Chemistry of Alkali Metal-unsaturated Hydrocarbon Adducts. III. Cleavage Reactions by Lithium–Biphenyl Solutions in Tetrahydrofuran[1]

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The cleavage of certain carbon–carbon and carbon–heteroatom linkages by means of the 2:1 lithium–biphenyl adduct (I) in tetrahydrofuran solution has been investigated both as a route to certain organolithium compounds and as a degradation procedure for some organic systems. Besides accelerating the rate of cleavage of certain organic compounds, in comparison with the speed of ordinary lithium metal cleavages, solutions of I readily effect the lithium metal rupture of certain ether and arylated ethane systems. By consideration of the cleavage facility toward I of a related series of compounds, certain electronic and structural features were found to favor reaction with this dissolved form of lithium metal. As an initial step toward understanding such metal cleavage reactions and the role of biphenyl and tetrahydrofuran in promoting their realization, the known facts concerning lithium metal cleavage reactions are discussed and classified. With reference to the recent physicochemical investigations concerning the nature of alkali metal–aromatic hydrocarbon adducts, the ease of cleavage of organic compounds by lithium is related to the ability of such systems to form transitory lithium metal adducts.

The alkali metal cleavage of bonds between carbon atoms, or between a carbon atom and a heteroatom, such as oxygen, nitrogen, or sulfur, has proved of great value in the synthesis of organometallic reagents and in the degradation of certain organic systems (equation 1). The formation of organoalkali compounds by the

$$R{-}E{-}R' + 2M \longrightarrow M{-}E{-}R' + M{-}R \ (E = O,S,NR,CR_2) \quad (1)$$

rupture of suitable ethers and arylated ethanes with sodium at 200°[2] or with sodium–potassium alloy at room temperature[3] has led to suitable synthetic procedures for these types. The feasible preparation of 2-phenyl-2-propylpotassium from methyl 2-phenyl-2-propyl ether and potassium[4] illustrates a useful application of this method. Even the less reactive alkali metal, lithium, has been employed successfully in recent cleavage reactions involving aryl fluorides,[5] benzyl ethers,[6] and heterocycles[7] in tetrahydrofuran solution. More recently, the cleavage of arylmethanes and -ethanes has been shown to be promoted by the use of lithium metal dispersions.[8]

Previous investigations have shown that lithium metal–unsaturated hydrocarbon adducts behave as strong bases toward pseudoacidic hydrocarbons.[9] Since such 1:1 or 2:1 adducts arise from the reversible adduction between alkali metals and the unsaturated component (equation 2),[10] the present study sought to evaluate the ability of the 2:1 lithium–biphenyl adduct (I) to serve as a solubilized source of lithium metal for organic cleavage reactions (reversal of equation 2). To this end a series of related systems was chosen, so as to include compounds either resistant to cleavage by lithium metal alone or undergoing only slight cleavage in refluxing tetrahydrofuran.[7] The results obtained from the attempted cleavages of such systems with tetrahydrofuran solutions of I are summarized in Table I.


(2)

I

The use of the 2:1 lithium–biphenyl adduct in tetrahydrofuran offers several advantages over similar reactions employing lithium metal alone in tetrahydrofuran. First, the homogeneous system I often permits the cleavage reactions to proceed more readily and affords higher yields of the cleavage products. (The yields reported for ordinary lithium metal alone in tetrahydrofuran are cited in the last column of Table I.) For example, the cleavage of triphenylamine by I in refluxing tetrahydrofuran occurs much more rapidly than with lithium metal (58% *vs.* 8%). Secondly, the ease of certain cleavages by I permits shorter reaction periods and lower temperatures to be employed. As organolithium compounds can be destroyed by their cleavage or metalating action on the solvent, milder reaction conditions allow the organolithium compound resulting from the cleavage to persist unchanged. The high yield of diphenylmethyllithium (83%), obtained by the cleavage of 1,1,2,2-tetraphenylethane, is a case in point. Longer reaction times required with lithium alone in tetrahydrofuran yield only solvent cleavage products.[8] Thirdly, in contrast to previous cleavages, only a slight excess of lithium metal as I over the stoichiometric amount is necessary in many cases. Fourthly, certain organolithium compounds can be prepared most conveniently by this approach. Pertinent examples are the cleavage of 1,1,2,2-tetraphenylethane and dibenzothiophene[7a] by I to provide diphenylmethyllithium[9] and the lithium salt of *o*′-mercapto-*o*-biphenylyllithium, respectively, in >80% yields. Fifthly, carbon–heteroatom linkages resistant to lithium metal alone in tetrahydrofuran[7a] can be ruptured by I. The dealkylation of anisole to give phenol and the ring opening of tetrahydrofuran itself to yield *n*-butyl alcohol recommend the use of I as an ether-cleavage reagent in degradation studies.[11] Consequently, com-

