10 min. the mixture was filtered and the solid was washed with dilute sulfuric acid. The washings were combined and extracted with ether, which was added to the filtrate. The ether solution was dried over magnesium sulfate and freed of solvent *in vacuo*, yielding 1.0 g. of white solid, m.p. 62.5–63.5°. Repetition of the above procedure with 26 g. of the dibromide afforded 11 g. (42%) of 2,2-dibromo-1,5-pentandiol, m.p. 69.5–71.5°.

Anal. Calcd. for $C_5H_{10}O_2Br_2$: C, 22.92; H, 3.85; Br, 61.01. Found: C, 23.09; H, 3.92; Br, 61.35.

2-Keto-1,5-pentandiol (VII).—Sodium acetate (0.3 g.) and acetic acid (2 ml.) were added to the above 2,3-dibromo-1,5-pentandiol (0.2 g.), the mixture was refluxed for 12 hr. and was finally poured into excess sodium bicarbonate solution. Extraction with three 20-ml. portions of ether, followed by drying of the extract over sodium sulfate and stripping of its solvent, yielded 0.05 g. (56%) of yellow oil. Essentially identical yields were obtained on larger scale runs. The oily product was characterized by conversion to its bis(2,4-dinitrophenylhydrazone), m.p. 241.5–242.5°.

Anal. Calcd. for $C_{17}H_{16}O_9N_8$: C, 42.86; H, 3.38; N, 23.52. Found: C, 42.95; H, 3.59; N, 22.53.

Conversion of 2-Keto-1,5-pentandiol to γ-Butyrolactone.—The above 2-keto-1,5-pentandiol (3.0 g.) was suspended in 0.40 *M* periodic acid (30 ml.), whereupon the oil slowly dissolved as reaction occurred. After solution was complete the mixture was saturated with sodium chloride and extracted with three 30-ml. portions of ether. Usual processing yielded a colorless oil which was distilled, b.p. 205–209°. The distillate was treated with phenylhydrazine. The resulting phenylhydrazide had m.p. 93–95°. The latter boiling point accords with that reported[12] for γ-butyrolactone; the latter melting point with that reported[13] for the phenylhydrazide of γ-hydroxybutric acid.

Conversion of 2,2-Dibromo-1,5-pentandiol to 1,5-Pentandiol.—The above 2,2-dibromo-1,5-pentandiol (7.8 g.) was dissolved in methanol (30 ml.). A solution of sodium borohydride (2.4 g.) dissolved in 2 *N* sodium hydroxide (2.2 ml.) and diluted to 24 ml. was added slowly to the diol solution at a rate such as to maintain gentle reflux, after which the mixture was stirred for 10 min. and the methanol was distilled on the steam bath. The resulting oily residue was dissolved in water and the solution was extracted with three 30-ml. portions of ether. The extract was dried and stripped of solvent in the usual way, leaving 2.34 g. (75%) of colorless oil which was purified by distillation. Its boiling point (235–240°)[8] and the identity of its infrared spectrum with that of an authentic sample indicated the product to be 1,5-pentandiol.

Alternative Synthesis of 3,3-Dibromo-2-hydroxytetrahydropyran (IV).—As an additional structure proof of 3,3-dibromo-2-hydroxytetrahydropyran, an alternative synthesis of this substance was undertaken employing known tetrahydropyran derivatives as intermediates. Dihydropyran (5.4 g.) was dissolved in ether (30 ml.) and the solution was cooled to −16°, then treated dropwise with bromine (10 g.) at such a rate as to keep the temperature below −10°. After completion of the addition the mixture was stirred for 20 min., and the resulting solution of 2,3-dibromotetrahydropyran (IX) was employed directly in the next step.[6] The solution was treated with additional ether (60 ml.) and a suspension of lead hydroxide (10 g.) in water (60 ml.), then the three-phase mixture was stirred for 12 hr. with a "Vibro-stirrer." The solid was filtered and rinsed with ether and the ether layer was separated and dried over magnesium sulfate. Solvent removal yielded 6.34 g. of white solid, m.p. 71–75°, in fair agreement with the value (m.p. 79–80°) reported by Paul[9] for 3-bromo-2-hydroxytetrahydropyran (X). The latter product (6.34 g.) was dissolved in acetic acid (60 ml.), and the solution was chilled in an ice bath to 16° and treated dropwise with a solution of bromine (11 g.) in acetic acid (40 ml.) at such a rate that the temperature remained below 20°. The mixture was stirred for an additional 12 hr. and the excess bromine and acetic acid were removed at diminished pressure leaving an amber oil. This was dissolved in ether (150 ml.) and processed as before to yield an amber oil which crystallized after 12 hr. It was washed with petroleum ether and recrystallized from benzene, 1.4 g. (8.4% over-all), m.p. 98.1–98.5°. The infrared spectrum of this sample was identical with that of the 3,3-dibromo-2-hydroxytetrahydropyran described above.

