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WADC TECHNICAL REPORT 54-532

PART 2

HIGH-TEMPERATURE HYDRAULIC FLUIDS

Part 2 — Development of Base Stock

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FOREWORD

This progress report was prepared by Monsanto Chemical Company, Research and Engineering Division, Chemical Research Department, Dayton, Ohio, under USAF Contract No. AF 33(616)-2623. This contract was initiated under Project No. 7331, "Hydraulic Fluids", Task No. 73313, "Hydraulic Fluids", formerly RDO No. 613-15, "Hydraulic Fluids and Lubricants", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Dr. H. Rosenberg and Lt. D. A. Rausch acting as Project Engineers.

This report covers period of work from November, 1954 to July, 1955.

We acknowledge the help of Mr. Morris R. Ort who conducted the reduction experiments on 2-ethyl-2-butyl propanol and prepared norbornylene, and of Mr. Donald Beasecker who made the infrared analyses.

WADC TR 54-532 Part 2

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ABSTRACT

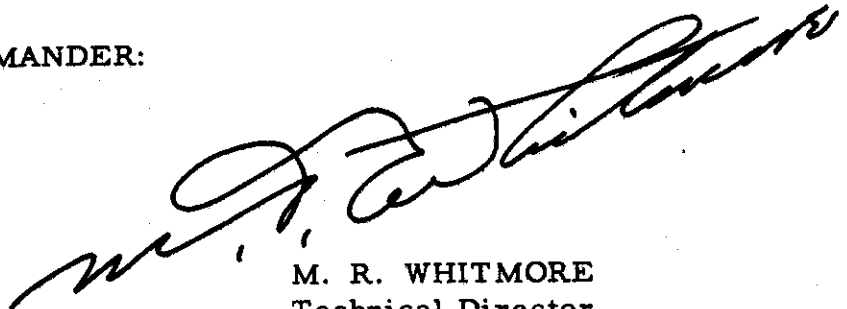
Fifty compounds have been screened for thermal stability.

Tert-alkylcarbinyl sebacates have been shown to be remarkably more stable (104-122°F) than n-alkyl sebacates. One new tert-alkylcarbinol, 2,2,4-trimethyl-1-pentanol, and eight new esters were synthesized. A polyarylphosphonate as a V.I. improver for thermally stable trialkylphosphate appeared to degrade on heating. A sufficient number of aromatic ethers were made and tested to reaffirm the high thermal stability of this chemical class and to indicate a high probability that the melting points of the aromatic ethers can be sufficiently lowered, without sacrifice in their thermal properties, to make them promising as base stock for high temperature functional fluids.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

Contrails

TABLE OF CONTENTS

	<u>Page</u>
I. INTRODUCTION	1
II. DISCUSSION	1
Synthesis	1
Alcohols	1
Esters	6
Ethers	8
Thermal Stability.	8
Esters	9
Ethers	13
Suggestions for Future Work	14
III. EXPERIMENTAL	15
Physical Testing	15
Isoteniscope Decomposition Studies	15
Isoteniscope vs Thermal Screening	18
Synthesis	25
Alcohols	25
Esters	32
Ethers	39

Continued
LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	Physical Properties of Esters	7
2	Comparison of Thermal Stabilities of Octyl Sebacates	9
3	Comparison of Thermal Stabilities of Octyl Esters	12
4	Viscosities of Solutions of Polyarylphosphonates in Tricresyl Phosphate	13
5	Vapor Pressure and Isothermal Rates of Pressure Rise of Tri(tetradecyl)dodecylsilane	16
6	Summary of Isoteniscope Measurements	18
7	Thermal Stability Tests	20

Contrails

I. INTRODUCTION

The final report (WADC TR 54-532) which preceded this report covered an extensive literature search on thermal stability, viscosity and vapor pressure data through eleven classes of chemicals. This literature review was paralleled with a screening program of available chemicals. As a result of this study a research program was proposed for the development of a high-temperature (700°F) hydraulic fluid base stock.

This final report covers work done between November, 1954 and July, 1955 toward the execution of these proposals with extension in scope to also cover base stock for high-temperature lubricants. More specifically, it covers the synthesis and thermal stability screening of esters of tert-alkylcarbinols, the synthesis and screening of some poly-aryl phosphonates as viscosity index improvers; and the synthesis and screening of some aryl ethers and alkyl aromatics.

This report is divided into three main sections: Introduction, Discussion and Experimental. Several unsuccessful attempted syntheses are reported.

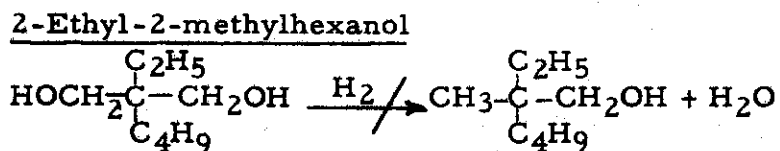
II. DISCUSSION

Synthesis

The three main divisions in the synthesis section are alcohols, esters, and ethers. The following discussion of thermal stability will also follow this arrangement.

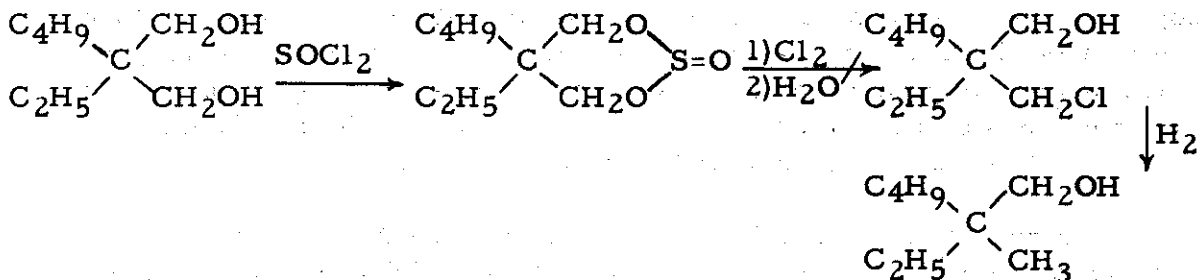
Alcohols

To determine the thermal stability of organic and inorganic esters in which thermal decomposition by the elimination of an olefin is inhibited, it was necessary to synthesize the esters and the intermediate alcohols required for their preparation. We are concerned here with tert-alkylcarbinols high enough in molecular weight to yield esters of sufficiently low volatility to be subjected to our thermal decomposition test (WADC TR 54-532).



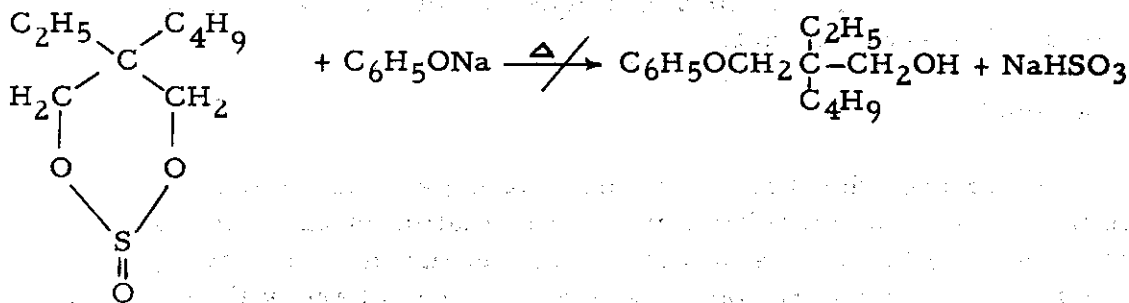
1, 3-Propanediol gives excellent yields of propanol on reduction with copperchromium oxide (Connor, R., Adkins, H., J. Am. Chem. Soc., 54, 4678 [1932]). Attempts were therefore made to reduce the commercially available 2-butyl-2-ethyl-1, 3-propanediol to 2-ethyl-2-methylhexanol using both copperchromium oxide and Raney nickel catalyst. Reduction products obtained with both catalysts were identified as 2-ethylhexanol.

After the direct reduction of 2-butyl-2-ethylpropanediol failed, indirect reduction of this diol via 2-butyl-2-methyl-3-chloropropanol was attempted. It was thought that this compound could be



obtained from the chlorination of the cyclic sulfite of 2-butyl-2-ethylpropanediol since the chlorination of ethylene sulfite has been reported to yield the chlorosulfite ester of β -chloroethanol (Viard, M. J., U.S. Patent 2,684,977). No product corresponding to the desired 3-chloropropanol was isolated from this reaction.

2-Butyl-2-ethyl-3-phenoxypropanol

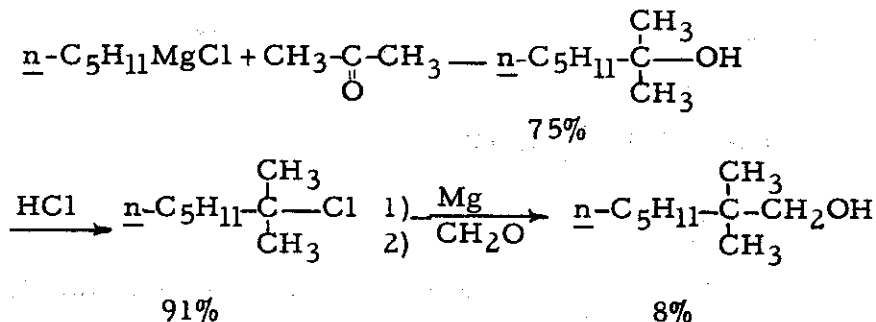


2-Hydroxyethyl β -naphthyl ether is obtained in excellent yield from the reaction of sodium β -naphthoxide and ethylene sulfite in boiling toluene (Carlson, W. W., and Cretcher, L. H., J. Am. Chem. Soc., 69, 1952 [1947]). It is predicted in WADC TR 54-532 report that neopentyl aryl-type ethers should have high thermal stability, and if this is borne out, esters from 2-butyl-2-ethyl-3-phenoxypropanol should also possess a high order of thermal stability. Utilization of the intermediate 2-butyl-2-ethyltrimethylene sulfite and sodium phenoxide under the same conditions

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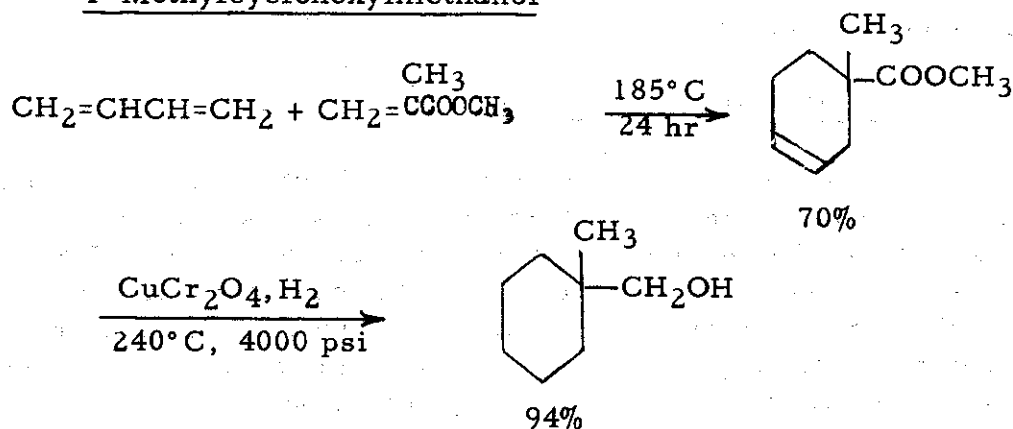
as described for ethylene sulfite and sodium β -naphthoxide appeared to be an interesting route to such mixed ethers. However, only unchanged cyclic sulfite was recovered from the reaction. This reaction remains intriguing and should proceed under suitable reaction conditions, such as with an improved solvent and a higher temperature.

2, 2-Dimethyl-1-heptanol



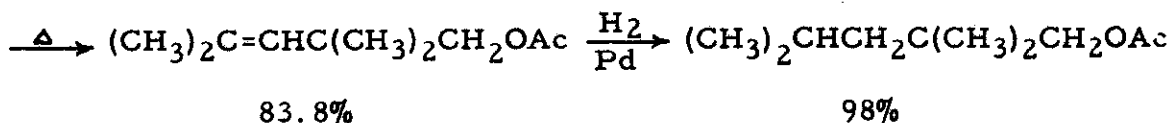
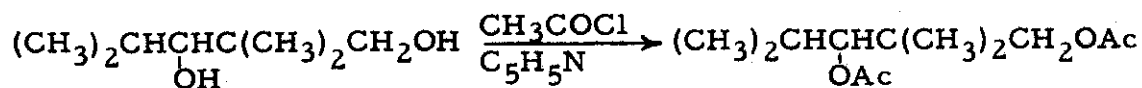
2, 2-Dimethyl-1-heptanol was prepared in an overall yield of 5% from *n*-amyl chloride by the procedure of Whitmore, F. C., et al., J. Am. Chem. Soc., 55, 406, 1559 (1933). The Grignard reaction of 2-methyl-2-heptylmagnesium chloride and formaldehyde proceeded in lower yield than that reported by Whitmore, presumably because the reaction was carried out on a larger scale and at a higher concentration. This lengthy synthesis with its inherent low yields was abandoned for more desirable routes to such carbinols.

1-Methylcyclohexylmethanol



This alcohol was synthesized by the catalytic reduction of 1-carbomethoxy-1-methyl-3-cyclohexene, which was prepared by the procedure of Roberts, J. D., Jeydel, A. K., and Armstrong, R., J. Am. Chem. Soc., 71, 3248 (1949).

Continued
2, 2, 4-Trimethyl-1-pentanol



98%

The route shown by the above equations provided the 2, 2, 4-trimethyl-1-pentanol in excellent yield (75%).

The reduction of 2, 2, 4-trimethyl-3-pentenyl acetate to the 2, 2, 4-trimethyl-1-pentanol in one step using a copper chromate catalyst containing barium at 230°C/4000 psig yielded a small amount of the desired pentanol. Other than a poisoned catalyst, there is no explanation for this failure and this procedure is still regarded as the method of choice in any extensive study.

Direct dehydration of 2, 2, 4-trimethyl-1, 3-pentanediol to 2, 2, 4-trimethyl-3-penten-1-ol over activated alumina at 400°C gave only low boiling fractions, which distilled at a much lower temperature than the desired alcohol.

