[CONTRIBUTION FROM THE UNIVERSITY OF TORONTO]

Adducts of Alkali Metals with Azobenzene

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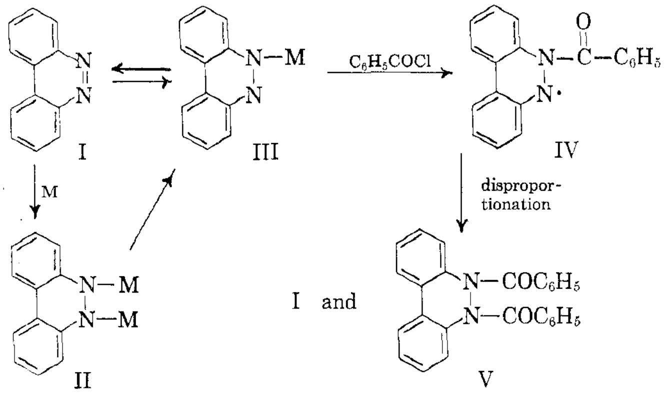
Adducts have been prepared directly from azobenzene and two atom equivalents of lithium, sodium, and potassium. In general these dimetal adducts are less reactive than the analogous stilbene-dimetal adducts. Benzyl chloride, which couples to diphenylethane upon treatment with stilbene-disodium adduct, gives a good yield of *N,N'*-dibenzyl-*N,N'*-diphenylhydrazine. Normal alkyl halides and methyl sulfate give only *N,N'*-disubstituted hydrazobenzenes but secondary and tertiary halides, and a phosphate, give *N*-monosubstituted hydrazobenzene. Isopropyl methanesulfonate, however, gives both mono- and disubstituted hydrazobenzenes. The monosubstituted hydrazobenzenes may be obtained from the diphenylhydrazyl metal, which is derived from equivalent amounts of the dimetal adduct and hydrazobenzene. The nature of azobenzene-monometal adducts has not been demonstrated but they are probably not free radicals.

In their comprehensive report on the addition of alkali metals to aromatic unsaturated compounds Schlenk and Bergmann[1] mention the reaction of azobenzene with sodium in ethyl ether to form an unidentified precipitate. They were more successful in the use of potassium phenylbiphenylethyl as a source *in situ* of metal; they obtained an adduct comprising 1 atom of potassium per mole of azobenzene. Later Wittig[2] prepared *N,N*-'dilithiumdiphenylhydrazyl by treatment of hydrazobenzene with methyllithium in ethyl ether. When he treated this indirectly prepared di-adduct with an equivalent of azobenzene in ethyl ether a color change occurred. The resulting system was equivalent to *N*-monolithium diphenylhydrazyl and was designated by Wittig as a free radical, C_6H_5-N-N(Li)C_6H_5.

Thus, the direct addition of alkali metals to azobenzene was not accomplished, but several adducts from analogs were reported. A disodium adduct in ethyl ether from azomethane and from 1,10-dimethyl dibenzopyridazine[3] was reported, and later both disodium and dilithium adducts were obtained from dibenzopyridazine I in ethyl ether.[4] The latter dimetal adducts II (M = Na or Li) were converted to monometal adducts (1:1 metal and azo compound) by treatment of dibenzopyridazine in the manner described previously.[2,5] A characteristic color change and also magnetic susceptibility measurement have persuaded Wittig *et al.* that the monometal adduct system contains about 50% of the free radical III in mobile equilibrium with I and II. Furthermore they postulated that the reaction product of the radical III and benzoyl chloride, *N*-benzoyl dibenzopiperazine, IV, disproportionates into the dibenzoyl derivative, V, and I (the actual products).



By use of 2,5-dioxahexane as the reaction medium we have obtained the dimetal adducts of azobenzene with lithium, sodium, and potassium in quantitative yield. Presumably the dilithium adduct is identical with Wittig's product from hydrazobenzene and methyllithium since it gives the same alkylation derivatives. By use of a modified Schlenk tube[5] shaken horizontally at 25° to 30° with metal of about 3-cm.[2] surface at 240 cycles per min. it has been found that addition occurs more slowly with azobenzene than with stilbene (Table I).

While the differences in rate can in part be attributed to the electropositivity of the metal and to the bond degeneracy in the unsaturated compound, the physical state of the metal surface seems to be highly important. Table I shows that use of a Waring Blendor operating at 8000 r.p.m. markedly increases the rate of adduct formation.

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(1) W. Schlenk and E. Bergmann, *Ann.*, **463**, 1 (1928).

(2) G. Wittig, *Angew. Chem.*, **53**, 241 (1940).

(3) G. Wittig and O. Sticknoth, *Ber.*, **68B**, 928 (1935).

(4) G. Wittig and A. Schumacker, *Ber.*, **88**, 234 (1955).

(5) J. W. B. Reesor, J. G. Smith, and G. F Wright, *J. Org. Chem.*, **19**, 940 (1954).

TABLE I

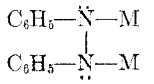
Addition of Metals to Unsaturated Compounds (0.25 mole per liter) in 2,5-Dioxahexane

Unsaturated Compound	Metal	Solution Initial	Color Final	Ppt. Color	Reaction time (hr.)	Reaction Vessel
Stilbene[a]	Na	Green	Red	—	2	Schlenk
Azobenzene[a]	Li	Green	Light yellow	Yellow	40–50	Same
Azobenzene[a]	Na	Green	Red	Red	12	Same
Azobenzene[a]	K	Brown	Red	Red	6	Same
Azobenzene[a]	Li	Green	Yellow	Yellow	2	Waring Blendor

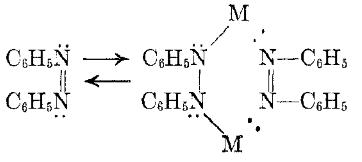
[a] (trans)

There is evidence for solvation of the alkene-dimetal adducts in the solid[6] form and in solution,[7] but no firm decision can be made about solvation of dimetal adducts of azobenzene. However, it is notable that the color of Wittig's dilithium diphenylhydrazyl in ether is different from our azobenzene-dilithium adduct in dioxahexane, although the two organometallic compounds are evidently identical except for the solvate. If this is evidence for coordination then the bond with 2,5-dioxahexane must be strong in the yellow solid azobenzene-dilithium adduct since the latter does not change color under 0.001 mm. at 40–50° for one hour.

