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Chemistry of Alkali Metal-unsaturated Hydrocarbon Adducts. I. Metalations with Lithium Metal Adducts of Biphenyl Systems[1]

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A detailed study of the model 1:1 adduct of lithium metal and biphenyl in tetrahydrofuran solution (I) as a metalating agent toward pseudoacidic hydrocarbons has led to an excellent synthetic method for certain organolithium compounds. In addition, new insight has been gained as to the mechanism of such metalations and the importance of lithium metal adducts in the reduction of aromatic hydrocarbons. The reaction of I with the individual phenylmethanes, $(C_6H_5)_nCH_{4-n}$ (n = 1–3), was found: (a) to proceed more readily and to a greater extent when n = 3; (b) to be catalyzed by lithium piperidide and by a solid lithium phase; (c) not to evolve hydrogen gas, but rather to involve simultaneous reduction of the biphenyl; (d) to proceed more slowly than the reaction of the 1:1 lithium–phenylcyclohexene adduct with the phenylmethane; and (e) to lead eventually to phenylcyclohexane if one-sixth an equivalent of biphenyl is treated with one equivalent each of lithium and the phenylmethane. In the light of these findings the reaction of lithium metal with fluorene was reinvestigated and reinterpreted as involving autometalation by lithium–fluorene adducts. As an extension, a modified Birch-type reduction of polycyclic aromatic hydrocarbons *via* lithium-adduct formation in tetrahydrofuran and alcoholysis is suggested.

Schlenk and co-workers[2] made the fundamental discovery that polyunsaturated organic compounds form adducts with alkali metals slowly in hydrocarbon solution or more rapidly in ethyl ether solution. Similar alkali metal–hydrocarbon adducts have been postulated as transitory intermediates in metal reductions involving alcohols,[3] liquid ammonia,[4,5] or amines.[6] The observation that more basic ethers, such as methyl ether and 1,2-dimethoxyethane, markedly increase the rate of metal–hydrocarbon interaction and allow the preparation of relatively stable solutions has made such adducts more accessible for further study.[7] Recent re-examination of the sodium and potassium metal adducts of aromatic hydrocarbons in basic ether solvents by means of paramagnetic susceptibility[8] and electron spin resonance[9] measurements has demonstrated that the 1:1 and 2:1 metal–hydrocarbon adducts are formed by electron-transfer processes. Consequently, the 1:1 adducts are to be viewed as metal cation–aromatic radical anion pairs.

The synthetic chemistry of metal–hydrocarbon adducts, especially those of sodium, has received periodic attention. That the sodium adducts can react with carbon dioxide and active hydrogen compounds, like typical active organometallic compounds, was noted in the original study of Schlenk and co-workers.[2] Subsequent research has extended the synthetic utility of these adducts.[7,10] Although lithium metal–hydrocarbon

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[1] Presented at the 138th American Chemical Society Meeting, New York, N.Y., September 11–16, 1960. A preliminary communication of a portion of this work appeared in *Chem. Ind.* (London), 470 (1961).

[2] For a comprehensive treatment of this research, *cf.* W. Schlenk and E. Bergmann, *Ann.*, **463**, 1–322 (1928).

[3] R. Willstätter, F. Seitz, and E. Bumm, *Ber.*, **61**, 871 (1928).

[4] A. J. Birch, *Quart. Rev.*, **4**, 69 (1950).

[5] For a recent discussion of metal reductions in liquid ammonia, *cf.* A. P. Krapcho and A. A. Bothner-By, *J. Am. Chem. Soc.*, **81**, 3658 (1959).

[6] R. A. Benkeser, R. E. Robinson, and H. Landesman, *ibid.*, **74**, 5699 (1952).

[7] N. D. Scott, J. F. Walker, and V. I. Hansley, *ibid.*, **58**, 2442 (1936).

[8] T. L. Chu and S. C. Yu, *ibid.*, **76**, 3367 (1954).

[9] *Cf.*, *inter alia*: (a) D. Lipkin, D. E. Paul, J. Townsend, and S. I. Weissman, *Science*, **117**, 534 (1953); (b) G. J. Hoijtink, E. de Boer, P. H. van der Meij, and W. P. Weyland, *Rec. trav. chim.*, **74**, 277 (1955); **75**, 487 (1956); (c) D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956); (d) T. R. Tuttle, Jr., and S. I. Weissman, *ibid.*, **80**, 5342 (1958); and (e) A. Carrington, F. Dravnieks, and M. C. R. Symons, *J. Chem. Soc.*, 947 (1959).

[10] (a) J. F. Walker and N. D. Scott, *J. Am. Chem. Soc.*, **60**, 951 (1938); (b) A. Jeanes and R. Adams, *ibid.*, **59**, 2608 (1937); (c) G. F. Wright, *ibid.*, **61**, 2106 (1939); (d) A. G. Brook, H. L. Cohen, and G. F. Wright, *J. Org. Chem.*, **18**, 447 (1953); and (e) H. Normant and B. Angelo, *Bull. soc. chim. France*, 354 (1960).

adducts have been utilized to form alkyl, carboxyl, and similar derivatives of the original hydrocarbon,[2,10d,11] the wide utility and significance of lithium metal–hydrocarbon adducts in organic chemistry have not been appreciated. Inspired by the physicochemical characterization of 1:1 metal–hydrocarbon adducts as metal cation–radical anion pairs and by the importance of organolithium compounds in organic synthesis, the present study was undertaken to learn more about the chemical properties of 1:1 lithium metal–aromatic hydrocarbon adducts. To evaluate the ability of such systems to serve as strong bases (anionic character), the model 1:1 adduct of lithium metal and biphenyl in tetrahydrofuran was studied in detail. As will be apparent from the subsequent discussion, biphenyl was the hydrocarbon selected because of its kinship with other systems of interest. Thus the success of Gilman and co-workers in promoting lithium metal cleavage reactions of heterocycles,[12a] certain ethers,[12b] fluorenes,[12c] and disilanes[12d] by the use of tetrahydrofuran in place of ethyl ether suggested to us a relationship between metal-adduct formation and lithium metal cleavage reactions in tetrahydrofuran(THF).[13]

The interaction of equivalent amounts of lithium metal and biphenyl in THF gave a blue-green solution of the 1:1 adduct (I). However, it appears that higher lithium adducts can be formed with an excess of lithium metal; in 0.5 *M* biphenyl solutions maximum lithium–biphenyl ratios of 2.5:1.0 have been attained.[14] This contrasts with the behavior of the sodium–biphenyl system in THF, where the 1:1 adduct is reported to form to the extent of 37% and no 2:1 adduct is detectable.[8]

