This compound, m.p. 135°, was prepared using a procedure analogous to the preparation of the two preceding mercuric chloride addition compounds.

Anal. Calcd. for $C_{20}H_{48}Cl_2HgS_2Si_2$: Si, 8.2; C, 35.3; H, 7.1. Found: Si, 7.9; C, 34.4; H, 6.6.

Hydrogen sulfide, solvents, and other reagents were purchased from the usual sources. *Spectro grade iso-octane* was purchased from Phillips Petroleum Company. All were found to possess satisfactory physical constants. Molecular refractions were calculated using the data of Warrick.[19]

BUFFALO, N. Y.

---

[19] E. L. Warrick, *J. Am. Chem. Soc.*, **68**, 2455 (1946).

[CONTRIBUTION FROM THE CHEMICAL DIVISION, DENVER RESEARCH INSTITUTE, UNIVERSITY OF DENVER]

Alkylpolyphenyls. I. 4′-Alkyl-*m*-terphenyls[1]

JOSEF J. E. SCHMIDT, JOHN A. KRIMMEL, AND THOMAS J. FARRELL, JR.[2]

Received August 17, 1959

A series of 4′-alkyl-*m*-terphenyls have been prepared for potential use as high temperature hydraulic fluids and lubricants. An improved synthesis of 4′-bromo-*m*-terphenyl has been developed.

In connection with a study on the preparation of potential hydraulic fluids and lubricants of high thermal stability and wide liquid range, the authors have prepared a number of alkylbiphenyls and alkylterphenyls. Compounds of the alkylpolyphenyl type were chosen for investigation as it was expected that the well established thermal stability of such "chain-type" aromatic structures as biphenyl and the terphenyls might also be found to some extent in their derivatives.

Although biphenyl and the terphenyls are rather high melting compounds, it is known, especially from the study of biphenyl derivatives, that the introduction of an alkyl group into the nucleus greatly extends the liquid range of the compound. While numerous alkylbiphenyls are known, only a very few alkyl terphenyls have been reported; however the information available for the biphenyls is sufficient to make certain correlations concerning the substitution of alkyl groups on the terphenyl nucleus.

A study of the alkylbiphenyls revealed that substitution of an alkyl group at any position in the molecule lowered the melting point of the parent compound, substitution in the 2- or 3-position producing much greater lowering than substitution in the 4-position. This same depression was postulated for substitution in the terminal nucleus of the terphenyl molecule and was confirmed by the few examples reported in the literature. It was further postulated that substitution in the inner ring of a terphenyl molecule should depress the melting point; however, a literature survey revealed only one such compound, 5′-methyl-*m*-terphenyl,[3] and this compound, perhaps because of its molecular symmetry, had a melting point of 130°, somewhat higher than that (87°) of *m*-terphenyl. It was also evident that increased symmetry of the substituted alkyl group would lead to an increased melting point for the corresponding alkyl derivative. For example, melting points have been reported for certain 2-alkylbiphenyls as follows: *n*-propyl, −11.26°[4]; isopropyl, 24.46°[4]; *n*-butyl, −9.65° and −13.71°[4]; isobutyl, glass;[5] *sec*-butyl, 8.12°[5]; and *tert*-butyl, 31–34°.[6] This trend has been confirmed by our work which shows that the normal alkyl derivatives generally have lower pour points than the branched alkyl derivatives.

In considering the terphenyls, the *ortho* and *meta* isomers are much more attractive starting materials, from the standpoint of providing derivatives of wide liquid range, than is the *para* isomer due to the much lower melting points of the first two isomers.

Among the alkylpolyphenyls which have been prepared in this laboratory are 2-, 3-, and 4-monoalkylbiphenyls; 2- and 3-monoalkyl-*o*-terphenyls; 2-, 3-, 4-, and 4′-monoalkyl-*m*-terphenyls and 2-, 3-, and 4-monoalkyl-*p*-terphenyls. Other alkylterphenyls have been prepared by the Friedel-Crafts reaction, which by its inherent nature usually gave products of indefinite composition. While the 2- and 3-substituted alkyl derivatives will be described in a subsequent publication, the 4′-alkyl-*m*-terphenyls are discussed in this communication.

