[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Nitration of Cyclopropane in the Vapor Phase. Nitrocyclopropane[1]

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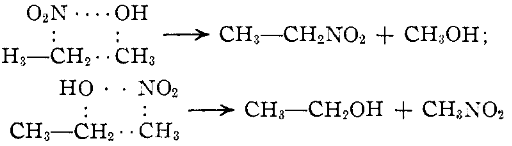
Reaction of cyclopropane with nitric acid or nitrogen dioxide in the vapor phase yields nitrocyclopropane, identified by reduction to cyclopropylamine with iron and hydrochloric acid or Raney nickel and hydrogen. Cyclopropylamine was also prepared from cyclopropanecarboxylic acid and hydrazoic acid in sulfuric acid. Nitrocyclopropane does not form salts in strong alkaline media at 25°. The lack of reactivity of nitrocyclopropane with bases is related to the increase in internal strain involved in conversion of the nitrocycloalkane into its nitronate anion.

Discussion

Two types of homogeneous reactions occur simultaneously in nitration of homologs of methane to yield nitroalkanes.[3] These reactions are (a) replacement of hydrogen atoms by nitro groups and (b) replacement of alkyl radicals by nitro groups. There are, at present, two pertinent general mechanisms that have been proposed to explain the formation of lower nitroalkanes by nitration of higher paraffins: (1) nitration is intimately related to oxidation of alkanes and results in formation of alkoxy radicals,[4] decomposition of which leads to lower alkyl radicals and carbonyl compounds; subsequent reactions of the lower alkyl radicals with nitrating agents yield the corresponding nitroalkanes, and (2) replacement of alkyl groups occurs by bimolecular reaction of a hydrocarbon with nitric acid resulting in formation of lower nitro compounds and alcohols.[5] In the nitration of propane to yield alkyl-substitution products by the second of these mechanisms, two modes of reaction are possible, and thus, nitroethane and nitromethane should be formed along with methanol and ethanol (equation 1).[6] It is also possible that alkyl replacement by a similar mechanism involves reaction of the alkane with dinitrogen tetroxide (even though highly dissociated at elevated temperatures) or its equivalent. Thus, if carbon–nitrogen attachment occurs during addition, nitromethane and nitroethane would be expected as fission products from nitration of propane.



$$\begin{array}{l} O_2N\cdots OH \\ \ \ \vdots \qquad \vdots \\ CH_3-CH_2\cdot\cdot CH_3 \end{array} \longrightarrow CH_3-CH_2NO_2 + CH_3OH;$$

$$\begin{array}{l} \quad HO\cdot\cdot NO_2 \\ \quad\ \vdots \qquad \vdots \\ CH_3-CH_2\cdot\cdot CH_3 \end{array} \longrightarrow CH_3-CH_2OH + CH_3NO_2 \quad (1)$$

In order to study the various addition mechanisms that have been proposed, nitration of the strained alicyclic hydrocarbon, cyclopropane, was investigated. If the addition reactions play important roles, nitration of cyclopropane with nitric acid or dinitrogen tetroxide should yield either 3-nitro-1-propanol[7a] or 1,3-dinitropropane.[7b,c]

The nitration of cyclopropane with nitric acid and with nitrogen dioxide was investigated at relatively short exposure times (up to 2.5 seconds) over temperatures ranging from 390–455° in the presence of large excesses of the cycloalkane. Some decomposition and oxidation of the reaction mixtures occurred at temperatures above 390°; however, nitrocyclopropane (3.6 to 15.0% conversion) was obtained with either of the two nitrating agents. In experiments conducted at lower temperatures (335–390°) and longer exposure times (in order to minimize thermal isomerization of cyclopropane to propene and oxidative-decomposition of the reaction product) the only nitration product which could be isolated was nitrocyclopropane. On the basis of these experiments, it has been concluded that the proposed addition reactions of the various nitrating agents with an aliphatic hydrocarbon do not play an important role in the alkyl-replacement processes occurring in the vapor phase. Interpretation of the results of this investigation in terms of the oxidative mechanism involving alkoxy radicals as intermediates (mechanism 1) is premature at present because of the lack of information concerning the decomposition of cycloalkoxy radicals and the chemistry of the $\cdot CH_2-CH_2-CH{=}O$ radical. Nitrations of the higher cycloalkanes, cyclopentane[1,2,3b] and cyclohexane,[1,2,3b] are being reinvestigated in order to obtain information related to these points and will be a subject of future communication.