3,3-Dibromo-2-tetrahydropyryl Ether (VIII).—3,3-Dibromo-2-hydroxytetrahydropyran (3 g.) was dissolved in glacial acetic acid (25 ml.), and the resulting yellow solution was allowed to stand for 48 hr., then stirred at 90° for 10 min. On cooling 1.7 g. (59%) of white solid precipitated, m.p. 157–157.4°.

Anal. Calcd. for $C_{10}H_{14}O_3Br_4$: C, 23.94; H, 2.80; Br, 63.69; mol. wt., 502. Found: C, 23.77, 23.86; H, 2.82, 2.95; Br, 62.80, 62.86; mol. wt. (Rast), 467.

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[12] S. S. G. Sircar, *J. Chem. Soc.*, 901 (1928).

[13] J. Seib, *Ber.*, **60**, 1399 (1927).

Reactions of *o*-Methoxyphenylmagnesium Bromide with Hindered Ketones[1]

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o-Methoxyphenylmagnesium bromide has been found to react in the 1,2-manner with 2-mesitoyl-2′-methoxybiphenyl and 2-mesitoylbiphenyl. It also effects methoxyl group displacement in 2-duroyl-2′-methoxybiphenyl.

Diaryl ketones containing one mesityl or duryl group are extremely resistant to 1,2-addition by organometallic compounds. Success has been reported with certain aryllithium reagents,[3] but 1,2-addition of Grignard reagents has been observed only with the methyl reagent[4] and certain reagents of the allyl type.[5]

We now wish to report 1,2- addition of the aryl-

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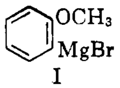
[2] United States Rubber Co. Fellow, 1955–1956.

[3] R. C. Fuson, G. P. Speranza, and R. Gaertner, *J. Org. Chem.*, **15**, 1155 (1950).

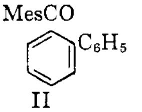
[4] R. C. Fuson and J. A. Robertson, *J. Org. Chem.*, **7**, 466 (1942); R. C. Fuson, M. D. Armstrong, W. E. Wallace, and J. W. Kneisley, *J. Am. Chem. Soc.*, **66**, 681 (1944).

[5] W. G. Young and J. D. Roberts, *J. Am. Chem. Soc.*, **66**, 2131 (1944).

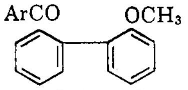
magnesium halide, *o*-methoxyphenylmagnesium bromide (I), to 2-mesitoylbiphenyl (II) and to 2-mesitoyl-2′-methoxybiphenyl (III).



I

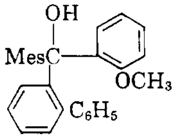


II

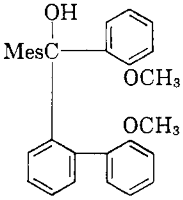


III. Ar = Mes
IIIa. Ar = Dur

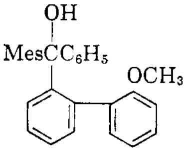
The yields of carbinols IV and V were 15 and 29%, respectively. Failure was encountered with the duryl analog IIIa, which would be expected to exhibit more resistance to 1,2-addition than the mesityl ketone III.



