containing 3 drops of methyl red (0.1%)-brom cresol green (0.1%) indicator. The dimethylamine was determined by titration of the boric acid solution with 0.01 *N* hydrochloric acid.

In separate experiments, the volatile organic base fraction was examined for the presence of trimethylamine by the sensitive quantitative procedure of Cromwell.[26] Trimethylamine was not present. The oxide of trimethylamine was prepared; it gave a positive ninhydrin reaction[11] and it was found to be absent in chromatographic analyses of reaction mixtures at *p*H 4–8.

C. **Determination of Carbon Dioxide.**—A reaction mixture (*p*H 7.0), containing N,N-dimethylglycine oxide-1-C^{14} (6.9 μmoles), tartaric acid (50 μmoles) and ferric nitrate nonahydrate (4 μmoles), was prepared in the usual way and allowed to react for 90 minutes at 23° in a flask connected to a sodium hydroxide trap. The solution was acidified with 1.0 ml. of 8.5% phosphoric acid and the system was flushed with nitrogen for 15 minutes. The carbon dioxide collected in the sodium hydroxide trap was counted[27] as barium carbonate. Runs at other *p*H values were made in the same way.

N,N-Dimethylglycine hydrochloride-1-C^{14} (7.1 μmoles) and glyoxylic acid (400 μmoles) gave no carbon dioxide under similar conditions (catalyst, tartrate, 23°, 90 minutes).

D. ***p*H Effects.**—Over the *p*H region where decarboxylation was the primary reaction it was observed that the *p*H rose as the reaction proceeded. Initial and final *p*H values were averaged to locate the points near *p*H 8 in Fig. 2.

BETHESDA, MD.

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[26] B. T. Cromwell, *Biochem. J.*, **46**, 578 (1950).

[27] C. V. Robinson, *Science*, **112**, 198 (1950).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF IOWA STATE COLLEGE]

Some Reactions of *o*-Halophenyllithium Compounds

BY HENRY GILMAN AND RICHARD D. GORSICH

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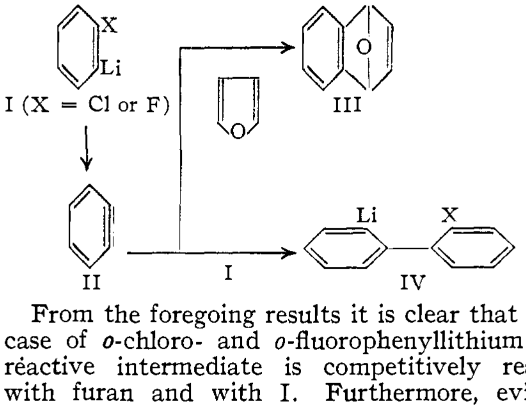
When *o*-chloro- and *o*-fluorophenyllithium are prepared at −90 and −60°, respectively, in the presence of furan and then carbonated, the main product is 1,4-dihydronaphthalene-1,4-endoxide (III) while the corresponding 2-carboxy-2′-halobiphenyl (IV) is obtained in small yields. *o*-Dibromobenzene and *n*-butyllithium in the presence of furan also give III under modified conditions. Only III is obtained when an RLi is added to a mixture of the *o*-bromohalobenzene and furan at a temperature above that at which the *o*-halophenyllithium compound is stable. Methyllithium and phenyllithium are equally effective in reacting with an *o*-halobromobenzene in the presence of furan to give excellent yields of III. 2-Chloro-2′-(triphenylsilyl)-biphenyl has been synthesized and compared with the bromo-isomer prepared by a less ambiguous method. The results are discussed and correlated.