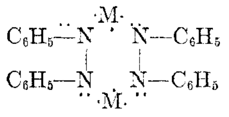
We have not yet been able to devise experiments such as those with stilbene-dimetal adducts and stilbene[5] in order to designate the present solutions as azobenzene-metal monoadducts. Treatment of the 1:1 azobenzene-metal system with carbon dioxide yields an equal mixture of azobenzene and hydrazobenzene, the latter being a decarboxylation product. Essentially the same behavior occurs with benzoyl chloride as with carbon dioxide, a 60% yield of *sym*-dibenzoyldiphenylhydrazine being produced. These reactions might seem to designate the system as a dimetal adduct (VI, M = Li, Na or K) to which the extra equivalent of azobenzene is coordinated (instead of dioxahexane) *via* its otherwise unshared electron pairs as the complex VII:



VI



VII



VIII

The characteristic color of the azobenzene-dimetal adducts affords an interesting qualitative exhibition of metal interchange. If the red azobenzene-dipotassium adduct in 2,5-dioxahexane is shaken for 2 days with lithium metal the color intensity decreases markedly and the appearance and reaction with water of the metallic lithium shows that it is coated with metallic potassium. The reverse reaction is apparent in the color change from yellow to orange-red when the azobenzene-dilithium adduct is shaken with potassium metal.

Wittig[2] reported that colorless diphenylhydrazyl dilithium (VI) in diethyl ether becomes brown when an equivalent of azobenzene is added to it. We too observe a color change when the yellow suspension of azobenzene-dilithium adduct in dioxahexane is treated with azobenzene, although the effect of the medium is apparent because the final color is different from that observed by Wittig. Our yellow suspension is dissolved to give a dark green solution. Likewise the red azobenzene-dipotassium adduct is dissolved by azobenzene in dioxahexane to give a color of much greater depth.

Despite evidence from reaction with carbon dioxide and benzoyl chloride it seems worthwhile to consider alternatives. It may be observed that by redistribution of electronic charge VII becomes VIII, analogous with a structure suggested for the alkene monometal adducts.[5] The latter also react with carbon dioxide as if they were dimetal adducts although in part they react with 2-chloropropane and triethyl phosphate to give coupling products and polymers expected from an intermediate free radical. We have not been able to isolate such products indicative of a transitory radical by treatment of the 1:1 azobenzene-metal system with 2-chloropropane. But these products would be tetrazanes and diazopolymers. The complex unstable mixture that we do obtain from the 1:1 azobenzene-metal system is not unexpected if these substances have indeed been formed.

Therefore we consider the 1:1 azobenzene-metal system to resemble VIII (with or without coordinated ether) in equilibrium with VI and azobenzene rather than an initial radical state like III which was suggested by Wittig for the monometal dibenzopiperazine system. A choice between these alternatives cannot be made by paramagnetic resonance absorption studies[8] because the spins in either may be expected to be uncoupled. However it

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[6] B. M. Mikhailov and N. G. Chernova, *Doklady Akad. Nauk, S.S.S.R.*, **74**, 939 (1950); *Chem. Abstr.*, **45**, 4698 (1951).

[7] A. G. Brook, H. L. Cohen, and G. F Wright, *J. Org. Chem.*, **18**, 447 (1953).

[8] D. Lipkin, D. E. Paul, J. Townsend, and S. I. Weissman, *Science*, **117**, 534 (1953).

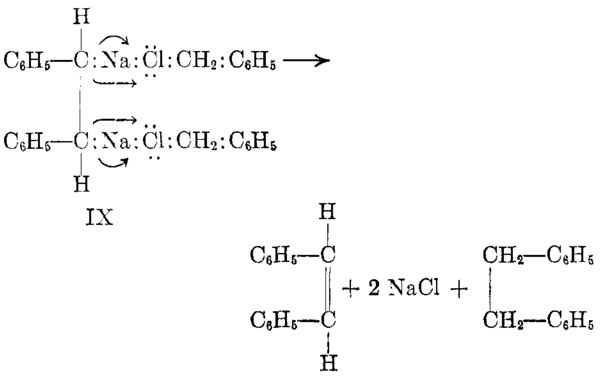
might be expected that a system initially containing free radicals as typified by III ought to convert 1,3-butadiene to its polymer. This gas is inert toward the azobenzene-monolithium system during 2 hr. at 25°.

In general the azobenzene-dimetal adducts, although less reactive than the stilbene-dimetal adducts, tend to form the same type of product. The lesser reactivity is not entirely disadvantageous since scission of ether molecules by the azobenzene-metal system is slight. For example the stilbene-disodium adduct attacks 2,5-dioxahexane to form 27% of diphenylethane in 8 days. By contrast the azobenzene-disodium adduct attacks 2,5-dioxahexane in 55 days to form not more than 13% of hydrazobenzene.

The reactions of azobenzene-dimetal adducts are listed in Table II.