The 4′-alkyl-*m*-terphenyl series was selected for the investigation of inner ring substitution due to the availability of 4′-bromo-*m*-terphenyl as a starting material. The bromination of *m*-terphenyl to give 4′-bromo-*m*-terphenyl has been re-

---

[1] This research was supported in whole by the United States Air Force under contract AF 33(616)-2939, monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

[2] Denver Research Institute Fellow 1956–57.

[3] C. Gastaldi and F. Cherchi, *Gazz. Chim. Ital.*, **45**, 11, 251 (1915); *Chem. Abstr.*, **10**, 1637 (1916).

[4] I. A. Goodman and P. H. Wise, *J. Am. Chem. Soc.*, **72**, 3076 (1950).

[5] I. A. Goodman and P. H. Wise, *Natl. Advisory Comm. Aeronaut. Tech. Note*, 2260, 29 pp. (1951); *Chem. Abstr.*, **45**, 7986 (1951).

[6] J. I. G. Cadogan, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 3352 (1954).

ported by Olgiati,[7] Cook and Cook,[8] and Bradsher and Swerlick.[9] Bradsher and Swerlick also prepared this compound from 4′-amino-*m*-terphenyl by the Sandmeyer method. The various procedures reported gave products which melted at 31°,[7] 36.5–37°,[9] or which did not solidify.[8] Bradsher and Swerlick also showed the presence of 4-bromo-*m*-terphenyl in the product prepared by the Cook and Cook method.

We first prepared 4′-bromo-*m*-terphenyl by the methods of Olgiati, and Cook and Cook, obtaining similar results to those reported. A change in procedure and more important, the purification of the product by fractional distillation through a glass-helices-packed column gave material which ultimately melted at 58°. This disagreement with the published values led us to the purification of 4′-bromo-*m*-terphenyl prepared by both the Olgiati, and Cook and Cook methods, and from both methods we obtained material agreeing with the melting point claimed by us for 4′-bromo-*m*-terphenyl. We have also studied the composition of various samples of 4′-bromo-*m*-terphenyl by gas chromatography methods which show that unless the product is carefully purified, it will contain impurities which will cause low melting points. Preparations by the Olgiati method contain *m*-terphenyl as the principal impurity, whereas preparations by the Cook and Cook method in addition, contain a higher boiling impurity, apparently the 4-bromo isomer first noted by Bradsher and Swerlick.

We also found that conditions existing during the solidification of 4′-bromo-*m*-terphenyl affected the melting point. At times products were obtained which melted over a range (for example 40–53°). Remelting and seeding with a crystal of 57° melting product gave complete solidification with a melting point of 53–54°.

Bradsher and Swerlick reported that in one preparation of 4′-bromo-*m*-terphenyl (from 4′-amino-*m*-terphenyl by the Sandmeyer method) the product first obtained melted at 40–42° and after recrystallization from ether-ethanol solution, the product attained a constant melting point of 36.5–37°. They stated that the initial high melting point was probably due to a small quantity of high melting impurity. We have not repeated this preparation. We have not been able to lower the melting point of any sample of 4′-bromo-*m*-terphenyl by recrystallization.

The preparation of a 4′-alkyl-*m*-terphenyl from 4′-bromo-*m*-terphenyl was accomplished by converting the bromide into the corresponding lithium or magnesium bromide compound, adding the desired aldehyde or ketone, dehydrating the resulting alcohol, and finally selectively hydrogenating the alkenyl-*m*-terphenyl to the desired 4′-alkyl-*m*-terphenyl.

Of the 4′-alkyl-*m*-terphenyls prepared, all had pour points (most of the derivatives did not crystallize) or melting points considerably below that of the parent hydrocarbon. This lowering of pour point combined with elevated boiling points has given compounds of wide liquid range.