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(1) (a) A preliminary communication covering a portion of this work appeared in *Chem. Ind.* (London), 470 (1961); (b) previous paper in this series: J. J. Eisch and R. M. Thompson, *J. Org. Chem.*, **27**, 4171 (1962).

(2) P. Schorigin, *Ber.*, **56**, 176 (1923).

(3) K. Ziegler and F. Thielmann, *ibid.*, **56**, 1740, 2453 (1923).

(4) (a) K. Ziegler, F. Crössman, K. Kleiner, and O. Schäfer, *Ann.*, **473**, 1 (1929); (b) K. Ziegler and H. Dislich, *Ber.*, **90**, 1107 (1957).

(5) H. Gilman and T. S. Soddy, *J. Org. Chem.*, **22**, 1121 (1957).

(6) H. Gilman, H. A. McNinch, and D. Wittenberg, *ibid.* **23**, 2044 (1958).

(7) (a) H. Gilman and J. J. Dietrich, *ibid.*, **22**, 851 (1957); *J. Am. Chem. Soc.*, **80**, 380 (1958); (b) earlier cleavage work utilizing lithium and dioxane: H. Gilman and D. L. Esmay, *ibid.*, **75**, 2947 (1953); H. Gilman, J. B. Honeycutt, and R. K. Ingham, *J. Org. Chem.*, **22**, 328 (1957).

(8) H. Gilman and B. J. Gaj, unpublished studies. We are indebted to Professor Gilman for communicating these results to us prior to their publication.

(9) J. J. Eisch and W. C. Kaska, *J. Org. Chem.*, **27**, 3745 (1962).

(10) (a) W. Schlenk and E. Bergmann, *Ann.*, **463**, 1 (1928); (b) N. D. Scott, J. F. Walker, and V. I. Hansley, *J. Am. Chem. Soc.*, **58**, 2442 (1936).

(11) C. D. Hurd and G. L. Oliver, *J. Am. Chem. Soc.*, **81**, 2795 (1959), have explored the cleavage of ethers by sodium in liquid ammonia recently.

TABLE I

CLEAVAGE REACTIONS BY THE 2:1 LITHIUM–BIPHENYL ADDUCT

	Reaction conditions			Products[a] (%)		
Compound (mole)	Concn. (mole/l.)	Temp., ° C.	Reaction time (hr.)	Major	Other	Reported yield of major product (with Li in tetrahydrofuran)
Fluorobenzene (0.10)	0.57	−10	2.0 [0.6][b]	Benzoic acid (50)	Triphenylcarbinol	...
	1.33	−10	1.0 [0.6]	Benzoic acid (70)		50[c]
Anisole (0.10)	0.57	66	2.0 [0.25]	Phenol (55)	[d]	0[e]
	1.33	66	4.5 [0.5]	Phenol (80)	[d]	0[e]
N,N-Dimethylaniline (0.10)	0.57	66	24	*N*-Methylaniline (2)		...
Phenyl ether (0.10)	0.57	0	2.0 [1.0]	Phenol (96)	Benzoic acid[f]	?[e]
Triphenylamine (0.10)	0.57	66	10	Diphenylamine (58)	Aniline (1.6)	8[e]
1,1,1-Triphenylethane (0.02)	0.40	66	6.0	Triphenylacetic acid (2)	[d]	...
1,1,1,2-Tetraphenylethane (0.02)	0.40	25	2.0	Triphenylacetic acid (93)	Phenylacetic acid	...
		66	2.0			
1,1,2,2-Tetraphenylethane (0.02)	0.40	25	2.0	Diphenylacetic acid (83)	5,5-Diphenyl-1-pentanol[g]	...
		66	2.0			
Dibenzothiophene (0.10)	0.30	0	2.0 [1.0]	3,4-Benzothiocoumarin (84)		49[e]
Carbazole (0.10)	0.57	66	20	Ammonia		...
Tetrahydrofuran	...	66	8.0	*n*-Butyl alcohol		

