that described by Fortune and Mellon.[12] Thus, to each aliquot was added 0.5 ml. of 15% hydrochloric acid, 2 ml. of 15% hydroxylamine hydrochloride, 10 ml. of a saturated sodium acetate solution and 10 ml. of 0.1% α-phenanthroline solution. The resulting red solution was diluted to 100 ml. and the color intensity measured in a round absorption cell approximately 22 mm. in diameter. A Fisher electrophotometer equipped with a green filter, $\lambda_{\max}$ approximately 525 mμ, was used for the color measurements. The difference between the absorption with and without added sulfinic acid is a measure of the precipitated ferric sulfinate which may be related to the amount of added sulfinic acid. The analysis was calibrated for each sulfinic acid by analyzing various aliquots of a standard solution of that acid[5,6] in the same manner as above. The first-order rate constants for the rearrangement of each of the sulfones listed in Table I were determined by plotting ln (100 − % reaction) *vs.* time in minutes. The slopes of the resulting straight lines were determined by the method of least squares and the rate constants so calculated are shown in Table I together with the number of runs for each sulfone. Except for phenyl 2,4-xylyl sulfone, 10 to 12 points were taken during each run and the run was carried to within 70–85% completion. With phenyl 2,4-xylyl sulfone, 15 points were taken up to 60 to 70% completion. Since the conversion with phenyl *o*-tolyl and phenyl 2,4-xylyl sulfones was only about 60%,[6] the analysis gave somewhat less satisfactory results than with the other sulfones, the standard deviation of a single measurement being about 5%. For the other sulfones this value was about 3%. The standard deviation of rate constants from successive runs was generally slightly greater than the above values but was not greater than 7%.

For mesityl phenyl, phenyl 2,6-xylyl and mesityl sulfones, the first-order plot gave a straight line which did not pass through the origin on extrapolation. The extrapolated link intersected the ordinate at a point representing the percentage of the over-all reaction accounted for by the first stage, for which see the Discussion. The "% reaction" which was plotted for these sulfones represents the fraction of the reaction in excess of this first stage.

Acknowledgment.—We wish to gratefully acknowledge the support of this work by the National Science Foundation and the Union Carbide and Carbon Chemicals Co.

LAFAYETTE, IND.

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[12] W. B. Fortune and M. G. Mellon, *Anal. Chem.*, **10**, 60 (1938).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

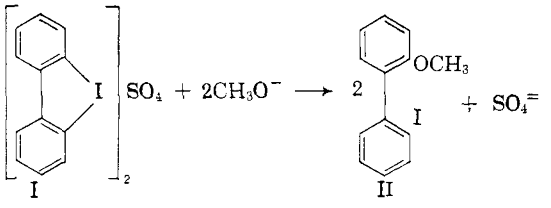
Synthesis of 2-Iodo-2'-Methoxybiphenyl. A New Route to *o*-Terphenyls[1]

BY REYNOLD C. FUSON AND ROBERT L. ALBRIGHT[2]

RECEIVED AUGUST 21, 1958

2-Iodo-2'-methoxybiphenyl has been prepared from biphenyleneiodonium sulfate by a three-step transformation. 2-Acetoxy-2'-iodobiphenyl, obtained by the action of sodium acetate on the iodonium sulfate, underwent methanolysis to give the corresponding phenol. Finally, the desired iodo methyl ether was produced by methylation of the phenol with methyl sulfate. The transformation was nearly quantitative at each step. The Grignard reagents made from 2-iodobiphenyl and 2-iodo-2'-methoxybiphenyl were condensed with duryl *o*-methoxyphenyl ketone to give the corresponding *o*-terphenyl derivatives. Carbonation of the Grignard reagent from the methoxy iodide yielded 2'-methoxy-2-biphenylcarboxylic acid.