2, 2-Dimethyl-n-alkan-1-ols

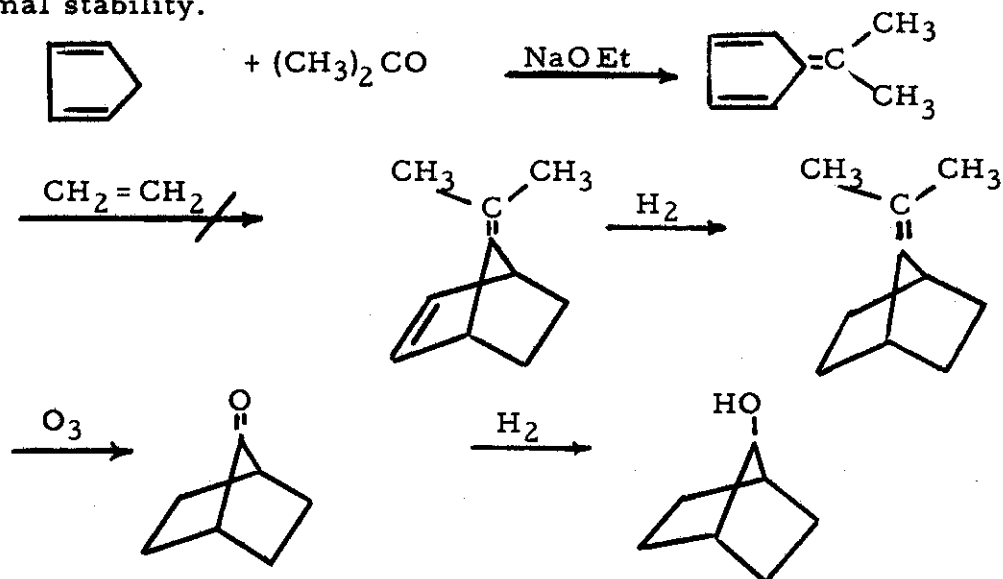
A scouting experiment was carried out to point out a possible commercial route to tert-alkylcarbinols. This was a telomerization reaction using ethylene and isobutyric acid as described in U.S. Patent 2, 433, -15 (Roland, J.R. Harmon, J.). Although conditions were far from optimum, some material, $\text{RC}(\text{CH}_3)_2\text{COOH}$, in the desired molecular weight range was obtained. Such acids should yield the desired 2, 2-dimethyl-n-alkan-1-ols by reduction.

7-Norbornanol

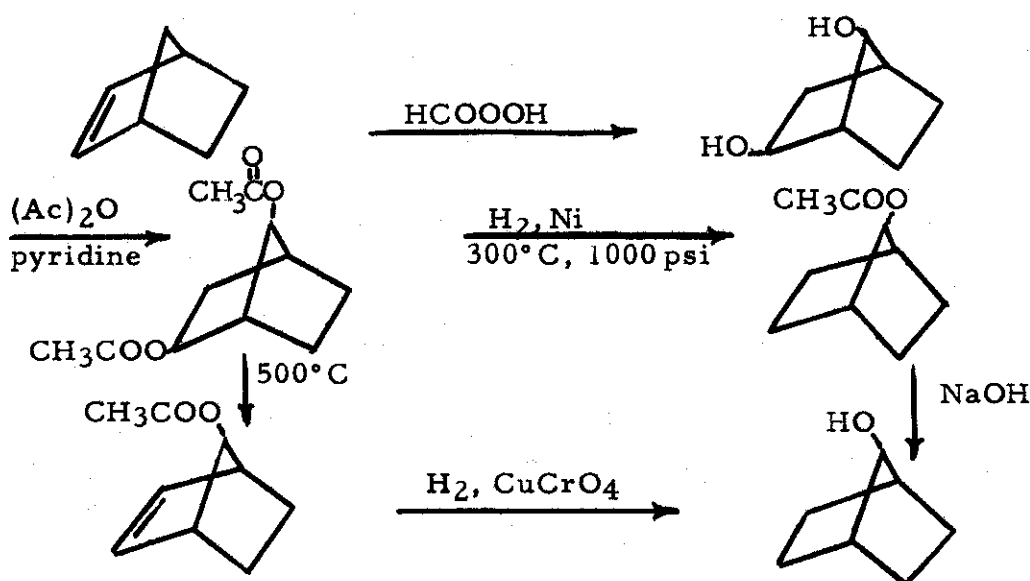
The inhibition of the thermal decomposition of esters by elimination of an olefin might be accomplished not only by replacing the β -hydrogen atoms of the alcohol moiety by alkyl groups but by so placing the acyloxy group on a caged structure that olefin formation

must violate Bredt's rule [cf. Prelog, V., Ruzicka, L., Baiman, P., and Frenkiel, L., *Helv. Chim. Acta*, 31, 92 (1948)]. Such esters might be more stable than esters of *tert*-alkylcarbinols because a caged compound should be more thermally stable than a linear one and the bond between oxygen and a bridgehead carbon atom should be more stable to heterolytic cleavage than an ordinary carbon-oxygen bond.

To test this hypothesis, the synthesis of 7-norbornanol was undertaken. The synthesis of this compound appeared more feasible than that of 1-norbornanol which would have been more desirable for enhanced thermal stability.



The first route, shown in the equation above, was patterned after the known Diels-Alder addition of dimethylfulvene and maleic anhydride (Kohler, E. P. and Koble, J., *J. Am. Chem. Soc.*, 57, 917 (1935)). The product isolated from the addition of ethylene, however, appeared to be the dimer of dimethylfulvene, and this route was abandoned.



Contrails

In a second route, shown above, the pyrolysis of 2,7-diacetoxynorbornane prepared from 2,7-dihydroxynorbornane /Kevart, H. and Vosburgh, W.G., J. Am. Chem. Soc., 76, 5400 (1954)/ gave a 10% yield of an acetoxy-norbornylene. Isolation of the theoretical amount of acetic acid and formation of much tar suggests that the desired reaction took place but that the product underwent a reverse Diels-Alder reaction. To avoid this, the pyrolysis was conducted under hydrogenating conditions and a 16% yield of an acetoxynorbornane was obtained. In this case, the isolation of some norbornane indicates the reaction conditions were too severe. It should, therefore, be possible to improve the yield greatly. Hydrolysis of the acetate yielded 7-norbornanol.

Esters

As previously indicated, in testing the hypothesis that esters of tert-alkylcarbinols should have greater thermal stability than esters of other aliphatic alcohols, it was necessary to synthesize numerous esters from the prepared carbinols.

The sebacates were prepared by the usual procedure of heating the acid in slight excess of the alcohol with sulfuric acid as a catalyst and azeotroping off the water with a hydrocarbon. The products were then further diluted with a solvent, washed free of acid, dried over anhydrous sodium sulfate and vacuum-distilled.

The silicates were prepared from tetraethyl silicate and the appropriate alcohol by ester interchange, using a trace of sodium as a catalyst. These products were distilled directly.

The borates were prepared by heating the alcohol and boric acid with or without an azeotroping agent for the water and the products were distilled directly.

Nonylphenyl carbonate was prepared in dioxane from sodium nonylphenoxide and phosgene. The phosphates and isophthalates were prepared from the acid chlorides and alcohol, with pyridine used as a scavenger for the hydrogen chloride generated in the reaction.

Table I on the following page lists the properties of the esters prepared.

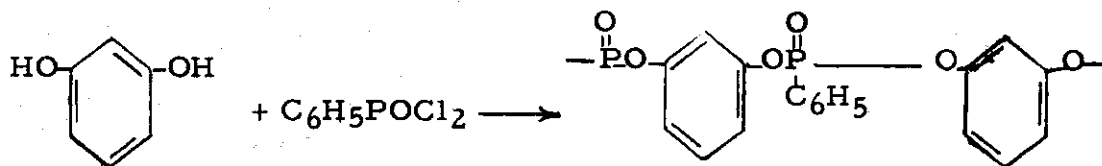
TABLE I

PHYSICAL PROPERTIES OF ESTERS

Ester	Yield, %	BP, °C/mm	n_D^{25}
*Bis(2, 2, 4-trimethylpentyl) sebacate	92	207-209/0.6	1.4471
Di(1-octyl) sebacate	82	213/0.5	1.4472
Dibenzyl sebacate	63	241-244/1.3	1.5173
*Bis(1-methylcyclohexylmethyl) sebacate	36	205-206/0.3	1.4729
*Bis(1-methylcyclohexylmethyl) adipate	73	186-188/0.7	1.4734
*Bis(1-methylcyclohexylmethyl) isophthalate	75	215-221/0.4	1.5172
Di(1-octyl) isophthalate	54	205-209/0.8	1.4850
*Tetrakis(2, 2, 4-trimethylpentyl) silicate	74	180-182/0.7	1.4325
*Tetrakis(1-methylcyclohexylmethyl) silicate	88	210/0.3	1.4732
Tetra-n-octyl silicate	80	199-204/0.3	1.4363
Tetra(2-ethylhexyl) silicate	--	184-185/0.7	1.4362
Tris(2-ethylhexyl) borate	--	138-140/0.35	1.4345
Tri(1-octyl) borate	66	104-165/0.45	1.4340
*Tris(1-methylcyclohexylmethyl) borate	75	170-175/0.3	1.4724
*Tris(2, 2, 4-trimethylpentyl) borate	92	144-146/0.7	1.4320/21°C
Tri(1-octyl) phosphate	38	187-189/0.15	1.4430
Bis(nonylphenyl) carbonate	92	258-263/1.0	1.5127

* New Compound

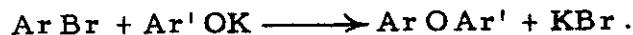
Three polymeric arylphosphonates were prepared by the reaction of dichlorophenylphosphine oxide with resorcinol, hydroquinone and bisphenol A, respectively, at a maximum temperature of 190°C using powdered tin as a catalyst according to Zeuftman, H. and McGillivray, R., Brit. 653, 489.



It was of interest to determine the effect of these phosphonates as viscosity index improvers of materials such as Aroclor 1248 and tricresyl phosphate (TCP) which have excellent thermal stability but poor viscosity-temperature characteristics. These polymers (size unknown) have good solubility in tricresyl phosphate, limited solubility in Aroclor 1248 and are insoluble in tri(n-dodecyl) silicon fluoride, tetra(2-ethylhexyl) silicate and tri-(n-dodecyl)borate.

Ethers

Although unsubstituted diaryl ethers are reported in the chemical literature to have excellent thermal stability, the class of aromatic ethers has not received much attention as possible base stocks for high temperature functional fluids. Several aromatic ethers were prepared by the Ullmann reaction,



They were found to possess a high thermal stability when unsubstituted or when the substituents were either halogen atoms or short-chain alkyl (ethyl or methyl) groups, but they were all solids.

The design of an aromatic ether having adequate rheological properties and oxidative stability without sacrifice in thermal stability, therefore, becomes the problem. As a beginning in a study of the effect of substituents on the thermal and rheological properties of diaryl ethers, several substituted aromatic ethers, having alkyl substituents higher than ethyl and methyl, were prepared by two methods: by Friedel-Crafts alkylation without concern for orientation and by the Ullmann reaction, where the orientation is known.

Thermal stability

Thermal stability screening tests of possible base stock materials were conducted by heating 10-20 gm samples of the material in glass in a nitrogen atmosphere for 10 hours at 545°F and at 690°F. The weight loss and viscosity change as a result of this treatment are a measure of thermal stability. The decomposition points of several compounds were determined by use of the isoteniscope.

The procedure and equipment for thermal stability screening were previously pictured and described in WADC TR 54-532, pp. 76-82.

The viscosity measurements (ASTM) were carried out as described in WADC TR 54-532, p. 91, on compounds which showed less than 10% weight loss when subjected to the thermal stability test at 690°F.

The results of the thermal stability screening tests are listed in Table 7 along with available melting and boiling points. (The numbers in parenthesis in the text refer to compounds in Table 7.) Several boiling temperatures were estimated from isoteniscope vapor pressure measurements.

Esters

As was anticipated, bis(1-methylcyclohexylmethyl) isophthalate (1) showed better stability than di(1-octyl) isophthalate (2), although the thermal stability at 690°F for both was very poor. Di(1-octyl) isophthalate showed no improvement at 545°F over bis(2-ethylhexyl) orthophthalate which was not anticipated.

Esters of 2,2-dialkyl-1,3-propanediols (11), $\text{RCOOCH}_2\text{C(R)}_2\text{CH}_2\text{OOCR}$, and of pentaerythritol (Hercoflexes) (12), $\text{C}(\text{CH}_2\text{OOCR})_4$, have no β -hydrogen atoms on the alcohol moiety and, as expected, had improved thermal stability over normal esters. They were not, however, stable enough for further consideration at 690°F, and were considerably less stable than esters of tert-alkylcarbinols. The difference in stability between esters of the glycols and esters of tert-alkylcarbinols is thought to be related to the proximity (1,3 positions) of the glycol ester functions.

n-Octyl, 2-ethylhexyl, 2,2,4-trimethylpentyl and 1-methylcyclohexylmethyl sebacates were compared in thermal stability by heating samples of each ester for 10 hours under nitrogen at the temperatures shown in Table 2.

Table 2

COMPARISON OF THERMAL STABILITIES OF OCTYL SEBACATES

<u>Sebacate</u>	<u>% Decomposition</u>				
	<u>282°C</u>		<u>319°C</u>		<u>341°C</u>
	<u>Acidity</u>	<u>Acidity</u>	<u>Distillate</u>	<u>Acidity</u>	<u>Distillate</u>
<u>n</u> -Octyl	0.92	21.2	46	69.0	100
<u>2</u> -Ethylhexyl	2.12	33.6	46	64.0	91
2,2,4-Trimethylpentyl	0.10	0.33	-	0.44	-
1-Methylcyclohexylmethyl	0.085	0.20	-	0.38	-

<u>Sebacate</u>	<u>% Viscosity Change at 210°F after Heating for 10 hours</u>				
	<u>230°C</u>	<u>259°C</u>	<u>282°C</u>	<u>319°C</u>	<u>341°C</u>
	<u>n</u> -Octyl	-1.05	-0.1	-0.80	-11.0(315)
<u>2</u> -Ethylhexyl	-0.5	-1.2	-0.85	-14.8	-
2,2,4-Trimethylpentyl	0	-0.7	-0.1	-2.1	-6.8
1-Methylcyclohexylmethyl	0	-0.59	-0.35	+0.26	-1.91

Contrails

The per cent decomposition (Table 2) was calculated from the amount of acid present after heating, and at the temperatures of 319°C and 341°C the per cent decompositions of n-octyl and 2-ethylhexyl sebacates were also measured by the weight of distillate collected as octene. These data show that from a thermal standpoint the tert-alkylcarbinyl sebacates have a useful temperature range of 40° to 50°C (104° to 122°F) higher than the sebacates of alcohols having β -hydrogen atoms.

The viscosity changes at 210°F were determined for the same four sebacates on heating at five different temperatures for 10 hrs under nitrogen. A plot of this viscosity data is shown in Fig. 1. Above 282°C the viscosity changes for n-octyl and 2-ethylhexyl sebacate are very rapid. After 10 hrs at 319°C both esters had deposited an appreciable amount of solid. No solid deposit was present in the tert-alkylcarbinyl esters after 10 hrs at 341°C. These data support the previous statement of a 40° to 50°C (104° to 122°F) increase in the useful temperature range for the sebacates of alcohols having no β -hydrogen atoms. This does not imply that these esters will have improved oxidative stability which has yet to be determined.

