at 70°, the reaction mixture was cooled, neutralized, and extracted with methylene chloride. The methylene chloride solution was extracted with a saturated solution of sodium bicarbonate and then with 5% sodium hydroxide. The O-benzoyl derivative IV (0.8 g., 10%), m.p. and m.m.p. 150–151°, was obtained from the methylene chloride solution. Acidification of the sodium hydroxide extract yielded a yellow solid which, on fractional crystallization from methanol, afforded 3.65 g. (69.4%) of unchanged I, m.p. and m.m.p. 108–109°, and 0.07 g. (2%) of diphenacyl sulfone (VI), m.p. 122–123° (lit.[5] m.p. 124–125°).

Anal. Calcd. for $C_{16}H_{14}O_4S$: C, 63.56; H, 4.67; S, 10.6. Found: C, 63.78; H, 4.11; S, 10.9.

It failed to produce a color with ethanolic ferric chloride or to form a derivative with copper acetate. Its infrared spectrum showed a sharp benzoyl carbonyl group peak at 1695 cm.$^{-1}$ (lit.[6] ν 1690 cm.$^{-1}$). Its ultraviolet spectrum had λ_{max} 253 mμ (ϵ 38,600), compared with λ_{max} 251 mμ (ϵ 15,300) for I. Its n.m.r.[10] spectrum had a singlet at τ 4.9 and a multiplet at 1.9–2.74 (ten protons).

B. With Phenylsodium in Toluene.—A hot solution of 4.95 g. (0.025 mole) of I in toluene was added to a stirred hot suspension of phenylsodium[11] in toluene, and the mixture was stirred at 60° for 2.5 hr. and then 1.7 g. (0.0125 mole) of methyl benzoate in 3 ml. of toluene was added and stirring at 60° was continued for a further 5 hr. The reaction mixture was cooled, treated with ethanol (to destroy excess of sodium), and then poured onto a slight excess of hydrochloric acid in the presence of ice. The product on working up as in the previous experiment gave 0.75 g. (20%) of diketo sulfone VI, m.p. 122°, and 3.71 g. (75%) of unchanged keto sulfone I.

Acknowledgment.—The authors thank Professor E. M. Philbin of this Department and Professor C. R. Hauser of Duke University, Durham, North Carolina, for advice.

[10] We are indebted to Dr. G. R. Bedford of Imperial Chemical Industries Ltd., Pharmaceuticals Division, Macclesfield, Cheshire, England, for this determination.

[11] See "Sodium Dispersions," U. S. Industrial Chemical Co., Division of National Distillers Production Corp., New York, N. Y., 1957, p. 36.

Azo-Hydrazone Conversion. III. The Autoxidation of Benzaldehyde Phenylhydrazones

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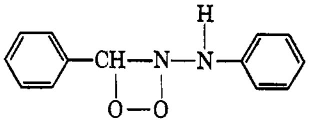
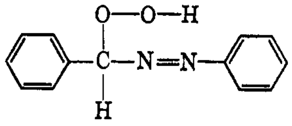
Received February 8, 1965

Busch and Dietz[2] reported that certain benzaldehyde phenylhydrazones can take up oxygen to form peroxides and assigned the structure I to these peroxides. Pausacker[3] determined the rate of oxidation by measuring the oxygen consumption. He suggested two other possible structures, II and III, for the oxidation product. Pausacker could not unequivocally distinguish between these two structures but favored structure II. Criegee and Lohans[4] compared the rates of oxidation of several series of substituted benzaldehyde phenylhydrazones. They found that although benzaldehyde phenylhydrazones take up oxygen readily, under the same conditions N-substituted benzaldehyde phenylhydrazones are not reactive with oxygen. On these bases, they also favored structure II for the autoxidation product and suggested a possible tautomerization (eq. 1). Structure IV comes close to Busch's formulation I.


I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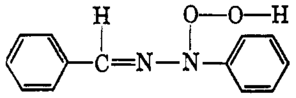
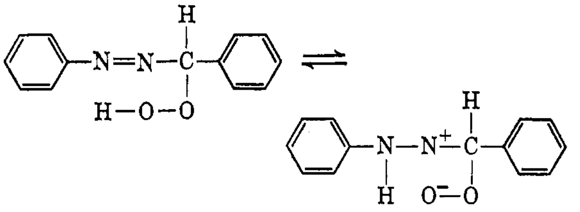

III


(1)

IV

However, no evidence other than the rate measurements has been given to distinguish among the above formulations, I, II, and III. This is possibly due to the instability of such oxidation products, which readily decompose at room temperature in the solid state as well as in solution.

