216°, could be isolated. This product was shown to be the *threo* isomer by comparison of m.p., mixed m.p. and infrared spectrum.

When 0.13 g. of *threo*-2-benzamido-1,2-diphenylethanol (the 215–216° compound) was subjected to the same treatment, 0.10 g. of only impure starting material could be recovered. No higher melting product was detected.

Reductions of Imabenzil.—(a) Sodium borohydride (0.60 g.) was added with stirring to a solution of 0.34 g. of imabenzil in 75 ml. of ethanol and the mixture refluxed for four hours. Partial concentration of the solution and the addition of water produced a precipitate which on filtration was crystallized fractionally from methanol; 0.11 g. of a compound, m.p. 239–240°, and 80 mg. of another, m.p. 214–215°, were isolated. These products could be shown to be the *erythro*- and *threo*-2-benzamido-1,2-diphenylethanols, respectively, by comparison of their m.p., mixed m.p. and infrared spectra.

(b) A solution of 1.31 g. (2.3 mmoles) of imabenzil in 75 ml. of ethanol was hydrogenated over palladium–charcoal catalyst at room temperature and pressure. The reaction was complete at the end of 26 hours and the uptake of 103 ml. (4.6 mmoles) of hydrogen. After filtration of the catalyst and evaporation of the filtrate, fractional crystallization of the product from methanol gave 0.69 g. of white flakes, m.p. 239–240°, and 0.43 g. of a substance, m.p. 215–216°. These compounds were again shown to be the above two epimeric 2-benzamido-1,2-diphenylethanols by mixed m.p. and infrared spectra. Distillation of the oil, remaining after complete removal of methanol from the mother liquor, yielded 60 mg. of a liquid whose infrared spectrum was indistinguishable from that of ethyl benzoate.

When 0.65 g. of imabenzil was exposed to catalytic hydrogenation conditions identical to those above except for the absence of hydrogen gas, 0.54 g. of slightly impure starting material, m.p. 191–193°, was the only isolable product.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Some Reactions of *o*-Halobromobenzenes with *n*-Butyllithium

BY HENRY GILMAN AND RICHARD D. GORSICH

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o-Fluorophenyllithium (I) and *o*-chlorophenyllithium (II) can be prepared in excellent yields at about −60 and −90°, respectively, by the interaction of the corresponding *o*-halobromobenzene with *n*-butyllithium. *o*-Bromophenyllithium (III) has been prepared in a 23% yield by employing a temperature of −100° and a reaction time of 7 minutes. The first two organolithium compounds on being allowed to warm to room temperature give 2-halo-2′-lithiobiphenyl and triphenylene (XIII). In the case of II at −65° only 2-chloro-2′-lithiobiphenyl (VII) and 2-(*o*-chlorophenyl)-2′-lithiobiphenyl (XI) have been derivatized whereas, at room temperature, only VII and XIII have been obtained. The possible routes of the reactions of I and II on warming and similarities to other reactions are discussed. In addition, 2-bromo-2′-carboxybiphenyl and 4-bromo-9,9-diphenylfluorene have been synthesized for comparison purposes.

Although *o*-fluorophenyllithium (I) had previously been considered too reactive to form derivatives as such,[1,2] we successfully obtained the benzophenone adduct in excellent yields.[3]

The inability of earlier workers to detect I can be ascribed to the reaction conditions employed. All of their reactions were carried out at temperatures in the vicinity of 0°, whereas all successful preparations of *o*-halophenyllithium compounds in this Laboratory were achieved below −50°. Attempts to prepare I and *o*-chlorophenyllithium (II) at −30° and 0° were unsuccessful.

In the course of our studies we have been able to carbonate I to *o*-fluorobenzoic acid (IV) in 83% yield at about −60° after adding the *o*-fluorobromobenzene to the *n*-butyllithium. In carrying out the addition in a reverse manner at the same temperature only a 42% yield of IV was obtained while a 15% yield of 2-fluoro-2′-carboxybiphenyl (X) was isolated. Furthermore, if the reaction mixture was allowed to warm to room temperature and then carbonated, the only acid isolated was X. In addition to this acid there was also obtained a 2.5% yield of triphenylene (XIII).

Similar results were obtained in the case of II although it appeared to be much more reactive than I, as was evidenced by the increased yield of coupling products under comparable conditions and also by the lower temperature required for its preparation in good yield. At −90°, II could be prepared in an almost quantitative yield as determined by carbonation. The method of carbonation, which was different from that used in the other runs, may be a promising one. Instead of pouring the mixture over a Dry Ice–ether slurry, powdered Dry Ice was added to the reaction mixture at −100° and then it was allowed to warm to room temperature.[4] The usual method, pouring of the reaction mixture into a Dry Ice–ether slurry, could not be used in this case since the temperature rise of the reaction mixture during carbonation was sufficient to give some 2-chloro-2′-carboxybiphenyl (IX). When the reaction was carried out employing conditions similar to those used for I, there was obtained about a 6% yield of *o*-chlorobenzoic acid (V) and an 18% yield of IX. With II the mode of addition was immaterial. By allowing II to warm to room temperature and then carbonating, a 22% yield of IX was obtained and a 7% yield of XIII was found in contrast to 2.5% of XIII obtained with I under similar conditions. By varying the reaction conditions it was possible to increase the yield of XIII to approximately 17%.

