4.64 g. (0.015 mole) of 4-bromo-*p*-terphenyl (m.p. 228–230°) and 75 ml. of ether. This suspension was stirred slowly at room temperature while 12.5 ml. (0.016 mole) of *n*-butyllithium solution[8] was added dropwise. After stirring 10 min. the reaction mixture became pink, though not quite clear, and the insoluble bromide was no longer evident. At this point Color Test II[9] was negative and Color Test I[10] was positive. The solution was poured jetwise into a stirred Dry Ice–ether slurry and stirring was continued until the ether had evaporated. The residual lithium salt was insoluble in water and had to be moistened with glacial acetic acid and stirred 1 hr. with 100 ml. of 10% hydrochloric acid in order to convert it to the free acid. This product was filtered and recrystallized from glacial acetic acid to give 2.18 g. (53%) of clear plates, m.p. 315–317°; reported[1] m.p. 315°.

Diphenyl-p-terphenyl-4-ylcarbinol. To a stirred solution of *p*-terphenyl-4-yllithium prepared as above was added 2.91 g. (0.016 mole) of benzophenone in 50 ml. of ether. After stirring for 5 min. Color Test I was negative, and the mixture was hydrolyzed with 30 ml. of saturated ammonium chloride solution. One hundred ml. of benzene was added and the layers were separated. The organic layer was evaporated to a gummy residue which was sucked dry on a Büchner funnel; yield 4.95 g. (80.1%); m.p. 213–216°. Two recrystallizations from 1:1 benzene–petroleum ether (b.p. 60–70°) raised the m.p. to 216–217°; yield 4.42 g. (72%).

Anal. Calcd. for $C_{31}H_{24}O$: C, 90.25; H, 5.87. Found: C, 90.10, 90.27; H, 6.04, 5.80.

4-Benzoyl-p-terphenyl. Upon addition of 1.65 g. (0.016 mole) of benzonitrile in 50 ml. of ether to 0.015 mole of *p*-terphenyl-4-yllithium solution, the mixture turned to a bright red-orange suspension, and Color Test I was negative after stirring for 5 min. The mixture was hydrolyzed with 30 ml. of 10% hydrochloric acid and worked up in the same fashion as the benzophenone adduct to give 2.95 g. (88.3%) of pale yellow material having a melting range of 192–195°. After four recrystallizations from 1:2 benzene–petroleum ether (b.p. 60–70°) the product melted at 196–197°.

Anal. Calcd. for $C_{25}H_{18}O$: C, 89.80; H, 5.42. Found: C, 90.14, 90.23; H, 5.61, 5.58.

4-Methyl-p-terphenyl. Addition of 2.02 g. (0.016 mole) of methyl sulfate in 50 ml. of ether to the terphenylyllithium solution as prepared above caused vigorous reflux and precipitation of a white solid. Color Test I was negative after stirring 10 min., and the mixture was hydrolyzed with 30 ml. of water. The layers were separated and the organic layer washed with water, dried and evaporated to a gummy residue. After drying on a Büchner funnel there remained 2.46 g. (67%) of white solid; m.p. 205.5–207°. Recrystallization from 1:2 benzene-petroleum ether (b.p. 60–70°) gave glassy prisms; m.p. 207–208°, as reported by France, Heilbron, and Hey.[3]

3-Methyl-p-terphenyl. A solution of 0.077 mole of *p*-biphenylyllithium[11] in 200 ml. of ether was added over a period of 30 min. to a stirred solution of 8.96 g. (0.080 mole) of 3-methylcyclohexanone in 50 ml. of ether. Color Test I was negative after stirring for 30 min., and the mixture was hydrolyzed with 50 ml. of 10% hydrochloric acid. The layers were separated and the aqueous layer was extracted with 50 ml. of benzene. The organic layer was filtered from a small amount of solid and distilled to remove the solvents. The solid (0.45 g.) proved to be impure quaterphenyl having a melting range of 260–285°. Two recrystallizations from toluene raised the m.p. to 315–317°; reported[12] m.p. 320° The residual oil was stirred and heated at 90–100° with 20 ml. of 20% sulfuric acid for 1 hr. The mixture was cooled and diluted with 30 ml. of water and 30 ml. of benzene. The layers were separated and the organic layer washed three times with 30 ml. portions of water, then distilled to remove the benzene. The residual oily solid was distilled at reduced pressure and three fractions were collected:

Fraction I: 1.64 g.; b.p. 55–57°/22 mm.
Fraction II: 6.41 g.; b.p. 85–98°/0.15 mm.
Fraction III: 7.77 g.; b.p. 152–158°/0.10 mm.