Isoteniscope determinations of pressure increase with temperature also demonstrate the increased stability of tert-alkylcarbinyl sebacates as compared to n-octyl sebacates. Fig. 3 shows that the rate of pressure increase of di(1-octyl) sebacate at 300°C is 0.08 mm Hg/sec while bis(1-methylcyclohexylmethyl) sebacate does not decompose at this rate until approximately 355°C is reached.

The data in Table 3 show that the thermal stability of borates and silicates prepared from tert-alkylcarbinols is not markedly improved over the isomeric n-alkyl esters. This is also borne out by the isoteniscope measurements of decomposition point and the isothermal rate of pressure change as shown in the dp/dt column of Table 6.

To accentuate differences in thermal stability as measured by weight loss, four isomeric silicates were heated for 10 hr at 730°F (Table 3). Until further data on the decomposition products of silicates are obtained, correlation of the differences in thermal stability of silicates and sebacates with decomposition mechanisms is largely speculative.

In view of the inherent high thermal stability of n-alkyl borates and silicates, less improvement might be expected in the thermal stability of such esters by the replacement of all β -hydrogen atoms in the alcohol moiety than would be shown by less stable esters, such as sebacates. The contrast between the improvement in stability of a sebacate and a borate resulting from the replacement of the β -hydrogen atoms of the alcohol moiety (data in Table 3) shows this to be the case.

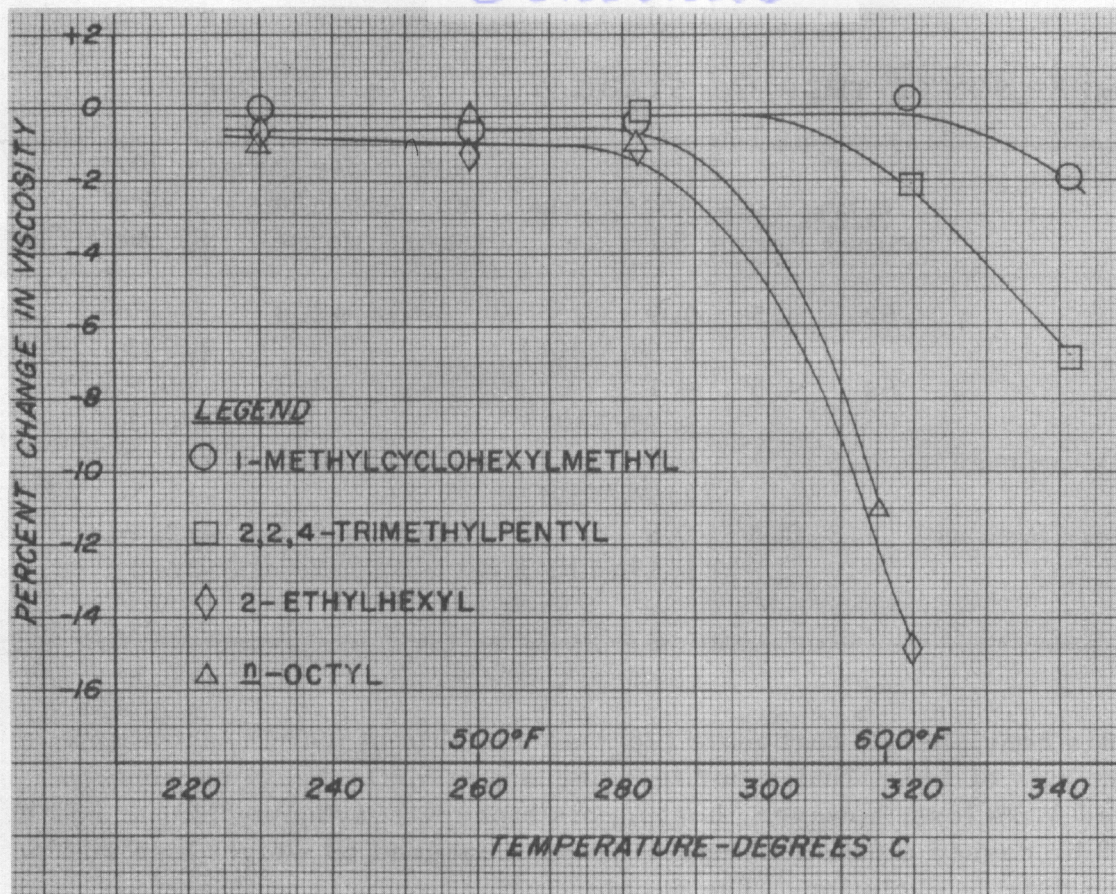


Figure 1 PERCENT VISCOSITY CHANGE AT 210° F
AFTER HEATING FOR 10 HOURS

Assuming decomposition via olefin elimination and the complete loss of volatile fragments, then at 690° F n-octyl and 2-ethylhexyl sebacates are 100% decomposed while the 2, 2, 4-trimethyl-1-pentyl and 1-methylcyclohexyl sebacate are only 14% and 2.2% decomposed respectively. In comparison, n-octyl and 2-ethylhexyl borate both undergo 5.5% decomposition while the 2, 2, 4-trimethyl-1-pentyl and 1-methylcyclohexylmethyl borate undergo 4.4% and 0.35% decomposition respectively.

The decrease in viscosity, especially of the 1-methylcyclohexylmethyl sebacate, silicate and borate, after 10 hrs heating at 690° F indicates a molecular change which has not involved the loss of volatile fragments. Infrared analyses of the 1-methylcyclohexylmethyl sebacate and silicates before and after heating indicated no detectable change. This observation will be studied further by subjecting a larger sample to the thermal treatment followed by an attempt to isolate decomposition fragments by fractionation. Nevertheless, sebacates of this structure, from a utility standpoint as lubricants, are regarded as materially more stable than n-alkyl sebacates and will be explored further.

COMPARISON OF THERMAL STABILITIES OF OCTYL ESTERS

<u>Alcohol</u>	<u>% Wt. loss, 690° F/10 hr</u>			<u>% Viscosity change at 100° F after heating 10hr at 690° F</u>		
	<u>Sebacate</u>	<u>Borate</u>	<u>Silicate</u>	<u>Sebacate</u>	<u>Borate</u>	<u>Silicate</u>
n-Octanol	62	4.5	0.9	--	+2.8	+1.0
			5.5%/730° F			+17.3
2-Ethylhexanol	64	4.5	4.1	--	-4.3	-0.2
			18.4%/730° F			+40.3
2,2,4-Trimethyl-1-pentanol	8.5	3.7	6.4	-18.1	-5.5	-16.0
			12.3%/730° F			-19.3
1-Methylcyclohexylmethanol	1.3	0.3	0.6	-20.9	-20.5	-22.4
			3.1%/730° F			-32.3

Bis(nonylphenyl) carbonate (26) was unstable at 690° F, showing a weight loss of 14%. Under our test procedure bis(biphenyl) carbonate showed 3.3% loss; however, heating bis(biphenyl) carbonate (25) at 380° C for 20 hr caused a 63% decomposition as measured by weight loss and by carbon dioxide evolution. The decomposition products of this experiment have not been identified, but it is hoped that a further study using copper as a decomposition catalyst might result in a better route to some aromatic ethers.

The titanates as shown by one example (24) do not appear very promising.

Since Aroclor 1248 and tricresyl phosphate (TCP) have high thermal stability but poor ASTM 100° to 210° F viscosity slope properties, it was of interest to determine the effect of polymeric phosphonates as viscosity index improvers for these materials and others. As indicated in Section II under synthesis, three polyaryl phosphonates were prepared, and the viscosities of solutions of these polyaryl phosphonates in tricresyl phosphate were determined; the results are shown in Table 4. As a result of these measurements, the 15% PP-1 in tricresyl phosphate was tested for thermal stability and the subsequent viscosity change is shown in Table 4 and also in Table 7, sample 28. This solution was filtered, because it was found that viscosity measurements on the filtered solutions were more reliable.

VISCOSITIES OF SOLUTIONS OF POLYARYLPHOSPHONATES
IN TRICRESYL PHOSPHATE

<u>Compounds</u>	<u>Kinematic Viscosity (cs)</u>		<u>ASTM Slope</u>
	<u>at 100° F</u>	<u>at 210° F</u>	
Tricresyl phosphate (TC)	29.88	4.123	0.866
5% PP-1 in TCP (not filtered)	49.30	5.743	0.824
10% PP-1 in TCP (not filtered)	84.94	8.14	0.789
15% PP-1 in TCP (filtered)	162.7	12.11	0.765
15% PP-1 after 10 hr at 690° F (lost 0.2% wt)	152.8	10.08	0.828
20% PP-1 in TCP (not filtered)	388.6	31.31	0.598
20% PP-2 in TCP (not filtered)	443.9	26.34	0.680
20% PP-3 in TCP (not filtered)	138.8	9.96	0.814

PP-1 = Treaction product of resorcinol and $C_6H_5POCl_2$
 PP-2 = Reaction product of hydroquinone and $C_6H_5POCl_2$
 PP-3 = Reaction product of bisphenol A and $C_6H_5POCl_2$

The resorcinol polymer (PP-1) dissolved 15% in tricresyl phosphate and filtered increased the viscosity by 445% and decreased the ASTM 100° - 210° F slope by 11.7%. This effect appeared interesting for a first attempt, as the order of magnitude of the molecular weight was unknown but was anticipated to be about 15,000. However, the viscosity measurements after 10 hr heating at 690° F were discouraging. Although the weight loss of the solution was very low (0.2%) the ASTM slope improvement of 11.7% fell to 4.3%. It would appear that some degradation of the polymer took place at this temperature.

Ethers

Aromatic-aliphatic mixed ethers (32, 33) were unstable in our tests

as predicted. Aromatic ethers which are unsubstituted or contain only halogen-, methyl-, or ethyl groups (34, 38, 39, 40) have outstanding thermal stability at 700° F but have melting points above room temperature.

If the melting point of an aromatic ether could be lowered and the general rheological properties improved without great sacrifice in thermal stability, this class of compounds would be very promising as possible base stocks for high temperature functional fluids. A study has been started, therefore, to determine the effect of kind and position of substituents on the rheological properties and thermal stability of aromatic ethers. The substituents to be considered initially are halogen, alkyl, and perfluoroalkyl groups.

As shown by compounds 35, 36, 37, 41, 42, alkyl substituents lower the ASTM slope from that of 1.1 for diphenyl ether. In particular, 3-n-pentadecylphenyl phenyl ether (42) has a slope of 0.708 which compares favorably with that of 0.69 for n-tetracosane (the hydrocarbon of analogous chain length if the phenyl groups in 3-n-pentadecylphenyl phenyl ether are each assigned a length of 4); the 100° F viscosity of the ether, however, is 17.21 as compared to 9.25 for the hydrocarbon. The monodecyl and hexapropyl diphenyl ethers (35, 36, 37) are liquids at room temperature and cyclohexylphenyl phenyl ether (41) has a pour point of less than -10° C. These improvements in the viscosity properties were, except for cyclohexylphenyl phenyl ether, achieved at the cost of a decrease in thermal stability. It will be necessary to obtain more data on the relation between thermal stability and the length and degree of branching of alkyl substituted diphenyl ethers.

Suggestions for Future Work

On the basis of our experimental work to date the following lines of investigation seem promising for the development of high temperature functional fluids.

(1) Tert-alkylcarbonyl esters such as glutarates, adipates and/or sebacates should be subjected to further screening tests for oxidative and hydrolytic stability in view of the 100° F improvement in thermal stability shown by these esters as compared to isomeric n-alkyl esters.

(2) Aromatic ethers should be investigated intensively as possible base stocks for high temperature functional fluids.

(3) The decomposition of aryl carbonates and sulfites should be investigated as possible routes to aryl ethers from substituted phenols.

(4) Polyaromatics should be investigated following an approach similar to that to be taken with aromatic ethers.

Contrails

(5) The effect of orthosubstitution on the hydrolytic stability of some phenyl esters should be investigated.

(6) The mode of thermal and hydrolytic decomposition of silicates and borates should be studied in order to design more stable molecules in these two classes.

(7) A study should be made on the development of more thermally stable V.I. improvers.

III. EXPERIMENTAL

Physical Testing

Isoteniscope Decomposition Studies

The thermal stability of several compounds was studied using the isoteniscope vapor pressure apparatus described previously (WADC TR - 54-532, pp. 85-91). The measurements made consisted of equilibrium vapor pressure below the "decomposition point" and isothermal rates of pressure change above the decomposition point. Since we aimed primarily at getting the latter data, complete vapor pressure data were not generally obtained. The data were used in several cases, however, for estimating normal boiling points in the absence of more firmly established values.

In the tests the isoteniscope sample bulbs were filled as previously described (WADC TR 54-532), sealed, and evacuated to ca 10^{-5} mm Hg. The bulb was then heated gently with a gas flame to drive out absorbed gases. The temperature during flaming was held below 150° - 225° C, depending on the stability of the compound as previously determined in the screening test. The gentle heating was continued after degassing to distill some of the sample into the isoteniscope manometer for subsequent use in the pressure measurements. Filling of the manometer in this manner is a modification of the technique described in WADC TR 54-532.

The "decomposition point" has been arbitrarily taken as the temperature at which the isothermal rate of pressure change, dp/dt , is equal to 10^{-4} mm Hg/sec. This value was chosen from studies on n-octacosane (data given in WADC TR 54-532); it is approximately the rate of pressure rise observed at the point (temperature) of departure of the vapor pressure curve from a straight line. It has been found that the values of $\log(dp/dt)$ generally fall on a straight line when plotted against the reciprocal of the absolute temperature, as might be expected, so that extrapolation to 10^{-4} mm Hg/sec can be done readily. The possibility of subjective errors in this method is much less than in the alternative method which involves choosing a point of tangency as the decomposition point.

Typical results to illustrate the isoteniscope measurements are given in Table 5. These data, taken on a sample of tri(tetradecyl)-dodecylsilane prepared at WADC, are also plotted (Fig 2) against the reciprocal of the absolute temperature. The vapor pressures follow a straight line reasonably well at lower temperatures but deviate more and more as higher temperatures are reached and decomposition is faster. The isothermal rates of pressure rise, dp/dt, also plotted on the semi-log graph, are seen to fall closely on a straight line; this was found, also, for the other compounds studied. For the silane, extrapolation of dp/dt to 10⁻⁴ mm Hg/sec gives 282°C as the decomposition point.

