ADDITION OF CARBANIONS TO AZOBENZENE IN LIQUID AMMONIA

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Azobenzene (I) has long been known to react with carbanions to afford products wherein the azobenzene is reduced to aniline and/or hydrazobenzene with concomitant oxidative dimerization of the organometallic (1). For example, such reactions have been realized in ethyl ether with various metallophenyl reagents where the metal has been lithium, sodium, beryllium, magnesium, manganese, and zinc; biphenyl was often observed as the oxidation product (1). More recently, azobenzene has been reduced to its radical anion by a wide variety of alkali enolates, alkoxides, and carbanions derived from hydrocarbons in dimethyl sulfoxide solutions (2).

In contrast, addition of organometallic reagents across the azo linkage of azobenzene to afford substituted hydrazines has but rarely been observed. Such additions to I appear to have been accomplished only with the highly reactive phenylcalcium iodide and phenylpotassium (1), and with phenyllithium (3) to afford triphenylhydrazine (II).
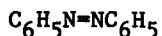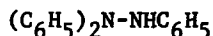
$$C_6H_5N=NC_6H_5 \qquad\qquad (C_6H_5)_2N-NHC_6H_5$$
$$\text{I} \qquad\qquad\qquad\qquad\quad \text{II}$$

This current study was prompted by the possibility that less reactive carbanions than those above might be oxidatively dimerized by azobenzene in liquid ammonia. Such an organic oxidizing agent would complement the inorganic ones previously reported in this solvent, for example, potassium permanganate (4).

Surprisingly, though, mixing of ethereal solutions of azobenzene with various carbanions in liquid ammonia has afforded products arising only from addition of the carbanions to the N-N double bond. Indeed, in no case studied to date with azobenzene have oxidative dimerizations of anions been observed in this laboratory.

The results are summarized in Table I. This Table shows that

sodiodiphenylmethane (III, M = Na) adds to azobenzene, presumably via anion IV', to afford hydrazine IV in 77% yield. Likewise, potassiodiphenylmethane (III, M = K) adds to I to give IV in 15-72% yield. It is interesting that the yields of IV in the latter reactions increase dramatically when shorter reaction periods are employed, and when the reaction mixtures are neutralized inversely rather than directly.
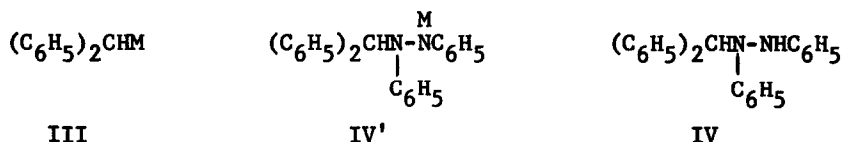
$$(C_6H_5)_2CHM \qquad\qquad (C_6H_5)_2CH\underset{\underset{C_6H_5}{|}}{\overset{\overset{M}{|}}{N}}-NC_6H_5 \qquad\qquad (C_6H_5)_2CH\underset{\underset{C_6H_5}{|}}{N}-NHC_6H_5$$

$$\text{III} \qquad\qquad\qquad \text{IV'} \qquad\qquad\qquad\qquad \text{IV}$$

TABLE I

Addition of Carbanions to Azobenzene in Liquid Ammonia

Substrate	MNH_2, M=	Time, min[a]	Neut'n mode[b]	Product	Yield, % [c]
Diphenylmethane	Na	5	In	IV	77
Diphenylmethane	K	10	In	IV	72
Diphenylmethane	K	10	Di	IV	50
Diphenylmethane	K	20	Di	IV	28
Diphenylmethane	K	120	Di	IV	15
3-Phenylphthalide	Na	5	In	V	30
4-Picoline	Na	5	In	VI	31
2-Methylpyrazine	Na	5	In	VII	39
Phenylacetamide	Na[d]	5	In	VIIIa	29
Phenylacetanilide	Na[d]	5	In	VIIIb	49
Phenylacetonitrile	Na	5	In	X	12

[a] Time before neutralization after addition of azobenzene completed.

