tilled to leave a liquid from which separated an additional 0.1 g. of hexaphenyldigermane melting over the range 338–344° (total yield 0.5 g., 8.3%). The mother liquor was dissolved in petroleum ether; then by volume reduction and cooling there was obtained 2.1 g. of crystals melting over the range 90–180°. This was recrystallized from the same solvent to give 1.3 g. (21%) of hexaphenyldigermoxane, m.p. 185–186°, and 0.2 g. (6%) of recovered fluorene melting over the range 115–119°.

A second run using the same quantities of materials gave almost exactly the same results.

Reaction of triphenylgermyllithium with dibenzofuran. Using the same procedure as above, the triphenylgermyllithium from 6.0 g. of hexaphenyldigermane was allowed to react with 3.4 g. (0.02 mole) of dibenzofuran. Work-up of the reaction mixture in the same manner as above yielded 1.6 g. (25%) of triphenylgermanecarboxylic acid, m.p. 184–186°, 0.4 g. (6.7%) of hexaphenyldigermane, m.p. 344–345°, 0.9 g. (14%) of triphenylgermyl triphenylgermanecarboxylate, m.p. 165–166°, and 0.7 g. (20.6%) of recovered dibenzofuran, m.p. 86–87°. No dibenzofuran-4-carboxylic acid was isolated.

Reaction of phenyllithium with fluorene in GDME. Phenyllithium was prepared in GDME by the reaction of bromobenzene (15.7 g., 0.1 mole) with lithium wire (1.47 g., 0.21 g.-atom) to give a deep green solution. Acid titration indicated a yield of 0.0283 mole or 28.3%.

To this stirred lithium reagent was added an excess of fluorene (12.2 g., 0.074 mole) dissolved in GDME. After the first addition an orange color appeared, however upon further stirring it was replaced by the blue-green color. When the addition of fluorene was complete the color remained orange. After stirring 22 hr. the mixture was carbonated and allowed to warm to room temperature. Work-up as previously mentioned gave 2.0 g. of light brown acid melting over the range 205–215°. Recrystallization from acetic acid gave 1.0 g. (25% based on phenyllithium) of fluorene-9-carboxylic acid, melting over the range 218–222°.

The ether layer was dried and the solvents distilled to leave a residue which was recrystallized from ethanol to give 8.0 g. (67%) of recovered fluorene, m.p. 116–118°.

Reaction of triphenylgermyllithium with bromine. A solution of triphenylgermyllithium from 6.0 g. of hexaphenyldigermane was cooled to −25°, then 2.4 g. (0.015 mole) of bromine dissolved in GDME was added dropwise while the temperature was maintained between −20° and −25°. When the addition was complete the mixture was stirred and allowed to warm to room temperature overnight. This mixture was filtered and the precipitate washed with ether, 10% hydrochloric acid, and hot petroleum ether to give 4.6 g. (78%) of hexaphenyldigermane, melting over the range 339–343°. The ether layer was dried and the solvents distilled to leave a residue which was recrystallized from ethanol to give 0.2 g. (2.6%) of bromotriphenylgermane, m.p. 138–140°.

The hexaphenyldigermane obtained from this reaction could not have been unreacted starting material because the solubility is such that very little dissolved in the solvent and any amount would be visible before the bromine was added, especially at the low temperatures used in the reaction.

A second run using exactly the same conditions and amounts of starting materials yielded 4.7 g. (78%) of hexaphenyldigermane and 0.9 g. (11.8%) of bromotriphenylgermane.

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Some Organolithium Compounds of Quinoline and 2-Phenylquinoline

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In a recent publication from this laboratory,[1] the first preparation of 1-isoquinolyl- and 2-quinolyllithium was reported. These organolithium reagents were prepared from 1-bromoisoquinoline and 2-bromoquinoline, respectively, by means of the halogen-metal interconversion reaction with *n*-butyllithium between −50 and −60°. When 1-isoquinolyl- and 2-quinolyllithium were carbonated, the predominant products were 1,1′-diisoquinolyl- and 2,2′-diquinolyl ketone, respectively, rather than the expected acids.

