Amorphous *m*-Phenoxylenes as Potential Lubricants

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THE RESULTS described were obtained in a study of materials for potential use as thermally stable, radiation-resistant lubricants. This program was not completed and has been dormant for over a year. In spite of the incomplete state of the data, they would appear of interest, if only to corroborate and extend previously announced results of similar investigations (*6, 9*).

The stated objective at the inception of this program, in late 1955, was the preparation and evaluation of base stocks for lubricants usable at 750° to 1000° F. in a radiation environment. These requirements were so severe that no materials then known could be utilized. Indeed, only a few classes of aromatic compounds were theoretically capable of providing likely candidate materials.

In selecting a material to serve as the base stock, primary consideration was given only the structural factors affecting liquid range and stability towards heat and nuclear radiation. The relatively poor thermal stability of aliphatic groups resulted in a search for a lubricant base stock from among wholly aromatic compounds such as polyaryls, aryl ethers, and arylsilanes. This selection was reinforced by the observation that, broadly speaking, the order of radiation stability parallels the order of thermal stability.

The insistence on wholly aromatic compounds leads to serious problems concerning the liquid range. The high molecular weights required to attain a sufficiently high boiling point also cause a concurrent, although not necessarily linear, increase in melting point. This tendency is particularly pronounced in the aromatic series. It was predicted that this difficulty could be surmounted by resorting to benzene derivatives linked exclusively through the meta positions. This prediction was based on the general observation that meta-substituted compounds have lower melting points than their ortho- and para-isomers. Furthermore, the lower melting points of the *p*-phenyl ethers as contrasted to the *p*-polyphenyls suggested that the goal of low-melting compounds might be realized in the *m*-phenyl ethers. In addition, arylsilanes of sufficient molecular dissymmetry may have relatively low melting points (*7, 11*). It was therefore concluded that unsymmetrical arylsilanes carrying *m*-phenoxylene substituents would afford low-melting materials.

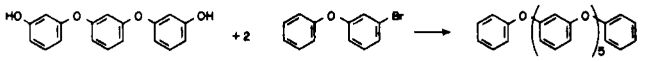
Accordingly, poly(*m*-phenoxylene) of the type $C_6H_5O(m\text{-}C_6H_4O)_nC_6H_5$, *m*-polyphenyls, and *m*-phenoxyphenylarylsilanes were synthesized. Data were obtained on flow points, boiling points, and thermal stabilities of most of the compounds. Some lubricity determinations were also made.

RESULTS

Poly(*m*-phenoxylene). These compounds were prepared by the Ullmann reaction of an aryl bromide with the potassium salt of a phenol in the presence of catalytic quantities of copper. Reaction temperatures varied from 175° to 250° C. and reaction times from 1 to several hours.

Three generalized reaction schemes for the preparation of intermediates and final products were attempted: reaction of a monohydric phenol with a monobromo compound; reaction of a monohydric phenol with a dibromo compound; and reaction of a dihydric phenol with a monobromo compound.

The first scheme includes the reaction of *m*-bromophenol with itself or with phenol, while the second includes the reaction of this compound with *m*-dibromobenzene. The third scheme was found to be largely impracticable. Thus, resorcinol failed to react under various conditions and the only partially successful application of this scheme was in the reaction of the dihydric phenol (I) to give II.


I
II

Here the final product exhibited lowered thermal stability, as shown by decomposition rates. Furthermore, residual hydroxyl content was indicated in the infrared spectrum of II. These observations do not necessarily imply that any dihydric phenol is a poor choice of starting material, since it is conceivable that compound I was contaminated with (isomeric ?) side-reaction products.

Compound I used in the above synthesis was prepared by the reaction of *m*-methoxyphenol and *m*-dibromobenzene. In all cases in which *m*-methoxyphenol was used as a starting material, the ultimate products showed relatively poor thermal stability and indications of residual hydroxyl content. The exact nature of the difficulty encountered in the use of *m*-methoxyphenol is not known at this time. One indication of the possible source of trouble is the observation that *m*-methoxyphenol and potassium hydroxide yield *m*-dimethoxybenzene and therefore, presumably, resorcinol. It has also been suggested (*8*), that part of the difficulty may be due to a rearrangement involving transfer of the methyl group from the oxygen atom to one of the ring carbon atoms. A third potential source of difficulty lies in carbon-carbon, rather than carbon-oxygen, coupling to give an isomeric product still containing a phenolic hydroxyl.

The physical constants and decomposition rates for the poly(*m*-phenoxylene) compounds are listed in Table I. The data presented in this table are "best" values.