IV



V

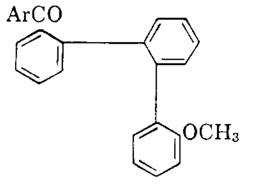


VI

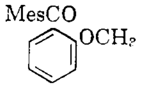
By contrast the action of phenylmagnesium bromide on ketone II produced no carbinol. From ketone III the corresponding carbinol VI was obtained, but in only 4% yield. This carbinol was readily synthesized (in 80% yield) from *o*-(*o*-methoxyphenyl)benzophenone and mesityllithium. It was also produced (in 60.5% yield) from 2-mesitoyl-2′-methoxybiphenyl (III) and phenyllithium. Carbinols IV and V were formed in 61 and 53% yield, respectively, by 1,2-addition of *o*-methoxyphenyllithium to ketones II and III.

From these experiments it would appear that the methoxyl group increases the tendency of *o*-methoxyphenylmagnesium bromide to effect 1,2-addition. If coordination of magnesium with the ether oxygen atom is intramolecular, the molecule would be very compact and perhaps more accessible at the reaction site.

Another unexpected product was obtained by the action of this reagent on 2-duroyl-2′-methoxybiphenyl (IIIa); the methoxyl group was displaced by the *o*-methoxyphenyl radical to give the terphenyl derivative VIIa.



VII. Ar = Mes
VIIa. Ar = Dur



VIII

A similar terphenyl derivative VII was obtained by treating mesityl *o*-methoxyphenylketone (VIII) with *o*-methoxyphenylmagnesium bromide, a change that could involve displacement of the methoxyl group from 2-mesitoyl-2′-methoxybiphenyl (III). From the method of synthesis it seems likely that terphenyl derivative VIII has the same structure as one previously reported.[6] In support of this hypothesis is the fact that the infrared and ultraviolet spectra of the two compounds are nearly superimposable. The new terphenyl however melts at 270–271° whereas the one described earlier melts at 160–161°. Models indicate that these isomers might have the *cis-trans* relationship. Attempts at interconversion, however, have not been successful. The compounds are being studied further.

Experimental[7]

Reaction of 2-Mesitoylbiphenyl (IIa). A. With *o*-Methoxyphenylmagnesium Bromide (I).—A solution of 4 g. of the ketone[8] in 50 ml. of benzene was added rapidly to a Grignard reagent prepared from 0.97 g. of magnesium, 7.86 g. of *o*-bromoanisole, and 60 ml. of ether. After the mixture had been heated under reflux for 20 hr., it was treated with a saturated solution of ammonium chloride. The product, isolated by conventional procedures, was an oil; it was placed on a column of 300 g. of alumina. Elution with 15:1 cyclohexane–ether gave mesityl-2-biphenylyl(*o*-methoxyphenyl) carbinol (IV) as a colorless solid; after two recrystallizations from ethanol, it melted at 155–156°, yield 0.8 g. (15%).

Anal. Calcd. for $C_{29}H_{28}O_2$: C, 85.26; H, 6.91. Found: C, 85.09; H, 7.05.

Its infrared spectrum contains bands assignable to a hydroxyl group (3480 cm.$^{-1}$), a methoxyl group (1240 and 1045 cm.$^{-1}$), a mesityl radical (855 cm.$^{-1}$), an *o*-disubstituted phenyl group (735 cm.$^{-1}$), and a monosubstituted phenyl group (703 cm.$^{-1}$). Elution with 10:1 cyclohexane–ether gave 0.8 g. (20%) of the original ketone; 5:1 cyclohexane–ether gave a colorless solid that appears to be mesityl 2-(*o*-methoxyphenyl)-6-phenylphenyl ketone. After two recrystallizations from absolute ethanol it weighed 0.28 g. (5.2%), m.p. 130–131°.

The infrared spectrum of the compound is consistent with that expected for mesityl 2-(*o*-methoxyphenyl)-6-phenylphenyl ketone. It contains bands assignable to an aromatic ketone (1660 cm.$^{-1}$), a methoxyl group (1250 and 1140 cm.$^{-1}$), an *o*-disubstituted phenyl group (757 cm.$^{-1}$), a monosubstituted phenyl group (705 cm.$^{-1}$).

Anal. Calcd. for $C_{29}H_{26}O_2$: C, 85.68; H, 6.45. Found: C, 85.34; H, 6.43.