In any of the carbonations achieved below −30° in which coupling products appeared, there was obtained simultaneously on extraction of the ethereal layer with sodium hydroxide an acidic oil. Numerous attempts to obtain a pure compound from this oil failed, but it is believed that some 2-(*o*-chloro-

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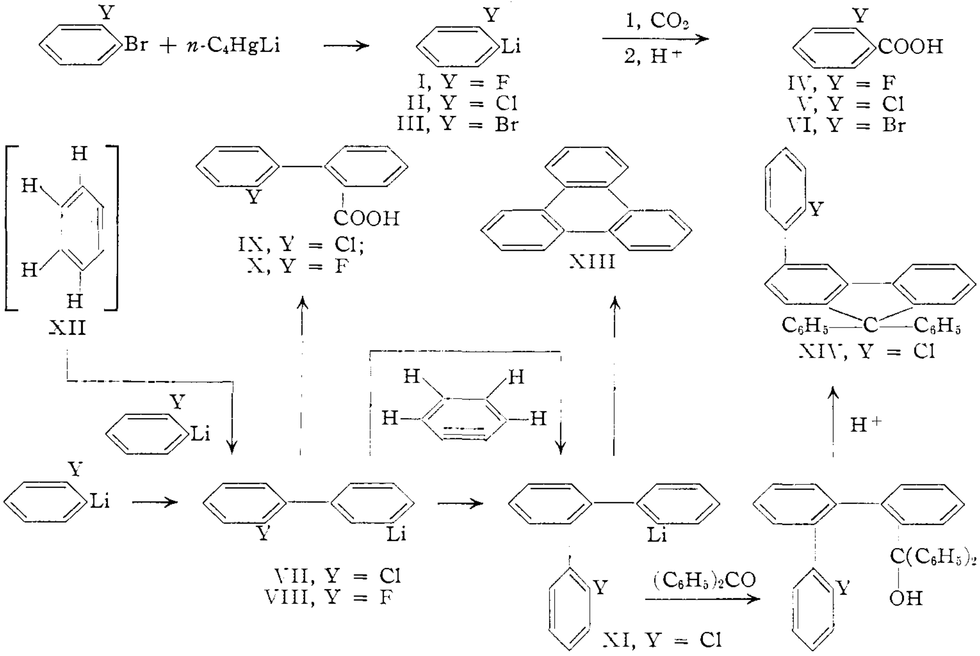
[1] G. Wittig, G. Pieper and G. Fuhrmann, *Ber.*, **73**, 1193 (1940).

[2] G. Wittig and W. Merkle, *ibid.*, **75**, 1491 (1942).

[3] H. Gilman and R. D. Gorsich, THIS JOURNAL, **77**, 3919 (1955).

[4] The high yield of acid obtained by adding carbon dioxide to II is somewhat surprising in view of the high yield of ketones obtained by H. Gilman and P. R. Van Ess, THIS JOURNAL, **55**, 1258 (1933), by passing carbon dioxide over the organolithium compound.



phenyl)-2′-carboxybiphenyl may have been present since the intermediate organolithium compound was derivatized successfully with benzophenone.

The studies concerned with *o*-bromophenyllithium (III) were limited; however, evidence indicated that it was more reactive than either the chloro or fluoro isomers. Employing a 7-minute reaction time at −100° afforded a 23% yield of *o*-bromobenzoic acid (VI), whereas after 45 minutes at the same temperature there was obtained only a trace of VI. The neutral products were not identified.

When II was treated with benzophenone at −65°, in addition to obtaining the benzophenone adduct of 2-chloro-2′-lithiobiphenyl (VII) isolated as 4-chloro-9,9-diphenylfluorene in 27% yield, about a 10% yield of the benzophenone adduct of 2-(*o*-chlorophenyl)-2′-lithiobiphenyl (XI) also was isolated. The carbinol was readily converted by glacial acetic acid to 4-(*o*-chlorophenyl)-9,9-diphenylfluorene (XIV).

The formation of VII, VIII, XI and XIII may have occurred by one of two possible routes, both of which are compatible with the evidence obtained. One route, using II as an example, could be visualized as first involving the displacement of the chlorine from II by the anion of another molecule of II to give VII. In a similar manner, XI could be formed by the interaction of VII with II. Subsequently, on warming, XI could undergo an intramolecular displacement to give XIII. This pathway, however, does not account for the enhanced reactivity of *o*-halophenyllithium compounds as compared to other halophenyllithium types.[5]

The second possible route appears to be more plausible than the first, involving as it does an intermediate which would nicely account for the increased reactivity of the *o*-halophenyllithium compounds. This highly reactive species, sometimes termed the "benzyne" intermediate XII, was first postulated by Wittig[6] as possibly arising in the metalation of fluorobenzene with phenyllithium. Roberts and co-workers[7] adduced good evidence for such a symmetrical intermediate when they showed that approximately equal amounts of aniline-1-C^{14} and aniline-2-C^{14} were obtained by the interaction of chlorobenzene-1-C^{14} with potassium amide.

Recently, such an intermediate was invoked to rationalize the reaction of diphenyl ether with phenylsodium[8] and fluoroanisoles with phenyllithium.[9,10] In the latter case it was shown that both *o*- and *m*-fluoroanisole, when treated with phenyllithium followed by carbonation, gave rise to a mixture of 2-phenyl-6-methoxybenzoic acid and 2-phenyl-3-methoxybenzoic acid. In a similar manner 1-fluoronaphthalene, when reacted with phenyllithium and then carbonated, gave rise to a

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[5] For example, *p*-chlorophenyllithium can be obtained in high yields at room temperature by the interaction of *p*-chlorobromobenzene with *n*-butyllithium. For other similar examples see H. Gilman, W. Langham and F. W. Moore, THIS JOURNAL, **62**, 2327 (1940).