In connection with a study of Grignard reagents containing ether functions[3] attention was directed to the reagents corresponding to the 2-halo-2'-alkoxybiphenyls. It was hoped that the iodo ethers of this series could be made by the action of alkoxide ions on biphenyleneiodonium salts. The iodonium salts had been made available by adaptation of the method of Beringer, Drexler, Gindler and Lumpkin[4] to 2-iodobiphenyl.[5] The first experiments designed to this end involved treatment of biphenyleneiodonium sulfate (I) with sodium methoxide.

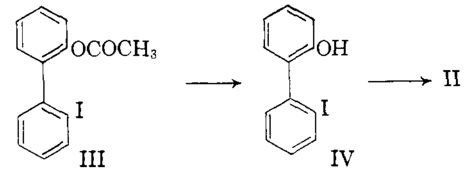


By analogy with similar experiments in the diaryliodonium series[6] it seemed possible that sodium methoxide might bring about displacement to give 2-iodo-2'-methoxybiphenyl (II).

It soon became evident that nucleophilic displacement with methoxide ion in the cyclic iodonium salts was much more difficult to accomplish than in the open-chain analogs. The products were biphenyl, 2-iodobiphenyl and 2,2'-diiodobiphenyl. None of the desired 2-iodo-2'-methoxybiphenyl (II) could be found.

An indirect method was developed, however, by which this compound could be made, the initial step of which was displacement by acetate ion. This reaction, which was carried out in boiling glacial acetic acid, proved to be catalyzed by copper salts. The product, 2-acetoxy-2'-iodobiphenyl (III), was obtained in nearly quantitative yields.

Methanolysis of the iodo acetate gave the corresponding phenol IV, which in turn was methylated to produce the methoxy iodide II. The yields in these steps were very high also.



The methoxy iodide formed a Grignard reagent as was shown by carbonation; the product was the known 2'-methoxy-2-biphenylcarboxylic acid (V).[7]

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[1] This investigation was supported in part by a grant from the Office of Ordnance Research, U. S. Army (Contract No. DA-11-022-ORD-874).

[2] Lubrizol Corporation Fellow, 1956–1958.

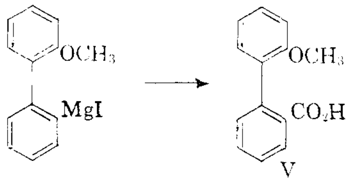
[3] R. C. Fuson and B. Freedman, *J. Org. Chem.*, **23**, 1161 (1958).

[4] F. M. Beringer, M. Drexler, E. M. Gindler and C. C. Lumpkin, THIS JOURNAL, **75**, 2705 (1953).

[5] J. Collette, D. McGreer, R. Crawford, F. Chubb and R. B. Sandin, *ibid.*, **78**, 3819 (1956).

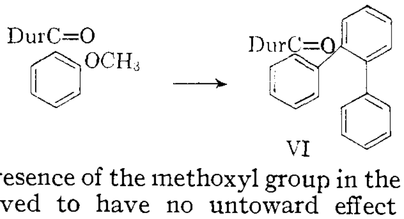
[6] F. M. Beringer, A. Brierley, M. Drexler, E. M. Gindler and C. C. Lumpkin, *ibid.*, **75**, 2708 (1953).

[7] H. G. Rule and E. Bretscher, *J. Chem. Soc.*, 925 (1927).



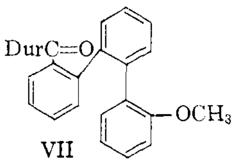
V

A principal source of interest in 2-halobiphenyl derivatives having substituents in the 2′-position was the possibility of using them, together with various hindered *o*-methoxyaryl ketones, to open a convenient route to the *o*-terphenyls carrying substituents in the 2- and 2″-positions. That this plan was eminently feasible was shown by the fact that the Grignard reagent made from 2-iodobiphenyl reacted smoothly with duryl *o*-methoxyphenyl ketone[8] to give 2-duroyl-*o*-terphenyl (VI).



