Experimental Section

The hydrogen bromide was CP grade from Matheson Co. The allenes, except 1,1-dimethylallene, were commercial chemicals; allene came from Matheson Co., the others from the Chemical Samples Co. 1,1-Dimethylallene was prepared by the method of Doering[17] and Hoffman.[18] All compounds were degassed before use and dried thoroughly over phosphorus pentoxide. The reaction system was a conventional all-glass apparatus except for the quartz reaction vessel, the quartz spiral Bourdon gauge, and the quartz medium-pressure mercury arc lamp (GE 100 W). Gas chromatography was done on apparatus connected directly to the reaction system, using hydrogen as the carrier gas, and either dinonyl phthalate columns or a mixture of di-2-ethylhexyl sebacate and dimethylsulfolane. Reaction times were short, usually less than 5 min, and were kept to less than 10% reaction in the kinetic runs. Product identification was largely by nmr, using 50% solutions in CCl_4 run in a Varian A-60 spectrometer. All gas-phase runs and reactions were carried out at least in triplicate, and under a variety of temperatures and pressures. The yields, relative reactivities, and activation energies are reproducible to *ca.* ±2%.

Registry No.—Allene, 463-49-0; methylallene, 590-19-2; 1,1-dimethylallene, 598-25-4; 1,3-dimethylallene, 591-96-8; tetramethylallene, 1000-87-9.

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[17] W. von E. Doering and P. M. LaFamme, *Tetrahedron*, **2**, 75 (1958).

[18] R. Hoffman, *ibid.*, **22**, 521 (1966).

N-Nitrenes. IX. The Reaction of 1,1-Dibenzylhydrazine Anions with Tosyl Azide, Oxygen, and Nitrous Oxide

GEN KOGA AND J.-P. ANSELME[1]

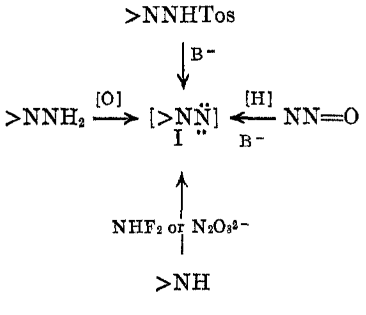
Department of Chemistry, University of Massachusetts, Boston, Massachusetts 02116

Received September 17, 1969

The diazo transfer reaction of tosyl azide to the anion and to the dianion of 1,1-dibenzylhydrazine gives bibenzyl, benzaldehyde dibenzylhydrazone, and 3,3-dibenzyl-1-tosyltriazene. The effect of temperature, the nature of the anion, and the conditions of the reactions, and the mechanisms by which these products are formed, are discussed. Evidence for the participation of N-azidodibenzylamine as an intermediate has been adduced. The reaction of the monoanion of 1,1-dibenzylhydrazine with nitrous oxide and with oxygen results in the formation of the same products (except for the triazene) as are obtained with tosyl azide.

Through the N-nitrene[2] intermediate I, moderate success has been achieved in the gross rationalization of the products formed in a number of reactions[3–8] (Scheme I). The sequence of events between the time the reactants are brought together and the isolation of the products is a matter of conjecture. The questions as to whether or not N-nitrenes are involved and their behavior under the reaction conditions being used are still unresolved.

SCHEME I



In order to eliminate as many parameters as possible, a method which would produce N-nitrenes directly was needed. By analogy with the generation of carbenes and nitrenes from the corresponding diazo alkanes and azides, N-azides (II) should give N-nitrenes (I) by loss of elemental nitrogen.

$$>\overset{-}{C}-\overset{+}{N}\equiv N \longrightarrow >C: + N_2 \tag{1}$$

$$-\overset{-}{N}-\overset{+}{N}\equiv N \longrightarrow -\ddot{N}: + N_2 \tag{2}$$

$$\underset{\text{II}}{>N-\underset{-}{\overset{-}{N}}-\overset{+}{N}\equiv N} \longrightarrow \underset{\text{I}}{>N-\ddot{N}:} + N_2 \tag{3}$$

A major portion of our research effort has been devoted to the development of new and mild methods of preparation of azides. Presumably, these techniques could be applied to the preparation of N-azides. The formation of azides and diazo alkanes[9] by the *diazo transfer* reaction to the anions of the appropriate amine derivatives has been reported.[10] Diazo alkanes were obtained from the reaction of oxygen and tosyl azide with anions of hydrazones[11] and by the *azido transfer* reaction of tosyl azide to ketimine anions.[10c]

We are now reporting the results of our investigations of the reactions of the monoanion and of the dianion of 1,1-dibenzylhydrazine with tosyl azide.

