

ate under a simple fractionating column. Slow distillation was continued until no more acetone could be detected in the distillate (four to six hours). The remaining isopropyl alcohol was removed *in vacuo*, the residue hydrolyzed by pouring into an excess of cold dilute hydrochloric acid, and the product isolated by extraction with ether, washing with water, drying and distillation. The properties of the lactones as obtained by fractionation through a 20-plate column appear in Table II.

**Hydrogenation of Lactones.**—All of the lactones in Table II were hydrogenated in absolute ethanol with Adams platinum oxide catalyst at room temperature. The uptake of hydrogen varied with pressure and concentration of the solution, being greatest (close to 2 moles) in dilute solution at atmospheric pressure. The experiments

summarized in Table III were run at 40 p. s. i. in 5–10% solution. There is evidence from titration experiments for the presence of some saturated lactones in the fore fractions in the distillation of the hydrogenation products of the two cyclohexenyl lactones, but no pure products were obtained.

### Summary

4-(1-Cyclohexenyl)- and 4-(1-cyclopentenyl)-butyrolactones and 5(1)-cyclohexenyl- and 5-(1-cyclohexenyl)-valerolactones have been synthesized. Hydrogenation of these lactones leads to hydrogenolysis of the lactone rings.

NEW HAVEN, CONN.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

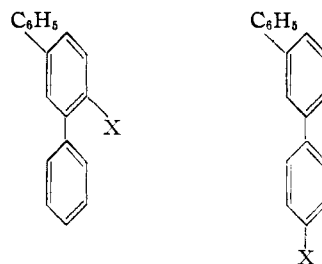
## Reactions in the *m*-Terphenyl Series<sup>1</sup>

By C. K. BRADSHER AND I. SWERLICK

In earlier work,<sup>2,3</sup> it was demonstrated that 2-benzoyl- and 2-benzoyl-4,5-dimethylbiphenyl are useful intermediates in the synthesis of certain phenylphenanthrene derivatives. Since it appeared probable that the closely related 4'-benzoyl-*m*-terphenyl (I)<sup>4</sup> might serve as a convenient starting material for the synthesis of some new diphenylphenanthrenes, experiments directed toward the synthesis of this previously unknown ketone (I) were undertaken. These experiments, together with others bearing on the problem of orientation in the *m*-terphenyl series, are the subject of the present communication.

Olgiati<sup>5</sup> showed that the bromination of *m*-terphenyl in carbon disulfide yielded a crystalline monobromo derivative (m. p. 31°) to which, on the basis of oxidation products, he assigned the structure of 4'-bromo-*m*-terphenyl (II). From this bromo compound, by heating with cuprous cyanide, we have obtained 4'-cyano-*m*-terphenyl (III). The reaction of this nitrile with phenylmagnesium bromide afforded the desired 4'-benzoyl-*m*-terphenyl (I) in 62% yield. The nitrile (III), on hydrolysis, yielded the new 4'-*m*-terphenoic acid (IV). This acid was found to lose water when treated with concentrated sulfuric acid, yielding a compound which is presumably 3-phenylfluorenone.

Cook and Cook,<sup>6</sup> by brominating molten *m*-terphenyl, obtained a liquid preparation which, on oxidation, gave evidence of only 4'-bromo-*m*-terphenyl (II). That this compound is the major product present is borne out by our observation that this liquid preparation gives fairly good yields of 4'-cyano-*m*-terphenyl. It is noteworthy that hydrolysis of the higher-boiling fraction from the



- |  |   |
|--|---|
| I, X = COC <sub>6</sub> H <sub>5</sub> | VI, X = COC <sub>6</sub> H <sub>5</sub> |
| II, X = Br                             | VII, X = Br                             |
| III, X = CN                            | VIII, X = CN                            |
| IV, X = COOH                           | IX, X = COOH                            |
| V, X = NH <sub>2</sub>                 | X, X = NH <sub>2</sub>                  |

nitrile synthesis yielded a small quantity of 4-*m*-terphenoic acid<sup>7</sup> (IX) (identified as the methyl ester), the first evidence that direct bromination of *m*-terphenyl may yield some of the unknown 4-bromo-*m*-terphenyl (VII). The previous disagreement<sup>5,6</sup> concerning the melting point of 4'-bromo-*m*-terphenyl, and the present evidence for the existence of 4-bromo- (VII) and 4-cyano-*m*-terphenyl (VIII) in our reaction products, made it seem worthwhile to prepare pure samples of these compounds.