The thermal stability of these compounds was studied by heating in a nitrogen atmosphere, distilling in air, and determining vapor pressure using either a Smith-Menzies type[10] or a Greene type[11] isoteniscope. A typical compound, 4′-*n*-heptyl-*m*-terphenyl showed a 4.7% weight loss when heated in a nitrogen atmosphere for 24 hr. at 370°. It could be distilled in air with only a slight change in refractive index. Vapor pressure measurements[12] showed the first deviation from the straight line plot of log pressure *vs.* 1/T at 262°. This temperature is considered to be the point of initial thermal decomposition. For comparison, di-2-ethylhexyl sebacate showed an initial thermal decomposition point of 290°. Other 4′-alkyl-*m*-terphenyls showed slightly higher initial decomposition points. The 4′-alkyl-*m*-terphenyls, as well as other alkylpolyphenyl compounds have shown good radiation stability.[12]

EXPERIMENTAL[13]

4′-Bromo-m-terphenyl. (a) *By the method of Olgiati.* *m*-Terphenyl, m.p. 87°, 138 g. (0.6 mole) was brominated in carbon disulfide solution as described by Olgiati.[7] Fractional distillation of the crude product through a column[14] gave 50-g. forecuts containing both *m*-terphenyl and 4′-bromo-*m*-terphenyl, and 75 g. of 4′-bromo-*m*-terphenyl, m.p. 54.5–56°, 40% yield. From a different preparation in which recrystallization instead of distillation was used, a product similar to that described by Olgiati was obtained.

(b) *By the method of Cook and Cook.* Molten *m*-terphenyl (Santowax M) was brominated at 90–95° as described by Cook and Cook.[8] Distillation using a 20 × 200 mm. Vigreux column gave fractions which either did not solidify or which developed small amounts of white crystals on prolonged standing. Similar results were noted by Cook and Cook. Fractionation of a portion of this product through a column[14] gave two fractions of interest, both of which were solidified by seeding with 4′-bromo-*m*-terphenyl (m.p. 57°): 1. indefinite m.p. 30–45° and 2. m.p. 50–53°, which on recrystallization from absolute ethanol gave a m.p. of 54–55°. These fractions are further described in the section on gas chromatography.

---

[7] L. Olgiati, *Ber.*, **27**, 3385 (1894).

[8] W. A. Cook and K. H. Cook, *J. Am. Chem. Soc.*, **55**, 1212 (1933).

[9] C. K. Bradsher and I. Swerlick, *J. Am. Chem. Soc.*, **72**, 4189 (1950).

[10] A. Smith and A. W. C. Menzies, *J. Am. Chem. Soc.*, **32**, 1412 (1910).

[11] H. Greene, *Anal. Chem.*, **28**, 428 (1956).

[12] A detailed discussion of the use of vapor pressure measurements to determine thermal stability and radiation stability of alkylpolyphenyls will be subjects covered in future publications from this laboratory.

[13] All melting points and boiling points are uncorrected. Microanalyses by Huffman Microanalytical Laboratories, Wheatridge, Colo.

[14] 600 × 25mm., vacuum jacketed, packed with 1/8″ multiturn glass helices.

(c) *By direct bromination in ethylene dichloride.* To a stirred solution of 1380 g. (6 mole) of *m*-terphenyl (Santowax M)[15] and 1100 ml. of ethylene dichloride, heated to about 80°, were added several ml. of bromine, several iron nails (freshly cleaned with hydrochloric acid) and several drops of water (to promote the formation of hydrogen bromide). As soon as the bromine vapors disappeared, the reaction mixture was cooled to room temperature. A total of 815 g. (5.1 moles) of bromine[16] was added over a period of 16 hr. The reaction mixture was cooled in an ice-water bath and filtered to remove about 75 g. of a red-brown solid. Recrystallization of this material from ethanol gave white plates, m.p. 235–236° which did not depress the melting point of 4-bromo-*p*-terphenyl, which was prepared by the bromination of *p*-terphenyl. The filtrate was steam distilled to remove ethylene dichloride and hydrogen bromide. The steam distillation residue was washed several times with water by decantation and dried by heating under reduced pressure. The crude bromide was purified by distillation through a column.[14] Two distillations were used, the first to separate the product into a low boiling yellow forecut, containing some *m*-terphenyl, 50 g.; *m*-terphenyl, 150 g.; intermediates, 60 g.; crude 4′-bromo-*m*-terphenyl, 1280 g.; and higher boiling residue, 150 g. Careful refractionation of the crude 4′-bromo-*m*-terphenyl through the same column gave the following fractions: 1. *m*-terphenyl, 40 g., m.p. 87°, b.p. 162°/1.3 mm.; 2. intermediate fractions containing both *m*-terphenyl and 4′-bromo-*m*-terphenyl, 215 g., b.p. 162–183/1.5 mm.; 3. 4′-bromo-*m*-terphenyl, 970 g., b.p. 183°/1.5 mm., m.p. 55–56°; and 4. higher boiling material and residue, 55 g.