[6] G. Wittig, *Naturwiss.*, **30**, 696 (1942).

[7] J. D. Roberts, H. E. Simmons, Jr., L. A. Carlsmith and C. W. Vaughn, THIS JOURNAL, **75**, 3290 (1953).

[8] A. Lüttringhaus and K. Schubert, *Naturwiss.*, **42**, 17 (1955).

[9] R. Huisgen and H. Rist, *ibid.*, **41**, 358 (1954).

[10] Additional information strongly supporting the "benzyne" intermediate has been presented very recently by G. Wittig and L. Pohmer, *Angew. Chem.*, **67**, 348 (1955). This evidence is closely related to the present report since it involves the interaction of *o*-fluorobromobenzene with lithium amalgam in ether and in furan. Their results have been interpreted as first involving the formation of the "benzyne" intermediate from *o*-fluorobromobenzene and lithium amalgam followed by a Diels–Alder reaction of the intermediate with furan to give 1,4-dihydronaphthalene-1,4-endoxide.

Recently, evidence in agreement with the results reported in this communication has been presented by G. H. Hall, R. Piccolini and J. D. Roberts, THIS JOURNAL, **77**, 4540 (1955). The latter workers attempted unsuccessfully to alkylate the anion from fluorobenzene with methyl iodide in liquid ammonia solution containing equal molar amounts of fluorobenzene and potassium amide. This in accord with our unsuccessful attempts to derivatize *o*-fluorophenyllithium at −30°. See, also, E. F. Jenny and J. D. Roberts, *Helv. Chim. Acta*, **38**, 1248 (1955). See also, the studies by H. Heaney, F. G. Mann and I. T. Millar, *J. Chem. Soc.*, 1 (1956) which appeared just before receipt of proof of this article.

mixture of 1-phenyl-2-naphthoic acid and 2-phenyl-1-naphthoic acid. On the other hand, 2-fluoronaphthalene not only afforded the aforementioned acids but also gave 2-phenyl-3-naphthoic acid. The formation of the above mixtures was explained by postulating the existence of the symmetrical "benzyne" and "naphthyne" intermediates, respectively.

The above examples closely parallel the reactions described in this paper with the main difference being that in this work the halogen–metal interconversion reaction was utilized, whereas previous workers essentially made use of a metalation reaction. Since the halogen–metal interconversion reaction can be achieved under more moderate conditions than metalation,[11a,11b] the former method is superior for isolating reactive intermediates.

The instability of the *o*-halophenyllithium compounds at higher temperatures may well be associated with XII. For example, when II is warmed to an appropriate temperature, it may be converted partially to XII which, in turn, because of its reactivity could interact with unconverted II to give VII or it could react further with VII to yield XI.

The formation of triphenylene (XIII) seems to be due to an intramolecular displacement involving XI rather than by the condensation of three molecules of XII, as has been suggested by earlier workers.[8] Two pieces of evidence seem to favor the intramolecular displacement, the first being that XIII and the benzophenone adduct of XI are never isolated together. At room temperature only XIII is found while at −65° only the benzophenone adduct can be obtained. Furthermore, the yield of XIII is comparable to that of the benzophenone adduct. Secondly, since VII is also present when the reaction mixture is warmed to room temperature, one would expect XII to react with VII rather than with itself. In addition, no other products indicative of XII reacting with itself were found.

Earlier workers[12] concerned with the formation of triphenylene from sodium and chlorobenzene had suggested that the former compound may have been formed by the interaction of three "phenylene" radicals. Another explanation deserving consideration might be similar to the one given above. Sodium could react with chlorobenzene to give phenylsodium which in turn could metalate chlorobenzene to give II (sodium analog). The latter intermediate, because of the reaction conditions, would have only a very temporary existence and would very likely give rise to some XII which could react with more of II (sodium analog) to give XIII. The other products obtained from the reaction, biphenyl, *o*-terphenyl and 2,2′-diphenylbiphenyl, could have been formed by a series of reactions of phenyllithium with XII followed by hydrolysis. The benzene formed in the reaction could have been formed either by the hydrolysis of phenylsodium or by the metalation of chlorobenzene with phenylsodium.

2-Bromo-2′-carboxybiphenyl and 4-bromo-9,9-diphenylfluorene were synthesized for the purpose of comparing their infrared spectra with those of the chloro isomers. The former compound was prepared by interacting one equivalent of *n*-butyllithium with one equivalent of 2,2′-dibromobiphenyl at approximately −20°. Subsequent carbonation afforded a 38% yield of the desired acid. The 4-bromo-9,9-diphenylfluorene was prepared in a similar manner by derivatizing the intermediate organolithium compound with benzophenone rather than with carbon dioxide. Because of the difficulty in purifying the intermediate carbinol[13] the impure material was converted directly into 4-bromo-9,9-diphenylfluorene by means of glacial acetic acid. The yield was 41%.