[a] The indicated yields are for products in a practical grade of purity. [b] Bracketed figures indicate the fractional hour of total reaction time consumed in adding the compound to be cleaved. [c] Ref. 5. [d] A slow, apparent gas evolution was observed in these cases. [e] Ref. 7a. [f] This acid was isolated from a run terminated by carbonation. [g] This product is reported for the first time by Gilman and Gaj (ref. 8).

pounds undergoing slow cleavage in solutions of I will have to compete with solvent attack by I. This limits the cleavages attainable with this reagent. However, the foregoing observations indicate that more rapid reaction and higher yields may be expected by the use of I in other lithium cleavage reactions, such as those reported in the interesting study of Gilman and Dietrich.[7a,12]

In order to gain insight into those factors operative in determining the course and ease of metal cleavage reactions, the behavior of certain groups of related compounds toward I is worthy of special note. First, as judged both by the temperature at which the cleavage proceeds and the extent of reaction,[13] the apparent ease of cleavage of C_6H_5Z increases as $Z = N(CH_3)_2$, OCH_3, F. Secondly, the replacement of methyl groups in the substrate by phenyl groups enhances the tendency to undergo cleavage: $C_6H_5—O—C_6H_5 > C_6H_5—O—CH_3$ and $C_6H_5—N(C_6H_5)_2 > C_6H_5—N(CH_3)_2$. A similar enhancement is seen in replacing hydrogen by phenyl groups: consider the greater ease with which $(C_6H_5)_3C—CH_2C_6H_5$ and $(C_6H_5)_2CH—CH(C_6H_5)_2$ undergo cleavage in comparison with $(C_6H_5)_3C—CH_3$. Thirdly, *o,o′*-bridged biphenyl derivatives which are cleaved only slowly or not at all by lithium metal in tetrahydrofuran are cleaved more rapidly by I. The rapid cleavage of dibenzothiophene at 0° and the slow cleavage of even the resistant carbazole ring by I illustrate this point.

As to the mechanism of these cleavage reactions, the extensive investigations[14] on the formation of stable 1:1 and 2:1 alkali metal (Na,K)–aromatic hydrocarbon adducts in donor solvents, such as 1,2-dimethoxyethane and tetrahydrofuran, suggest that similar lithium metal adducts may be important intermediates in these cleavage processes. Taken together with the previous findings of Gilman and co-workers on the cleavage of heterocyclic systems by lithium metal alone in tetrahydrofuran,[7a] the present results can best be interpreted in terms of such intermediate lithium adducts. Among the aromatic systems undergoing cleavage, certain structural classes can be discerned. There are, in the first place, *o,o′*-bridged biphenyls, which are able to react with lithium metal alone in tetrahydrofuran.[1b,7a,9] In these cases the formation of dark blue-green solutions accompanies the exothermic cleavage of the compounds. The fact that biphenyl itself,[9,14b] fluorene,[9] and phenanthridine[1b] have been shown to form stable or transitory lithium metal adducts in tetrahydrofuran with the formation of dark green solutions points to the intervention of 1:1 and/or 2:1 lithium adducts (II) in the cleavage of dibenzofuran, dibenzothiophene, and N-substituted carbazoles also.

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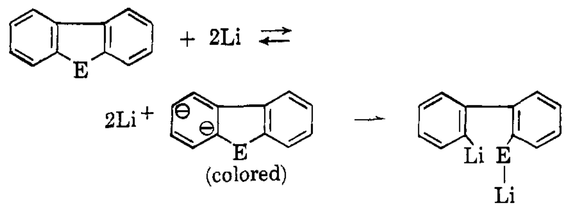
(12) The use of the 2:1 lithium–biphenyl adduct in tetrahydrofuran furnishes a completely homogeneous solution of "lithium." However, the amount of biphenyl can be reduced, since it functions as a carrier. Separation of acidic or basic cleavage products from the biphenyl poses no difficulty.