The composition of the residue is still under investigation. It has however, been shown to contain 4-bromo-*p*-terphenyl. This compound was isolated from the ethanol extraction of the distilled residue as white plates, m.p. 236–237° which did not depress the melting point of known 4-bromo-*p*-terphenyl. This compound was also converted into the lithium derivative by *n*-butyllithium and hydrolyzed to give a product which, after recrystallization from ethanol, melted at 213° and did not depress the melting point of a known sample of *p*-terphenyl (m.p. 215°).

The principal product, 4′-bromo-*m*-terphenyl, was obtained as an almost colorless, viscous, liquid which slowly solidified. It usually melted over a 1° range between the temperatures of 53 and 57°; however, sometimes a sample was obtained which started to melt as low as 35°. This could be converted into the higher melting material. Specifically, a sample of 4′-bromo-*m*-terphenyl melting at 45–52° was remelted and seeded with a small crystal of this compound melting at 57°. The resulting solid had a melting point of 52–54°. Recrystallization of 4′-bromo-*m*-terphenyl, m.p. 56–57°, twice from absolute ethanol, once from hexane, and finally from absolute ethanol gave a product which melted at 58°. This is somewhat higher than the values reported in the literature, 31°,[7] 36.5–37°.[9]

During the course of this investigation and related work approximately 40 kg. of 4′-bromo-*m*-terphenyl have been prepared by this method.

Anal. (m.p. 58°). Calcd. for $C_{18}H_{13}Br$: C, 69.92; H, 4.24; Br, 25.85. Found: C, 69.86; H, 4.29; Br, 25.90.

Anal. (m.p. 54–55°). Found: C, 70.45; H, 4.09; Br, 25.50.

(d) *Analysis by gas chromatography.*[17] Various samples of 4′-bromo-*m*-terphenyl (I) were analyzed using a 4-ft. column packed with polyethylene, a carrier gas of helium and temperatures of 305–320°. Samples were shown to contain, in addition to I, the following impurities: *m*-terphenyl (II), and an unidentified product higher boiling than I (possibly 4-bromo-*m*-terphenyl) (III), in the amounts indicated. Percentages were estimated from the areas beneath each peak. I prepared by Olgiati method, 11% of II, 2% of III. I prepared by Olgiati method and purified by fractional distillation, m.p. 54.5–56°, trace of II and 0.5% of III. I prepared by Cook and Cook method, purified by fractional distillation and melting 30–45°, 7.5% of II, and 3.5% of III. I, Cook and Cook as preceding and m.p. 50–53°, trace of II and 9% of III. I, m.p. 52–53°, 0.4% of II and 1.7% of III. I, m.p. 58°, no trace of either II or III. I, to which 1.99% of II had been added, 2.2% of II.

4-Bromo-p-terphenyl. *p*-Terphenyl (Santowax P) was brominated in a manner similar to that described for *m*-terphenyl, with the exception that bromination was carried out in refluxing ethylene dichloride. The product was purified by distillation and recrystallization from benzene and from ethanol, m.p. 234°; lit.[1] 228°, 230–232°.[18]

4′-Alkyl-m-terphenyls. These compounds were prepared from 4′-bromo-*m*-terphenyl by the same method which is described in general terms below with specific results being given in Tables I and II.