Fraction I was unreacted 3-methylcyclohexanone. Fraction II was impure biphenyl; m.p. and mixed m.p. with pure biphenyl 67–69°. The product in fraction III (crude 1-*p*-biphenylyl-2-methylcyclohexene) was dehydrogenated by heating with 2.05 g. (0.064 g.-atom) of sulfur for 5 hours at 205–210°. The resulting reddish solid was distilled at 145–150°/0.04 mm., and the product recrystallized from ethanol to give 3.88 g. (21%, based on *p*-biphenylyllithium) of pale yellow needles, having a melting range of 110–117°. This material was sublimed at 100°/0.01 mm. to give 3.02 g. of white powder; m.p. 122–124°. After two recrystallizations from ethanol the product[13] melted at 125.5–126°.

Anal. Calcd. for $C_{19}H_{16}$: C, 93.44; H, 6.56. Found: C, 93.44; H, 6.71.

2-Methyl-p-terphenyl. This material was prepared by condensation of 0.077 mole of *p*-biphenylyllithium with 8.96 g. (0.080 mole) of 2-methylcyclohexanone in the same manner as the 3-methyl isomer. After dehydration with 20% sulfuric acid, there was recovered 1.42 g. of unreacted 2-methylcyclohexanone and 4.92 g. of biphenyl before the main fraction: 7.64 g. of what is presumed to be a mixture of 1-(*p*-biphenylyl)-3-methylcyclohexene and 1-(*p*-biphenylyl)-5-methylcyclohexene; b.p. 138–151°/0.10 mm. This material was heated with 1.96 g. (0.061 g.-atom) of sulfur for 8 hr. at 200–210° and distilled to give 4.13 g. of pale yellow solid; b.p. 125–140°/0.05 mm. Three recrystallizations from ethanol removed all sulfur and left 1.92 g. (10.4%); m.p. 93–94°. France, Heilbron, and Hey[3] reported 91–92°.

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[8] H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *J. Am. Chem. Soc.*, **71**, 1499 (1949).

[9] H. Gilman and J. Swiss, *J. Am. Chem. Soc.*, **62**, 1847 (1940).

[10] H. Gilman and J. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

[11] H. Gilman, W. H. Langham, and F. W. Moore, *J. Am. Chem. Soc.*, **62**, 2327 (1940).

[12] F. Ullman and G. M. Meyer, *Ann.*, **332**, 52 (1904).

[13] The m.p. reported[3] was 169–170°. Information kindly supplied by Prof. D. H. Hey in a private communication said that their compound was 4-acetamidodiphenyl.

Coupling Reactions with Some Organolithium Compounds in Tetrahydrofuran

HENRY GILMAN AND BERNARD J. GAJ

Received October 23, 1956

Several investigations concerning the reactions of *n*-butyllithium with dihalobenzene compounds have been reported recently. Depending upon conditions and solvents used, a variety of products have been obtained from these reactions. One such investigation[1] described the reactions of *o*-diiodobenzene and *o*-dibromobenzene with magnesium, lithium and *n*-butyllithium in various solvents to yield a series of coupling products. The formation

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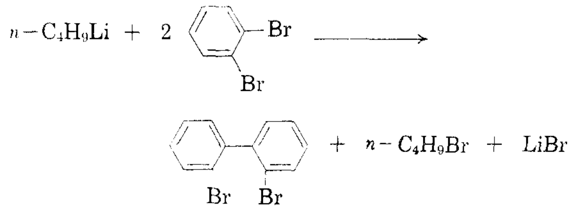
[1] H. Heaney, F. G. Mann, and I. T. Millar, *J. Chem. Soc.*, 1 (1956).

of these coupling products in the reactions involving *o*-diiodobenzene has been postulated to proceed through the initial formation of 2,2′-diiodobiphenyl as an intermediate. However, neither 2,2′-diiodobiphenyl nor 2,2′-dibromobiphenyl could be isolated from the reaction mixtures.