Results

The monoanion and the dianion of 1,1-dibenzylhydrazine were prepared by addition of the appropriate

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[1] To whom all inquiries should be addressed. Fellow of the Alfred P. Sloan Foundation.

[2] In this discussion, it is by no means implied that the involvement of N-nitrenes as fully developed entities has been proven.

[3] For a summary, see C. G. Overberger, J.-P. Anselme, and J. G. Lombardino, "Organic Compounds with Nitrogen-Nitrogen Bonds," The Ronald Press Co., New York, N. Y., 1966, p 89.

[4] C. G. Overberger, M. Valentine, and J.-P. Anselme, *J. Amer. Chem. Soc.*, **91**, 687 (1969).

[5] L. A. Carpino, *J. Org. Chem.*, **30**, 736 (1965), and previous papers.

[6] (a) D. M. Lemal, *et al.*, *J. Amer. Chem. Soc.*, **85**, 1944 (1963); (b) *ibid.*, **86**, 2395 (1964).

[7] (a) C. L. Bumgardner, K. J. Martin, and J. P. Freeman, *ibid.*, **85**, 97 (1963); (b) C. L. Bumgardner and J. P. Freeman, *ibid.*, **86**, 2233 (1964).

[8] D. M. Lemal and T. W. Rave, *ibid.*, **87**, 393 (1965).

[9] Diazo alkanes can formally be considered as N-nitrenes (iii) and can be viewed as arising from N-azidimines (III).

$$\underset{\text{III}}{>C=N-N_3} \xrightarrow{-N_2} \underset{\text{i}}{>C=\overset{+}{N}=\overset{-}{N}} \longleftrightarrow \underset{\text{ii}}{>\overset{-}{C}-\overset{+}{N}\equiv N} \longleftrightarrow \underset{\text{iii}}{>C-\underset{..}{\overset{..}{N}}-N}$$

[10] (a) G. Koga and J.-P. Anselme, *Chem. Commun.*, 446 (1968); (b) J.-P. Anselme and W. Fischer, *Tetrahedron*, **25**, 855 (1969); (c) J.-P. Anselme, W. Fischer, and N. Koga, *ibid.*, **25**, 89 (1969).

[11] (a) W. Fischer and J.-P. Anselme, *J. Amer. Chem. Soc.*, **89**, 5312 (1967); N. Koga and J.-P. Anselme, unpublished results. (b) W. Fischer and J.-P. Anselme, *Tetrahedron Lett.*, 877 (1968).

TABLE I

PRODUCTS OF THE REACTION OF ANIONS OF 1,1-DIBENZYLHYDRAZINE WITH *p*-TOLUENESULFONYL AZIDE, NITROUS OXIDE, AND OXYGEN[a]

Anion	Temp (conditions)	Hydrazine consumed, mmol	Bibenzyl, %	Hydrazone,[b] %	Triazene, %	$TosNH_2$,[c] %	$TosN_3$ recovered, mmo
Mono-	Room	18.6	49	30	. . .	33	7.4
Mono-	Low	20.1	23	30	16	37	Traces
Mono-	Low[d]	19.2	11	16	28	35	4.2
Di-	Room	24.6	42	10	. . .	82	Traces
Di-[e]	Low[d]	>95%	Traces	14	13	83	3.8
Mono-[f,g]	Room (O_2)	20.1	27	22	. . .		
Mono-[f,h]	Room (N_2O)	10.8	12	11	. . .		

[a] Percentage yields are corrected for recovered 1,1-dibenzylhydrazine. Thirty millimoles of 1,1-dibenzylhydrazine was used except as noted otherwise. An equivalent amount of tosyl azide was used. [b] N,N-Dibenzylbenzalhydrazone; percentage yield based on reaction 10. [c] Percentage yields are based on the amount of uncovered tosyl azide. [d] Reverse addition (anion added to tosyl azide). [e] Twenty millimoles of hydrazine and 40 mmol of tosyl azide were used. [f] See Experimental Section. [g] Dibenzylamine (19%) and benzoic acid (12%) were also isolated. [h] An unknown compound (0.3 g, mp 92–93.5°) having NH (3225 cm^{-1}) and C=O (1690 and 1650 cm^{-1}) absorptions was also isolated. The results of the elemental analysis suggest the formula $C_{14}H_{14}N_2O$.