Arylsilanes. The arysilanes were prepared mainly by the reaction of the appropriate lithium aryl with either a silane or, in a few cases, a chlorosilane. *o*-Biphenylyllithium and *p*-biphenylyllithium were prepared directly from lithium and the corresponding bromo compound in a manner analogous to the preparation of phenyllithium (*1*). All other lithium derivatives were prepared by metal-halogen interchange from the corresponding bromo compound and *n*-butylithium (*2*).

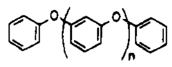
Physical constants and decomposition rates for the arylsilanes are given in Table II.

***m*-Polyphenyl.** The *m*-polyphenyl was prepared by decomposition of the mono-Grignard derivative of a *m*-dihalobenzene with catalytic quantities of cobaltous chloride.

Initially the major problem seemed to be that of preventing the average molecular weight from reaching too high a value, but this problem was solved by the addition of monobromobenzene as a chain stopper. All the products contained residual amounts of halide which proved to be virtually impossible to remove completely and which apparently lowered the thermal stability.

Attempts to isolate pure compounds by fractional distillation at reduced pressure were unsuccessful, so that

Table I. Physical Constants and Thermal Stabilities of Poly(*m*-phenoxylene)

Compound, 	Flow Point, °F.	B. Pt., ° F. at Various Pressures, Mm.				Decomposition Temperature, ° F. *dp/dt*	
		10	100	500	760	0.001 mm. Hg/sec.	0.014 mm. Hg/sec.
n = 1	136[a](58° C.)				698[b]		
n = 2	10[c]				865[d]		
n = 3	54	644	824	985	1030[e]	735	833
n = 4	67	678	870	1050	1112[e]	703	806
n = 5	80	790	975	1146	1202[e]	743	830

[a] Melting point. [b] Value determined in open test tube. [c] Distillation Products Industries has recently announced the availability of this material in the solid form with m. pt. 35° to 40° C. [d] Calculated value. [e] Extrapolated value.

Table II. Physical Constants and Thermal Stabilities of Arylsilanes

Compound	M. Pt. (*m*) or Flow Pt. (*f*), ° F.	B. Pt.,° F. at Various Pressures, Mm.				Decomposition Temperature, ° F. *dp/dt*	
		10	100	500	760	0.001 mm. Hg/sec.	0.014 mm. Hg/sec.
o-Biphenylyl-*p*-biphenylyldiphenylsilane	270 (*m*)(132° C.)	652	832	1004	1060[a]	760	850
o-Biphenylyl-*m*-phenoxyphenyl-diphenylsilane	130 (*f*)	631	802	954	1004[a]	712	814
m-Phenoxyphenyltriphenylsilane	98 (*f*)				960[a]		
Bis(*m*-phenoxyphenyl)diphenylsilane	110 (*f*)	690	831	958	990[a]	690	763
Tris(*m*-phenoxyphenyl)phenylsilane	110 (*f*)						
Tetrakis(*m*-phenoxyphenyl)silane	112 (*f*) 212 (*m*)(100° C.)						
[3-(3′-Phenoxyphenoxylene)phenyl]-triphenylsilane	111 (*f*)	633	832	1025	1087[a]	615	705

[a] Extrapolated value.

Table III. Thermal Stabilities of Various Aromatic Compounds

Compound	Decomposition Rate, *dp/dt* = 0.014 Mm. Hg/Sec. at ° F.
A. Polyphenyl	
p-Quaterphenyl	826[a]
m-Poly(phenyls) (mixed polymers containing 2% by weight halide)	734[b]
B. Tetraarysilanes	
p-Biphenylylytriphenylsilane	799[a]
o-Biphenylyl-*p*-biphenylyl-diphenylsilane	850[b]
o-Biphenyloxytriphenylsilane	815[b]
o-Biphenylyl-*m*-phenoxyphenyl-diphenylsilane	814[b]
Bis(*m*-phenoxyphenyl)diphenylsilane	763[b]
C. Poly(phenoxylene)	
[Phenoxybi(*p*-phenoxylene)]benzene or bis(*p*-phenoxyphenyl) ether	824[c]
[Phenoxy-*m*-, *p*-bi(phenoxylene)]benzene or *m*-phenoxyphenyl-*p*-phenoxyphenyl ether	821[c]
[Phenoxytri(*m*-phenoxylene)]benzene	832[b]
[Phenoxytetra(*m*-phenoxylene)]benzene	806[b]
[Phenoxypenta(*m*-phenoxylene)]benzene	830[b]

[a] Reference (*5*). [b] Present work. [c] Reference (*4*).

distillates containing mixtures of polyphenyls were used for the determination of properties. A typical mixture, distilled over a temperature range calculated to include *m*-penta-, hexa-, septa-, and octaphenyl, contained 2% by weight of halide (calculated as chloride) and had a flow point of 84° C. (183° F.) By comparison, the crystalline melting points of *m*-penta-, hexa-, and octaphenyl are 117°, 147°, and 129° C. (*3*), respectively. The mixture is glasslike (but not brittle) at room temperature; no crystallization has been observed after a period of over 1 year.