(13) Although competitive experiments, such as between fluorobenzene and anisole *vs.* limited amounts of I would be desirable to make the degree of reactivity more precise, the concurrent occurrence of cross *ortho* metalation by the organolithium compounds formed—*e.g.*, the destruction of phenyllithium, formed from fluorobenzene, by the *ortho* metalation of anisole—severely hampers the feasibility of such experiments.

A complication that may lower the yield of phenyllithium isolated from fluorobenzene and I is the known tendency of phenyllithium to metalate fluorobenzene in ether solution to yield biphenyl derivatives. [G. Wittig, G. Pieper, and G. Fuhrmann, *Ber.*, **73**, 1193 (1940).] Moreover, since this side reaction proceeds by *ortho* metalation of fluorobenzene, tetrahydrofuran would be expected to favor this side reaction. *Cf.* H. Gilman and S. Gray, *J. Org. Chem.*, **23**, 1476 (1958), for the enhancement of rates of metalation by organolithium compounds in this solvent.

(14) *Cf., inter alia:* (a) D. Lipkin, D. E. Paul, J. Townsend, and S. I. Weissman, *Science*, **117**, 534 (1953). (b) T. L. Chu and S. C. Yu, *J. Am. Chem. Soc.*, **76**, 3367 (1954). (c) G. J. Hoijtink, E. de Boer, P. H. van der Meij, and W. P. Weygand, *Rec. trav. chim.*, **74**, 277 (1955); **75**, 487 (1956). (d) D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956). (e) T. R. Tuttle, Jr., and S. I. Weissman, *ibid.*, **80**, 5342 (1958). (f) A. Carrington, F. Dravnieks, and M. C. R. Symons, *J. Chem. Soc.*, 947 (1959).



(3)

II

E = O,S,[N—R, CH_2, CH=N]

With N-substituted carbozoles (E = N—R), the adduct can eliminate R—Li to form the stable lithium salt of carbazole[7a]; with fluorene (E = CH_2), the lithium adduct of type II has been shown to abstract protons from uncomplexd fluorene to yield fluorenyllithium and hydrofluorenes[9]; and, finally, with phenanthridine

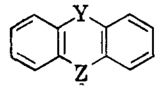
(E = CH=N)

the intermediate radical–anion

$(\mathrm{E} = \dot{\mathrm{C}}\mathrm{H}-\mathrm{N}^{\ominus}\ \mathrm{Li}^{\oplus})$

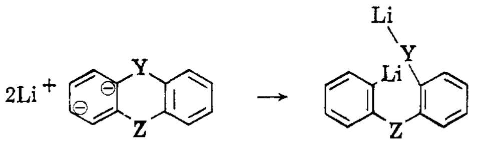
has been found to couple to produce a dimer or to form a dianion adduct (II).

The second class of compounds cleaved by lithium are the dibenzo derivatives of the heterocyclic system III,



III

where Y, Z = O, N—R, S. Here it appears that the attachment of two electronegative atoms to a benzene ring makes the rings sufficiently electron-attracting to promote lithium adduct formation and cleavage:

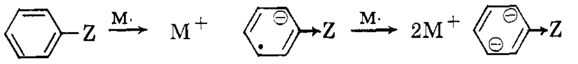


(4)

IV

Again, in these cases transitory blue-green colors are observed during the course of the cleavages.[7a] The reported preference for cleaving carbon–sulfur bonds (Y = S, Z = O and Y = S, Z = NR) over carbon–oxygen or carbon–nitrogen bonds may be related to the lower bond energy of carbon–sulfur linkages (C—S, 65; C—N, 73; C—O, 86 kcal./mole[15]).

