The Action of Bromine in Acetic Acid on Dihydropyran and Some of Its Derivatives

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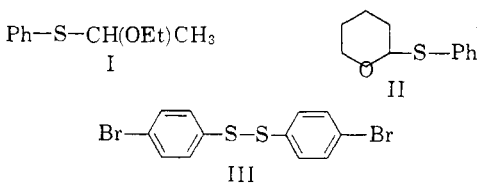
The action of bromine in acetic acid on phenyl 2-tetrahydropyryl sulfide (II) results in the formation of di(4-bromophenyl) disulfide (III) and a crystalline dibromide, $C_5H_8O_2Br_2$(IV). As the latter had unusual chemical and pharmacological properties its structure establishment was undertaken. Reduction of IV with lithium aluminum hydride led to 2,2-dibromo-1,5-pentandiol (VI), which could be readily hydrolyzed to 2-keto-1,5-pentandiol (VII) or reduced with sodium borohydride to 1,5-pentandiol. The structure of VII followed from its cleavage with periodate to γ-butyrolactone. These data require that IV have the constitution 3,3-dibromo-2-hydroxytetrahydropyran. The structure of IV was confirmed by its independent synthesis *via* known tetrahydropyran derivatives. The action of bromine in acetic acid on dihydropyran yielded 3,3-dibromo-2-acetoxytetrahydropyran (V), which was spontaneously hydrolyzed to IV on standing. In acetic acid solution IV gradually underwent intermolecular dehydration, affording 3,3-dibromo-2-tetrahydropyryl ether (VIII).

Several years ago one of us investigated the action of bromine in acetic acid on alkyl and aryl tetra-*O*-acetyl-β-D-thioglucopyranosides[2] and on phenyl tetra-*O*-acetyl-β-D-selenoglucopyranoside.[3] These reactions, in contrast to the bromination of phenyl poly-*O*-acetyl-D-glycopyranosides where only nuclear bromination was observed,[4] involved the cleavage of the thio- or seleno-glucoside, the conversion of the carbohydrate moiety into tetra-*O*-acetyl-α-D-glucopyranosyl bromide and the formation of diphenyl disulfide or diphenyl diselenide. Since such cleavage reactions were quite unexpected and since their mechanism[5] appeared rather complex it appeared to us desirable to extend our previous studies to such acyclic analogs as phenyl 1-ethoxyethyl sulfide (I) and to such heterocyclic noncarbohydrate analogs as phenyl 2-tetrahydropyryl sulfide (II).



Phenyl 1-ethoxyethyl sulfide (I) b.p. 77.2° (2.5 mm.), was prepared by the action of potassium thiophenoxide on ethyl 1-chloroethyl ether. The interaction of bromine with a solution of I in acetic acid resulted in the formation of di(4-bromophenyl) disulfide (III) as the only readily isolable product. The reaction of I thus qualitatively paralleled that of phenyl tetra-*O*-acetyl-β-D-thioglucopyranoside, with the exception that the thiophenyl moiety of I underwent additional nuclear bromination.

Phenyl 2-tetrahydropyryl sulfide (II), b.p. 110–112° (1 mm.), resulted on reaction of potassium thiophenoxide with 2-bromotetrahydropyran.[6] Reaction of II with bromine in acetic acid again yielded di(4-bromophenyl)disulfide (III) from its thiophenyl moiety, while its tetrahydropyran moiety engendered a white crystalline substance having the composition $C_5H_8O_2Br_2$ (IV). Further investigation disclosed that the latter crystalline dibromide could be prepared more readily directly from dihydropyran. Treatment of dihydropyran with bromine in acetic acid yielded a viscous oil, $C_7H_{10}O_3Br_2$ (V), which underwent spontaneous hydrolysis producing the above crystalline IV and acetic acid.