As a continuation of some of our earlier studies concerned with *o*-halophenyllithium compounds,[1] we have investigated further some of their reactions and possible routes by which these organometallic compounds couple to form new organolithium compounds. In order to obtain a better understanding of the various transformations, the elegant procedure of Wittig and Pohmer[2] was employed in this present work. These workers successfully interacted *o*-bromofluorobenzene with lithium amalgam in furan to obtain 1,4-dihydronaphthalene-1,4-endoxide (III), a strained molecule which has been formulated as arising *via* a Diels–Alder reaction between furan and the benzyne intermediate (II). Furthermore, the reactive species II has been postulated as being formed from *o*-fluorophenyllithium after the latter has been generated by the interaction of *o*-bromofluorobenzene and lithium amalgam.[3] In view of these results it was hoped that furan could be used in a similar fashion to trap any intermediate which might arise during the break-down of *o*-halophenyllithium compounds (I). *o*-Fluoro- and *o*-chlorophenyllithium were prepared at −60 and −90°, respectively. A relatively large excess of furan was added in each case and then the mixtures were allowed to warm to −50° for the chloro-isomer and −10° for the fluoro-isomer. Since Color Test I[4] was positive in both cases at these temperatures, the mixtures were carbonated. The run involving *o*-bromochlorobenzene afforded 41% of III and 11% of 2-carboxy-2′-chlorobiphenyl; with *o*-bromofluorobenzene the yield of III was 67% while 4% of 2-carboxy-2′-fluorobiphenyl was isolated.

A modified procedure was used with *o*-dibromobenzene since it was found in previous studies that *o*-bromophenyllithium is a short-lived intermediate.[1] Consequently, *o*-dibromobenzene was added to a mixture of furan and butyllithium. The yield of III was 68%; however, as might be expected and will be explained later, no acid was isolated.



(1)

(2)

From the foregoing results it is clear that in the case of *o*-chloro- and *o*-fluorophenyllithium some reactive intermediate is competitively reacting with furan and with I. Furthermore, evidence substantiates that such a competitive reaction occurs only when the organolithium compound is formed first independently of the other reactants. In order to ascertain that no metalation reaction

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[1] H. Gilman and R. D. Gorsich, THIS JOURNAL, **78**, 2217 (1956); this reference contains a general survey of relevant literature citations.

[2] G. Wittig and L. Pohmer, *Angew. Chem.*, **67**, 348 (1955). See G. Wittig and L. Pohmer, *Chem. Ber.*, **89**, 1334 (1950), for details about which we have just learned, after returning proof, of study mentioned in their prior communication.

[3] It is interesting to note that the same reaction in the absence of furan gives diphenylene and triphenylene; G. Wittig and W. Herwig, *Ber.*, **87**, 1511 (1954).

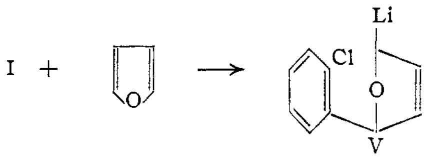
[4] H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

ensued between furan and I followed by another similar metalation between the halobenzene and 2-furyllithium at a warmer temperature, an attempt was made to metalate chlorobenzene under conditions used for the competitive reactions. No acid was detected after carbonation; most of the chlorobenzene was recovered.

At this time the most plausible explanation for the presence of coupling product in the competitive reaction is one involving II, although an alternate explanation has been proposed recently for a related reaction.[5] Intuitively the halide in I would not be expected to be displaced by a nucleophile because the high electron density in the position adjacent to the chlorine atom should hinder such an approach. Also, nucleophilic aromatic substitution reactions are facilitated by electron-withdrawing groups and not electron-donating substituents.[6] It is conceivable the anion of I may displace the halogen in another molecule of I either just before or during the formation of the reactive intermediate II.[7]

The rapid conversion of *o*-bromophenyllithium to II did not allow its preparation prior to the addition of furan, and, as a result, the concentration of *o*-bromophenyllithium probably was so slight that the main reaction was between II and furan.

The reaction path leading to III might involve a nucleophilic attack of I on furan or the more likely reaction of II with furan. Of the two possibilities, it appears better to rationalize on the basis of II being the key intermediate. If I is considered as being the attacking species, a reaction path (3) might be expected. Evidence indicates that an intermediate such as V is less likely to undergo ring closure to give the highly strained molecule III than would an intermediate arising from interaction of II with furan.[8] If V were formed as an intermediate, ring closure at such a low temperature would be doubtful in view of polar effects and formation of the strained molecule III.[6,9] The formation of V *via* I is unprecedented since there is no known instance wherein furan is attacked in such a manner. In fact under these conditions furan is inert to such an attack, and at warmer temperatures the only product formed is 2-furyllithium.[10]

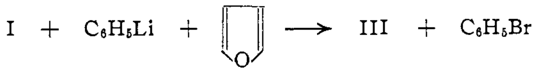


V (3)

On the basis of the aforementioned discussion wherein II has been visualized as the intermediate in the various reactions, it would be expected that if compound I were generated at a temperature above that at which it is stable, the concentration of I would be negligible and no coupling product (IV) should be detected. This has been verified by adding butyllithium to a mixture of furan and an *o*-bromohalobenzene at temperatures considerably higher than those at which the stability of I has been well-established. For example, when butyllithium is added to a mixture of *o*-bromochlorobenzene and a large excess of furan, only III has been isolated. No acids were found to be present. The same was found to be true for the fluoro- and bromo-isomers, although in the latter case the results are not as significant as for the former two.