Monosubstituted benzene derivatives, C_6H_5Z, may be considered as the third and the least reactive class of compounds toward lithium. How readily such systems will react with lithium or lithium–biphenyl(I) depends upon the nature of Z. Evidence indicates that the more readily C_6H_5Z can add alkali metal to yield radical–anion $[M^+ (C_6H_5^{\odot})^-]$ and/or dianion intermediates $[2M^+(C_6H_5^{\odot})^{-2}]$, the more readily cleavage will proceed. Thus, although polynuclear hydrocarbons, such as biphenyl, naphthalene, and phenanthrene,[14] form 1:1 and/or 2:1 alkali metal–hydrocarbon adducts in donor solvents at room temperature, benzene (Z = H) does not.[14e] However, benzene derivatives with electron-withdrawing substituents, such as nitrobenzene (Z = NO_2)[16] and benzonitrile (Z = CN),[17] form 1:1 alkali metal adducts in donor ether solvents at room temperature. An extension of this observation suggests that electron-withdrawing substituents favor the formation of radical-anion intermediates and hence cleavage:



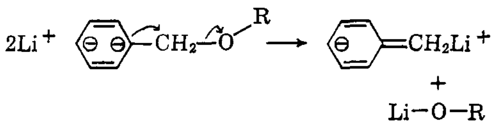
(5)

V VI

(Whether V actually then will undergo cleavage or will couple also depends on the nature of Z.)

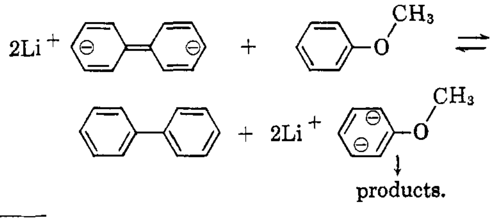
If one measures this electron-withdrawal by either the σ_m or σ_p values of Z, the observed ease of cleavage for the series, $C_6H_5F > C_6H_5OCH_3 > C_6H_5N(CH_3)_2$, parallels the decrease in the σ values of the substituents.[18] The greater ease of cleavage of phenyl ether and triphenylamine, compared with anisole and N,N-dimethylaniline, respectively, can be related to the greater electron-withdrawing power of O—C_6H_5 over O—CH_3, and of $N(C_6H_5)_2$ over $N(CH_3)_2$. A similar interpretation is possible for the arylated ethanes.

In situations where Z contains several linkages, the bond preferentially cleaved seems to be controlled by the anionic stability of the fragments, as in the cleavage of benzyl alkyl ethers to yield benzyllithium and lithium alkoxide,[6] rather than lithium benzylate and an alkyllithium:



(6)

In light of the foregoing discussion, therefore, the role of the lithium–biphenyl adduct(I) in effecting the cleavage of compounds, such as anisole and the tetraphenylethanes (which do not react readily with ordinary lithium metal in tetrahydrofuran) and in facilitating other cleavage reactions is to provide an homogeneous source of lithium for adduct formation under mild conditions by electron transfer[19,20]:



(7)

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[15] T. L. Cottrell, "The Strengths of Chemical Bonds." 2nd ed., Butterworths Scientific Publications, London, England, 1958, pp. 274–276.

[16] (a) T. L. Chu, G. E. Pake, D. E. Paul, J. Townsend, and S. I. Weissman, *J. Phys. Chem.*, **57**, 504 (1953); (b) R. L. Ward, *J. Chem. Phys.*, **30**, 852 (1959).

[17] (a) W. Schlenk and E. Bergmann, *Ann.*, **463**, 57 (1928); (b) R. L. Ward, *J. Chem. Phys.*, **32**, 1592 (1960).

[18] The σ_{para} values for F, OCH_3, and $N(CH_3)_2$ are +0.062, −0.170, and −0.600, respectively; the corresponding σ_{meta} values are +0.337, +0.115, and −0.211. For nitrobenzene and benzonitrile, whose radical-anions have been fully characterized (Ref. 16b and 17b), the substituents, NO_2 and CN, also have positive σ_{para} (+0.778 and +0.628) and σ_{meta} (+0.710 and +0.678) values. *Cf.* H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

[19] For a discussion of the relative electron affinities of aromatic hydrocarbons, *cf.* ref. 14d. The series, benzene ≪ phenanthrene < naphthalene < anthracene, naphthacene, was determined by interacting one hydrocarbon with the preformed radical–anion (1:1 sodium–hydrocarbon adduct) of another hydrocarbon.

[20] For the rapidity of electron transfer between radical–anions and aromatic hydrocarbons in tetrahydrafuran, *cf.* R. L. Ward and S. I. Weissman, *J. Am. Chem. Soc.*, **76**, 3612 (1954).