Experimental[14]

***o*-Fluorophenyllithium. (A) Addition of *n*-Butyllithium to *o*-Fluorobromobenzene.**—In a flask previously dried and flushed with nitrogen was placed a solution of 6 g. (0.0342 mole) of *o*-fluorobromobenzene in 55 ml. of dry ether. To this rapidly stirred solution cooled by means of a Dry Ice–acetone-bath to approximately −65° was added 37 ml. of a 0.98 *N* *n*-butyllithium solution[15] over a period of 6 minutes, while not allowing the temperature to rise above −45° during the addition. Immediately following the addition, Color Test I[16] was positive while Color Test II[17] was negative. As soon as the color tests were completed the reaction mixture was carbonated by pouring it jet-wise over a Dry Ice–ether slurry. After warming to room temperature, the carbonated mixture was hydrolyzed with water. The ethereal layer was separated and washed with two 50-ml. portions of 5% sodium hydroxide. The extracts were combined with the original aqueous layer and the resulting solution was boiled to remove the ether and then was acidified with concentrated hydrochloric acid. The resulting milky solution deposited 1.4 g. of crystalline material melting over the range 90–94° after standing overnight. This crude material was recrystallized three times from water to give 0.55 g. (15% based on *o*-fluorobromobenzene) of 2-fluoro-2′-carboxybiphenyl melting at 137.5–138.5°. The acid also can be conveniently recrystallized from an ethanol–water pair.

Anal. Calcd. for $C_{13}H_9FO_2$: C, 72.21; H, 4.20; neut. equiv., 216. Found: C, 72.28, 72.09; H, 4.09, 4.19; neut. equiv., 216.

The infrared spectrum of the acid as a carbon disulfide solution showed a strong band at 13.2 μ indicative of 1,2-disubstitution and was very similar to the spectrum of 2-bromo-2′-carboxybiphenyl synthesized by a less ambiguous method.

The filtrates from the crystallizations mentioned above were combined and extracted with ether. The ether was distilled and the residue was crystallized from a minimum of water to give, on cooling, filtering and drying, 1.7 g. of material melting over the range 124–128°. Two additional crystallizations from water yielded a product melting at 125–126°. The total yield of *o*-fluorobenzoic acid was 2.0 g. (42%).

A mixed melting point of the above acid with an authentic specimen prepared by the oxidation of *o*-fluorotoluene with potassium permanganate showed no depression.

(B) Addition of *o*-Fluorobromobenzene to *n*-Butyllithium.—The procedure was essentially the same as that described

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[11] (a) See R. G. Jones and H. Gilman, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, Chap. 7. (b) "Organic Reactions," Vol. VIII, 1954, Chap. 6.

[12] W. E. Bachmann and H. T. Clark, THIS JOURNAL, **49**, 2089 (1927).

[13] In general this type of carbinol appears to be difficult to purify. A procedure for the purification of a similar carbinol, 2-biphenylyldiphenylcarbinol, is given by R. G. Clarkson and M. Gomberg, THIS JOURNAL, **52**, 2881 (1930).

[14] All reactions involving organometallic compounds were carried out in a dry, oxygen-free atmosphere and all melting points are uncorrected. The infrared spectra were run on a Baird Associates double beam infrared spectrometer in the sodium chloride region.

[15] H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, THIS JOURNAL, **71**, 1499 (1949). The yield of *n*-butyllithium was determined according to a procedure described by H. Gilman and A. H. Haubein, *ibid.*, **66**, 1515 (1944).

[16] H. Gilman and F. Schulze, *ibid.*, **47**, 2002 (1925).

[17] H. Gilman and J. Swiss, *ibid.*, **62**, 1847 (1940).

above. A solution of 8 g. (0.0457 mole) of *o*-fluorobromobenzene in 60 ml. of ether was added to 34 ml. of a 1.35 *N* *n*-butyllithium solution cooled to about −70° during 5 minutes. Subsequent carbonation, hydrolysis and work-up of the crude acid yielded 5.8 g. of pale brown needles melting over the range 120–124°. A recrystallization from water gave 4.7 g. of white needles melting at 126-127°. From the mother liquor there was obtained an additional 0.62 g. of acid melting at 126–127°. The total yield of *o*-fluorobenzoic acid, identified by a mixed melting point with an authentic sample, was 5.32 g. (83%). No other acid was isolated.

o-**Chlorophenyllithium. (A) Preparation at −60°.**—In a 250-ml., three-necked flask were placed 44 ml. of an ethereal solution containing 0.06 mole of *n*-butyllithium and an additional 20 ml. of ether. To this rapidly stirred solution cooled to about −70° was slowly added a solution of 11.5 g. (0.06 mole) of *o*-chlorobromobenzene in 40 ml. of ether during 5 minutes. The temperature was maintained below −50° during the addition. Carbonation in the manner described above required one minute after the addition was completed. After hydrolysis and separation of the aqueous and ethereal layers, the hot aqueous layer was acidified with hydrochloric acid. A brown oil separated and solidified after the mixture cooled to room temperature. The yield of amorphous solid was 3.6 g. The crude material was crystallized from petroleum ether (b.p. 60–70°) to give a granular solid which, after drying, melted over the range 133–137°. An additional crystallization from an ethanol–water pair gave 1.2 g. (17%) of 2-chloro-2′-carboxybiphenyl melting at 138–139°.

Anal. Calcd. for $C_{13}H_9ClO_2$: C, 67.10; H, 3.90; neut. equiv., 233. Found: C, 67.06, 67.11; H, 4.02, 3.98; neut. equiv., 236.