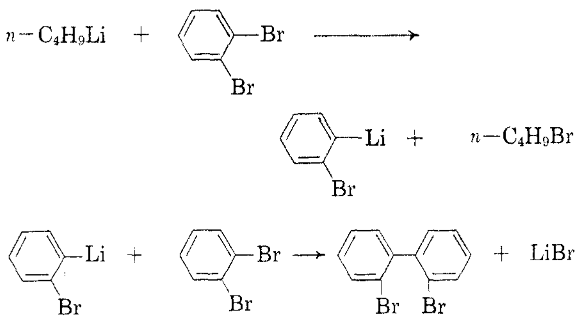
Another investigation[2] described the reactions of *o*-dibromobenzene, *o*-chlorobromobenzene and *o*-fluorobromobenzene with *n*-butyllithium in ethereal solution at low temperatures to yield upon carbonation, *o*-bromobenzoic, *o*-chlorobenzoic and *o*-fluorobenzoic acids, respectively. Upon warming the reaction mixtures prior to carbonation, the various *o*-halophenyllithium reagents underwent coupling reactions to yield such products as 2-halo-2′-lithiobiphenyl, 2-(*o*-halophenyl)-2′-lithiobiphenyl and triphenylene. However, in no case was any 2,2′-dihalobiphenyl isolated. It was suggested that one possible route to these coupling products might involve the "benzyne" intermediate.[3] Recent chemical evidence from this laboratory strongly supports such an intermediate.[4]

The present investigation has shown that one equivalent of an ethereal solution of *n*-butyllithium reacts instantaneously at −78° with two equivalents of *o*-dibromobenzene, dissolved in tetrahydrofuran, to give as the main product, 2,2′-dibromobiphenyl in yields ranging from 67 to 74%.



Similarly, when *p*-dibromobenzene and *p*-chlorobromobenzene were dissolved in tetrahydrofuran and treated with an ethereal solution of *n*-butyllithium in a 2:1 ratio, there resulted 4,4′-dibromobiphenyl and 4,4′-dichlorobiphenyl, respectively. However, the yields of the latter two compounds were much lower than that of 2,2′-dibromobiphenyl.[5]

Although the mechanism of the reaction in tetrahydrofuran has not been extensively studied, it is conceivable that *o*-bromophenyllithium is formed as an intermediate *via* a halogen-metal interconversion reaction between *o*-dibromobenzene and *n*-butyllithium, and that this in turn can couple with *o*-dibromobenzene to give the final product, 2,2′-dibromobiphenyl.



This reaction path is compatible with the route postulated for the formation of various coupling products obtained by the reaction of *o*-diiodobenzene with *n*-butyllithium in benzene and petroleum ether.[1] In these particular reactions the postulated intermediate was 2,2′-diiodobiphenyl.

From the foregoing discussion, there is a strong inference that the solvent may play an important role in the reaction of *n*-butyllithium with a dihalobenzene compound. In further support of this conclusion, it has been found that when *o*-dibromobenzene is interacted with *n*-butyllithium in diethyl ether under identical conditions and using the same quantities of reactants employed in the run carried out in tetrahydrofuran, no 2,2′-dibromobiphenyl was isolated. The only products were an unidentified ether-insoluble material and a highly viscous oil.

It is also a well established fact that *p*-chlorobromobenzene and *p*-dibromobenzene, when reacted with *n*-butyllithium in diethyl ether, undergo a normal halogen-metal interconversion reaction to give *p*-chlorophenyllithium and *p*-bromophenyllithium, respectively, in high yields.[6] However, we found that in these cases the mode of reaction is changed when tetrahydrofuran is used as the solvent.

