

Anal. Calcd. for $C_{22}H_{17}ClO_5S$: C, 60.64; H, 5.02. Found: C, 60.65; H, 4.96.

t-Butyl *o*-(*p*-Nitrophenylthio)-perbenzoate.—*o*-(*p*-Nitrophenylthio)-benzoic acid was prepared in a 22% yield by the procedure of Mann and Turnbull³⁷; m.p. 226–227° (lit.³⁷ 227–228°). This acid (10 g., 0.036 mole) was refluxed with excess thionyl chloride for several hours. Removal of the thionyl chloride by distillation left impure acid chloride, which was recrystallized from ether-pentane; 8.0 g. (0.027 mole, 75%), m.p. 131–132°. Treatment of this acid chloride with *t*-butyl hydroperoxide in the presence of pyridine in the usual manner prepared the perester in 46% yield, m.p. 84–84.5°.

Anal. Calcd. for $C_{17}H_{17}NO_5S$: C, 58.77; H, 4.93. Found: C, 59.00; H, 4.87.

Galvinoxyl.—The radical scavenger, galvinoxyl, was synthesized by the method of Kharasch and Joshi³⁸; m.p. 154–155° (lit.³⁸ 157°).

Decomposition of *t*-Butyl *o*-Phenylthio-perbenzoate in Acetic Acid.—The perester (0.13 g., 0.00043 mole) in 4 ml. of acetic acid in a sealed tube was heated on a steam-bath for 2 hours. The tube was opened, a small amount of ethanol was added and the volatile materials were distilled. The addition of 2,4-dinitrophenylhydrazine reagent caused the precipitation of the dinitrophenylhydrazone of acetone; yield 15% (16 mg., 0.000067 mole), m.p. 124–125° (lit.³⁹ 126°).

t-Butyl *o*-Methylsulfonylperbenzoate (V).—Technical grade *o*-mercaptobenzoic acid was methylated with alkaline dimethyl sulfate according to the procedure of Friedlaender,⁴⁰ and the methylated acid was oxidized to *o*-methylsulfonylbenzoic acid by the method of Arndt, Kirsch and Nachtwey.⁴¹ Treatment of this acid with thionyl chloride yielded the acid chloride (88%), m.p. 59–60°.

Anal. Calcd. for $C_9H_7O_3ClS$: C, 43.94; H, 3.21. Found: C, 44.20; H, 3.48.

A solution of the acid chloride (4.0 g., 0.018 mole) in 75 ml. of ether was added slowly to a solution of *t*-butyl hydroperoxide (2.55 g., 0.028 mole) and pyridine (1.6 g., 0.020 mole) in 100 ml. of ether.

The mixture was allowed to stir overnight, then was filtered to remove pyridinium hydrochloride. Chromatography through

basic alumina, eluting with ether, removed *t*-butyl hydroperoxide. Recrystallization from ether-pentane yielded the perester, 1.06 g. (0.003 mole, 17%), m.p. 74–75°.

Anal. Calcd. for $C_{12}H_{16}O_5S$: C, 52.94; H, 5.88. Found: C, 52.89; H, 6.03.

t-Butyl Dibenzothiophene-4-percarboxylate (VI).—A solution of dibenzothiophene-4-carboxylic acid chloride^{42,43} (3.72 g., 0.015 mole) in 500 ml. of methylene chloride was added slowly to a stirred solution of pyridine (2.0 g., 0.0253 mole) and *t*-butyl hydroperoxide (1.7 g., 0.0189 mole) in 75 ml. of methylene chloride at 0°. The mixture was stirred at 0° for 6 days, then filtered to remove pyridinium chloride and chromatographed through basic alumina, eluting with ether. The crude perester was recrystallized from ether-pentane to give 0.67 g. (0.0023 mole, 15%) of VI, m.p. 79–80°.

Anal. Calcd. for $C_{17}H_{16}O_5S$: C, 68.00; H, 5.33. Found: C, 67.66; H, 5.36.

t-Butyl Thioxanthone-4-percarboxylate (VII).—Treatment of thioxanthone-4-carboxylic acid^{44,45} with excess thionyl chloride produced the acid chloride in 69%, m.p. 202–204°. Perester VII was prepared in a 14% yield from this acid chloride in a manner analogous to the preparation of VI; m.p. 132–133° dec.

Anal. Calcd. for $C_{18}H_{16}O_4S$: C, 65.83; H, 4.91. Found: C, 65.55; H, 4.83.

Kinetic Analysis.—A description of the technique employed may be found in part II of this series.¹

The rate constants were determined by the method of least squares.⁴⁶

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(37) F. G. Mann and J. H. Turnbull, *J. Chem. Soc.*, 747 (1951).

(38) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1435 (1957).

(39) R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956.

(40) P. Friedlaender, *Ann.*, **351**, 390 (1907).

(41) F. Arndt, A. Kirsch and P. Nachtwey, *Ber.*, **59**, 1074 (1926).

(42) H. Gilman and A. L. Jacoby, *J. Org. Chem.*, **3**, 108 (1938).

(43) H. Gilman and S. Avakian, *J. Am. Chem. Soc.*, **68**, 2104 (1946).

(44) H. Gilman and D. L. Esmay, *ibid.*, **75**, 278 (1953).

(45) F. Mayer, *Ber.*, **43**, 584 (1910).

