move all oxygen. On addition of 6 g. of potassium ferricyanide the solution turned milky at once from separation of p-terphenyl. The flow of nitrogen was continued for 20 min. and the white solid was collected, washed, and dried; yield 0.84 g. (95.5%), m.p. 211–212°. Crystallization from dioxane or methanol gave shiny flakes, m.p. 212° (lit.[2] 212°).

No change in speed of reaction or yield was observed when the reaction was run without nitrogen. If potassium ferricyanide is added to a solution of the acid in alkali (25°) and the mixture is swirled on a hot plate, the oxidation can be completed in about 5 min.

Oxidation of Δ²-Dihydronaphthalene-trans-1,4 dicarboxylic Acid[11] (8).—A solution of 100 mg. of the diacid and 0.5 g. of potassium ferricyanide in 10 ml. of 1 N sodium hydroxide was prepared at room temperature and let stand for 2 hr. Acidification with dilute hydrochloric acid liberated carbon dioxide and precipitated 75 mg. (96%) of α-naphthoic acid. Crystallization from methanol–water afforded colorless needles, m.p. 161–162°; a mixture melting point determination with an authentic sample showed no depression.

Oxidation of Δ¹-Dihydronaphthalene-1,4-dicarboxylic Acid[11] (9).—A solution of 100 mg. of the diacid and 0.5 g. of potassium ferricyanide in 10 ml. of 1 N sodium hydroxide was heated on the steam bath for 3 hr. and acidified. The product that precipitated (65 mg., 83%) after crystallization melted at 161–162° and did not depress the m.p. of authentic α-naphthoic acid.

When the oxidation was conducted as above but at room temperature for 11 hr., acidification precipitated starting material; α-naphthoic acid was obtained after a reaction period of 30 hr.

Oxidation of Δ³-Dihydronaphthalene-trans-1,2-dicarboxylic Acid[11] (13).—A solution of 200 mg. of the diacid in 10 ml. of 1 N sodium hydroxide was flushed with a stream of oxygen-free nitrogen, treated with 2 g. of potassium ferricyanide, and heated on the steam bath for 1.5 hr. in a nitrogen atmosphere. The yellow solution was cooled and acidified, and the product that precipitated (135 mg., 86%) on crystallization from n-hexane melted at 185–186° and gave no depression when mixed with β-naphthoic acid.

The oxidation proceeded equally well when air was not excluded. β-Naphthoic acid was obtained under the same conditions but at room temperature for 4 days.

Oxidation of Δ²-Dihydronaphthalene-1,2-dicarboxylic Acid[11] (14).—A solution of 150 mg. of the diacid and 0.6 g. of potassium ferricyanide in 8 ml. of 1 N sodium hydroxide was warmed on the steam bath for 30 sec. and let stand at room temperature for 4 hr. Acidification with hydrochloric acid gave a white solid and ether extraction afforded 105 mg. of β-naphthoic acid, identified by m.p. and mixture m.p. determinations.

Oxidation of Δ³,⁵-Cyclohexadiene-trans-1,2-dicarboxylic Acid (18).—This acid was prepared according to Baeyer[13] except that glacial acetic acid was used instead of 50% acetic acid; the yield rose from 56 to 80%.

A solution of 1 g. of the diacid and 5 g. of potassium ferricyanide in 30 ml. of 1 N sodium hydroxide was heated on the steam bath for 15 min., cooled, and acidified. After collection of precipitated benzoic acid, a further crop was isolated by ether extraction; total yield 0.68 g. (98%); identification by m.p. and mixture m.p.

Attempted Oxidations.—Samples of meso-1,2-diphenylsuccinic acid and trans-1,4-tetralindicarboxylic acid were refluxed; the starting materials were recovered unchanged.

The Diazene–Hydrazone Rearrangement

BY DAVID M. LEMAL, FREDRIC MENGER, AND EUGENE COATS

The course of thermal decomposition of a series of 1,1-dialkyl-2-benzenesulfonylhydrazine sodium salts has been found to be highly solvent dependent. Tetrazenes are the major products when the solvent is tetraglyme, but rearrangement to hydrazones occurs competitively with or to the exclusion of tetrazene formation with diethylene glycol the solvent. In contrast to the dialkyl analogs, 1,1-diphenyl-2-benzenesulfonylhydrazine sodium salt yields diphenylamine in both solvents, and no rearrangement product (azobenzene) was isolated. Mechanistic implications of these observations are discussed and certain of them are tested experimentally.

Aminonitrenes (1), called diazenes, have been proposed as intermediates in the oxidation of 1,1-disubstituted hydrazines,[1–3] in the thermal decomposition of 1,1-disubstituted 2-sulfonylhydrazine salts,[4,5] in the base-catalyzed decomposition of 1,1-disubstituted 2-chlorohydrazines,[1b] in the reduction (particularly by

sodium hydrosulfite) of nitrosamines,[2,6,7] and most recently in the reaction of secondary amines with difluoroamine.[7] Tetrazenes have been the usual products of reactions which proceed via diazenes, whether the substituent groups were aryl or alkyl.[8] Special features

$$\left\{ >\ddot{N}\!-\!\underset{\cdot\cdot}{N}: \longrightarrow >\overset{+}{N}\!=\!\underset{\cdot\cdot}{\bar{N}}: \right\}$$

1
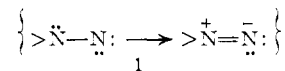
in the substituents can lead to cleavage of the carbon–nitrogen bond of the intermediate, however, with the formation of molecular nitrogen accompanied by disproportionation, coupling, and/or fragmentation products.[1–7]

Among representatives of a single type of diazene intermediate, arylbenzyl- or arylallyldiazenes, rearrangement to hydrazones has been observed. Thus Carter and Stevens[5] recently discovered that decomposition in aqueous or ethanolic alkali of a series of 1-aryl-1-benzyl-2-sulfonylhydrazines (2) leads to the corresponding hydrazones 3, and earlier Busch and Lang[9] had shown that oxidation of a 1-aryl-1-benzylhydrazine (4) gave either the hydrazone or the tetrazene 5 or both. Carter and Stevens concluded that the rate-determining

(1) See, for example: (a) L. A. Carpino, A. A. Santilli, and R. W. Murray, J. Am. Chem. Soc., **82**, 2728 (1960); C. G. Overberger and L. P. Herin, J. Org. Chem., **27**, 417 (1962); (b) C. G. Overberger and B. S. Marks, J. Am. Chem. Soc., **77**, 4104 (1955); C. G. Overberger, Record Chem. Progr., **21**, 21 (1960).

(2) 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).

(3) (a) W. R. McBride and H. W. Kruse, J. Am. Chem. Soc., **79**, 572 (1957); (b) W. H. Urry, H. W. Kruse, and W. R. McBride, ibid., **79**, 6568 (1957); (c) W. R. McBride and E. M. Bens, ibid., **81**, 5546 (1959).