Although the role played by the solvent in the reaction is unknown as yet, investigations of similar reactions in tetrahydrofuran to test its generality and utility are now being carried out.

This preparation of 2,2′-dibromobiphenyl is interesting also from a synthetic viewpoint since previous to this, the only satisfactory means for preparing 2,2′-dibromobiphenyl was a multistep process involving diazotization of 2,2′-diaminobiphenyl.[7,8] The procedure described in this communication offers several advantages over the older methods. The over-all yield is probably higher, there are fewer steps involved, and the reaction can be achieved quite rapidly.

This reaction is now finding extensive use in

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[2] H. Gilman and R. D. Gorsich, *J. Am. Chem. Soc.*, **78**, 2217 (1956).

[3] See ref. 2 for leading references concerning the "benzyne" intermediate.

[4] Unpublished work of H. Gilman and R. D. Gorsich utilizing the techniques of Wittig has shown that the intermediate can be captured by means of furan to give a Diels-Alder adduct.

[5] The optimum conditions for the preparation of 4,4′-dibromobiphenyl and 4,4′-dichlorobiphenyl have not been worked out as yet.

[6] H. Gilman, W. Langham, and F. Moore, *J. Am. Chem. Soc.*, **62**, 2327 (1940).

[7] Heinz-Werner Schwechten, *Ber.*, **65B**, 1605 (1932).

[8] J. J. Dobbie, J. J. Fox, and A. J. H. Gauge, *J. Chem. Soc.*, **99**, 684, 1618 (1911).

this laboratory for the preparation of 2,2′-dibromobiphenyl, which is an important intermediate in the preparation of some cyclic organosilicon compounds.[9]

EXPERIMENTAL[10]

2,2′-Dibromobiphenyl. To a stirred solution of 47.26 g. (0.2 mole) of *o*-dibromobenzene in 450 ml. of anhydrous tetrahydrofuran[11] was added 76.4 ml. of an ethereal solution containing 0.1 mole of *n*-butyllithium[12] (molarity determined by the double titration method).[13] The *o*-dibromobenzene solution was cooled to the minimum temperature afforded by a dry ice–acetone bath, and the rate of addition was such that the temperature was not allowed to rise more than 5°. The reaction was instantaneous as was evidenced by a negative Color Test I[14] and Color Test II[15] immediately after completion of the addition.

The yellow-green reaction mixture was allowed to warm to 5° and then was hydrolyzed with 100 ml. of 5% hydrochloric acid. The resulting layers were separated and the aqueous layer was extracted with four 20-ml. portions of ether. The ether washings were combined with the original organic layer and dried over anhydrous sodium sulfate, filtered and concentrated by distillation until the distillation temperature reached 70°. The residue was treated with 50 ml. of absolute ethanol and cooled to give 11.74 g. of 2,2′-dibromobiphenyl, m.p. 80–81°. The filtrate was decolorized with activated charcoal, filtered and concentrated by evaporation to give an additional 11.26 g. of less pure product, m.p. 78–81°, or a total yield of 73.7%. One recrystallization from absolute ethanol gave pure 2,2′-dibromobiphenyl, m.p. 80–81°. A mixed melting point with an authentic sample showed no depression.

In a similar run, using 11.80 g. (0.05 mole) of *o*-dibromobenzene in 100 ml. of tetrahydrofuran and 19 ml. of 1.33 N *n*-butyllithium, there was obtained 5.18 g. (66.5%) of 2,2′-dibromobiphenyl, m.p. 79–80°.

o-Dibromobenzene and n-butyllithium in diethyl ether. To a stirred solution of 11.8 g. (0.05 mole) of *o*-dibromobenzene in 100 ml. of anhydrous diethyl ether, cooled to −78°, was added an ethereal solution containing 0.025 mole of *n*-butyllithium at such a rate that the temperature was not allowed to rise more than 5° during the addition. A white suspension developed in the pale yellow solution after only a few drops of *n*-butyllithium had been added. The reaction mixture exhibited a negative Color Test I immediately upon completion of the addition. The main product isolated after work-up in the usual manner was an unidentified ether insoluble white solid which melted over the range 304–340° with decomposition. A small amount of an unidentified yellow oil was obtained also.

