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Alkali Metal Reduction of Aromatic Nitro Compounds

VAIDEESWARAN KALYANARAMAN AND MANAPURATHU VERGHESE GEORGE*[1]

Department of Chemistry, Indian Institute of Technology, Kanpur, India

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The reaction of nitrobenzene with lithium in tetrahydrofuran gave a mixture of products consisting of azobenzene, 2-anilinoazobenzene, 2,2′- and 2,4′-dianilinoazobenzenes, anilinodibenzopyridazine, and unidentified polymeric azo compounds. Similar products were obtained from the reaction of nitrosobenzene with lithium, whereas the reaction of azoxybenzene gave exclusively azobenzene. It has been suggested that radical anion intermediates are involved in these reactions. Substituted nitro compounds react in a manner analogous to that of nitrobenzene, whereas nitroanilines are unchanged under similar conditions. Compounds such as 4-bromoazoxybenzene and 2-chloronitrobenzene undergo both deoxygenation and dehalogenation reactions on treatment with lithium in THF. 2,2′-Dinitrobiphenyl, on the other hand, gave dibenzopyridazine and a trace of carbazole on treatment with lithium in ether solvents. Under similar conditions, however, 2,2′-dinitrodiphenyl ether did not give any cyclized product.

Aromatic nitro compounds, in general, are reduced in basic medium to the corresponding azoxy, azo, and hydrazo derivatives, whereas they are converted to the corresponding amines under strongly acidic conditions or under catalytic hydrogenation.[2]

The deoxygenation of nitro and nitroso compounds have been brought about by several reagents to give a variety of products depending on the reaction conditions and the nature of the reagents.[3] Aryl nitro compounds, for example, have been reduced to the corresponding azo derivatives in fairly good yields by metal hydrides[4-6] and thallium.[7]

The reaction of nitrobenzene with sodium in liquid ammonia is very complex and may warrant further investigation.[8] However, sodium amalgam has been reported to reduce aromatic nitro compounds to the corresponding azoxy and azo compounds.[2] Lukashevich[9] had observed the formation of mono- and disodium adducts of nitrobenzene, as well as nitrosobenzene in ether solvents. Addition of alkali metals to nitro compounds in aprotic solvents has been reported to give rise to radical anion intermediates and several groups of workers have examined the esr spectra of some of these intermediates.[10] We previously examined the electronic spectra of the radical anions of a few nitrobenzene derivatives and some of the intermediates formed on treatment with alkali metals.[11,12]

The radical anion of nitrobenzene has been reported to undergo oxidation to nitrobenzene in air[13] or disproportionation to nitrobenzene and phenylhydroxylamine in aqueous solution.[14] The chemistry of nitrobenzene radical anion and the products formed in these reactions, however, have not been investigated in detail. This article describes investigations of the reactions of some aromatic nitro compounds with alkali metals in ether solvents.

Results and Discussion

Reaction of Nitrobenzene with Lithium in Tetrahydrofuran.—Treatment of nitrobenzene with lithium in THF under nitrogen atmosphere gave a mixture of products consisting of azobenzene (**2**) (34%), 2-anilinoazobenzene (**3**) (12%), 2,2′-dianilinoazobenzene (**4**) (0.5%), 2,4′-dianilinoazobenzene (**5**) (0.5%), and a trace of anilinodibenzopyridazine (**6**) (Scheme I). In addition, an unidentified mixture of polymeric azo compounds was also isolated from this reaction. The identities of products **2**–**6** have been established on the basis of analytical results and independent syntheses, whereever possible.

The assignment of structure **3** was accomplished on the basis of its elemental analysis ($C_{18}H_{15}N_3$), mass spectrum (mol wt 273), and ir spectrum, which indicated a weak N–H band at 3340 cm^{-1} which was unaffected by dilution (intramolecular hydrogen bonding).[15] The assignment of **3** was confirmed by an independent synthesis from 2-aminodiphenylamine and nitrosobenzene.[16]

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(1) To whom inquiries should be addressed.

(2) For some general references concerning the reduction of nitro compounds, see P. A. S. Smith, "Open Chain Nitrogen Compounds," Vol. 2, W. A. Benjamin, New York, N. Y., 1966, pp 422–430.

(3) For some of these deoxygenation reactions, see (a) J. I. G. Cadogan, *Quart. Rev., Chem. Soc.*, **22**, 222 (1968); J. H. Boyer in "The Chemistry of Nitro and Nitroso Groups," Vol. 1, H. Feuer, Ed., Interscience, New York, N. Y., 1969, p 260.

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(10) For some of these studies, see (a) A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **33**, 825 (1960); (b) R. L. Ward, *J. Amer. Chem. Soc.*, **83**, 1296 (1961); (c) T. A. Glaxton, W. M. Fox, and M. C. R. Symons, *Trans. Faraday Soc.*, **63**, 2570 (1967).

(11) V. Kalyanaraman, C. N. R. Rao, and M. V. George, *Tetrahedron Lett.*, 4889 (1969).

(12) C. N. R. Rao, V. Kalyanaraman, and M. V. George, *Appl. Spectrosc. Rev.*, **3**, 153 (1970).

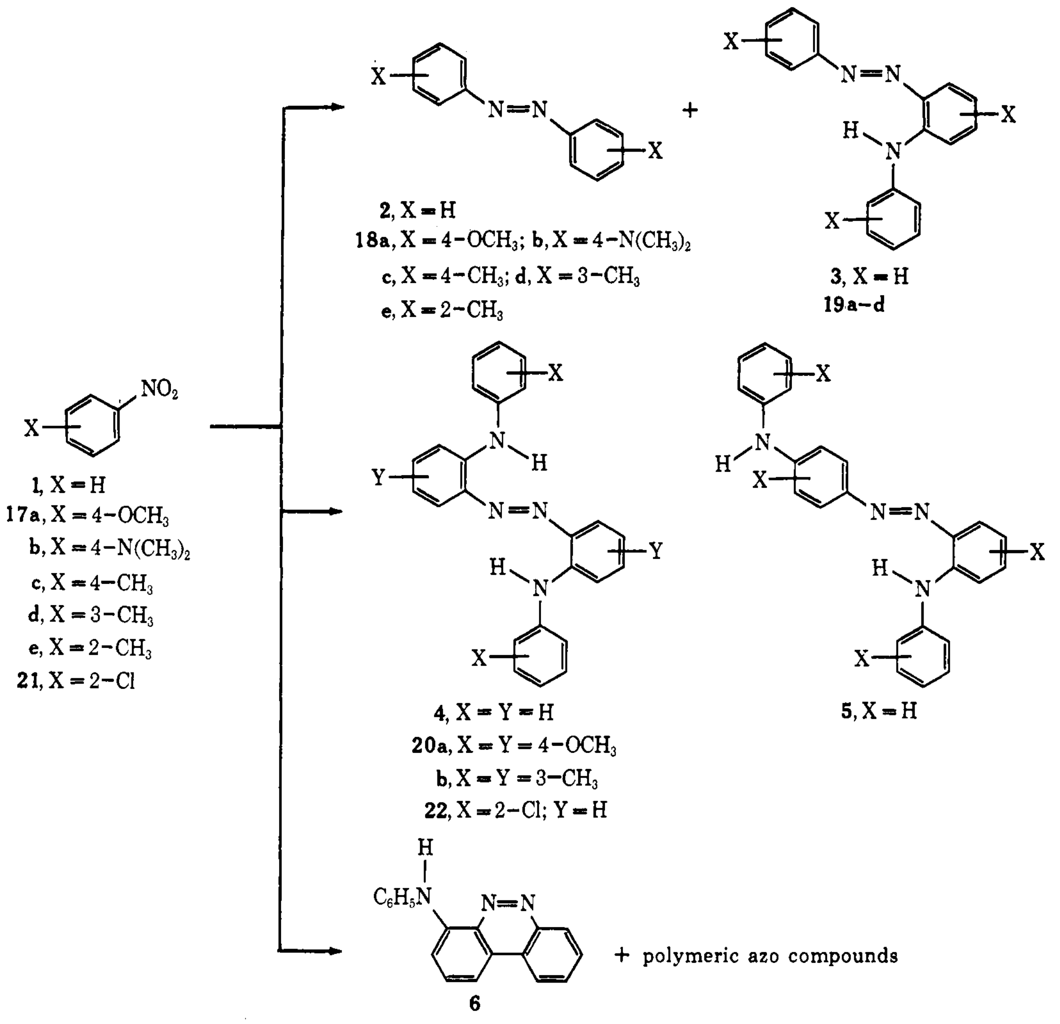
(13) G. A. Russell and A. G. Bemis, *Inorg. Chem.*, **6**, 403 (1967).