(4) (a) L. A. Carpino, Chem. Ind. (London), 172 (1957); J. Am. Chem. Soc., **79**, 4427 (1957); **84**, 2196 (1962); **85**, 2144 (1963); R. L. Hinman and K. L. Hamm, ibid., **81**, 3294 (1959); W. Baker, J. F. W. McOmie, and D. R. Preston, Chem. Ind. (London), 1305 (1960); J. Chem. Soc., 2971 (1961); (b) D. M. Lemal, T. W. Rave, and S. D. McGregor, J. Am. Chem. Soc., **85**, 1944 (1963).

(5) P. Carter and T. S. Stevens, J. Chem. Soc., 1743 (1961).

(6) C. G. Overberger, L. G. Lombardino, and R. G. Hiskey, J. Am. Chem. Soc., **80**, 3009 (1958); C. G. Overberger and N. P. Marullo, ibid., **83**, 1378 (1961).

(7) C. L. Bumgardner, K. J. Martin, and J. P. Freeman, ibid., **85**, 97 (1963).

(8) An interesting exception is discussed in footnote 17.

(9) M. Busch and K. Lang, J. prakt. Chem., **144**, 291 (1936).

TABLE I

ULTRAVIOLET DATA[a]

Compound	λ_{max}, mμ	log ϵ
Tetrazenes		
Tetramethyl-[b]	277	3.92
Tetraethyl-[c]	285	3.90
Tetraisopropyl-[d]	291	4.05
Hydrazones		
Formaldehyde methyl-	233	3.69
Acetaldehyde ethyl-	232	3.68
Acetone isopropyl-	228	3.70
Formaldehyde dimethyl-[3a]	236	3.71
Acetaldehyde dimethyl-[e]	238	3.71

[a] Solvent is methanol unless otherwise specified. [b] Lit. (W. E. Bull, J. A. Seaton, and L. F. Audrieth, *J. Am. Chem. Soc.*, 80, 2516 (1958)) λ_{max} 277 (3.92) in ethanol and in water. [c] Ethanol is the solvent; lit. (note b) λ_{max}^{EtOH} 285 (3.88). [d] The spectrum was measured in heptane. [e] This compound was prepared as a model.
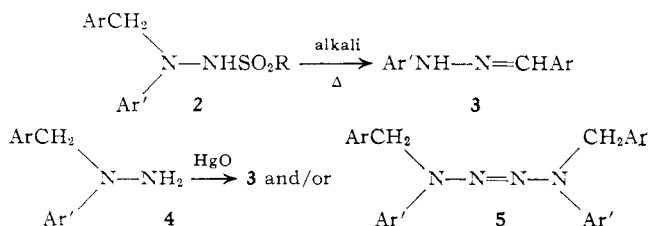
hydrazone rearrangement is broader in scope than previously recognized and have adduced additional evidence regarding its mechanism.

1,1-Dialkyl-2-benzenesulfonylhydrazine Sodium Salts.—Pyrolysis of the salts **6a–c**[10] was studied at 110–120° in tetraglyme and in diethylene glycol (DEG).[11] In the former (aprotic) solvent all three salts gave good yields of the corresponding tetrazenes (**7a**,[3a] 74%; **b**,[3c] 80%; **c**, 72%), which were isolated by distillation and purified by gas–liquid chromatography (g.l.c.) (**7a**) and by adsorption chromatography on alumina (**7b,c**). Spectral data for these compounds appear in Tables I and II. When heated in the protic solvent DEG, on the other hand, **6a** gave no detectable tetrazene. The major product was isolated by distillation at ∼0.1 mm. into a Dry Ice trap during the brief interval required for the reaction to run its course.

TABLE II

NUCLEAR MAGNETIC RESONANCE DATA[a]

Compound	Solvent	Position, τ	J, c.p.s.		Form	Assignment
Tetramethyltetrazene	CDCl₃	7.17			Singlet	Methyl
Tetraethyltetrazene	CDCl₃	8.91	7.5		Triplet	Methyl
		6.76	7.5		Quartet	Methylene
Tetraisopropyltetrazene	CDCl₃	8.86	7		Doublet	Methyl
		6.08	7		Septet	Methine
Formaldehyde methylhydrazone	Acetone-d_6	7.28	4		Doublet[b]	Methyl
		3.67, 4.09	11.5	AB	Quartet	Methylene
Acetaldehyde ethylhydrazone	Acetone-d_6	8.95	7		Triplet	Methyl (of ethyl)
		7.02	7		Quartet	Methylene (of ethyl)
		8.28	5	syn[c] {	Doublet	Methyl (of ethylidene)
		3.13	5	{	Quartet	Methine (of ethylidene)
		8.37	5	anti[c] {	Doublet	Methyl (of ethylidene)
		3.63	5	{	Quartet	Methine (of ethylidene)
Acetone isopropylhydrazone	Acetone-d_6	8.94	6.5		Doublet	Methyl (of isopropyl)
		6.76	6.5		Septet	Methine (of isopropyl)
		8.34, 8.20			Singlets	Methyls (of isopropylidene)
1-Ethyl-3-methyldiaziridine	CDCl₃	8.85	7		Triplet	Methyl (of ethyl)
		8.62	5		Doublet	Methyl (of ethylidene)
		7.5				Methylene and methine

[a] All n.m.r. spectra were measured with a Varian A-60 spectrometer at 60 Mc. and calibrated using hexamethyldisiloxane as internal standard (τ 9.94 in CDCl₃, 9.93 in acetone-d_6). Relative areas were consistent in all cases with structural assignment. [b] The splitting arises from spin coupling with the amine proton, which does not appear in the spectrum. Addition of D₂O causes the doublet to coalesce. [c] These assignments were based on the assumption that the less hindered *syn* form should predominate in the mixture. The relative chemical shifts of methyl and methine protons in the two forms are in agreement with the assignments (G. Karabatsos, R. A. Taller, and F. M. Vane, *J. Am. Chem. Soc.*, 85, 2327 (1963)).

step in sulfonylhydrazine salt decomposition was loss of RSO₂⁻ to form the diazene. The reaction rate was

ArCH₂
\
   N—NHSO₂R $\xrightarrow[\Delta]{alkali}$ Ar′NH—N=CHAr
/
Ar′   **2**   **3**

ArCH₂   ArCH₂   CH₂Ar
\   \   /
 N—NH₂ $\xrightarrow{HgO}$ 3 and/or   N—N=N—N
/   /   \
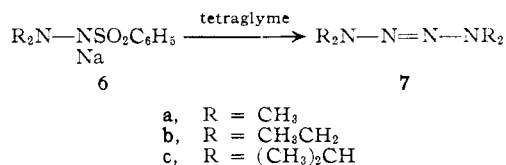Ar′ **4**   Ar′   **5**   Ar′

not a sensitive function of R, consistent with the fact that electron-withdrawing (donating) character in R would stabilize (destabilize) *both* the sulfonylhydrazine anion and the sulfinate anion. The English authors showed that the rearrangement was intramolecular, but they were noncommittal regarding the pathway from diazene to hydrazone.