Recently, spectral properties of phenylhydrazones have been shown to be quite different from those of the tautomeric azo compounds.[5–9] It is interesting, therefore, to re-examine the structures of the products from the autoxidation of phenylhydrazones by spectral methods. In the present work, the autoxidation of several benzaldehyde phenylhydrazones has been carried out at room temperature and in an atmosphere of oxygen. The stability of these products depends largely on the *para* substituents of the benzaldehyde moiety and increases in the following order: $Cl < H \leq CH_3 < OCH_3$. While the *p*-chloro-substituted product often decomposes readily in the process of crystallization, the *p*-methyl-substituted product can be recrystallized from benzene and stored at 0° for several hours. The *p*-methoxy-substituted product decomposes very slowly at room temperature; it can be stored at about 0° for several weeks without decomposition. These products have been taken for the spectral study of their chemical structures.

Yao and Resnick[5] reported that the ultraviolet absorption spectra of phenylhydrazones differ from those of the phenylazo compounds obtained from the coupling of benzenediazonium ion to α-substituted acetoacetanilides and acetoacetic acid esters. The former have a weak band at 285 to 295 mμ and a stronger band at wave length longer than about 320 mμ. The latter, which have a phenylazo group attached to an aliphatic carbon, show a characteristic band at 270 to 280 mμ.[5,7]

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[1] To whom communications should be sent: Scientific Laboratory, Ford Motor Co., Dearborn, Mich.

[2] M. Busch and N. Dietz, *Ber.*, **47**, 3281 (1914).

[3] K. H. Pausacker, *J. Chem. Soc.*, 3478 (1950).

[4] R. Criegee and G. Lohans, *Ber.*, **84**, 219 (1951).

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[9] H. C. Yao, *ibid.*, **29**, 2959 (1964).

TABLE I

CHEMICAL SHIFTS (δ, p.p.m.) OF THE VARIOUS PROTONS IN THE N.M.R. ABSORPTION SPECTRA OF THE PHENYLHYDRAZONES AND THE AZO HYDROPEROXIDES

Compd.	Benzene ring	-CH=N-	=N—NH-	$-\underset{H}{\underset{\mid}{C}}{—}N{=}N-$	-OOH	$-CH_3$
V	7.3, 7.7 (11)[a]	6.9	8.6 (1)	...	...	...
VI	7.2, 7.5 (10)[a]	6.9	8.5 (1)	...	...	...[b]
VII	7.0, 7.6 (10)[a]	7.1	8.4 (1)	...	...	3.8 (3)
IX	7.4, 7.6 (10)	...	...	6.1 (1)	10.4 (1)	...
X	7.3, 7.7 (9)	...	...	6.0 (1)	10.3 (1)	...[b]
XI	7.0, 7.6 (9)	...	...	6.0 (1)	10.3 (1)	3.8 (3)

[a] Values in parentheses are the number of protons estimated from the relative area of the peaks. In Compounds V, VI, and VII, the proton peaks from the benzene ring are overlapped with those from -CH=N- group and the proton numbers given are the sums of the protons in these two groups. [b] Methyl proton peaks of VI and X are overlapped with the side bands of solvent proton peaks.

As shown in Figure 1, the ultraviolet absorption spectra of the benzaldehyde phenylhydrazones V, VI, VII, and VIII show two absorption bands at 285 and 350 mμ characteristic of typical phenylhydrazones. The ultraviolet absorption spectra of their oxidation products show a strong band at 270 to 280 mμ, indicating that they are phenylazo compounds rather than phenylhydrazones. This evidence favors structure II for the oxidation product rather than structure III, which retains the phenylhydrazone structure.