Organolithium compounds other than butyllithium have been found equally suitable if not somewhat superior for generating the reactive species II at moderate temperatures. A 75% yield of III has been obtained with phenyllithium while with methyllithium yields up to 84% of III have been isolated. This is surprising because, in the past, methyllithium has been found to be very ineffective in halogen–metal interconversion reactions.[11] The unusual effectiveness in this case may be attributed to the formation of the highly reactive intermediate II.

In order to substantiate that a halogen–metal interconversion reaction was the initial step in the reaction between *o*-bromochlorobenzene and phenyllithium, the latter compound was synthesized from iodobenzene and lithium. Recovery of bromobenzene in a good yield supports the above proposal. No attempt was made to recover methyl bromide when methyllithium was used.



A reaction between *o*-dichlorobenzene and butyllithium in the presence of furan was unsuccessful. Carbonation, after stirring at room temperature for 1 hr., afforded only 2-furoic acid. It is conceivable that conditions might be varied so as to effect a reaction since there is evidence that a reaction occurs between butyllithium and *o*-dichlorobenzene in the absence of furan.[13]

Recent related work can be correlated with the results in this communication together with pre-

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(5) An ion-pair mechanism has been formulated in explaining the interaction of chlorobenzene with sodium amide; A. A. Morton, *J. Org. Chem.*, **21**, 593 (1956).

(6) J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 273 (1951).

(7) It has been shown that benzyne can be formed either *via* a stepwise or concerted mechanism depending on the halogen being eliminated when metalation reactions are involved. However, in this case these findings do not necessarily apply since it cannot be assumed that the initial step is similar in both cases; J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, THIS JOURNAL, **78**, 601 (1956); see also, J. D. Roberts, C. W. Vaughan, L. A. Carlsmith and D. A. Semenow, *ibid.*, **78**, 611 (1956).

(8) In distinguishing between the two paths, it is not pertinent whether the interaction of benzyne with furan is a polar reaction or a four-center-type reaction. Since there is no sharp line between the latter two types of reaction mechanisms, it is difficult to rationalize by which one the benzyne interacts with furan; J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, pp. 450–461.

(9) Previous studies (ref. 1) showed that an intermediate such as 2-(*o*-chlorophenyl)-2′-lithiobiphenyl does not undergo ring closure below approximately −50° to give the planar, non-strained system, triphenylene.

(10) In general, metalation reactions proceed smoothly only at room temperature or higher when diethyl ether is the solvent; H. Gilman and J. W. Morton, Jr., "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, Chap. 6.

(11) Methyllithium interconverts only with very reactive halides such as *o*-bromoanisole. Phenyllithium is generally more effective but has the disadvantage of occasionally participating in side-reactions (ref. 12).

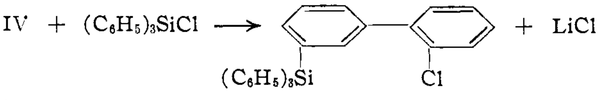
(12) R. G. Jones and H. Gilman, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 343.

(13) R. D. Gorsich, unpublished studies.

