pressure, yielding 4.02 g of crude product, which was dissolved in hexane and chromatographed on Merck alumina. Elution with hexane gave 1.20 g (20%) of pentenone: bp 99–101° (0.32 mm); nmr 1.21 (d, J = 6 Hz, CH_3CH), 2.10 (br s, 3 H, CH_3), 2.15 (m, 1 H, CH), 6.49 (br s, 1 H, vinyl CH), 7.13 (m, 3 H, ArH), 7.62 ppm (m, 2 H, ArH); ir 3.35, 5.95, 6.25 μ. This material could not be obtained completely homogenous to glc and was characterized by mass spectrometry, molecular ion at m/e 188.

Cyclization of 3,4-Dimethyl-1-phenyl-2-penten-1-one. A.—A solution of 0.10 g (0.53 mmol) of 3,4-dimethyl-1-phenyl-2-penten-1-one in 1.0 ml of dry benzene was added to a chilled slurry of 0.227 g (1.7 mmol) of aluminum chloride in 4.0 ml of dry benzene. The reaction mixture was stirred at ice bath temperature for 1 hr and then heated at reflux for 2 hr. Isolation of the product in the manner previously described gave 0.095 g (95%) of a viscous oil which was shown by glc to consist of 3,4-dimethyl-1-phenylpentan-1-one (4) and 3,3,4-trimethyl-1-tetralone (1) in a ratio of 6:94, respectively.

B.—A solution of 0.4 g (2.1 mmol) of 3,4-dimethyl-1-phenyl-2-penten-1-one in 5.0 ml of benzene-d_6 was added to a chilled, stirred slurry of 0.64 g of aluminum chloride in 15 ml of benzene-d_6. The reaction was carried out and the product was isolated as described above to give 0.36 g (90%) of viscous oil. The crude product was dissolved in benzene and chromatographed on alumina. Ether eluted the product, which was shown to be homogenous by vapor phase chromatography and the nuclear magnetic resonance and infrared spectra of which were identical with those of 3,4,4-trimethyl-1-tetralone obtained from the Friedel–Crafts reaction of 3,4,4-trimethylbutyrolactone and benzene.

Registry No.—**1**, 2981-99-9; **2**, 2981-96-6; **3**, 2982-01-6; **4**, 32557-33-8; **5**, 2977-36-8; **11**, 32557-35-0; benzene, 71-43-2; ethyl 3,4-dimethyl-2-pentenoate, 6570-79-2; 3,4-dimethyl-2-pentenoic acid, 32557-37-2; 3,4-dimethylpentanoic acid, 3302-06-5.

Interaction of Carbanions with Azobenzene and Related Compounds[1a,b]

EDWIN M. KAISER* AND GREGORY J. BARTLING[1c]

Department of Chemistry, University of Missouri, Columbia, Missouri 65201

Received March 30, 1971

Reaction of alkali salts of active hydrogen compounds with azobenzene follow three general pathways: (1) addition to afford substituted hydrazobenzenes; (2) oxidation–reduction to often give dimer of the active hydrogen compound; and (3) addition–elimination to afford anils. In contrast to earlier work, the current study has ascertained that the most general pathway for such reactions is addition. Thus, the synthesis of 21 new hydrazobenzenes, prepared by three different methods, is reported. The addition reactions, apparently kinetically controlled in ammonia, proceed *via* intermediate monoanions of the hydrazobenzenes as evidenced by a trapping experiment with benzoyl chloride. Redox reactions have currently been observed only in two rather special cases: 9,10-dipotassioacenaphthene with azobenzene, and lithiodiphenylmethane with a highly conjugated azo compound. Interaction of either the monoalkali or geminal dialkali salts of phenylacetonitrile with azobenzene has given an interesting cyanoenamine, presumably *via* a novel "base-catalyzed" deamination. Similar deaminations have been observed with other systems, including some hydrazobenzenes, to afford anils. Certain of the latter conversions are rationalized by considering the thermodynamic and kinetic acidities of the hydrazobenzenes.