The two halides (II and VII) were prepared from the appropriate amines by the Sandmeyer reaction. The 4'-bromo-*m*-terphenyl (II) prepared from a pure sample of 4'-amino-*m*-terphenyl<sup>8</sup> (V) melted several degrees higher than the product<sup>5</sup> obtained by direct bromination.

The 4-amino-*m*-terphenyl (X), prepared from the known<sup>7</sup> 4-*m*-terphenoic acid by the Curtius reaction, was converted to the corresponding bromo compound (VII). The new 4-cyano-*m*-terphenyl (VIII) was obtained by dehydration of the corresponding amide by means of phosphorus trichloride.

Goodman and Lowy<sup>7</sup> have investigated the

(1) This work was aided in part by a grant from the Duke University Research Council.

(2) Bradsher, *THIS JOURNAL*, **66**, 45 (1944).

(3) Bradsher and Wissow, *ibid.*, **68**, 2149 (1949).

(4) *Chemical Abstracts* numbering.

(5) Olgiati, *Ber.*, **27**, 3385 (1894).

(6) Cook and Cook, *THIS JOURNAL*, **55**, 1212 (1933).

(7) Goodman and Lowy, *ibid.*, **60**, 2155 (1938).

(8) Wardner and Lowy, *ibid.*, **54**, 2510 (1932).

Friedel and Crafts reaction between benzoyl chloride and *m*-terphenyl and have shown the product to be 4-benzoyl-*m*-terphenyl (VI). While this evidence would appear to be conclusive, the directness of the Friedel and Crafts method warranted a restudy of the reaction to determine whether the desired 4'-benzoyl-*m*-terphenyl (I) might not be an undetected by-product. The Friedel and Crafts reaction in nitrobenzene, essentially as described by Goodman and Lowy, yielded a complex mixture from which, by repeated recrystallization from methanol, two isomeric ketones, m. p. 120.5-121.5° and 112-112.5°, were obtained. Judging from the yields of crude product, the higher melting ketone was present in larger quantity (29%) than the lower (10%). The lower melting ketone was identical in every respect with 4'-benzoyl-*m*-terphenyl, but the higher melting ketone melted about four degrees higher than had been reported (117°) by Goodman and Lowy<sup>7</sup> for 4-benzoyl-*m*-terphenyl (VI). That the higher melting point observed was not due to the presence of disubstitution products was demonstrated by synthesis of 4-benzoyl-*m*-terphenyl (VI) by the Friedel and Crafts reaction between 4-*m*-terphenoyl chloride and benzene. It was found that the oxime of VI undergoes the Beckmann rearrangement to yield 4-benzoyl-amino-*m*-terphenyl.

In the hope of finding a method suitable for the preparation of the 4'-benzoyl-*m*-terphenyl (I) in a pure condition, we undertook to apply the Perrier<sup>9</sup> procedure in the benzoylation reaction. When the benzoyl chloride-aluminum chloride complex was dissolved in a small volume of carbon disulfide, and *m*-terphenyl added, no precipitate was observed and none appeared even after the mixture was refluxed for four hours and allowed to stand overnight in the refrigerator. Decomposition of the solution with ice and hydrochloric acid, and a single recrystallization of the product afforded almost pure 4'-benzoyl-*m*-terphenyl in a yield of 69%. It will be recalled that this compound was the less plentiful isomer in the Friedel and Crafts reaction in nitrobenzene.

The modified Perrier method was also used to prepare 4'-*m*-toluyl- and 4'-*p*-toluyl-*m*-terphenyl and the structure of each was demonstrated by the Grignard synthesis. The Perrier method failed with *o*-toluyl, *p*-bromobenzoyl, and *o*-chlorobenzoyl chlorides.

