BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 1054—1058 (1966)

The Chemistry of Polyazanes. III. The Reaction of Nitrosobenzene with Hydrazine and Phenylhydrazine

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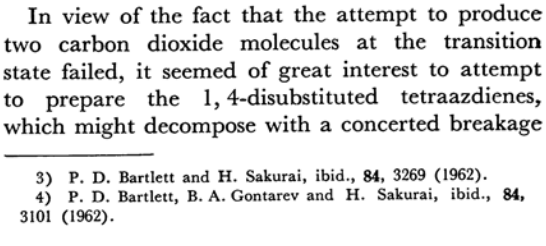
(Received October 19, 1965)

The reaction between nitrosobenzene and hydrazine was studied. Aniline and nitrogen were found to be the products, but it was not certain whether or not phenyltriazene existed as an intermediate. Then the reaction between nitrosobenzene and phenylhydrazine was studied. The products were azoxybenzene, diphenylamine, benzene and nitrogen. The reaction between *p*-nitrosotoluene and phenylhydrazine yielded 4, 4′-azoxytoluene, 4-methyldiphenylamine, benzene and nitrogen. The mechanisms of these reactions were discussed on the basis of these findings.

It has been of interest to seek for the initiators which form free radicals at low temperatures. *t*-Butyl triphenylperacetate is an unstable perester, decompositing at lower temperatures to yield free radicals, but this compound cannot be used as an initiator, since one of the free radicals produced, the triphenylmethyl radical, is so stable that it does not initiate polymerization.

The possibility of producing two carbon dioxide molecules to further hasten decomposition while still producing highly-reactive radicals has been explored in the study of di-*t*-butyl peroxalate,[1,2] but later work[3,4] has suggested that in decomposing these peroxalates form only one molecule of carbon dioxide in the transition state.



$$\mathrm{Me_3CO\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}\underset{\underset{O}{\|}}{C}\text{-}O\text{-}OCMe_3}\ \begin{array}{l} \nearrow\!\!\!\!\!/\!/ \ \mathrm{Me_3CO\cdot + CO_2} \\ \qquad \mathrm{+ CO_2 + \cdot OCMe_3} \\ \searrow \ \mathrm{Me_3CO\cdot + CO_2} \\ \qquad \mathrm{+ \cdot \underset{\underset{O}{\|}}{C}\text{-}O\text{-}OCMe_3} \end{array}$$

In view of the fact that the attempt to produce two carbon dioxide molecules at the transition state failed, it seemed of great interest to attempt to prepare the 1, 4-disubstituted tetraazdienes, which might decompose with a concerted breakage

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[1] P. D. Bartlett, E. P. Benzing and R. E. Pincock, *J. Am. Chem. Soc.*, **82**, 1762 (1960).

[2] P. D. Bartlett and R. E. Pincock, ibid., **82**, 1769 (1960).

[3] P. D. Bartlett and H. Sakurai, ibid., **84**, 3269 (1962).

[4] P. D. Bartlett, B. A. Gontarev and H. Sakurai, ibid., **84**, 3101 (1962).

TABLE I. PRODUCTS OF THE REACTION BETWEEN NITROSOBENZENE AND HYDRAZINE

Run	Reactants,* mmol.		Other additives	$\frac{(C_6H_5NO)}{(N_2H_4)}$	Solvent	Products, mmol.			$\%C_6H_5$ Accounted for
	C_6H_5NO	N_2H_4				$C_6H_5NH_2$	C_6H_5NO	$C_6H_5N{=}NC_6H_5$	
1	1.00	1.60		0.625	CH_2Cl_2 2 ml.	0.855	0	0.0697	99.4
2	9.99	9.94		1.00	CH_2Cl_2 20 ml.	7.73	2.67	0	104
3	22.3	8.92		2.50	MeOH 20 ml.	5.16	7.79	1.92	75.5
4	20.8	10.8	MeONa 2.0 mmol	1.93	MeOH 20 ml.	8.00	0	4.90	85.6

* Reactants were mixed below −30°C, and then the mixture was gradually warmed up to room temperature.