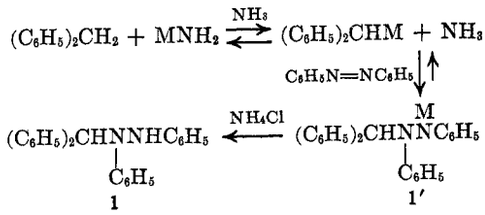
Previously, it has been shown that carbanions usually transfer an electron to the azo linkage of aromatic azo compounds in solutions of ether[2a] or dimethyl sulfoxide,[2b] resulting in reduction of the nitrogen–nitrogen double bond and, sometimes, in isolation of the oxidative dimer of the carbanion.[2a] Only rarely, though, have such reactions resulted in ionic addition of carbanions across the azo linkage to give substituted hydrazo compounds. Thus, the highly reactive phenylpotassium,[2a] phenylcalcium iodide,[2a] and phenyllithium[3] have been observed to so add to azobenzene to afford 1,1,3-triphenylhydrazine in low yields.

Our initial interest in azobenzene and related compounds stemmed from their potential use as oxidants in the dimerization of carbanions in liquid ammonia.[4] Instead of the expected oxidation–reduction reactions, though, these interactions have been found to constitute a presumably general synthesis of arylated hydrazines. This paper describes the three methods developed to effect such syntheses and illustrates not only interesting solvent and temperature effects, but also discusses novel base-catalyzed deaminations of certain of the hydrazine products.

Results and Discussion

Initial efforts were directed toward interacting the monoalkali salts of diphenylmethane with azobenzene in liquid ammonia. Surprisingly, aside from some recovered starting materials, only hydrazine **1**, the product arising from addition across the azo linkage, was isolated in variable yields (Scheme I); the expected dimeric product, 1,1,2,2-tetraphenylethane, was absent. The highest yields of **1** were realized by employing sodium or potassium cations for relatively short reaction periods (5–10 min) and by inversely neutralizing the reaction mixtures[5] (method A). For

SCHEME I



1 1′

(1) (a) Supported by the Petroleum Research Fund, administered by the American Chemical Society, on Grant 3710-A. (b) A preliminary report has been published; see E. M. Kaiser and G. J. Bartling, *Tetrahedron Lett.*, 4357 (1969). (c) Shell Fellow, 1971.

(2) (a) H. Gilman and J. C. Bailie, *J. Org. Chem.*, **2**, 84 (1937), and references cited therein; (b) 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 references 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) Inverse neutralization involves the pouring of a reaction mixture into ammonia containing excess ammonium chloride.

TABLE I
PREPARATION OF $RNNHC_6H_5$
C_6H_5

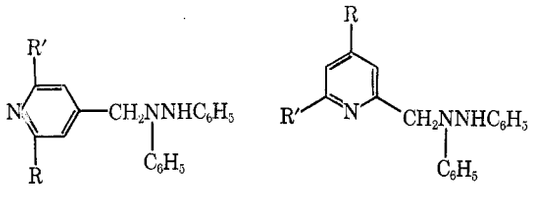
Active hydrogen compound, RH	Product	Mp, °C	Yields,[a] % A	B	C	Ir, cm^{-1}	Calcd, % C	H	N	Found % C	H	N
Diphenylmethane	1	115–119[b]	77	49	92	3290 (NH)	85.66	6.34	7.99	85.47	6.41	7.89
4-Picoline	2	124–126[c]	31	51	97	3240 (NH)	78.50	6.23	15.26	78.70	6.40	15.45
2,4-Lutidine	3	116–117[c]	5–10		82	3230 (NH)	78.85	6.63	14.52	79.06	6.58	14.46
2,4,6-Collidine	4	168–170[b]	28		77	3210 (NH)	79.16	6.99	13.85	79.25	7.08	13.78
2-Picoline	5	112–113[c]	0	29	69	3250 (NH)	78.50	6.24	15.26	78.51	6.05	15.11
2,4-Lutidine	6	142–144[b]		47[d]		3270 (NH)	78.85	6.63	14.52	79.00	6.70	14.38
2,6-Lutidine	7	119–121[b]			83	3270 (NH)	78.85	6.63	14.52	79.07	6.45	14.47
2,4,6-Collidine	8	104–105[c]		63[d]		3320 (NH)	79.16	6.99	13.85	79.16	7.04	13.80
2-Methylpyrazine	9	90–91[e]	39			3280 (NH)	73.87	5.84	20.28	74.00	5.68	20.43
2-Methylquinoline	10	137–140[c]	50			3230 (NH)	81.19	5.90	12.91	81.10	5.90	12.88
p-Tolunitrile	11	119–121[b]		19	73	3320 (NH) 2230 (CN)	80.23	5.73	14.04	80.15	5.67	13.89
3-Phenylphthalide	12	171–172[b]	30			3270 (NH)	79.56	5.14	7.14	79.41	5.12	7.21
2-Phenylacetamide	13	94–97[f]	29[g]			3500 (OH)[h] 3330 and 3175 (NH)	73.17[h]	7.22[h]	11.11[h]	73.05	7.09	10.93
2-Phenylacetanilide	14	134–137[e]	49[g]			3300, 3370 (NH)	79.33	5.90	10.68	79.16	5.99	10.75