Mesityl-2-biphenylyl(*o*-methoxyphenyl)carbinol (IV) was prepared also by the action of *o*-methoxyphenyllithium on 2-mesitoylbiphenyl (II). A solution of 0.6 g. of the ketone and 20 ml. of benzene was added over a 5-min. period to the lithium reagent prepared from 0.278 g. of lithium and 3.74 g. of *o*-bromoanisole in 40 ml. of ether. The reaction mixture was stirred at room temperature for 2 hr. and under reflux for an additional hour. After 15 ml. of water had been added, the organic phase was removed, washed with water, and dried over sodium sulfate. Distillation of the solvent left the carbinol as a colorless solid which, after two

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(6) R. C. Fuson and R. L. Albright, *J. Am. Chem. Soc.*, **81**, 487 (1959).

(7) All melting points are uncorrected. The infrared spectra were measured with a Perkin-Elmer Model 21B spectrophotometer by Mr. Paul E. McMahon, Mrs. Mary Verkade, and Mr. William Dalton. The NMR spectra were measured by Mr. Oliver W. Norton with a Varian high resolution spectrophotometer (Model V-4300B with super-stabilizer) at 60 mc. with tetramethylsilane as an internal standard.

(8) R. C. Fuson, M. D. Armstrong, and S. B. Speck, *J. Org. Chem.*, **7**, 297 (1942).

recrystallizations from ethanol–benzene, weighed 0.5 g. (61%), m.p. 155–156°.

Anal. Calcd. for $C_{29}H_{28}O_2$: C, 85.26; H, 6.91. Found: C, 85.14; H, 6.95.

Its infrared spectrum was superimposable on that of the carbinol made with the Grignard reagent, and a mixture melting point determination with the two samples showed no lowering.

B. With Phenylmagnesium Bromide.—A solution of 4.5 g. of the ketone in 50 ml. of benzene was added over a 10-min. period to a solution of the Grignard reagent prepared from 1.095 g. of magnesium and 7.76 g. of bromobenzene in 60 ml. of ether. The reaction mixture was heated at reflux for 20 hr.; 50 ml. of 1 *N* hydrochloric acid was then added. The product, an oil, was placed on a column of 300 g. of activated alumina. Elution with 15:1 cyclohexane–ether gave a colorless solid that appears to be mesityl 2,6-diphenylphenyl ketone. After two recrystallizations from absolute ethanol it weighed 1.05 g. (19%), m.p. 162–163°.

Anal. Calcd. for $C_{28}H_{24}O$: C, 89.32; H, 6.43. Found: C, 89.45; H, 6.44.

The infrared spectrum contains bands assignable to an aromatic ketone (1667 cm.$^{-1}$), a 1,2,3-trisubstituted phenyl group (811 cm.$^{-1}$), and a monosubstituted phenyl group (777, 755, and 694 cm.$^{-1}$). No carbinol was detected.

Reaction of Mesityl *o*-Methoxyphenyl Ketone with *o*-Methoxyphenylmagnesium Bromide.—The Grignard reagent prepared from 15.72 g. of *o*-bromoanisole in 50 ml. of ether was added over a 30-min. period to a solution of 14.26 g. of the ketone in 100 ml. of benzene. The solution was then heated at reflux for 1 hr. A solution of 12 ml. of concd. hydrochloric acid in 110 ml. of water was added slowly; the product, an oil, was dissolved in 30 ml. of hot ethanol, and the solution allowed to cool in a refrigerator. 2-Mesitoyl-2′-methoxybiphenyl (III) separated as yellow crystals, m.p. 89–92°, yield 17 g. (92%). Two additional recrystallizations of the ketone from ethanol raised the melting point to 93–95°.[9]

When 4 moles of the Grignard reagent were used with 1 mole of ketone, and the period of heating was extended to 20 hr., the results were different. The product, a red oil, was chromatographed on an alumina column; elution with 5:1 cyclohexane–ether yielded mesityl-*o*-(*o*′-methoxybiphenylyl)-*o*-methoxyphenylcarbinol (V) as a colorless solid which, after two recrystallizations from absolute ethanol, melted at 146.5–147.5°, yield 19%.

Anal. Calcd. for $C_{30}H_{30}O_3$: C, 82.16; H, 6.90. Found: C, 82.35; H, 7.