vious findings.[1] In the related work, 2,2′-diiodobiphenyl has been postulated as an intermediate in the reaction of *o*-diiodobenzene with butyllithium and lithium in non-polar solvents.[14] It is unlikely that *o*-iodophenyllithium would be present as such in any appreciable concentration in view of the instability of *o*-bromophenyllithium at −110°, and, especially since a refluxing mixture of benzene and petroleum ether (b.p. 40–60°) was employed. Since the *o*-diiodobenzene was added to butyllithium, an intermediate such as 2-iodo-2′-lithiobiphenyl (formed according to scheme 2) would be expected to react further with butyllithium to give 2,2′-dilithiobiphenyl.[15] The latter, in turn, could interact with two equivalents of II to give 2,2′-bis-(*o*-lithiophenyl)-biphenyl. This compound could partially couple with butyl iodide, formed during the interconversion reaction, to give 2,2′-bis-(*o*-*n*-butylphenyl)-biphenyl.[16] The remaining organodilithium compound would give the corresponding acid after carbonation. When lithium interacted with *o*-diiodobenzene, the major product was triphenylene. This is not too surprising since it is quite possible that in this case the intermediate, 2-iodo-2′-lithiobiphenyl, would tend to react preferentially with II instead of with lithium, and as a result one would get 2-(*o*-iodophenyl)-2′-lithiobiphenyl, a type of molecule which has been shown to undergo readily ring closure to yield triphenylene.[10]

Caution should be exercised in interpreting all reactions of *o*-bromohalobenzenes with RLi compounds as proceeding *via* the benzyne intermediate. Recent investigations infer that the solvent plays an important role in the reaction of a bromohalobenzene with an RLi compound. For example, it has been found in this Laboratory that two equivalents of *o*-dibromobenzene in tetrahydrofuran interact with one equivalent of butyllithium to give good yields of 2,2′-dibromobiphenyl. Apparently, *o*-bromophenyllithium couples with *o*-dibromobenzene rather than pass through the benzyne intermediate.[17]

2-Chloro-2′-(triphenylsilyl)-biphenyl has been prepared by allowing an ethereal solution of *o*-chlorophenyllithium to warm in the presence of triphenylchlorosilane. A small amount of triphenylene was isolated also. The former compound probably is formed *via* the organolithium compound (IV, X = Cl). The corresponding bromo-isomer has been prepared in a less ambiguous manner by means of a monohalogen–metal interconversion reaction between 2,2′-dibromobiphenyl and butyllithium followed by reaction with triphenylchlorosilane. The infrared spectra of the two compounds compared favorably.



Experimental[18]

Reactions of *o*-Halophenyllithium Compounds in the Presence of Furan. (a) ***o*-Chlorophenyllithium.**—The *o*-chlorophenyllithium was prepared at −90° by adding a pre-cooled solution of 19.16 g. (0.10 mole) of *o*-bromochlorobenzene in 25 ml. of dry diethyl ether, during 17 min., to 80 ml. of a stirred ethereal solution containing 0.10 mole of *n*-butyllithium[19] and cooled to −100° by means of an ethanol–ether–liquid nitrogen slurry.[1] The temperature was not allowed to rise above −90° during the addition. After stirring the reaction mixture at −90° for 45 min., 48 g. of redistilled furan (Eastman) was added, and then the resulting solution was stirred between −75 and −70° for 10 min. The mixture was allowed to warm further to −50°, becoming quite milky at −65°. The reaction mixture then was stirred for 2.5 hr. at the minimum temperature afforded by a Dry Ice–acetone-bath. Subsequently the mixture was cooled to −95° and carbonated by adding powdered Dry Ice. The reaction mixture was allowed to warm to room temperature, whereupon, hydrolysis was effected with water. The aqueous layer was separated from the organic layer and was warmed to expel dissolved ether, cooled and then acidified with sulfuric acid. A brown precipitate was filtered, dissolved in ethanol, decolorized with Norit-A and then water was added slowly until the solution was slightly cloudy. On cooling, there crystallized 0.53 g. of acid melting at 139–140°. A mixed melting point with an authentic sample of 2-carboxy-2′-chlorobiphenyl obtained previously[1] showed no depression.

The organic layer was extracted with three 50-ml. portions of 5% sodium hydroxide. Acidification of the basic extract and subsequent work-up left an oil which crystallized after standing for 2 weeks. This material then was extracted with 5% sodium bicarbonate and after acidification with concentrated hydrochloric acid, there was deposited 0.72 g. of acid melting at 137–139°. The total yield of 2-carboxy-2′-chlorobiphenyl was 1.25 g. (10.7%).