[a] Method A, 1 equiv each of potassium amide (or sodium amide), RH, and azobenzene in liquid ammonia; method B, 1 equiv each of lithium diisopropylamide, RH, and azobenzene; method C, 2 equiv each of lithium diisopropylamide and RH, 1 equiv of azobenzene. [b] Recrystallized from ethanol. [c] Recrystallized from cyclohexane. [d] 1 equiv of *n*-butyllithium was used as the base. [e] Recrystallized from aqueous ethanol. [f] Recrystallized from 2-propanol. [g] 2 equiv of sodium amide were employed. [h] This compound was obtained as a monosolvate (2-propanol).

example, sodiodiphenylmethane and azobenzene gave **1** in yields of 77 and 67% upon inverse neutralization after reaction periods of 5 and 15 min, respectively. Similarly, potassiodiphenylmethane afforded **1** in yields of 70 and 28% after 20-min reaction periods upon inverse and direct neutralization, respectively; direct neutralization of a similar 2-hr reaction using the potassium cation gave **1** in only 15% yield.

The above results are similar to the previously reported condensations of certain carbanions with aldehydes and ketones in ammonia and may be ascribed to the competition of a kinetically controlled addition reaction *vs.* a thermodynamically controlled reversion reaction.[6] In the current study, this would mean that the formation of **1′** is kinetically controlled and that, after some time, the active hydrogen compound, diphenylmethane, is reversibly regenerated along with alkali metal amide (Scheme I). The alkali metal amide then adds to or complexes with the azobenzene in a thermodynamically controlled process to possibly afford $C_6H_5N(M)$–$N(NH_2)C_6H_5$. Although attempts to isolate or trap this latter adduct were unsuccessful in addition reactions where reversion had occurred or in blank experiments involving potassium amide and azobenzene, both systems exhibited a unique purple color not seen in any other current reaction. More importantly, hydrazine **1** was found to be unstable to catalytic amounts of potassium amide in ammonia, since such treatment caused it to reverse to diphenylmethane and azobenzene. This result suggests that neutral diphenylmethane and neutral azobenzene are more thermodynamically stable than neutral hydrazine **1**.[6] In this reversion reaction, small amounts of **1′** would be formed which reverse to azobenzene and potassiodiphenylmethane; the latter salt would be protonated by un-ionized **1** to give diphenylmethane and **1′**. The process then would be repeated until all of **1** has been exhausted. A similar situation is thought to prevail when the normal addition reactions of carbanions with azobenzene are directly neutralized.

In addition to alkali salts of diphenylmethane, a wide variety of other carbanions were condensed with azobenzene in liquid ammonia (method A) as well as by means of an additional base–solvent system, lithium diisopropylamide in THF–hexane (method B). Moreover, the use of a twofold excess of carbanion over azo compound (method C), prepared by this latter base, proved even more successful. The results are listed in Table I. This table shows that diphenylmethane was condensed by each of the three methods to afford hydrazine **1** in fair to excellent yields. Similarly, the 4- and 2-picolyl anions were reacted to give hydrazines **2** and **5**, respectively. Likewise, 2,4-lutidine and 2,4,6-collidine, converted to their 4-lithio derivatives by lithium diisopropylamide, were condensed with azobenzene to give adducts **3** and **4**, respectively. Finally, 2,4-lutidine, 2,6-lutidine, and 2,4,6-collidine, converted to their 2-lithio salts by *n*-butyllithium, were similarly condensed to afford hydrazines

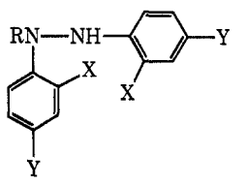


2, R = R′ = H
3, R = CH_3; R′ = H
4, R = R′ = CH_3

5, R = R′ = H
6, R = CH_3; R′ = H
7, R = H; R′ = CH_3
8, R = R′ = CH_3

(6) E. M. Kaiser and C. R. Hauser, *J. Org. Chem.*, **31**, 3873 (1966).