Table 5

VAPOR PRESSURE AND ISOTHERMAL RATES OF PRESSURE RISE OF TRI(TETRADECYL)DODECYL SILANE

Temperature, °C	Reciprocal Abs. Temp. 10 ³ /T°K	Pressure, (1) mm Hg	dp/dt, mm Hg/Sec
197	2.128	0.85	--
228.5	1.994	2.5	--
251.5	1.906	3.7	--
271.5	1.836	6.2	--
293	1.766	10.1	--
314	1.703	15.7	.0016
315	1.701	17.7	
329	1.661	--	.0045
344	1.620	--	.013
356	1.589	--	.035
367	1.561	--	.0715

(1) Pressures are not given for temperatures above 315°C, although some of the higher pressures used in determining dp/dt are shown in Fig 2.

Decomposition points, estimated boiling points and vapor pressures at 700°F (=371°C), obtained from isoteniscope data on several other compounds are listed in Table 6 along with per cent weight loss at 690°F as observed in the thermal stability screening test (Table 7). Isothermal rates of pressure rise for these same substances are plotted in Fig 3.

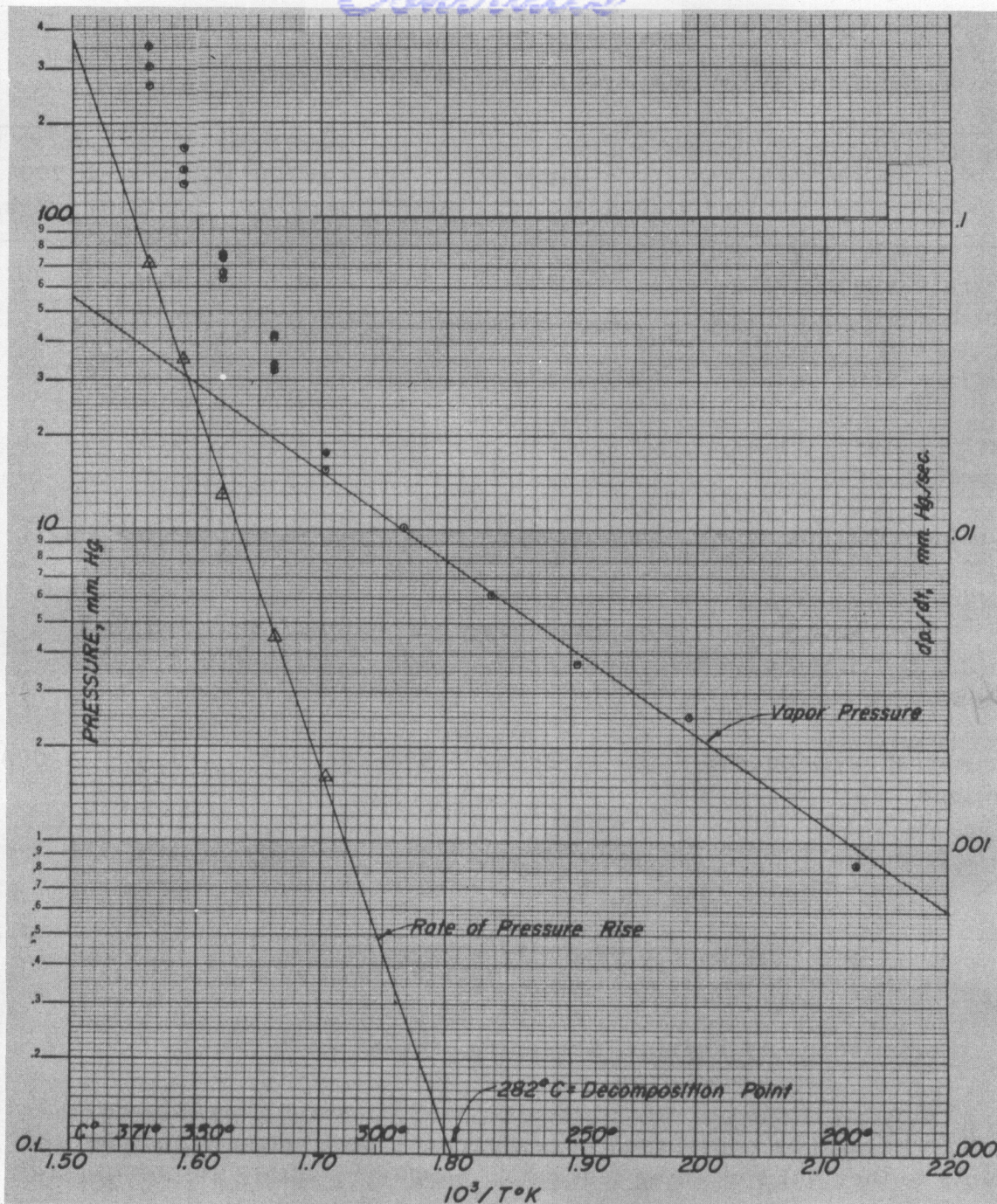


Figure 2 VAPOR PRESSURE AND DECOMPOSITION RATES OF TRI(TETRADECYL)DODECYLSILANE

SUMMARY OF ISOTENISCOPE MEASUREMENTS

	Curve	Decomp. Pt, °C	BP, °C	Vapor Press at 700° F mm, Hg	% Wt loss at 690° F	dp/dt at 700° F mmHg/sec
Tetra(1-methylcyclohexylmethyl) silicate	1	250	435	175	0.6	0.34
Tetra(<u>n</u> -octyl) silicate	2	255	476	118	0.9	0.14
Di(1-methylcyclohexylmethyl) sebacate	5	250	468	120	1.3	0.19
<u>n</u> -Octyl stearate	8	227	385	560	33.6	4
Di(<u>n</u> -octyl) sebacate	6	223	--	--	62	9
Di(2, 2, 4-trimethylpentyl) sebacate	7	227	390	485	8.5	1
Tri(tetradecyl)dodecylsilane	3	281	594	47	1.9	0.090
<u>n</u> -Octacosane	4	295	412	340	4.3	0.14

Isoteniscope vs Thermal Screening

Volatility, mode of decomposition, and possibly a number of other factors have to be considered in comparing isoteniscope decomposition points to thermal screening test data. However, within a class (esters one class, and octacosane and the silane the other) the "per cent weight loss at 690° F" ranks the compounds in about the same order as does the decomposition point and the values of dp/dt extrapolated to 700° F.

Except that the isoteniscope method requires 2-3 times the labor involved in the thermal stability screening tests, the methods are interchangeable. Each has some advantages. The screening test, run with 10-20 gm of sample, provided material for further analysis and study. Also, volatile decomposition products can be collected and analyzed for study of mechanism. With the isoteniscope, decomposition products

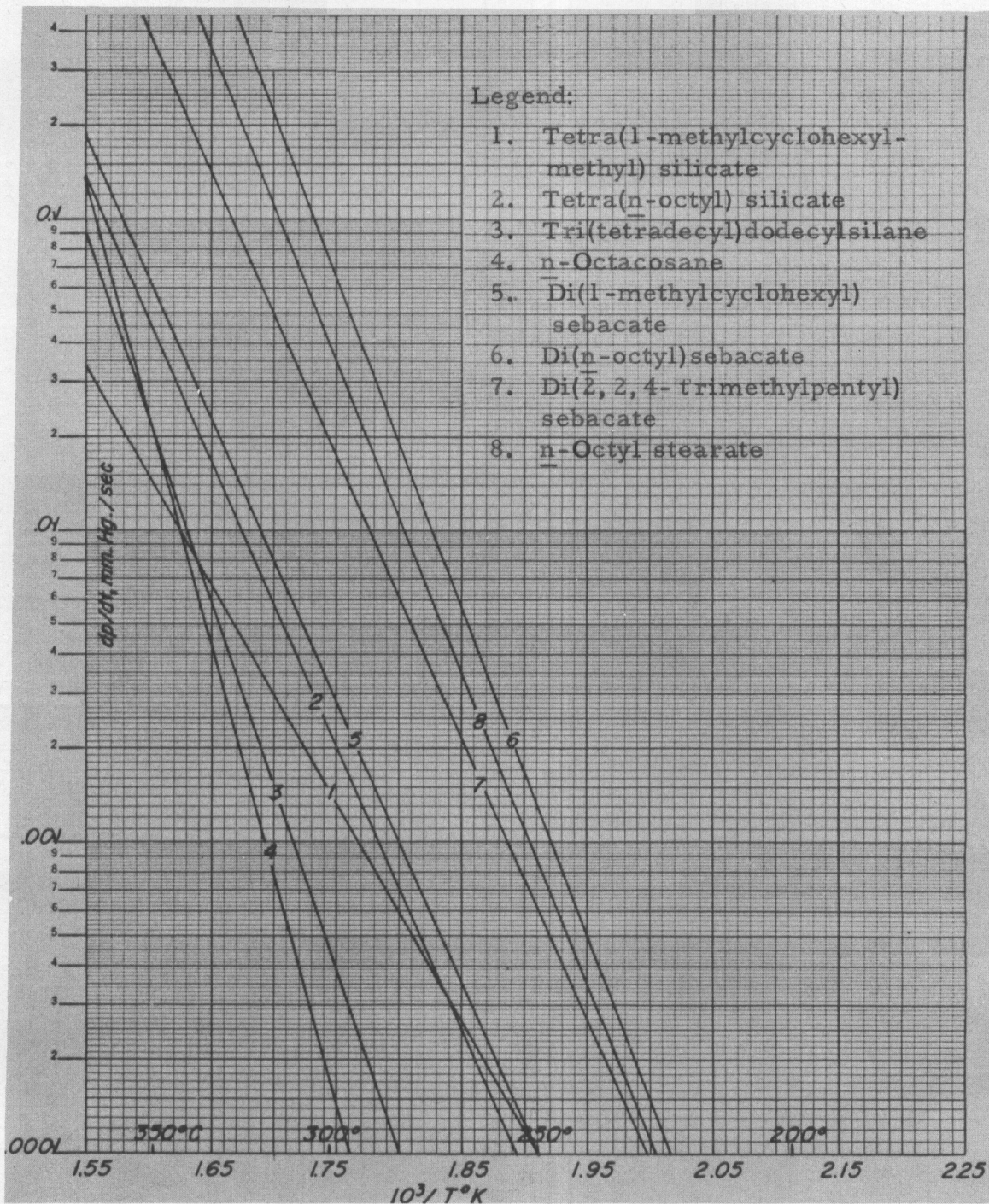


Figure 3 ISOTHERMAL RATE OF PRESSURE RISE IN ISOTENISCOPE

THERMAL STABILITY TESTS

Compound No. (3)	Compound (1)	MP (2) °C	BP °C/mm Hg	Weight Percent Loss		Viscosity cs		ASTM Slope
				545°F	690°F	100°F	210°F	100° to 210°F
1	Bis(1-methylcyclohexylmethyl) isophthalate (a) after 545°F heat after 690°F heat	L	215-221/0.4	0.3	>50			
2	Di(1-octyl) isophthalate (a) after 545°F heat	L	205-209/0.8	7.3				
3	Bis(2-ethylhexyl) phthalate (b) 545°F 690°F			4.2	>50			
4	Di(1-octyl) sebacate (a) 545°F 690°F	L		2.6	62			
5	Bis(2-ethylhexyl) sebacate (a) 545°F 690°F	L	190-192/0.05	1.4	64			
6	Bis(2,2,4-trimethylpentyl) sebacate (a) 545°F 690°F	L	207-209/0.6 (390°C) ⁶	0.3	8.5	14.97 14.92 12.25	3.827 3.821 3.417	0.672 0.672 0.665
7	Bis(1-methylcyclohexylmethyl) sebacate (a) 545°F 690°F	L	205-206/0.3 (468°C) ⁶	0.2	1.3	49.38 39.04	7.625 6.636	0.680 0.706
8	Bis(1-methylcyclohexylmethyl) adipate (a) 690°F	L	186-188/0.7		5.5	38.26 35.66	6.011 5.563	0.728 0.749
9	Dibenzyl sebacate (a) 690°F	L	241-244/1.15-1.3		7.8	16.63 13.37	3.984 3.374	0.691 0.712
10	1-Octyl stearate (a) 545°F 690°F	34	205-207/1	0.2	33.6	11.16 11.02 Solid	3.258 3.226 5.840(9)	0.663 0.664 -
11	Mixed pelargonate and laurate of 2,2-dimethyl-1,3-propanediol(a) 545°F 690°F	L	175-226/0.5	0.5	23			
12	Hercoflex 600 (1) 545°F 690°F	L		0.75	20.9			

Table 7 (Cont'd)

Compound No. (3)	Compound (1)	MP (2) °C	BP °C/mm Hg	Weight Percent Loss		Viscosity cs		ASTM Slope 100° to 210°F	
				545°F	690°F	100°F	210°F		
13	Tri(1-octyl) borate (a) 545°F 690°F	L	164-165/0.45	0.3	4.5	6.499	2.086	0.754	
						6.473	2.078	0.754	
						6.680	2.168	0.736	
14	Tris(2-ethylhexyl) borate (a) 690°F	L	138-140/0.35		4.5	6.286	1.935	0.802	
						6.016	1.878	0.806	
15	Tris(2,2,4-trimethylpentyl) borate (a) 690°F	L	144-146/0.7		3.7	7.739	2.255	0.774	
						7.310	2.173	0.779	
16	Tris(1-methylcyclohexylmethyl) borate (a) 545°F 690°F	~24	170-175/0.3	0.2	0.3	188.2	10.09	0.868	
						186.5	10.03	0.869	
						149.6	9.22	0.864	
17	Tri-o-cresylborate (f) 545°F 690°F	L		0.5	0.5	47.08	4.068	1.010	
						54.03	4.223	0.996	
						55.16	4.304	0.981	
18	Tris(2-cyclohexylcyclohexyl) borate (f) 545°F 690°F	S		0.9	>90				
19	Tetra(1-octyl) silicate (a) 690°F 730°F	L	192-204/0.2 (476°C) ⁶		0.9 (5.5)	6.871	2.341	0.687	
						6.945	2.397	0.669	
						8.058	2.721	0.647	
20	Tetra(2-ethylhexyl)silicate (a) 690°F 730°F	L	184-185/0.7		4.1 (18.4)	6.815	2.244	0.715	
						6.800	2.284	0.700	
						9.558	3.003	0.652	
21	Tetrakis(2,2,4-trimethylpentyl) silicate (a) 690°F 730°F	L	180-182/0.7		6.4 (12.3)	9.517	2.888	0.678	
						7.992	2.553	0.706	
						7.676	2.507	0.686	
22	Tetrakis(1-methylcyclohexylmethyl) silicate (a) 690°F (after 1st 10 hr) 690°F (after 2nd 10 hr) 730°F	L	210/0.3 (435°C) ⁶			183.6	14.48	0.726	
						0.6			
						1.4	142.4	12.85	0.710
						(3.1)	124.2	12.03	0.709
23	Isooctyl polysilicate (a) 545°F (after 1st 10 hr) 545°F (after 2nd 10 hr) 690°F (after 1st 10 hr) 690°F (after 2nd 10 hr)	L	255-320/1.0		7.4 1.4				
						21.3			
						11.9			