In a related fashion, the rapidity of lithium metal cleavage reactions in tetrahydrofuran,[7a] compared to the sluggishness of the same reactions in ethyl ether or dioxane,[7b] can be ascribed to the promotion of lithium metal adduct formation (II, IV, and VI) through the greater solvating power of the tetrahydrofuran (more donor solvent) for the resulting lithium metal cation.[10]

Experimental[21]

Starting Materials.—The tetrahydrofuran was shaken with successive portions of sodium hydroxide pellets, refluxed for 24 hr. over fresh sodium slices, and then distilled from the sodium metal. (For routine preparative work such tetrahydrofuran could be used directly after the sodium–metal distillation.) 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 and were dried before use. The refractive indices of the liquids and the melting points of the solids agreed well with the reported values.

Melting points given in this paper are corrected.

General Procedure for Cleavage Reactions by Agency of the 2:1 Lithium–Biphenyl Adduct.—In most cases the cleavage reactions were conducted in a 500-ml., three-necked, round-bottomed flask equipped with a Friedrichs condenser, sealed paddle stirrer, and a pressure-equalized addition funnel. After the oven-dried apparatus was assembled, it was purged thoroughly with dry nitrogen. Thereafter 150 ml. of tetrahydrofuran was distilled into the reaction apparatus so prepared. Under an emerging stream of nitrogen 15.4 g. (0.10 mole) of biphenyl and 1.54 g. (0.22 g.-atom) of small pieces of freshly cut lithium ribbon were added to the tetrahydrofuran. The heterogeneous system was stirred vigorously under a nitrogen atmosphere for 1–2 hr., during which time the lithium dissolved exothermically to form a deep blue-green solution. The system was brought to the desired temperature (by cooling or by heating to the reflux temperature) while 0.1 mole of the compound to be cleaved (dissolved in 25 ml. of anhydrous ethyl ether) was introduced into the 2:1 lithium–biphenyl adduct (I) solution. The experimental conditions and the yields of cleavage products are summarized in Table I. Individuating features of work-up and product characterization are detailed in the following paragraphs.

Tetrahydrofuran.—Extensive heating of tetrahydrofuran solutions of I caused disappearance of the characteristic blue-green color and the formation of reddish brown—or deep violet—colored solutions. The decomposition was shown to involve attack on the solvent and proceeded more rapidly if lithium piperidide was present (by addition of 1 mole % of piperidine to I). Hydrolysis of the reaction system, followed by the separation, drying and fractional distillation of the organic layer through a 20-cm. glass helices-filled column resulted in 4.0 g. of crude product, b.p. 97–115°. Redistillation provided 2.5 g. of colorless *n*-butyl alcohol, b.p. 114–115°, $n^{24}\text{D}$ 1.3990 (lit. b.p. 117–118°, $n^{25}\text{D}$ 1.3993), whose infrared spectrum was identical with that of an authentic sample.

Fluorobenzene.—Employing a volume of 150 ml. of tetrahydrofuran and altering the biphenyl between 0.002–0.20 mole had no pronounced effect on the yield of phenyllithium obtained at −10°. Slurry carbonation resulted in crude yields of benzoic acid between 40–50%. Enhanced yields were obtained by reducing the volume of tetrahydrofuran to 50 ml. (incomplete solution of the lithium metal) and by diluting the reaction mixture with 50 ml. of anhydrous ethyl ether prior to carbonation (Table I). Infrared spectra of the crude acids (m.p. 110–118°) revealed essentially pure benzoic acid admixed with a small apparent content of an *ortho*-substituted benzoic acid (*e.g.*, *o*-phenylbenzoic acid) by the distinct band at 750 cm.$^{-1}$.[13]

Anisole.—The resulting brown reaction system was treated with 100 ml. of water and the separated organic layer extracted with dilute aqueous sodium hydroxide solution. Combination of the aqueous extracts, acidification with dilute hydrochloric acid, saturation with salt, and extraction with ether allowed the isolation of the phenol. The dried and carefully evaporated ether extracts yielded the semisolid phenol. A sample was treated with methanolic bromine–potassium bromide to produce *p*-bromophenol, m.p. 62–64°, from dilute methanol. A mixture melting point with an authentic specimen was undepressed.