The dibromide IV proved to have some rather remarkable chemical properties. In 10% sodium hydroxide it yielded a yellow solution (A) which instantly gave a precipitate on treatment with silver nitrate. When air was bubbled through the yellow alkaline solution a deep wine-red color (B) was produced. If the latter red solution (B) were acidified it became yellow (D), reverting again to the red state on addition of excess alkali. Catalytic hydrogenation of the red alkaline solution (B) also produced a yellow solution (A) which, on treatment with a stream of air, again returned to its original red color (B). Acidification of the catalytically reduced yellow solution (A) gave rise to a colorless solution (C), whose yellow color (A) was again regenerated by addition of excess alkali. Catalytic reduction of the acidic yellow solution (D) afforded the acidic colorless solution (C), which could be reconverted to the yellow state (D) by treatment with an air stream. With no implication as to chemical identity, this series of reversible color transformations is summarized in Chart I.

(1) The authors are indebted to the Abbott Laboratories for funds which supported a portion of this investigation.

(2) W. A. Bonner, *J. Am. Chem. Soc.*, **70**, 770 (1948).

(3) W. A. Bonner and Ann Robinson, *J. Am. Chem. Soc.*, **72**, 356 (1950).

(4) C. D. Hurd and W. A. Bonner, *J. Am. Chem. Soc.*, **67**, 1764 (1945).

(5) W. A. Bonner, *J. Am. Chem. Soc.*, **70**, 3491 (1948).

(6) R. Paul, *Compt. rend.*, **198**, 375, 1246 (1934).

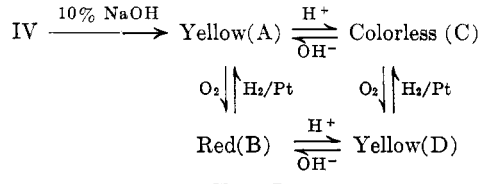


Chart I

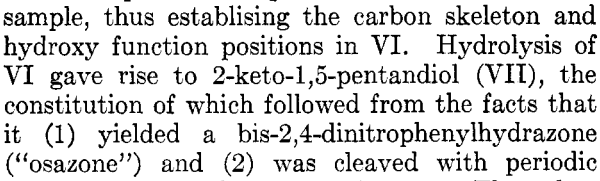
Thus the yellow substance arising on treatment of IV with alkali proved qualitatively to be both an acid-base indicator and an oxidation-reduction indicator. In addition to these chemical peculiarities, the crystalline dibromide IV also exhibited several interesting physiological characteristics. One of us (MR) observed that small concentrations of IV had a distinct paralyzing action on goldfish. Subsequent pharmacological testing of this substance[7] indicated it to have a mild central stimulating activity with a definite depressant component in mice, that it was slightly active in parasitological tests on the tapeworm, that it produced a transient loss of the righting reflex in dogs (at 100 mg./kg.) and that it was quite nontoxic to mice. That such interesting chemical and pharmacological properties should reside in a compound containing only five carbon atoms was quite intriguing to us, and it appeared of paramount importance to gather such chemical evidence as would permit a structural assignment to the dibromide IV, $C_5H_8O_2Br_2$.

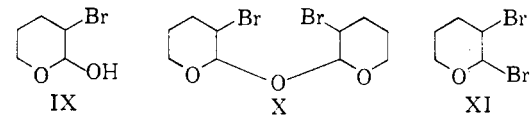
Lithium aluminum hydride reduction of IV yielded a solid bromine-containing alcohol which proved to be 2,2-dibromo-1,5-pentandiol (VI).

$$HO—CH_2CH_2CH_2CBr_2CH_2—OH$$
VI

$$HO—CH_2CH_2CH_2—CO—CH_2—OH$$
VII

Sodium borohydride reduction of the latter afforded the known[8] 1,5-pentandiol, identified by infrared spectral comparison with an authentic sample, thus establising the carbon skeleton and hydroxy function positions in VI. Hydrolysis of VI gave rise to 2-keto-1,5-pentandiol (VII), the constitution of which followed from the facts that it (1) yielded a bis-2,4-dinitrophenylhydrazone ("osazone") and (2) was cleaved with periodic acid to form γ-hydroxybutyrolactone. These degradative experiments argue for 3,3-dibromo-2-hydroxytetrahydropyran (IV) as the structure of our crystalline $C_5H_8O_2Br_2$, and for 3,3-dibromo-2-acetoxytetrahydropyran (V) as the structure of its sirupy acetate precursor, $C_7H_{10}O_3Br_2$. On standing in acetic acid, IV gradually underwent intermolecular dehydration with the production of what appeared to be 3,3-dibromo-2-tetrahydropyryl ether (VIII), m.p. 157°. This ready conversion of IV into VIII is reminiscent of the behavior ascribed by Paul[9] to 2-hydroxy-3-bromotetrahydropyran (IX), which spontaneously reverts to 3-bromo-2-tetrahydropyryl ether (X) on standing moist.