The present study of the decomposition of a series of 1,1-disubstituted 2-benzenesulfonylhydrazine salts was initiated in an effort to shed further light on the behavior of diazenes. We have found that the diazene–

After purification by g.l.c., the colorless, mobile oil (43% yield) was recognized to be formaldehyde methylhydrazone (**8a**)[12] by its microanalysis and spectra (Tables I and II). Since this substance had been

R₂N—NSO₂C₆H₅ $\xrightarrow{tetraglyme}$ R₂N—N=N—NR₂
      Na
    6   **7**

      a, R = CH₃
      b, R = CH₃CH₂
      c, R = (CH₃)₂CH

known previously only as a crystalline dimer of questionable purity,[13] its identity was confirmed by hydrolysis to formaldehyde and methylhydrazine (characterized as the 2,4-dinitrophenylhydrazone and the bisulfate salt, respectively).[14] Rearrangement was again

(10) Satisfactory carbon, hydrogen, and nitrogen analyses were obtained for all new compounds.

(11) In all runs, even in tetraglyme, the salts were entirely in solution.

(12) Tetramethyltetrazene (7a) does not yield any 8a when heated at 120° in DEG.

(13) E. Müller and W. Rundel, *Ber.*, 90, 1299, 1302 (1957).

(14) When 8a was permitted to stand at room temperature for a few weeks crystals were deposited which analyzed for the dimer. A single

observed when **6b** was allowed to decompose in DEG. The distillate in the cold trap was proved to be acetal-

$$(CH_3)_2N-NSO_2C_6H_5 \xrightarrow[\text{Na}]{\text{DEG}} CH_3NH-N=CH_2$$

$$\textbf{6a} \qquad\qquad\qquad \textbf{8a}$$
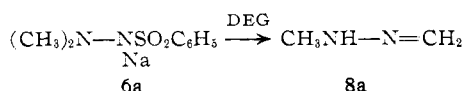
dehyde ethylhydrazone[15] (**8b**, 70% yield) by comparison with an authentic sample after further purification by g.l.c. In the hydroxylic solvent, **6c** gave substantial quantities of both tetrazene **7c** (54%) and the rearranged product, acetone isopropylhydrazone[16] (**8c**, 17%).

Tetrazenes are formed by attack of the diazenes upon starting material with subsequent loss of sodium benzenesulfinate or (less likely) by dimerization of the diazenes. Assuming that the diazenes are also intermediates in the rearrangement to hydrazones (*vide infra*), the most obvious pathway for rearrangement would be simple 1,2-shift of an alkyl group followed by tautomerization of the resulting azo compound[5] (*e.g.*, **9** → **10** → **8b**; mechanism 1). Alternatively, tautomerization could be the first step in the transformation.[17] Should the 1,3-dipolar species **11** be formed from the tautomeric diazene **9**, for example, subsequent migration of the ethyl group would lead directly to the observed hydrazone (mechanism 2). Ring closure of **11** to an isohydrazone (diaziridine, **12**) deserves consideration since it is conceivable that this substance could reopen to the hydrazone under the reaction conditions (mechanism 3).
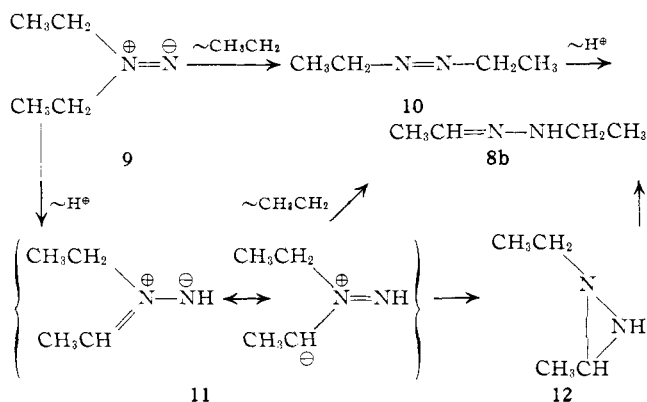

In order to test mechanism 1 it was necessary to learn whether or not azoethane (**10**) was stable under the conditions required for the decomposition of **6b**. Azo compounds are known to tautomerize readily to the corresponding hydrazones, but the fortunate discovery was made that the decomposition can be effected in an

attempt to prepare authentic **8a** from formaldehyde and methylhydrazine yielded crystalline material, but no monomer.

(15) F. M. Beringer, J. A. Farr, and S. Sands, *J. Am. Chem. Soc.*, **75**, 3984 (1953).

(16) H. L. Lochte, W. A. Noyes, Jr., and J. R. Bailey, *ibid.*, **44**, 2556 (1922).

(17) A variety of reagents oxidize N-aminotetrahydroisoquinoline to the dimer i (E. Höft and A. Rieche, *Angew. Chem.*, **73**, 907 (1961)). The dimerizing species is very likely the resonance-stabilized zwitterion ii derived by a prototropic shift from an initially formed diazene (iii).
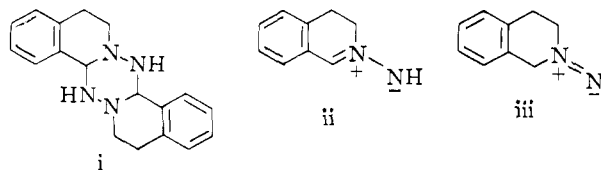
exceedingly gentle manner. *A solution of 1,1-diethyl-2-benzenesulfonylhydrazine in DEG containing slightly less than 1 equivalent of DEG sodium salt was allowed to stand 2 hr. at 25° and ~0.1 mm. The hydrazone of 8b distilled in −70% yield.*[18] Repetition of this experiment at atmospheric pressure with azoethane present yielded a product rich in azoethane as well as hydrazone, thereby proving that mechanism 1 cannot be the pathway for the diazene–hydrazone rearrangement.

Diaziridine **12**[19] (Table II) was synthesized from acetaldehyde, ethylamine, and, hydroxylamine-O-sulfonic acid. The colorless oil displayed N–H stretching absorption in the infrared ($\lambda_{max}^{CHCl_3}$, 3.0 μ), showed end absorption only in the ultraviolet, oxidized hydriodic acid rapidly at room temperature as expected for a diaziridine,[20] and gave a correct C, H, and N analysis. Not unexpectedly, this compound was isolated unchanged when subjected to the mild conditions described above for hydrazone formation. Hence mechanism 3, like 1, is clearly wrong.