(14) B. Kastening, *Electrochim. Acta*, **9**, 241 (1964).

(15) For examples of similar intramolecular hydrogen bonding in ortho-substituted azobenzene, see (a) E. Sawicki and D. Gerber, *J. Org. Chem.*, **21**, 410 (1956); (b) L. Skulski, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **14**, 29 (1966); *Chem. Abstr.*, **64**, 19367 (1966).

(16) H. Zollinger, "Azo and Diazo Chemistry," Interscience, New York, N. Y., 1964.

SCHEME I



Compound **4**, mp 158° dec, obtained in the reduction of nitrobenzene analyzed for $C_{24}H_{20}N_4$ (mol wt 364, mass spectrometry). Allan and Swan[17] had reported the formation of a compound, mp 160°, identified as 2,2′-dianilinoazobenzene, in the reduction of 2-nitrodiphenylamine with zinc and sodium hydroxide. The uv spectral characteristics of this compound were in agreement with those of **4**, thereby suggesting the identity of **4** as 2,2′-dianilinoazobenzene. Further confirmation of the structure of **4** was derived from an independent synthesis involving the oxidation of 2-aminodiphenylamine using nickel peroxide[18,19] to afford a product identical with **4**.

Compound **5**, mp 120° dec, also analyzed for $C_{24}H_{20}N_4$ (mol wt, 364, mass spectrometry) and its ir spectrum was found to be similar to that of **4** except in the NH region. The presence of two NH stretching bands at 3400 and 3260 cm^{-1} is in agreement with the assigned structure. In the electronic spectrum of 2-anilinoazobenzene (**3**), the longest wavelength absorption maximum is observed at 457 nm. The corresponding para isomer, namely 4-anilinoazobenzene, is reported to have an absorption band at 420 nm.[20] In 2,2′-dianilinoazobenzene (**4**), the absorption maxima are observed at 288 nm (ϵ 32,300), 323 (10,500), and 504 (13,500). In compound **5**, the corresponding absorption maxima were observed at 290 nm (ϵ 32,400), 325 (15,300), and 472 (6900). Thus, the electronic spectrum of **5** is similar to that of **4**, except that the long-wavelength band has undergone a hypsochromic shift with a decrease in intensity. In addition, **5** and the 4,4′-dianilino derivative differ considerably in their melting points (120° *vs.* 238°,[21] respectively). An attempted synthesis of **5** employing the condensation of 2-aminodiphenylamine with 4-nitrosodiphenylamine, however, was not successful.

In addition to the azo- and anilinoazobenzenes obtained in the reduction of nitrobenzene, we have also isolated a small quantity of a light red compound tentatively assigned structure **6** on the basis of elemental analysis ($C_{18}H_{13}N_3$), mass spectrum (mol wt 271), and ir spectrum (–N=N– and intramolecular hydrogen bonding). In addition, the uv spectrum displayed maxima characteristic of dibenzopyridazine chromophore (λ_{max} 297, 338, 354, 364, 372, and 510 nm).

A probable route to the formation of azobenzene (**2**) in the reaction of nitrobenzene with lithium is shown in Scheme II. In this scheme we assume that the initially formed radical anion intermediate **8** is converted to nitrosobenzene (**7**) through the dianion intermediate **9**. Further reaction of lithium with nitro-

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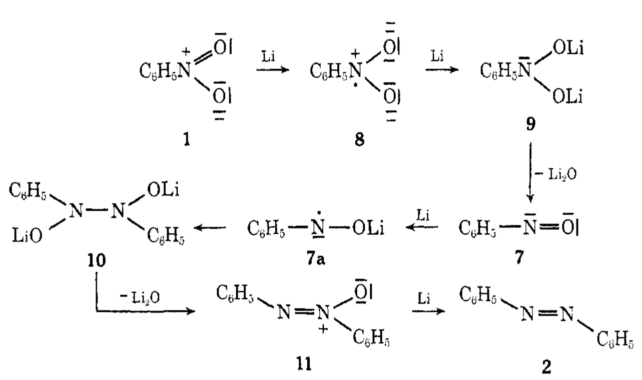
[18] K. Nagakawa and T. Tsuji, *Chem. Pharm. Bull.*, **11**, 296 (1963); *Chem. Abstr.*, **59**, 3827 (1963).

[19] K. S. Balachandran and M. V. George, unpublished results.

[20] G. M. Badger, R. G. Buttery, and G. E. Lewis, *J. Chem. Soc.*, 1888 (1954).

[21] M. Colonna and M. Angeletti, *Bull. Sci. Fac. Chim. Ind. Bologna*, **18**, 160 (1960); *Chem. Abstr.*, **55**, 23414 (1961).

SCHEME II



sobenzene should result in the formation of a new radical anion intermediate **7a**, which can be transformed to azoxybenzene (**11**) through the intermediate **10**. Azoxybenzene will undergo further deoxygenation in presence of lithium to azobenzene. It might be mentioned in this connection that azobenzene itself will undergo further addition in the presence of lithium to give a dianion derivative.[22] However, under the conditions of work-up, the hydroazobenzene that will be formed is rapidly oxidized back to azobenzene.

In order to test for the intermediacy of nitrosobenzene (**7**) and azoxybenzene (**11**), the reaction of both with lithium in THF was examined. Treatment of **7** with excess lithium in THF at room temperature gave a 53% yield of azobenzene. Under similar conditions, **11** afforded a nearly quantitative yield of azobenzene. Furthermore, a 3% yield of **11** was isolated from the reaction of nitrobenzene with lithium in ether at 0°. The changes observed in the time-dependent electronic spectra of nitrobenzene radical anion also support the intermediate formation of nitrosobenzene and azoxybenzene.[11,12] During the course of our studies, we had observed that 4 equiv of lithium metal is required for the complete reduction of every mole of nitrobenzene. However, stopping the reaction at intermediate stages led only to the partial conversion of nitrobenzene to azobenzene. This observation is in agreement with the fact that the intermediates such as nitrosobenzene and azoxybenzene are reduced under much lower potentials than nitrobenzene itself.[23]

The formation of 2-anilinoazobenzene (**3**), 2,2′-dianilinoazobenzene (**4**), and 2,4′-dianilinoazobenzene (**5**) may be explained in terms of the coupling of radical intermediates as shown in Scheme III. One of the probable modes for the formation of **3** is through a coupling of the radical anion of azobenzene (**12a**) with the addition product of lithium to nitrosobenzene to give the intermediate **13**, which can ultimately lead to **15**. Under the conditions of work-up, **15** will be converted to **3**. Similarly, the formation of both **4** and **5** may be rationalized through the reaction of the radical anion intermediate **16** as shown in Scheme III. From a study of the esr spectrum of the radical anion of azobenzene, it is known that the electron density is greater at the ortho position of the aromatic ring,[24] a fact which is in tune with our observation concerning the predominance of the ortho-substituted azobenzene derivatives. The exact mode of formation of the pyridazine derivative **6** in the reduction of nitrobenzene is not very clear. It is feasible that one of the radical anion intermediates such as **16** (Scheme III) may be undergoing oxidative cyclization leading to the formation of **6**.