The unique orientation observed in the Perrier reaction is not solely a consequence of the use of carbon disulfide, for this solvent, in the Friedel and Crafts procedure, gave a mixture similar to that observed with nitrobenzene. It appears that there is actually a difference in orientation which arises when aluminum chloride and benzoyl chloride are used as a preformed complex, rather than separately.

The authors are indebted to the Monsanto

Chemical Company for a generous gift of *m*-terphenyl.

### Experimental

**4'-Bromo-*m*-terphenyl (II).** (a) By Direct Bromination.—*m*-Terphenyl was brominated in carbon disulfide solution as described by Olgiani<sup>5</sup> except that the product was fractionated (b. p. 198-200° (2 mm.)) before it was crystallized from ethanol by cooling in a Dry Ice-acetone mixture; white crystals, m. p. 31-33° (lit.<sup>5</sup> 31°) were obtained in 37% yield.

(b) By the Sandmeyer Method.—Ten grams of 4'-amino-*m*-terphenyl hydrochloride<sup>8</sup> was suspended in a mixture containing 40 ml. of acetic and 40 ml. of 48% hydrobromic acid and the suspension cooled to 0-5° while a solution of 2.4 g. of sodium nitrite in 10 ml. of water was added dropwise. A hydrobromic acid solution of cuprous bromide was added and after one hour, the mixture was heated for a few minutes on the steam-bath. The product washed with concentrated sulfuric acid, sodium hydroxide solution, and with water, was purified by vacuum distillation, and by low temperature crystallization from ether-ethanol solution. It was obtained as white needles, 4.2 g. (38%), m. p. 40-42°. This probably contained a small quantity of a high-melting impurity, for on recrystallization, a constant m. p. of 36.5-37° was obtained.

*Anal.*<sup>10</sup> Calcd. for C<sub>13</sub>H<sub>11</sub>Br: Br, 25.85. Found: Br, 26.01.

**4'-Cyano-*m*-terphenyl (III).**—A mixture consisting of 20 g. of 4'-bromo-*m*-terphenyl,<sup>5</sup> 15.4 g. of cuprous cyanide, 70 ml. of pyridine, a few crystals of cupric sulfate, and a few drops of toluenitrile was heated in a sealed tube for twenty-four hours at 225°. The reaction mixture was poured into dilute hydrochloric acid and extracted with benzene. The benzene layer was washed, dried and concentrated, and the residue crystallized from methanol, yielding 10.3 g. (63%) of white needles, m. p. 67-68°.

In our earlier experiments, the crude product was purified only by vacuum-distillation, the fraction boiling at 207-212° (1 mm.) being used in further reactions. The analytical sample, purified by recrystallization from methanol, melted at 69-70°.

*Anal.* Calcd. for C<sub>13</sub>H<sub>11</sub>N: C, 89.38; H, 5.13. Found: C, 89.40; H, 5.43.

**4'-Benzoyl-*m*-terphenyl (I) by Use of the Grignard Reagent.**—To a solution of phenylmagnesium bromide prepared from 14 g. of bromobenzene, 9.2 g. of 4'-cyano-*m*-terphenyl (III) (b. p. 207-212° (1 mm.)) in 14 ml. of ether was added. The mixture was refluxed overnight, and then decomposed with ice and hydrochloric acid. The acid solution was refluxed for two hours. The dark-green gum which separated was crystallized from methanol (Darco) to give 7.5 g. (62%) of white crystals, m. p. 111-111.5°.

*Anal.* Calcd. for C<sub>20</sub>H<sub>15</sub>O: C, 89.79; H, 5.42. Found: C, 89.63; H, 5.48.

**4'-Benzyl-*m*-terphenyl.<sup>11</sup>**—Ten grams of 4'-benzoyl-*m*-terphenyl, 2.4 g. of sodium hydroxide, and 6 ml. of 100% hydrazine hydrate were added to 30 ml. of diethylene glycol, and the mixture refluxed for three hours. It was then heated without the condenser until the temperature reached 195°, and finally refluxed for an additional five hours. The reaction mixture was poured into water, extracted with ether, and the ethereal extract was washed, dried, and concentrated. After removal by filtration of about one gram of an unidentified high melting material, the residue was crystallized from ether-methanol as white cubes, m. p. 69-70°; yield 3.8 g. (40%).