of three bonds, with the expulsion of two molecules of nitrogen. It is known that nitrosobenzene reacts with aniline to yield azobenzene, and it seemed plausible that the reaction between nitrosobenzene and hydrazine might yield a tetraazdiene. Therefore, the reaction between nitrosobenzene and hydrazine has been investigated:

$$C_6H_5NO + H_2NC_6H_5 \rightarrow C_6H_5\text{-N=N-}C_6H_5$$

$$2C_6H_5NO + N_2H_4 \xrightarrow{?} C_6H_5\text{-N=N-N=N-}C_6H_5$$

During the investigation of various polyazanes, we have come across a paper, written by Mills, reporting that the reaction between nitrosobenzene and phenylhydrazine yields nitrogen and azobenzene.⁵⁾

$$C_6H_5NO + H_2NNHC_6H_5 \rightarrow N_2 + C_6H_5\text{-N=N-}C_6H_5$$

Since the reaction between nitrosobenzene and aniline yields azobenzene, one would expect that the reaction between nitrosobenzene and phenylhydrazine would yield 1, 3-diphenyltriazene, which is a well-characterized, stable compound:

$$C_6H_5NO + H_2NNHC_6H_5 \xrightarrow{?} C_6H_5\text{-N=N-NH-}C_6H_5$$

Obviously the reaction of nitrosobenzene and phenylhydrazine yielding azobenzene is not straightforward; it therefore calls for further investigation. Therefore, the reaction between nitrosobenzene and phenylhydrazine and the reaction between *p*-nitrosotoluene and phenylhydrazine have been investigated and will be described in this paper.

Results and Discussion

The Reaction between Nitrosobenzene and Hydrazine.—When nitrosobenzene was mixed with hydrazine in dichloromethane at −50—−78°C most of the nitrosobenzene remained as a solid due to its low solubility at low temperatures, unless a great amount of the solvent was used. However, when the solution was warmed up to about −30°C, a homogeneous solution with a light green color was obtained; the color did not appear to change when the solution was kept at this temperature. Apparently, nitrosobenzene and hydrazine do not react at this temperature. When however, the solution was further warmed up to about −8°C, the green color of nitrosobenzene began to change to a yellowish brown, with an evolution of nitrogen. The evolution of nitrogen was complete after the solution had been kept at room temperature for three hours. Besides the nitrogen evolved, the products of the reaction were aniline, azobenzene and unreacted nitrosobenzene, as is shown in Table I. In any case, the gas chromatographic analysis showed the absence of benzene, which is a product likely to be formed if 1, 4-diphenyl-1, 3-tetraazdiene was formed. Apparently, one mole of hydrazine reacted with only one mole of nitrosobenzene, and aniline and nitrogen were produced. It is not certain whether or not phenyltriazene was present as the intermediate.

$$C_6H_5NO + N_2H_4 \rightarrow (C_6H_5\text{-N=N-}NH_2\ ?) \rightarrow C_6H_5NH_2 + N_2$$

Dimroth prepared phenyltriazene by reducing phenyl azide with stannous chloride and dry hydrogen chloride in absolute ether at −20°,C and then by purifying the phenyltriazene through its copper derivative, which was then decomposed with aqueous potassium cyanide at a low temperature:⁶⁾

$$C_6H_5\text{-N=N}^{+}\text{=N}^{-} \xrightarrow{SnCl_2} C_6H_5\text{-N=N-}NH_2$$

Phenyltriazene was found to be in the form of colorless leaflets melting at 50°C, and it was very unstable. It rapidly decomposed into aniline anp nitrogen n all solvents at room temperature:

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5) C. Mills, *J. Chem. Soc.*, **67**, 925 (1895).