Influence of the Solvent, Alkali Metal, and Temperature on the Reduction of Nitrobenzene.—With a view to improving the yield of azobenzene formed in the reaction of nitrobenzene with lithium, we have varied the solvents and alkali metals. The results of these studies are summarized in Table I. It has been observed that changing the solvent from tetrahydrofuran to 1,2-dimethoxyethane, dioxane, or diethyl ether had very little effect on the composition of the product mixture. The yield of azobenzene in these cases varied from 19 to 43%, increasing with solvents of increased dielectric constant and also with increasing temperatures. The yield of azobenzene was very poor (1–7%) when either sodium or potassium was used and this may be due to the relatively poor solubilities of the intermediates formed in these cases.

TABLE I
INFLUENCE OF SOLVENT, TEMPERATURE, AND ALKALI METAL ON THE YIELD OF AZOBENZENE IN THE REDUCTION OF NITROBENZENE

Solvent	Metal	Temp, °C	Time, hr	Azobezene yield, %
Diethyl ether	Lithium	0–5	24	8
Diethyl ether	Lithium	30	24	19
Tetrahydrofuran	Lithium	0	24	25
Tetrahydrofuran	Lithium	30	16	34
1,2-Dimethoxyethane	Lithium	30	24	43
Dioxane	Lithium	30	24	30
Tetrahydrofuran	Sodium	30	24	7
Tetrahydrofuran	Potassium	30	48	1

Reaction of Substituted Nitrobenzenes with Lithium in Tetrahydrofuran.—In continuation of our studies we have examined the reaction of a few substituted nitrobenzenes with lithium for evolving a convenient method for the preparation of azo compounds. Treatment of different monosubstituted nitro compounds with lithium in THF at room temperature gave rise to the corresponding azo compounds in varying yields. Table II summarizes the results of these studies.

Reaction of Aromatic Dinitro Compounds with Lithium.—In continuation of our studies we have examined the reactions of a few dinitro compounds with alkali metals, for evolving a convenient route to the synthesis of cyclic azo compounds. Treatment of 2,2′-dinitrobiphenyl (**23**) with lithium in tetrahydrofuran gave a 45% yield of dibenzopyridazine (**24**) and a trace of carbazole (**25**) (Scheme IV). A similar yield of **24** was obtained when the reaction of **23** was carried out with sodium in 1,2-dimethoxyethane. On the basis of analogy to the formation of azobenzene from nitrobenzene (Scheme II), one would assume that the reduction of **23** is proceeding through radical anion intermediates. The esr spectrum of a solution of **23** in THF after treatment with alkali metals such as

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[22] For some of these addition reactions, see (a) J. W. B. Reesor and G. F. Wright, *J. Org. Chem.*, **22**, 375 (1957); (b) M. V. George, D. Wittenberg, and H. Gilman, *J. Amer. Chem. Soc.*, **81**, 361 (1959); (c) M. V. George, P. B. Talukdar, and H. Gilman, *J. Organometal. Chem.*, **5**, 397 (1966); (d) S. S. Dua and M. V. George, *ibid.*, **9**, 413 (1967); (e) *ibid.*, **10**, 219 (1967).

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[24] R. K. Gupta, Ph.D. Thesis, Indian Institute of Technology, Kanpur, India, 1968.