TABLE II

REACTION PRODUCTS OF 1,1-DIBENZYLHYDRAZINE ANIONS WITH TOSYL AZIDE, OXYGEN, AND NITROUS OXIDE[a]

Anion	Temp (conditions)	Hydrazine recovered	Bibenzyl	Hydrazone	Triazene	$TosNH_2$	$TosN_3$
Mono-	Room	2.40	1.65	0.85	. . .	1.70	1.45
Mono-	Low	2.10	0.85	0.90	1.20	1.90	Traces
Mono-	Low[b]	2.30	0.40	0.46	2.00	1.80	0.25
Di-	Room	1.20	1.90	0.35	. . .	4.20	Traces
Di-	Low[b]	Traces	Traces	0.43	0.96	2.85	0.30
Mono-	Room[c] (O_2)	2.10	1.00	0.66	. . .	. . .	. . .
Mono-	Room[d] (N_2O)	4.10	0.25	0.18	. . .	. . .	. . .

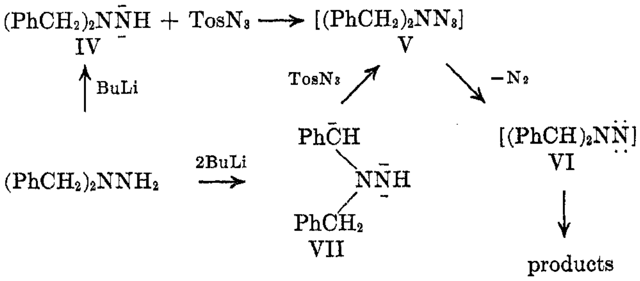
[a] All weights are in grams; see also footnotes to Table I. [b] Reverse addition (anion added to tosyl azide). [c] Other products identified follow: dibenzylamine, 0.77 g; benzoic acid, 0.3 g. [d] A compound, mp 92–94° ($C_{14}H_{14}N_2O$), was also isolated.

amount of *n*-butyllithium to the hydrazine. Then a solution of tosyl azide in tetrahydrofuran was added and the reaction was allowed to proceed. In addition to recovered 1,1-dibenzylhydrazine and tosyl azide and the expected by-products (tosylamide and nitrogen gas), the following compounds were isolated and characterized in the various runs: bibenzyl (VIII), benzaldehyde dibenzylhydrazone (IX), and 3,3-dibenzyl-1-tosyltriazene (X). The results are collected in Tables I and II along with the data from the reaction of the monoanion of 1,1-dibenzylhydrazine with oxygen and with nitrous oxide.

Discussion

By analogy to the reaction of primary amine anions with tosyl azide, N-azidodibenzylamine (V) may be viewed as the first product of the reaction of the monoanion (IV) of 1,1-dibenzylhydrazine with tosyl azide (Scheme II). Whether or not V has any real existence even as a highly unstable intermediate is not certain at this time, although the evidence presented later would seem to support such an assumption.[12] The results of the reaction depicted below, as well as those of the dianion VII of dibenzylhydrazine[13] with tosyl azide, can be most easily rationalized *via* the intermediacy of the N-nitrene VI. Similarly, the products of the reaction of IV with nitrous oxide and oxygen are also best explained in terms of VI.

SCHEME II



An examination of the data of Table I indicates that the expected fragmentation product bibenzyl (VIII) is formed in all cases, even though it is not necessarily the main product. The formation of bibenzyl *via* the intermediacy of dibenzylaminonitrene (VI) had been previously postulated,[3–8] although direct

$$(PhCH_2)_2NNH_2 + BuLi \longrightarrow \begin{bmatrix}\text{monoanion}\\ \text{dianion}\end{bmatrix} \xrightarrow{TosN_3}$$

$$\underset{\text{VIII}}{PhCH_2CH_2Ph} + \underset{\text{IX}}{PhCH{=}NN(CH_2Ph)_2} + \underset{\text{X}}{(PhCH_2)_2NN{=}NTos} \quad (4)$$

evidence for this intermediate was still lacking. However, recent reports[14] as well as the early work of Urry, McBride, and coworkers,[15] while not proving

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[12] Two N-azidamines have been reported previously: (a) H. Bock and K.-L. Kompa, *Z. Anorg. Allg. Chem.*, **332**, 238 (1964); (b) N. Wyberg and A. Gieren, *Angew. Chem., Int. Ed. Engl.*, **1**, 664 (1962).