A priori, the remaining pathway under consideration, mechanism 2, has some rather dubious features. In particular, migration of an alkyl group in the zwitterion **11** is strongly reminiscent of the Stevens rearrangement,[21] but the latter reaction ordinarily fails when only simple alkyl groups are available for migration. The apparent inconsistency worsens when **11** is compared in stabilization with a typical Stevens ylid intermediate in which negative charge resides only on carbon. Nitrogen can share anionic charge in the delocalized zwitterion **11**, and *both* resonance forms place the opposite charges on adjacent atoms. Finally, if mechanism 2 is correct, rearrangement of **11** must not only occur, but must also be very rapid relative to simple ring closure to a diaziridine. These objections notwithstanding, the presently available experimental data on the diazene–hydrazone rearrangement are best accommodated by mechanism 2.[22]

The influence of solvent hydroxyl groups on the decomposition pathway of **6a–c** reminds one of solvent effects on the pyrolysis of tosylhydrazone salts. Just as aprotic solvents favor "carbenoid" and hydroxylic media "cationoid" decomposition of tosylhydrazones,[23] it is attractive to postulate that compounds **6a–c** fragment to diazenes in aprotic solvents but give the conjugate acids, diazenium ions ($>\overset{+}{N}=NH$), in protic media. According to this view, diazenes would be responsible for tetrazene formation and diazenium ions would undergo rearrangement to hydrazones. Work of McBride and co-workers indicates, however, that dialkyldiazenium ions are reasonably stable species at room temperature[3]; n.m.r. studies in our laboratory[24] have confirmed this and established that 1,1-dialkyl-2-arenesulfonylhydrazines ionize rapidly and reversibly (the

(18) The rate of decomposition was so rapid (see Experimental) that the reactions run earlier in DEG at 110–120° may well have been complete or nearly so by the time the reaction mixture had come to temperature.

(19) E. Schmitz and D. Habisch, *Ber.*, **95**, 680 (1962).

(20) E. Schmitz and R. Ohme, *ibid.*, **94**, 2166 (1961); E. Schmitz, *Angew. Chem.*, **74**, 437 (1962).

(21) L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, pp. 740, 741.

(22) On the basis of early experiments the authors originally favored mechanism 1, considering 2 unlikely for the reasons cited. They wish to thank a referee for stimulating them to test mechanism 1 more carefully.

(23) J. W. Powell and M. C. Whiting, *Tetrahedron*, **7**, 305 (1959); L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959).

(24) D. M. Lemal, C. D. Underbrink, and T. W. Rave, to be published.

extent of ionization is small) to diazenium ions and sulfinite ions in highly polar hydroxylic solvents in the cold. The sulfonylhydrazine *salts* show a much smaller tendency to dissociate into diazenes and sulfinate ions at room temperature. Solutions of the sulfonylhydrazines containing either no added base or several equivalents of it are quite stable relative to solutions containing a moderate amount of base. These facts indicate that free sulfonylhydrazine is necessary for fast decomposition in the cold[25]; *i.e.*, that the initially formed intermediate is a diazenium ion which is subsequently attacked by base. Thus the previously described decomposition of 1,1-diethyl-2-benzenesulfonylhydrazine in basic DEG at room temperature must proceed *via* the ion 13, which can then lose a proton in either of two ways. Ordinarily, removal of a proton from nitrogen is much faster than from carbon even in cases where rather large pK_a differences favor formation of the anion on carbon. For this and other reasons it is presumed that the diazene 9 is formed from 13.[26] The reaction is very likely reversible in DEG, however, so it is not clear whether 9 or 13 or both function as direct precursors for zwitterion 11.[27] A transition state such as that shown
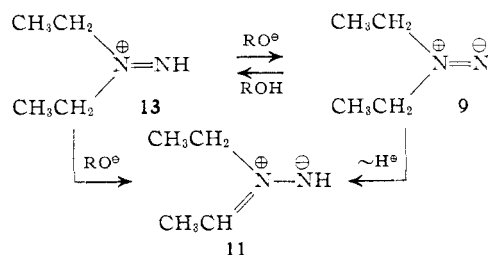
below could lead from 9 to 11 without involving 13.
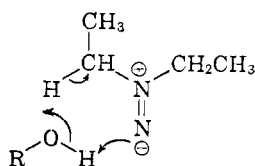
In the light of the above discussion of the rearrangement mechanism, the dramatic influence of solvent on reaction pathway becomes readily understandable. Whereas tetrazene formation requires only the generation of diazenes, rearrangement to a hydrazone apparently does not occur unless a 1,3-dipolar intermediate tautomeric with the diazene is produced. In an aprotic solvent there is no hydroxyl group to facilitate concerted proton transfer from carbon to nitrogen as in the transition state diagrammed above, nor is there any proton source to permit stepwise tautomerization proceeding *via* the diazenium ion. Hence it is not surprising that diazenes generated in tetraglyme survive sufficiently long to react intermolecularly producing tetrazenes.[28]

(25) Since solvolysis by the hydroxylic solvent assures the presence of some free sulfonylhydrazine even when an entire equivalent of base is used, diazenium ions are produced rapidly in such solutions.

(26) This view is supported by the fact that careful neutralization of acidic aqueous solutions containing dialkyldiazenium ions leads quantitatively to tetrazenes.[3]

(27) When the decomposition of a sulfonylhydrazine salt, particularly an aryl-substituted salt,[24] is conducted at elevated temperatures in *strongly* basic protic media as in the work of Carter and Stevens,[5] it is probable that diazenium ions play at best a minor role. It should be borne in mind that pyrolysis proceeds smoothly in hot aprotic solvents where the diazene can form, but not its conjugate acid.

(28) The state of aggregation of the salt may also influence whether inter-

1,1-Diphenyl-2-benzenesulfonylhydrazine Sodium Salt.

—With the observation that 1,1-dialkyl as well as 1-aryl-1-benzyl- (or allyl-) 2-sulfonylhydrazine salts are capable of rearranging, it became desirable to learn whether or not the 1,1-diaryl derivatives could show analogous behavior, yielding azo compounds. Carter and Stevens[5] had reported that 1,1-diphenyl-2-*p*-toluenesulfonylhydrazine was inert to "boiling dilute alkali," but earlier Carpino[29] had noted without experimental detail that "alkaline degradation" of 1,1-diphenyl-2-benzenesulfonylhydrazine gave diphenylamine (26% yield). In our laboratory the corresponding sodium salt (14) was heated in DEG solution at 240° for 3 hr. Conventional work-up followed by chromatography of the crude product on alumina gave no discernible azobenzene, but diphenylamine (15), identified by mixture melting point and spectral comparison with an authentic sample, was obtained in about 80% yield. Though the yield of amine was lower, results were similar with refluxing triglyme as the solvent (225°). Again in sulfolane (240°)[30] the major product was diphenylamine (70%), accompanied not by azobenzene but by an unidentified colorless crystalline compound