A comparison of the infrared spectra of the phenylhydrazones with those of their oxidation products favors structure II rather than structure I for the oxidation products. For example, the spectra of the oxidation products show a strong OH stretching band at 3.08 to 3.18 μ, a -CH- stretching band at 3.45 μ, and a -CH- deformation band at 7.10 to 7.16 μ.[10] These bands are not found in the infrared spectra of the parent phenylhydrazones. In addition, the sharp -NH stretching band at about 3.00 to 3.02 μ which is present in the infrared spectra of all the benzaldehyde phenylhydrazones is not found in the spectra of their oxidation products.

These phenylhydrazones and their oxidation products have been examined further by means of n.m.r. absorption spectra (Table I). The assignments of the various proton peaks are based on the reported data in n.m.r. spectra of the phenylhydrazones and related compounds. The -CH=N- and =N—NH- proton peaks of the phenylhydrazones are often found to be close to or overlapped by the phenyl proton peaks.[11-13] For example, the =N—NH- peaks of heptaldehyde phenylhydrazone, acetone phenylhydrazone, and cyclohexanone phenylhydrazone occur at 8.2 p.p.m.[12] The -CH=N- proton peak of 2,4-dinitrophenylhydrazones occurs at 7.8 to 8.1 p.p.m.[13] The $-CH_2—N=N-$ proton peak of benzylazo compounds is at 5.7 p.p.m.[11,14] The replacement of one of the H-atoms with an -OOH group can probably shift the proton peak of the remaining H-atom from 5.7 p.p.m. to 6.0 p.p.m. The -C—OOH proton peaks of the hydroperoxides obtained from the oxidation of 2,5-hexanedione occur at 10.61 and 10.75 p.p.m.[15] The absence of both -CH=N- and =N—NH- and the presence of -CH—N=N- and -OOH proton peaks in the n.m.r. spectra of the oxidation products favor structure II rather than structure I or III.

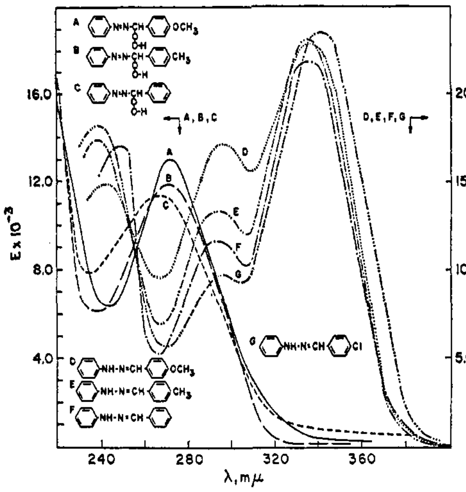

Figure 1.—The ultraviolet absorption spectra of the phenylhydrazones and the azo hydroperoxides.

Chemical evidence also shows that the autoxidation products are probably the azo hydroperoxides. For example, the decomposition of *p*-methoxybenzylazobenzene α-hydroperoxide (XI) to yield *p*-anisic acid and benzene indicates that the hydroperoxide group is attached to the methinyl carbon atom (structure II) rather than the nitrogen atom (structure III).

These spectral and chemical findings, therefore, indicate that a hydrazone to azo conversion occurs in the autoxidation of the benzaldehyde phenylhydrazones.

Experimental

Benzaldehyde phenylhydrazones were prepared by mixing the stoichiometric amounts of benzaldehyde and phenylhydrazine in methanol solution with the addition of a few drops of glacial acetic acid. The white solids collected were recrystallized from alcohol. Approximately quantitative yields were obtained. The following phenylhydrazones were prepared: benzaldehyde phenylhydrazone (V), m.p. 156–158° (lit.[16] m.p. 158°); *p*-tolualdehyde phenylhydrazone (VI), m.p. 113–114° (lit.[16] m.p. 114°); *p*-anisaldehyde phenylhydrazone (VII) m.p. 120–121° (lit.[16] m.p. 120°); and *p*-chlorobenzaldehyde phenylhydrazone (VIII), m.p. 127° (lit.[16] m.p. 127°). The infrared spectra of V, VI, VII, and VIII show a sharp -NH stretching band at 3.00 to 3.02 μ.

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[10] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 13.

[11] T. W. Milligan and B. C. Minor, *J. Org. Chem.*, **27**, 4663 (1962).

[12] R. O'Connor, Jr., *ibid.*, **26**, 4375 (1961). For comparison, the value of −120 c.p.s. (at 40 Mc. and relative to water as zero) was converted to 8.2 p.p.m. (relative to tetramethylsilane as zero).