VI

The presence of the methoxyl group in the 2′-position proved to have no untoward effect on the condensation of 2-methoxy-2′-biphenylylmagnesium iodide with duryl *o*-methoxyphenyl ketone. The reaction took place readily to form 2-duroyl-2″-methoxy-*o*-terphenyl (VII) in a yield of 81.2%.



VII

Since many similar displacements of *o*-methoxyl groups have been effected in hindered aromatic ketones, this method of synthesis of the *o*-terphenyl derivatives serves to establish their structures. Moreover, the structures are fully confirmed by the elemental analyses and the infrared spectra.

Experimental[9]

Biphenyleneiodonium Sulfate.—The procedure was that of Collette, McGreer, Crawford, Chubb and Sandin.[5] The crude biphenyleneiodonium bisulfate, obtained in a 97.1% yield, melted with decomposition at 261–263°. When a solution of this product (15.0 g.) in 500 ml. of boiling water was allowed to cool slowly to room temperature, very light tan rhombic crystals were formed. Cooling the mixture in the refrigerator caused the separation of an additional crop of crystals which had the form of white needles and proved to be the bisulfate, m.p. 268–269°.

The rhombic crystals were found to be biphenyleneiodonium sulfate, m.p. 275–276° dec. The yield in various runs ranged from 88.4% to nearly quantitative.

Anal.[10] Calcd. for $C_{24}H_{16}I_2O_4S$: C, 44.05; H, 2.47. Found: C, 43.80, H, 2.64.

Action of Sodium Methoxide on Biphenyleneiodonium Sulfate.—The sulfate (9.5 g., 14.5 mmoles) was placed in 60 ml. of anhydrous methanol which was then heated to boiling. To the suspension, kept under nitrogen, was added dropwise a hot solution of sodium methoxide prepared by dissolving 3.34 g. (145.1 mg. at.) of sodium in 55 ml. of anhydrous methanol. During the addition the reflux temperature rose to 73°. Stirring was started at the beginning of the addition and continued for 23.5 hr. (at 73–75°) after it was completed. To the white colloidal suspension, cooled in ice-water, was added 75 ml. of ether and 60 ml. of dilute hydrochloric acid. Stirring was continued for another 0.5 hr., and the mixture was filtered to remove a white solid (1.86 g.) which proved to be biphenyleneiodonium chloride, yield 20.4%. It began to decompose at 265° but did not melt when heated to 300°.

A mixture of other products, isolated by conventional procedures, formed a light yellow oil, which was fractionated by distillation through a Holtzmann column at a pressure of 0.7–1.0 mm. The first fraction (b.p. 76–110° at 0.9–1.0 mm.) yielded crude biphenyl (0.52 g., 11.6%), which melted at 64–67°. Two sublimations (65° at 3.0 mm.) afforded white platelets melting at 69–70°. A mixed melting point determination with an authentic sample of biphenyl showed no depression.

The second fraction (4.20 g., 51.7%), collected at 115–118° at 0.8 mm., gave a positive Beilstein test for halogen and an infrared spectrum that is superimposable on that of 2-iodobiphenyl. The spectrum[11] has bands at 702, 751 and 3065 cm.$^{-1}$, which can be assigned, respectively, to monosubstituted phenyl, *o*-disubstituted phenyl and aromatic hydrogen.

A later fraction (1.18 g.), collected at 130–150° at 0.7 mm., was found to contain 2,2′-diiodobiphenyl which, after two recrystallizations from ethanol, melted sharply at 110° (reported melting points 108°[12] and 109°[13]), yield 0.63 g., 5.35%. The compound was identified by reference to elemental analysis, comparison of infrared spectra and a mixed melting point determination with an authentic specimen of 2,2′-diiodobiphenyl. No depression of the melting point occurred. The infrared spectrum has absorption peaks at 756 and 3065 cm.$^{-1}$ that can be assigned, respectively, to *o*-disubstitution and aromatic hydrogen.