TABLE II

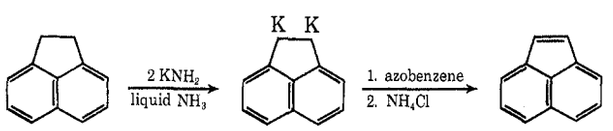
PREPARATION OF 

Active hydrogen compound, RH	Product	Method[a]	X	Y	Mp, °C	Yield, %	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
Diphenylmethane	16	A	Cl	H	152–154[b]	20	71.59	4.81	6.68	71.57	4.87	6.41
4-Picoline	17	B	Cl	H	155–156[c]	53	62.79	4.40	12.21	63.00	4.31	12.19
2-Picoline	18	B	Cl	H	95–96[d]	36	62.79	4.40	12.21	62.90	4.34	12.22
2-Methylquinoline	19	B	Cl	H	109–110[e]	7	67.00	4.35	10.66	67.25	4.47	10.76
p-Tolunitrile	20	C	Cl	H	128–130[e]	68	65.22	4.11	11.41	65.28	4.22	11.28
Phenylacetanilide	21	C	Cl	H	168–169[b]	6[f]	67.53	4.59	9.09	67.80	4.58	9.08
4-Picoline	22	B	H	Cl	135–136[g]	44	62.79	4.40	12.21	62.71	4.41	12.21

[a] See footnote *a*, Table I. [b] Recrystallized from 2-propanol. [c] Recrystallized from cyclohexane. [d] Recrystallized from 30–60° petroleum ether. [e] Recrystallized from benzene–ethyl acetate. [f] 2 equiv of lithium diisopropylamide were employed. [g] Recrystallized from benzene.

6, **7**, and **8**, respectively.[7] In all of the above reactions, method C was clearly superior to the other methods and is recommended as the one of choice for synthetic purposes. The superiority of method C is probably due to favorable shifts in equilibria toward intermediates like **1′** (Scheme II).

Certain other active hydrogen compounds were also condensed with azobenzene to give hydrazines. Thus, 2-methylpyrazine and 2-methylquinoline gave compounds **9** and **10**, respectively. Likewise, *p*-tolunitrile and 3-phenylphthalide gave **11** and **12**, while phenylacetamide and phenylacetanilide, which were converted to their 1,3-disodio salts,[8] gave adducts **13** and **14**, respectively. Interestingly, interaction of 9,10-dipotassioacenaphthene, prepared by treatment of acenaphthene with 2 equiv of potassium amide, and azobenzene afforded acenaphthylene (**15**) and hydrazobenzene (eq 1). In the current study, the latter reaction constitutes the only example of an oxidation–reduction reaction effected by azobenzene.

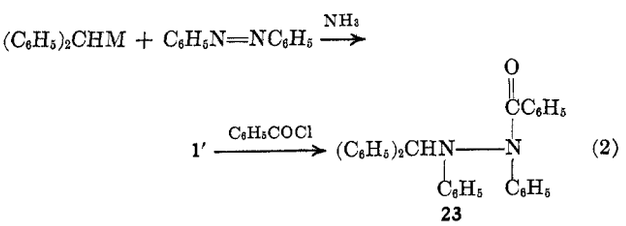


15 (1)

Incidentally, methods B and C were successful only when the addition of the azobenzene to the solutions of the carbanions were effected at low temperatures. For example, hydrazine **1** was obtained in only 18% yield when the condensation was carried out at 25° (method B), but the yield increased to 40% when the temperature was maintained at −78°. Models indicate that **1** is not entirely free of rotational restrictions. Thus, it is attractive to explain the above temperature effects in terms of steric compression in intermediates like **1′**; such compression should be felt less at lower temperatures than at higher ones.