(46) W. J. Youden, "Statistical Methods for Chemists," John Wiley and Sons, Inc., New York, N. Y., 1951.

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The Decomposition of Certain 1,1-Disubstituted 2-Arenesulfonylhydrazine Salts

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The behavior in ether solvents at elevated temperatures of *N*-benzenesulfonamidopyrrolidine, *N*-tosylamidopyrrolidine and *N*-benzenesulfonamidocarbazole sodium salts has been studied. Mechanisms are proposed for the observed decompositions and inferences are drawn regarding the chemistry of diazenes (aminonitrenes).

Introduction

Oxidation of 1,1-disubstituted hydrazines generally leads to tetrazenes, often in quantitative yields. Certain 1,1-dialkylhydrazines undergo fragmentation when oxidized, however, yielding nitrogen and the products of disproportionation and/or coupling of the alkyl groups. This so-called "abnormal" reaction has been observed only where one² or both^{3,4} of the α -carbons bears a substituent capable of stabilizing charge or radical character (*e.g.*, aryl or cyano) in the transition state for decomposition. Fragmentation

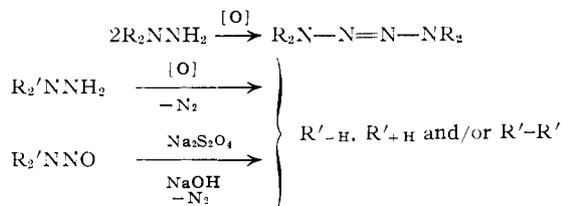
(1) Monsanto Summer Research Fellow, 1961; du Pont Summer Research Fellow, 1962.

(2) C. G. Overberger and L. P. Herin, *J. Org. Chem.*, **27**, 417 (1962); L. A. Carpino, A. A. Santilli and R. W. Murray, *J. Am. Chem. Soc.*, **82**, 2728 (1960).

(3) C. G. Overberger, *Rec. Chem. Progr.*, **21**, 21 (1960).

(4) See for example, C. G. Overberger, N. P. Marullo and R. G. Hiskey, *J. Am. Chem. Soc.*, **83**, 1374 (1961); C. G. Overberger and L. P. Herin, *J. Org. Chem.*, **27**, 2423 (1962).

also occurs in sodium hydrosulfite reductions of nitrosamines (which normally give hydrazines), but only if these special substituents are present.^{4,5} Carpino discovered that the base-catalyzed decomposition of

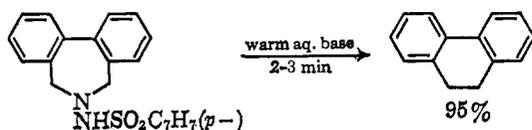


1,1-dibenzyl-2-benzenesulfonylhydrazine gave nitrogen and bibenzyl in high yield,⁶ and fragmentation in an analogous fashion has been shown to occur with a

(5) C. G. Overberger and N. P. Marullo, *J. Am. Chem. Soc.*, **83**, 1378 (1961).

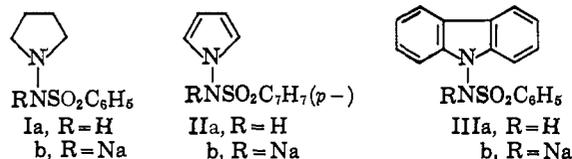
(6) L. A. Carpino, *ibid.*, **79**, 4427 (1957).

variety of other arenesulfonylhydrazines bearing benzylic substituents.^{7,8} For example⁸

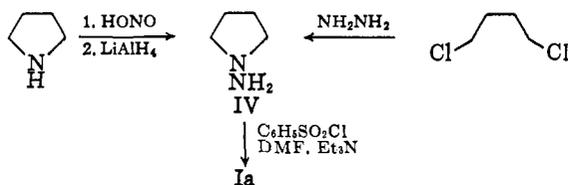


It has been postulated,³ though by no means proved, that all of the processes described above share a common intermediate, namely, an aminonitrene (called a diazene, $>N-N \longleftrightarrow >\overset{+}{N}-\overset{-}{N}$) which either fragments or survives sufficiently long to react intermolecularly, giving tetrazene.⁹ McBride and co-workers have adduced convincing evidence for the existence of diazenes in certain oxidations of 1,1-dialkylhydrazines and have demonstrated that the conjugate acids of certain diazenes (diazonium ions) are remarkably stable species (e.g., $(CH_3)_2\overset{+}{N}=\overset{-}{N}H$).^{10,11}

The present work was undertaken in order to gain greater insight into the chemistry of diazenes. Attention was focused on the Carpino reaction since it appeared to be particularly well suited for generating these species in inert media. With very few exceptions, examples of this reaction had employed hydrazines bearing benzylic substituents, and the usual reaction medium had been warm aqueous base.¹² We chose to investigate the behavior of arenesulfonylhydrazine salts having other types of substituents, and to eliminate or minimize reactions with the medium by using ethers (diglyme and tetraglyme) as the solvents. The first salts to come under our scrutiny were the aminopyrrole derivatives Ib, Iib and IIIb; decomposition of other arenesulfonylhydrazine salts will be the subject of future publications.