The character of the 1:1 lithium–biphenyl adduct (I) as a base was examined by the metalation of the phenylmethanes under comparable conditions. The extent of metalation of the pseudoacids was determined by carbonation and the isolation of the substituted acetic acid

$$(C_6H_5)_nCH_{4-n} \xrightarrow{\text{Li—}(C_6H_5)_2} (C_6H_5)_nCH_{3-n}Li \xrightarrow[\text{2. } H_3O^+]{\text{1. } CO_2} (C_6H_5)_nCH_{3-n}COOH \quad (1)$$

TABLE I

METALATIONS BY LITHIUM–BIPHENYL ADDUCTS IN TETRAHYDROFURAN

Hydrocarbon, RH	Moles,[a] RH. Li	Molar ratio, hydrocarbon. biphenyl	Time, hr.	Temperature (°C. ± 2)	Yield of RLi, %
Triphenylmethane	0.022	1.0	9.0	30	92
	0.015	1.0	4.5	30	61
	0.022	1.0	3.5	66	98
	0.022	6.0	18.0	30	82
Diphenylmethane	0.022	1.0	18.0	30	63
	0.022	1.0	3.5	66	43
	0.022	1.0	7.0	66	34
	0.022	6.0	27.0	30	52
Toluene	0.022[b]	1.0	18.0	30	~1[c]

[a] In 75 ml. of tetrahydrofuran. [b] A 100% excess of toluene was employed. [c] The phenylacetic acid was characterized as its *p*-bromophenacyl ester.

The results of various runs with I and with other lithium–biphenyl ratios are summarized in Table I. The over-all metalation reaction was found to display the following characteristics. First, all the phenylmethanes ($n = 1$–3) are metalated by I, but with decided differences in *ease* and *extent;* at 30° triphenylmethane was almost quantitatively metalated (92%) under conditions where diphenylmethane and toluene reacted to give the phenylmethyllithium in yields of about 50% and less than 1%, respectively. At the reflux temperature of THF, triphenylmethane and diphenylmethane were metalated in 98 and 43% yields, respectively, under comparable conditions. On the other hand, maximal extent of metalation observed with triphenylmethane and I was 98% and with diphenylmethane and I, 63%. Secondly, the displaced hydrogen is not evolved as hydrogen gas, but instead reduces the biphenyl. Thirdly, the metalation proceeds almost to the same extent, but at a slower rate, when equivalent quantities of lithium metal and the phenylmethane are used with only one-sixth an equivalent of biphenyl; in this case the biphenyl accepts all the displaced hydrogen of the pseudo acid and is reduced thereby to phenylcyclohexane. Fourthly, the lithium in the adduct I is accounted for by the formation of equivalent amounts of the phenylmethyllithium. Fifthly, as was shown by comparison runs with I and triphenylmethane (Table II) the rate of metalation is accelerated by the presence of small amounts of lithium piperidide or a solid lithium metal phase. Sixthly, certain lithium adducts of partially reduced biphenyls, such as 1-phenylcyclohexene, are kinetically better metalating agents than I itself. This follows from the observation that under comparable conditions triphenylmethane and the 1:1 lithium–1-phenylcyclohexene adduct gave a yield of trityllithium twice that obtained from tri-

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(11) *Cf.*, for example, A. D. Petrov, E. P. Kaplan, Z. I. Letina, and I. P. Egorov, *Zh. Obshch. Khim.*, **28**, 608 (1958) [*Chem. Abstr.*, **52**, 17169 (1958)], who report the reaction between lithium and biphenyl in ether with the subsequent addition of *n*-butyl bromide to yield supposedly 4-*n*-butyl-1,4-dihydrobiphenyl (19%) and 1,4-di-*n*-butyl-1,4-dihydrobiphenyl (11%). However, more recent work suggests that 2,5-dihydrobiphenyls, rather than 1,4-dihydrobiphenyls, are formed in the hydrolysis of the lithium–biphenyl adduct [I. P. Egorov, E. P. Kaplan, Z. I. Letina, V. A. Shliapochnikov, and A. D. Petrov, *J. Gen. Chem U.S.S.R.* (Eng. Transl.), **28**, 3284 (1958)].

(12) (a) H. Gilman and J. J. Dietrich, *J. Org. Chem.*, **22**, 851 (1957); *J. Am. Chem. Soc.*, **80**, 380 (1958); (b) H. Gilman, H. A. McNich, and D. Wittenberg, *J. Org. Chem.*, **23**, 2044 (1958); (c) H. Gilman and R. Gorsich, *ibid.*, **23**, 550 (1958); and (d) H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, **80**, 608 (1958).

(13) A subsequent paper will deal with the role of aromatic radical-anions in such metal cleavage reactions.

(14) With the assumption that there is no lithium cleavage of the solvent at room temperature and with allowance for 2:1 adducts, the data indicate either that biphenyl forms higher adducts with lithium or that some additional lithium metal is dissolved after the manner of alkali metals in liquid ammonia. *Cf.* M. C. R. Symons, *Quart. Rev.*, **13**, 99 (1959).

TABLE II

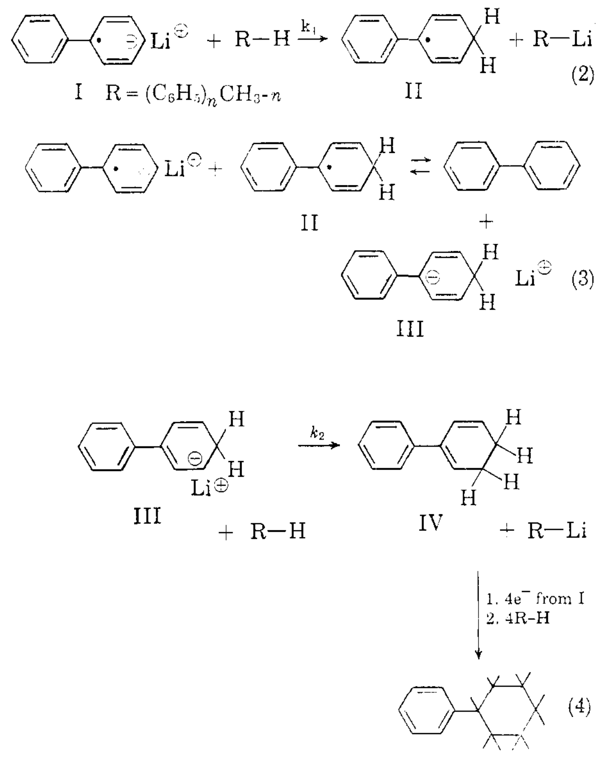
INTERACTION OF THE 1:1 LITHIUM–BIPHENYL ADDUCT WITH TRIPHENYLMETHANE[a]

