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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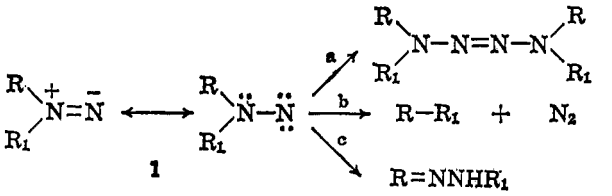
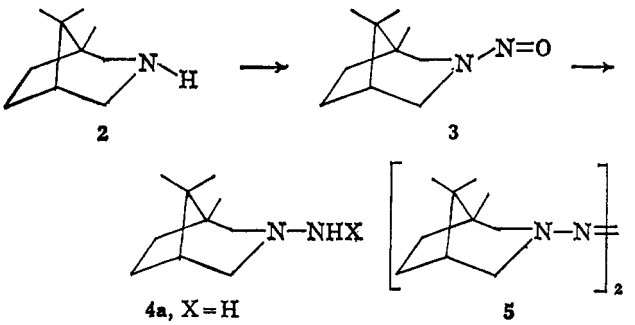
Received January 22, 1965

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



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

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

(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.

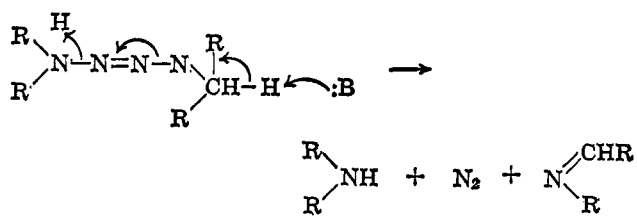
n.m.r. spectrum (at 1.09, 1.01, 0.96, and 0.91 p.p.m. from TMS in a ratio of 3:2.0:2.7:1.4, respectively), the assignment of its structure is based on its mode of formation, a correct elemental analysis, acidic hydrolysis to camphidine, and reduction to a hydrazine. The presence of *four* methyl peaks may be explained either by *syn–anti* isomerism of the nitroso group or by a chair–boat equilibrium of the ring system. In either of these cases one of the methyl groups must experience different shielding in the two forms. Furthermore a multiplet appears at 4.2 p.p.m. and can be attributed to the α-methylene protons. This multiplet is absent in the spectra of the other compounds in the camphidine series and the chemical shift is in accord with the data of Karabatsos[7] for N-nitrosamines. Reduction of the nitrosamine was effected by sodium dithionite and afforded the hydrazine **4a** as an oil which was very susceptible to air oxidation. It was therefore isolated and purified as the N-acetyl derivative **4b** which could be hydrolyzed in hydrochloric acid to the stable hydrochloride **4c**. The acetylation product showed a band at 3290 cm.$^{-1}$ in its infrared spectrum (N–H) indicating the presence of a primary amino group in **4a**. The hydrazine hydrochloride was converted to the N-*p*-toluenesulfonyl derivatives by the method of Carpino.[3a]

Oxidation of the hydrazine in boiling ethanol yielded the tetrazene **5** (analysis and ultraviolet spectrum[8]). G.l.c. analysis did not disclose the presence of any camphane. Oxidation by bromine in a variety of solvents, and at several different temperatures (refluxing aqueous sodium hydroxide, acetic acid, dioxane, and valeric acid) produced only decomposition products and yielded no camphane (g.l.c. analysis). In several experiments one-half the theoretical amount of nitrogen expected in pathway b was obtained. This may be explained by a primary formation of tetrazene followed by its acid- or base-catalyzed decomposition.[9] Pyrolysis of the solid sodium salt of the *p*-toluenesulfonhydrazide at 210° led to a product with a wide melting point range. This material was apparently a mixture of camphidine and imines on the basis of a band at 1645 cm.$^{-1}$ in the infrared spectrum of this material which can be attributed to a C=N group, and the fact that the material may be hydrogenated cleanly to camphidine. When the same sodium salt was pyrolyzed at 200° as a tetraglyme solution, a 37% yield of the tetrazene **5** was obtained and g.l.c. and t.l.c. examination showed a trace (<1%) of camphane. This amount proved too small to be isolated. An increase in the pyrolysis temperature resulted only in drastic decomposition. It seems therefore that N-aminocamphidine reacts as an unexceptional 1,1-disubstituted hydrazine.

(7) G. J. Karabatsos and R. A. Taller, *J. Am. Chem. Soc.*, **86**, 4373 (1964).

(8) Tetrazenes have characteristic absorption maxima at about 285 mμ (log $\epsilon \sim 4$). A summary of such data is given in ref. 1.