$$(C_6H_5)_2N-NSO_2C_6H_5 \xrightarrow[Na]{>200°} (C_6H_5)_2NH$$

<div align="center">14   15</div>
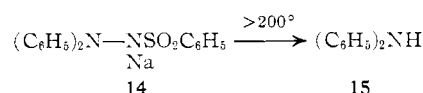
Decomposition of the sodium salt of N-benzenesulfonamidocarbazole has been shown to give carbazole in excellent yield, and evidence has been adduced that the tetrazene 16 is an intermediate in this transformation.[4b] It is thus reasonable to postulate that tetraphenyltetrazene (17) is a precursor of diphenylamine in the decomposition of 14. The experiment giving carbazole did not constitute an adequate test of the ability of diaryldiazenes to rearrange, since geometrical restrictions on the potential migrating group could well have prevented rearrangement. Hence the present experiments, in which the phenyl groups are unlinked, provide the first clear-cut evidence that the tendency toward rearrangement in the diaryl series is slight.
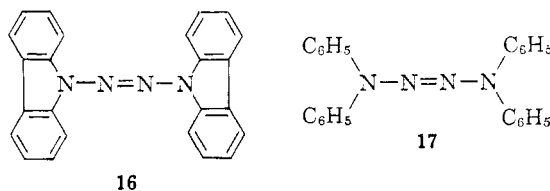
Since no 1,3-dipolar tautomer is possible for a diaryldiazene, the failure to observe rearrangement with 1,1-diaryl-2-benzenesulfonylhydrazine salts indirectly lends support to the mechanism proposed above for the diazene–hydrazone transformation. The mechanism further predicts, of course, that rearrangement of 1-aryl-1-alkyldiazenes (whether the alkyl groups be benzyl, allyl, or yet-untried simple alkyl) proceed exclusively

or intramolecular reaction occurs. This factor would favor tetrazene formation relative to rearrangement when the solvating power of the medium is decreased, as is observed.

(29) L. A. Carpino, Abstracts, 130th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1956, p. 18-O.

(30) Much more vigorous conditions are required for the formation of a diaryldiazene (or diaryldiazenium ion) than for its dialkyl analog because of the greatly reduced electron-donating ability of the arylated nitrogen atom.[4b,5,24]

via aryl rather than alkyl migration. Present efforts in our laboratory are directed toward testing this prediction and toward intercepting the hypothetical 1,3-dipolar intermediate in the diazene–hydrazone rearrangement.

Experimental[31]

N-Nitrosodiethylamine.—This preparation was based on the procedure of Hart.[32] Concentrated hydrochloric acid, 83 ml., was placed in a 500-ml. 3-neck flask and cooled in ice. To this was added dropwise with stirring 73 g. (1 mole) of distilled diethylamine (Eastman). Slightly more acid was added at the end of this step in order that the mixture be barely acid to litmus. The solution was warmed to 70–75° and 79 g. (1.1 moles) of sodium nitrite in 100 ml. of distilled water was added over the course of 1 hr. Concurrently, 10 ml. of 2 N hydrochloric acid was added in 3 portions to ensure that the reaction mixture was maintained slightly acidic. Stirring and heating were continued 2 hr. after the addition was completed; the (top) organic layer was separated after cooling. The aqueous phase was saturated with salt and extracted 3 times with ether. When the combined organic layers had been dried over potassium carbonate, the ether was stripped, leaving a brown oil which was distilled through a 10-in. vacuum-jacketed Vigreux column. The distillate weighed 85.5 g. (84%), b.p. 71–72 at 20 mm. (lit.[33] 174.5° at 777 mm.).

N-Nitrosodiisopropylamine was prepared according to the above method using distilled diisopropylamine (Eastman). The nitroso compound was a liquid, b.p. 87–88° at 18 mm. (91% yield).

1,1-Diethylhydrazine.—The following procedure is based on that of Vogel.[33] A 3-l. 3-neck flask was fitted with a dropping funnel, a condenser protected with a drying tube, and a strong glass stirrer. To this was added 1 lb. of dry ether and 27 g. (0.71 mole) of lithium aluminum hydride. The mixture was boiled under reflux for 90 min. and then cooled in ice. A solution of 51 g. (0.5 mole) of N-nitrosodiethylamine in 50 ml. of ether was added over the course of 2.5 hr. Immediately after all the nitrosamine had been added, rather violent frothing ensued, but the large flask prevented any loss of material. Vigorous stirring was necessary at all times. When the reaction had subsided (after 3 or 4 min.), an additional 150 ml. of ether was added and the mixture stirred 45 min. at 0° followed by 45 min. at room temperature. The flask was again cooled in ice; 60 ml. of water was added dropwise with great caution. With the excess lithium aluminum hydride thus destroyed, 300 ml. of 20% sodium hydroxide was added and the ether decanted from the suspension. The aqueous suspension was washed with many portions of ether, so that the final volume of ether was about 1.5 l. This was dried over potassium carbonate and the solvent evaporated. The residue was distilled from potassium hydroxide through a vacuum-jacketed Vigreux column. The product boiling from 98–99° (25.5 g., 58%) was collected and stored in a tight container in the refrigerator (lit.[33] b.p. 98.5–99.5°).

1,1-Diisopropylhydrazine.—When N-nitrosodiisopropylamine was reduced by the above procedure, starting material was recovered in greater than 90% yield. Accordingly, in another run 27 g. (0.71 mole) of lithium aluminum hydride was dissolved in tetrahydrofuran (450 ml.) instead of ether. The nitrosamine (65 g., 0.5 mole) in 40 ml. of tetrahydrofuran was added dropwise over the course of 1 hr. at room temperature. After the mixture had been boiled under reflux 5 hr., it was cooled in ice and worked up in essentially the same manner as that described for diethylhydrazine; 32 g. (55%), b.p. 130–132°, of diisopropylhydrazine was isolated.

1,1-Dimethyl-2-benzenesulfonylhydrazine.—The general sulfonylation method devised by Carpino[4a] was used here. Distilled Eastman *unsym*-dimethylhydrazine (6.02 g., 0.1 mole) was mixed with 10.16 g. (0.1 mole) of distilled triethylamine in a 250-ml. erlenmeyer flask that had been cooled in ice; 50 ml. of distilled

Eastman White Label dimethylformamide was introduced, and a solution of 17.66 g. (0.1 mole) of benzenesulfonyl chloride in 20 ml. of dimethylformamide was added dropwise with constant stirring over 10 min. The thick slurry was stored overnight in the refrigerator. When the mixture was poured into cold water, crystals separated. These were collected by filtration, washed with water, and recrystallized twice from methanol–water. The final crop weighed 8.0 g. (40%) and melted at 95–96°.