$Li—(C_6H_5)_2$, moles	Normality[b] in THF	$(C_6H_5)_3CH$, moles	Catalyst, equiv.	Yield of $(C_6H_5)_3C—COOH$, % Crude	Pure[g]
0.0226	0.332	0.0226	...	19.6[c]	18.3
0.0228	0.336	0.0228	...	21.7[c]	20.3
0.0232	0.334	0.0225	0.0007 $C_5H_{11}N$[d]	...	56.1
0.0228	0.334	0.0228	0.0012 Li[e]	30.9[f]	29.5
0.0224	0.335	0.0224	0.0012 Li[e]	36.8[f]	35.1

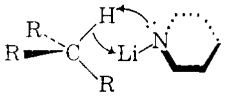
[a] Reaction time, 5.75 hr.; temperature, 28 ± 1°. [b] Determined by titration of hydrolyzed aliquots by standard acid. [c] The blank run averaged about a 20% yield of trityllithium. [d] The freshly purified, anhydrous piperidine reacted with I promptly to give lithium piperidide. [e] Since these runs are initially heterogeneous, the solution of the lithium seems to depend upon the rate of stirring. [f] The variation in yield seems related to the rate of stirring. [g] The pure yield was determined by measuring the apparent neutralization equivalent and assuming phenyldicarboxycyclohexadiene to be the impurity.

phenylmethane and I (42.4% *vs.* 19.2%). The smooth formation of phenylcyclohexane from one equivalent of biphenyl and six equivalents each of lithium metal and triphenylmethane also supports this view.

These observations are consistent with the metalation following the pathway described in equations 2–4:



That proton abstractions, as typified by equations 2 and 4, are probably rate-determining accords with the observed acceleration of the metalation by lithium piperidide and the greater ease of metalating triphenylmethane, compared with diphenylmethane (98% *vs.* 43% at 66°). The catalytic action of lithium piperidide is consonant with assistance in proton abstraction in the rate-determining step, the nucleophilic attack by the unshared electron pair on the nitrogen aiding proton exchange[15]



VI

R = C_6H_5 or H

In this view the lithium piperidide would facilitate proton transfer to I in the following fashion[16].

$$(C_6H_5)_3CH + C_5H_{10}NLi \rightleftharpoons (C_6H_5)_3CLi + C_5H_{10}NH \quad (5)$$

$$C_5H_{10}NH + \underset{\text{I}}{(C_6H_5\dot{-}C_6H_5)Li} \rightleftharpoons C_5H_{10}NLi + \underset{\text{II}}{(C_6H_5\cdot C_6H_6)} \quad (6)$$

In addition, the greater resonance stabilization of the trityl anion, anticipated in the transition state (such as VI for the catalyzed run) should facilitate proton loss from triphenylmethane, compared with diphenylmethane.

As mentioned previously, it appears that anions such as III and/or radical anions such as that of IV can compete successfully with the radical anion of I for the pseudo acid, R—H (*e.g.*, $k_2 > k_1$). In the metalation of triphenylmethane by I the neutral organic product was principally recovered biphenyl, admixed with highly reduced biphenyls, such as phenylcyclohexane. The greater kinetic basicity of anions of reduced biphenyls, such as of 1-phenylcyclohexene (VII), compared with that of biphenyl (I), is consistent with an anion having a

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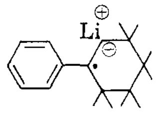
(15) A similar instance of the acceleration of metalations by lithium piperidide has been observed and interpreted in like fashion by R. Huisgen and J. Sauer, *Angew. Chem.*, **72**, 100 (1960), for the metalation of halobenzenes by phenyllithium.

(16) Although equation 5 is written as reversible, the equilibrium constant is not known. G. Wittig, *Experientia*, **14**, 389 (1958), states qualitatively that piperidine discharges the color of trityllithium (solvent not given), but C. H. Horning and F. W. Bergstrom, *J. Am. Chem. Soc.*, **67**, 2110 (1945), have prepared trityllithium in ether solution from triphenylmethane and lithium diethylamide. Taking diethylamine and piperidine as comparable in acidity, we believe that a measurable equilibrium for equation 5 is reasonable.



VII

more localized negative charge and hence a greater kinetic basicity.[17]

Finally, the accelerating influence of small amounts of added lithium metal on the metalation of triphenylmethane by I may be due to the formation of more basic 2:1 lithiumbiphenyl adducts which abstract a proton from R—H more rapidly.[18]

The use of lithium–biphenyl adducts to prepare organolithium compounds from hydrocarbons having a feasible kinetic and thermodynamic acidity has the advantage of experimental simplicity and readily accessible starting materials. Triphenylmethyllithium and diphenylmethyllithium are most conveniently prepared in essentially quantitative and 50–60% yields, respectively, by this method.[19] Other pseudoacidic hydrocarbons and active hydrogen compounds having an estimated p$K_a \leq 35$ (diphenylmethane)[20] should be metalated in satisfactory yield. The presence of biphenyl and reduced biphenyls usually does not interfere, even in the preparation of neutral organic derivatives (*e.g.*, the preparation of 1,1,1-triphenylethane from trityllithium and methyl iodide in 80% yield). Steam distillation usually suffices to remove the biphenyl products. In addition, the amount of biphenyl can be reduced to one-sixth an equivalent in the preparation of the organolithium compound. Rates of metalation are somewhat slower, but yields of triphenylmethyllithium (82% *vs.* 98%) and diphenylmethyllithium (52% *vs.* 63%) are comparable.

Certain other systems having methylene groups adjacent to carbonyl or azomethine linkages give modest yields of metalation products. Quinaldyllithium and the lithium salt of cyclohexanone were formed from 2-methylquinoline and cyclohexanone, respectively, and I in about 30% yields. The intrusion of side reactions, such as the attack of I upon the solvent (at higher temperatures, forming *n*-butyl alcohol[13]), the cleavage of the tetrahydrofuran by the organolithium compound produced, and radical-coupling and aldol condensations of the pseudo acid by agency of I, all tend to lower the yield of metalated product from the weaker pseudo acids. Despite these limitations the use of lithium–aromatic hydrocarbon adducts will make many benzylic-like organolithium compounds more accessible.