(9) E. Fischer and H. Troschke [*Ann.*, **199**, 294 (1879)] noted that the products of tetrazene decomposition were nitrogen, amines, and imines and their hydrolysis products.



Experimental

N.m.r. spectra were run on a Varian high-resolution 60-Mc. instrument using tetramethylsilane as an internal standard (all values are given as p.p.m. from TMS). Infrared and ultraviolet spectra were run on a Perkin-Elmer Model 237 and a Bausch and Lomb Spectronic 505, respectively. Microanalyses were performed by the Scandanavian Microanalytical Laboratory and by the Spang Microanalytical Laboratory.

Camphidine (2).—Camphidine hydrochloride was prepared using the procedure of Corey and Hertler[4] except that hydrogen chloride was used instead of hydrogen bromide. The hydrochloride melted at 288–290° dec. The free base was obtained by dissolving the hydrochloride in water and making the solution basic (pH 12) with 10% sodium hydroxide solution. The precipitate was extracted with ether and the solution was dried over anhydrous magnesium sulfate and concentrated to dryness. Camphidine was obtained as a white fluffy powder, m.p. 188–190°, in yields of 38 to 52%.

A *p*-nitrobenzenesulfonamide derivative, m.p. 143–144° (rhomboids from methanol), was obtained by treatment of the free base with *p*-nitrobenzenesulfonyl chloride using a Hinsberg procedure.

Anal. Calcd. for $C_{16}H_{22}N_2O_4S$: C, 56.78; H, 6.56; N, 8.27. Found: C, 56.30; H, 6.68; N, 8.17.

The Reaction of Camphidine with Carbon Tetrachloride.—Camphidine (1.0 g. 6.5 mmoles) was dissolved in carbon tetrachloride (10 ml.) from a freshly opened bottle (Baker Analyzed reagent) and allowed to remain at room temperature in a Pyrex flask under ambient light conditions. Needle-like crystals begin to appear within 1 hr. and a total of 1.1 g. of a solid, m.p. 282–284°, was filtered off at the end of 68 hr. This material was recrystallized by dissolving in a 10:1 ethyl acetate–methanol mixture followed by boiling off the methanol until crystals began to appear. Camphidine hydrochloride (0.53 g., 43%), m.p. 288–290 dec., was obtained. The infrared spectrum of this material was identical with the spectrum of camphidine hydrochloride prepared by the procedure of Corey and Hertler.

Anal. Calcd. for $C_{10}H_{20}ClN$: C, 63.28; H, 10.64; N, 7.38. Found: C, 63.45; H, 10.64; N, 7.39.

N-Nitrosocamphidine (3).—Camphidine (10 g., 0.0655 mole) was dissolved in glacial acid (180 ml.), and sodium nitrite (5 g., 0.0725 mole) in water (35 ml.) was added slowly with stirring. The resulting solution was stored at room temperature overnight and then concentrated to one-fifth of its volume. Water was added to the oil and the mixture was extracted with ether. The ether was dried and concentrated to a pasty solid which could be crystallized from an ethanol–water mixture, yielding N-nitrosocamphidine (9 g., 75%). An analytical sample was recrystallized from methanol–water, m.p. 166.5–167°.

Anal. Calcd. for $C_{10}H_{18}N_2O$: C, 65.88; H, 9.95; N, 15.37. Found: C, 65.89; H, 9.96; N, 15.21.

This material gave a negative Lieberman's nitroso test and exhibited four unsplit peaks in its n.m.r. spectrum at 1.09, 1.01, 0.96, and 0.91 and a multiplet centered at 4.2 p.p.m.

Hydrolysis of N-Nitrosocamphidine.—N-Nitrosocamphidine (120 mg., 0.79 mmole) was refluxed with concentrated hydrochloric acid (3 ml.) for 1.5 hr. The solution was made basic with 10% sodium hydroxide solution and extracted with ether. The dried ether solution was concentrated and camphidine (75 mg., 75%) was obtained. This material was conclusively identified by conversion to its *p*-nitrobenzenesulfonyl derivative, m.p. 143–144°.