Next, several condensations of carbanions with chlorinated azobenzenes were realized, mostly by employing methods B and C. The results, listed in Table II, are similar to those realized above on the parent azo compound. Thus, 2,2′-dichloroazobenzene was condensed with diphenylmethane, 4-picoline, and 2-picoline to give hydrazines **16**, **17**, and **18**, respectively. This azo compound was also condensed with 2-methylquinoline, *p*-tolunitrile, and phenylacetanilide to give **19**, **20**, and **21**, respectively. Finally, 4,4′-dichloroazobenzene was condensed with 4-picoline to give **22**. Although the yields in these reactions were, at best, only fair, the material balances were excellent, unreacted starting materials being quantitatively recovered. These results would suggest that the anions in the current study are not displacing the halides in the molecules. Such nucleophilic aromatic substitutions have been reported on certain azobenzenes containing an *o*-methoxy group.[9] It should be mentioned that attempted condensations of certain carbanions with 4,4′-dimethylazobenzene failed, presumably because of the limited solubility of this compound; even if this compound were soluble, though, the substituent effects of the methyl groups would be expected to decrease the reactivity of the azo linkage toward addition reactions.

The above condensations of carbanions with azobenzene probably proceed *via* a nucleophilic addition type of mechanism similar to that observed with carbonyl compounds. This was demonstrated by trapping the proposed intermediate **1′** in the reaction of potassiodiphenylmethane with azobenzene by means of benzoyl chloride. Thus, in addition to obtaining some of **1**, benzoyl derivative **23** was obtained in low yield (eq 2).



23 (2)

One condensation of an active hydrogen compound with azobenzene deserves special mention. Thus, reaction of sodio- or lithiophenylacetonitrile, prepared by means of the corresponding alkali amides in ammonia, or of dilithiophenylacetonitrile, prepared by *n*-

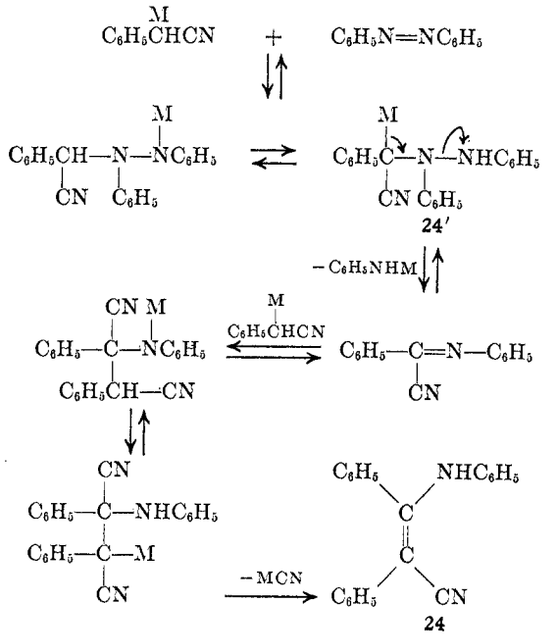
(7) A manuscript is currently in preparation dealing with the different site of metalation of polymethylpyridines as a function of the base.

(8) R. B. Meyer and C. R. Hauser, *J. Org. Chem.*, **26**, 3696 (1961).

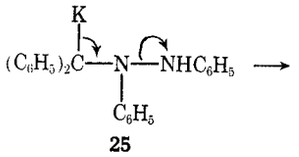
(9) For example, see S. Bozzini, A. Risaliti, and A. Stener, *Tetrahedron*, **26**, 3927 (1970).

butyllithium in THF–hexane,[10] all surprisingly afforded cyanoenamine **24** in low yield (Scheme II). Product **24**, pictured as arising from the elimination of the alkali metal derivative of aniline from **24′** to give benzoyl cyanide anil, was not expected since deminations are usually promoted by acid catalysts. A similar reaction has been reported in the addition of potassiophenylacetonitrile to nitrosobenzene in *tert*-butyl alcohol[11] where the leaving group is potassium oxide (or hydroxide).

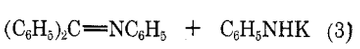
SCHEME II



The novel base-catalyzed deamination reaction proposed in Scheme II was also observed in certain other cases. For example, treatment of hydrazine **1** with 1 molecular equiv of potassium amide in liquid ammonia cleanly afforded benzophenone anil (**26**). This anil can be pictured as arising *via* ionization of the benzhydrylic proton of **1** to give **25** followed by loss of *N*-potassioaniline (eq 3).