The foregoing study on the metalating characteristics of lithium–biphenyl adducts prompted a reinvestigation of a recent report[12c] that fluorene (VIII) and lithium metal in THF react to produce fluorenyllithium (IX) and lithium hydride:

VIII + 2 Li IX + LiH (7)

Since fluorene can be viewed as 2,2′-methylenebiphenyl, the present workers felt that lithium–fluorene adducts similar to I might be involved in the facile formation of IX in THF and that the displaced hydrogen reduced a portion of the fluorene, instead of forming lithium hydride. Quantitative monitoring of the lithium consumption ruled out the formation of lithium hydride. The reaction scheme shown in equation 7 would require that 1.0 mole of fluorene and 1.0 g.-atom of lithium metal give a maximum yield of 0.5 mole of fluorenyllithium. If the 0.5 mole of lithium hydride in turn were to react with the 0.5 mole of fluorene to yield more IX, hydrogen gas would be evolved.[21] In repeating the fluorene–lithium metal interaction no gas evolution was observed and it was shown that 1.0 mole of VIII and 0.82 g.-atom of lithium metal reacted to yield 0.83 mole of IX (by carbonation). Hence, as in metalations, by the 1:1 lithium–biphenyl adduct (I), all the lithium metal consumed in the fluorene reaction appears in the resulting organolithium compound. The balance of the fluorene was accounted for by the column chromatographic isolation of a neutral oil (X) which was shown by vapor phase chromatography to be a mixture of at least three components. The presence of unchanged fluorene in this mixture was ruled out on the basis of chromatographic retention times. The infrared spectrum of the neutral oil X possessed moderate bands at 1595, 1615, 1645, and 1670

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(17) Work in progress in this laboratory suggests that lithium metal adducts of aromatic hydrocarbons show a decrease in relative kinetic basicity as the amount of conjugation increases: naphthalene ≫ anthracene ~ biphenyl ≫ phenanthrene. Resonance energies computed from observed heats of hydrogenation increase in the order: naphthalene (61 kcal./mole), biphenyl (71), anthracene (84), phenanthrene (92). *Cf.* G. W. Wheland, "Resonance in Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1955, p. 132.

(18) Even when employing 1:1 ratios of lithium metal and biphenyl, it cannot be excluded that some 2:1 adduct exists in equilibrium with the 1:1 adduct. Although this possibility has been ruled out for 1:1 sodium and potassium adducts of naphthalene and biphenyl in dilute solutions,[8,9] the situation need not be the same for lithium. Hence, such small amounts of the 2:1 lithium–biphenyl adduct could be the kinetically better metalating species. This would not alter the validity or tenor of the previous arguments, however.

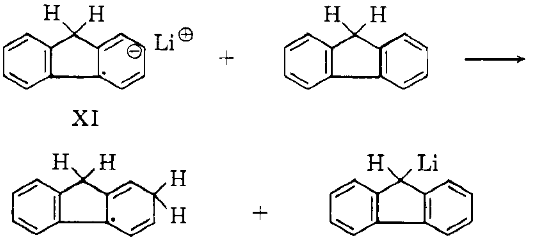
(19) (a) *Cf.* P. Tomboulian, *J. Org. Chem.*, **24**, 229 (1959), for a survey of previous preparative methods for tritylithium; (b) H. Gilman and R. L. Bebb, *J. Am. Chem. Soc.*, **61**, 109 (1939), found that *n*-butyllithium metalated diphenylmethane in 20% yield; (c) Lithium metal reacts with triphenylmethane extremely slowly in THF; even with lithium dispersions reaction times ranging up to 7 days are necessary (H. Gilman, personal communication).

(20) W. K. McEwen, *ibid.*, **58**, 1124 (1936).

(21) G. W. H. Scherf and R. K. Brown, *Can. J. Chem.*, **38**, 2450 (1960), report that the reaction of fluorene with lithium metal in various ether solvents such as 1,2-dimethoxyethane and tetrahydrofuran was accompanied by hydrogen gas evolution. Accordingly, they have formulated the lithium–fluorene reaction as yielding IX and one equivalent of hydrogen gas. In this study no gas evolution whatsoever was observed when fluorene was reacted with lithium metal in THF at room temperature (several check runs).

(broad) cm.$^{-1}$. Since indene exhibits prominent bands at 1595, 1617, 1670, and 1690 (broad) cm.$^{-1}$, the neutral oil may contain some 1,2,3,4-tetrahydrofluorene. Finally, an elemental analysis of the oil gives carbon (90.93%) and hydrogen (9.07%) values approaching that of a hexahydrofluorene (C, 90.64% and H, 9.36%). Therefore, it appears that X may be a mixture of the *cis* and *trans* isomers of 1,2,3,4,10,11-hexahydrofluorene and at least one tetrahydrofluorene. It is of interest to note that the reduction of fluorene by six equivalents of lithium metal and 1-propanol in THF gave in 73% yield an oil whose infrared spectrum was superposable with that of X and whose vapor phase chromatogram again showed three components with the same retention times as those in X.[22]

The foregoing data should be coupled with the observation that the lithium metal in THF reacted with fluorene with the initial formation of a dark green coating on the metal surface. Consequently, it is clear that lithium–fluorene adducts (1:1 and/or 2:1) (XI) are formed initially on the metal surface and these then abstract protons from fluorene to produce fluorenyllithium (compare the reaction of I with diphenylmethane)



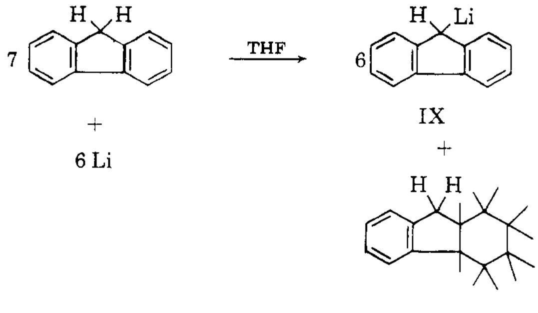
(8)

XI

XII

IX

The resulting radical XII could gain another electron from ureacted lithium to form an anion which could metalate more fluorene. As in the biphenyl case (equations 2–4) partially reduced fluorenes should form kinetically stronger radical anion bases. Thereby a portion of the fluorene becomes reduced to tetrahydro- and hexahydrofluorenes:



(9)

IX

According to equation 9, 1.0 mole of fluorene would react with 0.86 g.-atom of lithium to yield 0.86 mole of IX. Formation of solely tetrahydrofluorene, on the other hand, would prescribe that 1.0 mole of fluorene and 0.80 g.-atom of lithium give 0.80 mole of IX. Again, the experimentally determined equivalents of 1.0 mole of fluorene reacting with 0.82 g.-atom of lithium to provide 0.83 mole of IX point to a mixture of tetrahydro- and hexahydrofluorenes as by-products.