Reduction of N-Nitrosocamphidine.—N-Nitrosocamphidine (4.55 g., 0.025 mole) was dissolved in ethanol (75 ml.) and 20% sodium hydroxide solution (45 ml.) was added. The solution was refluxed and stirred under nitrogen for 20 min. and then sodium dithionite (20 g.) was added in small portions. After the addition was complete the mixture was stirred and refluxed for 8 hr. Water was then added and the mixture was extracted with fresh ether. The ether was dried and concentrated to an oil (3 g.) which was shown to be a mixture of eight components by thin layer chromatography. It gave a positive Tollens test and seemed to darken on exposure to air. Hence, further purification was not attempted, and the material was converted to its N-acetyl derivative. The oil was suspended in 5% sodium hydroxide solution (20 ml.) and acetic anhydride (15 ml.) was added. An immediate precipitate appeared which was filtered after 30 min. of stirring. N'-Acetyl-N-aminocamphidine (3.2 g., 61% based on N-nitrosocamphidine), m.p. 178–179.5°, was ob-

tained. An analytical sample was prepared by recrystallization from cyclohexane, m.p. 179.5–180°.

Anal. Calcd. for $C_{12}H_{22}N_2O$: C, 68.52; H, 10.56; N, 13.31. Found: C, 68.35; H, 10.46; N, 13.10.

The infrared spectrum ($CHCl_3$) showed bands at 3290 (N–H), 1678 (C=O), and 1665 cm.$^{-1}$.

N-Aminocamphidine Hydrochloride (4c).—N′-Acetyl-N-aminocamphidine (2.5 g., 0.012 mole) was dissolved in concentrated hydrochloric acid (10 ml.) and water (25 ml.) and heated on the steam bath for 5 hr. The solution was evaporated to dryness on a rotary evaporator (steam bath) and N-aminocamphidine hydrochloride (2.3 g., 95%) was obtained, m.p. 218–220°. An analytical sample was prepared by recrystallization from ethyl acetate containing a small amount of methanol, m.p. 220–221°.

Anal. Calcd. for $C_{10}H_{21}ClN_2$: C, 58.64; H, 10.35; N, 13.67. Found: C, 58.70; H, 10.39; N, 13.53.

N′-*p*-Toluenesulfonyl-N-aminocamphidine (4d).—The tosyl hydrazide was prepared by the method of Carpino.[3a] N-Aminocamphidine hydrochloride (2.3 g., 11.8 mmoles) was dissolved in dimethylformamide (50 ml.) and triethylamine (3.3 ml., 23.6 mmoles) was added. A white precipitate appeared immediately. *p*-Toluenesulfonyl chloride (2.5 g., 13.1 mmoles) was added in small portions to the stirred mixture at 0°. After the addition was complete, it was stirred for an additional 15 min. at 0° and then quenched in water (250 ml.). The oil which was formed crystallized on overnight standing. The *p*-toluenesulfonhydrazide, m.p. 102.8–103.5°, was recrystallized from methanol–water and a total yield of 2.6 g. (68%) was obtained by repeated concentration of the mother liquors.

Anal. Calcd. for $C_{17}H_{26}N_2O_2S$: C, 63.32; H, 8.12; N, 8.68. Found: C, 63.27; H, 8.26; N, 8.57.

Oxidation of N-Aminocamphidine with Mercuric Oxide.—N-Aminocamphidine·HCl (204 mg., 1.0 mmole) was dissolved in 95% ethanol (13 ml.) and stirred at reflux under a nitrogen atmosphere. Sodium methoxide in methanol (3.3 ml. of a 0.304 *M* solution) was added to form the free base. Then yellow mercuric oxide (460 mg., 2.1 mmoles) was added in one portion. The mixture was stirred and refluxed for 0.5 hr. and filtered hot through Celite. The filtrate was warmed to the boiling point and water was added until a permanent cloudiness appeared. The tetrazene **5** was obtained (100 mg., 62%), m.p. 224–225°, and was recrystallized from ethanol, λ_{max} (ethanol) 287 mμ (log ε 4.10).

Anal. Calcd. for $C_{20}H_{36}N_4$: C, 72.24; H, 10.91; N, 16.84. Found: C, 72.08; H, 11.04; N, 16.79.

Pyrolysis of the Sodium Salt of N′-*p*-Toluenesulfonyl-N-aminocamphidine.—N′-*p*-Toluenesulfonyl-N-aminocamphidine (625 mg., 2 mmoles) was dissolved in methanolic sodium methoxide (3.85 ml. of a 0.65 *M* solution) and the resulting solution was concentrated to dryness *in vacuo* and on the steam bath. The solid sodium salt was transferred to a glass tube, sealed, and heated to 220–230° in an oil bath. A sublimate (50–60 mg.) appeared during the course of 1 hr. The residue was then cooled, dissolved in water, and acidified, and *p*-toluenesulfinic acid (melting point, mixture melting point, and infrared spectrum) was isolated. The sublimate, m.p. 167–200°, had a strong absorption at 1650 cm.$^{-1}$. Hydrogenation of this material in acetic acid (4 ml.) with PtO_2 (40 mg.) took up 1.25 equiv. of hydrogen based on an equimolar mixture of camphidine and the corresponding imine. The catalyst was filtered off and the acetic acid was evaporated *in vacuo*. The resultant oil was converted to the *p*-nitrobenzenesulfonamide (70 mg., 63%), m.p. 143–144°.