6) O. Dimroth, *Ber.*, **40**, 2378 (1907).

$$C_6H_5\text{-}N{=}N\text{-}NH_2 \rightarrow C_6H_5NH_2 + N_2$$

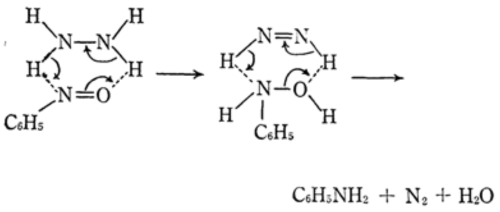
It seemed of interest to determine whether or not the phenyltriazene was the intermediate at the reaction between hydrazine and nitrosobenzene. Attempts have been made to find experimental conditions where nitrosobenzene and hydrazine react and yet the product (presumably phenyltriazene) does not decompose to yield nitrogen. Whether nitrosobenzene has reacted or not can be determined from the loss of the light green color. However, it was found that the loss of the green color was always accompanied by the evolution of nitrogen, even though the solution was warmed up very slowly. In an attempt to facilitate the reaction between the hypothetical phenyltriazene and another mole of nitrosobenzene, sodium methoxide was added to the reaction mixture, but there was no essential difference in the products.

These experimental findings can be explained by either of the following two assumptions:

(A) Nitrosobenzene reacts with hydrazine to form phenyltriazene, which is so unstable that it immediately decomposes before reacting with another mole of nitrosobenzene.

(B) Nitrosobenzene reacts with hydrazine to yield aniline and nitrogen, without going through phenyltriazene as the intermediate.

The mechanism B may best be described in the following scheme:



The experimental findings described so far are not sufficient for us to make a choice between these two mechanisms, but the experimental evidence to be described below for the reaction between nitrosobenzene and phenylhydrazine seems to indicate that the reaction between nitrosobenzene and hydrazine is best described by the mechanism B.

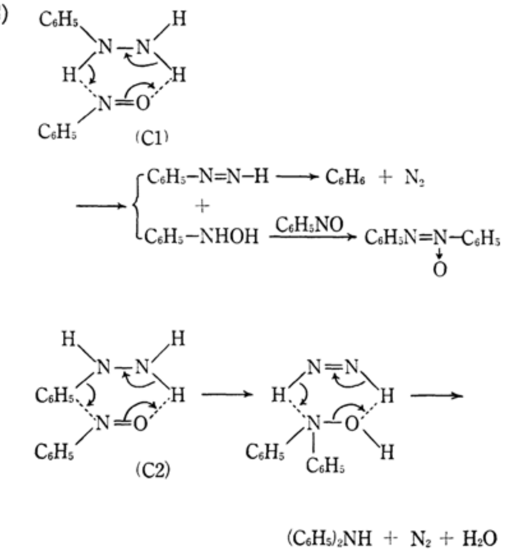
The Reaction between Nitrosobenzene and Phenylhydrazine.—Phenylhydrazine was added drop by drop to a stirred solution of nitrosobenzene in dichloromethane at room temperature until no more evolution of nitrogen occurred. The products of the reaction were then identified by the use of elution chromatography and by a study of the infrared spectra; the results are summarized in Table II.

TABLE II. PRODUCTS OF THE REACTION BETWEEN NITROSOBENZENE AND PHENYLHYDRAZINE

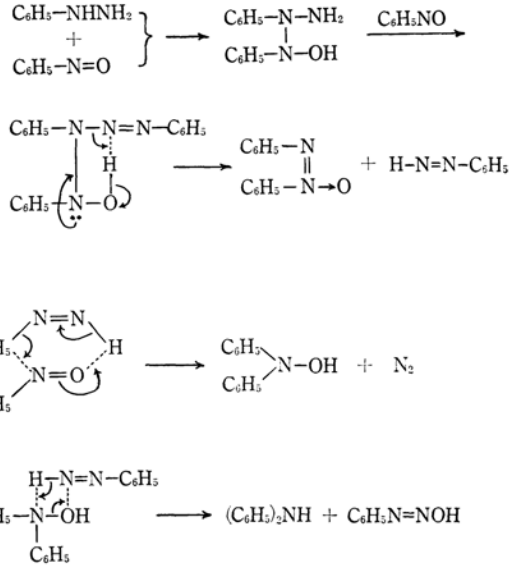
Reactant	Nitrosobenzene	10.0 mmol.
	Phenylhydrazine	3.95
Product	Benzene	1.90 mmol.
	Azoxybenzene	3.59
	Diphenylamine	1.38
%C_6H_5 of C_6H_5NO	accounted for	81.7%
%C_6H_5 of $C_6H_5N_2H_3$	accounted for	83.0%