The preparation of 4-quinolyllithium was effected in the same manner as was the 2-isomer. 4-Bromoquinoline was treated with *n*-butyllithium between −50 and −60° for 20 min. The approximate yield of 4-quinolyllithium (80%) was determined by a reaction with benzophenone to give the tertiary carbinol, α,α-diphenyl-4-quinolinemethanol.

The similarity in the reactivity of the 2- and 4-position in quinoline led the authors to consider the possibility that the carbonation of 4-quinolyllithium might yield 4,4′-diquinolyl ketone as the 2-isomer had yielded 2,2′-diquinolyl ketone. The only product that could be detected, however, from the carbonation of 4-quinolyllithium was 4-quinolinecarboxylic acid which was isolated in a yield of 39%. Two possible explanations for the failure of 4-quinolyllithium to form the ketone, in appreciable quantities, on carbonation are as follows: the lesser degree of reactivity of 4-quinolyllithium as compared to the 2-isomer, or the 4-quinolyllithium's effective reactivity was reduced due to its insolubility in diethyl ether at −50°.

The preparation of 2-(*p*-lithiophenyl)- and 2-(*m*-lithiophenyl)quinoline was achieved also by the use of the halogen-metal interconversion reaction. 2-(*p*-Bromophenyl)- and 2-(*m*-bromophenyl)quinoline were treated with *n*-butyllithium at −20° for 20 min. The yields of 2-(*p*-lithiophenyl)- and 2-(*m*-lithiophenyl)quinoline, based on the crude acids obtained on carbonation, were 75 and 70%, respectively.

The preparation of 2-(*p*-lithiophenyl)- and 2-(*m*-lithiophenyl)quinoline in such good yields was of particular interest because Summers[2] had attempted earlier to prepare the isomeric 7-(*p*-lithiophenyl)quinoline by treating 7-(*p*-bromophenyl)-quinoline with *n*-butyllithium at −50°, but was

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[1] H. Gilman and T. S. Soddy, *J. Org. Chem.*, **22**, 565 (1957).

[2] R. M. Summers, Doctoral Dissertation, Indiana University, Bloomington, Ind., 1954.

able to isolate only starting material from the reaction. This fact indicates that the bromo derivatives of the pyridinoid portion of quinoline probably enter into the halogen-metal interconversion reaction more readily than the corresponding bromo derivatives of the benzenoid portion of quinoline.

EXPERIMENTAL[3]

4-Quinolyllithium. Into a 250-ml., round-bottomed flask were introduced 100 ml. of anhydrous ether and 0.015 mole of *n*-butyllithium in 16 ml. of anhydrous ether. This solution was cooled to −50°. To this solution was added 3 g. (0.015 mole) of 4-bromoquinoline. A yellow suspension formed and Color Test II A[4] was negative after 10 min., but Color Test I[5] was positive.

α,α-Diphenyl-4-quinolinemethanol. To the stirred solution of 4-lithioquinoline, prepared in the preceding experiment, was added dropwise 2.7 g. (0.015 mole) of benzophenone in 100 ml. of ether. After the addition of 80 ml. of the ethereal solution Color Test I[5] was negative. The reaction mixture turned light yellow, and a white, curdy precipitate formed. On hydrolysis with an ice cold saturated solution of ammonium chloride, a white solid settled between the water and ether layers. The solid was removed by filtration and dried. The yield of crude product was 80%. On recrystallization from an ethanol-benzene (1:2) pair the m.p. was 246–248° (lit. value 247–248°).[6]

4-Quinolinecarboxylic acid. Into a 3-necked, elongated flask, which was equipped with a stopcock on the bottom and an attached Dry Ice–acetone bath, was introduced 0.015 mole of *n*-butyllithium in 100 ml. of ether. This solution was cooled to −50°, and 3 g. (0.015 mole) of 4-bromoquinoline was added. The reaction mixture was stirred for 20 min. at −50°. The stopcock was opened, and the yellow suspension flowed jetwise into a vigorously stirred Dry Ice–ether slurry. The carbonation mixture was worked up in the usual manner. The basic extract was acidified to a *p*H of 6 and concentrated from 100 to 50 ml. The *p*H was lowered to 1, at which time the organic acid separated in fine white crystals. The m.p. of the acid was 249.5–250° (lit. value 253–254°),[7] and the yield was 39%. No products could be isolated from the ether extract.