[b] In = inverse neutralization (addition of reaction mixture to ammonium chloride in ammonia), Di = direct neutralization.

[c] Material balances in all cases were nearly quantitative.

[d] Two molecular equivalents of sodium amide were employed.

Table I also shows that 3-sodio-3-phenylphthalide, α-sodiopicoline, and α-sodiopyrazine add to azobenzene to afford hydrazines V, VI and VII in fair yields, respectively. That such additions to I are not limited to monoanions was demonstrated by the condensations of disodiophenylacetamide and
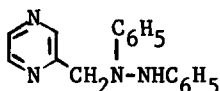
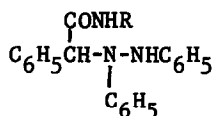disodiophenylacetanilide with I to give hydrazines VIIIa and VIIIb,
respectively.

V

VI

VII

$$\begin{array}{c} CONHR \\ | \\ C_6H_5CH\text{-}N\text{-}NHC_6H_5 \\ | \\ C_6H_5 \end{array}$$
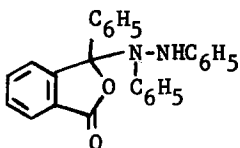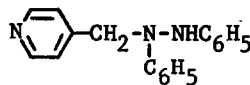
VIIIa, R = H
    b, R = C_6H_5

Unexpectedly, even the weakly nucleophilic sodiophenylacetonitrile (IX)
adds to azobenzene, but the product isolated was the enamine X. Formation of
X can be rationalized by *in situ* elimination of N-sodioaniline (a base-
catalyzed deamination) to form the anil of benzoyl cyanide, followed by
addition of a second equivalent of IX and subsequent elimination of cyanide
ion (after a proton shift). Enamine X has also been obtained by reaction of
IX with nitrosobenzene in ammonia (5).

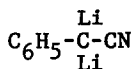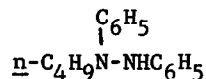$$\begin{array}{c} Na \\ | \\ C_6H_5CHCN \end{array}$$
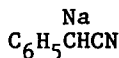
IX
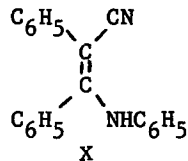
X

Incidentally, tetrahydrofuran (THF) has also been found to be a suitable
solvent for addition of certain organolithium reagents to azobenzene. Thus,
1,1-dilithiophenylacetonitrile (XI) and n-butyllithium add to I to afford
enamine X and hydrazine XII in fair yields, respectively.

$$\begin{array}{c} Li \\ | \\ C_6H_5\text{-}C\text{-}CN \\ | \\ Li \end{array}$$

XI

$$\begin{array}{c} C_6H_5 \\ | \\ \underline{n}\text{-}C_4H_9N\text{-}NHC_6H_5 \end{array}$$

XII

The success of the present method is apparently due to the recognition

that addition of carbanions to azobenzene is kinetically controlled; this was demonstrated by adding the hydrazine IV to ten mole percent (catalytic amount) of potassium amide in ammonia to afford azobenzene and hydrazobenzene; none of hydrazine IV was present in the products as indicated by tlc. Thus, to maximize the yields of the desired hydrazines, short reaction periods and inverse neutralization of the reaction mixtures must be employed to prevent reversion of intermediate anions like IV' to more thermodynamically stable products.

It appears that the presently described convenient and rapid additions of carbanions to azobenzene should consitute a general method for synthesizing new and interesting substituted hydrazines. The scope and limitations, metallic cation effects, and thermodynamic versus kinetic control in such additions are currently being investigated.

References:

1. See H. Gilman and J. C. Bailie, J. Org. Chem., 2, 84 (1937), and references cited therein.
2. G. A. Russell, R. Konaka, E. T. Strom, W. C. Danen, K.-Y. Chang, and G. Kaupp, J. Amer. Chem. Soc., 90, 4646 (1968), and earlier work cited therein.
3. P. F. Holt and B. P. Hughes, J. Chem. Soc., 764 (1954).
4. E. M. Kaiser, J. Amer. Chem. Soc., 89, 3659 (1967).
5. See H. G. Aurich, Chem. Ber., 98, 3917 (1965).