The infrared spectrum of the acid as a carbon disulfide solution was very similar to that of the fluoro and bromo isomers.

The aqueous portion from which the oil settled was extracted with two 50-ml. portions of ether. Distillation of the ether on a steam-bath left 0.7 g. of a white solid which was crystallized from a minimum of water to yield 0.6 g. (6.4%) of *o*-chlorobenzoic acid melting at 137–138°. A mixed melting point of the acid with an authentic sample showed no depression.

The neutral ethereal layer was washed with 50 ml. of 5% sodium hydroxide resulting in the formation of an aqueous layer, ethereal layer and an oil. The layers were separated and then the oil was re-acidified, dissolved in ether and dried over anhydrous sodium sulfate. Distillation of the ether left 1.9 g. of oil which did not solidify on long standing. An unsuccessful attempt was made to purify the material.

The ethereal layer obtained after separating the oil yielded only *n*-butyl bromide after removal of the solvent.

(B) Preparation at −90°.—A solution of 7.68 g. (0.04 mole) of *o*-chlorobromobenzene in 40 ml. of ether was added, over a period of 2 minutes, to 29 ml. of an ethereal solution containing 0.04 mole of *n*-butyllithium and diluted to 175 ml. with more ether. Prior to the addition, the *n*-butyllithium solution was cooled to about −100° by means of an ethanol–ether–liquid nitrogen-bath. The addition was carried out at approximately −100° and then the mixture was stirred at −90° for 30 minutes. Subsequently the mixture was cooled to about −100° again and a large excess of Dry Ice was added to the rapidly stirred solution. The cooling bath was removed and the mixture was allowed to warm to room temperature. After working up the *o*-chlorobenzoic acid as described previously there was obtained 5.83 g. (93%) of acid melting at 137.5–139°. A mixed melting point with an authentic specimen showed no depression.

o-**Bromophenyllithium.**—To a stirred solution of 9.43 g. (0.04 mole) of *o*-dibromobenzene in 200 ml. of dry ether and cooled to about −110° was added, during 5 minutes, 32.5 ml. of a 1.31 *N* *n*-butyllithium solution. During the addition the temperature rose to about −100°. Seven minutes after the addition was completed, the reaction mixture was carbonated in a manner described in the preceding run. After working up the mixture in the usual manner, there was obtained 1.87 g. (23%) of *o*-bromobenzoic acid melting at 144-146°. A mixed melting point with an authentic sample showed no depression and the infrared spectra of the two compounds were identical.

After drying the organic layer over anhydrous sodium sulfate, evaporation of the solvent left a liquid which was further distilled to give 6.05 g. (64.5%) of *o*-dibromobenzene. A comparison of the infrared spectrum and refractive index with that of the starting material showed the two compounds to be identical.

In another run employing similar quantities of reactants and comparable reaction conditions, the reaction mixture was stirred at −100° for 45 minutes after the addition of *n*-butyllithium was completed. Carbonation and subsequent working up of the reaction mixture gave an oil after acidification. The oil was separated and after allowing the aqueous portion to stand for several weeks, there was isolated 0.3 g. of *o*-bromobenzoic acid melting at 145–146°. The acid was identified by a mixed melting point with an authentic sample.

All attempts to purify the oil failed even though it was distinctly soluble in 5% sodium bicarbonate.

o-**Chlorophenyllithium Warmed to 22°.**—A solution of 9.58 g. (0.05 mole) of *o*-chlorobromobenzene in 35 ml. of ether was added to 77 ml. of an ethereal solution containing 0.05 mole of *n*-butyllithium in a manner described above. The reaction mixture was stirred at −70° for 10 minutes and then was allowed to warm slowly over a 2-hour period to 22°. At 0° the reaction mixture became very cloudy in appearance. Subsequently the mixture was carbonated and after hydrolysis the two layers were separated. Acidification and working up of the oil as previously described for 2-chloro-2′-carboxybiphenyl yielded 1.28 g. (22%) of the latter compound melting at 136.5–138°.

The ether was slowly allowed to evaporate from the ethereal layer, leaving impure lustrous plates of triphenylene which was recrystallized from *n*-propyl alcohol to give 0.26 g. (7%) of white needles melting at 193–195°. The picrate of triphenylene, melting at 223–224°, was prepared according to a method described earlier[12] and a mixed melting point with an authentic sample showed no depression.[18]

Most of the *n*-propyl alcohol was distilled from the filtrate and the residue was dissolved in ether. Extraction of the ethereal solution and subsequent separation of the various layers yielded 0.65 g. of light brown oil.

o-**Chlorophenyllithium and Benzophenone (A) At −90°.**—The *o*-chlorophenyllithium was prepared at −100° as described previously from 9.58 g. (0.05 mole) of *o*-chlorobromobenzene and 0.04 mole of *n*-butyllithium. The reaction mixture was stirred at −90° for 30 minutes after which there was added 7.28 g. (0.04 mole) of benzophenone. The mixture was allowed to warm to room temperature, hydrolyzed with 5% hydrochloric acid, and the ethereal layer was separated and dried over anhydrous sodium sulfate. The ether was distilled leaving a glassy material on cooling. This material was dissolved in petroleum ether (b.p. 60–70°) and on cooling there was deposited 6.7 g. of white granules melting at 91–93°. Concentration of the mother liquor afforded an additional 1.54 g. of product. The total yield of *o*-chlorophenyldiphenylcarbinol was 8.24 g. (68%). The infrared spectrum of the compound as a carbon disulfide solution was very similar to that of *o*-fluorophenyldiphenylcarbinol.