25

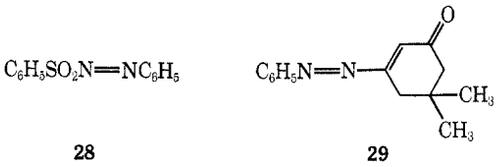


(3)

26 **27**

That treatment of hydrazine **1** with potassium amide afforded **26** (presumably *via* **25**) is particularly interesting when compared with the base-catalyzed reversion of **1** to diphenylmethane and azobenzene described above. It thus appears that **1** may interact with base either at the nitrogen hydrogen to give **1** which can eliminate potassiodiphenylmethane, or at the benzhydrylic hydrogen to give **25** which can eliminate *N*-potassioaniline. It is attractive to explain such differences in products in terms of kinetic *vs.* thermodynamic acidities. Based on rapid exchange reactions with deuterium oxide, the N–H, but not the benzhydrylic protium, readily and completely exchanges as evidenced by nmr spectroscopy. Therefore, we suggest that, kinetically, the N–H is more acidic than the benzhydrylic proton of **1** and rapidly, but reversibly, is ionized. We further suggest that, thermodynamically, the benzhydrylic proton is more acidic than the N–H since the resulting carbanion (**25**) is more highly resonance stabilized than is the nitrogen anion (**1′**). Once **25** is formed, though, it apparently eliminates *N*-potassioaniline (**27**) immediately, since all attempts to trap **25** have failed and only anil **26** has been obtained.

Finally, certain condensations of lithiodiphenylmethane were attempted on two azo compounds other than those directly related to azobenzene. Thus, interaction of this carbanion with azo sulfone **28** at 25° afforded anil **26** in 21% yield along with an equivalent amount of benzenesulfonamide. The mechanism of this conversion is presumably similar to that shown in eq 3. Surprisingly, though, reaction of lithiodiphenylmethane with the novel azo compound **29** failed to give either addition or elimination product. Instead, oxidation–reduction occurred, since 1,1,2,2-tetraphenylethane was obtained in 72% yield.



28 **29**

All of the hydrazines described above appear to be new. Their structures were supported by infrared spectroscopy and by correct elemental analyses (Tables I and II) and, in some cases, by nmr spectroscopy.

The currently described condensations of azobenzene and its derivatives with various organometallic reagents should be capable of extension to afford a wide variety of highly substituted hydrazines. Moreover, products of addition, elimination, and oxidation–reduction can be expected from these reactions, with the reaction path obviously dependent on specific structural characteristics of the azo compound. Methods by which these characteristics may be correlated with reaction paths to allow prediction of the products are at present unknown. Even more interesting is the broader area of condensations of carbanions with "novel" electrophiles of which azobenzene may be considered to be the first example.

Experimental Section[12]

Preparation of Substituted Hydrazobenzenes.—Tables I and II list the specifics for each of the hydrazines prepared in this study. Examples illustrating the preparation of *N*-diphenylmethylhydrazobenzene by means of each of the methods follow.

Method A.—To a stirred solution of 0.05 mol of potassium amide (or sodium amide) in 350 ml of anhydrous liquid ammonia[13] was added a solution of 8.4 g (0.05 mol) of diphenylmethane in 50 ml of anhydrous ethyl ether. After 30 min, the resulting solution was treated with a solution of 9.1 g (0.05 mol) of azobenzene in 30 ml of ether added during 5 min. The now blue-

(10) E. M. Kaiser and C. R. Hauser, *J. Amer. Chem. Soc.*, **88**, 2348 (1966).

(11) H. G. Aurich, *Chem. Ber.*, **98**, 3917 (1965).

(12) Infrared spectra were measured on a Perkin-Elmer Model 237B grating infrared spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

(13) See C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. React.*, **8**, 122 (1954).

green mixture was stirred for an additional 5 min and then poured with stirring into 300 ml of ammonia containing 20 g of ammonium chloride. After allowing the solvents to evaporate, the solid residue was extracted with benzene. Upon concentration, a red oil was obtained which solidified upon standing.[14] The crude solid was purified as indicated in Table I.