SCHEME III

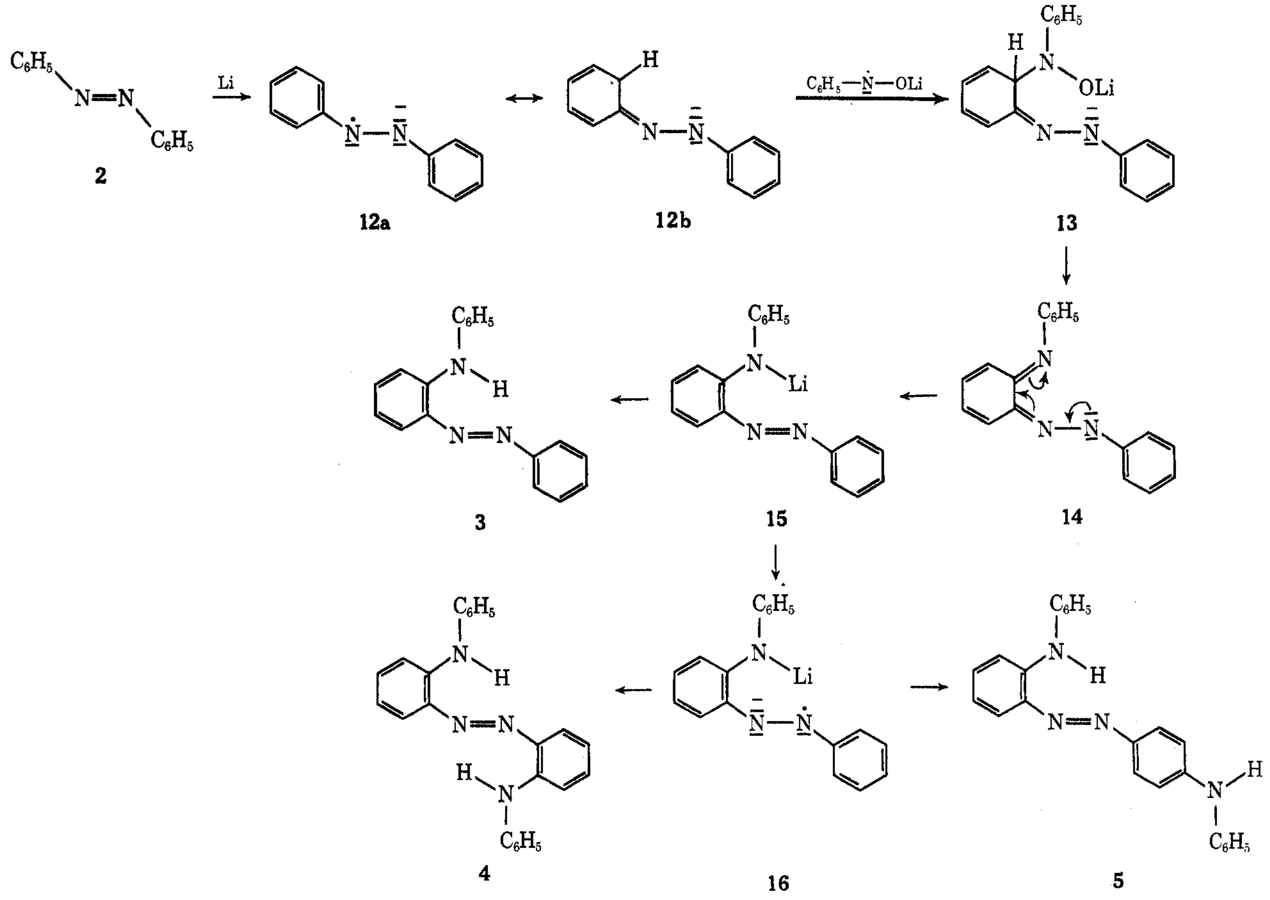


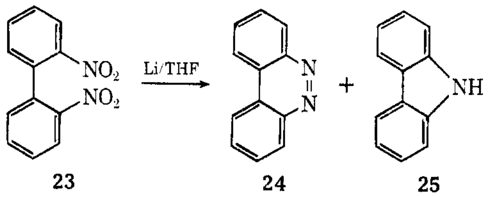
TABLE II

PRODUCTS OBTAINED FROM THE REACTION OF AROMATIC NITRO COMPOUNDS WITH LITHIUM IN THF

Nitro compd	Products (yield, %)
4-Nitroanisole (**17a**)	4,4′-Azoanisole (**18a**) (25); 2-(*p*-anisidino)-4,4′-azoanisole (**19a**) (18); 2,2′-bis(*p*-anisidino)-4,4′-azoanisole (**20a**) (1)
4-Nitro-*N*,*N*-dimethylaniline (**17b**)	4,4′-Bis(*N*,*N*-dimethylamino)azobenzene (**18b**) (18); 2-(*p*-*N*,*N*-dimethylamino)-4,4′-bis(*N*,*N*-dimethylamino)azobenzene (**19b**) (2)
4-Nitrotoluene (**17c**)	4,4′-Azotoluene (**18c**) (19); 2-(*p*-toluidino)-4,4′-azotoluene (**19c**) (0.6); 4,4′-azoxytoluene (0.5)
3-Nitrotoluene (**17d**)	3,3′-Azotoluene (**18d**) (31); 2-(*m*-toluidino)-5,5′-azotoluene (**19d**) (12); 2,2′-bis(*m*-toluidino)-5,5′-azotoluene (**20d**) (0.2)
2-Nitrotoluene (**17e**)	2,2′-Azotoluene (**18e**) (22)
2-Chloronitrobenzene (21)	2,2′-Bis(*o*-chloroanilino)azobenzene (22) (2)
2-Bromonitrobenzene	No definite product
4-Nitroaniline	Unchanged starting material
3-Nitroaniline	Unchanged starting material
4-Nitroacetanilide	Unchanged starting material

Li, Na, and K supports this view.[25] It might be pointed out in this connection that the esr spectrum of a solution of **23** on prolonged treatment with alkali metals corresponds to the spectrum of the radical anion of dibenzopyridazine (**24**).[25]

SCHEME IV



23 **24** **25**

In order to examine whether the reduction of 2,2′-dinitrodiphenyl ether (**26**) would give rise to the corresponding cyclic azo compound, dibenzo[1.4.5]oxadiazepine (**27**) we have studied the reaction of **26** with lithium in THF. It was observed that the initially formed radical anion intermediate does not undergo further reaction and the starting material was recovered unchanged in appreciable yields, on work-up. However, the reaction of **26** with sodium in tetrahydrofuran resulted in the cleavage of this molecule, and a small quantity of 2-nitrophenol (**28**) was isolated from this run. Similarly, the reaction of 1,8-dinitronaphthalene with lithium did not give rise to any of the cyclic products.

Reaction of Aromatic Nitroso and Azoxy Compounds with Lithium.—Treatment of nitrosobenzene with lithium in tetrahydrofuran gave a 53% yield of azobenzene and a 11% yield of 2-anilinoazobenzene (**3**). The formation of **3** in this reaction would be an indirect support to the reaction sequences shown in Scheme II. Similarly, a 28% yield of 4,4′-bis(*N*,*N*-dimethylamino)azobenzene was obtained from 4-nitroso-*N*,*N*-dimethylaniline. It might be mentioned

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[25] J. Subramanian and P. T. Narasimhan, private communication.

in this connection that Kauffman and Hage[26] were able to isolate a 48% yield of 4,4′-azoxytoluene in the reduction of 4-nitrosotoluene with sodium in ether solvents, whereas *N*-(*p*-tolyl)hydroxylamine was formed when excess sodium was employed. Also, it has been reported that phenyllithium reacts with aromatic nitro and nitroso compounds to give lithium derivatives of hydroxylamine, phenol, and diphenylamine.[27]

The reaction of azoxybenzene with lithium in THF gave a nearly quantitative yield of azobenzene. Similarly, 4,4′-azoxyanisole, on treatment with lithium was deoxygenated to the corresponding 4,4′-azoanisole in 99% yield. A similar observation was made by Kauffman and coworkers,[28] who were able to isolate a 80% yield of azobenzene from the reaction of azoxybenzene with alkali metals. In the reaction of α-4-bromoazoxybenzene with lithium, however, the product isolated was a 40% yield of azobenzene, suggesting thereby that a debromination step is also involved in this reaction.

Mass Spectral Fragmentation of Arylamino-Substituted Azobenzenes.—We have examined the mass spectral fragmentation pattern of a few arylaminoazobenzenes that were obtained during the course of the present studies. In this connection, the mass spectra of 2-anilinoazobenzene, 2,2′-dianilinoazobenzene, 2,4′-dianilinoazobenzene, and 2,2′-bis(*p*-anisidino)-4,4′-azoanisole were examined. The base peaks in all these compounds have been due to the molecular ions. Bowie and coworkers[29] have recently examined the mass spectra of several azobenzenes and have found that the base peak in these compounds has been due to biphenyl and biphenylene ions, arising through the loss of nitrogen. Similar loss of nitrogen has been observed in related systems.[30] However, we find that, in the arylaminoazobenzene examined by us, the loss of nitrogen is not very significant. The major fragmentation modes appeared to be the cleavage of the arylamino moiety and also of the loss of aryl groups, Without exception, all these compounds showed ions arising through skeletal rearrangements and many metastable peaks were also observed in the spectra.

Experimental Section

All melting points are uncorrected and were taken in a Thomas-Hoover melting point apparatus. Ir spectra were determined on either a Perkin-Elmer Model 137 or 521 infrared spectrometer. Electronic spectra were recorded in a Cary 14 spectrophotometer. Nmr spectra were recorded on a Varian HR-100 spectrometer using TMS as an internal standard. Mass spectra were recorded on a CEC 21-110 B mass spectrometer with 40 μA ionizing current and an ionizing voltage of 70 eV.

Starting Materials.—Solvents such as diethyl ether, 1,2-dimethoxyethane, tetrahydrofuran, and dioxane, used in the present studies, were purified by standard procedures and distilled over sodium. Reagent grade samples of nitrobenzene, 2-nitrotoluene, 3-nitrotoluene, 4-nitrotoluene, 4-nitroanisole, 2-chloronitrobenzene, 3-nitroaniline, 4-nitroaniline, 4-nitroacetanilide, 1,8-dinitronaphthalene, 4-nitrosodiphenylamine, azoxybenzene, 4,4′-azoxyanisole, and 2-aminodiphenylamine were purified either by distillation or recrystallization before use. 4-Nitro-*N*,*N*-dimethylaniline,[31] mp 163° (75% yield), 2,2′-dinitrobiphenyl,[32] mp 124° (50% yield), 2,2′-dinitrodiphenyl ether,[33] mp 111° (50% yield), nitrosobenzene,[34] mp 65–66° (40% yield), 4-nitroso-*N*,*N*-dimethylaniline,[35] mp 87° (80% yield), and 4-bromoazoxybenzene,[36] mp 73° (45% yield), were prepared by reported procedures.