The products and the yields from dimethyl sulfate and from 1,3-dichloropropane are the same as those reported by Wittig,[2] thus confirming the identity of his dilithium diphenylhydrazyl with our adduct. The products and yields from *n*-propyl chloride, *tert*-butyl chloride, and 1,4-dichlorobutane are comparable with corresponding alkylations of stilbene-dimetal adducts but a notable contrast is observed with benzyl chloride. This halide reacts with the stilbene-disodium adduct yielding only diphenylethane, stilbene, and sodium chloride but with azobenzene the main product is *sym*-*N*,*N*′-dibenzylhydrazobenzene, XI.

We are interpreting this difference in terms of homopolar versus heteropolar scissions within transient complex intermediates. The homopolar scission is depicted in structure IX for the reaction of benzyl chloride with stilbene-disodium adduct.



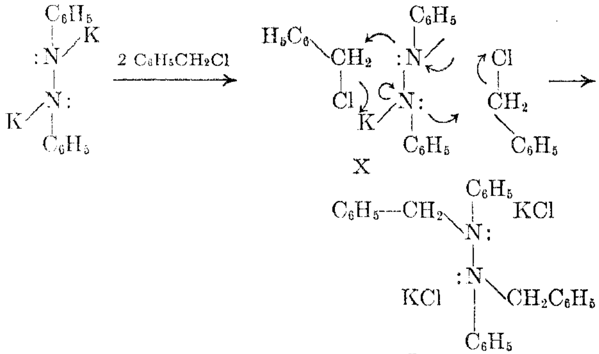
IX

TABLE II

AZOBENZENE-DIALKALI METAL ADDUCTS AND VARIOUS REAGENTS AT A TEMPERATURE OF 0–25°

Reagent	Metal of Diadduct	No. of Moles	Duration of Reaction (Hr.)	*N*,*N*′-Disubstituted Hydrazobenzene (% Yield)	*N*-Monosubstituted Hydrazobenzene (% Yield)	Azobenzene (% Recovered)	Other Products (% Yield)
Methyl sulfate	Na	0.01	0.3	92			
	Li	0.01	0.3	96			
n-Propyl chloride	Na	0.01	5.5	74		1	
Benzyl chloride	K	0.01	5.5	74	1	7	1,2-Diphenylethane **8**
1,3-Dichloropropane	Na	0.01	1.1	70		7	
1,4-Dichlorobutane	Na	0.01	4.5	90		4	
	Na	0.11	—	90		—	
	K	0.01	3	90		3	
Iso-propyl chloride	Li	0.01	12 days	—	30	40	
	K	0.01	30	2	77	3	
Iso-propyl bromide	Li	0.06	—		73		
	K	0.01	2		81		
Isopropyl iodide	Li	0.01	1		78		
	K	0.01	1		77		
Triisopropyl phosphate	K	0.01	14 days	1	60	27	
Isopropyl methane sulfonate	Na	0.01	48	20	66		
Isopropyl chloride	Li	0.01	Methyl sulfate added after 22 hr.	86 (*N*,*N*-dimethyl)			
t-Butyl chloride	Li	0.01	11 days	21			25 Hydrazobenzene
	Na	0.01	50	23			
Ethylene	K	0.01	8	No reaction			
2,5-Dioxahexane	Na	0.01	Methyl sulfate added after 55 days	49 (dimethyl)	26 (monomethyl)		5 Hydrazobenzene

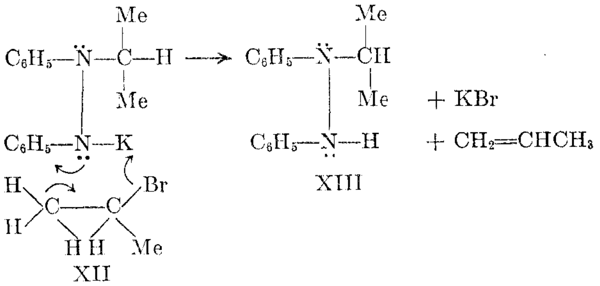
In contrast to this homopolar concerted electron redistribution is the heteropolar shift depicted in structure X for reaction of benzyl chloride with the azobenzene-dipotassium adduct in which the unshared nitrogen electron pairs may play a part.



Of course, the isolation of 8% of diphenylethane and 7% of azobenzene in the latter reaction shows that homopolar scission also must be occurring to a lesser extent.

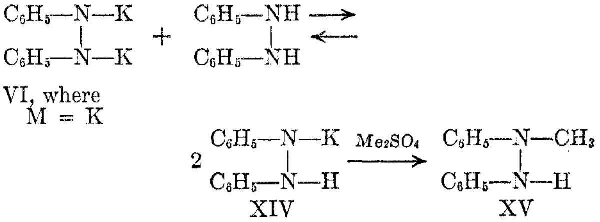
In contrast to reactions of isopropyl halides with the stilbene-dimetal adducts (which yield both mono- and dialkylated diphenylethanes) are the slower reactions with azobenzene-dimetal adducts. From the latter only monoalkylated hydrazobenzenes (XIII) are obtained. The reaction with isopropyl chloride is particularly slow, and product yields may not be significant because of long-term contamination. However, the inertness of the system has been demonstrated by addition of methyl sulfate 22 hr. after the isopropyl chloride is introduced. The 86% yield of methyl derivative shows that the halide has not reacted appreciably.

The stepwise concerted mechanism suggested[5] for reaction of isopropyl halides with stilbene-dimetal adducts may be applied to azobenzene-dimetal adducts. A relatively rapid alkylation at one nitrogen is thought to be followed by a slow replacement of metal by hydrogen (β on propyl) at the second nitrogen atom in the transitory XII.