(B) At −65°.—The reaction of 9.58 g. (0.05 mole) of *o*-chlorobromobenzene with the same amount of *n*-butyllithium was carried out at about −65° as described previously. Four minutes after the addition of the *o*-chlorobromobenzene was completed, a solution of 7.28 g. (0.045 mole) of benzophenone in 35 ml. of ether was added. Subsequently the reaction mixture was hydrolyzed with water and the organic layer was separated. After drying the organic layer over anhydrous sodium sulfate and then distilling the ether and *n*-butyl bromide, there remained a very viscous, milky oil. This material was refluxed in petroleum ether (b.p. 60–70°) and the white, insoluble powder was filtered and crystallized from ethanol to give 0.70 g. (9.4%) of 2-(*o*-chlorophenyl)-2′-(diphenylhydroxymethyl)-biphenyl melting at 211–213°. The analytical sample melted at 213-214°.

In another run a 13% yield of the latter carbinol was obtained by extending the reaction time to 50 minutes.

Anal. Calcd. for $C_{31}H_{23}ClO$: C, 83.30; H, 5.19; mol. wt., 429. Found: C, 83.02, 83.01; H, 4.91, 5.07; mol. wt. (Rast), 422.

The infrared spectrum as a carbon disulfide solution was

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[18] A sample of the picrate of triphenylene was kindly furnished by Dr. Hans T. Clark.

TABLE I

REACTIONS BETWEEN *o*-XC_6H_4X' AND *n*-C_4H_9Li[a]

	Halide	Mole[b]	Reaction temp., °C.	Reaction time, min.	Derivatives and yields, %
1	*o*-FC_6H_4Br	0.029	−70	90	*o*-FC_6H_4COOH (74)[c]
2	*o*-FC_6H_4Br[d]	.046	−50	5	*o*-FC_6H_4COOH (39), *o,o'*-$FC_6H_4C_6H_4COOH$ (13)
3	*o*-FC_6H_4Br	.029	25[e]	105	*o,o'*-$FC_6H_4C_6H_4COOH$ (26), triphenylene (2.5)
4	*o*-ClC_6H_4Br[f]	.065	−50	5	*o,o'*-$ClC_6H_4C_6H_4COOH$ (15), *o*-ClC_6H_4COOH (0.5)
5	*o*-ClC_6H_4Br	.05	Reflux[g]		Triphenylene (16.5)[h]
6	*o*-ClC_6H_4Br	.06	0	20[i]	No acidic material[j]

[a] The runs listed in this table are ones not described in the Experimental section. [b] An equivalent amount of *n*-C_4H_9Li was used in every run. [c] A trace of *o,o'*-$FC_6H_4C_6H_4COOH$ was also isolated. [d] The *n*-C_4H_9Li was added to *o*-FC_6H_4Br. [e] *o*-FC_6H_4Li was prepared by adding *n*-C_4H_9Li to *o*-FC_6H_4Br in the usual manner before allowing the mixture to warm. [f] *n*-C_4H_9Li was added to *o*-ClC_6H_4Br. [g] *o*-ClC_6H_4Br and *n*-C_4H_9Li reacted at −60° and then the reaction mixture was allowed to warm to 20° during 45 minutes. Subsequently, the mixture was cooled again to −70° at which temperature another 0.05 mole of *o*-ClC_6H_4Br and *n*-C_4H_9Li were added. The mixture was stirred at room temperature for 4.5 hours and then refluxed for 6 hours. [h] Distillation afforded 1.38 g. of pale yellow liquid boiling over the range 78–85° at 0.006 mm., $n^{25}D$ 1.5555, and another fraction, 1.0 g., boiling over the range 85–90° at 0.005 mm., $n^{25}D$ 1.5617, d_{25} 1.047. The infrared spectrum of the liquid showed bands at 3.22, 3.4 and 13.2 μ characteristic of aliphatic C–H, aromatic C–H and *o*-disubstitution, respectively. [i] Time of addition. [j] In working up the neutral fraction, the crude oil was chromatographed on alumina and the only material isolated was an unidentified compound melting over the range 111–115°. The compound gave a negative halogen test, did not form a picrate and was very soluble in most organic solvents.

compatible with the structure assigned to the above compound. There were strong absorption bands at 2.44, 3.34, 13.3 and 13.7 μ characteristic of a hydroxyl group, an aryl group, 1,2-disubstitution and a phenyl group, respectively. No other bands were observed in the range 12–15 μ.

To further substantiate the structure, a small amount of carbinol was refluxed in glacial acetic acid for several minutes. The product was crystallized twice from ethanol to give what is believed to be 4-(*o*-chlorophenyl)-9,9-diphenylfluorene melting at 209.5–210.5°.

Anal. Calcd. for $C_{31}H_{21}Cl$: C, 86.80; H, 4.94. Found: C, 86.79, 86.89; H, 5.11, 5.26.

The infrared spectrum as a carbon disulfide solution was compatible with the assigned structure. There were three sharp bands at 13.2, 13.4 and 13.7 μ which were somewhat similar to three bands exhibited by 4-bromo- and 4-chloro-9,9-diphenylfluorene in the same region and are probably characteristic of 1,2,3-trisubstitution, 1,2-disubstitution and a phenyl group, respectively. Also, a mixed melting point with the parent carbinol showed a depression of about 30°.