Table 7 (Cont'd)

Compound No. (3)	Compound (1)	MP (2) °C	BP °C/mm Hg	Weight Percent Loss		Viscosity cs		ASTM Slope
				545°F	690°F	100°F	210°F	100° to 210°F
24	Tetra(2-ethylhexyl) titanate (e) 545°F 690°F	L		0.8	84			
25	Bis(biphenyl)carbonate (a) 690°F	193-196			3.3			
26	Bis(nonylphenyl) carbonate (a) 690°F	L	258-263/1.0		14			
27	Tricresyl phosphate (b) 545°F 690°F	L		0.3		29.88 34.08 0.5 54.41	4.123 4.434 5.877	0.866 0.864 0.870
28	15% Polymer PP-1(4) in tricresyl phosphate (a) 690°F	L				162.7 0.2 152.8	12.11 10.08	0.765 0.827
29	Tri(1-octyl) phosphate (a) 545°F	L	187-189/0.15 ca 95					
30	Pydraul F-9 (b) 545°F 690°F	+5°F (pour)		0.4		51.26 45.90 0.8 58.83	5.725 4.742 4.827	0.836 0.911 0.967
31	Decyl 1,4,5,6,7,7-hexachlorobicyclo 2.2.1-5-heptene-2-yl ether (a) 545°F	-65°F (pour)	170-174/0.3- 0.5		59			
32	4,4'-Bis(2-ethylhexoxy)-octachlorobiphenyl (a) 545°F	S	255-265/0.2- 0.5		16.0			
33	4,4'-Bis(1-methylcyclohexylmethoxy)-x,x,x',x'-tetrachlorobiphenyl (a) 690°F	S	250-310/0.3		48			
34	Bis(p-bromophenyl) ether (a) 690°F	58-60	201-203/12		0.3			
35	x-Dodecylphenyl phenyl ether(8)(a) 690°F	L	191-198/0.5			21.26 6.0 13.14	3.643 2.862	0.833 0.823
36	x'-Dodecylphenyl phenyl ether(8)(a) 690°F	L	197-212/0.5-0.8			7.2 29.97 17.42	4.63 3.477	0.797 0.794
37	Hexapropyldiphenyl ether (a) 690°F	S-L	164-167/0.8			1895 3.3 496.9	16.51 11.76	1.075 0.995

Table 7 (Cont'd)

Compound No. (3)	Compound (1)	MP (2) °C	BP °C/mm Hg	Weight Percent Loss		Viscosity cs		ASTM Slope
				545°F	690°F	100°F	210°F	100° to 210°F
38	1,4-Bis(4-ethylphenoxy)benzene (a) 690°F	52-54	195-200/0.6		0.1			
39	1,4-Bis(3,5-dimethylphenoxy)benzene (a) 690°F	95-100	182-184/0.5		0.1			
40	Bis(p-phenoxyphenyl) ether (a) 690°F	107-109	215-221/1		0.1			
41	Cyclohexylphenyl phenyl ether (a) 690°F	L	154-161/1.2			15.58 15.65	2.977 2.988	0.862 0.862
42	3-n-Pentadecylphenyl phenyl ether (a) 690°F	30-35	211-214/0.7		0.7	17.21 15.38	3.960 3.677	0.706 0.708
43	o-Chlorophenyl p-nonylphenyl ether (a) 690°F	L			10.0			
44	Dibenzofuran 690°F	87	288		>98			
45	Tri(n-dodecyl)silicon fluoride (a) 690°F	L	255-265/0.25		1.7	19.31 19.25	4.611 4.649	0.652 0.652
46	Tri(p-fluorophenyl)silicon fluoride (a) 690°F	~20	162-165/1.0		1.9	13.41 14.36	2.138 2.278	1.060 1.031
47	Silicone (DC550 fluid) (h) 690°F	L			0.3	75.73 79.55	18.77 19.36	0.417 0.420
48	Silicone (DC710 fluid) (h) 545°F 690°F	-10°F		0.2	0.2	235.3 244.4 249.9	29.39(5) 30.01(5) 30.02(5)	0.521 0.522 0.527
49	Tris(tetradecyl)dodecylsilane (g) 690°F	L	594(6)		1.9	43.23 41.24	8.261 8.095	0.603 0.602
50	Aroclor 1248 (b) 545°F 690°F	-7 (pour)	330-370	0.2	0.2	48.45 47.67 48.54	3.312 3.302 3.317	1.153 1.148 1.150
51	Aroclor 1254 (b) 690°F 690°F (7)	8-12 (pour)	365-390		0.04 0.7	478.9 461.5	5.085 6.059	1.321 1.288
52	Triamylbiphenyl (a) 690°F	L	155-161/0.45		3.7	42.76 44.79	4.900 5.112	0.865 0.864
53	Retene (c) 545°F 690°F	98.5	394	0.2	0.3			

Compound No. (3)	Compound (1)	MP (2) °C	BP °C/mm Hg	Weight Percent Loss		Viscosity cs		ASTM Slope 100° to 210°F
				545°F	690°F	100°F	210°F	
54	n-Octacosane (c) 545°F 690°F	59-61	412.5	0.2	4.3			
55	Polybutene (Oronite 24) (d) 545°F	L		9.2				
56	1,2,3,4,7,7-Hexachloro-6-hexylbicyclo [2.2.1]-2-heptene (a) 545°F 690°F	-55°F (pour)	141-165/0.15- 0.9	5.8	63			
57	Benzoic anhydride (j) 545°F 690°F	43	360	1.1	>24			

Notes to Table 7:

1. Source of samples:

- (a) Monsanto, laboratory preparation
- (b) Monsanto, production
- (c) Eastman Kodak Co.
- (d) Oronite Chem. Co.
- (e) Titanium Pigment Corp.
- (f) Pacific Coast Borax Co.
- (g) Rosenberg, H., W.A.D.C., Dayton
- (h) Dow-Corning Co.
- (i) Hercules Powder Co.
- (j) Eastern Chemical Corporation

- 2. The symbols S and L indicate the physical state, solid or liquid, at room temperature.
- 3. Samples numbered 3, 27, 32, 48, 51, 54, 55 were reported in WADC TR 54-532, Table 25. These are repeated here for comparison.
- 4. Reaction product of resorcinol and C₆H₅POCl₂.
- 5. Kinematic viscosity measured at 212.0°F.
- 6. Boiling points obtained by extrapolation from low temperature vapor pressure data.
- 7. Sample tube was open to air for this test.
- 8. Position of substituents unknown.
- 9. Residue after 690°F run is probably stearic acid (MP 69°C).

are not effectively separated, and, as the sample is small (2 cc), only a small amount is left for further testing or analysis. The isoteniscope does, however, provide good vapor pressure data.

Synthesis

Alcohols

2-Ethyl-2-methylhexanol

Raney Nickel reduction (unsuccessful). A 1000 cc stainless steel rocking autoclave was charged with 160 gm (1 mole) of 2-butyl-2-ethyl-1,3-propanediol and 16 gm of Raney nickel catalyst. The charged bomb was flushed with hydrogen and pressurized to 3000 psig. The temperature was gradually raised to 250°C where it was held with rocking for 6.5 hours. On cooling down, the residual hydrogen pressure was 2600 psig. The contents of the bomb were emptied and the bomb was rinsed with ethanol. After filtering to remove the catalyst the solution was fractionated through a 2-ft heated Vigreux column:

Fraction	Yield/gm	BP °C/mm Hg	n ²⁵ D
1	72	92.5°/23	1.4295
2	34	88° - 95°C/0.25 to 0.40	
	15	residue	

Hydroxyl value of fraction 1: Calcd. for C₈H₁₈O: (2-ethylhexanol): 13.05. Found: 13.01. The infrared spectrum of fraction 1 was identical with that of 2-ethylhexanol, n²⁵D 1.4295.

Analyses of fraction 2: Calcd for C₉H₂₀O₂ (diol): C, 67.5; H, 12.5. Found: C, 67.3; H, 12.66.

Copper Chromite reduction (unsuccessful). Reduction was carried out as before using 16 gm of copper chromite and 2700 psig hydrogen pressure at 250°C for 5 hours. On cooling, the residual pressure was 2300 psig. The product was worked up as before.

A small amount of forerun was collected but the main fraction, 113 gm, distilled at 90°-90.5°C/21 mm, n²⁵D 1.4295. Anal. Calcd for C₈H₁₈O; C, 73.8; H, 13.85; Hydroxyl value, 13.05. Found: C, 74.77; H, 14.0; Hydroxyl value, 12.75. The product is 2-ethylhexanol.

2-Butyl-2-ethyl-3-phenoxypropanol

2-Butyl-2-ethyltrimethylene sulfite. To 160 gm (1 mole)

of 2-butyl-2-ethyl-1,3-propanediol (Carbide & Carbon) was added dropwise with stirring and cooling 40 gm (0.33 mole) of thionyl chloride at 35° - 45°C. Then 80 gm (0.67 mole) of thionyl chloride was added rapidly with heating so that the temperature stayed at 35° - 45°C. The mixture was heated at 70°C for 20 min and allowed to cool. The colorless product, bp 132° - 135°C/15 mm; n^{25}_D 1.4602, weighed 204 gm (98% yield). Anal. Calcd for $C_9H_{18}O_3S$: C, 52.40; H, 8.79; S, 15.54. Found: C, 53.37; H, 9.00; S, 14.57.

2-Buty-2-ethyl-3-phenoxypropanol (unsuccessful). Twenty-three grams (1 mole) of sodium was dissolved with stirring in a solution of 94 gm (1 mole) of phenol in 1000 cc of toluene. To the stirred sodium phenoxide solution was added 400 gm (1.93 mole) of 2-butyl-2-ethyl-trimethylene sulfite and the mixture was refluxed at 114°C for 14 hours. The solid was filtered off and the toluene removed by distillation. Distillation of the residue yielded 303 gm of material: bp 129° - 130°C/12 mm; n^{25}_D 1.4595.

The solid was treated with 500 cc of 3N sodium hydroxide and extracted with toluene. The toluene solution was washed, toluene was removed by distillation, and the residue was distilled. Two fractions were collected: fraction 1, 28 gm, bp 132° - 133°C/12 mm, n^{25}_D 1.4585; fraction 2, 13 gm, bp 137° - 140°C/12 mm, n^{25}_D 1.4582.

The 303 gm and 28 gm distillates were considered to be recovered starting material, an 86% recovery. A similar, but successful, reaction between sodium naphthoxide and ethylene sulfite is reported by Carlson, W. W., and Cretcher, L. H., J. Am. Chem. Soc., 69, 1952 (1947).

Chlorination of 2-butyl-2-ethyltrimethylene sulfite. Chlorine was bubbled with stirring into 204 gm (0.97 mole) of 2-butyl-2-ethyltrimethylene sulfite irradiated internally with ultraviolet light. After the reaction had been carried out for 90 min at 15° - 20°C and then 30 min at 30°C, 100 gm (theory 71 gm) of chlorine had been absorbed. The light yellow product darkened overnight to a deep purple color having a strong odor of sulfur dioxide. The product was unaffected by treatment with 1% hydrochloric acid solution (to hydrolyze the expected chlorosulfuric ester of 2-butyl-3-chloro-2-ethylpropanol). Steam distillation gave 60 gm of an oil, n^{25}_D 1.4845, along with a large amount of non-volatile tars. The oil could not be separated into any definite fractions by distillation through an 8 in. column packed with 4 mm glass helices. The boiling point range was 45° - 85°C/0.5 mm; n^{25}_D 1.4654 - 1.4963. The calculated boiling point is 90°C/0.5 mm (Kinney, C. R., J. Org. Chem., 7, 111 (1942).

2,2-Dimethyl-1-heptanol

1,1-Dimethyl-1-hexanol. This alcohol was prepared in 74%

yield (1538 gm) by the action of n-amylmagnesium chloride on acetone, according to the procedure of Whitmore, F. C. and Williams, F. E., J. Am. Chem. Soc., 55, 406 (1933).

1,1-Dimethyl-1-hexyl chloride. This chloride was prepared in 91% yield (1480 gm) by the action of dry hydrogen chloride on 1,1-dimethyl-1-hexanol at -10°C , according to the procedure of Whitmore, F. C., and Williams, F. E., J. Am. Chem. Soc., 55, 406 (1933).

2,2-Dimethyl-1-heptanol. This alcohol was prepared in an 8% yield (54 gm) by the action of 1,1-dimethyl-1-hexylmagnesium chloride on gaseous formaldehyde according to the procedure of Whitmore, F. C., and Badertscher, D. E., J. Am. Chem. Soc., 55, 1559 (1933).

1-Methylcyclohexylmethanol

4-Carbomethoxy-4-methylcyclohexene. A 3-liter stainless steel bomb was charged with 600 gm (6 moles) of methyl methacrylate (Rohm and Haas), 595 gm (11 moles) of 1,3-butadiene (Matheson) and 6 gm of hydroquinone. The bomb was heated to 185°C in two hours. This temperature should be approached carefully because somewhat above 200°C the reaction proceeds so rapidly that the temperature rises to 500°C in two minutes. After 18 hours at 185°C the bomb was cooled, and the contents were distilled through a 3-ft column packed with 6-mm glass helices. There was obtained 651 gm (70% yield based on methyl methacrylate) of a viscous colorless liquid: bp $71^{\circ} - 72.4^{\circ}\text{C}/13\text{ mm}$, $n^{25}_{\text{D}} 1.4569$. Reported, Roberts, J. D., Jeydel, A. K., and Armstrong, R., J. Am. Chem. Soc., 71, 3248 (1949): bp $64^{\circ} - 65^{\circ}\text{C}/10\text{ mm}$, $n^{20}_{\text{D}} 1.4600$.

1-Methylcyclohexylmethanol. A 3-liter stainless steel bomb was charged with 640 gm (4.2 moles) of 4-carbomethoxy-4-methylcyclohexene and 75 gm of copper chromite catalyst. The bomb was pressured with hydrogen to 2200 psig at 23°C and heated in 4 hours to 235°C . Hydrogen was added as necessary to maintain a pressure of 3000 - 4000 psig at $230^{\circ} - 240^{\circ}\text{C}$. The theoretical amount of hydrogen was absorbed in 6 hours. The bomb was cooled, the catalyst removed from the product by filtration and the product distilled through a 3-ft column packed with 6-mm glass helices. There was obtained 507 gm (94% yield) of a colorless, viscous liquid having a camphor-like odor: bp $85^{\circ} - 86^{\circ}\text{C}/3\text{ mm}$; $n^{25}_{\text{D}} 1.4660$. Anal. Calcd for $\text{C}_8\text{H}_{16}\text{O}$: C, 74.94; H, 12.58. Found: C, 74.86; H, 12.63.