(a) *Alkyl-4′-m-terphenylylcarbinols.* To a stirred solution of 4′-bromo-*m*-terphenyl dissolved in diethyl ether (300 ml. per mole of bromide), cooled to 0°, was added an ethereal solution containing the exact molar equivalent of *n*-butyllithium (molarity determined by the double titration method)[19] at a rate of 2 moles per hr. A yellow-white precipitate formed after about one third of the *n*-butyllithium solution had been added. To the 4′-*m*-terphenylyllithium so formed was added the molar equivalent of the desired aldehyde or ketone to form an alkyl- or dialkyl-4′-*m*-terphenylylcarbinol. With the exception of 5-nonanone, 6-undecanone, and 7-tridecanone, which were prepared by the oxidation of the corresponding alcohols, and *n*-dodecanal which was prepared by the dehydrogenation of *n*-dodecanol, all aldehydes and ketones were commercially available, but were purified by distillation prior to use. For several preparations, 4′-*m*-terphenylylmagnesium bromide in diethyl ether or tetrahydrofuran was used; however the reaction in diethyl ether proceeded slowly and the reaction in tetrahydrofuran was sometimes (but not always) difficult to initiate. We have prepared 4′-*m*-terphenylylmagnesium bromide in tetrahydrofuran in 89% yield. We feel that this reagent has not been fully exploited.

The alcohols so prepared were usually purified by distillation. For those alcohols which were not purified by distillation, the lower boiling products were removed by distillation to approximately the boiling point of the alcohol.

(b) *4′-Alkenyl-m-terphenyls.* The alkyl- or dialkyl-4′-*m*-terphenylylcarbinol was dehydrated by heating with 5% by weight of anhydrous copper sulfate for a period of 1 to 2 hr., during which time the reaction temperature reached a maximum of 250° and approximately 80% of the theoretical amount of water was condensed and collected. The crude 4′-alkenyl-*m*-terphenyl was filtered to remove solid materials and purified by distillation. The *cis* and *trans* isomers were not separated.

(c) *4′-Alkyl-m-terphenyls.* The 4′-alkenyl-*m*-terphenyl was selectively hydrogenated to the 4′-alkyl-*m*-terphenyl in a rocking autoclave using Raney nickel catalyst, pressures of 1000 to 1500 p.s.i. and temperatures up to 80°. If only a small amount of the 4′-alkenyl-*m*-terphenyl was available, hexane was used as a solvent. The 4′-alkyl-*m*-terphenyls were purified by distillation through a 20 × 200 mm. Vigreux column. All 4′-alkyl-*m*-terphenyls were prepared in 20- to 40-g. quantities with the exception of the heptyl and

---

[15] Both Santowax M and *m*-terphenyl, obtained by the distillation or recrystallization of Santowax M were used as starting materials to give similar final products.

[16] In this run a deficiency of bromine was used in an effort to reduce polybromination. In later runs, the theoretical amount was used without causing an objectionable increase in polybromination.

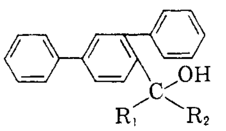
[17] We thank Mr. George E. Bohner, Jr., for the gas chromatography analyses.

[18] J. v. Braun, G. Irmisch, and J. Nelles, *Ber.*, **66B**, 1471 (1933).

[19] H. Gilman and A. E. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).