*Anal.* Calcd. for C<sub>27</sub>H<sub>23</sub>: C, 93.71; H, 6.29. Found: C, 93.93; H, 6.31.

**4'-*m*-Terphenoic Acid (IV).**—Two grams of 4'-cyano-*m*-terphenyl (III) was dissolved in 10 ml. of acetic acid and to the mixture, at the boiling point, 48% hydrobromic

(9) Perrier, *Bull. soc. chim.*, [3] 31, 859 (1904).

(10) Analyses by Micro-Tech Laboratories, Skokie, Illinois.

(11) Cf. Huang-Minlon, *This Journal*, 68, 2487 (1946).

acid was added until the solution became saturated with respect to the nitrile. After it had been refluxed for forty-eight hours, the solution was diluted, and the resulting precipitate recrystallized from methanol, yielding 0.7 g. (32%) of analytically pure, long white needles, m. p. 168–169°.

*Anal.* Calcd. for  $C_{19}H_{14}O_2$ : C, 83.19; H, 5.14. Found: C, 83.13; H, 5.31.

The methyl ester was obtained from methanol as colorless plates, m. p. 75.5–78°.

*Anal.* Calcd. for  $C_{20}H_{16}O_2$ : C, 83.30; H, 5.59. Found: C, 83.42; H, 5.61.

**3-Phenylfluorenone.**—4'-*m*-Terphenoic acid (IV, 0.1 g.) was suspended in 15 ml. of cold, concentrated sulfuric acid and the mixture allowed to stand for fifteen minutes. The mixture was poured into water, and the product collected, washed and recrystallized from ethanol as yellow needles, m. p. 100.5–101°.

*Anal.* Calcd. for  $C_{19}H_{12}O$ : C, 89.04; H, 4.72. Found: C, 89.10; H, 4.96.

**4-*m*-Terphenoic Acid (IX) from Bromo-*m*-terphenyl.**—Bromo-*m*-terphenyl as prepared by the procedure of Cook and Cook<sup>6</sup> could not be made to crystallize, but did give satisfactory yields of 4'-cyano-*m*-terphenyl (III) on reaction with cuprous cyanide. The higher-boiling (above 234°) (1 mm.) fraction (5.1 g.) from one such preparation (starting from 42 g. of bromo compound), on hydrolysis, yielded 0.5 g. of crude acid (m. p. 217–219°), the methyl ester of which melted at 124°. The ester was demonstrated to be methyl 4-*m*-terphenoate by comparison with a sample (m. p. 124–124.5°) prepared by esterification of the known<sup>7</sup> 4-terphenoic acid (IX).

*Anal.* Calcd. for  $C_{20}H_{16}O_2$ : C, 83.30; H, 5.59. Found: C, 83.07; H, 5.50.

**4-*m*-Terphenoic Acid from 4-Aceto-*m*-terphenyl.**—This acid has been prepared previously by the hypochlorite oxidation of 4-aceto-*m*-terphenyl,<sup>7</sup> but the following modified procedure was found to give better yields and to be better adapted to the use of large quantities of material.

A solution of 15 g. of 4-aceto-*m*-terphenyl in 50 ml. of xylene was added to 500 ml. of 5% sodium hypochlorite solution containing a small quantity of dioxane. The mixture was refluxed for two days, during which time an insoluble sodium salt precipitated. The salt was collected, washed by boiling in benzene, collected and washed with ether; yield 15 g.

A portion of the above salt (13.8 g.) was dissolved in hot glacial acetic acid and the filtered solution acidified further by addition of dilute hydrochloric acid. The acid which precipitated was recrystallized from methyl alcohol as white plates, m. p. 222–223° (lit.<sup>7</sup> 221°); yield 10 g. (66%).