Nitrocyclopropane, a new compound, was identified by reduction with iron and hydrochloric acid or Raney nickel and hydrogen to cyclopropylamine,[8] identified as N-cyclopropylbenzamide[8] and as N-cyclopropyl-N′-phenylthiourea.[8] Cyclopropylamine, for purposes of comparison, was also prepared by a new method: reaction of cyclopropanecarboxylic acid and hydrazoic acid in the presence of sulfuric acid (equation 2, the Schmidt reaction[9]).

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[1] Preliminary results of this investigation were presented at the 109th Meeting of the American Chemical Society, Organic Division, in Atlantic City, N. J., April 11, 1946.

[2] Initial experiments are part of the Ph.D. thesis of Harold Shechter, Purdue University, June, 1946.

[3] (a) H. B. Hass, E. B. Hodge and B. M. Vanderbilt, *Ind. Eng. Chem.*, **28**, 339 (1936); (b) H. B. Hass and H. Shechter, *ibid.*, **39**, 817 (1947).

[4] (a) C. E. Boord, "Third Symposium on Combustion, Flame and Explosion Phenomena," William and Wilkins Co., Baltimore, Md., 1949, pp. 416–424; (b) H. B. Hass and L. B. Alexander, *Ind. Eng. Chem.*, **41**, 2266 (1949); (c) G. B. Bachman, L. M. Addison, J. V. Hewitt, L. Kohn and A. Milliken, *J. Org. Chem.*, **17**, 906 (1952).

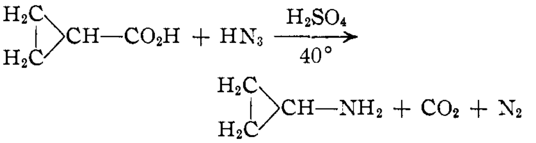
[5] R. H. Ewell, private communication; H. B. Hass and E. F. Riley, *Chem. Revs.*, **32**, 380 (1943). These four-center reactions are analogous to that of: $H_2 + I_2 \rightleftarrows 2HI$; H. Eyring, THIS JOURNAL, **53**, 2537 (1931); *Trans. Faraday Soc.*, **34**, 3 (1938).

[6] Lower alcohols are produced in the nitration of alkanes; however, the yields are much lower than those of their corresponding nitroalkanes,[3b]

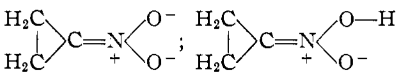
[7] (a) L. Henry, *Bull. acad. roy. Belg.*, [3], **33**, 412 (1897); (b) F. Keppler and V. Meyer, *Ber.*, **25**, 1710 (1892); (c) J. P. Kispersky, H. B. Hass and D. E. Holcomb, THIS JOURNAL, **71**, 516 (1949).

[8] N. Kishner, *Chem. Zentr.*, **76**, I, 1704 (1905).

[9] H. Wolff, "The Schmidt Reaction," in R. Adams, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 307.