The formation of benzene, azoxybenzene and diphenylamine can be explained by either of the following two mechanisms, C and D:

(C)



(D)



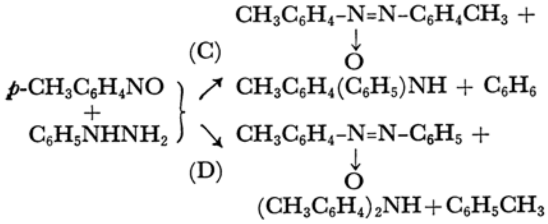
Although the mechanism C looks more attractive than the mechanism D, the products of the reaction are consistent with the mechanism D as well. Therefore, the reaction between *p*-nitrosotoluene and phenylhydrazine was investigated in order to find out which of these two mechanisms is better applicable to these reactions.

The Reaction between *p*-Nitrosotoluene and Phenylhydrazine.—*p*-Nitrosotoluene and phenylhydrazine were allowed to react in the same manner as in the case of nitrosobenzene and phenylhydrazine. The rate of the evolution of nitrogen was less vigorous than in the case of nitrosobenzene. The products of the reaction are summarized in Table III.

Table III. Products of the reaction between *p*-nitrosotoluene and phenylhydrazine

Reactant	*p*-Nitrosotoluene	10.0 mmol.
	Phenylhydrazine	4.37
Product	Benzene	1.63 mmol.
	4, 4′-Azoxytoluene	3.37
	4-Methyldiphenylamine	0.79
	Phenylhydrazine	0.63
$\%CH_3C_6H_4$ of $CH_3C_6H_4NO$ accounted for		75.3%
$\%C_6H_5$ of $C_6H_5N_2H_3$ accounted for		69.8

If the mechanism C is right, the products should be 4, 4′-azoxytoluene, 4-methyldiphenylamine and benzene. On the other hand, if the mechanism D is right, the products should be 4-methylazoxybenzene, 4, 4′-dimethyldiphenylamine and toluene:

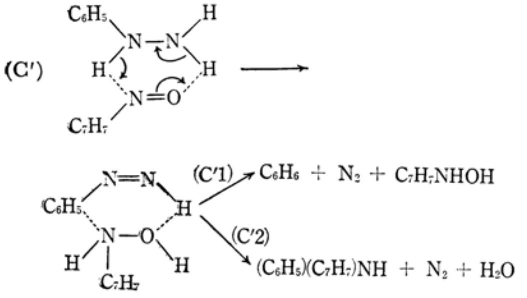


$$p\text{-}CH_3C_6H_4NO + C_6H_5NHNH_2 \xrightarrow{(C)} CH_3C_6H_4\text{-}N{=}\underset{\overset{\downarrow}{O}}{N}\text{-}C_6H_4CH_3 + CH_3C_6H_4(C_6H_5)NH + C_6H_6$$

$$p\text{-}CH_3C_6H_4NO + C_6H_5NHNH_2 \xrightarrow{(D)} CH_3C_6H_4\text{-}N{=}\underset{\overset{\downarrow}{O}}{N}\text{-}C_6H_5 + (CH_3C_6H_4)_2NH + C_6H_5CH_3$$

The products of the reaction shown in Table III contradict the mechanism D, but they are consistent with the mechanism C.

The mechanism C assumes both phenylhydroxylamine and diphenylhydroxylamine as intermediates. However, a modified mechanism, C′, is possible, which assumes only phenylhydroxylamine as an intermediate:



According to the mechanism C′, combined phenyldiimide and *p*-tolylhydroxylamine either depart from each other to yield benzene and nitrogen according to the step C′1, or react further in a solvent cage to yield 4-methyldiphenylamine according to the step C′2. The ratio of C′1 to C′2 can be calculated from the yields of benzene and 4-methyldiphenylamine to be 2.06; in other words, 67% of the reaction proceeds by C′1, while 33% proceeds by C′2. In th ecase of nitrosobenzene, the ratio of C′1 to C′2 is 1.38; in other words, 58% of the reaction proceeds by C′1, while 42% proceeds by C′2.