General Procedure for the Reaction of Aromatic Nitro Compounds with Lithium.—In general, a mixture of the aromatic nitro compound with an excess of lithium metal (4–5 g-atoms) in a solvent such as tetrahydrofuran was shaken under an atmosphere of dry nitrogen.[37] In order to ensure a clean surface of the metal throughout, a few broken glass chips were added to the reaction mixture. On completion of the reaction, the excess of metal was removed by filtration under nitrogen and the solvent was stripped under vacuum. The residue was successively extracted with solvents such as benzene and acetone. Further separation and purification of the individual components were achieved through repeated chromatography over alumina.

Reaction of Nitrobenzene with Lithium.—A mixture of 2.5 g (20 mmol) of nitrobenzene and 0.7 g (0.1 g-atom) of lithium was shaken in tetrahydrofuran (60–75 ml) for about 16 hr. The reaction mixture became brown at first, and turned later to violet and finally deep brown. In several successive runs, a total of 22.1 g (0.18 mol) of nitrobenzene was treated with the requisite amount of lithium and the mixture of products thus obtained was extracted with hot benzene (2 l.) to give 17.2 g of a dark brown mass. This material was dissolved in benzene (50 ml) and chromatographed on alumina. Elution of the column with a mixture (3:1) of petroleum ether (bp 60–80°) and benzene gave 9.8 g of a red, viscous material. The residual material on the column was eluted out with hot ethanol and this eluate was mixed with the ethanol extract of the original reaction mixture (the residue left behind after extraction with benzene). Removal of the solvent gave 4.4 g of a violet-brown, viscous material which was worked up subsequently.

The red, viscous solid (9.8 g) obtained earlier was chromatographed thrice over alumina using petroleum ether to give 5.6 g (34%) of azobenzene (**2**), mp and mmp 68°. Further elution of the column with a mixture (5:1) of petroleum ether and benzene gave 1.9 g (12%) of 2-anilinoazobenzene (**3**), which melted over the range 50–54°. Repeated recrystallizations from methanol gave a pure product of **3** which melted at 56°.

Anal. Calcd for $C_{18}H_{15}N_3$: C, 79.12; H, 5.50; N, 15.39; mol wt, 273. Found: C, 79.31; H, 5.88; N, 15.50; mol wt (mass spectrometry), 273. Ir spectrum (KBr) ν_{max} 3340 (NH) and 1450 cm^{-1} (N=N); uv spectrum (cyclohexane) λ_{max} 288 nm (ε 30,200), 322 (22,500), and 457 (10,700).

The violet-brown mass (4.4 g) obtained from the ethanol extract was rechromatographed on alumina. Elution with a mixture (3:1) of petroleum ether and benzene gave 40 mg of azobenzene, mp and mmp 68°. Further elution with a mixture (2:1) of petroleum ether and benzene gave 0.2 g of a maroon-colored product, melting over the range 100–130° (darkens around 70°). The residue on the column was again extracted with ethanol to give 3.2 g of a dark-colored solid, which was subsequently worked up.

Further chromatography of the maroon-colored product (mp 100–130°) over alumina using petroleum ether gave 77 mg (0.5%) of 2,4′-dianilinoazobenzene (**5**), which melted at 120° dec after recrystallization from petroleum ether.

Anal. Calcd for $C_{24}H_{20}N_4$: C, 79.12; H, 5.50; N, 15.39; mol wt, 364. Found: C, 79.40; H, 6.08; N, 15.38; mol wt (mass spectrometry), 364. Ir spectrum (KBr) ν_{max} 3400 (NH),

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[26] T. Kauffman and S. M. Hage, *Angew. Chem., Int. Ed. Engl.*, **2**, 156 (1963).

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[34] G. H. Coleman, C. M. McCloskey, and F. A. Stuart, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 668.

[35] G. M. Bennett and E. V. Bell, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1959, p 223.

[36] A. Angeli and B. Valon, *Atti Accad. Naz. Lincei*, **21**, 55 (1912); *Chem. Abstr.*, **6**, 1137 (1912).

[37] For purification of nitrogen, see L. J. Brady, *Ind. Eng. Chem., Anal. Ed.*, **20**, 1034 (1948).

3260 (NH), and 1490 cm^{-1} (N=N); uv spectrum (cyclohexane) λ_{max} 290 nm (ϵ 32,400), 325 (15,500), and 472 (6800).

Further elution of the chromatographic column using a mixture (4:1) of petroleum ether and acetone gave 85 mg (0.5%) of 2,2′-dianilinoazobenzene (4), mp 158° dec (lit.[17] mp 160°), after recrystallization from a mixture (1:1) of benzene and ethanol.

Anal. Calcd for $C_{24}H_{20}N_4$: C, 79.12; H, 5.50; N, 15.39; mol wt, 364. Found: C, 79.00; H, 5.68; N, 15.24; mol wt (mass spectrometry), 364. Ir spectrum (KBr) ν_{max} 3400–3250 (NH) and 1455 cm^{-1} (N=N); uv spectrum (cyclohexane) λ_{max} 288 nm (ϵ 32,300), 323 (10,500), and 500 (13,500).

The dark brown material obtained earlier was dissolved in about 35 ml of a mixture (1:1) of benzene and acetone and chromatographed over alumina. Elution of the column with a mixture (3:1) of petroleum ether and benzene gave 11 mg of a pink-colored compound melting at 135–137°. Recrystallization from petroleum ether gave 6 mg of a pure sample of anilinodibenzopyridazine (6), mp 138.5°.

Anal. Calcd for $C_{18}H_{13}N_3$: mol wt, 271. Found: mol wt (mass spectrometry), 271. Ir spectrum (CCl_4) ν_{max} 3280 (NH) and 1460 cm^{-1} (N=N); uv spectrum (cyclohexane) λ_{max} 241 nm (ϵ 38,300), 297 (42,600), 338 (2900), 354 (4300), 364 (3700), 372 (5400), and 510 (4500).

Further elution of the chromatographic column with a variety of solvents did not lead to the isolation of any definite product.

Influence of Solvent, Temperature, and the Alkali Metals on the Reaction of Nitrobenzene. A. Solvent.—In a typical run, 2.5 g (20 mmol) of nitrobenzene and 0.7 g (0.1 g-atom) of lithium were mixed together in 70 ml of tetrahydrofuran. On completion of the reaction, the mixture was worked up as described earlier and the yield of azobenzene was assessed. Similarly, the reaction was repeated in different solvents such as 1,2-dimethoxyethane, dioxane, and diethyl ether and Table I summarizes the results of these studies.

B. Temperature.—In a repeat run involving the reaction of nitrobenzene with lithium, the reaction was carried out around 0–5°, instead of at room temperature in ether medium. Work-up of the mixture in the usual manner gave a 8% yield of azobenzene and 60 mg (3%) of a product, identified as azoxybenzene, mp and mmp 36°. However, when the same reaction was carried out in tetrahydrofuran around 30°, a 25% yield of azobenzene was obtained after a reaction time of 24 hr (Table I).

C. Alkali Metals (Na and K).—Treatment of 2.5 g (20 mmol) of nitrobenzene with 2 g (0.09 g-atom) of sodium in 75 ml of tetrahydrofuran and work-up of the mixture in the usual manner gave 120 mg (7%) of azobenzene and 1 g (40%) of unchanged nitrobenzene, identified through its ir spectrum.

In a repeat run, 2.5 g (20 mmol) of nitrobenzene was treated with 3.5 g (0.09 g-atom) of potassium in 75 ml of tetrahydrofuran. Work-up of the mixture as in the earlier cases, after a 48-hr reaction time, gave 14 mg (2%) of azobenzene, mp and mmp 68°, and 1.6 g (65%) of unchanged nitrobenzene, identified through its ir spectrum.