Synthesis of the Arenesulfonylhydrazines. **N-Benzenesulfonylamidopyrrolidine (Ia).**—Nitrosation followed by lithium aluminum hydride reduction transformed pyrrolidine into its N-amino derivative IV,¹³ which was even more readily accessible by the reaction of 1,4-dichlorobutane with hydrazine. The Carpino method¹



(7) R. L. Hinman and K. L. Hamm, *J. Am. Chem. Soc.*, **81**, 3294 (1959); W. Baker, J. F. W. McOmie and D. R. Preston, *Chem. Ind. (London)*, 1305 (1960), *J. Chem. Soc.*, 2971 (1961); L. A. Carpino, *J. Am. Chem. Soc.*, **84**, 2196 (1962).

(8) L. A. Carpino, *Chem. Ind. (London)*, 172 (1957).

(9) Dimerization of the aminonitrene is the most obvious route to tetrazene, but attack of the nitrene on a longer-lived species such as the starting material followed by an elimination is a far more likely pathway.

(10) W. R. McBride and H. W. Kruse, *J. Am. Chem. Soc.*, **79**, 572 (1957); W. H. Urry, H. W. Kruse and W. R. McBride, *ibid.*, **79**, 6568 (1957).

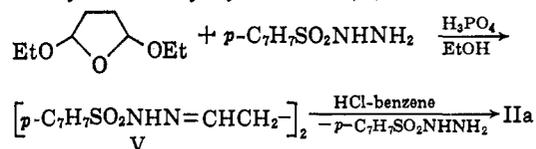
(11) W. R. McBride and E. M. Bens, *ibid.*, **81**, 5546 (1959).

(12) 1-Aryl-1-benzyl-2-sulfonylhydrazines rearrange to hydrazones under the conditions of the Carpino reaction (P. Carter and T. S. Stevens, *J. Chem. Soc.*, 1743 (1961)). Similarly, oxidation of certain 1-arylbenzylhydrazines gives hydrazones (M. Busch and K. Lang, *J. prakt. Chem.*, **144**, 291 (1936)). It is likely that both reactions involve diazene intermediates.

(13) J. H. Biel, U. S. Patent 2,932,646 (1960); (*Chem. Abstr.*, **54**, 17436a (1960); M. Rink and M. Mehta, *Naturwissenschaften*, **48**, 51 (1961).

for sulfonylation, which employs the sulfonyl chloride in dimethylformamide containing triethylamine, was found to be superior to more common procedures in the preparation of the sensitive Ia.

N-Tosylamidopyrrole (IIa) was prepared from 2,5-diethoxytetrahydrofuran and tosylhydrazine *via* succinaldehyde bistosylhydrazone (V).¹⁴



N-Benzenesulfonylamidocarbazole (IIIa).—The nitrogen of carbazole, in contrast to that of pyrrole, is sufficiently basic that N-nitrosation is facile, and zinc in acetic acid¹⁵ reduces the N-nitroso compound to the hydrazine VI. Lithium aluminum hydride is an equally satisfactory reducing agent, though reductive cleavage of the N-N bond competes with hydrazine formation.¹⁶

Sulfonylation of the hydrazine in dimethylformamide containing triethylamine gave the bisbenzenesulfonyl derivative VII¹⁷ even when equimolar amounts of base and chloride were used. The formation of VII indicates that the monosulfonyl derivative was converted to its anion which then was sulfonylated much more rapidly than the starting material. N-Aminocarbazole is a weaker base than N-aminopyrrolidine and its monosulfonyl derivative should be a stronger acid than the pyrrolidine analog, so the contrast in outcome of the two sulfonylation experiments is not surprising. Pyridine was substituted for triethylamine in order to minimize salt formation with the monosulfonyl compound, but the product under these conditions was a neutral substance which lacked sulfur altogether (VIII, C₁₃H₁₀N₂O). The spectral properties of VIII, notably the presence in the infrared spectrum of N-H stretching and amide I bands at 3.16 and 5.94 μ , respectively, identified it as N-formamidocarbazole, the product of a modified Vilsmeier reaction. Benzenesulfonyl chloride and hot pyridine, in the absence of dimethylformamide, converted N-aminocarbazole into a weakly acidic compound, C₁₈H₁₄N₂O₂S, recognizable by its infrared, ultraviolet, and n.m.r. spectra (see Experimental) as the desired monobenzenesulfonyl derivative IIIa. It is of interest that treatment of the bis-derivative VII with sodium methoxide in hot diglyme also led to III accompanied by its N-methyl homolog IX.¹⁸ The latter obviously arose through attack of IIIb on the initially-formed methyl benzenesulfonate.

Decomposition of the Salts.¹⁹ **N-Benzenesulfonylamidopyrrolidine Sodium Salt (Ib).**—Destruction of Ib

(14) D. M. Lemal and T. W. Rave, *Tetrahedron*, in press.

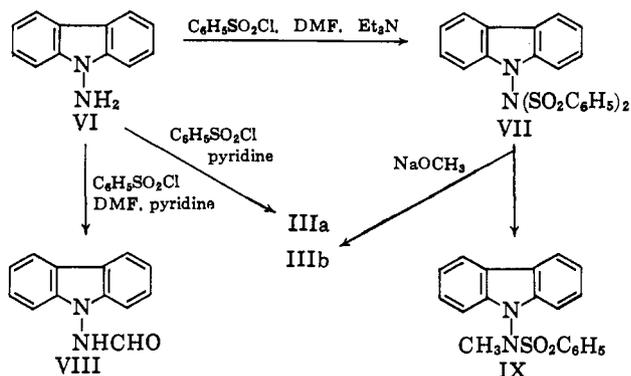
(15) H. Wieland and A. Susser, *Ann.*, **392**, 169 (1912).