**4-*m*-Terphenamide.**—Two grams of 4-*m*-terphenoic acid (IX) was refluxed with 20 ml. of thionyl chloride till the evolution of hydrogen chloride ceased. The solution was added dropwise to an ice-cold ammonia solution. The resulting solid was collected, washed with water, and recrystallized from ethanol as small white plates, m. p. 204–206°; yield 1.44 g. (72%). The analytical sample melted at 206–206.5°.

*Anal.* Calcd. for  $C_{19}H_{15}ON$ : C, 83.49; H, 5.53; N, 5.13. Found: C, 83.58; H, 5.51; N, 5.04.

The amide failed to undergo the Hofmann reaction.

**4-Cyano-*m*-terphenyl (VIII).**—One gram of the amide (above) was refluxed for five hours with 15 ml. of phosphorus trichloride, and the solution filtered and poured on ice. The product was collected, washed and recrystallized from methanol as white crystals, m. p. 94–95°; yield 0.77 g. (82.5%). The analytical sample melted at 97°.

*Anal.* Calcd. for  $C_{19}H_{13}N$ : C, 89.38; H, 5.13; N, 5.49. Found: C, 89.43; H, 5.12; N, 5.33.

**4-*m*-Terphenoylhydrazide.**—Seven grams of methyl *m*-terphenoate (prepared from the acid in 83% yield), 80 ml. of amyl alcohol, and 40 ml. of 100% hydrazine hydrate were refluxed together for twelve hours. The amyl alcohol

was removed by steam distillation, and the product collected, washed with water, and crystallized from ethanol as white plates, m. p. 170–173°; yield 6 g. (86%). The analytical sample melted at 172–173°.

*Anal.* Calcd. for  $C_{19}H_{15}N_2O$ : C, 79.14; H, 5.59; N, 9.72. Found: C, 78.97; H, 5.58; N, 9.70.

**4-Amino-*m*-terphenyl Hydrochloride.**<sup>12</sup>—Six grams of the above hydrazide was dissolved in 50 ml. of acetic acid and cooled in an ice-bath while a solution of 0.9 g. of sodium nitrite in 9 ml. of water was added dropwise. The flask containing the pasty mixture was removed from the ice-bath and allowed to stand for two and one-half hours. The mixture was diluted with water and the white precipitate collected.

The crude azide was dissolved in acetic acid and sufficient concentrated hydrochloric acid was added to make the solution saturated with respect to the azide. After it had been refluxed for two hours, the mixture was cooled, neutralized with ammonia, and the resulting solid collected, washed and dried. It was dissolved in ether, and hydrogen chloride passed through, precipitating 4 g. (68%) of white crystals.

**4-Amino-*m*-terphenyl (X).**—A sample of the above hydrochloride was suspended in a mixture of methanol and 10% sodium hydroxide solution, and the mixture heated to boiling. The product was recrystallized from ethanol-water as light pink plates, m. p. 101.5–102°.

*Anal.* Calcd. for  $C_{18}H_{15}N$ : N, 5.71. Found: N, 5.95.

**4-Benzoylamino-*m*-terphenyl.**—The amine (above) was benzoylated in pyridine solution and recrystallized from ethanol as long white needles, m. p. 180.5–181°.

*Anal.* Calcd. for  $C_{25}H_{19}NO$ : N, 4.01. Found: N, 4.01.

**4-(*N,N*-Diacetylamino)-*m*-terphenyl** was formed when the amine (X) was refluxed for two hours with acetic anhydride. It was obtained as long white needles from ethanol-water, m. p. 145–146°.

*Anal.* Calcd. for  $C_{22}H_{19}NO_2$ : N, 4.25. Found: N, 4.28.

**4-Bromo-*m*-terphenyl (VII).**—Five grams of the hydrochloride of 4-amino-*m*-terphenyl (X) was diazotized in acetic acid and treated with cuprous bromide by a procedure essentially that used in the preparation of 4'-bromo-*m*-terphenyl (II). After distillation under reduced pressure, the product was fractionally crystallized from benzene-ethanol solution yielding two compounds, a high-melting compound (m. p. 155–157°) (1.73 g.) and the expected 4-bromo-*m*-terphenyl (VII) (m. p. 84–85.5°; yield 3 g. (54.5%)). The analytical sample consisted of small white needle clusters, m. p. 91.5–92°.