Synthesis of 2-Anilinoazobenzene (3).—A mixture of 2-aminodiphenylamine (0.92 g, 5 mmol) and nitrosobenzene (0.53 g, 5 mmol) was dissolved in 10 ml of glacial acetic acid and was left at room temperature for 36 hr. The deep red reaction mixture was diluted with cold water and extracted with a mixture (1:1) of ether and benzene, after neutralization with potassium hydroxide. Removal of the solvent under vacuum gave a product which was chromatographed on alumina. Elution with a mixture (5:1) of petroleum ether and benzene gave 100 mg (7%) of **3**, which melted at 56° on recrystallization from methanol. Comparison of this compound with a sample of **3** obtained in the reaction of nitrobenzene with lithium revealed that they were identical. There was no depression in their melting points when they were mixed together and also their ir spectra were identical.

Synthesis of 2,2′-Dianilinoazobenzene (4).—A mixture of 0.92 g (5 mmol) of 2-aminodiphenylamine and 4.5 g of nickel peroxide in 100 ml of dry benzene was stirred at room temperature for 5 hr. Removal of the unchanged nickel peroxide and solvent under vacuum gave a product which was chromatographed on alumina. Elution with benzene gave 12 mg (0.5%) of **4**, which melted at 158° dec, on recrystallization from a mixture (1:1) of benzene and ethanol. There was no depression in the melting point of this material when mixed with a sample of **4** obtained in the reaction of nitrobenzene with lithium. The ir spectra of these two samples were also identical.

Attempted Synthesis of 2,4′-Dianilinoazobenzene (5).—A mixture of 4-nitrosodiphenylamine (1 g, 5 mmol), 2-aminodiphenylamine (0.92 g, 5 mmol), and glacial acetic acid (10 ml) was left at room temperature for 24 hr. Work-up of the mixture as in the case of **3** resulted in the recovery of a 20% yield (0.2 g) of unchanged 2-aminodiphenylamine, mp and mmp 80°, and a 60% yield (0.6 g) of 4-nitrosodiphenylamine, mp and mmp 144°.

Repetition of this experiment under different conditions, such as treatment of the reagents in pyridine, acetic acid, or aqueous sodium hydroxide, did not give rise to the desired product. In a separate run, when the reagents were heated in acetic acid in a sealed tube for 6 hr, only polymeric materials could be isolated.

Reaction of 4-Nitroanisole with Lithium.—Treatment of 4-nitroanisole (**17a**)) (9.2 g, 0.06 mol) with lithium (1.8 g, 0.26 g-atom) in tetrahydrofuran (120 ml) for a period of 18 hr gave a deep brown reaction mixture. Removal of the solvent under vacuum gave a mixture of products which was extracted with hot benzene, and the benzene-soluble product (7.2 g) was chromatographed on alumina. Elution with benzene gave 4.2 g of a red solid which, when fractionally crystallized from ethanol, yielded 1.8 g (25%) of 4,4′-azoanisole (**18a**), mp and mmp 161–162°. Removal of the solvent from the mother liquor gave a product which was rechromatographed on alumina. Elution with a mixture (2:1) of petroleum ether and benzene gave a yellow solid which, when fractionally crystallized from methanol, yielded 1.3 g (18%) of 2-(*p*-anisidino)-4,4′-azoanisole (**19a**), mp 108°.

Anal. Calcd for $C_{21}H_{21}N_3O_3$: C, 69.42; H, 5.80; N, 11.57; mol wt, 363. Found: C, 69.52; H, 5.80; N, 11.53; mol wt (mass spectrometry), 363. Ir spectrum (CCl_4) ν_{max} 3400 (NH), 3230 (NH), and 1470 cm^{-1} (N=N); uv spectrum (tetrahydrofuran) λ_{max} 288 nm (ϵ 17,000), 347 (18,000), and 451 (15,000); nmr spectrum (CCl_4) 3.69 (3 H, methoxy), 3.75 (3 H, methoxy), 3.79, (3 H, methoxy), 7.18 (11 H, multiplet, aromatic), and 10.5 ppm (1 H, NH).

Further elution of the column with a mixture (1:1) of petroleum ether and benzene gave 90 mg (1%) of 2,2′-bis(*p*-anisidino)-4,4′-azoanisole (**20a**), which melted over the range 163–165°, after recrystallization from a mixture (1:1) of benzene and ethanol.

Anal. Calcd for $C_{28}H_{28}N_4O_4$: C, 69.42; H, 5.80; N, 11.57; mol wt, 484. Found: C, 69.44; H, 5.30; N, 11.57; mol wt (mass spectrometry), 484. Ir spectrum (KBr) ν_{max} 3360 (NH), 3300 (NH), and 1495 cm^{-1} (N=N); uv spectrum (tetrahydrofuran) λ_{max} 298 nm (ϵ 33,900), 342 (14,500), 493 (23,400); nmr spectrum ($CDCl_3$) 3.96 (6 H, methoxy), 4.03 (6 H, methoxy), 7.38 (14 H, multiplet, aromatic), and 10 ppm (2 H, NH).

Reaction of 4-Nitro-*N*,*N*-dimethylaniline (17b) with Lithium.—Treatment of 8.3 g (0.05 mol) of **17b** with 1.8 g (0.25 g-atom) of lithium in tetrahydrofuran for 36 hr gave a dark red reaction mixture. Removal of the solvent under vacuum gave a mixture of products which was extracted with a hot mixture (1:1) of benzene and acetone and chromatographed over alumina. Elution of the column with benzene gave 1.2 g (18%) of 4,4′-bis(*N*,*N*-dimethylamino)azobenzene (**18b**), mp and mmp 272–274°.

Further elution of the column with benzene gave 87 mg (2%) of 2-(*p*-*N*,*N*-dimethylaminoanilino)-4,4′-bis(dimethylamino)azobenzene (**19b**), which melted at 243–244° after recrystallization from benzene.

Anal. Calcd for $C_{24}H_{30}N_6$: C, 71.64; H, 7.46; N, 20.89. Found: C, 71.70; H, 7.77; N, 21.06. Ir spectrum (KBr) ν_{max} 3322 (NH) and 1471 cm^{-1} (N=N); uv spectrum (tetrahydrofuran) λ_{max} 252 nm (ϵ 17,000), 320 (10,100), 448 (31,400), and 468 (33,300).

Reaction of 4-Nitrotoluene (17c) with Lithium.—A mixture of 11 g (0.08 mol) of **17c** and 2.5 g (0.36 g-atom) of lithium in 200 ml of tetrahydrofuran was allowed to stand at room temperature for 18 hr, with constant shaking. Removal of the unchanged metal and solvent under vacuum gave 7 g of a brown viscous solid which was chromatographed over alumina. Elution of the column with petroleum ether gave 1.6 g (19%) of 4,4′-azotoluene (**18c**), which melted at 146° (mixture melting point) after recrystallization from ethanol. Further elution of the column with a mixture (3:1) of petroleum ether and benzene afforded a red substance which was recrystallized from methanol to give 50 mg (0.6%) of 2-(*p*-toludino)-4,4′-azotoluene (**19c**), mp 112°.

Anal. Calcd for $C_{21}H_{21}N_3$: C, 80.00; H, 6.67; N, 13.34. Found: C, 80.30; H, 6.53; N, 13.77. Ir spectrum (CCl_4) ν_{max} 3400 (NH), 3230 (NH), and 1440 cm^{-1} (N=N); uv spectrum (tetrahydrofuran) λ_{max} 292 nm (ϵ 20,300), 353 (18,400), and 465 (11,100).