(16) (a) R. H. Poirier and F. Benington, *J. Am. Chem. Soc.*, **74**, 3192 (1952); (b) N. G. Gaylord, "Reductions with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, pp. 761, 762.

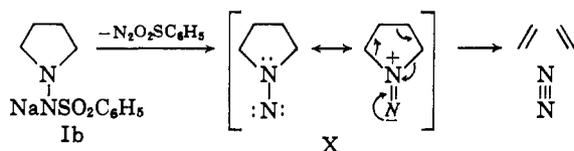
(17) Coupled with the insolubility of VII in aqueous alkali, microanalytical and spectral data (in particular the absence of N-H bending or stretching absorption in the infrared spectrum) established the structure of this compound.

(18) The ultraviolet spectrum of the neutral substance IX was superimposable upon that of IIIa, but the N-H absorption at 3.04 μ in the infrared spectrum of IIIa was absent in that of IX. With the exception of an additional sharp singlet at 6.66 τ (CCl₄) corresponding to three protons in the n.m.r. spectrum of IX, the n.m.r. spectra of the two compounds were virtually identical.

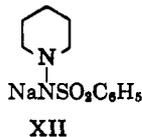
(19) All three salts (Ib, Iib, IIIb) were prepared by treatment of a methanolic solution of the sulfonylhydrazine with one equivalent of sodium methoxide in methanol; the solution was evaporated under reduced pressure. In order to expel remaining hydroxylic solvent the residue was shaken with glyme and the mixture stripped again. Diglyme or tetraglyme was added and the mixture was heated to the desired decomposition temperature.



was so rapid in hot diglyme that the solvent could hardly be brought to the reflux temperature (163°) before reaction was complete. Copious gas evolution and the appearance of a flocculent precipitate of sodium benzenesulfinate accompanied the decomposition. The gaseous products were allowed to pass through a trap cooled by Dry Ice, then through another surrounded by liquid nitrogen, and finally into a eudiometer. Virtually nothing condensed in the first trap, but much white solid accumulated in the second. The volume of uncondensable gas corresponded to as high as 77% of the total nitrogen present in the salt. The white solid was identified as ethylene by treatment with bromine and comparison of the infrared spectrum of the dibromide with that of an authentic sample. Measured volumetrically, ethylene yields ranged as high as 83% (see Experimental) based on fragmentation of the salt into sodium benzenesulfinate, nitrogen and two molecules of ethylene.²⁰



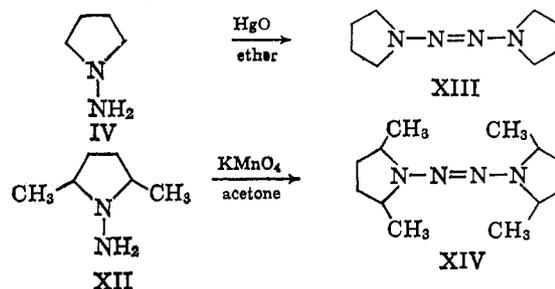
No cyclobutane is formed, but this alone does not preclude the possibility that the diazene X collapses to nitrogen plus a 1,4-diradical intermediate which fragments in a subsequent step. Other evidence discredits this conjecture, however. In particular, the facile decomposition of the sodium salt XI of the homologous sulfonylhydrazine, N-benzenesulfonamidopiperidine,²¹ is unaccompanied by evolution of nitrogen, presumably because no low-energy, concerted pathway for fragmentation is available to the diazene.



This is the first example of fragmentation (with C-N cleavage) of a 1,1-disubstituted hydrazine derivative lacking a stabilizing function or functions on the α -carbons.

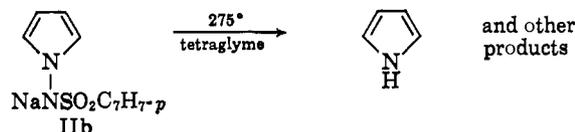
In striking contrast to the decomposition of Ib, oxidation of N-aminopyrrolidine with mercuric oxide or of N-amino-2,5-dimethylpyrrolidine (XII) with potassium permanganate²² leads to the tetrazenes XIII and XIV, respectively. We have found to be general this lack of parallelism between the decomposition of

1,1-disubstituted 2-arenesulfonylhydrazine salts and the oxidation of the corresponding hydrazines.²³ The reasons for the duality of mechanism are the subject of current investigation.