The neutral organic layer was dried over anhydrous sodium sulfate, and the solvent was allowed to slowly evaporate. The resulting crystalline material was sublimed at room temperature (*ca.* 25°) and 0.005 mm. to yield 5.84 g. (40.6%) of product melting at 54–55°. The reported melting point of 1,4-dihydronaphthalene-1,4-endoxide is 55–56°.[2]

The adduct was cleaved by passing hydrogen chloride into a methanolic solution containing 2.0 g. (0.0139 mole) of 1,4-dihydronaphthalene-1,4-endoxide (III) and refluxing for about 3 hr.[2] The yield of α-naphthol melting at 94–95° was 1.61 g. (80%). A mixed melting point with an authentic specimen showed no depression.

(b) ***o*-Fluorophenyllithium.**—The *o*-fluorophenyllithium was prepared in accordance with a procedure described previously[1] from 10.0 g. (0.057 mole) of *o*-bromofluorobenzene in 30 ml. of ether and 40.5 ml. of an ethereal solution containing 0.057 mole of *n*-butyllithium at approximately −60°. To the organolithium solution cooled to about −70° was added 49 g. of redistilled furan. The temperature was not allowed to rise above −60° during the furan addition. The reaction mixture was allowed to warm slowly to −50° and was maintained between −50 and −45° for 10 min.; between −45 and −40° for 10 min.; between −35 and −30° for 10 min.; between −30 and −25° for 10 min.; and, between −15 and −10° for 25 min. Since Color Test I was positive, the reaction mixture was cooled to −65° and then poured jet-wise into a slurry of Dry Ice and ether. The carbonated mixture was worked up as described in the preceding experiment. Acidification of

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[14] H. Heaney, F. G. Mann and I. T. Millar, *J. Chem. Soc.*, 1 (1956).

[15] Iodides are very reactive in interconversion reactions; see ref. 7.

[16] Alkyl iodides are more prone to be involved in coupling reactions than are other halides. For example, methyl iodide couples with 1-naphthyllithium to give a good yield of 1-methylnapthalene; H. Gilman and F. W. Moore, THIS JOURNAL, **62**, 1843 (1940); see, also, H. Gilman, C. G. Brannen and R. K. Ingham, *J. Org. Chem.*, **22**, in press (1957).

[17] This same type of reaction can be applied also to other bromohalobenzene isomers, *e.g.*, *p*-bromochlorobenzene yields 4,4′-dichlorobiphenyl. The latter reaction excludes the possibility of II being an intermediate in reactions carried out in tetrahydrofuran; H. Gilman and B. Gaj, *J. Org. Chem.*, **22**, in press (1957).

[18] All reactions involving organometallic compounds were carried out in a dry, oxygen-free nitrogen 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.

[19] 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).

the aqueous layer left needle-like crystals. These were combined with similar crystals obtained by acidification of the basic solution obtained after extracting the organic layer with 5% sodium hydroxide. Recrystallization of the 2-carboxy-2′-fluorobiphenyl from a mixture of ethanol and water yielded 0.23 g. (3.7%) of product melting at 138–140°. A mixed melting point with an authentic sample[1] of the acid showed no depression.

The organic layer on work-up as described above yielded a crystalline material which was sublimed at room temperature and 0.003 mm. to yield 5.49 g. (67%) of III melting at 54–55°.

(c) *o*-Bromophenyllithium.—A solution of 13.5 g. (0.057 mole) of *o*-dibromobenzene in 20 ml. of ether was added dropwise, during 15 min., to 70 ml. of an ethereal solution containing 0.057 mole of *n*-butyllithium and 61.5 g. of furan cooled to −110° by means of an ethanol–ether–liquid nitrogen slurry. The temperature remained between −110 and −100° during the addition. The reaction mixture was stirred at −65° for 1 hr., and, although Color Test I was negative, carbonation was effected in the same manner as described for *o*-chlorophenyllithium. Following the usual work-up no acid was isolated from the aqueous layer.

The crude adduct obtained from the organic layer was purified by sublimation at 45° and 0.005 mm. to yield 5.60 g. (68%) of pure III melting at 54.5–55.5°.