In conclusion, the tendency of aromatic hydrocarbons to form lithium metal adducts in THF and the strongly basic character of such adducts suggested a modified Birch reduction[4] procedure, wherein the lithium–hydrocarbon adduct is formed in THF and smoothly destroyed by adding a proton source such as an alcohol. Obviating the use of ammonia[4,5] and amines,[6] this approach may add flexibility to existing procedures for the reduction of conjugated systems in homogeneous media. In orienting experiments phenylcyclohexane has been obtained in 75% yield by treating biphenyl and six equivalents of lithium in THF with 1-propanol. In a similar fashion fluorene yielded a mixture of principally the hexahydrofluorenes containing some tetrahydrofluorne (*cf. supra*). Further work on the scope and limitations of this reduction method is underway.

Experimental[23]

Starting Materials.—The tetrahydrofuran was shaken with successive poritions of sodium hydroxide pellets, refluxed for 24 hr. over fresh sodium slices, and then distilled from the sodium metal. Thereupon the tetrahydrofuran was treated with lithium aluminum hydride and redistilled under a nitrogen atmosphere directly into the reaction vessel.

Lithium ribbon (containing 0.6% of sodium metal) was carefully scraped free of oxide and nitride while under dry benzene.

All organic chemicals employed were of reagent grade. The reported melting points of solids and the refractive indices of liquids agreed well with the reported values. Melting points given in this paper are corrected. To ensure the absence of moisture all solids were stored over phosphorus pentoxide or Molecular Sieves before use and all previously dry liquids were fractionally distilled just before use.

General Procedure for Metalation with the Lithium–Biphenyl Adduct (I).—Under a nitrogen atmosphere the solution of 1 molar equivalent of biphenyl in freshly distilled tetrahydrofuran was stirred with the freshly cut pieces of 1 g.-atom equivalent of lithium ribbon. The blue-green color of the lithium–biphenyl adduct appeared almost immediately on the metal surface. The suspension was stirred at room temperature until no more undissolved lithium metal was seen in the dark blue-green solution (except where the ratio of lithium to biphenyl was 6:1). Thereupon a tetrahydrofuran solution of the compound to be metalated was introduced from a nitrogen-filled pressure-equalized addition funnel. The reaction was allowed to proceed either at room temperature or at the reflux temperature of the solution. Essentially no gas was evolved during the metalation. Depending upon the pseudo acid, the blue-green color of the adduct I changed to dark red or faded completely.

The resulting organolithium compound was derivatized by treating the reaction mixture, previously cooled in an acetone–Dry Ice bath, with gaseous carbon dioxide, or by

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[22] Further work on the individual reduction products of fluorene is planned.

[23] Reactions involving lithium–hydrocarbon adducts were conducted in an atmosphere of dry, oxygen-free nitrogen. Pure commercial nitrogen was passed over bright copper gauze heated at 400° and then dried by passage through Molecular Sieves and phosphorus pentoxide.

pouring the reaction mixture into a slurry of crushed Dry Ice in anhydrous ether. After the carbonation mixture had reached room temperature, it was hydrolyzed and then treated with 5% potassium hydroxide solution. The neutral organic products were removed by ether extraction of the aqueous layer. Warming the aqueous layer to expel the dissolved organic solvent, cooling in an ice bath, and acidification with dilute sulfuric acid precipitated the organic acid. The acid was purified and then identified by means of a mixture melting point with an authentic specimen, neutralization equivalent, and infrared spectroscopy. The experimental conditions and yields are summarized in Table I. Typical details of significant runs are given below.

a. **Triphenylmethane.**—A solution of the lithium–biphenyl adduct I, prepared from 0.15 g. (0.023 g.-atom) of lithium and 3.40 g. (0.022 mole) of biphenyl in 50 ml. of tetrahydrofuran, was treated with a solution of 5.35 g. (0.022 mole) of triphenylmethane in 25 ml. of tetrahydrofuran. During 9 hr. at room temperature a rather thick, deep crimson solution was formed. After low-temperature gaseous carbonation and usual work-up 5.85 g. (92%) of triphenylacetic acid, m.p. 265–267°, dec., was obtained. The observed neutralization equivalent was 290 (theory, 288).

In a run of exactly the same size conducted at the reflux temperature for 3.5 hr. the yield of triphenylacetic acid was 6.19 g. (98%).

b. **Diphenylmethane.**—A solution of the adduct I, prepared as in section a, was treated with 3.70 g. (0.022 mole) of diphenylmethane in 25 ml. of tetrahydrofuran. After 18 hr. at room temperature the red reaction mixture was carbonated and worked up in the usual manner to afford 2.94 g. (63%) of crude diphenylacetic acid, m.p. 138–145°. Recrystallized from an ethanol–water pair this sample provided 2.47 g. (53%) of pure diphenylacetic acid, m.p. 146–148°. The observed neutralization equivalent was 212 (theory, 212).

In runs of exactly the same size conducted at the reflux temperature for 3.5 hr. and for 7 hr., the yields of pure diphenylacetic acid were 43% and 34%, respectively. Gradual attack of the diphenylmethyllithium upon tetrahydrofuran to form 5,5-diphenylpentanol[24] was indicated by the enhanced hydroxyl bond in the infrared spectra of the neutral organic products from the 7-hr. run.

c. **Toluene.**—A solution of the adduct I, prepared as in section a, was treated with 2.1 g. (0.023 mole) of toluene in 25 ml. of tetrahydrofuran. After 18 hr. at room temperature the usual work-up of the aqueous layer from the carbonation by acidification and ether extraction provided a small amount—*ca.* 0.1 g.—of crude phenylacetic acid. This oily product was treated with *p*-bromophenacyl bromide to prepare the *p*-bromophenacyl ester.[25] From ethanol the ester formed colorless platelets, m.p. 90–91°. A mixture melting point with authentic *p*-bromophenacyl phenylacetate (m.p. 90–91°) was undepressed.