Anal. Calcd. for $C_{12}H_8I_2$: C, 35.50; H, 1.99. Found: C, 35.78, H, 2.23.

2-Acetoxy-2′-iodobiphenyl.—A mixture of 10 g. (30.6 meq.) of biphenyleneiodonium sulfate, 5.0 g. of sodium acetate, 0.04 g. of cupric sulfate, 100 ml. of glacial acetic acid and 10 ml. of acetic anhydride was placed under nitrogen and heated under reflux, with stirring (Nichrome wire stirrer), for 72 hr. During this period the color of the mixture, originally light blue, changed to light tan.

The mixture was cooled to room temperature and filtered to remove the solid that had formed. The solid was washed six times with anhydrous ether, and the solution obtained by combining the ether washes with the filtrate was concentrated by evaporation of solvent under reduced pressure until a fluffy, white solid began to form. The solid, tan-colored mass produced by cooling the mixture was extracted with anhydrous ether until all the color had been removed (twelve extractions). Removal of the ether from the combined extracts left a tan oil, which was distilled at 0.05–0.1 mm. at 130° in a special sublimation tube. The tube, which was 3.3 cm. in diameter and 26 cm. in length and stood at an incline of 20° from the horizontal, had a constriction of 9 cm. from the bottom to collect the distillate. The 2-acetoxy-2′-iodobiphenyl was a clear colorless oil that solidified when transferred to a weighing flask; m.p. 54.5–55.5°, yield 10.32 g. or 99.8% of the theoretical. An analytical sample, prepared by distillation of a small amount of the white solid in a sublimation tube with an S-bend, melted at 55.0–55.5°. The infrared spectrum had absorption peaks that can be assigned to 2,2′-disubstituted biphenyl in which the two substituents are different (746 and 755 cm.$^{-1}$), an aromatic carbon–oxygen bond (1187 cm.$^{-1}$), the bond between the carbonyl carbon atom and the oxygen atom of an aryl acetate (1210 cm.$^{-1}$), a carbon–methyl bond (1367 cm.$^{-1}$), the carbonyl group of an aryl ester (1763 cm.$^{-1}$) and aromatic hydrogen (3050 cm.$^{-1}$).

Anal. Calcd for $C_{14}H_{11}IO_2$: C, 49.72; H, 3.28. Found: C, 49.63; H, 3.32.

Conversion of 2-Acetoxy-2′-iodobiphenyl to Dibenzofuran.—A mixture of 3.4 g. (10.0 mmoles) of the acetoxy iodide and

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(8) R. C. Fuson and W. C. Hammann, THIS JOURNAL, **73**, 1851 (1951).

(9) All melting points are corrected. All boiling points are uncorrected.

(10) The microanalyses were performed by Mr. Josef Nemeth, Mrs. R. Maria Benassi, Miss Clair Higham, Mrs. Frederick Ju and Mrs. H. Stingl.

(11) The infrared spectra were recorded by Mr. James Brader, Mr. Brian Cloonan, Mr. Paul McMahon and Miss Mary DeMott.

(12) L. Mascarelli and G. Benati, *Gazz. chim. ital.*, **38**, (II), 624 (1908).

(13) L. Mascarelli and D. Gatti, *ibid.*, **61**, 782 (1931).

50 ml. of 1 *N* sodium hydroxide solution was placed in an atmosphere of nitrogen and heated under reflux with stirring for 18 hr. During this time a white solid was deposited on the top of the flask. The reaction mixture was cooled, and the product isolated by usual procedures. The crude dibenzofuran melted at 80–81°, yield 1.7 g. (100%). Two recrystallizations from cyclohexane and one from ethanol afforded white platelets melting at 82.0–82.2° (reported melting points 80°[14] and 85°[15]). The infrared spectrum has bands that can be assigned to *o*-disubstituted phenyl (752 cm.$^{-1}$), an aryl–oxygen bond (1200 cm.$^{-1}$), skeletal vibrations of the biphenylene system (1494, 1588 and 1601 cm.$^{-1}$) and aromatic hydrogen (3025 cm.$^{-1}$).