2,2,4-Trimethyl-1-pentanol

2,2,4-Trimethyl-1,3-diacetoxypentane. To a vigorously stirred solution of 876 gm (6 mole) of 2,2,4-trimethyl-1,3-pentanediol in 1600 cc of benzene and 1050 gm (13.4 mole) of pyridine was added dropwise 942 gm (12 moles) of acetyl chloride. The temperature was held below 50°C during the acetyl chloride addition, and the mixture was

finally heated at 90°C for 1.5 hours. The cooled reaction mixture was diluted with 400 cc of benzene, washed free of pyridine hydrochloride, dried over anhydrous sodium sulfate and topped under water pump vacuum. Fractionation through an 8-in. Vigreux column yielded 1380 gm of the diacetate (90%): bp 115° - 116°C/10 mm, n_D^{25} 1.4308.

2, 2, 4-Trimethyl-3-penten-1-yl acetate. 2, 2, 4-Trimethyl-1, 3-diacetoxypentane (1281 gm, 5.57 mole) was dropped through a vertical pyrolysis tube at 494° - 517°C over a period of 17 hours and the effluent was collected under a water-cooled reflux condenser. The temperature for the most part was 496° - 500°C. Nitrogen was passed through the pyrolysis tube at a rate of 200 cc/min. The tube was a pyrex glass tube approximately 25 mm in diameter and 48 in. long, packed with Size 3 solid glass beads over a length of 32 in.; it was insulated and electrically heated over approximately 38 inches with separate heating elements for the top and bottom halves regulated by two powerstats. The temperature was measured by two thermocouples located at distances of approximately 8 in. and 24 in. in the bead bed. The thermocouples were inclosed in a central 63-mm glass thermowell.

The pyrolysis product was fractionated through a 90 x 2.5 cm column packed with 6-mm glass helices. By washing the forerun to remove acetic acid and redistilling the residue, a yield of 644.2 gm of a clear, colorless liquid was obtained: bp 74.5° - 75.5°C/12 mm, n_D^{25} 1.4357. Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.5; H, 10.6. Found: C, 70.0; H, 10.46. Two hundred and forty-one grams of diacetate, bp 112° - 118°C/12 mm, was recovered so that the yield based on unrecovered material was 83.8%.

2, 2, 4-Trimethylpentan-1-ol. Reduction of 2, 2, 4-trimethyl-3-penten-1-yl acetate at room temperature in a Parr Hydrogenation Apparatus using approximately 4% catalyst (palladium, 5% on carbon black) and 30 psig of hydrogen removed all the unsaturation as shown by infrared analysis.

The reduction product was filtered to remove the catalyst and 472 gm was hydrolyzed by refluxing for 5 hours in a solution of 1200 cc of absolute ethanol and 100 cc of water containing 111 gm of sodium hydroxide. The alcohol was removed by distillation, 200 cc of water was added and the top layer was separated and washed free of caustic with saturated salt solution. The alcohol was dried over anhydrous sodium sulfate and vacuum distilled through a 30-in. Vigreux column to yield 346 gm (96%) of 2, 2, 4-trimethylpentan-1-ol, bp 82° - 83°C/30 mm, n_D^{25} 1.4280.

Dehydration of 2, 2, 4-trimethyl-1, 3-pentanediol over Al_2O_3 (unsuccessful). An attempt was made to dehydrate 2, 2, 4-trimethyl-1, 3-pentene-1-ol by passing the diol over activated alumina. The catalyst tube described above in the preparation of 2, 2, 4-trimethyl-3-penten-1-yl

Continued

acetate was used, being charged with 8-mesh activated alumina instead of with glass beads.

In 2 hours 146 gm (1 mole) of 2, 2, 4-trimethyl-1, 3-pentane-diol was passed through the catalyst tube at a top half temperature of 390° - 404°C and a bottom half temperature of 378° - 400°C. It appeared from the powerstat settings that the alumina was a much poorer conductor than the glass beads, which may have resulted in an appreciably hotter than desired temperature for the outside catalyst surfaces.

During the dehydration, a great amount of gas was generated and 20 cc of water was collected (17 cc theory for monodehydration) along with 44.5 gm of liquid product. This liquid product (distillation range 70° - 112°C) on distillation through a 10-in. Vigreux column indicated that none of the desired alcohol was obtained.

Telomerization reaction

A one-liter stainless steel rocking autoclave was charged with 203 gm (6.85 mole) of isobutyric acid, 6 gm of benzoyl peroxide and 196 gm (7 mole) of ethylene. The autoclave was heated at 71° - 73°C for 18 hours. The initial pressure was 1100 psig and the final pressure 900 psig. An initial pressure of approximately 4000 psig was desired. The autoclave was cooled and vented and 649 gm of liquid product was obtained. Vacuum distillation through a 24-in. Vigreux column yielded the following fractions:

Fraction	Yield/gm	BP °C/mm Hg	n ²⁵ D
1	533	66° - 68°/18-19	1.3908
2	13	68° - 88°/16-17	1.3988
3	36.5	95° - 160°/16	1.4325
4	15.5	150° - 176°/16	1.4412
Residue	34		

Fraction 1 was regarded as essentially recovered isobutyric acid and fractions 3 and 4 had acid numbers of 360.5 and 259.3, respectively, which are in the range of the desired octanoic - decanoic acids.

7-Norbornanol

Dimethylfulvene. To a stirred solution of 92 gm (4 mole) of sodium in 1300 cc of absolute ethanol was added at 30° - 40° C in 10 min a solution of 220 gm (3.3 mole) of cyclopentadiene and 193 gm (3.3 mole) of acetone (Baker & Adamson, Reagent grade). The mixture was stirred for 10 min after addition was complete and then poured into 1.5 liters of water. The organic material was taken up by extraction with three 600-cc portions of chloroform, the combined chloroform extracts were washed with two 800-cc portions of water and dried over sodium sulfate. The residue which remained after the solvent and drying agent were removed was fractionated through a 20-in. Vigreux column yielding 249 gm (72%) of an orange liquid: bp 45° - 46° C/11 mm, n_D^{25} 1.5421. Reported [Thiele, J. Ber., 33, 671 (1900)]: bp, 40° C/11 mm.

Reaction of dimethylfulvene and ethylene (unsuccessful).

A one-liter bomb was charged with 106 gm (1 mole) of dimethylfulvene, 350 gm of ethylene and 1 gm of hydroquinone. The bomb was heated at 185° C (4000 psig) for 24 hours, at the end of which time no pressure drop had occurred. Distillation of the contents of the bomb through a 6-in. Vigreux column yielded 90 gm of an orange oil, bp 74° C/15 mm - 150° C/-2 mm, and 18 gm of tar. Since the desired product, 7-isopropylidene norbornylene, was expected to boil below 65° C/15 mm, it was concluded that ethylene did not add to dimethylfulvene in the Diels-Alder manner.

Fractionation of the orange oil through a 3-ft column packed with 4-mm glass helices gave 21 gm of a light-yellow liquid: bp, 107° - 114° C/1 mm; n_D^{25} 1.5281, which is probably the dimer of dimethylfulvene. Anal. Calcd for C₁₆H₂₀: C, 90.50; H, 9.50. Found: C, 89.65; H, 10.00.

2,7-Diacetoxynorbornane. Norbornylene (94 gm, 1 mole) was hydroxylated with performic acid according to the procedures of Kwart, H. and Vosburgh, W. G., J. Am. Chem. Soc., 76, 5400 (1954), to give 135 gm of crude 2,7-dihydroxynorbornane.

A solution of the dihydroxynorbornane, 500 cc of pyridine and 200 cc of acetic anhydride was heated at reflux for 1 hour. The cooled solution was then poured over a mixture of 800 gm of ice and 800 cc of water. The organic material was extracted with four 500-cc portions of ether; the combined ether extracts were washed with two 200-cc portions of 5% hydrochloric acid solution and one 100-cc portion of saturated sodium chloride solution and dried over sodium sulfate. The residue remaining after removal of the drying agent and solvent was fractionated through a 3-ft column packed with 4-mm glass helices to give 166 gm (92% yield based on norbornylene) of a colorless oil: bp 137° - 138° C/12 mm; n_D^{25} 1.4619. Anal. Calcd for C₁₁H₁₆O₄: C, 62.25; H, 7.60; Sap. Eq., 106.12. Found: C, 62.30; N, 7.82; Sap. Eq., 106.1, 106.4.

Contrails

Pyrolysis of 2,7-Diacetoxynorbornane. The pyrolysis was conducted in the apparatus described in preparation of 2,2,4-trimethyl-3-penten-1-yl acetate above. The temperature was maintained at 480° - 500°C during the reaction. The diacetoxynorbornane, 155 gm (0.7 mole), was introduced at the top of the column at a rate of 1 drop/sec and the vapors were flushed through the column by a stream of nitrogen. A total of 127 gm of a dark red liquid was collected in the condenser. A gas, non-condensable in dry ice, was formed which reacted slowly with bromine in carbon tetrachloride and 2% aqueous potassium permanganate. A large amount of tar was formed in the column.

Fractionation of the liquid through a 10-in. Vigreux column gave the following main fractions.

Fraction	Yield/gm	BP °C/mm Hg	n ₂₅ D
1	20	80° - 118°/12	1.3912
2	10	30° - 47° / 12	1.4039
3	6.5	71° - 80°/12	1.4690
4	2.5	90° - 135°/12	1.4822
5	62	135° - 145°/12	1.4624
6	8.2	145° - 170°/12	1.5037
Residue	10		black oil

Fraction 5 was starting material, 40% recovery, indicating that 93 gm (0.44 mole) of diacetoxynorbornane reacted. Fractions 1 and 2 contained 24 gm of acetic acid (theory 26.4 based on pyrolysis of only one acetoxy group). The infrared spectrum of fraction 3 showed an acetoxy group and a cis double bond, and the analysis agrees with that calculated for 7-acetoxynorbornylene. Anal. Calcd for C₉H₁₂O₂: C, 71.03; H, 7.95. Found: C, 71.84; H, 8.44. This represents a 10% yield based on unrecovered material. Fractions 4 and 6 were unidentified, except for the observation that 4 contains a ketonic function.

Catalytic reduction of 2,7-diacetoxynorbornane. A 300-cc steel bomb was charged with 61 gm (0.32 mole) of 2,7-diacetoxynorbornane, 5 gm of Raney nickel catalyst and 500 psig of hydrogen. The bomb was heated to 300°C and held at this temperature for 1 hour. Hydrogen was added once to keep pressure at 750-1000 psig. The bomb was cooled, the catalyst separated by filtration and washed with ethanol. Product and washings were combined and distilled through a 6-in. Vigreux column,

yielding the following fractions:

Fraction	Yield/gm	BP °C/mm Hg	n ²⁵ D
1	23	60 - 80/760	partially solidifies on cooling;
2	13	80 - 117/760	1.3672
3	10	117 - 120/760	1.3777
4	1	25 - 76/13	1.4434
5	8	76 - 81/13	1.4586

Fraction 3 was acetic acid, n²⁵D 1.3718, and fraction 2 was a mixture of ethanol and acetic acid. The solid formed in fraction 1, isolated by filtration, weighed 8 gm, melted at 84° - 85°C and did not react with bromine nor 2% potassium permanganate solution. Properties of bicyclo(2.2.1)heptane have been reported / Thomas, C. L., Ind. Eng. Chem., 36, 310 (1944) /, to be mp, 86° - 87°C; bp, 105°C. The filtrate had n²⁵D 1.3674 and is mostly ethanol.

The analysis for fraction 5 corresponded to that calculated for acetoxynorbornane and represented a 16% yield. Anal. Calcd for C₉H₁₄O₂: C, 70.10; H, 9.15. Found: C, 70.48, H, 9.26.

Hydrolysis of 7-acetoxynorbornane. A mixture of 2 cc of fraction 5 from hydrogenation of 2,7-diacetoxynorbornane and 10 cc of 25% sodium hydroxide solution was heated under reflux for 12 hours. The cooled mixture was then extracted with three 15-cc portions of ether, the combined ether extracts were washed with three 10-cc portions of saturated sodium sulfate solution and dried over sodium sulfate. The semi-solid obtained by removal of solvent and drying agent was crystallized from 8 cc of Skelly solve yielding 1 gm of white crystals. The crystals were sublimed at 60°C/15 mm and melted at 150° - 151.5°C. A mixture with an authentic specimen of exo-2-norbornanol (mp, 128° - 129°C) melted at 126° - 134°C. Anal. Calcd for C₇H₁₂O: C, 74.95; H, 10.79. Found: C, 73.62, H, 10.44.

Esters

Bis(1-methylcyclohexylmethyl) sebacate

A mixture of 108 gm (0.53 mole) of sebacic acid (Paragon), 158 gm (1.1 mole) of 1-methylcyclohexylmethanol, 1 gm of conc sulfuric acid and 50 cc of toluene was heated at reflux under a Dean and Stark trap until 17.5 cc (theory 19 cc) of water had collected. The reaction mixture was cooled and taken up in one liter of ether. The ether solution was

washed with four 100-cc portions of 5% sodium hydroxide solution and six 250-cc portions of water and dried over sodium sulfate. The residue after removal of solvent and drying agent, was fractionated in vacuo through a 10-in. column packed with 4-mm glass helices. There was obtained 166 gm (73% yield) of a colorless oil: bp 215° - 217°C/0.5 mm; n^{25}_D 1.4725. Anal. Calcd for $C_{26}H_{46}O_4$: C, 73.89; H, 10.97. Found: C, 74.17; H, 11.28.

Bis(1-methylcyclohexylmethyl) adipate

A mixture of 87 gm (0.6 mole) of adipic acid (Du Pont), 158 gm (1.25 mole) of 1-methylcyclohexylmethanol, 0.4 gm of conc. sulfuric acid and 60 cc of toluene was heated at reflux under a Dean and Stark trap until 20.5 cc (theory 21.6 cc) of water had collected. The reaction mixture was worked up as described above for the sebacate to yield 160 gm (73% yield) of a colorless oil: bp 186° - 188°C/0.7 mm; n^{25}_D 1.4734. Anal. Calcd for $C_{22}H_{38}O_4$: C, 72.09; H, 10.45. Found: C, 72.90; H, 10.01.

n-Octyl stearate

This compound was prepared for decomposition studies using the isoteniscope.

To a mixture of 142 gm (0.5 mole) of stearic acid and 75 gm (0.577 mole) of n-octyl alcohol was added 0.5 cc of conc. sulfuric acid as a catalyst and sufficient benzene to hold the reflux temperature at 120°C. The water was removed (8.5 cc; theory, 9cc in 45 minutes) using a Dean and Stark trap. The ester was dissolved in ether and washed free of acid. After drying the ether solution over anhydrous sodium sulfate and filtering, the ester was distilled through an 8-in. heated Vigreux column. The fraction (106 gm) boiling at 205° - 207°C/1 mm, n^{25}_D 1.4470, was collected as the desired compound.