N,N-Dimethylaniline.—The pale violet reaction system was treated with 150 ml. of water and 100 ml. of ether. The amine was extracted with dilute hydrochloric acid and subsequently recovered from the acidic extracts by treatment with sodium hydroxide and extraction with ether. Distillation of the residual oil from dried and evaporated ether extracts furnished a 98% recovery of N,N-dimethylaniline which was shown by infrared spectroscopy to have approximately a 2% content of N-methylaniline (bands at 1270, 1430, and 3450 cm.$^{-1}$).

Phenyl Ether.—The work-up for phenol was identical with that employed with anisole. In one run worked up by carbonation benzoic acid was identified, in addition to phenol.

Triphenylamine.—Usual hydrolytic work-up gave an organic layer which was dried and then freed of solvent. The residue was dissolved in 200 ml. of dry benzene and the solution thereupon saturated with hydrogen chloride gas. The precipitated amine salts were collected and then treated with dilute sodium hydroxide to liberate the free amines. Filtration afforded 9.8 g. (58%) of diphenylamine, m.p. 52–54°. Extraction of the turbid filtrate with ether, drying of the extract, and removal of the solvent gave 0.15 g. (1.6%) of aniline, identified as its N-acetyl derivative, m.p. 112–113.5°.

1,1,1-Triphenylethane.—Treatment of the resulting vivid red solution with carbon dioxide gas at −75° and hydrolytic work-up yielded a crude acidic fraction. Recrystallization from glacial acetic acid gave a 2% yield of triphenylacetic acid, identified by melting point and spectral comparison with an authentic sample.

1,1,1,2-Tetraphenylethane.—Analogous to the preceding case, work-up by low-temperature carbonation led to a 93% yield of triphenylacetic acid, m.p. 255–265°, dec. (infrared confirmation). Phenylacetic acid was detected in the aqueous, acidic filtrate.

1,1,2,2-Tetraphenylethane.—In this instance, the ethane was added as a solid to the tetrahydrofuran solution of biphenyl, before the lithium metal was added. Work-up by low-temperature carbonation provided high yields of diphenylacetic acid, whose crude melting points ranged 140–145°. Recrystallized from dilute ethanol, the acid melted at 146–148°.

Prolonged heating of the original cleavage mixture led to destruction of diphenylmethyllithium by attack on the tetrahydrofuran. Thus, a 0.050-mole run conducted at the reflux temperature for 8 hr. gave upon work-up only a 68% yield of diphenylacetic acid. Work-up of the neutral organic layer by distillation and finally steam distillation (to remove the biphenyl) left 5.0 g. (21%) of colorless oil, which upon careful drying displayed infrared bands at 1060 and 3400 cm.$^{-1}$ (primary alcohol). This appears to be 5,5-diphenyl-1-pentanol.[8]

Carbazole.—The carbazole was introduced into a partial solution of 2.31 g. (0.33 g.-atom) of lithium metal and 0.10 mole of biphenyl in tetrahydrofuran (the lithium–biphenyl adduction being allowed to preform for 1 hr.). After the heated solution was cooled, it was cautiously hydrolyzed. An overpowering odor of ammonia was evident and its presence was confirmed by indicator paper. The organic phase was extracted with dilute hydrochloric acid, but treatment of these aqueous extracts with base yielded no precipitate. This rules out the presence of 2-aminobiphenyl. Drying the original organic phase, removing the solvent, and fractionally recrystallizing the residue from alcohol afforded: 10.95 g. (65%) of crude carbazole, m.p. 232–243°; 1.27 g. of intermediate solid, m.p. 120–210°, and 19.2 g. of crude biphenyl melting under 100°.

That the ammonia was not solely due to adventitious lithium nitride stemming from the nitrogen atmosphere was shown by a run conducted under a pure argon atmosphere. Again ammonia was detected and the recovery of carbazole was incomplete.

Dibenzothiophene.—The dibenzothiophene dissolved in 75 ml. of tetrahydrofuran and 75 ml. of ethyl ether was introduced into a solution of I in tetrahydrofuran at 0°. Work-up by slurry carbonation and hydrolysis gave an aqueous layer whose acidification and digestion precipitated 17.8 g. (84%) of 3,4-benzothiocoumarin, m.p. 115–125°. Recrystallization from ethanol gave colorless needles, m.p. 131–132°.

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[21] The following lithium metal cleavage reactions 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.