Subsequent elution of the column with the same solvent gave

46 mg (0.5%) of 4,4′-azoxytoluene, which melted at 68° after recrystallization from ethanol. There was no depression in the melting point of this compound when mixed with an authentic sample of 4,4′-azoxytoluene, prepared by a reported procedure.[38]

Reaction of 3-Nitrotoluene (17d) with Lithium.—Treatment of 11 g of 3-nitrotoluene (**17d**) with 2.5 g (0.36 g-atom) of lithium in 250 ml of tetrahydrofuran for 14 hr at room temperature and work-up in the usual manner gave a mixture of products which was chromatographed on alumina. Elution with petroleum ether gave 2.6 g (31%) of 3,3′-azotoluene (**18d**) which melted at 53° (mixture melting point) after recrystallization from petroleum ether (bp 40–60°).

Further elution of the column with a mixture (3:1) of petroleum ether and benzene gave 1 g (12%) of 2-(*m*-toludino)-5,5′-azotoluene (**19d**), which melted at 56–57° after distillation under high vacuum, followed by fractional crystallization from methanol.

Anal. Calcd for $C_{21}H_{21}N_3$: C, 80.00; H, 6.67; N, 13.30. Found: C, 80.23; H, 6.91; N, 12.80. Ir spectrum (CCl_4) ν_{max} 3390 (NH), 3220 (NH), and 1450 cm^{-1} (N═N); uv spectrum (cyclohexane) λ_{max} 293 nm (ϵ 21,100), 323 (14,000), and 482 (8400); nmr spectrum ($CDCl_3$) 2.38 (6 H, methyl), 2.46 (3 H, methyl), 7.45 (11 H, multiplet, aromatic), and 10.2 ppm (1 H, NH).

Further elution of the column with a mixture (2:1) of petroleum ether and benzene gave a red, viscous material which was repeatedly chromatographed to give 17 mg (0.2%) of 2,2′-bis(*m*-toludino)-5,5′-azotoluene (**20d**), showing a single spot to tlc.

Anal. Calcd for $C_{28}H_{28}N_4$: N, 13.30. Found: N, 12.80. Ir spectrum (CCl_4) ν_{max} 3333 (NH) and 1480 cm^{-1} (N═N); nmr spectrum ($CDCl_3$) 2.29, 2.43 (12 H, methyl), and 6.99 ppm (14 H, multiplet, aromatic).

Reaction of 2-Nitrotoluene with Lithium.—A mixture of 4.1 g (0.03 mol) of 2-nitrotoluene and 1.1 g (0.15 g-atom) of lithium in 60 ml of tetrahydrofuran was stirred for 20 hr around 0–5°. Removal of the solvent under vacuum gave 2.6 g of a red, viscous solid which was chromatographed on alumina. Elution of the column with petroleum ether gave 650 mg (22%) of 2,2′-azotoluene, mp and mmp 54–55° after recrystallization from petroleum ether.

Reaction of 2-Chloronitrobenzene with Lithium.—2-Chloronitrobenzene (15.8 g, 0.01 mol) was treated with lithium (4.2 g, 0.06 g-atom) in tetrahydrofuran (200 ml) for a period of 4 hr around 0–5°. The reaction mixture was worked up in the usual manner to give 8.5 g of a dark, viscous material which was repeatedly chromatographed on alumina to give 1.8 g of a reddish-brown product which was subsequently chromatographed on silica gel. Elution of the column with petroleum ether gave 200 mg of 2,2′-bis(*o*-chloroanilino)azobenzene (**22**), which melted at 164° after recrystallization from petroleum ether.

Anal. Calcd for $C_{24}H_{18}N_4Cl_2$: C, 66.51; H, 4.16; N, 12.93. Found: C, 66.67; H, 3.99; N, 12.76. Ir spectrum (CCl_4) ν_{max} 3311 (NH) and 1450 cm^{-1} (N═N); uv spectrum (cyclohexane) λ_{max} 288 nm (ϵ 40,800), 320 (27,200), and 504 (15,300); nmr spectrum ($CDCl_3$) 7.65 (16 H, multiplet, aromatic) and 10.2 ppm (2 H, NH).

Attempted Reaction of 4-Nitroaniline with Lithium.—Treatment of 4-nitroaniline (4.1 g, 30 mmol) with lithium (1.4 g, 0.02 g-atom) in tetrahydrofuran (100 ml) for 24 hr and work-up in the usual manner led to the recovery of 3.8 g (93%) of unchanged 4-nitroaniline, mp and mmp 147°.

Attempted Reaction of 3-Nitroaniline with Lithium.—3-Nitroaniline (2.1 g, 15 mmol) was treated with lithium (0.7 g, 0.1 g-atom) in tetrahydrofuran (40 ml) for 18 hr. Removal of the unchanged metal and the solvent led to the recovery of 1.8 g (90%) of the starting 3-nitroaniline, mp and mmp 114°.

Attempted Reaction of 4-Nitroacetanilide with Lithium.—Treatment of 4-nitroacetanilide (1.8 g, 10 mmol) with lithium (0.35 g, 0.05 g-atom) in tetrahydrofuran (60 ml) for 8 hr and work-up of the reaction mixture as before gave 1.7 g (95%) of unchanged 4-nitroacetanilide, mp and mmp 210°.

Reaction of 2,2′-Dinitrobiphenyl (23) with Alkali Metals. A. With Lithium.—A mixture of 3.7 g (15 mmol) of **23** and 1 g (0.14 g-atom) of lithium was stirred in tetrahydrofuran (125 ml) for 12 hr. Work-up of the reaction mixture in the usual manner gave a dark brown mixture, which was chromatographed on alumina. Elution of the column with benzene gave 1.2 g (45%) of dibenzopyridazine (**24**), which melted at 156° after recrystallization from benzene. There was no depression in the melting point of this sample on admixture with an authentic sample of **24** prepared from **23** by lithium aluminum hydride reduction.[39] Further elution of the column with a mixture (3:1) of chloroform and benzene gave 26 mg of carbazole **25**, mp and mmp 252° after recrystallization from benzene.

B. With Sodium.—In a repeat run, 1.2 g (5 mmol) of **23** was treated with sodium (1.2 g, 0.5 g-atom) in 1,2-dimethoxyethane (60 ml). Work-up of the reaction mixture as before gave 450 mg (50%) of **24**, mp and mmp 156°.

Reaction of 2,2′-Dinitrodiphenyl Ether (26) with Alkali Metals. A. With Lithium.—2,2′-Dinitrodiphenyl ether (3.3 g, 13 mmol) was treated with lithium (0.8 g, 0.11 g-atom) in tetrahydrofuran (60 ml) for 48 hr with occasional stirring. Removal of the unchanged metal and the solvent under vacuum gave a brown material, which on recrystallization from methanol gave 2.3 g (77%) of unchanged starting material, mp and mmp 111°.

B. With Sodium.—In a repeat run, 2.6 g (10 mmol) of **26** was treated with 2.1 g (0.9 g-atom) of sodium in tetrahydrofuran for 28 hr. Removal of the unchanged metal and solvent under vacuum gave a material which was steam distilled after acidification with hydrochloric acid to give 215 mg (15%) of 2-nitrophenol, mp and mmp 44°.

Reaction of 1,8-Dinitronaphthalene with Lithium.—1,8-Dinitronaphthalene (3.1 g, 15 mmol) was treated with lithium (1.1 g, 0.15 g-atom) for 8 hr. Most of the metal was consumed during the course of the reaction. Removal of the solvent under vacuum gave a dark-colored, polymeric material from which no definite product could be isolated.