Dibenzyl sebacate

To a mixture of 178 gm (1.65 mole) of benzyl alcohol and 151.5 gm (0.75 mole) of sebacic acid was added 0.3 cc of sulfuric acid and sufficient benzene to azeotrope off the water and hold the reflux temperature below 150°C. The water (28 cc; theory, 29 cc) was collected in a Dean and Stark trap in 1 hour of reflux time. The reaction mixture was taken up in ether, washed free of acid and dried over anhydrous sodium sulfate. The solvent was removed under vacuum from the filtered solution and the residue was vacuum distilled through an 8-in. heated Vigreux column. There was collected 180 gm (63% yield) of dibenzyl sebacate: bp 241° - 244°C/1.1 to 1.3 mm; n^{25}_D 1.5173.

Bis(2, 2, 4-trimethyl-1-pentyl) sebacate

To a mixture of 70 gm (0.538 mole) of 2, 2, 4-trimethyl-1-pentanol and 50.5 gm (0.25 mole) of sebacic acid was added 0.5 cc of sulfuric acid and sufficient toluene to azeotrope off the water and hold the reflux temperature below 130°C. The theoretical amount of water (9 cc) was collected, using a Dean and Stark trap. Additional benzene was added and the ester was washed free of acid, dried over anhydrous sodium sulfate, and distilled through an 8-in. heated Vigreux column. There was collected 106.5 gm (92%) of bis(2, 2, 4-trimethyl-1-pentyl) sebacate: bp 207° - 209°C/0.6 mm; n_{D}^{25} 1.4471. Anal. Calcd for $C_{20}H_{50}O_4$: C, 73.3; H, 11.8. Found: C, 73.27; H, 11.76.

Bis(2-ethylhexyl) sebacate

To a mixture of 151.5 gm (0.748 mole) of sebacic acid and 210 gm (1.62 mole) of 2-ethylhexanol was added 0.3 cc of sulfuric acid and sufficient benzene to azeotrope off the water. The water (28 cc) was collected in a Dean and Stark trap. The final temperature was allowed to reach 170°C. Additional benzene was added and the product was washed free of acid, dried over anhydrous sodium sulfate, and vacuum distilled through an 8-in. heated Vigreux column. The fraction distilling at 218.5° - 220.5°C/1.1 to 1.3 mm was collected as the bis-(2-ethylhexyl) sebacate, n_{D}^{25} 1.4485.

Di(1-octyl) isophthalate

A mixture of 66 gm (0.4 mole) of isophthalic acid, 117 gm (0.9 mole) of n-octanol (Matheson, Coleman and Bell), 10 gm of conc. sulfuric acid and 100 cc of toluene was heated at reflux under a Dean and Stark trap until 15 cc of water (theory 14.5 cc) had collected. The reaction mixture was washed with two 100-cc portions of 10% sodium hydroxide solution and one 100-cc portion of water and dried over sodium sulfate. After removal of solvent and drying agent, distillation in vacuo through a 10-in. Vigreux column gave 83 gm (54% yield) of a light-yellow oil: bp 205° - 209°C/0.8 mm; n_{D}^{25} 1.4850. Anal. Calcd for $C_{24}H_{38}O_4$: C, 73.80; H, 9.80. Found: C, 73.83; H, 9.83.

Bis(1-methylcyclohexylmethyl) isophthalate

To a cooled solution of 83 gm (0.65 mole) of 1-methylcyclohexylmethanol in 200 cc of pyridine was added in 10 min 61 gm (0.3 mole) of isophthaloyl chloride. The chloride was prepared in 77% yield by the action of thionyl chloride on isophthalic acid according to Ruggli, P. and Knecht, K., Helv. chim Acta., 27, 1111 (1944). The mixture was then heated under reflux for 3 hours, cooled and poured into one liter of water. The precipitated oil was taken up in 400 cc of benzene and the aqueous phase extracted with two 200-cc portions of benzene. The combined

Contrails

benzene solution was washed with two 200-cc portions of 5% hydrochloric acid solution, two 200-cc portions of 5% sodium carbonate solution and one 200-cc portion of water and dried over Drierite. The residue which remained after the solvent and drying agent were removed gave on distillation in vacuo through a 10-in. Vigreux column 88 gm (75% yield) of a light-yellow oil: bp 215° - 221°C/ 0.4 mm; n_{25}^D 1.5172. Anal. Calcd for $C_{24}H_{34}O_4$: C, 74.57; H, 8.87. Found: C, 74.56; H, 8.86.

Tetrakis(2, 2, 4-trimethyl-1-pentyl) silicate

To a mixture of 87 gm (0.667 mole) of 2, 2, 4-trimethyl-1-pentanol and 29.7 gm (0.143 mole) of tetraethyl silicate was added 0.33 gm (0.0143 mole) of sodium and the temperature was slowly raised to the reflux, a Dean and Stark trap serving to collect the distillate. The distillate collected during 8 hours was 32 cc (theory 33.3), the temperature rising to 190°C in this period. The product was distilled through a 10-in. heated Vigreux column and the fraction distilling at 170° - 185°C/0.7 mm was collected and refractionated. Refractionation gave two fractions: fraction 1, 175° - 180°C/0.77 mm, n_{25}^D 1.4322; Fraction 2, 180° - 182°C/0.7 mm, n_{25}^D 1.4325. The two fractions (57.5 gm; 73.9%) were combined. Anal. Calcd for $C_{32}H_{68}O_4Si$: C, 70.5; H, 12.57. Found: C, 70.38; H, 12.57.

Tetraphenyl silicate

To a solution of 0.4 gm of sodium in 5 cc of anhydrous ethanol was added 63 gm (0.3 mole) of freshly distilled tetraethyl silicate and 113 gm (1.2 mole) of freshly distilled phenol. The temperature of the mixture was raised slowly to 190°C during 4 hours. The distillate, collected in a Dean and Stark trap, measured 62 cc (theory, 75 cc). The product was vacuum distilled through an 8-in. heated Vigreux column. The fraction distilling at 124° - 204°C/0.6 to 1 mm (88 gm) was refractionated and the following fractions were collected:

Fraction	Yield/gm	BP °C/mm Hg	n_{25}^D
1	15	125 - 160 / 0.9	1.5140
2	22	160 - 179 / 0.9	1.5418
3	18	179 - 198 / 1	1.5531
4	31	198 - 204 / 1	1.5680

Fraction 4 quickly solidified and melted at 59° - 60°C. Anal. Calcd for $C_{24}H_{20}O_4Si$: C, 71.9; H, 5.03. Found: C, 71.73; H, 5.02. The highest melting point reported was 53° - 54°C (Report No. 8, Contract No. AF 33(616)-168 by Stanford Research Institute).

Tetra(1-octyl) silicate

To a solution of 0.46 gm (0.02 mole) of sodium in 117 gm (0.9 mole) of *n*-octanol was added 42 gm (0.2 mole) of tetraethyl silicate (Carbide and Carbon). The mixture was heated under reflux until 45 cc (theory 47 cc) of ethanol had distilled, at which time the temperature was 240°C. The residue was distilled in vacuo through a 6-in. Vigreux column yielding 82 gm (80%) of a colorless oil: bp 199° - 204°C/0.3 mm; n^{25}_D 1.4363. Anal. Calcd for $C_{32}H_{68}O_4Si$: C, 70.52; H, 12.58; Si, 5.15. Found: C, 70.54; H, 12.58; Si, 4.98.

Tris(1-methylcyclohexylmethyl) borate

A mixture of 85 gm (0.66 mole) of 1-methylcyclohexylmethanol, 13.5 gm (0.22 mole) of boric acid and 40 cc of benzene was heated at reflux under a Dean and Stark trap until 11.5 cc of water (theory, 11.9 cc) had collected. The solvent was distilled at atmospheric pressure and the residue distilled in vacuo through a 10-in. Vigreux column. There was obtained 64 gm (75% yield) of a colorless oil: bp 170° - 175°C/0.3 mm; n^{25}_D 1.4724. Anal. Calcd for $C_{24}H_{45}O_3B$: C, 73.46; H, 11.55. Found: C, 72.41; H, 11.36.

Tri(1-octyl) borate

A mixture of 8 gm (0.13 mole) of boric acid, 55 gm (0.42 mole) of *n*-octanol and 20 cc of toluene was heated at reflux under a Dean and Stark trap until 7 cc (theory, 7 cc) of water had collected. Distillation in vacuo through a 6-in. Vigreux column gave 34 gm (66% yield) of a colorless oil: bp 164° - 165°C/0.5 mm; n^{25}_D 1.4340.

Tris(2,2,4-trimethyl-1-pentyl) borate

Boric acid (12.4 gm, 0.2 mole) was heated with 2,2,4-trimethyl-1-pentanol (83 gm, 0.637 mole) using benzene to azeotrope off the water at a maximum temperature of 170°C. The product was distilled through an 8-in. heated Vigreux column and 70.5 gm (88.5%) was collected as tris(2,2,4-trimethyl-1-pentyl) borate: bp 144° - 146°C/0.77 mm; n^{21}_D 1.4320. Anal. Calcd for $C_{24}H_{51}O_3B$: C, 72.3; H, 12.9. Found: C, 76.67; H, 14.46.

Tri(1-octyl) phosphate

To a stirred solution of 97 gm (0.75 mole) of *n*-octanol (Matheson, Coleman and Bell), 65 gm (0.82 mole) of pyridine and 120 cc of benzene was added dropwise at 0° - 10°C 38.2 gm (0.25 mole) of phosphorus oxychloride. The mixture was slowly warmed to 90°C, stirred at this temperature for four hours and then cooled. The pyridine hydrochloride was dissolved in 100 cc of water, the organic layer washed with 30 cc of water and dried over sodium sulfate. The residue which remained after the

Contrails

solvent and drying agent were removed was distilled in vacuo through a 6-in. Vigreux column, yielding 40 gm (38%) of a colorless oil: bp 187° - 189°C/0.15 mm; n_{D}^{25} 1.4430. Anal. Calcd for $C_{24}H_{51}O_4P$: C, 66.32; H, 11.83; P, 7.13. Found: C, 66.04; H, 11.63; P, 6.79.

Tris(2,2-dimethyl-1-heptyl) phosphate (unsuccessful)

To a stirred solution of 54 gm (0.37 mole) of 2,2-dimethyl-1-heptanol, 28.5 gm (0.36 mole) of pyridine and 60 gm of benzene was added dropwise 18.4 gm (0.12 mole) of phosphorus oxychloride at -5° - 5°C. The mixture was stirred for 18 hours at room temperature and then for 4 hours at 75°C. The pyridine hydrochloride was dissolved in 40 cc of water, the benzene solution was washed with 10 cc of water and dried over 5 gm of sodium sulfate. The residue which remained after the solvent and drying agent had been removed was distilled in vacuo through a 6-in. Vigreux column. When the pot temperature reached 205°C, the product decomposed rapidly. No tris(2,2-dimethyl-1-heptyl) phosphate was obtained.

Tris(1-methylcyclohexylmethyl) phosphate (unsuccessful)

To a stirred solution of 90 gm (0.7 mole) of 1-methylcyclohexylmethanol, 50 gm (0.63 mole) of pyridine and 100 cc of benzene was added dropwise 30.6 gm (0.2 mole) of phosphorus oxychloride at such a rate that the temperature was held at 0° - 10°C for 2 hours, heated to reflux over a 2-hour period, stirred at reflux for 4 hours and finally allowed to stand at room temperature overnight. From the cooled reaction mixture 61 gm of pyridine hydrochloride (theory, 63.3 gm) was isolated by filtration. The filtered reaction mixture was taken up in 500 cc of benzene, washed with five 50-cc portions of saturated sodium chloride solution and dried over Driertie. The residue which remained after the drying agent and solvent had been removed was distilled in vacuo. When the pot temperature reached 230°C, decomposition occurred with formation of 17 gm of tar. From the dry ice trap there was obtained 30 gm of a clear liquid. This liquid was distilled through a 3-ft column packed with 4-mm glass helices to give 22 gm of a colorless liquid: bp 135° - 136°C; n_{D}^{25} 1.4537. The analysis of a center cut corresponded to that calculated for C_8H_{14} . Anal. Calcd for C_8H_{14} : C, 87.19; H, 12.80. Found: C, 87.31; H, 11.96. The compound reacted with bromine and decolorized a 2% solution of potassium permanganate. The infrared spectrum resembled, but was not identical with, 1-methylcyclohexene, which indicates that 1-ethyl cyclohexene is a probable structure for the product.

Bis(biphenyl) carbonate

To a solution of 168 gm (0.988 mole) of p-hydroxybiphenyl in 600 cc of dioxane was added 22 gm (0.956 mole) of metallic sodium and

Contrails

the mixture was refluxed until all the sodium had dissolved. The dioxane had been previously freed of peroxides and other impurities by refluxing over sodium until no additional precipitate formed and finally was distilled over sodium. The solution was cooled to 50°C and phosgene (49 gm, 0.495 mole) was added to the vigorously agitated solution, with the temperature held below 60°C. After standing overnight the solution was brought to reflux for 1 hour, cooled, and poured into water. The solid carbonate was filtered off, washed with water, and air-dried; crude yield was 60 gm vs a theory of 180.8 gm. Recrystallization from benzene yielded a white crystalline product, mp 195° - 196°C. Rinke, I. J., *Rec. trav. chim.*, 62, 12-16 (1943) reports a melting point of 193°C.

Bis(nonylphenyl) carbonate

Twenty-three grams (1 mole) of sodium was dissolved by refluxing in a solution of 220 gm (1 mole) of nonylphenyl in 500 cc of dioxane, which had been purified by refluxing and distilling over sodium to remove peroxides and other impurities. When essentially all of the sodium had dissolved, phosgene was passed in to a weight gain of 50 gm (0.5 mole). On addition of the phosgene, a precipitate formed immediately. The reaction was refluxed for 6.5 hours and to the cooled solution was added 500 cc of ethyl ether. The precipitated sodium chloride was removed by filtration. The solvents were removed under vacuum and the product was twice fractionated through an 8-in. heated Vigreux column. The product is a very viscous, straw-colored liquid: bp 258° - 263°C/1 mm; n_{D}^{25} 1.5127. PB Report 574 reports isononylphenyl carbonate boils at 260° - 278°C/2 mm.

Poly(bisphenol A phenylphosphonate)

A mixture of dichlorophenylphosphine oxide (121.8 gm, 0.625 mole) and 145.35 gm of bisphenol A was heated for 11.5 hours at 170° - 190°C. Pea-size portions of powdered tin were added after 2.8 and 10 hours of heating. Water pump vacuum was applied for 1 hour, and the product was poured into an evaporating dish where it crystallized to a brownish, brittle resin. The product is soluble to the extent of 20% in tricresyl phosphate.