While the above degradative evidence appeared to us to establish structure IV on firm enough grounds, it nevertheless appeared desirable to confirm this conclusion synthetically by an independent synthesis of IV, proceeding through tetrahydropyran derivatives of known structure. The addition of bromine in ether to dihydropyran afforded the known[6] 2,3-dibromotetrahydropyran (XI) which, in the crude state, was subsequently hydrolyzed in the presence of lead hydroxide to the known crystalline 2-hydroxy-3-bromotetrahydropyran (IX).[9] Further bromination of the latter in acetic acid solution led to a sample of IV identical in all respects with that obtained above.

The chemical changes behind the reversible color phenomena summarized in Chart I as well as the pharmacological effects of similar tetrahydropyran derivatives are currently under investigation.

Experimental

Phenyl 1-Ethoxyethyl Sulfide (I).—Ethyl 1-chloroethyl ether[10] (10.9 g., 0.1 mole) was dissolved in chloroform (75 ml.). Potassium hydroxide (5.6 g., 0.1 mole) was dissolved in absolute ethanol (25 ml.) and thiophenol (10.2 g., 0.1 mole) was added. The latter solution was added in small portions to the chloroform solution, causing immediate warming and the precipitation of potassium chloride. On completion of the addition the mixture was refluxed for an additional 20 min., then cooled and filtered, rinsing with chloroform. The filtrate was washed with water, dried over sodium sulfate, and stripped of solvent *in vacuo* at 60° to yield 15.2 g. (83.5%) of clear, thin oil. The reaction was then duplicated on a threefold scale. The combined product from both reactions was distilled at 5 mm. through a semimicro Claisen flask: forerun, 9.4 g., b.p. 30–93°; main fraction, 40.7 g., b.p. 94–96°; pot residue, 6.0 g. The main fraction was redistilled through an 18-in. vacuum-jacketed semimicro Vigreux column. A 2-ml. forerun and residue were discarded and the main fraction, 36.8 g. (50.5%), was collected at 77.2–77.8° (2.5 mm.). It showed $n^{25}D$ 1.5325 and d_{21}^{21} 1.0275.

Anal. Calcd. for $C_{10}H_{14}OS$: C, 65.9; H, 7.74. Found: C, 65.8; H, 7.98. Molecular refraction: calcd. 54.4; found: 55.0.

Action of Bromine on Phenyl 1-Ethoxyethyl Sulfide.—Phenyl 1-ethoxyethyl sulfide (9.1 g., 0.05 mole) was dissolved in acetic acid (75 ml.) and treated under cooling with a solution of bromine (80 g., 0.5 mole) in acetic acid

(7) We are indebted to the Abbott Laboratories and to the Parke, Davis Co. for the pharmacological tests herein briefly described.

(8) B. Wojcik and H. Adkins, *J. Am. Chem. Soc.*, **55**, 4943 (1933).

(9) R. Paul, *Bull. soc. chim.* [5] **1**, 1397 (1934).

(10) M. D. Gauthier, *Ann. chim. phys.* [8], **16**, 311 (1909).