Anal. Calcd. for $C_{12}H_8O$: C, 85.69; H, 4.79. Found: C, 85.67; H, 4.94.

2-Hydroxy-2′-iodobiphenyl.—A mixture of 5.12 g. (15.15 mmoles) of the acetoxy compound, 70 ml. of anhydrous methanol and 1 drop of concentrated hydrochloric acid was heated under reflux for 10 hr. Most of the solvent was then distilled under reduced pressure; an additional 60 ml. of methanol was added, and the heating continued for 3 hr. Removal of the solvent left the crude 2-hydroxy-2′-iodobiphenyl as a very light tan oil, which was distilled in the special sublimation tube at 96–97° at 0.1 mm. The clear, colorless distillate became very viscous when cooled in the refrigerator and, when allowed to stand at room temperature, set to a hard, white solid, m.p. 62.5–63.0°, yield 4.3 g. (96%). The infrared spectrum has absorption peaks which can be attributed to disubstituted phenyl (748 cm.$^{-1}$), a phenol (1174 cm.$^{-1}$), aromatic hydrogen (3045 cm.$^{-1}$) and hydroxyl (3545 cm.$^{-1}$).

Anal. Calcd. for $C_{12}H_9IO$: C, 48.67; H, 3.06. Found: C, 48.88; H, 3.07.

2-Iodo-2′-methoxybiphenyl.—A solution prepared by adding 8.76 g. (29.6 mmoles) of 2-hydroxy-2′-iodobiphenyl to 50 ml. of 2 *N* sodium hydroxide was added, dropwise and with stirring, to 30 ml. (322 mmoles) of commercial methyl sulfate cooled to 5°. After the completion of the addition, which required about 15 min., the dropping funnel was rinsed with 10 ml. of 2 *N* sodium hydroxide solution. The mixture was stirred at 4–5° for 3 hr., allowed to come to room temperature, then stirred for an additional 18 hr. To the mixture, which had been cooled to 10° in an ice–water-bath, was added 200 ml. of 2 *N* sodium hydroxide solution at such a rate that the temperature did not rise above 15° (about 0.5 hr.). The bath was removed, and stirring continued for 20 hr. at room temperature. When the stirrer was stopped two layers formed. The heavy layer contained the iodo ether, which was isolated by conventional procedures and distilled in the special sublimation tube at 70–75° at 0.1 mm. In order to hasten the distillation the temperature was raised to 130° after about one-third of the material had been collected. The product solidified as it condensed in the cold part of the tube. Near the end of the distillation a small amount of methyl sulfate came over and was removed by washing the solid with dilute sodium hydroxide solution. The solid melted at 53.5–54.5°, yield 9.11 g. (99.4%). A solution of the compound in ethanol deposited an oil which when seeded changed to a solid melting at 54.5–56.0°. A cyclohexane solution of this material was allowed to evaporate slowly until a small amount of solvent remained. The colorless rhombohedra that had formed were collected on a filter, m.p. 56.5–57.5°. An analytical sample was prepared by sublimation at 80° and 2.5 mm. The sublimation, which required 4 days, gave 2-iodo-2′-methoxybiphenyl melting at 56.5–57.5° (reported[16] m.p. 58–59°). The infrared spectrum has bands which can be assigned to *o*-disubstituted phenyl (748 cm.$^{-1}$), a carbon–oxygen bond of an aliphatic ether (1029 cm.$^{-1}$), a carbon–oxygen bond of an aromatic ether (1250 cm.$^{-1}$), the skeletal vibrations of an aromatic system (1598 cm.$^{-1}$), aliphatic hydrogen (2930 cm.$^{-1}$) and aromatic hydrogen (3055 cm.$^{-1}$).