Anal. Calcd. for $C_8H_{12}N_2O_2S$: C, 48.04; H, 6.05; N, 14.01. Found: C, 48.31; H, 5.78; N, 14.21.

1,1-Diethyl-2-benzenesulfonylhydrazine.—The procedure was identical with that used for the dimethyl derivative. Several recrystallizations from benzene–heptane afforded purer material (m.p. 97.5–98.5°, 53%) than the product of recrystallization from methanol–water.

Anal. Calcd. for $C_{10}H_{16}N_2O_2S$: C, 52.60; H, 7.07; N, 12.27. Found: C, 52.77; H, 6.79; N, 12.33.

1,1-Diisopropyl-2-benzenesulfonylhydrazine.—Prepared and purified in the same manner as its diethyl analog, this hydrazine melted at 130–132° (64%).

Anal. Calcd. for $C_{12}H_{20}N_2O_2S$: C, 56.20; H, 7.86; N, 10.93. Found: C, 56.42; H, 7.80; N, 11.13.

Pyrolysis of 1,1-Dimethyl-2-benzenesulfonylhydrazine Sodium Salt (6a) in Tetraglyme.—A 100-ml. 3-neck flask was fitted with a water condenser which was connected to an efficient graduated trap. A three-way stopcock connected the trap with a nitrogen source and a mechanical pump; 50 ml. of tetraglyme[34] was placed in the flask and cooled to 0°. Ten grams (50 mmoles) of 1,1-dimethyl-2-benzenesulfonylhydrazine and 2.5 g. (54 mmoles) of 52% sodium hydride dispersion in mineral oil were added. The mixture was stirred magnetically under nitrogen for 30 min., warmed at room temperature, and stirred an additional 30 min. Finally the system was evacuated with the mechanical pump until the solution was free from bubbles. With the trap fully immersed in Dry Ice–acetone and the pressure at 0.1–0.2 mm., the pot temperature was raised to 110–120° in a preheated oil bath. The heating was discontinued after 15 min., during which a copious precipitate of sodium benzenesulfinate had formed and 2.2 g. (76%) of product had collected in the trap. Gas–liquid chromatographic analysis indicated that this material was about 98% one substance. Proof that the compound was tetramethyltetrazene depended on the n.m.r. and ultraviolet spectra (Tables I and II), which were measured on a sample purified by g.l.c. It should be noted that essentially the same yield of tetrazene was obtained when the experiment was run at atmospheric pressure rather than at 0.1–0.2 mm.

Pyrolysis of 1,1-Diethyl-2-benzenesulfonylhydrazine Sodium Salt (6b) in Tetraglyme.—The salt was prepared and the decomposition carried out as in the preceding experiment. In the present case the product was isolated by distillation directly from the reaction flask through a 10-in. vacuum-jacketed Vigreux at 0.1 mm. The Dry Ice-cooled receiver contained tetraethyltetrazene (84% yield), which was chromatographed on Fisher alumina using distilled heptane as the eluent; n.m.r. and ultraviolet spectra of the purified tetrazene, a colorless oil, are recorded in Tables I and II. Comparison of these with spectra of the crude product indicated that the crude product had been 95% pure.

Pyrolysis of 1,1-Diisopropyl-2-benzenesulfonylhydrazine Sodium Salt (6c) in Tetraglyme.—The procedure was identical with that for the diethyl analog. While being stirred at room temperature to ensure complete salt formation, the tetraglyme solution became cloudy, due perhaps to a small amount of spontaneous decomposition of the salt. After the pyrolysis, the product (b.p. 50° at 0.2 mm., 79%) was isolated by distillation from the reaction mixture through a Vigreux column using the solvent as a chaser. The oil was purified by dissolving it in heptane, extracting twice with water, drying over calcium chloride, and chromatographing on Fisher alumina with distilled heptane. The resulting colorless tetraisopropyltetrazene was identified by its n.m.r. and ultraviolet spectra (Tables I and II) and by microanalysis. Spectral comparison of the pure tetrazene with the crude material showed that the latter had been about 91% pure.

Anal. Calcd. for $C_{12}H_{28}N_4$: C, 63.10; H, 12.35; N, 24.53. Found: C, 63.10; H, 12.35; N, 24.38.

(31) All melting points were determined on a Kofler micro hot stage and are corrected. Analyses were performed by the Spang, Illini, and Scandinavian microanalytical laboratories. Infrared spectra were measured on a Perkin–Elmer Infracord and the ultraviolet spectra on a Cary recording spectrophotometer, Model 11S. A 2-m. column packed with Ucon Polar on Chromosorb-W (20%) was used for all g.l.c. separations.

(32) H. H. Hart, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 211.

(33) A. I. Vogel, W. T. Cresswell, G. H. Jeffery, and J. Leicester, *J. Chem. Soc.*, 514 (1952).

(34) The glyme, triglyme, and tetraglyme used in all experiments were freshly distilled from lithium aluminum hydride. The DEG (Eastman White Label) was distilled through a 10-in. vacuum-jacketed Vigreux column.

Pyrolysis of 1,1-Dimethyl-2-benzenesulfonylhydrazine Sodium Salt (6a) in Diethylene Glycol.—A 300-ml. 3-neck flask was equipped with a water-cooled condenser which led to a trap cooled by liquid nitrogen, thence to a nitrogen source and a mechanical pump; 100 ml. of diethylene glycol (DEG)[34] was introduced, followed by 2.5 g. (54 mmoles) of 52% sodium hydride dispersion in mineral oil. When the mixture had been stirred magnetically under nitrogen for 45 min., the solution was cleared of gas bubbles by evacuation. Ten grams (50 mmoles) of 1,1-dimethyl-2-benzenesulfonylhydrazine was added and the mixture stirred for a few minutes until solution was complete. The apparatus was evacuated to 0.1 mm.; the reaction solution was brought to 110–120° in a preheated oil bath. After 13 min., 2.0 ml. (62% yield) of colorless oil had collected in the cold trap, and no increase in the quantity resulted from continued heating and pumping. The by-product sodium benzenesulfinate was soluble in DEG and never isolated; g.l.c. analysis of the crude product, which was stored in a sealed container at −25°, revealed that a single compound comprised about 70% of the total material. There was no peak corresponding to tetramethyltetrazene. A second run was performed and the combined yield of about 4 ml. was fractionated on a 10-in. spinning band column. Analysis by g.l.c. of the main fraction indicated that no substantial purification had been achieved. Purification was finally accomplished by trapping the desired g.l.c. peak and recycling the trapped material through the g.l.c. apparatus. The impurities tailed badly, as did the major peak itself. Identification of the pure, colorless oil as formaldehyde methylhydrazone rested upon the microanalysis and spectra (Tables I and II).

Anal. Calcd. for $C_2H_6N_2$: C, 41.36; H, 10.40; N, 48.24. Found: C, 41.06; H, 10.55; N, 48.06.