N-Tosylamidopyrrole Sodium Salt (Ib).—Analogy to the decomposition of Ib suggested that Iib might disintegrate into sodium *p*-toluenesulfinate, nitrogen and acetylene. After Iib had been heated 1 hour in tetraglyme at 225° , however, it was possible to recover it unchanged in 86% yield. The impressive inertness of this salt may be understood as a reflection of the resonance stabilization of the pyrrole nucleus. In order that elimination of sulfinate ion occur, the resulting monovalent nitrogen with only a sextet of electrons (*i.e.*, nitrene nitrogen) must be stabilized by electron pair donation from the adjacent nitrogen, as suggested by Carter and Stevens.¹² In aliphatic diazenes this need is easily satisfied, but the lone electron pair of a pyrrole nitrogen is, of course, delocalized throughout the ring. Nitrenes which are not well stabilized by electron donation are high-energy, extremely reactive species, many of which have triplet ground states.²⁴

The salt Iib was slowly destroyed by prolonged heating in tetraglyme at 275° , and a complex array of products was formed in the dark mixture. Slow distillation during the pyrolysis yielded a nearly colorless liquid which was subjected to vapor phase chromatography. Pyrrole was discovered in the distillate ($\sim 10\%$ yield) and identified by its retention time. The assignment was confirmed by comparison of the mass spectral cracking pattern with that of authentic pyrrole. A likely mechanism for the formation of this substance will be considered below in connection with the decomposition of IIIb.



N-Benzenesulfonamidocarbazole Sodium Salt (IIIb).—As in the pyrrole case, this carbazole derivative should be reluctant to part with sulfinate ion due to delocalization of the lone pair of the carbazole nitrogen. The greater acidity of pyrrole relative to carbazole (and of cyclopentadiene, for example, compared with fluorene) suggests, however, that delocalization is more pronounced in the parent aromatic system than in the dibenzo analog. In any event, IIIb suffered decomposition at 275° in tetraglyme over a period of several hours. When the reaction mixture was poured into dilute aqueous base a dark solid precipitated; the infrared spectrum revealed that it was carbazole (89% after sublimation). A purified sample proved to be identical with authentic material as determined by melting point, mixture melting point, and spectra.²⁵

(20) For fragmentation reactions of cyclic azo compounds see C. G. Overberger, G. Kesslin and N. R. Byrd, *J. Org. Chem.*, **27**, 1568 (1962); S. G. Cohen, S. Hsiao, E. Saklad and C. H. Wang, *J. Am. Chem. Soc.*, **79**, 4400 (1957).

(21) D. M. Lemal and T. W. Rave, to be published.

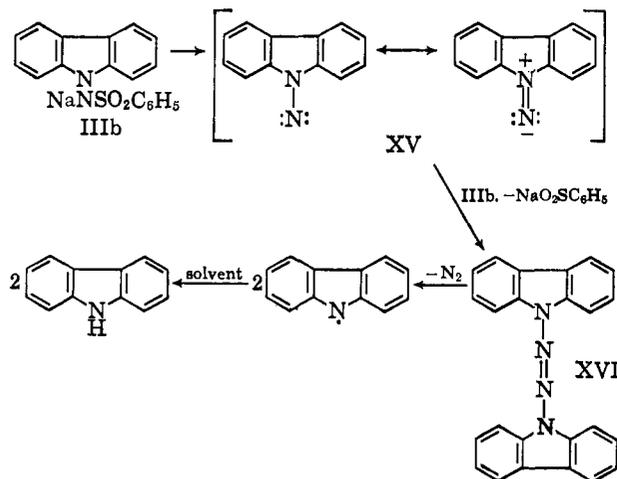
(22) C. G. Overberger, L. C. Palmer, B. S. Marks and N. R. Byrd, *J. Am. Chem. Soc.*, **77**, 4100 (1955).

(23) D. M. Lemal and F. Menger, unpublished results.

(24) G. Smolinsky, E. Wasserman and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3220 (1962), and references contained therein.

Formation of the tetrazene XVI *via* attack of the diazene XV on IIIb could explain the high yield of carbazole, for the tetrazene would be expected to decompose thermally to nitrogen and carbazolyl radicals which could abstract hydrogen from the solvent. To test this idea, XVI, prepared by the action of lead tetraacetate on N-aminocarbazole VI, was heated five minutes in tetraglyme at the boiling point. Dilution with water afforded carbazole in near-quantitative yield. Further support for the hypothesis that XVI was an intermediate in the decomposition of IIIb was provided by measurement of the uncondensable (by liquid nitrogen) gas evolved. This was identified as nitrogen mass spectrometrically, and its volume corresponded to a 77% yield in terms of the proposed mechanism.

Because of the vigor of the reaction conditions it is appropriate to consider the alternative possibility that the N-N bond of IIIb undergoes fission directly. The sulfonamido moiety would very likely abstract hydrogen from the solvent, giving benzenesulfonamide sodium salt. In the obvious control experiment, heating this salt in tetraglyme, no net increase in the volume of the system was observed.²⁶ Hence direct N-N scission, though not rigorously excluded, is clearly an unlikely pathway.²⁷



In summary, the marked contrast in lability of 1,1-dialkyl-2-arenesulfonylhydrazines *vis-a-vis* Iib and IIIb points up the dependence of the energy content of a diazene upon the basicity of the substituted nitrogen atom. Whether or not the diazene X is an intermediate in the fragmentation of Ib, loss of nitrogen is evidently concerted with formation of ethylene in this reaction. Lacking a low-energy pathway for disintegration in the fashion of Ib, IIIb decomposes to carbazole and nitrogen. The diazene XV and the tetrazene

(25) L. A. Carpio has mentioned that alkaline degradation of 1,1-diphenyl-2-benzenesulfonylhydrazine gives diphenylamine (26%) (Abstracts of the 140th National Meeting of the American Chemical Society, 1956, p. 18-0). The mechanism for this transformation probably parallels that for the decomposition of Ib to pyrrole and of IIIb to carbazole.