It is apparent that this is a steric argument though one may question *why hindrance should not be less* in XII than it is in the analogous carbon system in which both mono- and dialkylation occur. We attribute the difference to the greater covalence of the N—K bond (as contrasted to the C—K bond) which should accentuate steric effects. It has been observed that the alkylation is noticeably exothermic only during the first half of the reaction. Moreover, 20% of dialkylation can be effected if the highly reactive isopropyl methanesulfonate is used instead of the halide. It is probable that this dialkylation is due to the strong polarization in the ester rather than to a different concerted transition that it might undergo. As Table II shows, triisopropyl phosphate behaves like the halides.

The difference in the polarization of the first and second N—K linkages is shown also in the reaction of the azobenzene-dimetal adducts with substances containing active hydrogen. In contrast to solvolysis of the stilbene-dimetal adducts (which has not been effected in a stepwise manner) the azobenzene-dipotassium adduct can be converted to *N,N'*-diphenylhydrazylpotassium XIV. While this conversion may be accomplished with an alcohol like 1-butanol, the resultant potassium butoxide is troublesome if, subsequently, the system is treated with an alkylating agent. Consequently hydrazobenzene is preferred as a source of active hydrogen in order to avoid wastage of the alkylating substance.



Treatment of XIV with isopropyl bromide gives about the same yield of isopropylhydrazobenzene (XIII) as may be obtained directly from VI so that there is no advantage in the preparation and use of XIV for this purpose. However, dimethyl sulfate, which yields only dialkylation product from the adduct (VI), reacts with XIV to give a 26% yield of *N*-methylhydrazobenzene together with a 23% yield of *N,N'*-dimethylhydrazobenzene XVI. The formation of the dialkylation product indicates that VI and hydrazobenzene are in equilibrium with XIV.

Although the alkylation products shown in Table II have been authenticated by analysis[2] none of them has otherwise been characterized. We have chosen to establish the structure of three of the derivatives by hydrogenolysis. Using the recommended method[9] by which we obtained a 92% yield and a 46% conversion of hydrazobenzene to aniline we have treated *N,N'*-dimethylhydrazobenzene (XVI) with W-1 Raney nickel in ethanol for 4 hr. at 1000 p.s.i. The yield of *N*-methylaniline is 52% while 25% of XVI is recovered unchanged. This method is unsuccessful when applied to *N,N'*-diphenylpyrazolidine (XVII) because the ethanol behaves as a partial alkylating agent. However, the

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(9) L. W. Covert and H. Adkins, *J. Am. Chem. Soc.*, 54, 4116 (1932).

alternative choice of dioxane not only gives a nearly quantitative yield of *N*,*N'*-diphenyl-1,3-propanediamine but also enables the use of milder conditions (24°, atmospheric pressure, W-2 catalyst) in the medium.

The hydrogenolysis of *N*,*N'*-diphenylpyridazolidine proves to be much more difficult, and the compound is recovered unchanged under conditions used for XVI and XVII. When the pressure is increased to 4500 p.s.i. and the temperature to 150–160° in dioxane with W-2 catalyst hydrogenolysis is accompanied by hydrogenation and deamination. A 51% yield of *N*-cyclohexylpyrrolidine is obtained, corresponding with the behavior of other 1,2-diazacyclohexanes.[10–11]

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EXPERIMENTAL

All melting points have been corrected against reliable standards. X-ray diffraction powder patterns are reported as the strongest lines (*d*, Å) at intensities (I/I_1) using Cu K (Ni filtered) radiation. All petroleum ether used was alkene-free and peroxide-free, b.p. 60–70°.

Preparation and purification of reagents. Nitrogen, purified by passage through 3 washing towers of Brady's solution,[12] 2 towers of flake sodium hydroxide and a 2 × 10 inch length of Drierite, was used to protect all liquids during preparation and reaction. Purification of 2,5-dioxahexane was effected by reflux over sodium until addition of a few crystals of benzophenone formed a stable solution of the blue ketyl. Final distillation at 85° from this stored solution was carried out just prior to use. Alkyl halides were extracted with 80–96% sulfuric acid, washed with aqueous sodium bicarbonate, then water, and were dried with magnesium sulfate and distilled. Methyl sulfate, washed with bicarbonate solution and dried with magnesium sulfate was distilled (b.p. 76°/15 mm.). Technical azobenzene was distilled, b.p. 152–155° (11–14 mm.), then crystallized (3.4 ml./g.) at 0°C., filtered by suction and washed with cold ethanol (0.3 ml./g.). Recovery was 85%.

Preparation of azobenzene dimetal adducts. (1) The method described previously[5] was used, all glassware being flushed with nitrogen while it was externally flamed prior to use. The Schlenk tube containing a single piece of metal in excess and 0.01 mole of azobenzene per 40 ml. of dioxahexane was shaken until reaction was complete, then was decanted from excess metal.

(2) A stainless steel 1-l. Waring Blendor (Cenco No. 17235) container was modified to include a plug cock at the bottom and a Teflon gasket under the lid, which was equipped with ports for nitrogen influx and efflux or for sampling. This vessel was especially effective for decreasing the time of lithium addition; indeed it was necessary to employ strong air blast cooling for preparations as large as 0.1 mole.

General method for reactions of the adducts. The adduct prepared from 1.82 g. (0.01 mole) of azobenzene in 40 ml. of dioxahexane was transferred under nitrogen to a 100-ml. three-necked flask equipped with thermometer, dropping tube, and sealed stirrer. Addition of the reagent (0.022 mole) in 5 ml. of dioxahexane was carried out at 0–5°C. This temperature was maintained for 30 min. subsequent to addition and was then allowed to rise to 20–25°. When reaction was complete (no color change when an aliquot was exposed to air) the dioxahexane was vacuum-evaporated and the residue was dissolved in 30 ml. each of ethyl ether and water. The ether phase was washed with water and the combined aqueous phases were then washed with ether (30 ml.). This ether phase, washed with water, was combined with the first one and then evaporated under vacuum to leave the crude reaction product.