TABLE I

ALKYL-*m*-TERPHENYLYLCARBINOLS AND ALKENYL-*m*-TERPHENYLS



					Alkenyl-*m*-terphenyl			
R_1	R_2	Yield, %	B.P.	Mm.	Yield, %	B.P.	Mm.	n_D^{25}
C_2H_5	H	60	181	0.3	87	174	0.5[a]	
n-C_4H_9	H	60	203–207	0.25	78	186–188	0.3	
n-C_5H_{11}	H	79	234–237	0.8	52	200–210	0.7	
n-C_6H_{13}	H	85	214	0.4	66	170–174	0.3	1.6144[b]
n-C_8H_{17}	H	72	229	0.65[c]	94	218–222	0.6	1.6088[d]
n-$C_{10}H_{21}$	H	67	241	0.5[e]	81	235	0.6	1.5965
n-$C_{11}H_{23}$	H	45	Not distilled		77	238–242	0.4[f]	
Cyclohexyl	H	[g]			54	192–194	0.35[h]	
C_2H_5	C_2H_5	83	180–183	0.35	80	172	0.45	
n-C_3H_7	n-C_3H_7	60	194–199	0.6	79	166	0.15	1.6114
n-C_4H_9	n-C_4H_9	63	214	0.5	90	176	0.15	1.5985
n-C_5H_{11}	n-C_5H_{11}	50	Not distilled		73	193	0.3	1.5857
n-C_6H_{13}	n-C_6H_{13}	82	Not distilled		87	200	0.1	1.5779
C_2H_5	n-C_4H_9	42	185–192	0.4	66	170–174	0.3	1.6144
CH_3	n-C_6H_{13}	69	225–230	1.2	90	182–189	0.3	1.6037
CH_3	n-$C_{15}H_{31}$	81	Not distilled[i]		87	240–242	0.1	1.5570

[a] M.p. 102°. [b] *Anal.* Calcd. for $C_{25}H_{26}$: C, 91.97; H, 8.03. Found: C, 92.00; H, 8.00. [c] n_D^{25} 1.5882. [d] *Anal.* Calcd. for $C_{27}H_{30}$: C, 91.47; H, 8.53. Found: C, 91.58; H, 8.47. [e] n_D^{25} 1.5763. [f] M.p. 44–46°. [g] Carbinol dehydrated during preparation. [h] M.p. 85–88°. [t] M.p. 48–50°.

TABLE II

4'-ALKYL-*m*-TERPHENYLS

Alkyl Group	B.P.	Mm.	n_D^{20}	Pour Point[a]	Formula	Carbon, %		Hydrogen, %	
						Calcd.	Found	Calcd.	Found
n-C_3H_7-	153	0.3	1.6204	−7	$C_{21}H_{20}$	92.60	92.78	7.40	7.33
n-C_5H_{11}-	202–204	1.2	1.6050[b]	−15	$C_{23}H_{24}$	91.95	91.91	8.05	8.16
n-C_7H_{15}-	194–195	0.4	1.5921	−23	$C_{25}H_{28}$	91.41	91.35	8.59	8.60
n-C_9H_{19}-	212–214	0.55	1.5781	−26	$C_{27}H_{32}$	90.95	90.70	9.05	9.10
n-$C_{12}H_{25}$-	232	0.4	1.5675[b]	−23	$C_{30}H_{38}$	90.39	90.35	9.61	8.60
Cyclohexyl-[c]	196	0.5		75–77[d]	$C_{24}H_{24}$	92.26	92.33	7.74	7.47
$(C_2H_5)_2CH$-	164	0.3	1.6203	16	$C_{23}H_{24}$	91.95	92.10	8.05	7.60
$(n$-$C_3H_7)_2CH$-	185	0.6	1.6109	−12	$C_{25}H_{28}$	91.41	91.48	8.59	7.95
$(n$-$C_4H_9)_2CH$-	182	0.3	1.5953	−2	$C_{27}H_{32}$	90.95	91.63	9.05	8.39
$(n$-$C_5H_{11})_2CH$-	194	0.3	1.5749	−7	$C_{29}H_{36}$	90.48	90.44	9.52	9.26
$(n$-$C_6H_{13})_2CH$-	199	0.15	1.5641[b]	10	$C_{31}H_{40}$	90.23	90.18	9.77	9.62
$(C_2H_5)(n$-$C_4H_9)CH$-	168–170	0.3	1.5938	7	$C_{25}H_{28}$	91.41	91.51	8.59	8.49
$(CH_3)(n$-$C_6H_{13})CH$-	184	0.25	1.5944	−7	$C_{26}H_{30}$	91.17	91.16	8.83	8.55
$(CH_3)(n$-$C_{15}H_{31})CH$-	241–242	0.2		45[d]	$C_{35}H_{48}$	89.68	89.50	10.34	10.28

[a] Pour points were determined in °F. to the nearest 5° and converted into °C. for consistency with this table. [b] n_D^{20}. [c] Two other n-alkyl derivatives were prepared but are not included in this table due to unsatisfactory analyses: n-hexyl-, b.p. 206–210°/1 mm., n_D^{25} 1.6141, p.p. −4°; n-undecyl-, b.p. 219°/0.5 mm., n_D^{20} 1.5590, p.p. −32°. [d] Melting point.

nonyl derivatives which were prepared in kilogram quantities.