The infrared spectrum has bands assignable to a hydroxyl group (3520 cm.$^{-1}$), a methoxyl group (1250 and 1052 cm.$^{-1}$), a mesityl radical (846 cm.$^{-1}$), and an *o*-disubstituted phenyl group (750 cm.$^{-1}$). Elution with 5:1 cyclohexane–ether gave, after recrystallization from absolute ethanol, 2-mesitoyl-2′-methoxybiphenyl (III) melting at 93–95°,[9] yield 2.6%. It was identified by reference to its infrared spectrum and a mixture melting point determination. Elution with 4:1 cyclohexane–ether yielded a colorless solid which after recrystallization from absolute ethanol weighed 1.5 g. (9.2%), m.p. 175–176°.

Anal. Calcd. for $C_{30}H_{28}O_3$: C, 82.54; H, 6.47. Found: C, 82.29; H, 6.62.

The infrared spectrum contains absorption bands assignable to an aromatic ketone (1672 cm.$^{-1}$), aromatic skeletal vibrations (1600, 1509, 1475, and 1450 cm.$^{-1}$), and a methoxyl group (1250 and 1050 cm.$^{-1}$). These data are expected for 2,6-bis(*o*-methoxyphenyl)phenyl mesityl ketone. Elution with 1:1 cyclohexane ether gave a colorless solid which, after several recrystallizations from ethanol–benzene, weighed 1.1 g. (7.5%). This compound melted at 120–125°; at higher temperatures it solidified and remelted at 210–211°.

Anal. Calcd. for $C_{29}H_{26}O_2$: C, 85.68; H, 6.45. Found: C, 85.68; H, 6.50.

Its infrared spectrum has bands which can be assigned to an aromatic ketone (1670 cm.$^{-1}$), a methoxyl group (1250 and 1050 cm.$^{-1}$), and an *o*-disubstituted phenyl group (752 cm.$^{-1}$). These data are consistent with those expected for 2-mesitoyl-2″-methoxy-*o*-terphenyl (VII). The compound was sublimed and also heated above the melting point for several hours; in both instances it was recovered unchanged.

Reaction of 2-Mesitoyl-2′-methoxybiphenyl (III). A. With *o*-Methoxyphenylmagnesium Bromide.—To a solution of the Grignard reagent prepared from 8.42 g. of *o*-bromoanisole in 60 ml. of ether was added a solution of 5.0 g. of the ketone in 50 ml. of benzene. The mixture was heated at reflux for 20 hr. and treated with hydrochloric acid; the oily product was placed on a column of alumina. Elution with 5:1 cyclohexane–ether gave a colorless solid, which after two recrystallizations from absolute ethanol weighed 1.89 g. (29%), m.p. 146–148°. Its infrared spectrum and a mixture melting point determination showed it to be identical to the carbinol V described in the following paragraphs. Elution with 7:3 cyclohexane–ether gave gave 0.38 g. (6%) of mesitoyl 2,6-bis(*o*-methoxyphenyl)-phenyl ketone. The product from *o*′-methoxyl group displacement was not isolated.

B. With *o*-Methoxyphenyllithium. A solution of 0.43 g. of the ketone and 16 ml. of benzene was added over a 5-min. period to the lithium reagent prepared from 0.183 g. of lithium and 2.43 g. of *o*-bromoanisole in 20 ml. of ether. The mixture was stirred at room temperature for 2 hr. and then at reflux for another hour. Hydrolysis was effected by the addition of 15 ml. of water. The crude product was placed on a column of 50 g. of alumina. Colorless crystalline carbinol V was eluted with 5:1 cyclohexane–ether and after two recrystallizations from absolute ethanol weighed 0.3 g. (53%), m.p. 146–147°.

Anal. Calcd. for $C_{30}H_{30}O_3$: C, 82.16; H, 6.90. Found: C, 81.90; H, 7.10.

The infrared spectrum contains bands assignable to a hydroxyl group (3520 cm.$^{-1}$), a methoxyl group (1250 and 1052 cm.$^{-1}$), a mesityl radical (846 cm.$^{-1}$), and an *o*-disubstituted benzene ring (750 cm.$^{-1}$).