2-(p-Bromophenyl)quinoline. To a stirred solution of 39 g. (0.3 mole) of quinoline in 150 ml. of anhydrous ether at 0° was added dropwise a solution of 0.3 mole of *p*-bromophenyllithium[8] in 600 ml. of ether. The reaction mixture turned yellow and remained as such throughout the addition. Although the reaction mixture was stirred overnight, Color Test I[5] remained slightly positive. After refluxing the mixture for 1 hr., Color Test I[5] was negative. Hydrolysis of the reaction mixture was effected by pouring it into a saturated ammonium chloride solution. The ether layer was separated and dried over anhydrous sodium sulfate. After evaporation of the ether the crude product was dissolved in absolute ethanol. On recrystallization from absolute ethanol the pure compound was obtained as white platelets, m.p. 121–122°. The yield was 42%.

Anal. Calcd. for $C_{15}H_{10}BrN$: Br, 27.91. Found: Br, 27.71, 27.90.

2-(p-Carboxyphenyl)quinoline. Into a 3-necked, elongated flask which was equipped with a stopcock on the bottom and an attached Dry Ice–acetone bath, was introduced 0.02 mole of *n*-butyllithium in 17 ml. of anhydrous ether. To this solution, cooled to −45°, was added over 5 min., a solution of 0.02 mole of 2-(*p*-bromophenyl)quinoline in 80 ml. of ether and 20 ml. of benzene. The reaction mixture turned green, but the temperature remained constant. After stirring for 25 min. Color Test IIA[4] was negative, and Color Test I[5] was positive. The reaction mixture was carbonated by opening the stopcock at the bottom of the reaction vessel which permitted the reaction mixture to flow jet-wise onto a Dry Ice–ether slurry.

The basic extract was acidified, and the solid which precipitated was filtered off. The crude yield was 75%. Recrystallization of the crude product from ethanol yielded white needles, m.p. 252–253° (lit. value 248–249°).[9]

m-Bromophenyllithium. To a stirred solution of 0.2 mole of *m*-dibromobenzene in 140 ml. of ether at −35° was added 0.2 mole of *n*-butyllithium in 135 ml. of ether at −35°. The temperature rose to −20°, after which it was again cooled to −35°. At 3-, 6-, 9-, 12-, and 15-min. intervals 50-ml. aliquots were removed and carbonated. The carbonation mixtures were worked up in the usual manner. The optimum yield, in the times examined, of crude *m*-bromobenzoic acid (72%) was realized at the 15-min. interval. The melting point of the pure acid was 152–154°.

2-(m-Bromophenyl)quinoline. To the stirred solution of 6.5 g. (0.05 mole) of quinoline in 50 ml. of ether at 0° was added dropwise 0.037 mole of *m*-bromophenyllithium in ether at −25°. The reaction mixture was yellow at the end of the addition. Hydrolysis of the reaction mixture was effected by pouring it into a saturated solution of ammonium chloride. The ether extract was dried over sodium sulfate. On evaporation of the ether the residue was oxidized with nitrobenzene for 10 min. at 140°. The nitrobenzene was distilled under reduced pressure, and the residue recrystallized from 95% ethanol. The melting point of the pure compound was 74.5–76°, and the yield was 65%.

Anal. Calcd. for $C_{15}H_{10}BrN$: Br, 27.91. Found: Br, 27.72, 27.84.

2-(m-Carboxyphenyl)quinoline. To a stirred solution of 0.01 mole of *n*-butyllithium in 50 ml. of ether at −30° was added 2.5 g. (0.009 mole) of 2-(*m*-bromophenyl)quinoline. The reaction mixture turned green. At the end of 20 min. Color Test IIA[4] was negative, and Color Test I[5] was positive. The reaction mixture was carbonated by pouring jet-wise onto a Dry Ice–ether slurry. On working up the carbonation mixture in the usual manner the basic extract yielded 1.5 g. of crude acid upon acidification. This amount was equivalent to a 70% yield. The crude acid on purification by recrystallization from 95% ethanol melted at 215–215.5°.

Anal. Calcd. for $C_{16}H_{11}NO_2$: N, 5.62. Found: N, 5.59, 5.68.

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[3] All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen, and all melting points are uncorrected.

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