(26) As in the decomposition of IIIb, the evolved gas was allowed to pass through a liquid nitrogen trap into the eudiometer; the atmosphere in the system was nitrogen. Slow decomposition in the control experiment was actually accompanied by a large and reproducible decrease in the volume of the system, indicating that nitrogen had dissolved in a small amount of material collected in the cold trap. When the pressure within the system was varied at the end of the experiment, large volume changes with a slight time lag were observed, as would be expected for the establishment of equilibrium between the liquid and gas phases. This phenomenon did not occur in the decomposition of IIIb.

(27) Since many high-energy nitrenes successively abstract two hydrogens from suitable solvents,²⁴ the formation of VI in the decomposition of IIIb is conceivable. Cleavage of the N-N bond of this supposed intermediate should lead to carbazole and ammonia. Mass spectrometric scrutiny of the condensate in the liquid nitrogen trap revealed no more than trace quantities of ammonia, so the route to carbazole *via* VI can be disregarded.

XVI are believed to be intermediates in the transformation. It is proposed that the formation of pyrrole in the pyrolysis of Iib follows an analogous pathway.²⁸

Experimental²⁹

N-Benzenesulfonamidopyrrolidine (Ia).—N-Aminopyrrolidine (IV) was prepared by the reaction of 1,4-dichlorobutane with hydrazine (28% yield)³⁰ and by nitrosation of pyrrolidine followed by LiAlH₄ reduction¹³ (39% over-all). In 6 ml. of dimethylformamide (Eastman Kodak Co. White Label) were dissolved 1.54 g. (17.9 mmoles) of IV and 1.82 g. (17.9 mmoles, 2.50 ml.) of triethylamine, and the solution was cooled to 0°. Benzenesulfonyl chloride (3.18 g., 17.9 mmoles, 2.30 ml.) was added dropwise to the stirred solution; the mixture was allowed to stand overnight at 0°. Dilution with 30 ml. of ice-water gave a white precipitate which was washed with water and dried (2.93 g., 72%). Several recrystallizations from benzene-cyclohexane yielded white crystals, m.p. 186–187°. The infrared spectrum (chloroform) exhibited *inter alia* bands at 3.12 (N-H stretch), 6.91, 7.44, 7.55, 8.59 and 9.14 μ .

Anal. Calcd. for C₁₀H₁₄N₂SO₂: C, 53.02; H, 6.23; N, 12.38. Found: C, 53.20; H, 6.25; N, 12.42.

N-Aminocarbazole (VI).—N-Nitrosocarbazole was prepared and reduced with zinc and acetic acid by the method of Wieland and Susser,¹⁵ giving N-aminocarbazole (VI), m.p. 151–151.5°, lit.³¹ 151° (50% yield over-all). Reduction of N-nitrosocarbazole with lithium aluminum hydride according to the procedure of Poirier and Benington^{16a} yielded the N-amino derivative in 45% yield, m.p. 150–152°.

2,2-Bisbenzenesulfonyl-1,1-biphenylhydrazine (VII).—N-Aminocarbazole (VI, 12.5 g., 68 mmoles) and triethylamine (13.7 g., 136 mmoles, 19 ml.) were dissolved in 80 ml. of dimethylformamide, and the solution was cooled to 0°. Benzenesulfonyl chloride (24.4 g., 138 mmoles, 17.7 ml.) was added dropwise to the stirred solution. After an additional hour of stirring at room temperature, the solution was allowed to stand in the refrigerator overnight. The reaction mixture was added to 300 ml. of ice-water, and the precipitated solid collected by filtration. The yield was 31.4 g. (50.5%) of white crystals, m.p. 231–232°, after several recrystallizations from ethanol-chloroform. The infrared spectrum (CHCl₃) showed *inter alia* bands at 3.31, 7.21, 7.51, 7.62, 8.45, 8.54, 9.21 and 11.42 μ .

Anal. Calcd. for C₂₄H₁₈N₂SO₄: C, 62.40; H, 3.89; N, 6.07. Found: C, 62.41; H, 3.74; N, 6.09.

N-Formamidocarbazole (VIII).—N-Aminocarbazole (VI, 1.82 g., 10 mmoles) was dissolved in 8 ml. of dimethylformamide containing 0.79 g. (0.8 ml., 10 mmoles) of pyridine; 1.76 g. (1.28 ml., 10 mmoles) of benzenesulfonyl chloride was added. The solution was stirred at 0° for 90 minutes, then allowed to stand in the refrigerator for 2 days. Addition of 75 ml. of water caused a yellow solid (0.78 g., 37%) to precipitate. Several recrystallizations of this material from ethanol yielded white crystals, m.p. 254–256°. The infrared spectrum (Nujol) exhibited characteristic bands at 3.16 (N-H stretch), 3.44, 5.94 (amide I), 6.14, 6.88, 7.25 and 8.11 μ .

Anal. Calcd. for C₁₃H₁₀N₂O: C, 74.30; H, 4.76; N, 13.40. Found: C, 74.26; H, 4.73; N, 13.21.