C. With Phenylmagnesium Bromide. A solution of 2.5 g. of the ketone in 30 ml. of benzene was added dropwise over a 60-min. period to a refluxing solution of the Grignard reagent prepared from 3.69 g. of bromobenzene in 60 ml. of ether. After the addition, the reaction mixture was heated under reflux for 10 hr.; it was hydrolyzed by slow addition of 30 ml. of 1 *N* hydrochloric acid. The product, a yellow oil, gave yellow crystals when cyclohexane was added. The solid was recrystallized from benzene and then ethanol, yield 0.63 g., m.p. 150–153°. The infrared spectrum contains bands assignable to a hydroxyl group (3470 cm.$^{-1}$), an aromatic ketone (1627 cm.$^{-1}$), a methoxyl group (1255 and 1030 cm.$^{-1}$), and a mesityl radical (847 cm.$^{-1}$). The spectrum is consistent with that expected for the keto alcohol which could form by coupling of 2-mesitoyl-2′-methoxybiphenyl.[10] The filtrates were concentrated, and the residual oil was taken up in 5 ml. of benzene and placed on a column of 160 g. of alumina. The first solid was eluted with 5:1 cyclohexane–ether; after two recrystallizations from absolute ethanol the colorless crystals weighed 0.12 g. (4%), m.p. 135–136°.

Anal. Calcd. for $C_{29}H_{28}O_2$: C, 85.26; H, 6.91. Found: C, 85.50; H, 6.88.

The infrared spectrum contains bands assignable to a hydroxyl group (3520 cm.$^{-1}$), a methoxyl group (1250 and 1050 cm.$^{-1}$), a mesityl radical (847 cm.$^{-1}$), an *o*-disubstituted phenyl group (760 and 746 cm.$^{-1}$), and a monosubsti-

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(9) R. C. Fuson, E. M. Bottorff, and S. B. Speck, *J. Am. Chem. Soc.*, **64**, 1450 (1942).

(10) R. C. Fuson and C. Hornberger, *J. Org. Chem.*, **16**, 631 (1951).

tuted phenyl group (700 cm.$^{-1}$). This spectrum is consistent with that expected for *o*-(*o*′-methoxybiphenylyl)mesitylphenylcarbinol (VI).

Elution with 5:1 cyclohexane–ether gave a small amount of another colorless solid, m.p. 126–130°. After two recrystallizations of the substance from absolute ethanol, the melting point was 130–131°. It proved to be identical to the compound identified earlier as mesityl 2-(*o*-methoxyphenyl)-6-phenylphenyl ketone. Elution with 9:1 ether–methanol gave an additional 0.4 g. of the keto alcohol (m.p. 149–152°), total yield 26%.

C. With Phenyllithium. A solution of 0.43 g. of the ketone in 15 ml. of benzene was added rapidly to a solution of phenyllithium prepared from 0.183 g. of lithium and 2.04 g. of bromobenzene in 35 ml. of ether. The reaction mixture was stirred at room temperature for 2 hr. and at reflux for 1 hr. The product, a light yellow oil, was placed on a column of 40 g. of activated alumina. Elution with 10:1 cyclohexane–ether gave colorless crystals that, after two recrystallizations from absolute ethanol, weighed 0.32 g. (60.5%), m.p. 135–136°.

Anal. Calcd. for $C_{29}H_{28}O_2$: C, 85.26; H, 6.91. Found: C, 85.09; H, 7.01.

The infrared spectrum and a mixture melting point determination showed the substance to be identical to carbinol VI.

Reaction of *o*-(*o*-Methoxyphenyl)benzophenone with Mesityllithium. A solution of 0.58 g. of the ketone,[11] in 30 ml. of ether was added over a 15-min. period to mesityllithium prepared from 0.278 g. of lithium and 3.98 g. of bromomesitylene in 40 ml. of ether. The reaction mixture was stirred at room temperature for 90 min. and then poured over 30 g. of cracked ice. The product, an oil, was placed on a column of 135 g. of alumina. The colorless carbinol was eluted with 5:1 cyclohexane–ether and after recrystallization from absolute ethanol weighed 0.64 g. (80%), m.p. 135–136°.

Anal. Calcd. for $C_{29}H_{28}O_2$: C, 85.26; H, 6.91. Found: C, 85.17; H, 6.96.