[13] The deep red color of the dianion suggests that it exists in a large part as the C,N dianion; *i.e.*, the second proton is removed from the α carbon.

[14] R. W. Atkinson and C. W. Rees, *Chem. Commun.*, 1230 (1967); C. W. Rees, *et al.*, *ibid.*, 146, 147, 377 (1969).

[15] W. R. McBride and H. W. Kruse, *J. Amer. Chem. Soc.*, **79**, 572 (1957); W. H. Urry, H. W. Kruse, and W. R. McBride, *ibid.*, **79**, 6568 (1957); W. H. Urry, P. Szecsi, C. Ikoku, and D. W. Moore, *ibid.*, **86**, 2224 (1964).

the existence of VI, add credence to its postulation as the direct source of bibenzyl.

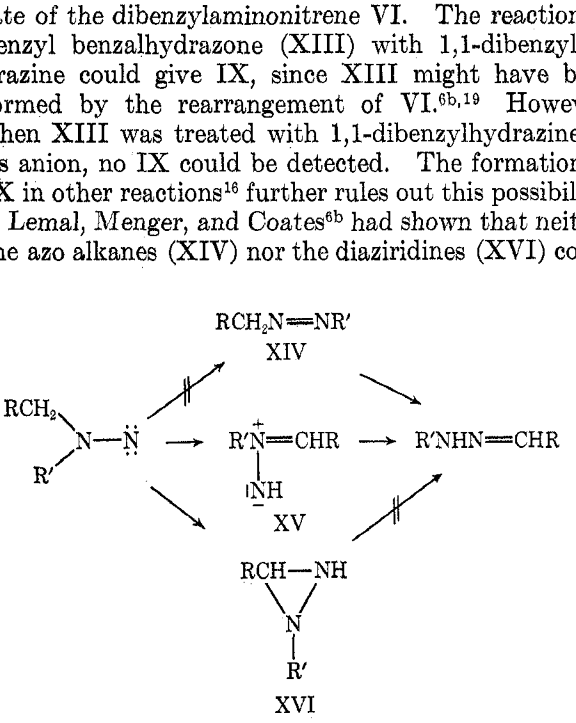
The isolation of benzaldehyde dibenzylhydrazone (IX), sometimes in substantial quantities, was unexpected at first sight. It had never been recognized[16] previously as one of the reaction products of VI. The only report of products of a related nature was that of Urry and Ikoku,[17] who found the hydrazones XII as one of the products of dialkylaminonitrenes (XI).

$$\underset{\text{XI}}{2(\mathrm{RCH_2})_2\mathrm{NN}\colon} \longrightarrow \underset{\text{XII}}{(\mathrm{RCH_2})_2\mathrm{NN{=}CHR}} \qquad (5)$$

$$\mathrm{R} = \mathrm{H, alkyl}$$

The formation of benzaldehyde dibenzylhydrazone (IX) as a ubiquitous product of our studies[18] indicated that this was a result of major significance in the overall fate of the dibenzylaminonitrene VI. The reaction of benzyl benzalhydrazone (XIII) with 1,1-dibenzylhydrazine could give IX, since XIII might have been formed by the rearrangement of VI.[6b,19] However, when XIII was treated with 1,1-dibenzylhydrazine or its anion, no IX could be detected. The formation of IX in other reactions[16] further rules out this possibility.

Lemal, Menger, and Coates[6b] had shown that neither the azo alkanes (XIV) nor the diaziridines (XVI) could be intermediates in the *diazene–hydrazone* rearrangement. These authors reluctantly accepted the azomethine imine (XV)[20] as a tentative intermediate despite what they felt were serious reservations. We suggest that XV is, indeed, the intermediate leading not only to hydrazones of the type reported by Lemal and his group,[6b] but also to IX.[21]



(6)