The petroleum ether was distilled from the remaining solution and the residue was distilled under reduced pressure to first yield 2.13 g. of a liquid which solidified when seeded with a crystal of benzophenone and was identified as such by comparison of the infrared spectra.

The second fraction gave 0.87 g. of a glass-like material boiling over the range 120–130° at 0.005 mm. The third fraction consisted of a similar material.

Fraction three was refluxed in ethanol and the insoluble material was filtered to give 0.05 g. of material melting at 206–208°. From the highly fluorescent filtrate there crystallized 0.28 g. of needles melting at 209–211°. An additional crystallization from ethanol raised the melting point to 215–217°.

The residue from the distillation was refluxed in ethanol for approximately 3 hours and then was decolorized with Norit-A and filtered while hot. From the filtrate there was obtained 0.90 g. of light yellow amorphous crystals melting at 215–218°. Recrystallization from glacial acetic acid gave needles melting at 219–220° and finally an additional crystallization from petroleum ether (b.p. 60–70°) gave 4-chloro-9,9-diphenylfluorene melting at 221–222°.

The material from fraction three showed no depression in melting point when admixed with the compound obtained from the residue. The total yield of 4-chloro-9,9-diphenylfluorene was 1.2 g. (27%).

Anal. Calcd. for $C_{25}H_{17}Cl$: C, 85.11; H, 4.85; Cl, 9.96. Found: C, 85.05, 85.13; H, 4.85, 4.92; Cl, 9.62.

The infrared spectrum of the compound as a carbon disulfide solution was similar to that of 4-bromo-9,9-diphenylfluorene, synthesized by a less ambiguous method.

In another run employing 0.07 mole of *o*-chlorobromobenzene, the reaction was carried out at −100° and then was stirred at −90° for 15 minutes and at −65° for 25 minutes. Subsequently, it was cooled to −100° when 10 g. of benzophenone was added. Working up of the reaction mixture in a manner analogous to that described above gave 0.92 g. of 2-(*o*-chlorophenyl)-2'-(diphenylhydroxymethyl)-biphenyl and 0.80 g. of 4-chloro-9,9-diphenylfluorene.

The third distillation fraction formed an oil which deposited clumps of crystals after standing about one week in an ethanol–water mixture. The yield of white crystals melting over the range 58–62° was 1.4 g. After three recrystallizations from an ethanol–water mixture there was obtained a small amount of material melting at 89–91°. A mixed melting point with an authentic sample of *o*-chlorophenyldiphenylcarbinol showed no depression and a comparison of the infrared spectra showed the two to be identical. Due to some impurities, however, most of the remaining material could not be purified in a similar manner.

4-Bromo-9,9-diphenylfluorene.—To a rapidly stirred solution of 5.0 g. (0.016 mole) of 2,2'-dibromobiphenyl in 55 ml. of dry ether cooled to −20° was slowly added, during 8 minutes, 13.5 ml. of an ethereal solution containing 0.016 mole of *n*-butyllithium. The temperature was maintained between −20 and −25° during the addition. When the addition was completed, the reaction mixture was stirred at −15° for 1 hour and at −10° for 15 minutes. A solution of 2.92 g. (0.016 mole) of benzophenone in 40 ml. of ether was added to the very milky mixture in 5-ml. portions, always maintaining the temperature between −10 and −15°. A negative Color Test I was obtained after adding 35 ml. of the benzophenone solution. The mixture was hydrolyzed and the insoluble bis-2,2'-(diphenylhydroxymethyl)-biphenyl was filtered and crystallized from ethanol to give 0.7 g. (9%) of the latter carbinol melting at 254–256°.

The organic layer was separated, dried and the solvent was distilled leaving a light brown, viscous oil which was subsequently dissolved in refluxing glacial acetic acid and on cooling there was deposited 2.6 g. (41%) of product melting at 202–204°. Two further crystallizations from ethanol yielded an analytical sample melting at 213.5–214.5°.

Anal. Calcd. for $C_{25}H_{17}Br$: C, 75.60; H, 4.31; Br, 20.09. Found: C, 75.58, 75.43; H, 4.39, 4.20; Br, 20.01.

2-Bromo-2'-carboxybiphenyl.—An ethereal solution containing 0.032 mole of 2,2'-dibromobiphenyl was treated with an equivalent amount of *n*-butyllithium according to the procedure described above. The reaction mixture was carbonated and the aqueous layer was separated. The latter layer, on acidification, gave 3.3 g. of white powder melting at 130–132°. This crude material was dissolved in 5% sodium bicarbonate and acidified with acetic acid. The solid was filtered and the filtrate was then acidified with sulfuric acid. The white precipitate was filtered and crystallized from an ethanol–water mixture to give 1.57 g. of acid melting at 142–143°.

The ethereal layer was extracted twice with 5% sodium hydroxide. Acidification of the extracts gave 1.80 g. of acid melting at 140–142°. An additional crystallization from petroleum ether (b.p. 60–70°) gave 1.43 g. of acid melting at 142–143°.

The total yield of 2-bromo-2′-carboxybiphenyl was 3.4 g. (38%). The analytical sample melted at 144.5–146°.