Chromatographic separation of products. (1) *On silicic acid.* The crude reaction product was dissolved in a minimum of hexane and the solution was applied to a 1 × 10 cm. column of Mallinckrodt 100-mesh chromatographic silicic acid, 20% water. Elution with hexane removed combined azobenzene with mono- and dialkylated hydrazobenzenes. Subsequently hydrazobenzene could be eluted by a 95:5 hexane-methanol mixture.

(2) *On alumina.* A special column was prepared to obviate "coning" because of the detailed separation which was required. Just above the 1 × 40 cm. column to contain the 100–200 mesh Alcan alumina (activated at 150° for 24 hr.) was *concentrically sealed* a tube of slightly larger diameter. A glass rod of 2.5-mm. diameter was then equipped with trigonally arranged spacers to fit the bottom and top of the enlargement and to allow the bare glass rod to extend halfway down (20 cm.) and in the center of the tube which subsequently was filled to a depth of 40 cm. with the alumina suspended in hexane.

The eluate (in petroleum ether solution) freed from hydrazobenzene by the silicic acid column was subsequently separated on these alumina columns. The substances, if they were present, appeared in the following order: diphenylethane, *sym*-di-*n*-propylhydrazobenzene, *sym*-dimethylhydrazobenzene, *N*-isopropylhydrazobenzene, *N*-methylhydrazobenzene, hydrazobenzene.

Scission of 2,5-dioxahexane. A solution of 0.0095 mole of azobenzene-disodium adduct in 40 ml. of dioxahexane was shaken at 20–25° 55 days and then treated with 2.60 g. (0.021 mole) of dimethyl sulfate at 0–5°. The crude product (2.064 g.) was isolated by ether extraction leaving an aqueous phase that contained 439 mg. of sodium ion (calcd. for 0.01 mole of adduct, 460 mg.). Chromatography on silica gel gave 0.09 g. (5%) of hydrazobenzene. Separation of the remainder on alumina yielded 1.03 g. (49%) of *N*,*N'*-dimethylhydrazobenzene (XVI) and 0.524 g. (26%) of *N*-methylhydrazobenzene (XV).

Reaction with dimethyl sulfate. A solution of 2.60 g. (0.021 mole) of dimethyl sulfate in 5 ml. of dioxahexane was added dropwise to 0.01 mole of azobenzene-disodium adduct at 0–5°. The color changed from deep red to light orange at the end of addition, and then to light yellow when the system was warmed to 20°. The residue after solvent evaporation was treated with 5 ml. of 1*N* aqueous sodium hydroxide for 12 hr. The system was extracted with ether to remove 2.12 g. of crude product which was dissolved in hot methanol. The solution, cooled to 0°, precipitated an oil which crystallized on further cooling. The methanol was decanted at 0° and the magma was redissolved in hot methanol; cooling yielded 0.43 g., m.p. 32.5–33°. The evaporated filtrates left a residue which was dissolved in petroleum ether and then applied to an alumina column. A further 1.53 g. of *N*,*N'*-dimethylhydrazobenzene, m.p. 32.5–33.0°, was obtained. Total yield was 92% of the theoretical. A similar experiment with the dilithium adduct gave a 96% yield.

Reaction with n-propyl chloride. The disodium adduct (0.01 mole) was treated with 1.73 g. (0.022 mole) of *n*-propyl chloride, b.p. 46.5°. Reaction was completed in 5.5 hr. The crude product, 2.479 g., crystallized from 20 ml. hot methanol, gave 1.47 g. of yellow crystals, m.p. 70–71°. The evaporated mother liquor, chromatographed on alumina yielded 0.818 g. more of *N*,*N'*-di-*n*-propylhydrazobenzene. Crystallization from hot methanol gave 1.976 g. (74%), m.p. 71.5–72°.

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(10) A. Katzenellenbogen, *Ber.*, **34,** 3828 (1901).

(11) S. Racine, *Ann.*, **239,** 71 (1887).

(12) L. J. Brady, *Ind. Eng. Chem.* (*Anal. Ed.*), **20,** 1034 (1948).

Anal. Calcd. for $C_{18}H_{24}N_2$: C, 80.7; H, 8.96; N, 10.4. Found: C, 80.7; H, 8.98; N, 10.3.

Reaction with benzyl chloride. Azobenzene-dipotassium adduct (0.01 mole) was treated with 2.78 g. (0.022 mole) of benzyl chloride, b.p. 63° (8 mm.). Much heat was evolved and an addition time of 35 min. was needed to hold the temperature to 5° by means of an ice-water bath. The resulting blue system became yellow-orange after five hours at 25°. The crude product, 3.58 g. from the ether extract, was thrice extracted with 5-ml. portions of boiling petroleum ether leaving 2.54 g. (70%) of *N,N'*-dibenzylhydrazobenzene, m.p. 123–124°. Three crystallizations from ethyl ether (20 ml. per g.) gave 0.50 g., m.p. 126.5–127.0°.

Anal. Calcd. for $C_{26}H_{24}N_2$: C, 85.7; H, 6.59; N, 7.69. Found: C, 85.4; H, 6.73; N, 7.50.

The x-ray diffraction pattern was: [10] 4.87; [9] 4.29; [8] 3.24; [7] 3.83; [6] 7.69; [5] 3.53; [4] 7.96, 7.43. The petroleum ether extract was chromatographed on alumina by means of petroleum ether to give 151 mg. of diphenylethane, m.p. 51–52° (8%), 193 mg. of azobenzene, m.p. 65–66° (7%), 159 mg. of dibenzylhydrazobenzene, m.p. 123–124° (4%) and 25 mg. of *N*-benzylhydrazobenzene, m.p. 71–72° (1%). Known products were identified by mixture melting point.