Hydrolysis of Formaldehyde Methylhydrazone.—A sample (0.16 g.) of partially purified product from the preceding experiment was placed in a 2-in. test tube containing 5 drops of water and 1 of concentrated sulfuric acid; the solution was allowed to stand at room temperature for several hours. Ten drops of 95% ethanol was added, followed by excess fresh 2,4-dinitrophenylhydrazine solution. The resulting precipitate was separated by filtration, washed, and recrystallized twice from ethanol–water. The 2,4-dinitrophenylhydrazone (45%) melted at 166–167.5°. An authentic sample of formaldehyde 2,4-dinitrophenylhydrazone melted at 166.5–167.5°; and the mixture melting point showed no depression.

A derivative of the other hydrolysis fragment, methylhydrazine, was obtained by mixing 0.20 g. of partially purified formaldehyde methylhydrazone, 0.5 ml. of water, 0.4 g. of sulfuric acid, and 1.0 ml. of methanol. While the mixture was kept at 0°, the formaldehyde was entrained by a slow stream of nitrogen. After about 30 min. crystals separated which were collected by filtration and recrystallized twice from methanol. Both this product (26% yield) and the authentic bisulfate salt of methylhydrazine melted at 142–143° (lit.[35] 142°); the mixture melting point was undepressed.

Pyrolysis of 1,1-Diethyl-2-benzenesulfonylhydrazine Sodium Salt (6b) in DEG.—The method was that used for pyrolysis of the dimethyl analog. In the present experiment, run on the same scale, the cold trap contained 2.5 ml. (2.0 g., 78%). This crude material was 89% pure as judged by g.l.c. and by ultraviolet spectral comparison with a sample purified twice by g.l.c. Ultraviolet and n.m.r. spectra (Tables I and II) of the pure compound indicated that it was acetaldehyde ethylhydrazone. Azoethane, synthesized by the method of Renaud and Leitch,[36] was isomerized with base to authentic acetaldehyde ethylhydrazone. This sample had an n.m.r. spectrum and a g.l.c. retention time identical with those of the compound produced in the pyrolysis reaction.

Pyrolysis of 1,1-Diisopropyl-2-benzenesulfonylhydrazine Sodium Salt (6c) in DEG.—The procedure described for the dimethyl analog was again followed. In this case, however, the trapped material constituted only 21% of the theoretical calculated for the hydrazone. This crude oil, which was better than 82% pure, was further purified by g.l.c.; n.m.r. and ultraviolet spectra (Tables I and II), coupled with microanalytical data, sufficed to identify the product as acetone isopropylhydrazone.

Anal. Calcd. for $C_6H_{14}N_2$: C, 63.09; H, 12.36; N, 24.54. Found: C, 62.98; H, 12.41; N, 24.80.

The remainder of the product was obtained by distilling the

(35) G. von Brüning, *Ann.*, **253**, 5 (1889).

(36) R. Renaud and L. C. Leitch, *Can. J. Chem.*, **32**, 545 (1954).

reaction mixture through a Vigreux column using the solvent as a chaser. Tetraisopropyltetrazene (59% crude yield) comprised approximately 92% of the distillate. As in the previous preparation of this substance, the tetrazene was purified by chromatography on Fisher alumina and shown to be identical in terms of ultraviolet and n.m.r. spectra with the material isolated from the decomposition of the sulfonylhydrazine salt in tetraglyme.

Acetaldehyde Dimethylhydrazone.—To an ice-cold solution of 20 g. of acetaldehyde in 50 ml. of water was added dropwise with magnetic stirring 20 g. of 1,1-dimethylhydrazine (Eastman). The solution was saturated with sodium hydroxide, the organic layer separated, and the product distilled twice from potassium hydroxide. A middle cut (b.p. 90–90.5°), free from impurities detectable by g.l.c., was used for the ultraviolet spectrum (Table I).

1-Ethyl-3-methyldiaziridine (12).[19]—Prepared from ethylamine, acetaldehyde, and hydroxylamine-O-sulfonic acid by method of Schmitz for 3,3-dimethyldiaziridine,[20] the 1-ethyl-3-methyl derivative was a colorless oil which showed only end absorption in the ultraviolet and which oxidized hydriodic acid at room temperature (a characteristic of diaziridines). The n.m.r. (Table II) and infrared ($\lambda_{max}^{CHCl_3}$ 3.0 μ) spectra were consistent with the structure assignment. Partial decomposition of the diaziridine occurred during g.l.c. as indicated by the presence of a constant quantity of volatile impurity no matter how pure the injected material.

Anal. Calcd. for $C_4H_{10}N_2$: C, 55.79; H, 11.70; N, 32.54. Found: C, 55.66; H, 11.54; N, 32.40.

Decomposition of 1,1-Diethyl-2-benzenesulfonylhydrazine Sodium Salt (6b) at Room Temperature.—In a 10-ml. round-bottom flask was placed 479 mg. (2.10 mmoles) of 1,1-diethyl-2-benzenesulfonylhydrazine; to this was added with a syringe 3.0 ml. (1.95 mmoles) of 0.65 M DEG sodium salt in DEG.[34] The flask was connected through two U-shaped traps (in series) to a mechanical pump. While the reaction mixture was stirred magnetically, the system was evacuated to ~0.1 mm. and the trap closer to the reaction vessel was immersed in liquid nitrogen. Interestingly, the reaction mixture began to boil as soon as the pressure was lowered, and an appreciable quantity of distillate appeared in the trap during the few minutes required for the hydrazone to dissolve completely. After the system had been maintained at ~0.1 mm. for 2 hr. the product was rapidly redistilled by allowing the cold trap to warm to room temperature while the other trap was cooled in liquid nitrogen. The purpose of the second distillation was to remove a small amount of solvent which had condensed in the original cold trap. Analysis by g.l.c. indicated that the product, a virtually colorless oil (148 mg.), was ~85% acetaldehyde ethylhydrazone (8b), identified by comparison of retention time with an authentic sample. Thus the yield of hydrazone based on hydrazine is ~70% (~75% based on the quantity of alkali used).

In another run 150 μl. (1.3 mmoles) of azoethane[36] was added to the reactants and the mixture was stirred 3.5 hr. under an atmosphere of nitrogen. With these exceptions, the experiment was conducted identically with the preceding one. The volatile products were again collected by vacuum distillation at room temperature; g.l.c. analysis revealed about 70% as much azoethane as hydrazone in the distillate, thereby proving that the azo compound cannot be an intermediate in the reaction producing hydrazone.

1-Ethyl-3-methyldiaziridine (12, 150 μl.) was substituted for azoethane in an experiment identical with that immediately preceding. Analysis of the product by g.l.c. demonstrated that isohydrazone had survived the reaction conditions. Roughly equal amounts of the hydrazone and its isomer were present.