DISCUSSION

Thermal Stability. As thermal stability is greatly affected by the presence of trace amounts of impurities, due care was exercised in the preparation, purification, and evaluation of the materials. Nevertheless, the limitations of the experimental method are such that it is questionable whether the accuracy of the decomposition temperatures is greater than ±25° F.

The results obtained in this work, and by others (*6*, *9*), indicate that aromatic compounds of the type of polyphenyl, polyphenoxylene, and tetraarylsilanes have thermal decomposition rates (pressure rise) of 0.014 mm. of mercury per second in the range of 800° to 850° F. Table III shows a list of compounds in the three classes and indicates that within the limits of experimental error there is no major difference in thermal stability in these classes. Moreover, Table III illustrates the vitally important points that meta-substitution does not exert any more unfavorable influence on thermal stability than does para-substitution, and tetraarylsilanes are neither more nor less stable than other wholly aromatic compounds—i.e., in a silane structure, the silicon atom exerts no unusual influence on the stability of the rest of the compound.

Liquid Range. Of the two factors which determine liquid range, the boiling point and the melting point, the latter is the characteristic which is more influenced by molecular configuration. Some variation in boiling point is noted, of course, due to differences in molecular structure, but these variations are generally of a lower order of magnitude than those observed in the melting point. Since aromatic compounds in general have markedly high melting points, the subject of influence of structure on this property received a large share of attention.

It was postulated that meta-disubstituted benzene derivatives, particularly ethers and silanes, might possess markedly low melting points. This postulate has been shown to be correct, inasmuch as the poly(*m*-phenoxylenes), with the exception of *m*-bisphenoxybenzene, are all liquids as indicated by the flow points given in Table I. In contrast, the corresponding poly(*p*-phenoxylenes) are crystalline compounds with melting points ranging from 110° C. for the ether with four benzene rings to 173° C. for the one with six benzene rings.

The marked influence of the *m*-phenoxylene unit is also exemplified in the silane series. The amorphous character conferred by this moiety is strikingly illustrated by comparison of the properties of *o*-biphenylyl-*p*-biphenylyldiphenylsilane, *o*-biphenylyl-*m*-phenoxyphenyldiphenylsilane, and bis(*m*-phenoxyphenyl)diphenylsilane. The first compound is a crystalline solid melting at 132° C. (270° F.) while the other two are amorphous solids with flow points of 130° and 110° F., respectively.

The higher flow points of the silanes as compared to those of the ethers is ascribed to the presence of the tetra-substituted silicon atom which confers a "branched-chain" effect.

Oxidation Stability. Conventional oxidation-corrosion tests were not made. However, in order to define the lower temperature at which such testing should begin, some preliminary experiments involving thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed. Figure 1 shows the results for TGA runs of $C_6H_5O\text{-}(m\text{-}C_6H_4O)_4C_6H_5$ in atmospheres of argon and a mixture of oxygen and nitrogen. The plots of weight change *vs.* temperature indicate that in both atmospheres the samples begin to lose weight at a detectable rate in the 350° to 360° C. (660° to 680° F.) region. Figure 2 shows the DTA results for the same compound in atmospheres of argon and air, respectively. The plot for the run in air indicates that an appreciable exothermic reaction begins at about 350° C. (660° F.). The plot for the run in argon is somewhat difficult to interpret, but indicates an endothermic reaction beginning at 300° or 400° C. depending on the base line which is chosen.

Isoteniscope studies on this compound indicate a decomposition rate (dp/dt) of 0.001 mm. Hg per second at 373° C., a temperature which lies in the same region in which noticeable changes are observed in DTA and TGA.

The results found by DTA, TGA, and isoteniscope measurements make it appear that oxidation will be of concern only in temperature regions at which thermal decomposition will occur.

Lubricity. The results of some Shell-4-ball wear tests on some silanes and one poly(*m*-phenoxylene) are given in Table IV. The average wear scar values given in the table are considerably higher than those found in similar tests on compounded diesters, pentaerythritol esters, chlorinated phenylsiloxanes, naphthenic petroleum fraction, and alkylarylsilanes, the values for which are in the range of 0.3 to 0.7 (*10*).