Anal. Calcd for $C_{13}H_{11}IO$: C, 50.34; H, 3.58; I, 40.92. Found: C, 50.64; H, 3.73; I, 41.14.

2-Duroyl-*o*-terphenyl.—Freshly ground magnesium (0.26 g., 10.7 mg. at.) and a very small crystal of iodine were placed in a flask which was then flushed with dry nitrogen. Anhydrous ether (7 ml.) was added, and the mixture allowed to stand for 15 min. Then 3 ml. of a solution of 3.0 g. (10.7 mmoles) of 2-iodobiphenyl in 5 ml. of dry ether was added. The stirrer was started, and the remainder of the solution of the iodide was added dropwise over a period of 0.5 hr. The mixture was heated with a lamp during this time and for an additional 1.5 hr., at the end of which time nearly all the magnesium had disappeared.

To the dark tan Grignard reagent was added within 10 min. a solution of 2.87 g. (10.7 mmoles) of duryl *o*-methoxyphenyl ketone in a mixture of 20 ml. of anhydrous ether and 25 ml. of dry benzene. The reaction mixture developed a reddish-brown color and deposited a precipitate. An additional 10 ml. of dry benzene was added, and the mixture—now orange colored—was heated under reflux for 22 hr. During this period the temperature of the mixture rose from 40 to 78°. The usual isolation procedure yielded the crude ketone as a brown solid which, when washed with cold cyclohexane, became light yellow, m.p. 161–162.5°, yield 2.14 g. (51.2%). Two recrystallizations of the product from absolute ethanol raised the melting point to 165.5°. The infrared spectrum has bands corresponding to monosubstituted phenyl (697 cm.$^{-1}$), *o*-disubstituted phenyl (742, 752 and 766 cm.$^{-1}$), the duryl group (868 cm.$^{-1}$), skeletal vibrations of a conjugated aromatic system (1590 cm.$^{-1}$), a conjugated aromatic ketone group (1674 cm.$^{-1}$), aliphatic hydrogen (2915 cm.$^{-1}$) and aromatic hydrogen (3060 cm.$^{-1}$).

Anal. Calcd. for $C_{29}H_{26}O$: C, 89.19; H, 6.71. Found: C, 88.93; H, 6.63.

2-Duroyl-2″-methoxy-*o*-terphenyl.—The procedure was very similar to that described for 2-duroyl-*o*-terphenyl. In several attempts, however, the Grignard reagent failed to form; apparently the concentration of the solution of the iodide in contact with the magnesium is critical. In the successful run a solution of 2 g. (6.45 mmoles) of 2-iodo-2′-methoxybiphenyl in 10 ml. of anhydrous ether was poured over 0.31 g. (12.91 mg. at.) of freshly ground magnesium to which a small crystal of iodine had been added. Reaction began immediately with the magnesium that was in contact with the iodine. When the reaction was well underway stirring and heating were started. After the mixture had been heated under reflux for 0.5 hr., an additional 10 ml. of ether containing 2.01 g. (6.48 mmoles) of the iodide was added all at once. After the initial, vigorous reaction had subsided, the reaction mixture was heated under reflux for an additional 2.5 hr. At the end of this time only a very small amount of magnesium remained.