More of the monobenzylhydrazobenzene, m.p. 50–61°, was obtained from the column by benzene elution. It was crystallized from petroleum ether (10 ml. per g.) at 0°.

Anal. Calcd. for $C_{19}H_{18}N_2$: C, 83.2; H, 6.57; N, 10.2. Found: C, 82.8; H, 6.76; N, 9.9.

N,N'-Diphenylpyrazolidine. Azobenzene-disodium adduct (0.01 mole) was treated with 1.20 g. (0.011 mole) of 1,3-dichloropropane, b.p. 125°, in 5 ml. of dioxahexane at 0–5°. Evolution of heat was apparent during the 70-min. reaction period. The crude product (2.19 g.) was crystallized from ethanol, 1.23 g., m.p. 96–98°. The mother liquor was evaporated *in vacuo* and dissolved in 3 ml. of petroleum ether (b.p. 60–70°). This solution was chromatographed on alumina to yield 87 mg. (5%) of azobenzene and 0.33 g. more of the *N,N'*-diphenylpyrazolidine (total yield 70%).

N,N'-Diphenylpyridazolidine. To 0.01 mole of azobenzene-disodium adduct was added at 0–5° a solution of 1.30 g. (0.01 mole) of 1,4-dichlorobutane. Reaction was complete in 4.5 hr. The crude product (2.55 g.) was dissolved in 50 ml. of methanol; crystals appeared at 0°. A second crystallization from 20 ml. of methanol gave 2.08 g. (85%) of diphenylpyridazolidine, m.p. 105.5–106°. Two more crystallizations (10 ml. per g.) raised the melting point to 106.4–106.9°.

Anal. Calcd. for $C_{16}H_{18}N_2$: C, 80.7; H, 7.55; N, 11.8. Found: C, 80.8; H, 7.49; N, 11.9.

The x-ray diffraction pattern was: [10] 4.168; [9]5.86; [8] 5.211; [7] 6.55; [6] 8.42, 2.93; [5] 3.437, 3.118; [4] 4.41, 3.897.

The liquors from the first and second crystallizations were combined, vacuum-evaporated, and steam-distilled to yield 71 mg. (4%) of azobenzene in the distillate and 127 mg. (5%) of diphenylpyridazolidine in the residue after it was crystallized from methanol. A similar reaction with the dipotassium adduct (3 hr.) yielded 90% of the desired product and 3% of azobenzene.

Reactions with isopropyl halides. The crude products of the reactions described in Table II were chromatographed on silicic acid but no hydrazobenzene was found. Chromatography on alumina gave the yields and products described in Table II. Purification of *N*-isopropylhydrazobenzene, m.p. 88.0–88.4°, was accomplished by the initial crystallization from petroleum ether (10 ml./g.) at 0°, treatment of its petroleum ether solution (30 ml./g.) with Norite at 25° for 10 min. and a final crystallization from a 90/10 methanol/water mixture (15 ml./g.) at 25°.

Anal. Calcd. for $C_{15}H_{18}N_2$: C, 79.7; H, 7.97; N, 12.4. Found: C, 79.5; H, 8.14; N, 12.3.

The x-ray pattern was: [10] 4.35; [9] 5.60; [8] 9.50; [7] 5.24; [6] 4.77; [5] 3.80, 3.21; [4] 3.66, 3.30; [3] 7.76.

N,N'-Diisopropylhydrazobenzene, m.p. 93.0–93.5°, was purified by repeated (5 times) crystallization from methanol (10 ml./g.) at 0°.

Anal. Calcd. for $C_{18}H_{24}N_2$: C, 80.6; H, 8.96; N, 10.4. Found: C, 80.3; H, 8.95; N, 10.4.

The x-ray diffraction pattern was: [10] 4.247; [9] 3.751; [8] 8.75; [7] 11.18, 7.02; [6] 5.71; [5] 5.50; [4] 3.035, 2.928.

Reaction with triisopropyl phosphate. Azobenzene-dipotassium adduct (0.01 mole) was treated with 4.93 g. (0.022 mole) of triisopropyl phosphate, b.p. 78–79° (2–3 mm.), n_D^{20} 1.4057, d_D^{20} 0.986. The reaction was very slow and is not recommended as a source of *N*-isopropylhydrazobenzene.

Isopropyl methanesulfonate (by R. Kullnig). Following the prescribed method[13] 30 g. (0.5 mole) of 2-propanol (purified by distillation after an hour reflux over aluminum isopropoxide) was mixed with 50 ml. of barium oxide-dried pyridine. To the solution at 115° was added dropwise 63 g. (0.55 mole) of methanesulfonyl chloride in 20 ml. of pyridine cooled to −15°. Addition of the cold solution required 20 min. under strict exclusion of water. After 1 hr. at −10° and overnight at +4° the system was treated slowly with about 50 g. of cracked ice and 100 ml. of 2*N* sulfuric acid to dissolve crude salts. The crude product was separated by 4 extractions with 40-ml. portions of chloroform. The extract combination, washed twice with 40 ml. of cold 2*N* sulfuric acid, 20 ml. of ice cold water, thrice with 20 ml. per time of saturated aqueous sodium bicarbonate, then four times with ice cold water. The cold nonaqueous phase was then dried overnight by magnesium sulfate. The solvent was removed *in vacuo*, finally at 0.35 mm. The chloroform-free residue was molecularly distilled at 30° (0.02 mm.) to yield 59 g. (85%) of ester, d_4^{20} 1.145, n_D^{20} 1.4173, m.p. 5.5–6.5°.