[13] D. Y. Curtin, J. A. Gourse, W. H. Richardson, and K. L. Rinehart, *ibid.*, **24**, 93 (1959). For comparison, the values of −104 to −118 c.p.s. (at 40 Mc. and relative to water as zero) were converted to 7.8 to 8.1 p.p.m. (relative to tetramethylsilane as zero).

[14] B. H. Arison, A. E. Erickson, N. R. Tienner, and E. F. Schoenewaldt, *Chem. Ind.* (London), 1627 (1958).

[15] N. A. Milas and A. Golubovic, *J. Org. Chem.*, **27**, 4319 (1962).

Benzylazobenzene α-hydroperoxide (IX) was prepared by dissolving 10 g. of benzaldehyde phenylhydrazone in 200 ml. of benzene. The solution was stirred while oxygen was bubbled through the solution until the phenylhydrazone was completely converted to azo hydroperoxide (as determined from the ultraviolet absorption spectrum of the reaction mixture). The solution was concentrated under vacuum and a yellow solid precipitated out. The mixture was cooled with ice and filtered. The solid was recrystallized twice from benzene and dried under vacuum, m.p. 67–68° (lit.[2] m.p. 65–66°), yield 64%.

Anal. Calcd. for $C_{13}H_{12}N_2O_2$: N, 12.3.. Found: N, 12.1. The infrared spectrum of IX has characteristic bands at 3.18, 3.45, and 7.16 μ.

***p*-Methylbenzylazobenzene α-hydroperoxide (X), *p*-methoxybenzylazobenzene α-hydroperoxide (XI), and *p*-chlorobenzylazobenzene α-hydroperoxide (XII)** were prepared from VI, VII, and VIII, respectively, using same procedure as for IX. X, fine white needles, showed m.p. 69–70° (yield 70%).

Anal. Calcd. for $C_{14}H_{14}N_2O_2$: N, 11.6. Found: N, 11.8. The infrared spectrum of X has characteristic bands at 8.18, 3.45, and 7.10 μ.

XI, long white needles, showed m.p. 88–89° (yield 85%).

Anal. Calcd. for $C_{14}H_{14}N_2O_3$: C, 65.1; H, 5.4; N, 10.8. Found: C, 65.7; H, 5.4; N, 11.5.

XII, yellowish needles, showed m.p. 64–65° dec. (yield ~60%). It decomposed to become brown tar after it was dried under vacuum.

Spectroscopic Measurements.—Ultraviolet absorption spectra were determined in methanol solution using a Beckman DU spectrophotometer. The results are shown in Figure 1. Infrared absorption spectra were obtained in a Fluorolube mull using a Perkin-Elmer 237 spectrophotometer. N.m.r. absorption spectra were obtained in acetonitrile solution with tetramethylsilane as an internal reference using a Varian A-60 analytical n.m.r. spectrometer. The results are listed in Table I.

Decomposition of *p*-Methoxybenzylazobenzene α-Hydroperoxide, XI. A.—Two grams of XI was dissolved in 200 ml. of benzene and then stored at room temperature for 2 weeks. During this time the yellow solution turned red. The solution was then concentrated under vacuum to about 50 ml. Another 50 ml. of petroleum ether (b.p. 30–60°) was added. A yellowish solid was precipitated. The solid was recrystallized from a benzene–petroleum ether mixture, m.p. 183–184° (lit.[16] m.p. of anisic acid 184°). A mixture melting point with an authentic sample indicated that the product is anisic acid, yield 30%.

B.—The decomposition of XI was also carried out in chloroform solution. The decomposition was so rapid that the azo hydroperoxide was added slowly and in small amounts. Two grams of XI was added to about 60 ml. of chloroform. The solution was then shaken with dilute aqueous sodium hydroxide solution. The aqueous layer was separated and acidified with acetic acid and a white solid precipitated. The solid precipitate was recrystallized from a benzene–petroleum ether mixture. Anisic acid (m.p. 183–184°) was obtained in about 60% yield. The chloroform solution was transferred into a volumetric flask and diluted to 100 ml. with chloroform. This solution (10 μl.) was injected into a gas chromatograph. The chromotographic curve was compared with that from a benzene–chloroform solution of known composition, and it was found that the decomposition of *p*-methoxybenzylazobenzene α-hydroperoxide can yield benzene in approximately 50% yield.