At this point 4 ml. (about one-fourth) of the Grignard reagent was removed for use in the carbonation experiment to be described later. To the remaining Grignard reagent was added dropwise over a 15-min. period a solution of 2.32 g. (8.65 mmoles) of duroyl *o*-methoxyphenyl ketone in a mixture of 30 ml. of dry benzene and 10 ml. of anhydrous ether. The reaction mixture immediately assumed a reddish-brown color which changed successively to brown, yellow, blue-green, blue and purple. Heating of the mixture under reflux for 4 hr. caused the temperature to rise from 40 to 63°. The highly colored mixture was cooled to 5°, and 50 ml. of dilute hydrochloric acid was added. Stirring was continued at 5° for 0.5 hr. The crude ketone, isolated in the usual way, was a white solid melting at 133–153°. A little warm cyclohexane was added, and the solid was crushed into fine particles. After the mixture had been cooled, the solid was collected on a filter, washed thoroughly with cold cyclohexane and dried, m.p. 159.5–160.5°, yield 2.71 g. An additional 0.24 g., in the form of light yellow needles melting at 167–168°, was obtained from the cyclohexane wash liquor. The total weight of product was 2.95 g. (81.2%). The analytical sample was prepared by two recrystallizations from absolute ethanol, m.p. 161.2–161.6°. The infrared spectrum has absorption peaks that can be assigned to *o*-disubstituted phenyl (750 cm.$^{-1}$), the duryl group (869 cm.$^{-1}$), the methyl-oxygen bond of an ether (1032 cm.$^{-1}$), the carbon–oxygen bond of an aryl ether (shoulder at 1252 cm.$^{-1}$), the conjugated carbonyl group of an aromatic ketone (1675 cm.$^{-1}$), aliphatic hydrogen (2910 cm.$^{-1}$) and aromatic hydrogen (3060 cm.$^{-1}$).

Anal. Calcd. for $C_{30}H_{28}O_2$: C, 85.68; H, 6.71. Found: C, 85.50; H, 6.85.

2′-Methoxy-2-biphenylcarboxylic Acid.—The 4 ml. of Grignard reagent mentioned earlier was injected into a slurry of solid carbon dioxide and anhydrous ether. When the

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(14) H. v. Niederhäusern, *Ber.*, **15**, 1119 (1882).

(15) P. Sabatier and A. Mailhe, *Compt. rend.*, **151**, 492 (1910).

(16) L. Mascarelli and D. Gatti, *Atti IV Congr. Naz. chim. pura applicata* (1932), 503 (1933).

mixture had warmed to 0° it was acidified with dilute hydrochloric acid. The aqueous layer was extracted with benzene, and the benzene solution combined with the organic layer. The acidic product was taken up in 2 *N* sodium hydroxide solution and precipitated with hydrochloric acid. The 2′-methoxy-2-biphenylcarboxylic acid, after one recrystallization from benzene, formed light tan crystals, m.p. 149.5–150.5° (reported[7] m.p. 152–153°). A mixed melting point with an authentic sample showed no depression. The infrared spectrum has peaks ascribable to a 2,2′-disubstituted biphenyl in which the substituents are different (740 and 760 cm.$^{-1}$), a methoxyl group (1023, 1126 and 1253 cm.$^{-1}$), skeletal vibrations of a conjugated aromatic system (1500, 1590 and 1598 cm.$^{-1}$), an aromatic acid (1687 cm.$^{-1}$) and the hydroxyl group of a carboxylic acid (broad band at 2520–2660 cm.$^{-1}$).

URBANA, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES AND THE CHEMISTRY DIVISION, RESEARCH DEPARTMENT, U. S. NAVAL ORDNANCE TEST STATION]

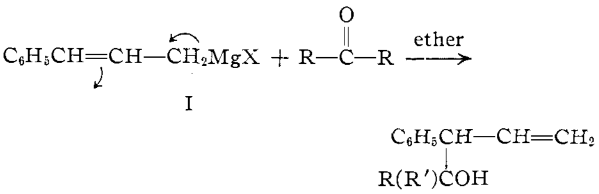
Allylic Rearrangements. XLIV. Reactions of Cinnamylmagnesium Bromide in Liquid Ammonia[1]

BY WILLIAM G. YOUNG AND WILLIAM P. NORRIS

RECEIVED JULY 10, 1958

Cinnamylmagnesium bromide forms highly colored precipitates in liquid ammonia below −50°. The color of the precipitate is attributed to the phenylallyl carbanion which was formed by solvation of the carbon–magnesium bond by the ammonia. Treatment of the colored precipitate with oxygen yields cinnamaldehyde.