Anal. Calcd. for $C_4H_{10}O_3S$: C, 34.7; H, 7.29. Found: C, 34.4; H, 7.23.

For characterization the ester (1.1 g., 0.008 mole) and 2-naphthol (1 g., 0.007 mole) in 3 ml. of acetone were refluxed with 1.5 g. (0.0014 mole) of anhydrous sodium carbonate for 2 hr. The solid was filtered off and the filtrate evaporated. The residue was heated 1 hr. with 5 ml. of 20% aqueous sodium hydroxide in 3 ml. of ethanol. The system was taken up in ether and the solution was washed with water, dried with magnesium sulfate, and evaporated. Crystallization of the residue from ethanol gave 2-isopropyl-2-naphthyl ether, m.p. 40–41°.[14]

N,N'-Diisopropylhydrazobenzene. Azobenzene-disodium adduct (0.01 mole) was treated in the usual manner with 3.04 g. (0.022 mole) of isopropyl methanesulfonate. The products were separated by the successive elution from alumina by petroleum ether. In this way a yield of 0.53 g. (20%) of diisopropylhydrazobenzene was obtained in addition to a 66% yield of monoisopropylhydrazobenzene.

Reaction with tert-butyl chloride. Azobenzene-disodium adduct (0.01 mole) was treated with 1.95 g. (0.021 mole) of 2-chloro-2-methylpropane, b.p. 51°, during 50 hr. The crude product (2.34 g.) was dissolved in 4 ml. of petroleum ether and chromatographed on alumina. The eluate yielded 0.543 g. of crystals, m.p. 53–56°, crystallized from petroleum ether (Norite) and then from methanol-water (4:1) at 0°. This pure *N-tert*-butylhydrazobenzene melted at 57–57.6°.

Anal. Calcd. for $C_{16}H_{20}N_2$: C, 80.0; H, 8.34; N, 11.7. Found: C, 79.8; H, 8.45; N, 11.5.

Reaction with ethylene. The nitrogen atmosphere above 0.01 mole of azobenzenedipotassium adduct was displaced with ethylene (pressure, 1 cm. of mercury) dried by passage through concentrated sulfuric acid. After 4 hr. of stirring at 0–5° and 4 hr. more at 25° the system was bleached by addition of 0.4 g. (0.022 mole) of water in 5 ml. of dioxahexane. The hydrazobenzene, 1.82 g. (99%), m.p. 124–127°, was characterized by mixture melting point.

Reactions of azobenzene-monometal adducts. The monolithium adduct is prepared simply by addition of 0.01 mole

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(13) M. Zief, H. G. Fletcher, and H. R. Kirschen, *J. Am. Chem. Soc.*, **68**, 2744 (1946).

(14) F. Bodroux, *Bull. soc. chim.* (3), **19**, 573 (1898).

of azobenzene to 0.01 mole of azobenzene-dilithium adduct.

(1) *Reaction with carbon dioxide.* The reaction mixture was decolorized by displacement of the nitrogen with dry gaseous carbon dioxide. After shaking with water and ether, the ether layer was evaporated, then chromatographed by petroleum ether through silica gel to yield 0.01 mole of azobenzene. The aqueous layer slowly precipitated 1.76 g. of hydrazobenzene (48%), m.p. 125–127°, mixture m.p. 126–128°.

(2) *Reaction with butadiene.* The nitrogen over the monolithium adduct was displaced by butadiene-1,3 dried by passage through flake sodium hydroxide. After 15 hr. the system was cooled and the butadiene was displaced by carbon dioxide. After separation as described above the recovery of azobenzene was quantitative and the hydrazobenzene, m.p. 125–127°, mixture m.p. 126–128°, was obtained in 94% yield after spontaneous decomposition of the carbamic acid.

(3) *Reaction with benzoyl chloride.* Azobenzene-monopotassium adduct (0.01 mole) was treated with 1.41 g. (0.01 mole) of benzoyl chloride, b.p. 86° (17 mm.) dissolved in 5 ml. of dioxahexane. An ice water bath was required to hold the temperature to 0–5°. The crude product, 2.65 g., obtained from the ether extract, was extracted four times with 5-ml. portions of hot petroleum ether leaving a residue of 1.64 g. This residue crystallized from methanol (10 ml. per g.) at 0° gave 1.18 g. (60%) of *N*,*N*′-dibenzoylhydrazobenzene, m.p. 159–159.5°.[15] The recovery of azobenzene (0.816 g., 90%) was effected by chromatography through alumina. X-ray pattern for the dibenzoyl derivative: [10] 5.86; [9] 3.66; [8] 9.21; [7] 4.39, 3.73; [6] 4.07; [5] 8.84, 5.43; [4] 3.01.

Reactions of potassium N,N′-diphenylhydrazyl. (1) *Prepared with 1-butanol; product isopropylhydrazobenzene.* A solution of 1-butanol (0.55 g., 0.009 mole) in 6 ml. of dioxahexane was added during 5 min. to 0.01 mole of azobenzene-dipotassium adduct in 40 ml. of dioxahexane at 0–5°. In order to characterize the resulting dark red solution it was stirred for 15 min. and then was treated with 1.35 g. (0.011 mole) of isopropyl bromide. The color of the system became dark brown within 30 min. and remained so for 2 hr. more at 25°. The system was rechilled to 0–5° and a second 0.011 mole of halide was added. The color became yellow-orange within 1 hr. The crude product (2.11 g.) was chromatographed by petroleum ether, first on silicic acid and then on alumina. Azobenzene (0.265 g., 15%), hydrazobenzene (0.58 g., 32%) and N-isopropylhydrazobenzene (1.14 g., 51%) were obtained.