The third compound isolated in the reactions with tosyl azide, 3,3-dibenzyl-1-tosyltriazene (X), is the first member of a novel class of compounds, 3,3-dialkyl-1-tosyltriazenes.[22] Low temperatures and high concentration of tosyl azide favored the formation of X, the generation of which can be viewed as arising directly from the reaction of the anions with tosyl azide (reaction 9). However, in view of the beneficial effect of low temperature on its formation and its yield, it is more likely that X was generated from the reaction

$$(\mathrm{PhCH_2})_2\mathrm{N}\underset{-}{\bar{\mathrm{N}}}\mathrm{H} + \mathrm{TosN_3} \longrightarrow (\mathrm{PhCH_2})_2\mathrm{NNH}\underset{-}{\bar{\mathrm{N}}}\mathrm{Tos} \xrightarrow{\mathrm{TosN_3}} \underset{\text{X}}{(\mathrm{PhCH_2})_2\mathrm{NN{=}NTos}} \qquad (7)$$

of either N-azidodibenzylamine (V) or dibenzylaminonitrene (VI) with tosyl azide.

The data of Table I also indicate that the total percentage yield of VIII, IX, and X amounts to 49–79%. The notable exception is that of the low-temperature, reverse-addition reaction of the dianion with a 100% excess of tosyl azide. If the dianion VII is involved, the formation of complex products (as indicated by the formation of tars) would be expected from the reaction of a second molecule of tosyl azide at the α carbon; it is also the only case in which practically none of the starting hydrazine could be recovered.[23]

It is evident from our data that the triazene is being formed at the expense of bibenzyl at lower temperature while the hydrazone yield remains the same. When reverse addition and low temperatures are used, the triazene becomes the major product. This could indicate that V (or VI) may have longer lifetime under these conditions. The complete absence of X in the reaction of tosyl azide with VII, at room temperature, along with the rather high conversion into bibenzyl, suggest that fragmentation is the preferred route. The following mechanisms are suggested as likely paths to explain our results.

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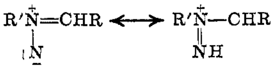
[16] Reexamination of the literature indicated that indeed hydrazones of types IX and XII had been formed. Busch and Weiss [*Ber.*, **33**, 2701 (1900)] isolated IX by heating 1,1-dibenzylhydrazine in ethanol and acetic acid. Evidently, air oxidation had occurred to give VI, which then gave IX. Similarly, the reduction of N-nitrosodibenzylamine also gave IX. In complete agreement with the results, Overberger and Marks [*J. Amer. Chem. Soc.*, **77**, 4101 (1955)] isolated a minor product, mp 86–87°, from the oxidation of 1,1-dibenzylhydrazine with *t*-butyl hypochlorite in basic medium; it was assigned the structure of tribenzylhydrazine and formed a picrate, mp 140–141°. An authentic sample of IX melts at 86–87° and its picrate melts at 137–139°. Subsequently, Overberger, Lombardino, and Hiskey [*J. Amer. Chem. Soc.*, **80**, 3009 (1958)] reported that lithium in liquid ammonia gave, in addition to some bibenzyl, "tribenzylhydrazine." There seems to be little doubt that Overberger and his group indeed obtained IX, both from the reduction of N-nitrosodibenzylamine and from the reaction of 1,1-dibenzylhydrazine with *t*-butyl hypochlorite. Carter and Stevens [*J. Chem. Soc.*, 1743 (1961)] isolated substantial amounts of the hydrazones corresponding to IX. Overberger and Marullo [*J. Amer. Chem. Soc.*, **83**, 1378 (1961)] obtained IX in 65% yield from the oxidation of 1,1-dibenzylhydrazine with potassium bromate in strongly acidic solution.

[17] W. H. Urry and C. Ikoku, Abstracts, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan 1964, p 25c. W. H. Urry, A. L. Olsen, E. M. Bens, H. W. Kruse, and C. Ikoku, *U. S. Gov. Res. Develop. Rep.*, **40**, 107 (1965); *Chem. Abstr.*, **64**, 14078*d* (1966).

[18] It has also been isolated in other oxidation studies carried out in our laboratories. These results will be the subject of a future paper.

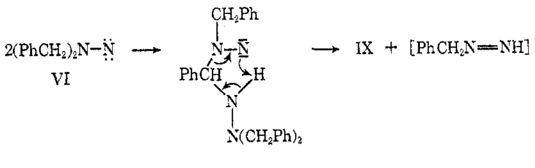
[19] M. Busch and K. Lang, *J. Prakt. Chem.*, **144**, 291 (1936).