Poly(resorcinol phenylphosphonate)

A mixture of 97.45 gm (0.5 mole) of dichlorophenylphosphine oxide and 56.1 gm (0.51 mole) of resorcinol was heated with stirring for 2 hours at 140° - 150°C. The temperature was raised to 170° - 180°C, a pea-size portion of powdered tin was added and the heating was continued for 5 hours and for 1 hour longer under waterpump vacuum. The molten mass was poured into an evaporation dish where it crystallized to a brittle amber resin. This resin is soluble to the extent of 10% in tricresyl phosphate and Aroclor 1248.

Poly(hydroquinone phenylphosphonate)

A mixture of 121.8 gm (0.625 mole) of dichlorophenylphosphine oxide and 70.12 gm (0.6375 mole) of hydroquinone was heated at 140° - 168°C for 2.5 hours. The temperature was raised to 170° - 180°C and a portion of powdered tin (pea-size) was added and heating was continued for 2 hours; a second portion of powdered tin (about 1/3 the size of the first) was added, and heating was continued for four additional hours. During the last hour of heating 10 mm of vacuum was applied to remove the hydrochloric acid. The amber-colored resin is soluble (10%) in tricresyl phosphate but less than 10% soluble in Aroclor 1248.

Ethers

Bis(p-bromophenyl) ether

To a stirred solution of 680 gm (4 mole) of diphenyl ether and 1 gm of iodine in 700 cc of carbon disulfide was added dropwise during 2 hours 475 cc (8.7 mole) of bromine. The reaction mixture was allowed to stand overnight and then the solvent was stripped off under a water pump. The residue was distilled in vacuo through a 10-in. Vigreux column, yielding 1188 gm (90% yield) of a colorless solid: mp 58° - 60°C. Reported [Hoffmeister, Ann., 159, 210 (1871)]: mp 59° - 60°C.

Bis(p-phenoxyphenyl) ether

A stirred mixture of 282 gm (3 mole) of phenol, 112 gm (2 mole) of potassium hydroxide and 70 cc of toluene was refluxed vigorously under a Dean and Stark trap until 37 cc of water had been removed. Then the toluene was distilled, the temperature was raised to 200°C and 164 gm (0.5 mole) of bis(p-bromophenyl) ether and 10 gm of copper powder was added. A vigorous reaction took place, carrying the temperature to 245°C. The reaction mixture was stirred at 245°C for 4 hours and then poured into 500 cc of water. The organic material was taken up in 1.5 liters of chloroform and the chloroform solution was washed with four 300-cc portions of water and dried over Drierite. The residue which remained after the drying agent and solvent had been removed was distilled in vacuo through a 10-in. Vigreux column, yielding 130 gm (75%) of a tan solid: mp 107° - 109°C; bp 215° - 221°C/1mm.

1,4-Bis(4-ethylphenoxy)benzene

A stirred mixture of 267 gm (2.2 mole) of p-ethylphenol (Eastman), 112 gm (2.0 mole) of potassium hydroxide and 50 cc of toluene was heated at reflux under a Dean and Stark trap until 42 cc of water had been collected. The toluene was distilled, the temperature was raised to 200°C and 117 gm (0.5 mole) of p-dibromobenzene and 8 gm of copper powder were added.

Contrails

After the initial vigorous reaction the mixture was stirred at 250°C for 3.5 hours and then poured into a mixture of 500 gm ice, 500 cc water and 50 gm potassium hydroxide. The organic material was taken up by extraction with three 400-cc portions of ether, the combined ether extracts were washed with one 200-cc portion of 10% sodium hydroxide solution and three 300-cc portions of water and dried over sodium sulfate. The residue which remained after the drying agent and solvent were removed was distilled in vacuo through a 10-in. Vigreux column and yielded 109 gm (69%) of a tan solid: mp 52° - 54°C; bp 195° - 200°C/0.6 mm. Anal. Calcd for C₂₂H₂₂O₂: C, 82.98; H, 6.97. Found: C, 83.22; H, 7.03.

1,4-Bis(3,5-dimethylphenoxy)benzene

A mixture of 175 gm (1.43 mole) of 3,5-dimethylphenol (Shell Development Co.) and 73 gm (1.3 mole) of potassium hydroxide was heated at 120°C and 15 mm pressure for 30 min. Then 75 gm (0.32 mole) of p-dibromobenzene (Eastman) and 5 gm copper powder were added and the mixture was stirred at 240°C for 4 hours. The hot mixture was poured into 400 cc of water and the organic material was taken up by extraction with three 500-cc portions of ether. The combined ether extract was washed with three 200-cc portions of 10% potassium hydroxide solution and two 200-cc portions of water and dried over sodium sulfate. The residue which remained after the drying agent and solvent were removed was distilled in vacuo through a 10-in. Vigreux column. There was obtained 70 gm (69% yield based on p-dibromobenzene) of a solid: mp 95° - 100°C; bp 180° - 185°C/0.4 mm. Anal. Calcd for C₂₂H₂₂O₂: C, 82.98; H, 6.97. Found: C, 83.12; H, 7.03.

4,4'-Bis(1-methylcyclohexylmethoxy)x,x,x',x'-tetrachlorobiphenyl

A mixture of 72 gm (0.2 mole) of Aroclor 1260, 77 gm (0.6 mole) of 1-methylcyclohexylmethanol, 17.6 gm (0.44 mole) of sodium hydroxide and 100 cc of toluene was heated at reflux under a Dean and Stark trap. The temperature was increased gradually from 140° - 220°C over an 18-hour period by removing toluene, at which time 7.8 cc (theory, 8 cc) of water had collected. The reaction mixture was taken up in 100 cc of benzene washed successively with 150 cc of water, 100 cc of 5% sodium hydroxide, and 100 cc of saturated sodium chloride solution and dried over sodium sulfate. The residue which remained after solvent and drying agent had been removed was distilled in vacuo through a 6-in. Vigreux column. There was obtained 73 gm (68%) of a yellow glass: bp 250° - 310°C/0.3 mm. Anal. Calcd for C₂₈H₃₄O₂Cl₄: C, 61.77; H, 6.29; Cl, 26.05. Found: C, 60.08; H, 5.98; Cl, 27.89.

Bis/p(3-pyridoxy)phenyl/ether

A stirred mixture of 95 gm (1 mole) of 3-hydroxypyridine (Aldrich Chemical), 50 gm (0.9 mole) of potassium hydroxide and 50 cc

Control

of toluene was refluxed under a Dean and Stark trap until 18 cc of water had been collected. The toluene was distilled, the temperature was raised to 170° C and 98 gm (0.3 mole) of bis(p-bromophenyl) ether and 5 gm of copper powder were added. After the initial reaction, the mixture was stirred at 240° C for 4 hours and then poured into 500 gm of ice. The organic material was taken up in 1.5 liters of chloroform and the chloroform solution was shaken with sodium sulfate and treated with charcoal. The residue which remained after the chloroform had been stripped off was distilled in vacuo through a 10-in. Vigreux column, yielding 32 gm (30% yield based on bis(p-bromophenyl) ether of a tan solid: mp 66° - 68° C; bp 240° - 245° C/0.4 mm. Anal. Calcd for C₂₂H₁₈O₂N₂: C, 73.74; H, 5.06; N, 7.82. Found: C, 74.29; H, 4.68; N, 8.41.

3-n-Pentadecylphenylphenyl ether

A stirred mixture of 121 gm (0.4 mole) of 3-n-pentadecylphenol (Irvington Chemicals), 20 gm (0.35 mole) of potassium hydroxide and 50 cc of toluene was heated at reflux under a Dean and Stark trap until 8 cc of water had been collected. The toluene was distilled, the temperature was raised to 180° C and 47 gm (0.3 mole) of bromobenzene and 5 gm of copper powder were added. After the initial reaction the mixture was stirred at 240° C for two hours, and then cooled to 70° C and poured into 500 cc of 5% potassium hydroxide solution. The organic material was taken up by extraction with four 300-cc portions of ether, and the combined ether extract was washed with two 300-cc portions of 10% sodium hydroxide solution and three 300-cc portions of saturated sodium sulfate solution and dried over sodium sulfate. The residue which remained after the solvent and drying agent were removed was distilled in vacuo through a 10-in. Vigreux column and gave 86 gm (65% yield) of a light-yellow solid: mp 30° - 32° C; bp 211° - 214° C/0.7 mm. Anal. Calcd for C₂₇H₄₀O: C, 85.21; H, 10.59. Found: C, 85.18; H, 10.50.

Cyclohexylphenyl phenyl ether

This reaction yielded a mono derivative instead of the desired di-substituted diphenyl ether.

To a stirred solution of 170 gm (1 mole) of diphenyl ether in 500 cc of carbon disulfide was added 150 gm (1.27 mole) of aluminum chloride followed by 326 gm (2 mole) of cyclohexyl bromide added dropwise at room temperature. The reaction mixture was stirred for 5 hours and then poured onto ice. Sufficient ethyl ether was added to facilitate washing the mixture free of acid. The solvent was removed under water pump vacuum and the residue was twice fractionated through a 10-in. heated Vigreux column. After the first fractionation most of the product remained as a soft, sticky, black, undistillable residue.

Contrails

On the second fractionation, three straw-colored oily fractions were collected:

Fraction	Yield/gm	BP, °C/mm Hg	n^{25}_D
1	48	154 - 161/1 to 1.2	1.5695
2	10.5	161 - 193/1.1 to 1.3	1.5691
3	13.0	193 - 217/1.3	1.5672

Anal. of fraction 1, Calcd for cyclohexyldiphenyl ether: $C_{18}H_{20}O$:
C, 85.6; H, 7.98. Found: C, 85.85; H, 8.08.

Bis(p-diphenylether)-1,4-butane (unsuccessful)

This reaction yielded no material which could be regarded as the desired compound.

To a vigorously stirred solution of 340 gm (2 mole) of diphenyl ether in 800 cc of carbon disulfide was added 300 gm (2.25 mole) of aluminum chloride followed by the dropwise addition at room temperature of 64 gm (0.5 mole) of 1,4-dichlorobutane over a period of 6 hours. The reaction was stirred for 5 hours and poured onto ice. It was taken up in ether, washed free of acid, and the solvent was removed under water pump vacuum. The residue gave two fractions on vacuum fractionation: fraction 1, 190 gm, bp $128^\circ - 130^\circ C/15$ mm, n^{25}_D 1.5780; fraction 2, 34 gm, bp $130^\circ - 131^\circ C/15$ mm, n^{25}_D 1.5773. These two fractions were probably diphenyl ether: bp $130^\circ C/15$ mm; n^{25}_D 1.5781. The viscous residue was very black.

Di(dodecyl)diphenyl ether

Dodecylchloride (205 gm, 1.0 mole) was added dropwise with stirring at $40^\circ - 45^\circ C$ to a solution of 85 gm of diphenyl ether (0.5 mole) in 300 cc of carbon disulfide containing 72 gm of aluminum chloride (0.54 mole). Stirring was continued for 6 hours at $40^\circ - 45^\circ C$ after which time the reaction mass was poured onto ice. Sufficient ether was added to produce top layer separation and the ether solution was washed free of acid. After drying over anhydrous sodium sulfate the ether and carbon disulfide were removed under water pump vacuum, and the residue was vacuum distilled through an 8-in. electrically heated Vigreux column. After two fractionations, two reddish-colored liquid fractions were collected. Fraction 1: 42 gm, bp $194^\circ - 198^\circ C/0.5$ mm, n^{27}_D 1.5245; Anal. Calcd for monododecyldiphenyl ether, $C_{24}H_{34}O$: C, 85.1; H, 10.12. Found: C, 85.59; H, 10.17. Fraction 2: 20 gm, bp $198^\circ - 212^\circ C/0.5-0.8$ mm, n^{27}_D 1.5205. Residue, 80 gm, decolorized with charcoal; n^{27}_D 1.5066; Anal. Calcd for didodecyldiphenyl ether,

C₃₆H₅₈O: C, 85.2; H, 11.5. Found: C, 85.24; H, 10.9.

Hexapropyldiphenyl ether

n-Propylchloride (247.8 gm, 3.15 mole) was added dropwise with stirring to a solution of 85 gm (0.5 mole) of diphenyl ether dissolved in 300 cc of carbon disulfide containing 75 gm (0.562 mole) of aluminum chloride. During the addition the temperature remained at 25°C without cooling. The reaction was stirred for 5 hours and heated at 45°C for 4 hours, after which time it was poured onto ice, taken up in ether and washed free of acid. After the mixture was dried over anhydrous sodium sulfate, the solvent was removed under water pump vacuum and the product was vacuum fractionated through an 8-in. heated insulated Vigreux column. There were collected two fractions of a viscous red oil: fraction 1, 86 gm, bp 164° - 167°C/0.8 mm; fraction 2, 30 gm, bp 167° - 196°C/0.8 mm. Anal. of fraction 2, Calcd for hexapropyldiphenyl ether, C₃₀H₄₆O: C, 85.2; H, 10.97. Found: C, 84.17; H, 10.21; S, 0.26.

The trace of sulfur probably accounts for the mercaptan-like odor.

Triamylbiphenyl

To a stirred solution of 154 gm (1.0 mole) of biphenyl dissolved in 400 cc of carbon disulfide containing 6 gm of aluminum chloride was added dropwise 265 gm (2.5 mole) of *n*-amyl chloride. The reaction was stirred at reflux for 2 hours and then poured onto ice. Sufficient ethyl ether was added to give top layer separation and the solution was washed free of acid, dried over anhydrous sodium sulfate and topped under water pump vacuum to remove the solvents. Two vacuum fractionations through an 8-in. electrically heated insulated Vigreux column yielded:

Fractions	Yield/gms	BP, °C/mm	n _D ²⁸
1	36.0	127 - 139/0.4	1.5540
2	21.0	139 - 151/0.4	1.5432
3	104.5	155 - 161/0.45	1.5377
4	40.0	163 - 168/0.45	1.5345
5	46.0	168 - 175/0.45	1.5321 ^{29°}
6	31.0	176 - 187/0.45	1.5310 ^{30°}

Infrared analyses of fraction 3 indicated the alkyl groups were straight chains, both rings were substituted and *p* and *m* substitution was present. Anal. Calcd for triamylsubstitution, C₂₇H₄₀: C, 88.93; H, 11.06. Found: Fraction 3, C, 89.75; H, 10.91; Fraction 6, C, 89.55; H, 11.11.

Decomposition of bis(biphenyl) carbonate

Di(biphenyl)carbonate (29 gm, 0.793 mole) was heated for 20 hours at 380°C using refluxing *m*-terphenyl as the heating medium. The carbon dioxide generated was collected in Ascarite. The Ascarite gained 2.051 gm and the sample lost 2.2 gm. The theory for total decomposition is 3.49 gm. The sample was 63% decomposed.