Pyrolysis of the Sodium Salt of N′-*p*-Toluenesulfonyl-N-aminocamphidine in Tetraglyme.—N′-*p*-Toluenesulfonyl-N-aminocamphidine (625 mg., 2 mmoles) was dissolved in methanolic sodium methoxide (2.9 ml. of a 0.74 *M* solution), and the resulting solution was concentrated to dryness on the steam bath and *in vacuo*. The dry sodium salt was dissolved in tetraglyme (25 ml., dried by passing through a column of chromatographic grade alumina). The solution was heated in an oil bath at 200° and after a few minutes a white precipitate appeared. After a total heating time of 15 min., the mixture was quenched in 60 ml. of ice water. The aqueous solution was extracted with ether and the resultant ethereal solution was washed with water and saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. Concentration to dryness afforded the tetrazene **5** (120 mg. 37%), m.p. 223–224°. In a similar experiment the white material which had formed during the pyrolysis was filtered, dissolved in water, and acidified. It proved to be *p*-toluenesulfinic acid (melting point, mixture melting point, and infrared spectrum). The filtrate (tetraglyme solution) was subjected to gas–liquid chromatography (silicone rubber column, oven temperature 145°, and helium flow rate of 60 cc./min.) and camphane was detected by comparing retention times of an observed peak with an authentic sample. Control experiments revealed that no other component of the system had a similar retention time. The filtrate was also subjected to thin layer chromatography on silica gel with a $CaSO_4$ binder and again camphane was detected. The estimated amount (g.l.c.) was about 0.5% and the isolation of this amount was not attempted.

Acknowledgment.—The author wishes to thank Dr. G. O. Dudek for obtaining the n.m.r. spectra and Mr. Samuel Stein for many valuable discussions.

The Photodehydrogenation of Levopimaric Acid in the Presence of Sulfur

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Received December 2, 1964

The photosensitized oxidation of the pine gum resin acids has been described.[2] In an attempt to replace oxygen with sulfur in this reaction, we found that levopimaric acid in ethanol in the presence of sulfur, visible light, and air gave off hydrogen sulfide, exhibited a total loss of conjugated dienic unsaturation, and yielded dehydroabietic acid on work-up of the mixture. No sensitizing dye was used in the reaction. In the absence of sulfur, visible light, or air, no reaction was observed. None of the other pine gum resin acids, namely palustric, neoabietic, abietic, pimaric, isopimaric, and dehydroabietic acids reacted to any extent under the same conditions. In the reaction of levopimaric acid in ethanol, the sulfur in dispersion or in solution may act as a sensitizer for the visible light.

The photochemical reaction was then attempted in carbon disulfide in which all reactants, including sulfur, were soluble. It was observed that isomerization of levopimaric to abietic acid took place. Neither sulfur nor air was found necessary. No reaction took place in the dark. It was noted that the isomerization proceeded to completion when the light was turned off in the middle of a run. It would thus appear that irradiation in carbon disulfide results in the formation of an acidic[3] (or possibly basic[4]) substance which catalyzes the isomerization of levopimaric acid to abietic acid.[3,4]

Experimental

Reaction of Levopimaric Acid with Sulfur, Light, and Air in 95% Ethanol.—To a solution of 8.16 g. of levopimaric acid ($[\alpha]_D$ −273°) in 2700 ml. of 95% ethanol was added 8.64 g. of flowers of sulfur. The dispersion was charged to a 2700-ml. reactor[2] equipped with an internal 40-w. daylight fluorescent lamp bulb and four external 15-w. fluorescent lamps. Aeration and irradia-

(1) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture. Article is not copyrighted.

(2) W. H. Schuller and R. V. Lawrence, *J. Am. Chem. Soc.*, **83**, 2563 (1961).

(3) D. E. Baldwin, V. M. Loeblich, and R. V. Lawrence, *ibid.*, **78**, 2015 (1956).

(4) W. H. Schuller and R. V. Lawrence, *J. Org. Chem.*, **30**, 2080 (1965).