[20] In one of its resonance forms, XV could be regarded as a "diimide ylide."



$$\mathrm{R'}\overset{+}{\underset{\underset{\underline{\mathrm{N}}}{|}}{\mathrm{N}}}{=}\mathrm{CHR} \longleftrightarrow \mathrm{R'}\overset{+}{\underset{\underset{\mathrm{NH}}{\|}}{\mathrm{N}}}{-}\mathrm{CHR}$$

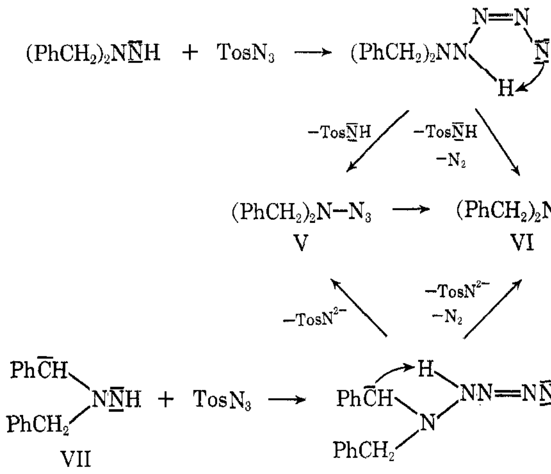
[21] The formation of IX does not necessarily require XV and could involve nitrene insertion and give IX; however, the likelihood of VI reacting with itself, as shown in the reaction below, is remote.



[22] The dimethyl analog has also been prepared and characterized. The nmr spectra of the 3,3-dialkyl-1-tosyltriazenes exhibited *two* sharp, well-defined peaks for the α hydrogens. See G. Koga and J.-P. Anselme, *Chem. Commun.*, 894 (1969).

[23] The oxidation products of the monoanion with oxygen amounts to 63% total yield (benzoic acid divided by 2). Nitrous oxide is known to be a much less effective *diazo transfer* agent.[10a]

Formation of N-azidodibenzylamine (V) and/or dibenzylaminonitrene (VI) is depicted in reaction 8.

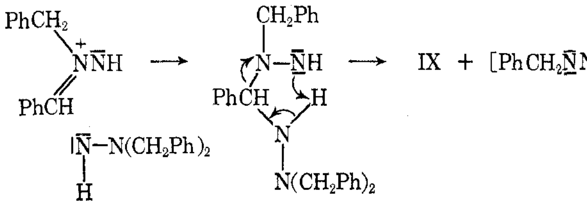


(8)

Formation of bibenzyl (VIII) is depicted in reaction 9.

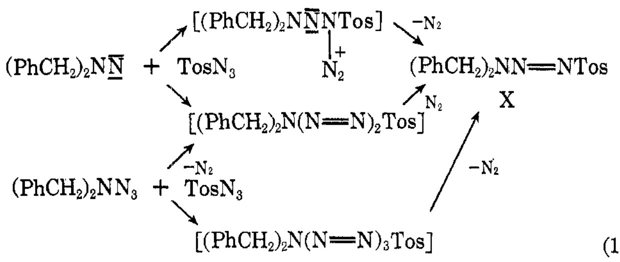
$$(PhCH_2)_2NN \xrightarrow{-N_2} PhCH_2CH_2Ph + N_2 \qquad (9)$$

Formation of benzaldehyde dibenzylhydrazone (IX) is depicted in reaction 10.



(10)

Formation of 3,3-dibenzyl-1-tosyltriazene (X) is depicted in reaction 11.



(11)

The ultimate goal of our program has been to prepare N-azidamines (II) as sources of N-nitrenes (I). The evidence that we have gathered so far suggests that, indeed, both the N-azidamine V and the N-nitrene VI are formed in our reactions. Supporting evidence for the formation of V was obtained from the following experiments. After the anion IV was treated with tosyl azide at −50°, the temperature was allowed to rise to 0–10°. The solvent was evaporated from an aliquot, and infrared spectral examination of the pasty residue showed, in addition to the azide band of tosyl azide at 2120 cm^{-1}, a small absorption at 2060 cm^{-1}. The ratio of the two bands was *ca.* 3:1. The bulk of the reaction mixture was allowed to warm to 15° and quenched with ice–water. Extraction with ether, followed by washing with dilute hydrochloric acid and evaporation of the solvent, gave an oil which showed the same two bands but with the ratio of the 2120- and 2060-cm^{-1} bands increased to 10:1. Upon standing at room temperature, the oil evolved gas; the following day, the band at 2060 cm^{-1} had completely disappeared and a 30% yield of bibenzyl was obtained. If the reaction mixture, having reached room temperature, was cooled back to −50° and triphenylphosphine was added, no significant yield of bibenzyl was obtained. Presumably, the triphenylphosphine reacted with the N-azidodibenzylamine[12a] to form the triphenylphosphine adduct; however, attempts to isolate it from the complex reaction mixture failed.