The Synthesis and Reactions of N-Aminocamphidine and Some of Its Derivatives

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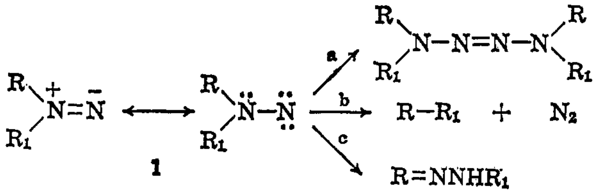
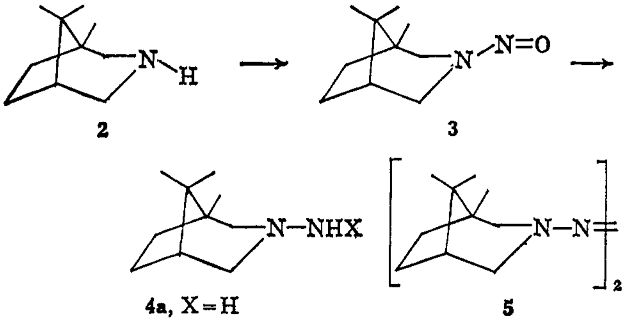
Received January 22, 1965

Aminonitrenes (**1**) have been postulated as intermediates in a variety of reactions. The fate of these reactive species depends on the nature of the R group and the following pathways have been observed: (a) dimerization to form tetrazenes, (b) carbon–nitrogen bond cleavage to form nitrogen, and (c) rearrangement to form hydrazones.[1] Coupling of the two R groups is often obtained in pathway b and yields as high as 95% have been observed. However, pathway b occurs only in compounds which have benzylic C–N bonds,[3a] α-cyano C–N bonds,[3b] C–N bonds in strained ring systems,[3c] and in systems where multiple bonds are concomitantly formed.[3d] Although there are several examples of this reaction in cyclic systems, no bridged bicyclic compound has ever been investigated. It was felt, therefore, that a study of the reactions of N-aminocamphidine (**4a**) and some of its derivatives might be useful since it is a slightly strained molecule and the intermediates resulting from the decomposition of the aminonitrene would be held in close proximity, facilitating the coupling reaction (to camphane). In addition, any rearrangement which might be observed would provide a clue as to the nature of these intermediates.



The synthesis of N-aminocamphidine is outlined below. Camphidine (**2**) was synthesized by lithium aluminum hydride reduction of camphorimide using a modification of Corey's procedure.[4] It was noted that when camphidine was dissolved in carbon tetrachloride, a 43% yield of camphidine hydrochloride was obtained.[5] Nitrosation of camphidine was effected by sodium nitrite in acetic acid. Although the N-nitroso compound **3** did not give a Lieberman's nitroso test[6] and did exhibit four unsplit peaks in the methyl region of its



4a, X = H
b, X = $COCH_3$
c, X = H_2Cl
d, X = *p*-$SO_2C_7H_7$

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(1) A summary of these reactions is given by D. M. Lemal, F. Menger, and E. Coats, *J. Am. Chem. Soc.*, **86**, 2395 (1964).

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

(3) (a) L. A. Carpino, *J. Am. Chem. Soc.*, **79**, 4427 (1957); (b) C. G. Overberger and B. S. Marks, *ibid.*, **77**, 4104 (1955); (c) C. Bumgardner, K. J. Martin, and J. P. Freeman, *ibid.*, **85**, 97 (1963); (d) D. M. Lemal, T. W. Rave, and S. D. McGregor, *ibid.*, **85**, 1944 (1963).

(4) W. R. Hertler and E. J. Corey, *J. Org. Chem.*, **24**, 572 (1959).

(5) The reaction of amines with carbon tetrachloride to give the corresponding hydrochlorides is well documented. See T. G. Bonner and R. A. Hancock, *Chem. Ind.* (London), 267 (1965), and references cited therein.

(6) A. I. Vogel, "A Textbook of Practical Organic Chemistry Including Qualitative Organic Analysis," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1962, p. 649.