Metalation of Triphenylmethane with Lithium and Limited Biphenyl.—Treatment of 0.15 g. (0.023 g.-atom) of lithium pieces and 0.57 g. (0.0037 mole) of biphenyl in 50 ml. of tetrahydrofuran with 5.35 g. (0.022 mole) of triphenylmethane in 25 ml. of the solvent caused the appearance of a red color 15 min. after mixing. During 18 hr. of stirring at room temperature only negligible gas evolution was noted and the lithium metal was almost completely consumed. Usual carbonation work-up provided an 82% yield of triphenylacetic acid, m.p. 263–265°, dec.

Metalation of Diphenylmethane with Lithium and Limited Biphenyl.—Treatment of 5.05 g. (0.030 mole) of diphenylmethane with 0.23 g. (0.033 g.-atom) of lithium pieces and 0.77 g. (0.005 mole) of biphenyl in 75 ml. of tetrahydrofuran for 27 hr. gave upon carbonation 3.32 g. (52%) of crude diphenylacetic acid, m.p. 138–143°. Recrystallization from dilute ethanol gave 2.58 g. (41%) of pure acid, m.p. 146–148°.

Isolation of Phenylcyclohexane from Lithium-Limited Biphenyl Metalations.—A mixture of 1.63 g. (0.234 g.-atom) of lithium pieces and 2.57 g. (0.017 mole) of biphenyl in 75 ml. of tetrahydrofuran was allowed to stir for 30 min. to form an intense blue-green solution with suspended lithium. Over a period of 30 min. a solution of 24.43 g. (0.10 mole) of triphenylmethane in 100 ml. of tetrahydrofuran was introduced. The deep red solution was stirred for 90 hr. at room temperature and then carbonated. Usual work-up provided 25.6 g. (89%) of triphenylacetic acid. The dried ether extract was evaporated and chilled. The semisolid residue was filtered and the oily filtrate was fractionally distilled. The fraction boiling at 123–125° (23 mm.), $n^{25}\text{D}$ 1.5278, 1.2 g., possessed an infrared spectrum superposable with that of an authentic sample of phenylcyclohexane.

Comparative Metalation of Triphenylmethane by the Lithium–Biphenyl Adduct I.—To obtain information as to the possible catalytic influence of added lithium piperidide and of solid lithium metal on the rate of metalation by the adduct I, identical runs were conducted in the presence or absence of proposed catalysts. As a means of comparison the amount of triphenylmethyllithium formed at 28 ± 1° after 5.75 hr. was determined by terminal carbonation and isolation of triphenylacetic acid. The crude acid obtained was most likely contaminated with phenyldicarboxycyclohexadiene[26] (neut. equiv. 122), resulting from the carbonation of the residual adduct I. Consequently, the purity of the isolated crude triphenylacetic acid was estimated by means of the equation,

$$y = \frac{x}{288} + \frac{(\text{wt. of sample} - x)}{122}$$

where y is the equivalents of base consumed by a sample of the isolated acid and x is the weight of pure triphenylacetic acid. The results of such comparative runs are listed in Table II. As two typical blank runs indicate, the reproducibility of the triphenylacetic acid yields is about ±2%. A typical blank run was conducted as follows.

A solution of 3.56 g. (0.0231 mole) of biphenyl in 50 ml. of tetrahydrofuran was stirred with 0.16 g. (0.0231 g.-atom) of lithium pieces for 1.75 hr. Thereupon the green solution was siphoned by nitrogen pressure through a glass filter into a 300-ml. calibrated flask equipped with an addition funnel and nitrogen connection. (The transfer was completed by rinsing the previous flask with fresh tetrahydrofuran.) The volume of the lithium–biphenyl solution was adjusted to the calibration mark and an aliquot was withdrawn, hydrolyzed, and titrated with standard acid. The solution contained 0.0228 g.-atom of lithium on this basis. Then a solution of 5.56 g. (0.0228 mole) of triphenylmethane in 20 ml. of tetrahydrofuran was added in one portion from the pressure-equalized addition funnel and the funnel was rinsed with 5 ml. of solvent. The reaction solution (final volume = 75 ml.) was stirred at 28 ± 1° for 5.75 hr., whereupon the red solution was cooled in a Dry Ice–acetone bath and treated with gaseous carbon dioxide. Upon usual work-up 1.43 g. (21.7%) of crude triphenylacetic acid was isolated, melting over the range, 190–210°, and having an observed neutralization equivalent of 264. By calculation this acid was estimated to be 93% pure.

Reaction of Fluorene with Lithium Metal in Tetrahydrofuran.—A solution of 16.62 g. (0.10 mole) of fluorene in 400

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[24] In a personal communication Professor Henry Gilman has informed us that 5,5-diphenylpentanol can be obtained from the interaction of *sym*-tetraphenylethane with lithium metal dispersions in refluxing tetrahydrofuran (H. Gilman and B. Gaj, unpublished studies).

[25] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "Systematic Identification of Organic Compounds," 4th ed., John Wiley and Sons, Inc., New York, N.Y. 1956, p. 200.

[26] A. G. Brook, H. L. Cohen, and G. F. Wright, *J. Org. Chem.*, **18**, 462 (1953).

ml. of tetrahydrofuran was stirred with 0.77 g. (0.11 g.-atom) of lithium pieces at room temperature for 18 hr. Initially the metal surface became coated with a green material and the solution thereafter became greenish black. Eventually the solution turned orange. No gas evolution was observed during the reaction period. The reaction mixture was then poured through a coarse filter into a slurry of Dry Ice in anhydrous ether. The lithium remaining on the filter was rinsed with anhydrous ether and then cautiously dissolved in water. By titrating an aliquot of the resulting lithium hydroxide solution with standardized acid it was determined that 0.20 g. of lithium metal was recovered and hence that 0.57 g. (0.082 g.-atom) of the metal was consumed in the fluorene reaction.

The carbonation mixture was treated with 5% potassium hydroxide solution and with ether. The aqueous layer yielded upon acidification 17.40 g. (82.8%) of 9-fluorenecarboxylic acid, m.p. 218–226°. Recrystallization from glacial acetic acid yielded colorless needles, m.p. 230.5–232°.