N-Benzenesulfonamidocarbazole (IIIa).—A solution of 18.2 g. (0.1 mole) of VI, 17.69 g. (0.1 mole) of benzenesulfonyl chloride and 150 ml. of pyridine was boiled under reflux for 10 hr. The cooled solution was poured into 500 ml. of ice-water, and the resulting suspension was made very basic with NaOH. The alkali-insoluble material, collected by filtration and recrystallized several times from ethanol-chloroform, was identified as VII. When the basic filtrate was neutralized with concentrated HCl, a heavy black oil separated which crystallized when triturated with ethanol. The yield was 20.0 g. (65%) of white crystals, m.p. 179–180° after several recrystallizations from ethanol. The infrared spectrum (chloroform) exhibited characteristic bands at 3.04 (N-H stretch), 3.42, 6.92, 7.43 and 8.58 (sulfonamide) and 9.17 μ .

Anal. Calcd. for C₁₈H₁₄N₂SO₄: C, 67.05; H, 4.38; N, 8.68. Found: C, 66.95; H, 4.27; N, 8.88.

Conversion of 2,2-Bisbenzenesulfonyl-1,1-biphenylhydrazine to IX and IIIa.—A solution of 12 g. (26 mmoles) of VII in

(28) NOTE ADDED IN PROOF.—Since the submission of this paper it has been reported that the reaction of difluoroamine with aziridine, azetidide and 3,3,5-trimethylpyrazoline leads, presumably *via* diazene intermediates, to fragmentation products (C. L. Bumgardner, K. J. Martin and J. P. Freeman, *J. Am. Chem. Soc.*, **85**, 97 (1963)). The parallel with IVb decomposition is obvious.

(29) Melting points were determined on a Kofler micro hot-stage. Elemental analyses were performed by Spang Microanalytical Laboratory and Illini Microanalytical Laboratory.

(30) For an analogous transformation see ref. 22.

(31) A. V. Blom, *J. prakt. Chem.*, **94**, 77 (1916).

anhydrous methanol containing 52 mmoles of sodium methoxide was evaporated to dryness *in vacuo*. Glyme³² (75 ml.) was added to the resulting salt and the mixture was stripped again. After the addition of 150 ml. of diglyme, the mixture was boiled under reflux for 15 hr., cooled, and added to 500 ml. of ice-water. Three extractions with chloroform followed by evaporation of the chloroform yielded 2.0 g. (36%) of a white solid (IX), m.p. 99–100° after several recrystallizations from ethanol. The infrared spectrum (CHCl₃) exhibited *inter alia* bands at 3.27, 6.94, 7.38 and 8.59 (sulfonamide), 8.29 and 9.19 μ .

Anal. Calcd. for C₁₉H₁₆N₂SO₂: C, 67.80; H, 4.79. Found: C, 67.79; H, 4.78.

When the aqueous solution from above was acidified with concentrated HCl, a solid (5.0 g., 60%) precipitated which was identified as IIIa by its m.p. (179–180°) and infrared spectrum.

Pyrolysis of N-Benzenesulfonamidopyrrolidine Sodium Salt (Ib).—In 5 ml. of diglyme contained in a 100-ml. two-necked round-bottomed flask was dissolved 0.581 g. (2.57 mmoles) of Ia. One neck of the flask was equipped with a stoppered 50-ml. pressure-equalizing dropping funnel containing 2.50 ml. of *n*-butyl Cellosolve, 1.149 N in its sodium salt (2.75 mmoles), in 15 ml. of diglyme. The second neck was attached to a water condenser connected successively (by 8 mm. Pyrex tubing) to a U-tube cooled by Dry Ice, a U-tube immersed in liquid nitrogen, a 500-ml. mercury eudiometer, and an open-end manometer. The system was equilibrated at room temperature and atmospheric pressure under nitrogen. When the contents of the dropping funnel had been added to the reaction flask, the solution was boiled under reflux for 1 hr. After cooling to room temperature the system was readjusted to atmospheric pressure; 41 ml. (740 mm., 25°, 64%) of nitrogen had been evolved. The proximal end of the liquid nitrogen trap was opened and capped quickly. The coolant was removed, and the frozen ethylene (*vide infra*) rapidly melted then boiled, causing a volume expansion of 106 ml. (740 mm., 25°, 83%) after correction had been made for the thermal expansion of the nitrogen in the trap.

It should be noted that the experiment described above is merely representative since the yields were variable. Nitrogen yields ranged from 59–77%, while ethylene yields ranged from 43–83%. Yields of total gas ranged from 50–77%. A variety of experimental conditions, including the use of preformed salt and of a Toepler pump to circulate nitrogen within the system (thereby assuring complete transfer of ethylene to the liquid nitrogen trap), failed to achieve reproducibility.

In another experiment carried out in similar fashion, the liquid nitrogen trap containing the frozen gas was removed from the system with the coolant still in place; excess bromine was introduced into the trap, and the ends were sealed. When the trap had warmed to room temperature, 3 ml. of saturated aqueous Na₂SO₃ was added to destroy the excess bromine. The organic layer was extracted with 0.5 ml. of carbon disulfide; the extract was dried over MgSO₄ and its infrared spectrum measured. Comparison with the spectrum of an authentic sample showed that the product was 1,2-dibromoethane.