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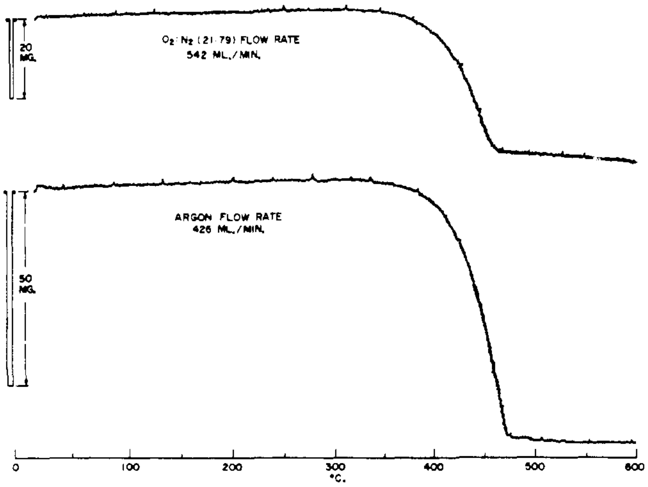

Figure 1. Thermogravimetric analysis of $C_6H_5O(m\text{-}C_6H_4O)_4C_6H_5$
Temperature rise. 150° C./hr.

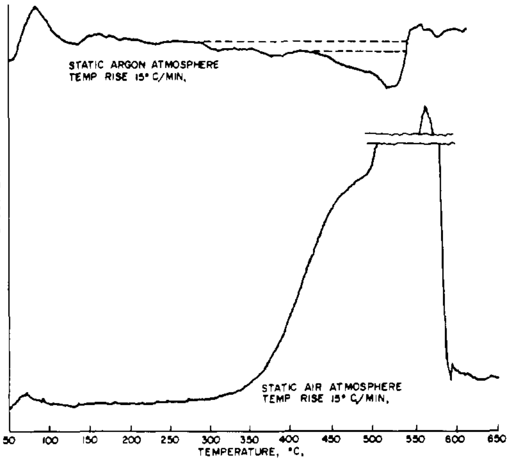

Figure 2. Differential thermal analysis of $C_6H_5O(m\text{-}C_6H_4O)_4C_6H_5$

Table IV. Shell 4-Ball Wear Tests

Speed. 600 r.p.m. Specimens. M-1 tool steel

Material	Load, Kg.	Av. Wear Scar, Mm. 500° F.	700° F.
Silanes,[a] duration 30 min.			
2-Thienyltriphenylsilane	10	1.86	1.52
	50	2.13	1.65
p-Biphenylyltriphenylsilane[b]	10	...	2.4
2-Biphenyloxytriphenylsilane	10	...	2.53
Poly(*m*-phenoxylene),[c] duration 1 hr.			
$C_6H_5O(m\text{-}C_6H_4O)_3C_6H_5$	10	...	1.42

[a] Silane tests conducted by S.F. Murray, Bearing and Lubricant Center, General Engineering Laboratory, General Electric Co., Schenectady, N. Y.

[b] Sample courtesy Leonard Spialter, Chemistry Research Laboratory, Wright Air Development Command, Wright-Patterson Air Force Base, Ohio.

[c] *m*-Phenoxylene test conducted by H.G. Wilson, Flight Propulsion Laboratory, General Electric Co., Evendale, Ohio.

LITERATURE CITED

(1) Adams, Roger, "Organic Reactions," Vol. VI, p. 352, Wiley, New York, 1951.
(2) *Ibid.*, p. 353.
(3) Alexander, R.L., *J. Org. Chem.* 21, 1464 (1956).
(4) Blake, E.S., Hammann, W.C., Abstracts 135th Meeting, ACS, p. 11-L, 1959.
(5) Blake, E.S., Edwards, J.W., Hammann, W.C., Reichard, T., *WADC Tech. Rept.* **54-532**, Part III, Table 6, p. 43, Monsanto Chemical Co., Dayton, Ohio, April 1957.
(6) Blake, E.S., Edwards, J.W., Hammann, W.C., Reichard, T., Quarterly Progr. Rept., Table 3, pp. 11-13, Feb. 10 to May 10, 1957, Monsanto Chemical Co., Dayton, Ohio.
(7) Gilman, Henry, *et al.*, *WADC,Tech. Rept.* **53-426**, Parts I-V, Iowa State College, Ames, Iowa, 1953-1958.
(8) Mahoney, C.L., Barnum, E.R., Kerlin, W.W., Sax, K.J., Saari, W.S., Abstracts 135th Meeting, ACS, p. 14-Q, 1959.
(9) Mahoney, C.L., Saari, W.S., Sax, K.J., Kerlin, W.W., Barnum, E.R., Williams, P.H., Quarterly Progr. Rept. No. 1, p. 13, March-May 1958, Shell Development Co., for Wright Air Development Command, Emeryville, Calif.
(10) Schwartz, A.A., personal communication, General Engineering Laboratory, General Electric Co., Schenectady, N. Y., 1959.
(11) Spialter, Leonard, Priest, D.C., Harris, C.W., *J. Am. Chem. Soc.* 77, 6227 (1955).

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