The dried organic extract was carefully freed from solvent to give 3.50 g. (accounting for *ca.* 20% of the original fluorene) of pale yellow oil. This product did not solidify when chilled. To remove the color the oil was chromatographed on alumina and eluted with petroleum ether (b.p. 30–60°). After removal of the solvent the recovered oil was colorless. Its infrared spectrum showed noteworthy bands at 930, 950, 970, 1020, 1210, 1325, 1595, 1615, 1645, and 1670 (broad) cm.$^{-1}$. This spectrum was completely superposable with the infrared spectrum of the reduced fluorene obtained from lithium metal and 1-propanol (*cf. infra*).

Gas chromatography of the neutral oil on a 10% silicone oil–firebrick column revealed at least three components: one well resolved peak and a symmetrical double peak with relative areas of 1.0:1.44. The oil was fractionally distilled under reduced pressure to yield a main fraction boiling at 55° (0.1 mm.), n^{25}D 1.5535. This still consisted of the same three components, as shown by vapor phase chromatography.

Anal. Calcd. for $C_{13}H_{14}$: C, 91.71; H, 8.29. Calcd. for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.93; H, 9.07.

Reduction of Biphenyl.—In 300 ml. of tetrahydrofuran 30.84 g. (0.20 mole) of biphenyl and 8.4 g. (1.21 g.-atoms) of lithium metal pieces were stirred for 1 hr., in order to form a dark green suspension. Over a period of 90 min. 87 g. (1.44 moles) of anhydrous 1-propanol, containing 2 ml. of dry piperidine, was added dropwise. Almost no gas evolution was noted until the latter part of the addition period. Moreover, the blue-green color of the lithium-biphenyl system was finally discharged permanently only toward the end of alcohol addition. After a further 4-hr. stirring period the mixture was hydrolyzed with 200 ml. of dilute hydrochloric acid and 300 ml. of ether were introduced. The ether layer was separated, dried, and evaporated. The residual oil was fractionally distilled at 19 mm. to afford a main fraction of 24.1 g. (75%) of phenylcyclohexane, n^{27}D 1.5281. Vapor phase chromatography on a 10% silicone oil–firebrick column showed one major component with impurities composing less than 4% of the composition. This phenylcyclohexane possessed an infrared spectrum superposable with an authentic sample prepared from cyclohexene and benzene (n^{27}D 1.5235).[27]

Reduction of Fluorene.—In an analogous fashion 33.20 g. (0.20 mole) of fluorene, 9.16 g. (1.32 g.-atoms) of lithium pieces, 1 ml. of piperidine, and 300 ml. of tetrahydrofuran were stirred for 2 hr. at room temperature. The orange solution (with suspended lithium) became dark green as 92 g. (1.53 moles) of anhydrous 1-propanol was added dropwise during a 2.5-hr. period. After 1 hr. of reflux the reaction mixture was worked up in the usual way. Fractional distillation of the dried and evaporated ether extract yielded a main fraction, b.p. 132–135° at 15 mm., n^{20}D 1.5565, 25.1 g. (73%, calculated as hexahydrofluorene). Vapor phase chromatography of this fraction on a 10% silicone oil–firebrick column showed the presence of at least three components: one sharply resolved peak followed by two closely associated peaks (relative areas of first peak to second double peak, 1.0:1.6). The infrared spectrum of this oil was superimposable with that obtained from the reaction of fluorene and lithium metal with carbonation work-up. The bands at 1615 and 1670 (broad) cm.$^{-1}$ may indicate the presence of a double bond conjugated with a benzene ring (possibly 1,2,3,4-tetrahydrofluorene). As a model spectrum the infrared spectrum of indene was examined: pronounced bands were displayed at 1617 and 1690 (broad) cm.$^{-1}$. From the observed boiling point and refractive index of a redistilled fraction (b.p. 122–123° at 12 mm., n^{25}D 1.5558) it is believed that the other components are the *cis* and *trans* isomers of 1,2,3,4,10,11-hexahydrofluorene[28] (*cf.* analytical data given below).

In another run of the fluorene reduction the reduced fluorene was carefully fractionally distilled and the main cut boiling at 113–114° (8 mm.), n^{25}D 1.5521, was analyzed. Found: C, 91.15; H, 8.87. This again suggests a mixture of tetrahydrofluorenes (C, 91.71; H, 8.29) and the 1,2,3,4,10,11-hexahydrofluorenes (C, 90.64; H, 9.36). The vapor phase chromatogram showed at least three components.

Related Metalations. a. Quinaldine.—A solution of 7.70 g. (0.050 mole) of biphenyl in 125 ml. of tetrahydrofuran was stirred with 0.77 g. (0.11 g.-atom) of lithium pieces for 30 min. to form a dark green solution. Then a solution of 14.3 g. (0.10 mole) of quinaldine in 10 ml. of dry ethyl ether was introduced over the course of 5 min. The system temporarily became dark yellow in color and heat was evolved. After 21 hr. of stirring at room temperature the system was refluxed for 3 hr. Thereupon the resulting solution was cooled and then treated with 18.2 g. (0.10 mole) of benzophenone dissolved in 40 ml. of dry ethyl ether. After a final 2-hr. reflux period the system was hydrolzyed. The white precipitate was filtered off and washed with ether. Further product was obtained by separating the organic solvent layer, drying it, and removing the solvent. The residual viscous orange oil was dissolved in 75 ml. of methanol. Chilling gave additional colorless product. The combined amount of crude product melting at 145–153° was 11.4 g. (35%). From absolute ethanol, colorless needles of quinaldydiphenylcarbinol were obtained, m.p. 159–160°.[29] Treatment with a warm solution of concentrated sulfuric acid in glacial acetic acid dehydrated the carbinol to form 1,1-diphenyl-2(2-quinolyl)ethylene, m.p. 102–103° (from ethanol).[29]

b. Cyclohexanone.—A solution of 1.70 g. (0.011 mole) of biphenyl in 80 ml. of tetrahydrofuran was stirred with 0.31 g. (0.044 g.-atom) of lithium pieces for 30 min. With cooling 4.32 g. (0.044 mole) of cyclohexanone in 50 ml. of tetrahydrofuran were introduced into the green solution during a 30-min. period. After an additional 20 min. of stirring the color had faded almost completely. Toward the end a reddish color reappeared. The solution was cooled in an ice bath and treated with 6.06 g. (0.050 mole) of allyl bromide in 50 ml. of dry ethyl ether over a 30-min. period. The solution became colorless at first and then yellow. After 30 min. at reflux the solution was hydrolyzed. The ether layer was separated, washed with saturated sodium chloride solution, and stored over Drierite. The solvent was removed by fractional distillation and the residue then fractionated at 11 mm. A fraction boiling at 70–85° weighed 1.6 g. (26%), n^{20}D 1.4650. A 2,4-dinitrophenylhydrazone of this product melted at 144–145°. 2-Allyl-

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[27] A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 151.