*Anal.* Calcd. for  $C_{13}H_{13}Br$ : C, 69.92; H, 4.24; Br, 25.85. Found: C, 70.21; H, 4.40; Br, 25.70.

The high-melting solid (m. p. of the analytical sample 162.5–163°) was not a monobromo *m*-terphenyl.

*Anal.* Calcd. for  $C_{13}H_{11}Br_2$ : Br, 51.34. Found: Br, 50.34.

**Benzoylation of *m*-Terphenyl in Nitrobenzene.**—Benzoylation of *m*-terphenyl (29 g.) by the action of benzoyl chloride (18 g.) in nitrobenzene (270 ml.) and in the presence of aluminum chloride (19 g.) was carried out essentially as described by Goodman and Lowy.<sup>7</sup> When the vacuum-distilled reaction product was crystallized from methanol, 12 g. (29%) of crude 4-benzoyl-*m*-terphenyl (IV), m. p. 116–117°, was obtained. By repeated recrystallization, an analytical sample consisting of white plates was obtained, m. p. 120.5–121.5° (lit.<sup>7</sup> 117°).

*Anal.* Calcd. for  $C_{25}H_{19}O$ : C, 89.79; H, 5.42. Found: C, 89.83; H, 5.52.

On concentration of the filtrate from the crude 4-benzoyl-*m*-terphenyl, 4 g. (9.6%) of crude 4'-benzoyl-*m*-terphenyl (III) was obtained, m. p. 110–111°. Recrystallization yielded white parallelepiped (m. p. 112–112.5°) which gave no depression of melting point when

(12) Cf. Windaus and Raiche, *Ann.*, **537**, 157 (1939).

mixed with an authentic sample of the ketone (I) prepared by the Grignard method.

**4-Benzoyl-*m*-terphenyl (IV) from 4-Terphenoic Acid (IX).**—Three grams of 4-terphenoic acid was heated with 15 g. of thionyl chloride until there was no further evolution of hydrogen chloride. The excess thionyl chloride was then removed under reduced pressure, and the residue taken up in 100 ml. of anhydrous benzene. After addition of 3 g. of aluminum chloride, the mixture was heated to 40° for a few minutes, and then allowed to stir overnight at room temperature. Worked up in the usual way, the reaction mixture yielded a solid which, on repeated recrystallization from benzene, yielded a small quantity of white plates, m. p. 119.5–121°. This material did not depress the melting point of the higher-melting ketone obtained by the benzoylation of *m*-terphenyl.

**Oxime of 4-Benzoyl-*m*-terphenyl.**—A mixture consisting of 2 g. of ketone (VI), 2 g. of hydroxylamine hydrochloride and 20 ml. of pyridine was refluxed for three hours. The product was obtained by pouring the mixture into ice water, and recrystallizing the resulting solid from pyridine-ethanol as small white plates, m. p. 192–194°; yield 0.7 g. (33.5%). The analytical sample melted at 193–194°.

*Anal.* Calcd. for C<sub>25</sub>H<sub>19</sub>ON: N, 4.01. Found: N, 4.10.

**Beckmann Rearrangement of the Oxime of 4-Benzoyl-*m*-terphenyl.**—A mixture consisting of 0.7 g. of the oxime (above), 0.7 g. of phosphorus pentachloride and 15 ml. of anhydrous ether was allowed to stand for twenty-four hours. The solvent was evaporated, and the residue decomposed with ice water. The resulting solid was collected, washed, and recrystallized from ethanol yielding 0.35 g. (50%) of white needles, m. p. 176–177°. Recrystallization of this material gave a product (m. p. 178.5–179°) which did not depress the melting point of a sample of 4-benzoylamino-*m*-terphenyl obtained by benzoylation of the amine.