Addition of RLi to a Mixture of Furan and *o*-Bromohalobenzene. (a) **n-Butyllithium and *o*-Bromofluorobenzene.**—To a rapidly stirred solution of 7.00 g. (0.04 mole) of *o*-bromofluorobenzene in 15 ml. of ether and 41 g. of furan was added 30 ml. of an ethereal solution containing 0.042 mole of *n*-butyllithium. The addition funnel containing the *n*-butyllithium was jacketed and cooled by means of Dry Ice and acetone. The temperature of the reaction mixture was maintained between −30 and −25° during the addition which required 15 min. Color Test I was negative on completion of the addition. The mixture was warmed to −20° and poured into water. The organic layer was separated, dried over anhydrous sodium sulfate, filtered, and finally the ether and excess furan were distilled on a steam-bath. A small amount of *n*-butyl bromide was distilled under reduced pressure, and the remaining material was sublimed at room temperature and 0.003 mm. to yield 3.90 g. (68%) of III.

The results of the interaction of *n*-butyllithium with the *o*-chloro- and *o*-bromo-isomers are given in Table I.

TABLE I

REACTIONS OF *o*-XC_6H_4Br WITH RLi IN THE PRESENCE OF FURAN

Run	Halide[a]	Halide, mole	RLi[b]	Temp., °C.[c]	Furan, g.[d]	Addn. time, min.	Yield of 1,4-dihydronaphthalene-1,4-endoxide, %
1	*o*-ClC_6H_4Br	0.042	*n*-C_4H_9Li	−40[e]	41	15[f]	64
2	*o*-BrC_6H_4Br	.042	*n*-C_4H_9Li	−50[e]	41	12[f]	80
3	*o*-ClC_6H_4Br	.026	CH_3Li	−20	30	10[g]	84
4	*o*-BrC_6H_4Br	.032	CH_3Li	−35	35	10[h]	77
5	*o*-FC_6H_4Br	.026	C_6H_5Li[i]	−30[j]	29	10	74[k]

[a] RLi was added to the halide in every run. [b] Equivalent amount of RLi was used in all runs. [c] Temperature during the addition of the RLi. [d] In all runs 15 ml. of dry diethyl ether was admixed with the furan. [e] Mixture warmed to −10° before hydrolyzing with water. [f] Negative Color Test I after addition. [g] Mixture warmed to −10° and carbonated after 10 min. [h] Color Test I was positive on completion of the addition. A negative Color Test I resulted after warming to −10°. The mixture was hydrolyzed with water. [i] C_6H_5Li prepared from C_6H_5Br. [j] Warmed to −20° before hydrolysis. [k] Recovered 1.18 g. (30%) of C_6H_5Br, $n^{20}D$ 1.5578.

(b) **Methyllithium and *o*-Bromofluorobenzene.**—Nineteen milliliters of an ethereal solution containing 0.026 mole of methyllithium[20] was added during 7 min. to a rapidly stirred solution of 4.38 g. (0.025 mole) of *o*-bromofluorobenzene in 15 ml. of ether and 29 g. of furan. The temperature of the reaction mixture during the addition was maintained between −10 and −12°. The reaction mixture was carbonated and worked up as described previously. No acid was found in the acidified aqueous layer. The organic layer was worked up as usual, and the crude adduct was sublimed at room temperature and 0.003 mm. to yield 3.01 g. (84%) of III.

The results of the interaction of methyllithium with the *o*-chloro- and *o*-bromo- isomers are summarized in Table I.

(c) **Phenyllithium and *o*-Bromochlorobenzene.**—The phenyllithium was prepared by adding a solution of 11.3 g. (0.055 mole) of iodobenzene in 60 ml. of ether to a suspension of 12.1 g. of lithium wire cut into small pieces and contained in 100 ml. of ether. The mixture was cooled with an ice-bath during the addition which required 2.5 hr. The mixture was stirred in the ice-bath for 2 hr. after the addition was complete and at room temperature for another 2 hr. After concentrating the mixture to 45 ml., a single acid titration indicated the yield to be 0.053 mole; 25 ml. of this solution was added, during 7 minutes, to a stirred solution of 5.75 g. (0.03 mole) of *o*-bromochlorobenzene in 10 ml. of diethyl ether and 31 g. of furan, while maintaining the temperature between −25 and −30°. The mixture was stirred at −30° for 25 min. and then was hydrolyzed with water. The two layers were separated and the organic layer was worked up in the usual manner. After distilling the ether and excess furan, the remaining material was distilled at 155–160° (745 mm.) to give 3.33 g. (71%) of bromobenzene, $n^{20}D$ 1.5585. The infrared spectrum was identical with that of a pure sample of bromobenzene.