Method B.—To a solution of 5.0 g (0.05 mol) of diisopropylamine in 200 ml of anhydrous THF was added, *via* a hypodermic syringe, 32 ml (0.05 mol) of 1.6 *M* *n*-butyllithium in hexane.[15] After stirring for 15 min, the yellow solution was treated with 8.4 g (0.05 mol) of diphenylmethane in 50 ml of THF and the mixture was stirred for 1 hr. Upon cooling to −78° by means of a Dry Ice–acetone bath, the mixture was then treated during 5 min by the dropwise addition of a solution of 9.1 g (0.05 mol) of azobenzene in 50 ml of THF. After stirring for 5 min, the mixture was poured into 400 ml of water containing excess ammonium chloride. The organic phase was separated, the aqueous phase was extracted with benzene, and the extracts were combined. Removal of the solvent by distillation yielded crude solid product which was purified as indicated in Table I.

Method C.—This method is identical with method B except for the use of 0.5 equiv (4.5 g, 0.025 mol) of azobenzene. The yields thus reported in Tables I and II are based on azobenzene.

Conversion of Acenaphthene to Acenaphthylene.—Solid acenaphthene (7.7 g, 0.05 mol) was added in portions to a solution of 0.1 mol of potassium amide in 350 ml of liquid ammonia.[13] After 30 min, the dark green mixture was treated with a solution of 9.1 g (0.05 mol) of azobenzene in 50 ml of ether and the mixture was stirred for 4 hr. At the end of this time, the mixture was directly neutralized by the addition of ammonium chloride and worked up as in method A above to give a red oil which was chromatographed on alumina with benzene, then methanol, to give 11.3 g of material. The latter was treated with a solution of 11.0 g (0.05 mol) of picric acid in 30 ml of boiling ethanol to afford 10.1 g (53%) of acenaphthylene picrate, mp and mmp 201–203° (lit.[16] mp 201–202°).

Preparation of 1-Anilino-2-cyano-1,2-diphenylethylene (24).—To 0.05 mol of sodium amide in 300 ml of liquid ammonia was added a solution of 5.8 g (0.05 mol) of phenylacetonitrile in 50 ml of ether. After stirring briefly, the mixture was treated with a solution of 9.1 g (0.05 mol) of azobenzene in 50 ml of ether added during 10 min. The mixture was stirred for 5 min, then neutralized and worked up as above. The resulting red oil (16.6 g) was chromatographed on alumina using benzene and ethyl acetate as eluents to give 3.7 g of yellow solid. Recrystallization of the solid from alcohol gave 0.9 g (6.0%) of fine yellow needles: mp 203–204° (lit.[11] mp 202–203.5°); ir (Nujol) 3250 (NH), 2200 (CN), 1240, 1030, and 750 cm^{-1}.

Anal. Calcd for $C_{21}H_{16}N_2$: C, 85.11; H, 5.44; N, 9.45. Found: C, 85.31; H, 5.48; N, 9.30.

Similar results were obtained by employing lithium amide in ammonia or with 2 equiv of *n*-butyllithium in THF–hexane.

Preparation of *N*-Diphenylmethyl-*N'*-benzoylhydrazobenzene (25).—To a solution of 0.05 mol of lithiodiphenylmethane in THF at −78° was added during 5 min a solution of 0.025 mol of azobenzene in THF as in method C above. The resulting mixture was treated immediately with a solution of 7.0 g (0.05 mol) of benzoyl chloride in THF added during 5 min. After stirring for 1 hr at −78°, the dark blue mixture was poured into 600 ml of water containing excess ammonium chloride. The organic layer was separated and the aqueous layer was extracted several times with benzene. Removal of the solvent gave 17.8 g of a thick orange oil which was crystallized from acetone to give 2.6 g (23%) of product **25**: mp 194° dec; ir (Nujol) 1650 (C=O), 1590, 1280, 1235, and 1155 cm^{-1} (aromatic).

Anal. Calcd for $C_{32}N_{26}N_2O$: C, 84.55; H, 5.77; N, 6.16. Found: C, 84.77; H, 5.66; N, 5.90.