The reaction of the monoanion of 1,1-dibenzylhydrazine with nitrous oxide can be visualized as proceeding through the same steps as when tosyl azide is used. In the case of oxygen, none of the triazene X can be formed; however, dibenzylamine and benzoic acid were isolated in substantial yields.

The results of the study reported here can be summarized as follows. *Diazo transfer* of tosyl azide to the monoanion (or dianion) of 1,1-dibenzylhydrazine gives N-azidodibenzylamine (V), which is moderately stable at low temperatures. The loss of nitrogen from V generates dibenzylaminonitrene (VI), which can lose nitrogen to give bibenzyl (VIII) or tautomerize to the azomethine imine XV. The reaction of VI (or IX) with tosyl azide would give 3,3-dibenzyl-1-tosyltriazene. Under the strongly basic conditions prevailing in our reaction, benzaldehyde dibenzylhydrazone (IX) is probably formed according to reaction 10. It is clear, however, that a whole gamut of mechanisms may be operative, depending upon the conditions under which VI is generated.

Experimental Section

All melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Infracord. Analyses were performed by the MHW Laboratories, Garden City, Mich. The alkyllithium compounds were used as received from α-Inorganics, Beverly, Mass. The preparation of the anions and all the reactions with tosyl azide were carried out under a nitrogen atmosphere. The compounds obtained were identified by their physical constants and by comparison of their infrared spectra with those of authentic samples.

Dibenzylhydrazine Anion Solution.—*n*-Butyllithium (30 mmol) in hexane was added during the course of 30 min to a solution of 6.4 g (30 mmol) of 1,1-dibenzylhydrazine in 100 ml of tetrahydrofuran under a nitrogen atmosphere with cooling and efficient stirring. The initially colorless solution turned deep wine red toward the end of the addition. Twice the amount of *n*-butyllithium was used with prolonged stirring after the addition to prepare the dianion solution. In this case, the deep red color developed much sooner.

Reaction with Nitrous Oxide.—Dibenzylhydrazine monoanion solution in a 300-ml pressure bottle was stirred at room temperature for 12 hr under 20–40-psi pressure of nitrous oxide. The color of the reaction mixture turned light tan after the introduction of nitrous oxide. The reaction mixture was then poured into cold water and extracted with ether. The ethereal extract was washed with 1 *N* hydrochloric acid to separate the basic fraction and dried over magnesium sulfate. Evaporation of the solvent gave a neutral residue which was chromatographed. The basic fraction was distilled *in vacuo* after a conventional work-up.

Reaction with Tosyl Azide at Room Temperature.—To the dibenzylhydrazine anion solution was added dropwise a solution of 5.9 g (30 mmol) of tosyl azide in 20 ml of tetrahydrofuran at room temperature. From the initially light orange solution, a white solid soon precipitated. After the completion of the addition, the reaction mixture was stirred for 1–2 hr at room temperature. The reaction mixture was worked up as previously described.

Reaction with Tosyl Azide at Low Temperature.—The hydrazine anion solution was cooled to −50 to *ca.* −60° in Dry Ice–isopropyl alcohol. A solution of 5.9 g (30 mmol) of tosyl azide in 20 ml of tetrahydrofuran was added to the above solution during the course of 1 hr with efficient stirring. The reaction mixture became reddish brown and gas began to evolve slowly and amounted to a total of *ca.* 15 mmol (350–400 ml) before all of the tosyl azide was added. After the completion of the addition, the temperature was allowed to rise slowly to room temperature. A white solid precipitated at −10°. The total volume of evolved nitrogen amounted to *ca.* 30–40 mmol (750–800 ml). The reaction mixture was worked up as usual.