(d) *Viscosities of 4'-alkyl-m-terphenyls.* The following viscosity data were obtained: viscosity c.s. at 100°F., 210°F., and ASTM slope 100–210°F. For *n*-heptyl- 64.89, 6.18, 0.85; *n*-nonyl- 72.88, 6.70, 0.84; *n*-undecyl- 64.43, 7.62, 0.77; (1-amylhexyl)- 245.76, 10.13, 0.92; and (1-butylamyl)- 394.68, 11.76, 0.99.

Thermal stability tests. (a) *By heating in inert atmosphere.* A 5-g. sample of the 4'-alkyl-*m*-terphenyl was placed in a sample tube, and fitted with a condenser and receiver to collect any low boiling material which might be formed. The sample tube was evacuated, filled with nitrogen, and kept under a slight positive pressure of nitrogen for the duration of the test. The sample tube was heated in an Aroclor bath at 370° for 24 hr. The following 4'-alkyl-*m*-terphenyls were tested: *n*-hexyl-, *n*-heptyl-, (1-methylheptyl)-, *n*-dodecyl-, (1-methylhexadecyl)-, and (1-hexylheptyl)-. All samples showed slight darkening at the end of the heating period and respective weight losses as follows: 4.7%, 7.2%, 8.0%, 0.8%, 3.8%, and 8.7%.

(b) *By distilling at atmospheric pressure in air.* Small samples of selected 4'-alkyl-*m*-terphenyls were distilled in air at 630 mm. All samples showed some decomposition, which was particularly evident for compounds with more than seven carbon atoms in the alkyl group. On distilling 4'-heptyl-*m*-terphenyl, n_D^{25} 1.5905, the first distillate was obtained at 368° with the major portion distilling at 396–400°. The distillate was light yellow in color, n_D^{25} 1.5925, and had a slight odor similar to that usually associated with aliphatic olefins. On distilling 4'-*n*-dodecyl-*m*-terphenyl, a fraction boiling at 140–164° was collected. It had an "aliphatic olefin" odor. Infrared spectra analysis showed the presence of a compound with terminal C=C stretching. The residue distilled to 367°. Other derivatives tested included the following: *n*-hexyl-, (1-methylheptyl)-, and (1-hexylheptyl)-.

(c) *By measurement of vapor pressure.* Vapor pressures were determined by use of the isoteniscope.[10, 11] The sample was placed in the isoteniscope and degassed at pressure of 1×10^{-4} mm. or less. In the Smith-Menzies-type isoteniscope, enough liquid was distilled to form a manometer in the capillary tube; this is, of course, unnecessary when using the Greene-type isoteniscope. The isoteniscope was heated in a furnace at a rate of -2° per min. Vapor pressure measurements were made by observing the nitrogen pressure in the system which (1) for the Smith-Menzies-type is required to balance the liquid height in the two arms of the isoteniscope manometer, and (2) for the Greene-type is required to force the liquid from the capillary tube to a level equal with the surrounding liquid. The logarithm of the vapor pressure was plotted against the reciprocal of the absolute temperature for each vapor pressure determination. Through the resulting points, two straight lines could be drawn, the first through points representing lower temperatures at which the sample was undecomposed; and the second, of steeper slope, through points representing higher temperatures at which some decomposition products were present. The intersection of these lines is taken as the point of initial thermal decomposition. The following decomposition temperatures were obtained for 4′-alkyl-*m*-terphenyls: *n*-amyl- 278°, *n*-heptyl- 262°, (1-methylheptyl)- 276°, and (1-methylhexadecyl)- 310°.

DENVER 10, COLO.