1,1-Diphenyl-2-benzenesulfonylhydrazine.—1,1-Diphenylhydrazine hydrochloride (Eastman, 2 g., 9.2 mmoles) was dissolved in a small volume of distilled sulfolane (Phillips Petroleum Co.). Benzenesulfonyl chloride (1.2 ml., 9 mmoles) was added and the solution was stirred overnight. When poured into ice-cold dilute acid, the dark reaction mixture deposited a brown oil which subsequently crystallized. The solid was collected by filtration and recrystallized from methanol–water, giving tan needles (1.98 g., 66%), m.p. 160–160.5°. An analytical sample (m.p. 164–165°) was prepared by further recrystallization from the same solvent.

Anal. Calcd. for $C_{18}H_{16}N_2O_2S$: C, 66.64; H, 4.97; N, 8.64. Found: C, 66.62; H, 4.97; N, 8.51.

Decomposition of 1,1-Diphenyl-2-benzenesulfonylhydrazine Sodium Salt (14).—Sodium hydride dispersion in mineral oil

(0.19 g., 3.6 mmoles) was dissolved in 100 ml. of DEG[34] under nitrogen and 1,1-diphenyl-2-benzenesulfonylhydrazine (1.0 g., 3 mmoles) was added. The resulting suspension was stirred until all of the sulfonylhydrazine was in solution as its sodium salt. The reaction mixture was boiled under reflux (238–240°) for 3 hr., still under a nitrogen atmosphere, and then poured into 300 ml. of dilute aqueous base. Extraction with several portions of ether followed; the combined extract was washed repeatedly with water and dried over magnesium sulfate. Removal of the ether yielded a dark residue which was chromatographed on Fisher alumina. The column was eluted successively with petroleum ether, petroleum ether–carbon tetrachloride, carbon tetrachloride–benzene, benzene; 0.43 g. of solid, m.p. 40.5–49°, was obtained from the carbon tetrachloride–benzene fraction. Purification by recrystallization from methanol–water raised the melting point to 53–54°. The compound was identified as diphenylamine (crude yield 83%) by infrared spectral and mixture melting point comparison with an authentic sample.

A similar pyrolysis was carried out in refluxing triglyme[34] (225°); again diphenylamine was the major product. The yield after purification by chromatography and repeated recrystallization was 40% (m.p. 53–54°).

When hot sulfolane (240–250°) was employed as the reaction medium, diphenylamine was isolated in 70% yield (m.p. 50–54°) by chromatography. Another crystalline substance was eluted prior to the amine. Sublimation or g.l.c. of this material gave colorless crystals which were shown to differ from diphenyl in g.l.c. retention time, but which were not further investigated.

No azobenzene was isolated in any of the above runs, despite the fact that the azo compound was recovered in substantial yield after being heated 3 hr. at about 240° in DEG.


Induced Decompositions of Di-t-butyl Peroxide in Primary and Secondary Alcohols[1]

BY EARL S. HUYSER AND CORWIN J. BREDEWEG[2]

Di-t-butyl peroxide undergoes an induced decomposition when heated at 125° in primary and secondary alcohols. The rate of decomposition of the peroxide in such alcohols is approximately first order in peroxide. Product analysis of the reaction of the peroxide in 2-butanol indicates that the attack of the alcohol-derived radical is exclusively at the oxygen–oxygen linkage of the peroxide. A mechanism involving the transfer of a hydrogen atom from an α-hydroxyalkyl derived from primary and secondary alcohols is suggested to account for both the induced decomposition and the major products of the reactions.

The kinetics of the decomposition of di-t-butyl peroxide have been studied both in the gas and liquid phases. In the gas phase, the rate of decomposition was found to be a reaction that was first order in peroxide, the rate-determining process being the homolytic rupture of the peroxide linkage yielding two t-butoxyl radicals.[3] The t-butoxyl radicals can decompose to

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO\cdot \qquad (1)$$
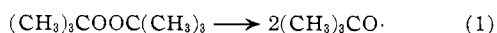
form methyl radicals and acetone and the products of such reactions depend on the subsequent reactions of the methyl radical. In solution, hydrogen abstrac-

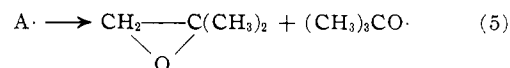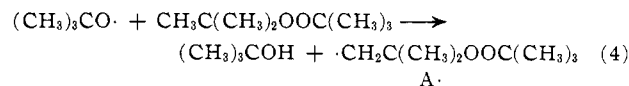$$(CH_3)_3CO\cdot \longrightarrow CH_3COCH_3 + CH_3\cdot \qquad (2)$$

tion from the solvent by the t-butoxyl radical producing t-butyl alcohol and a solvent-derived radical (reaction 3) competes with the fragmentation shown in reaction 2

$$(CH_3)_3CO\cdot + SH \longrightarrow (CH_3)_3COH + S\cdot \qquad (3)$$
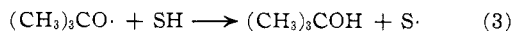
and the distribution of peroxide fragmentation products is solvent dependent.[4] Raley, Rust, and Vaughan

have shown that the rate of decomposition of the peroxide in cumene, tri-n-butylamine, and t-butylbenzene is a first-order reaction with essentially the same reaction rate observed for the gas phase reactions and concluded that in these solvents the decomposition of the peroxide is uncomplicated by any induced chain processes involving the solvent-derived radical.[4a]

There are, however, reported instances of induced decompositions of di-t-butyl peroxide. The neat liquid was found to decompose at a rate faster than that observed for decompositions in solution or in the gas phase.[5] The explanation given for this induced decomposition, based largely on the appearance of isobutylene oxide as a reaction product, involves attack of a hydrogen of the peroxide by a radical fragment producing the radical A· which decomposes into isobutylene oxide and the chain-carrying t-butoxyl radical. An induced decomposition of di-t-butyl peroxide, again involving the alkyl hydrogens of the

$$(CH_3)_3CO\cdot + CH_3C(CH_3)_2OOC(CH_3)_3 \longrightarrow$$
$$(CH_3)_3COH + \cdot CH_2C(CH_3)_2OOC(CH_3)_3 \quad (4)$$
$$A\cdot$$

$$A\cdot \longrightarrow CH_2\!\!-\!\!C(CH_3)_2 + (CH_3)_3CO\cdot \qquad (5)$$
$$\underset{O}{\diagdown\diagup}$$

peroxide, was noted in styrene polymerizations in which the peroxide was present.[6]

This paper is concerned with the decomposition of di-t-butyl peroxide in primary and secondary alcohols. Rate studies show that in such alcohols the peroxide

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(2) National Science Foundation Cooperative Fellow, 1961–1963. This paper is taken from the thesis submitted by C. J. B. in partial fulfillment of the requirements for the Ph.D. Degree from the University of Kansas, 1963.

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