Bistetramethylenetetrazene (XIII).—A solution of 3.1 g. (36 mmoles) of IV in 20 ml. of ether was cooled to 0°. Yellow mercuric oxide was added in portions to the solution until the yellow color remained; the solution was filtered and the filtrate evaporated to dryness. Two recrystallizations of the resulting yellow solid from ethanol–water yielded 1.36 g. (45%) of white crystals, m.p. 36–38°. The analytical sample, m.p. 37.5–38.5°, was prepared by sublimation. The ultraviolet spectrum in 95% ethanol exhibited a maximum at 282 m μ , ϵ 9860, with a shoulder at 255 m μ .

Anal. Calcd. for C₈H₁₆N₄: C, 57.12; H, 9.58; N, 33.30. Found: C, 57.26; H, 9.28; N, 33.24.

Thermal Behavior of N-Tosylamidopyrrole Sodium Salt (IIb). Attempted Pyrolysis at 225°.—The salt obtained by evaporating a solution of 1 g. (4.2 mmoles) of IIa and 10 ml. (4.8 mmoles) of 0.48 N sodium methoxide to dryness *in vacuo* was dissolved in 20 ml. of tetraglyme. The solution was heated at 225° for 1 hr.

and cooled. When 100 ml. of pentane was added a brown oil appeared which was separated and dissolved in water. Acidification of the aqueous solution with 5% HCl caused a brown solid to precipitate. Further dilution with pentane of the pentane–tetraglyme solution led to the separation of more dark oil from which a small additional amount of solid was obtained in the above fashion. Three recrystallizations of the combined precipitates (0.86 g., 86%) from benzene yielded white crystals (m.p. 142–143°) identified as IIa by mixture m.p. (141–143°) with an authentic sample.

Decomposition at 275°.—In 3.6 ml. of methanol containing 0.99 mmole of sodium methoxide was dissolved 0.206 g. (0.87 mmole) of IIa, and the solution was evaporated to dryness *in vacuo*. To remove residual methanol 5 ml. of glyme was added and then stripped *in vacuo*. A solution of the resulting white salt in 10 ml. of tetraglyme was boiled under reflux for 8 hr. under an atmosphere of nitrogen and volatile products were collected in an alembic. Vapor phase chromatography of the distillate on a 2-m. column packed with Ucon Polar on acid-washed Chromosorb P gave *inter alia* a peak with retention time identical with that of authentic pyrrole. Although the pyrrole peak and another of lesser area were incompletely resolved, it was possible to estimate the area under the pyrrole peak, and thus to estimate the yield: ~10%. Since pyrrole had the longer retention time of the two substances, the tail of the pyrrole peak was trapped and subjected to mass spectrometric analysis. The cracking pattern confirmed the structural assignment.

The black contents of the reaction flask were poured into 75 ml. of 2% aqueous NaOH, and the mixture was filtered. Acidification of the brown filtrate with concentrated HCl followed by cooling overnight failed to yield any starting material. The black residue from filtration proved to be intractable.

Pyrolysis of N-Benzenesulfonamidocarbazole (IIIb).—A solution of 1.181 g. (3.67 mmoles) of IIIa and 2.96 ml. (3.81 mmoles) of 1.300 N sodium methoxide in 10 ml. of anhydrous methanol was evaporated to dryness *in vacuo*. The resulting white salt was slurried in 15 ml. of tetraglyme; the mixture was boiled under reflux for 15 hr., cooled, diluted with 60 ml. of water, and made basic with 5% NaOH. The base-insoluble material was a brown solid (654 mg.) which from its infrared spectrum appeared to be primarily carbazole. Sublimation at 0.05 mm. and 110° gave a pale yellow solid (545 mg., 89%) which, after two recrystallizations from ethanol, was proved to be pure carbazole by m.p., mixture m.p., and infrared and ultraviolet analysis.

In 10 ml. of anhydrous methanol contained in a 50-ml. round-bottom flask were dissolved 1.188 g. (3.69 mmoles) of IIIa and 3.00 ml. (3.90 mmoles) of 1.300 N sodium methoxide, and the solution was evaporated to dryness *in vacuo*. Twenty milliliters of tetraglyme was added to the residue. The flask was connected to a pyrolysis train like that employed in the decomposition of Ib (but lacking the Dry Ice trap and using a 100-ml. eudiometer). When the mixture had been refluxed 15 hr., gas evolution was measured as in the Ib pyrolysis. The 35 ml. collected (750 mm., 24°, 77%) was shown to be at least 97% nitrogen by mass spectrometric analysis.

Bisbiphenylenetetrazene (XVI). Preparation.—Excess lead tetraacetate was added to a solution of 1.0 g. (5.5 mmoles) of VI in 20 ml. of acetonitrile at room temperature. A yellow solid (0.95 g., 94%) immediately precipitated. Several recrystallizations from diglyme afforded white crystals, m.p. 216° dec. (lit.¹⁵ 216°).

Anal. Calcd. for C₂₄H₁₆N₄: C, 80.00; H, 4.44; N, 15.56. Found: C, 80.08; H, 4.46; N, 15.57.

Pyrolysis.—A mixture of XVI (50 mg., 0.14 mmole) and tetraglyme (15 ml.) was boiled under reflux for 5 min. The resulting solution was cooled and poured into water. A solid precipitated which was identified as carbazole (45 mg., 96%) by its infrared spectrum.

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(32) The glyme, diglyme and tetraglyme used in these experiments had been distilled from LiAlH₄.