Reaction with Oxygen.—A rapid stream of oxygen was bubbled into the solution of dibenzylhydrazine monoanion for 30 min at room temperature. The color changed to light brown and to reddish brown toward the end of the reaction. There was no obvious heat evolution. The reaction mixture was worked up as before, with the exception that the washing with hydrochloric acid was omitted. The aqueous layer, after extraction with ether, gave a positive test for peroxide ion.

The Chromatographic Separation.—The crude reaction mixture, diluted with a small amount of benzene, was adsorbed on a column (i.d. 24 mm, length 600 mm) packed with 150 g of Fisher A540 alumina. The sequence of eluents and main eluates therefrom were as follows (Table III).

TABLE III

Fraction	Eluent	Eluate
1	Hexane	Bibenzyl
2	Hexane–benzene (1:1)	Tosyl azide
3	Benzene	Benzaldehyde dibenzylhydrazone
4	Benzene	Dibenzylhydrazine (O_2 reaction)
5	Benzene	Dibenzylamine (O_2 reaction)
6	Benzene–ether (1:1)	$C_{14}H_{14}N_2O$ compound (N_2O reaction)
7	Benzene–ether (1:1)	3,3-Dibenzyl-1-tosyltriazene

Although there were obtained many minor eluates, including benzaldehyde, along with above compounds, no effort was made to identify them.

In the case of the reaction with oxygen, the basic fraction was not separated from the rest of the reaction mixture.

3,3-Dibenzyl-1-*p*-toluenesulfonyltriazene.—A solution of 30 mmol of 1,1-dibenzylhydrazine monoanion (prepared under a nitrogen atmosphere) from 6.4 g (30 mmol) or hydrazine in 100 ml of dry tetrahydrofuran and 13.5 ml of 22% *n*-butyllithium was cooled to −50 to −60° in Dry Ice–isopropyl alcohol, and 5.9 g (30 mmol) of tosyl azide in 20 ml of tetrahydrofuran was added dropwise. After addition was completed, the solution was allowed to warm up gradually to *ca.* 10°. The initially reddish brown solution turned milky brown by the formation of a white precipitate. The reaction mixture was poured into ice–water and extracted with three 100-ml portions of ether. The combined ethereal extracts were washed successively with water, dilute hydrochloric acid, and water. After having been dried over magnesium sulfate, the solution was evaporated *in vacuo*.

The residual oil was chromatographed, and after the elution of other components, a white solid was obtained from the 1:1 benzene–ether fraction. The compound, mp 79–81°, weighed 1.20 g after recrystallization from carbon tetrachloride. It was characterized and identified as 3,3-dibenzyl-1-tosyltriazene from its elemental analysis and infrared and nmr spectra.[22]

Anal. Calcd for $C_{21}H_{21}N_3SO_2$: C, 66.47; H, 5.58; N, 11.07; S, 8.45. Found: C, 66.73; H, 5.45; N, 10.96; S, 8.34.

Its infrared spectrum, in addition to the expected aromatic and aliphatic bands, exhibited a strong absorption at 1145 and 1180 and at 1325 cm^{-1} ($-SO_2-$). The benzylic protons appeared as two sharp singlets at τ 4.97 and 5.10.[22]

Spectral Detection of N-Azidodibenzylamine.—The monoanion[24] of 1,1-dibenzylhydrazine was treated with 1 equiv of tosyl azide at −50 and −60° and allowed to warm to 0–10° as described above. The solvent was evaporated *in vacuo* below room temperature from a small aliquot. The pasty residue was bubbling on standing and showed two azide bands at 2120 and 2060 cm^{-1}. The former band, *ca.* three times stronger in intensity than the latter, is due to unreacted tosyl azide. The remaining portion of the reaction mixture was worked up as described before. The residual oil showed a much weaker (the ratio of the 2120:2060-cm^{-1} bands was *ca.* 10:1) but still discrete N-azide band which disappeared completely after standing overnight. Distillation of the residue gave bibenzyl in *ca.* 30% yield; the small discrepancy with the 23% yield given in Table I is due to the different isolation procedures.

Registry No.—Tosyl azide, 941-54-8; oxygen, 7782-44-7; nitrous oxide, 10024-97-2; IV, 23349-33-9; VII, 23349-34-0; X, 23349-35-1.

Acknowledgment.—The generous support of this work by the National Institutes of Health under Grant GM 13689-03 is hereby acknowledged with deep appreciation.

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[24] Methyllithium was used to prepare the monoanion in these experiments.