(25 ml.). Ice-cooling was employed during the addition, such that a temperature of 25° was maintained. The mixture then stood at room temperature for 2.5 hr., was transferred to a separatory funnel and was subsequently added in small portions to a slurry of ice and excess (48 g.) sodium thiosulfate. Sodium carbonate was added frequently to neutralize the reaction mixture, which was finally slightly alkaline. The yellow product separating during the addition was filtered and rinsed with water, and the filtrate was extracted with ether. Solvent removal from the extract afforded a negligible quantity (0.3 g.) of lachymatory oil which was discarded. The crude solid was dissolved in hot dioxane (50 ml.). The solution was filtered from 3 g. of inorganic material, treated with water until turbid, and allowed to crystallize as shining yellow platelets, 5.10 g., m.p. 92–93.5°. Recrystallization from dilute dioxane failed to raise the m.p. above 93.5–94°. The identity of the product as di(4-bromophenyl) disulfide (III) was established by mixed melting point (93.5–94°) with an authentic sample (m.p. 93–94°) prepared by the direct bromination of diphenyl disulfide according to the procedure of Bourgeois and Abraham.[11]

Phenyl 2-Tetrahydropyryl Sulfide (II). 2-Bromotetrahydropyran was prepared by treating dihydropyran (16.8 g.) with gaseous hydrogen bromide at 5–10° until the weight gain was 17.5 g., a procedure similar to that employed by Paul.[6] The crude yellow product was dissolved in cold chloroform (150 ml.), and the solution was treated slowly with a solution of potassium hydroxide (11.2 g.) and thiophenol (21 ml.) in absolute ethanol (75 ml.). Potassium bromide precipitated instantly with spontaneous warming. The slightly acidic solution was treated with sufficient alcoholic potassium hydroxide to make it just basic to litmus but not to phenolphthalein, then was heated under reflux for 30 min., cooled, and poured into water. The chloroform layer was washed thoroughly with water, dried over anhydrous sodium sulfate, and stripped of solvent *in vacuo*, yielding 29.3 g. of amber oil. The latter was fractionated through a 3-in. Vigreux column and a center cut, 16.4 g. (42.3%), b.p. 110–112° (1 mm.), was collected. This material was redistilled in the same apparatus and a center cut collected for analysis, $n^{23.5}$D 1.5705, $d_{21.5}^{24}$ 1.117.

Anal. Calcd. for $C_{11}H_{14}OS$: C, 68.0; H, 7.26. Found: C, 68.2; H, 7.39. Molecular refraction: calcd. 56.8; found: 57.1.

3,3-Dibromo-2-hydroxytetrahydropyran (IV) from Phenyl 2-Tetrahydropyryl Sulfide (II).—A solution of phenyl 2-tetrahydropyryl sulfide (5.00 g.) in acetic acid (125 ml.) containing bromine (13.2 ml.) was allowed to stand in a water bath at room temperature for 3 hr., then poured into ice water (500 ml.) containing an excess of sodium bisulfite. The solid material which precipitated was filtered and dried over phosphorus pentoxide, 4.40 g. (99%), m.p. 63–69°. Three recrystallizations (Norit) from dilute dioxane afforded pure di(4-bromophenyl) disulfide, m.p. 92°, no depression on admixture with an authentic sample. The filtrate from above was saturated with salt and extracted twice with ether, whereupon the extract was washed with water and sodium bicarbonate solution, dried over anhydrous sodium sulfate, and stripped of solvent *in vacuo*, affording 3.65 g. (54.5%) of amber oil. The latter was distilled, b.p. 96–98° (1 mm.); the distillate, 2.50 g., crystallized on cooling. The material was readily recrystallized three times by dissolving in a small amount of ethyl acetate, adding excess petroleum ether and chilling in ice water. The purified 2,3-dibromo-2-hydroxytetrahydropyran so obtained had m.p. 99.5°.

Anal. Calcd. for $C_5H_8O_2Br_2$: C, 23.12; H, 3.10; Br, 61.55; mol. wt., 259.9. Found: C, 23.09, 23.05; H, 3.18, 3.12; Br, 61.37, 61.49; mol. wt., 263, 258.

3,3-Dibromo-2-acetoxytetrahydropyran (V).—Dihydropyran (4.2 g., 0.05 mole) in acetic acid (125 ml.) was treated gradually with a solution of bromine (80 g., 0.5 mole) in acetic acid (25 ml.), cooling the reaction under the tap. The mixture was poured into ice water (500 ml.), treated with sodium bisulfite until clear and extracted with ether. The extract was washed with water, sodium bicarbonate solution, water, and finally dried over anhydrous sodium sulfate, filtered, and stripped of solvent. The residual amber oil, 7.00 g., was distilled, b.p. 120–122° (4.5 mm). Redistillation under the same conditions gave a sample having n^{25}D 1.5274 and d_{21}^{25} 1.848.