(2) *Prepared with hydrazobenzene; product N-methylhydrazobenzene.* An experiment otherwise identical with that in (*1*) except for use of hydrazobenzene instead of butanol yielded 12% of azobenzene, 32% of hydrazobenzene and 53% of isopropyldiphenylhydrazine.

In another experiment the potassium diphenyl hydrazyl (0.01 mole) was treated with 1.3 g. (0.01 mole) of methyl sulfate and product separation was effected as before. Yields were: 22% of hydrazobenzene, 23% of *N*,*N*′-diphenylhydrazine and 26% of *N*-methyl-*N*,*N*′-diphenylhydrazine, m.p. 74.0–74.5°. The latter substance was purified for analysis by two crystallizations from petroleum ether (30 ml./g.) at 0°.

Anal. Calcd. for $C_{13}H_{14}N_2$: C, 78.8; H, 7.07; N, 14.1. Found: C, 78.7; H, 7.15; N, 14.0.

X-ray diffraction pattern was: [10] 5.063; [9] 4.669; [8] 3.630; [7] 3.880; [6] 4.168; [5] 3.195; [4] 9.302; [3] 4.267.

Hydrogenolyses for structure proof. (1) *Of hydrazobenzene.* Hydrazobenzene (90 mg., 0.49 mmole) with approximately 0.1 ml. of W-1 Raney nickel catalyst and 10 ml. of absolute ethanol were shaken at 90–95° for 4 hr. at 1900 p.s.i. of hydrogen. After cooling the 50-ml. autoclave was vented, the catalyst removed, and the solvent evaporated *in vacuo.* The residual oil was dissolved in 5 ml. of dry pyridine and treated with 0.4 g. (0.2 mmole) of pure *p*-toluenesulfonyl chloride. After 5 hr. the excess acid chloride was hydrolyzed by 5 ml. of 10% aqueous sodium hydroxide. Hydrazobenzene (41 mg., 45%) was recovered by ether extraction. Acidification of the alkaline phase precipitated *N*-phenyl-*p*-toluene sulfonamide (0.11 g., 46%). X-ray pattern: [10] 4.19; [9] 5.77, 4.69; [7] 8.42, 3.74, 3.40; [6] 6.55.

(2) *Of N,N′-dimethyl-N,N′-diphenylhydrazine.* The reaction was carried out like that reported in (1). The *p*-toluenesulfonated product was chromatographed by petroleum ether on alumina activated at 47° to remove 25% of unchanged dimethyldiphenylhydrazine, m.p. 32.5–33.0°, mixture m.p. the same. Subsequent elution with methanol gave 52% of *N*-methyl-*N*-phenyl-*p*-toluenesulfonamide, m.p. 90–92°, mixture m.p. 91–93°.[16] The X-ray powder pattern of *N*-ethyl-*N*-phenyl-*p*-toluenesulfonamide is: [10] 9.93; [9] 4.29; [8] 4.766; [7] 7.075; [6] 8.11, 5.035, 3.076.

(3) *Of N,N′-diphenylpyrazolidine.* A semimicrohydrogenation apparatus was charged with 38 mg. (0.17 mmole) of *N*,*N*′-diphenylpyrazolidine, 0.1 ml. of W-2 Raney nickel catalyst and 5 ml. of pure peroxide-free dioxane. The system was stirred at 25° (15 lb.) until absorption (3.95 ml., 0.18 mmole at NTP) of hydrogen ceased. The product, 37 mg. (97%) was identified as *N*,*N*′-diphenyl-1,3-propanediamine by conversion to derivatives previously reported.[17]

Derivatives	Literature Constants[17]	Observed Constants
Amine	B.p. 244.5° (11 mm.)	B.p. 249–50° (18 mm.)
Dibenzoyl-	M.p. 135° (pale rose)	M.p. 125–125.5° (white)
Hydrochloride	M.p. 144° (mono)	M.p. 194–5°
Sulfate	M.p. 157° (mono)	M.p. 176–7°
Diacetyl-	M.p. 119°	M.p. 118.6–119°
Dinitroso-	M.p. 86°	M.p. 85.5–86°

Despite nonagreement with respect to the benzoyl derivative we consider these derivatives to establish the constitution.

(4) *Of N,N′-diphenylpyridazolidine.* A 50-ml. autoclave was charged with 5.13 g. (0.022 mole) of *N*,*N*′-diphenylpyridazolidine, 0.5 ml. of W-2 Raney nickel catalyst and 10 ml. of dioxane, then was heated to 150–160° for 36 hr. under 4500 p.s.i. of hydrogen. The catalyst was filtered off. The filtrate was evaporated *in vacuo* to leave 4.86 g. of an oil which did not show the color with concentrated hydrochloric acid that is typical of tetrasubstituted hydrazines.

The oil was distilled and the distillate, 3.80 g., b.p. 70–180° (5 mm.), was separated by redistillation into fractions. Fraction 1, b.p. 60–61° (2 mm.), boiled at 209–210° at 760 mm., n_D^{20} 1.4823, 1.68 g., was found to be a 51% yield of *N*-cyclohexylpyrrolidine since the picrate, m.p. 166.0–166.5°, does not depress the mixture m.p. of an authentic specimen. The x-ray diffraction pattern of this picrate was: [10] 10.64; [9] 4.02; [8] 5.34; [7] 6.15; [6] 3.48, 2.97. Fraction 2, b.p. 104° (0.007 mm.), n_D^{20} 1.4964, 1.50 g., was not identified. The picrate from acetone melts at 238–239° (dec.). Fraction 3, the residue, was 0.68 g. of brown viscous oil.

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