**Benzoylation of *m*-Terphenyl by Use of the Benzoyl Chloride-Aluminum Chloride Complex.**—The complex was formed by the cautious addition of 5.6 g. of benzoyl chloride to 5.8 g. of anhydrous aluminum chloride, followed by heating carefully until a homogeneous solution was formed. To the cooled complex, 25 ml. of carbon disulfide was added and the mixture refluxed until the complex had dissolved. The solution was cooled and 9.2 g. of *m*-terphenyl was added at such a rate that escape of hydrogen chloride did not become too rapid. The solution was then refluxed for four hours and allowed to stand in the refrigerator overnight. No insoluble complex precipitated.

The carbon disulfide was evaporated by means of a current of air and the residue decomposed with ice. The solid was collected and recrystallized from methyl alcohol, yielding 9.2 g. (69%) of product, m. p. 110–111.5°. Once recrystallized, the product melted at 111–112° and did not lower the melting point of a sample prepared by the Grignard procedure.

**4'-*m*-Toluyyl-*m*-terphenyl (a) by Use of the Perrier Complex.**—A solution of 1.4 g. of *m*-toluic acid in 10 ml. of thionyl chloride was refluxed for several hours and the excess thionyl chloride removed under reduced pressure. Dry benzene was added to facilitate the removal of the

last traces of thionyl chloride. To the crude acid chloride, 1.4 g. of aluminum chloride was added slowly, and the mixture heated cautiously until solution was obtained. The cooled melt was dissolved in 15 ml. of carbon disulfide and the solution cooled. When crystals started to appear, 2.3 g. of *m*-terphenyl was added. When the vigorous evolution of hydrogen chloride ceased, the mixture was refluxed for four hours, and was then allowed to stand overnight at room temperature. Since no solid complex separated, the entire solution was decomposed with ice and water, and the carbon disulfide evaporated. The residue was dissolved in ether and washed with 10% sodium bicarbonate solution and then with water. After the ether had been removed, the residue was crystallized from methanol as white needles, m. p. 95–97°; yield 1.1 g. (33%). The analytical sample melted at 98.5–99°.

(b) **By Use of the Grignard Reagent.**—A Grignard reagent was prepared from 3.6 g. of *m*-bromotoluene and to it was added dropwise a solution of 2 g. of 4'-cyano-*m*-terphenyl in 25 ml. of ether. The mixture was refluxed for four hours, and allowed to stand overnight. The solution was decomposed with dilute hydrochloric acid, the ether evaporated, and the acidic aqueous solution refluxed for two hours. The resulting product was taken up in benzene and the solution was washed and dried. The solvent was removed, and the residue was crystallized from methanol (Darco) as white needles, m. p. 93–96°; yield 1 g. (37%). Recrystallization gave a product (m. p. 97.5–98°) which did not depress the melting point of the material obtained by procedure a.

*Anal.* Calcd. for C<sub>26</sub>H<sub>20</sub>O: C, 89.62; H, 5.79. Found: C, 89.48; H, 5.72.

**4'-*p*-Toluyyl-*m*-terphenyl (a) by Use of the Perrier Complex.**—The procedure was similar to that used in preparing the *m*-toluyyl isomer. The product, 1.1 g. (33%) consisted of white needles from benzene-ethanol. The analytical sample melted at 180–181°.

(b) **By Use of the Grignard Reagent.**—The ketone was likewise prepared by the action of an excess of *p*-tolylmagnesium bromide on 2.55 g. of 4'-cyano-*m*-terphenyl as described for the isomer. The product, 1.55 g. (55%), melted at 180–181°, and did not depress the melting point of a sample prepared by use of the Perrier complex.

*Anal.* Calcd. for C<sub>26</sub>H<sub>20</sub>O: C, 89.62; H, 5.79. Found: C, 89.40; H, 5.61.

### Summary

Evidence has been found which suggests that 4-bromo-*m*-terphenyl is a by-product in the direct bromination of *m*-terphenyl.

The benzoylation of *m*-terphenyl in the Friedel and Crafts reaction gave not only the previously reported 4-benzoyl-*m*-terphenyl, but also a smaller quantity of 4'-benzoyl-*m*-terphenyl. Use of the benzoyl chloride-aluminum chloride (Perrier) complex resulted in benzoylation at the 4'-position exclusively. Several new *m*-terphenyl derivatives have been prepared.

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