In the case of the reaction between nitrosobenzene and hydrazine, we assumed a combination of intermediates, diimide and phenylhydroxylamine similar to that in the mechanism B. In this case, however, all the phenylhydroxylamine must have been reduced with diimide in a solvent cage, because if some phenylhydroxylamine departs from diimide without being reduced further, it should react with nitrosobenzene to yield azoxybenzene; the latter was not, however, found in any products studies of the reaction. These findings show the stronger reducing power of diimide compared with that of phenyldiimide.

As for the choice between the mechanisms C and C′, no experimental evidence is available which favors one over the other, although C′ appears a little more attractive than C.

Experimental

Materials.—Nitrosobenzene and *p*-nitrosotoluene were prepared by the reduction of nitrobenzene and *p*-nitrotoluene respectively.[7] Commercial hydrazine hydrate was dehydrated by refluxing it with sodium hydroxide.

4, 4′-Azoxytoluene was prepared by heating 500 mg. of 4, 4′-azotoluene in 2.5 ml. of acetic acid containing 0.1 ml. of 30% hydrogen peroxide in a water bath.[8] The yellow crystals obtained were recrystallized from ethanol, m. p. 70°C.

All the other chemicals were of the best grade commercially available and were used without further purification.

The Reaction between Nitrosobenzene and Hydrazine.—*Run. 1.*—To a solution of hydrazine (0.0512 g., 1.60 mmol.) in dichloromethane (2.587 g.), nitrosobenzene (0.1069 g., 1.00 mmol.) was added at −30°C. The transparent, light green solution thus obtained did not change when kept at −30°C. When it was gradually warmed up, the color changed to a yellowish green at −10°C, and nitrogen gas started to evolve at −8°C. The evolution of nitrogen ceased when the solution was kept for three hours at room temperature, and the color of the solution changed to a yellowish brown. The infrared specturm of the solution was completely accounted for by the absorption of aniline and azobenzene. 0.855 mmol. of aniline and 0.0697 mmol. of azobenzene were found to be present by the use of the absorptions at 1620 cm^{-1} (for aniline) and 1073 cm^{-1} (for azobenzene.).

Run 2.—The procedure was essentially the same as in Run 1, except that about equimolar amounts of

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[7] E. C. Horning, "Organic Syntheses," Coll. Vol. I, 668 (1955).

[8] T. Parsons, Jr., and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **58**, 269 (1936).

nitrosobenzene and hydrazine were used and the reactants solutions were degassed before mixing. The infrared specturm of the dichloromethane solution of the products was completely accounted for by the absorption of aniline and undecomposed nitrosobenzene. The amount of nitrosobenzene was determined by the use of an absorption at 1120 cm^{-1}.

Run 3.—A solution of hydrazine (0.286 g., 8.92 mmol.) in 20 ml. of methanol was placed in a container attached to one end of a U-shaped tube; solid nitrosobenzene (2.388 g., 22.3 mmol.) was placed in a container attached to the other end of the U-shaped tube. After these two had been degassed by the usual technique on a vacuum system, they were mixed at -78°C and then gradually warmed up. The evolution of gas started at -10°C, it became vigorous when the mixture was further warmed up to room temperature. The reaction had been completed in about three hours at room temperature. After the mixture had been kept at room temperature for one day, it was distilled in a vacuum; a greenish distillate and a brownish residue were thus obtained. The greenish distillate was found to be a methanol solution, with small amounts of nitrosobenzene and water, by a study of its infrared spectrum and by vapor-phase chromatography. No benzene was found in the distillate. The infrared spectrum of the brownish residue was completely accounted for by the absorption of aniline, nitrosobenzene and azobenzene.