Because of the high bath temperature (230°) encountered during the distillation, the adduct was converted to a dark brown material from which a trace of α-naphthol was sublimed. No other material was identified.

Three grams of III was refluxed under nitrogen for 4 hr. No adduct was recovered and the resulting product was a brown material very similar to the above material.

Attempted Metalation of Chlorobenzene in Furan with Butyllithium.—Twenty-two milliliters of an ethereal solution containing 0.03 mole of butyllithium was added, during 5 min., to a stirred solution of 3.48 g. (0.03 mole) of chlorobenzene in 15 ml. of diethyl ether and 30 g. of furan. The addition was carried out between −35 and −40° and was stirred at −30° for an additional 30 min. on completion of the addition. The mixture was cooled to −60° and carbonated in the usual manner. The aqueous layer on acidification, extraction with ether, and sublimation of the resulting solid gave 0.33 g. of 2-furoic acid, m.p. 130–132°. After distillation of solvent from the organic layer, there was obtained 2.06 g. (60%) of unreacted chlorobenzene. No Diels–Alder adduct was isolated.

2-Chloro-2′-(triphenylsilyl)-biphenyl.—An ethereal solution containing 0.10 mole of *o*-chlorophenyllithium was prepared at −70° in accordance with an earlier procedure. After stirring the organolithium solution at −70° for 1 hr., 10 g. (0.034-mole) of triphenylchlorosilane in 90 ml. of ether was added, and the reaction mixture was allowed to slowly warm to room temperature. Three hours after completion of the addition Color Test I was positive. Subsequently an additional 4.73 g. of triphenylchlorosilane in 25 ml. of ether was added, and then the mixture was allowed to stir at room temperature for 10 hr. The mixture was hydrolyzed with 5% hydrochloric acid. The ethereal layer was separated, dried over anhydrous sodium sulfate and the ether was distilled. The residue was suspended in warm petroleum ether (b.p. 60–70°) and the white solid (mostly triphenylsilanol) was filtered off. The filtrate was chromatographed on a column of alumina. Elution was effected with 100 ml. of petroleum ether followed by 400 ml. of a 1:1 mixture of petroleum ether and benzene. The white solid was then chromatographed on the same column and was eluted with a 1:1 mixture of petroleum ether and benzene. A total of

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[20] W. J. Hickinbottom, A. A. Hyatt and M. B. Sparke, *J. Chem. Soc.*, 2533 (1954).

9 fractions was collected. The oil from the second fraction when washed with ethanol gave a white solid which was crystallized from ethyl acetate to give 0.15 g. of tetraphenylsilane, identified by means of a mixed melting point with an authentic sample. Removal of the solvent from the third fraction left a yellow paste which was refluxed in petroleum ether. There was isolated 1.4 g. (13%) of product melting at 149–152°. Two additional crystallizations gave an analytical sample of 2-chloro-2′-(triphenylsilyl)-biphenyl melting at 157.5–158.5°.

Anal. Calcd. for $C_{30}H_{23}ClSi$: Si, 6.28. Found: Si, 6.23, 6.27.

Fraction four gave 0.25 g. of pale yellow plates melting at 194–196°. A mixed melting point with an authentic sample of triphenylene showed no depression.

2-Bromo-2′-(triphenylsilyl)-biphenyl.—A solution of 25 ml. (0.032 mole) of butyllithium was added over a period of 6 min. to a rapidly stirred solution of 10 g. (0.032 mole) of 2,2′-dibromobiphenyl in 100 ml. of dry ether. A temperature of −20° was maintained during the addition. After completing the addition, the mixture was stirred at −15° for 45 min. Subsequently 9.44 g. (0.032 mole) of triphenylchlorosilane dissolved in 85 ml. of ether was added at −15°, and the mixture was allowed to warm to room temperature. The mixture was stirred overnight at room temperature and then was refluxed for 7 hr. after which time Color Test I was positive. After adding 100 ml. of *n*-heptane, the resulting mixture was distilled until an internal temperature of 70° was reached, whereupon a negative color test was obtained after 20 min. The mixture was hydrolyzed with water. An insoluble material was filtered and crystallized from ethanol to give colorless needles, 1.92 g., m.p. 152–153°. Work-up of the filtrate as described in the preceding experiment yielded an additional 1.81 g. of product, m.p. 147–149°. The total yield of 2-bromo-2′-(triphenylsilyl)-biphenyl was 3.73 g. (24%). The analytical sample melted at 152.5–154°.