Reaction of *N*-Diphenylmethylhydrazobenzene (1) with Stoichiometric Amounts of Potassium Amide in Liquid Ammonia.—To 0.029 mol of potassium amide in 350 ml of ammonia was added a solution of 10.0 g (0.029 mol) of hydrazine **1** in 30 ml of THF. After 1 hr, the blue-green mixture was inversely neutralized and worked up as usual to give 9.9 g of a red oil. Crystallization of the oil from alcohol gave 0.6 g (6.2%) of 1,1,2,-2-tetraphenylethane, mp 208–210° (lit.[17] mp 209°); the ir of this compound was identical with that of an authentic sample. Concentration of the alcohol solution afforded 5.2 g (70%) of benzophenone anil (**26**): mp 113–115° (lit.[18] mp 113–114°); ir (Nujol) 1615 (C=N), 1590, 1225, 1140, and 955 cm^{-1} (aromatic).

Anal. Calcd for $C_{19}H_{15}N$: C, 88.67; H, 5.89; N, 5.44. Found: C, 89.10; H, 5.50; N, 5.36.

Reaction of *N*-Diphenylmethylhydrazobenzene with Catalytic Amounts of Potassium Amide in Liquid Ammonia.—This reaction was carried out exactly as described above, except for the use of only a catalytic amount (0.005 mol) of potassium amide. The work-up of the mixture afforded an orange oil which was chromatographed on alumina. Elution with ligroin followed by ligroin–benzene mixtures allowed isolation of 5.1 g of an orange oil which consisted of starting materials as analyzed by tlc and nmr. The middle fractions were combined to yield 0.3 g of 1,1,2,2-tetraphenylethane (3.1%), and concentration of the filtrate gave 0.4 g (5.4%) of benzophenone anil (**26**), mp 111–113°.

Reaction of Potassiodiphenylmethide with Phenylphenylsulfonyl Diimide (28).—To 0.025 mol of potassiodiphenylmethane in 350 ml of liquid ammonia, prepared as above, was added dropwise a solution of 6.1 g (0.025 mol) of **28** in ether. After stirring for 3 hr, the reaction mixture was inversely neutralized and worked up as above to give 1.3 g (21%) of benzophenone anil, mp 112–114°.

Interaction of Lithiodiphenylmethane with 5,5-Dimethyl-3-oxo-1-phenylazo-1-cyclohexene (29).—Lithiodiphenylmethane (0.05 mol) in 180 ml of THF, prepared by method B, was treated at 0° with a solution of 5.7 g (0.025 mol) of **29**[19] in 30 ml of THF added during 5 min. The resulting mixture was stirred for 30 min at 0°, then neutralized and worked up as above to afford, upon treatment with boiling alcohol, 6.0 g (72%) of 1,1,2,2-tetraphenylethane, mp 207–209°; the infrared spectrum was identical with that of an authentic sample.

Registry No.—**1**, 32812-31-0; **2**, 32812-32-1; **3**, 32812-33-2; **4**, 32812-34-3; **5**, 32812-35-4; **6**, 32812-36-5; **7**, 32812-37-6; **8**, 32812-38-7; **9**, 32812-39-8; **10**, 32812-40-1; **11**, 32812-41-2; **12**, 32812-42-3; **13**, 32812-43-4; **14**, 32812-44-5; **16**, 32812-45-6; **17**, 32812-46-7; **18**, 32812-47-8; **19**, 32812-48-9; **20**, 32812-49-0; **21**, 32812-50-3; **22**, 32812-51-4; **24**, 4686-15-1; **25**, 32819-57-1; **26**, 574-45-8; azobenzene, 103-33-3.

(14) In certain cases, the crude reaction mixtures were chromatographed on alumina and the products were eluted with benzene–ethyl acetate; unreacted azobenzene was always the first compound to be eluted.

(15) Obtained from the Foote Mineral Co., Exton, Pa.

(16) M. C. Kloetzel and H. E. Mertel, *J. Amer. Chem. Soc.*, **72**, 4786 (1950).

(17) A. Zagoumenny, *Ann. Chim. (Paris)*, **184**, 177 (1876).

(18) C. M. Rosser and J. J. Ritter, *J. Amer. Chem. Soc.*, **59**, 2179 (1937).

(19) A. J. Fatiadi, *J. Org. Chem.*, **35**, 831 (1970).