[28] 1,2,3,4,10,11-Hexahydrofluorene (*cis-trans* character unstated) is reported to boil at 137° (15 mm.) and to possess a refractive index of n^{20}D 1.5448 or n^{25}D 1.5589. *Cf.* J. W. Cooke and C. L. Hewett, *J. Chem. Soc.*, 1098 (1933).

[29] K. Ziegler and H. Zeiser, *Ann.*, **485**, 143 (1917).

cyclohexanone is reported to boil at 78–79° (11 mm.); n^{25}D 1.4662; 2,4-dinitrophenylhydrazone, m.p. 145–146°.[30]

Comparative Metalations of Triphenylmethane by Lithium–Biphenyl and by Lithium–Phenylcyclohexene.[31]—The relative kinetic basicites of the lithium adducts of biphenyl and of 1-phenylcyclohexene were compared by allowing each to react individually with triphenylmethane under identical conditions. Thus 0.060 mole of the hydrocarbon (either pure biphenyl or 1-phenylcyclohexene) was allowed to react with 0.050 g. atom of lithium pieces in 30 ml. of tetrahydrofuran at 28 ± 1°. After 2 hr. of stirring the lithium had dissolved to form a blue-green (biphenyl) or red (phenylcyclohexene) solution. Then 15.30 g. (0.0625 mole) of triphenylmethane, dissolved in 120 ml. of tetrahydrofuran, was added in one portion. The solution was stirred at the same temperature for 16 hr. and then carbonated in the usual way. Customary work-up gave the following yields of triphenylacetic acid: (a) from biphenyl: 2.76 g. of acid (19.2%); m.p. 261–264°; neut. equiv. 289. (b) from phenylcyclohexene: 6.11 g. of acid (42.4%); m.p. 263–265°; neut. equiv. 290.

Derivatives of Triphenylmethyllithium.—Non-acidic derivatives of trityllithium, prepared by the lithium–biphenyl method, were 1,1,1-triphenylethane (treatment with methyl iodide), (80%) and 3,3,3-triphenylpropanol (treat-with ethylene iodide) (89%). In these reactions it was found convenient to steam distil the hydrolyzed reaction mixture to remove the biphenyl and hydrobiphenyls. The residue could then be purified readily by filtration and recrystallization of the collected solid.

Determination of "Soluble" Lithium-Biphenyl Ratios.—Under nitrogen 3.70 g. (0.024 mole) of biphenyl and 0.50 g. (0.072 g.-atom) of lithium in 55 ml. of tetrahydrofuran were stirred in a calibrated flask to form the blue-green solution. Aliquots were withdrawn periodically, hydrolyzed, and titrated with standard acid. After 16 hr. at room temperature the "soluble" lithium attained a constancy of 2.5 ± 0.05 equivalents: 1.0 equivalent of biphenyl.

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[30] A. C. Cope, K. E. Hoyle, and D. Heyl, *J. Am. Chem. Soc.*, **63**, 1842 (1941).

[31] The following experiment was performed by Miss Deborah Drew, NSF undergraduate research assistant during the summer of 1961. The authors gratefully acknowledge her assistance in this and related studies.

Hydridic Reducing Agent—Group VIII Metal Compound. A New Catalyst System for the Polymerization of Acetylenes and Related Compounds. II

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The scope of a new catalytic reaction for the polymerization of acetylenic compounds was investigated. The catalyst system consists of a Group VIII metal compound plus a hydridic reducing agent. Polymerization was achieved with six out of seven of the Group VIII metals tried, iron compounds failing to cocatalyze these reactions. No metals outside of Group VIII were cocatalysts. Silane and simple alkali hydrides function as reducing agent cocatalysts, but are far less effective than the alkali boro and alumino hydrides. Nonhydridic reducing agents, even very powerful ones such as hydrazine, show little or no cocatalytic action.

The first paper in this series[1] described a new catalyst system for the polymerization of acetylenic compounds. This system consists of a compound of nickel plus an hydridic reducing agent. A typical example is nickel chloride plus sodium borohydride.

We now report extension of the scope of this reaction. The effects of other transition metal compounds were studied. In addition, a number of other variables such as different reducing agent cocatalysts were also investigated. A number of fundamental aspects of these reactions were also examined.

Experimental

Materials.—The various inorganic salts used were all either reagent grade or the nearest readily available equivalents. Solvents were reagent grade or equivalent. The reducing agents, except for the rather pure complex hydrides (as described in the first paper in this series[1]) were probably all contaminated by small quantities of oxidation products. The acetylenes used in these experiments were in most cases obtained from The Farchan Chemical Company and were used as received.

Bis(tri-*n*-butylphosphine)palladium Dichloride was prepared by mixing 1.78 g. of palladous chloride and 8.5 g. of tri-*n*-butylphosphine in 50 ml. of water. After storage for a couple of weeks in a freezer, the mixture deposited brilliant yellow plates. These were recrystallized from ethanol and dried, m.p. 66° in exact agreement with Mann.[2]

Bis(triphenylphosphine)platinum Dichloride.—Platinum chloride (2.66 g.) was dissolved in concentrated, air-free hydrochloric acid. The system was kept air-free with a stream of prepurified nitrogen. The pH was brought up to 8 with potassium hydroxide. The volume was made up to 50 ml. with distilled water. Triphenylphosphine (5.2 g.) in 50 ml. of hot ethanol was added. A yellow precipitate was formed immediately, and the original deep brown to pink color of the solution was discharged. The mixture was stirred magnetically under nitrogen for 7 hr. It was then filtered, washed extensively with water, ethanol, and finally with dry ethyl ether, and then dried. The product was a fine white powder with a slight grayish tinge, m.p. 290–295° (lit.[3] value 310°).

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[1] L. B. Luttinger, *J. Org. Chem.*, **27**, 1591 (1962).

[2] F. G. Mann, *J. Chem. Soc.*, 1549 (1954).

[3] K. A. Jensen, *Z. anorg. Chem.*, **229**, 225 (1936).