Anal. Calcd. for $C_{30}H_{23}BrSi$: Si, 5.71. Found: Si, 5.63, 5.45.

The infrared spectrum of the bromo-isomer as a carbon disulfide solution was very similar to that of the chloro-isomer, thus indirectly confirming the structure of the latter.

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AMES, IOWA

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Reactions of Trichloromethyl-1,3,5-triazine Derivatives with Amines[1]

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A method has been found which, by means of amines, permits the replacement by NHR-groups of all trichloromethyl groups attached to a 1,3,5-triazine ring. Use of diamines leads to longer chains of higher molecular 1,3,5-triazine compounds. In 1,3,5-triazine derivatives bearing both trichloromethyl and carbethoxy groupings, ammonia reacts first of all with one trichloromethyl group.

As is well known, the trichloromethyl groups of several organic compounds like chloral, trichloroacetic acid, trichloroacetone and others are split off upon reaction with alkali to form anions[2] which then, by combining with a proton, form chloroform. In connection with investigations on trichloromethyl-1,3,5-triazines,[3,4] especially 2-methyl-4,6-bis-trichloromethyl-1,3,5-triazine (I) and 2-phenyl-4,6-bis-trichloromethyl-1,3,5-triazine (II),[5] it was desirable to know whether these compounds reacted with bases analogously. The various replacement reactions of trichloromethyl groups attached to the 1,3,5-triazine ring by NHR-groups are described in the present article, along with some comparable observations on carbethoxytrichloro-1,3,5-triazines.

In the reaction of I or II with concentrated aqueous ammonia, only one of the two trichloromethyl groups turned out to be replaceable by the NH_2-group under very mild conditions, thus yielding 2-methyl-4-amino-6-trichloromethyl-1,3,5-triazine (III) and 2-phenyl-4-amino-6-trichloromethyl-1,3,5-triazine (IV), respectively. An attempt to replace the last trichloromethyl group by increasing the reaction temperature failed. Instead, at higher temperatures compound I yielded quantitatively 2-methyl-4-amino-6-hydroxy-1,3,5-triazine (V) upon reaction with aqueous ammonia and a mixture of III and V upon reaction with ethanolic ammonia solution.[6]

It was, however, desired to find a method by which all trichloromethyl groups attached to a triazine ring could be replaced by NHR-groups, because application of diamines would then lead to higher molecular compounds containing two or more 1,3,5-triazine rings linearly connected. This objective was achieved through working in OH-free media, like dioxane, chloroform and N,N-dimethylformamide.

Thus, by bubbling ammonia into a solution of I in N,N-dimethylformamide, 2-methyl-4,6-diamino-1,3,5-triazine (XI) was obtained. By the same

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(2) F. Arndt and B. Eistert, *Ber.*, **68**, 196 (1935).

(3) Ch. Grundmann and G. Weisse, *Chem. Ber.*, **84**, 684 (1951).

(4) Ch. Grundmann, H. Ulrich and A. Kreutzberger, *ibid.*, **86**, 181 (1953).

(5) K. Dachlauer, German Patent 682,391, Oct., 1939 (to I. G. Farbenindustrie A.-G.).

(6) These findings are in conformity with the results obtained from the action of concd. aqueous ammonia on 2,4,6-tris-trichloromethyl-1,3,5-triazine (VI) as reported by A. Weddige, *J. prakt. Chem.*, [2] **33**, 81 (1886). Only the first two trichloromethyl groups in VI could be replaced by the amino group with formation of 2-amino-4,6-bis-trichloromethyl-1,3,5-triazine (VII) and 2,4-diamino-6-trichloromethyl-1,3,5-triazine (VIII). Similar results were obtained when methylamine was used in place of concd. aqueous ammonia. The substitution by the NHR-group of the last trichloromethyl group in VI, however, could not even be forced under more severe conditions, and as end product only 2,4-diamino-6-hydroxy-1,3,5-triazine (IX) and 2,4-bis-methylamino-6-hydroxy-1,3,5-triazine (X), respectively, could be obtained.