Run 4.—The procedure was essentially the same as the one used for Run 3, except that sodium methoxide (2.0 mmol.) was added to the mixture.

The Reaction between Nitrosobenzene and Phenylhydrazine.—Phenylhydrazine was stirred, drop by drop, into a solution of nitrosobenzene (1.072 g., 10.0 mmol.) in dichloromethane (3.0 ml.) at room temperature. Reaction occurred with a vigorous evolution of nitrogen upon the addition of each drop of phenylhydrazine. When 0.4273 g. (3.95 mmol.) of phenylhydrazine was added, no more reaction occurred upon the addition of another drop of phenylhydrazine. When the dark red solution obtained was distilled, a colorless distillate and a dark red oil were obtained.

The colorless distillate was viewed against pure dichloromethane in the infrared region, and the spectrum was superimposable upon that of pure benzene. 1.90 mmol. of the benzene was found to be present by a comparison of the specturm with that of a solution containing a known amount of benzene.

1.1548 g. of dark red oil was chromatographed on about 25 g. of alumina. Fractions 1—6, eluted with petroleum ether - benzene, were in the form of light yellow crystals (0.6377 g.), melting at 34.5—35.5°C. Its infrared spectrum was identical with that of azoxybenzene. When recrystallized from ethanol, the crystals melted at 36°C; the melting point was not depressed when authentic azoxybenzene (m. p. 36°C) was mixed with these yellow crystals.

Fractions 8—11, eluted with benzene-ether, were in the form of colorless crystals (0.1770 g.), melting at 52—53°C. The infrared spectrum was identical with that of diphenylamine. When recrystallized, the crystals melted at 54°C, and the melting point was not depressed when authentic diphenylamine (m. p. 54°C) was mixed with these crystals. Fraction 7, eluted with benzene, was a mixture of azoxybenzene and diphenylamine; the amounts of the compounds were determined by a comparison of the infrared spectrum of the mixture with the spectra of authentic samples.

The Reaction between *p*-Nitrosotoluene and Phenylhydrazine.—Phenylhydrazine was stirred drop by drop into a solution of *p*-nitrosotoluene (1.2109 g., 10.0 mmol.) in dichloromethane (5.0 ml.) at room temperature. The evolution of nitrogen occurred less vigorously than in the case of nitrosobenzene and phenylhydrazine. When 0.4720 g. (4.37 mmol.) of phenylhydrazine was added, no more reaction occurred upon the addition of another drop of phenylhydrazine. When the dark orange solution was distilled, a colorless distillate and a brown solid were obtained.

The colorless distillate was viewed against pure dichloromethane in the infrared region; the spectrum was identical with that of pure benzene. 1.63 mmol. of benzene was found to be present by comparison with the spectrum of a solution containing a known amount of benzene.

1.1924 g. of a brown solid was chromatographed on about 25 g. of alumina. Fractions 1—9, eluted with petroleum ether - benzene, were light yellow crystals (0.7135 g.), melting at 69—70°C. Its infrared spectrum was identical with that of 4, 4′-azoxytoluene. The melting point was not depressed when authentic 4, 4′-azoxytoluene (m. p. 69—70°C) was mixed with these light yellow crystals.

Fractions 11—13, eluted with benzene - ether, were colorless needles (0.0729 g.), melting at 79—86°C. Its infrared spectrum was very similar to that of diphenylamine. When recrystallized from ligroin, the colorless needles melted sharply at 88—89°C, the melting point of authentic 4-methyldiphenylamine. Since diphenylamine melts at 54°C and 4,4′-dimethyldiphenylamine, at 79°C, this colorless crystalline amine can be identified with 4-methyldiphenylamine.

Fraction 10, eluted with benzene, weighed 0.0493 g. and was a mixture of 4, 4′-azoxytoluene and 4-methyldiphenylamine. The amounts of each compound were determined by a comparison of the infrared spectrum of the fraction 10 with the spectra of pure compounds.

Fractions 14 and 15, eluted with ether and methanol, were a black oil, weighing 0.1286 g., which was found to contain 0.0678 g. of unreacted phenylhydrazine.

Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.