Anal. Calcd. for $C_{13}H_9O_2Br$: C, 56.33; H, 3.27; neut. equiv., 277. Found: C, 56.44, 56.32; H, 3.33, 3.32; neut. equiv., 277.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF MEERUT COLLEGE, INDIA]

Behavior of Halogenated Nitrobenzenes with β-Diketones. Part I. 1-Chloro-2,4-dinitrobenzene and Acetylacetone

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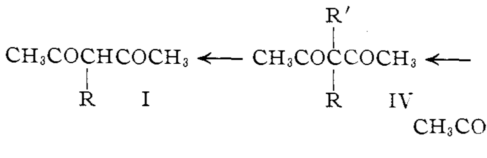
2,4-Dinitrophenyldiacetylmethane (I) and bis-(2,4-dinitrophenyl)-diacetylmethane (*II*) have been obtained by the interaction of 1-chloro-2,4-dinitrobenzene and acetylacetone and characterized. Their behavior with hydrazines, semicarbazide, hydroxylamine, etc., has been studied and cyclic compounds such as pyrazole, indole and isoxazole derivatives prepared. 6-Nitroanthranil has been isolated by the action of concentrated sulfuric acid on 2,4-dinitrophenylacetone and identified.

1-Chloro-2,4-dinitrobenzene easily reacts with the monosodium derivative of acetylacetone to form 2,4-dinitrophenyldiacetylmethane (I).[1] The sodium derivative of the latter reacts with 1-chloro-2,4-dinitrobenzene to form bis-(2,4-dinitrophenyl)-diacetylmethane (II) but fails to form a methyl derivative with methyl iodide. In the disubstituted compound II, the two dinitrophenyl groups appear to be linked to the same carbon atom, as acetylacetone yields the same dinitrophenyldinitrotolyl derivative IV whether it reacts first with chlorodinitrobenzene and then with chlorodinitrotoluene or in reverse sequence.



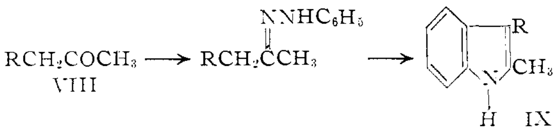
$$\underset{\mathrm{R}}{\mathrm{CH_3COCHCOCH_3}}\ \mathrm{I} \longleftarrow \mathrm{CH_3CO}\overset{\mathrm{R'}}{\underset{\mathrm{R}}{\mathrm{C}}}\mathrm{COCH_3}\ \mathrm{IV} \longleftarrow \mathrm{CH_3CO}\underset{\mathrm{R'}}{\mathrm{CH}}\mathrm{COCH_3}\ \mathrm{III}$$

R = 2,4-dinitrophenyl
R′ = 2,4-dinitro-5-tolyl

The bis-(2,4-dinitrophenyl)-diacetylmethane (II) resists hydrolysis by sulfuric acid, dilute or concentrated. This appears to be due to steric factors and is in agreement with the observation of Zaheer and Sidhu[2] that diethyl 2,4-dinitrophenyl-*n*-propylmalonate is not hydrolyzed due to the large size of the substituents. Its II ketonic groups, compared to those of the dinitrophenyl derivative, are very unreactive and do not condense with the usual reagents for the carbonyl group. The dinitrophenyldiacetylmethane (I), on the other hand, readily reacts with hydrazine hydrate, phenylhydrazine and semicarbazide hydrochloride. In alcoholic solution hydrazine hydrate gives a hydrazone as well as a pyrazole while other hydrazines give only the former; in acetic acid solution, however, only the pyrazole derivatives are obtained. With hydroxylamine hydrochloride in alcoholic or acetic acid solution the corresponding isoxazoles are formed. The structure of these isoxazoles and pyrazoles follows from the analogous derivatives of acetylacetone.[3,4]

Benzoyl chloride forms a derivative V with the sodium derivative of I in ether. The yield is poor by the Schotten and Baumann method and no benzoylation takes place with benzoyl chloride in pyridine solution. The benzoyl derivative is stable toward dilute or concentrated sulfuric acid and toward aniline, while with hot 2% alcoholic caustic potash it is hydrolyzed back to I and benzoic acid. This indicates that the benzoyl group is most likely linked to the oxygen atom rather than to the carbon atom of the methylene group. This view is also supported by the fact that identical products are not obtained by acetylation of chlorodinitrophenylbenzoylacetylmethane (VI) and benzoylation of chlorodinitrophenyldiacetylmethane (VII).

When heated with moderately concentrated sulfuric acid or aniline or even by passing hydrochloric acid gas through warm alcoholic solution, compound I is hydrolyzed to form a product which is found to be identical with 2,4-dinitrophenylacetone (VIII) obtained from ethyl (2,4-dinitrophenyl)-acetoacetate with dilute sulfuric acid.[5] This compound (VIII) readily forms a phenylhydrazone which when heated with fuming hydrochloric acid in absolute alcohol is cyclized to form 2-methyl-3-(2,4-dinitrophenyl)-indole (IX). The indole derivative fails to form the alkyl and acyl derivatives and is insoluble in hydrochloric acid, showing diminution of basic character due to presence of dinitrophenyl group in position 3.



$$\underset{\mathrm{VIII}}{\mathrm{RCH_2COCH_3}} \longrightarrow \mathrm{RCH_2}\overset{\mathrm{NNHC_6H_5}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3} \longrightarrow \mathrm{IX}$$

R = 2,4-dinitrophenyl

When heated with concentrated sulfuric acid at about 105–110° for two hours, compound I and also VIII yield another product X, m.p. 133°. This reduces Tollens reagent and potassium permangan-

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