Anal. Calcd. for $C_7H_{10}O_3Br_2$: C, 27.8; H, 3.32. Found: C, 27.4; H, 3.56. Molecular refraction: Calcd. 51.2; Found: 50.4.

The compound is assumed to have the indicated constitution in view of its spontaneous conversion to 3,3-dibromo-2-hydroxytetrahydropyran on standing. A sample of the oily product (2.2129 g.) was placed in a beaker and exposed to air. On standing 1 day the compound smelled strongly of hydrogen bromide and acetic acid and was partially solid. After another day the solidified material was placed *in vacuo* over potassium hydroxide for 2 days, whereupon it weighed 1.9050 g., corresponding to the exact weight loss required by the equation: $C_7H_{10}O_3Br_2 + H_2O \rightarrow C_5H_8O_2Br_2 + CH_3COOH$. The melting point of the crude product was 94–97°. After recrystallization from a mixture of ethyl acetate and petroleum ether the sample had m.p. 98.5° and showed no depression on admixture with the above 3,3-dibromo-2-hydroxytetrahydropyran.

When the above preparation was repeated with a larger quantity of dihydropyran (0.8 mole) a more complicated mixture of products was obtained. Vacuum distillation of the crude material afforded a range of fractions having higher refractive indices than noted above. These underwent only partial spontaneous hydrolysis of the sort previously noted. Furthermore, the pot residues from such distillations deposited crystals on standing. Recrystallization from 2-propanol yielded a product, m.p. 157.5–158°, which appeared identical with the 3,3-dibromo-2-tetrahydropyryl ether described below.

Anal. Calcd. for $C_{10}H_{14}O_3Br_4$: C, 23.94; H, 2.80. Found: C, 24.06, 24.20; H, 2.83, 2.87.

3,3-Dibromo-2-hydroxytetrahydopyran (IV) from Dihydropyran.—The above spontaneous hydrolysis of the acetate suggested a more convenient preparation of 3,3-dibromo-2-hydroxytetrahydropyran directly from dihydropyran. Dihydropyran (16.8 g., 0.2 mole) was dissolved in acetic acid (300 ml.) and bromine (160 g., 1 mole) was added dropwise, cooling the reaction vessel in an ice bath to keep the temperature below 25°. After completion of the addition the mixture was stirred for 12 hr. and the solution was poured into 1 l. of ice water and treated with sodium bisulfite (54 g.) to remove excess bromine. On addition of sodium chloride (115 g.) a yellow oil separated. This was extracted into four 150-ml. portions of ether. The extract was washed four times with 200-ml. portions of water and then twice with 100-ml. portions of 1.2 *M* sodium bicarbonate solution, then again with water. The extract was dried over sodium sulfate, filtered, and stripped of solvent *in vacuo*. On standing for 24 hr. the residual amber oil solidified. The solid was recrystallized as above, affording 9.7 g. (18.6%) of white product, m.p. 98.1–98.5°, elemental analysis similar to that above. Duplication of the above procedure employing 73.1 g. of dihydropyran and proportional quantities of other reagents was conducted exactly until the amber oil solidified. The solid was freed of oily impurities by repeated rinsing with ligroin and the residual product was recrystallized from benzene, 70.1 g. (31.5%), m.p. 98.1–98.5°.

2,2-Dibromo-1,5-pentandiol (VI).—A solution of lithium aluminum hydride (1.5 g.) in anhydrous ether (30 ml.) was treated dropwise with a solution of the above 3,3-dibromo-2-hydroxytetrahydropyran (6 g.) in ether (30 ml.) at such a rate as to maintain gentle reflux. The mixture was stirred for 10 min. then treated with a solution of ethyl acetate in ether to destroy the excess hydride. After

(11) E. Bourgeois and A. Abraham, *Rec. trav. chim.*, **30**, 421 (1911).

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°)[3] 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.

(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-

(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) 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).