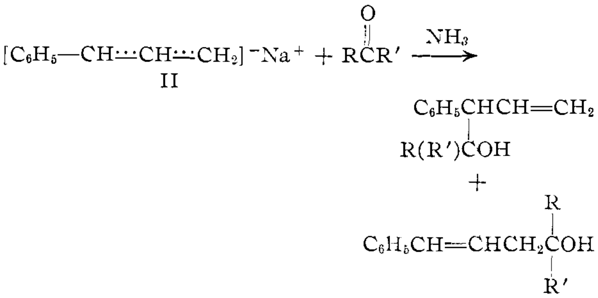
Cinnamylmagnesium halide in ethyl ether reacts with all but the most hindered carbonyl compounds to give α-phenylallylcarbinols. On the other hand,



$$C_6H_5CH{=}CH{-}CH_2MgX + R{-}\overset{O}{\overset{\|}{C}}{-}R \xrightarrow{\text{ether}} C_6H_5\underset{R(R')COH}{\underset{|}{C}H}{-}CH{=}CH_2$$

I

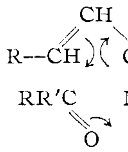
phenylallylsodium in liquid ammonia reacts with carbonyl reagents to give a mixture of both the α- and γ-phenylallylcarbinols.[2]



$$[C_6H_5{-}CH{\overset{...}{-}}CH{\overset{...}{-}}CH_2]^-Na^+ + R\overset{O}{\overset{\|}{C}}R' \xrightarrow{NH_3} C_6H_5\underset{R(R')COH}{\underset{|}{C}H}CH{=}CH_2 + C_6H_5CH{=}CHCH_2\overset{R}{\overset{|}{\underset{R'}{\underset{|}{C}}}}OH$$

II

Cinnamylmagnesium halide in ether is a covalent organometallic compound which exists predominantly or entirely in the primary configuration I.[3] The cyclic mechanism III proposed by Young and Roberts[4] to explain the nature of the products from addition reactions of carbonyl compounds and butenyl Grignard would explain how the primary cinnamyl Grignard reagent gives almost exclusively secondary addition products with carbonyl compounds.



III

Phenylallylsodium is a solid salt-like colored compound in inert solvents such as alkanes and ether and the electrophilic character of the sodium ion is quite important in coupling reactions with allylic halides, for instance.[5] In liquid ammonia, a polar solvent of relatively high dielectric constant, the ion pairs are dissociated and the sodium ions solvated so that the carbanion II reacts more or less independently. The amount of reaction at the α- or γ-positions depends on steric requirements of the two reactants and the relative reactivities of the α- and γ-positions.

Cinnamylmagnesium halide in ether reacts with aqueous acid to give a hydrocarbon product consisting of 75% allylbenzene and 25% propenylbenzene[6a,b] and when phenylallylsodium in pentane is added to excess methanol the hydrocarbon product is 74% allylbenzene and 26% propenylbenzene, essentially the same ratio.[5] If the phenylallylsodium is dissolved in liquid ammonia and treated with a proton donor the hydrocarbon mixture contains 85% propenylbenzene and 15% allylbenzene.

All reported reactions of cinnamylmagnesium halides have been carried out in ether or dioxane solutions, both solvents of low dielectric constant. The work reported here was carried out to see what effect ammonia, a high dielectric constant solvent, would have on the reactions of cinnamylmagnesium bromide.

When a concentrated ether solution of cinnamylmagnesium bromide was forced through a small capillary into well-stirred liquid ammonia at −76° a bright orange insoluble precipitate formed. This colored precipitate was stable for several hours at −76°. If the liquid ammonia mixture warmed up to −60° the orange precipitate changed to blue. At about −50° the blue color usually disappeared

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[1] Presented at the 133rd Meeting of the American Chemical Society, April 13, 1958, in San Francisco, Calif.

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