4,4′-Dibromobiphenyl. To a stirred solution of 23.59 g. (0.1 mole) of *p*-dibromobenzene in 100 ml. of anhydrous tetrahydrofuran, cooled to −15°, was added 40 ml. of an ethereal solution containing 0.05 mole of *n*-butyllithium at such a rate that the temperature did not rise above −10°. The reaction mixture darkened upon the addition of only a few drops of the *n*-butyllithium solution and a brown precipitate was noticed toward the end of the addition. Both Color Tests I and II were found to be negative immediately after the addition was completed. The reaction mixture was then warmed to 20° and hydrolyzed with 5% hydrochloric acid. The resulting layers were separated and the aqueous layer was extracted with three small portions of ether. The ether extracts were combined with the now homogeneous brown organic layer and dried over anhydrous sodium sulfate, filtered and concentrated by evaporation. A little ethanol was added to the residue which resulted in the formation of a yellow precipitate. This solid was removed by filtration to give 2.6 g. of crude 4,4′-dibromobiphenyl, m.p. 158–164°. Further concentration of the mother liquor gave an additional 1.81 g. of impure 4,4′-dibromobiphenyl and a heavy brown oil. The combined solids were recrystallized from a mixture of ethanol and benzene to give 2.14 g. of pure 4,4′-dibromobiphenyl, m.p. 168–169°, and an additional 1.14 g. of less pure material, m.p. 165–167° or a combined yield of 21%. A mixed melting point with an authentic specimen showed no depression.

In a similar reaction using the same quantities of materials, the addition was carried out while maintaining a temperature between −35 and −40°. Color Test I was positive after completing the addition. Upon warming the reaction mixture to −20° during a 30-min. period, a negative Color Test I was obtained. The mixture was worked up in the same manner as described above to give 4.99 g. of crude 4,4′-dibromobiphenyl, m.p. 144–160°. One recrystallization from benzene, after decolorizing with activated charcoal, gave 2.5 g. (16.4%) of pure 4,4′-dibromobiphenyl and 1.02 g. (6.7%) of less pure material, m.p. 165–168°.

4,4′-Dichlorobiphenyl. To a stirred solution of 38.29 g. (0.2 mole) of *p*-chlorobromobenzene in 200 ml. of anhydrous tetrahydrofuran, cooled to −40° by a dry ice–acetone bath, was added dropwise 85 ml. of 1.19 molar *n*-butyllithium in ether. During the addition, the reaction mixture was allowed to warm to −20°. It then was stirred at this temperature for an additional 15 min. before giving a negative Color Test I. The product was worked up in a manner similar to that described for 4,4′-dibromobiphenyl to give 6.0 g. of an oily brown solid which was dissolved in benzene, decolorized with activated charcoal, concentrated and cooled to give 2.24 g. (10%) of pure 4,4′-dichlorobiphenyl, m.p. 149–150°, and an additional 1.75 g. (7.8%) of less pure material, m.p. 144–148°.

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[9] H. Gilman and R. D. Gorsich, *J. Am. Chem. Soc.*, **77**, 6380 (1955).

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

[11] The tetrahydrofuran was dried and purified by first shaking with sodium hydroxide pellets, refluxing over sodium metal for several hours and finally distilling, immediately before use, from lithium aluminum hydride.

[12] H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *J. Am. Chem. Soc.*, **71**, 1499 (1949).

[13] H. Gilman and A. E. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).

[14] H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

[15] H. Gilman and J. Swiss, *J. Am. Chem. Soc.*, **62**, 1847 (1940).

Reactions of 1,3-Dienes with Activated Aldehydes, II

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Received November 21, 1956

In an earlier publication,[1] it was reported that chloral was observed to react with various 1,3-dienes to produce substituted 5,6-dihydro-1,2-pyrans through a Diels-Alder type of reaction.

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[1] W. J. Dale and A. J. Sisti, *J. Am. Chem. Soc.*, **76**, 81 (1954).