Reaction of Nitrosobenzene with Lithium.—Lithium metal (0.4 g, 0.06 g-atom) was added to a solution of nitrosobenzene (2.1 g, 20 mmol) in tetrahydrofuran (60 ml) and the reaction mixture was kept at room temperature for 28 hr, with occasional stirring. The solution, which was initially green, became dark brown at the end of this period. Removal of the solvent under vacuum gave a product which was chromatographed over alumina. Elution with petroleum ether gave 965 mg (53%) of azobenzene, mp and mmp 68°.

Further elution of the column with a mixture (5:1) of petroleum ether and benzene gave 190 mg (11%) of 2-anilinoazobenzene, mp and mmp 56°.

Reaction of 4-Nitroso-*N*,*N*-dimethylaniline with Lithium.—A mixture of 3 g (20 mmol) of 4-nitroso-*N*,*N*-dimethylaniline and 0.3 g (0.04 g-atom) of lithium in 50 ml of tetrahydrofuran was kept at room temperature for 18 hr. Removal of the unchanged metal and solvent under vacuum gave a brown solid which was chromatographed over alumina. Elution with benzene gave 750 mg (28%) of 4,4′-bis(*N*,*N*-dimethylamino)azobenzene, mp and mmp 272–273°.

Reaction of Azoxybenzene with Lithium.—Azoxybenzene (1 g, 5 mmol) was stirred with lithium (0.1 g, 0.014 g-atom) in tetrahydrofuran (40 ml) for a period of 30 min. Removal of the solvent under vacuum gave a product which was repeatedly extracted with hot benzene. Removal of the solvent from the benzene extract gave 0.9 g (99%) of azobenzene, mp and mmp 68° after recrystallization from ethanol.

Reaction of 4,4′-Azoxyanisole with Lithium.—4,4′-Azoxyanisole (1.3 g, 5 mmol) was dissolved in 40 ml of tetrahydrofuran and shaken with lithium (0.1 g, 0.014 g-atom) for 30 min. Work-up of the material as in the earlier case gave 1.2 g (99%) of 4,4′-azoanisole, mp and mmp 162°.

Reaction of α-4-Bromoazoxybenzene with Lithium.—A mixture of α-4-bromoazoxybenzene (2.1 g, 8 mmol) and lithium (0.14 g, 0.02 g-atom) in 50 ml of tetrahydrofuran was kept at room temperature for 1 hr with constant stirring. Removal of the solvent under vacuum gave a product which was extracted with hot benzene and the benzene-soluble portion was subsequently chromatographed over alumina. Elution of the column with petroleum ether gave 550 mg (40%) of azobenzene, mp and mmp 68°. Further elution with benzene gave a small quantity of an unidentified mixture of products.

Registry No.—**1,** 89-95-3; **2,** 103-33-3; **3,** 37436-61-6; **4,** 2074-94-4; **5,** 37436-63-8; **6,** 37436-64-9; **7,** 586-96-9; **17a,** 100-17-4; **17b,** 100-23-2; **17c,** 99-99-0; **17d,**

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99-08-1; **17e,** 88-72-2; **18a,** 501-58-6; **18b,** 6257-64-3; **18c,** 501-60-0; **18d,** 588-04-5; **18e,** 584-90-7; **19a;** 37436-65-0; **19b,** 37436-66-1; **19c,** 37436-67-2; **19d,** 37436-68-3; **20a,** 37436-69-4; **20d,** 37436-70-7; **21,** 88-73-3; **22,** 37436-71-8; **23,** 2436-96-6; **24,** 230-17-1; **25,** 86-74-8; **26,** 2217-65-4; **28,** 88-75-5; 2-aminodiphenylamine, 534-85-0; 4-nitrosodiphenylamine, 156-10-5; 4-nitroaniline, 100-01-6; 3-nitroaniline, 99-09-2, 4-nitroacetanilide, 104-04-1; azoxybenzene, 495-48-7, 4,4′-azoxyanisole, 1562-94-3; 2,4-bromoazoxybenzene, 16109-68-5.

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The Chemistry of Carbanions. XXII. C- *vs.* O-Acylation of Metal Enolates[1a]

HERBERT O. HOUSE,* ROBERT A. AUERBACH, MARTIN GALL,[1b] AND NORTON P. PEET

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

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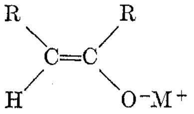
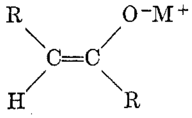
From a spectroscopic examination of metal enolates, the mercury(II) salts of ketones are found to exist as α-metalated ketones **2**, but salts with the metals lithium, sodium, zinc, and magnesium exist as enolate structures in which either contact ion pairs **4b** or solvent-separated ions **3** may be present. The existence of these metal enolates as solvent-separated ion pairs is favored (1) in a polar or a good solvating solvent, such as DME or DMF rather than ether; (2) by the presence of a metal cation such as lithium, sodium, or zinc rather than magnesium; and (3) by use of the trans (**1b**) rather than the cis (**1a**) stereoisomer of the enolate. In kinetically controlled reactions of metal enolates with acetylating agents, O-acylation is the favored reaction with α-metalated ketones **2** and with solvent-separated ion pairs **3**. The amount of of C-acylation is increased and may become the predominant reaction with metal enolates that exist as contact ion pairs **4b**. When the solvent and metal cation are kept constant, more C-acylation is obtained when acetyl chloride or acetyl bromide is used as the acylating agent rather than acetic anhydride or ketene.

Enolate anions **1** are members of a group of ambident nucleophiles that react wtih alkylating agents or acylating agents to form products with a new bond either at carbon or at oxygen.[2] When solutions of alkali metal enolates of monoketones in aprotic solvents are added slowly to an excess of reactive acylating agents such as (CH$_3$CO)$_2$O or CH$_3$COCl, the major products of this kinetically controlled processes are usually the O-acetylated derivatives corresponding in structure and stereochemistry to the starting enolates.[2b,3] However, several groups have noted that, even with reaction procedures that result in kinetically controlled acylation, mixtures of C- and O-acylated products may result, especially when the metal cation is halomagnesium rather than lithium or sodium.[2b,3a,4] The proportion of C-acylation is also enhanced by the use of relatively nonpolar solvents,[2b,3a,4] by use of the metal enolate stereoisomer **1a** with the metal alkoxide and the β substituent trans[3a,b,4b] and by the use of acid chlorides rather than acid anhydrides as acylating agents.[4b]

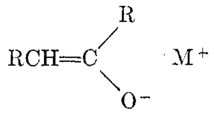

1a (cis enolate)

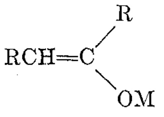

1b (trans enolate)

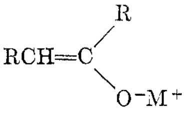
Consideration of this information has led us to the hypothesis that the reactions of ketone metal enolates can be explained by considering them to have one of three general structures: (1) structure **2** with a covalent carbon–metal bond; (2) solvent-separated ions **3**; or (3) either structure **4a** with a covalent metal–oxygen bond or the related contact ion pair **4b**. It is probable that many examples of the latter structures **4** will exist in solution as molecular aggregates (dimers, trimers, tetramers), especially with nonpolar solvents and in cases with small R groups which do not sterically impede aggregation.[5]


$R\underset{\underset{M}{|}}{C}H\underset{\underset{O}{\|}}{C}R$

2 (covalent)


3 (solvent-separated ions)


4a (covalent)


4b (contact ion pair)

In light of earlier discussions of ambident anions,[2] it would be expected that treatment with reactive acylating agents would lead to predominant O-acylation of enolates **2** and **3** and predominant C-acylation of enolates **4**. For this study we have prepared solutions of several metal enolates, determined the products

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