The infrared spectrum and mixture melting point determinations showed it to be identical with the samples of carbinol VI obtained by the reaction of phenylmagnesium bromide and phenyllithium with 2-mesitoyl-2′-methoxybiphenyl.

Reaction of Duryl *o*-Methoxyphenyl Ketone with *o*-Methoxyphenylmagnesium Bromide.—A solution of 10.0 g. of the ketone and 100 ml. of benzene was added over a 10-min. period to the Grignard reagent prepared from 27.8 g. of *o*-bromoanisole and 3.63 g. of magnesium in 120 ml. of ether. The mixture was then heated under reflux for 20-hr. and poured into a solution of 12.5 ml. of concd. hydrochloric acid and 150 ml. of cold water. The product, a yellow oil, was chromatographed on an alumina column. Elution with 4:1 cyclohexane–ether gave 2,2′-dimethoxybiphenyl, m.p. 153–154°. Elution with 3:2 cyclohexane–ether gave, after recrystallization from ethanol–benzene, 5.4 g. (41%) of 2-duroyl-2′-methoxybiphenyl, m.p. 154–155°. The compound was identified by reference to its infrared spectrum and a mixture melting point determination. Another solid from this elution (yield 0.1 g.) melted at 136–138°. By repeated recrystallization of the solid from ethanol two substances were obtained; one was 2-duroyl-2′-methoxybiphenyl and the other, a white fluffy solid, m.p. 182–183°, appears to be 2,6-bis(*o*-methoxyphenyl)phenyl duryl ketone. Elution with 1:4 cyclohexane–ether gave a colorless solid that weighed 1.25 g. (8%). It melted over the range 145–155°, resolidified around 200° and remelted at 260–265°. The analytical sample, prepared by sublimation, shows the same melting characteristics and the final melting point is at 270–271°.

Anal. Calcd. for $C_{30}H_{28}O_2$: C, 85.68; H, 6.71. Found: C, 85.73; H, 6.87.

Its infrared spectrum is that expected for 2-duroyl-2″-methoxy-*o*-terphenyl. Absorption at 1673 cm.$^{-1}$ is assignable to an aromatic ketone, at 1055 and 1245 cm.$^{-1}$ to a methoxyl group, and at 755 cm.$^{-1}$ to *o*-disubstituted benzene.

The high-melting ketone was heated above its melting point for several hours and recovered unchanged. The low-melting ketone[6] was sublimed and also heated above its melting point for several hours. It was also placed in glacial acetic acid and the solution heated at reflux for 8 hr.; it was recovered unchanged in each instance.

Reaction of 2-Duroyl-2′-methoxybiphenyl with *o*-Methoxyphenylmagnesium Bromide in the Presence of Magnesium Bromide.—The Grignard reagent was prepared from 5.81 g. of *o*-bromoanisole and 0.973 g. (excess) of magnesium in 20 ml. of ether. An ether solution of magnesium bromide was prepared according to the procedure of Pearson, Cowan, and Beckler.[12] A solution of 1.88 g. of freshly distilled ethylene bromide in 10 ml. of ether was allowed to react with the excess magnesium. A solution of 3.44 g. of ketone in 15 ml. of benzene was added rapidly to the reagent. The reaction mixture was heated at reflux for 20 hr.; a solution of 5 ml. of concd. hydrochloric acid in 100 ml. of water was then added slowly. The gummy brown product was dissolved in 15 ml. of benzene and placed on a column of 150 g. of alumina. Starting material and a colorless solid (m.p. 136–138°) were eluted with 3:2 cyclohexane–ether. A small amount of colorless solid (0.016 g.), eluted with 1:4 cyclohexane–ether, melted at 145–155°, resolidified around 200° and remelted at 256–272°. The infrared spectrum and a mixture melting point determination showed this compound to be that tentatively identified as 2-duroyl-2″-methoxy-*o*-terphenyl. Attempts to displace the methoxyl group from the starting ketone without the use of magnesium bromide were unsuccessful.

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[11] R. C. Fuson, R. J. Lokken, and R. L. Pedrotti, *J. Am. Chem. Soc.*, **78**, 6064 (1956).

[12] D. E. Pearson, D. Cowan, and J. D. Beckler, *J. Org. Chem.*, **24**, 504 (1959).