(2)

Nitrocyclopropane differs from its isomeric nitroölefins, the nitropropenes,[10] by its relative stability toward oxidation, addition of bromine, and the action of alkaline reagents. Nitrocyclopropane is not dissolved appreciably by strong aqueous bases; it does not form salts in homogeneous alkaline media at 25°. It is believed that the weak acidity of nitrocyclopropane and its lack of reactivity toward bases arises from the internal strain[11] involved in conversion of the small-ring nitrocycloalkane into its nitronate anion (I) or its nitronic acid (II). The inability of the carbon atom attached to the nitro group to undergo a change in coördination number from four to three recalls the failure to prepare cyclopropanone although its hydrate and methyl hemiacetal are known.[12] It is also of interest that the difficulty in forming the cyclopropanenitronate anion indicates again the importance of the contributions of resonance interaction (in addition to the electronegative nature of the nitro group) to the structure of an alkanenitronate anion (III).[13]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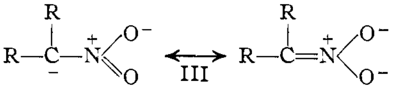
III

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Experimental

Apparatus.—The nitration apparatus, based on that described previously,[14] was constructed of Pyrex tubing (12 mm. o.d., reactor volume 800 ml.) immersed in a mixture of sodium and potassium nitrates. Reagents were injected directly into the reactor coil without being preheated. The products of reaction were condensed in a series of traps immersed in iced water, Dry Ice and acetone, and liquid air, respectively.

Materials.—Cyclopropane was obtained from the Mallinckrodt Company. Unreacted cyclopropane from each nitration experiment was recycled after it had been passed through water, a series of concentrated sodium hydroxide solutions, and anhydrous soda-lime and then distilled at atmospheric pressure. Commercial nitric acid (C.P., 69% HNO_3, sp. gr. 1.42) and dinitrogen tetroxide (Matheson Co.) served as nitrating agents.

Nitration of Cyclopropane with Dinitrogen Tetroxide.—Cyclopropane (2696 g., 64.2 moles) and dinitrogen tetroxide (316 g., 3.43 moles) were heated at atmospheric pressure in the gas phase at 420–455° and an exposure time of 2.36–2.44 seconds. Appreciable decomposition of the reaction mixture occurred under these conditions. The condensate collected at 0° was diluted with iced water, partially neutralized with aqueous sodium bicarbonate (5%), and extracted with ethyl ether. The condensate collected at −80° was distilled at atmospheric pressure to remove oxides of nitrogen and unreacted cyclopropane; the residue was diluted with iced water, neutralized with sodium bicarbonate, and extracted with ether. The ether extracts were combined, neutralized with aqueous sodium bicarbonate (2%), washed with saturated sodium chloride solution, dried over sodium sulfate, and then rectified at reduced pressure, in a column (12 × 1.5 cm.) packed with tantalum wire. After ether had been removed, **nitrocyclopropane** (45 g., 0.517 mole, 15.0% conversion based on N_2O_4 injected)[15] was obtained as a colorless distillate: b.p. 66.0–67.5° (58 mm.), 142.6–143.8° (751 mm.), $n^{20}D$ 1.4395, d^{20}_4 1.1358; *MR*D (found) 20.14, *MR*D (calcd.) 20.18. No residues or higher boiling materials were obtained from the distillations of the reaction products. The amount of recovered dinitrogen tetroxide was not determined.

Anal. Calcd. for $C_3H_5NO_2$: C, 41.38; H, 5.75; N, 16.09. Found: C, 41.56; H, 5.77; N, 15.72.

Nitration of Cyclopropane with Nitric Acid.—Reaction of cyclopropane (2016 g., 48.0 moles) and nitric acid (403.3 g. of 68% HNO_3, 4.36 moles) was effected in the vapor phase at a contact time of 1.9 seconds at temperatures ranging from 390–410°. Addition of oxygen failed to increase significantly the conversion to nitrocyclopropane. The condensate collected at 0° was diluted immediately with iced water, neutralized with dilute sodium bicarbonate and extracted with ethyl ether to prevent any excessive decomposition of the nitration product. The product condensed at −80° was distilled at atmospheric pressure to recover unreacted cyclopropane. The distillation residue was neutralized and dissolved in ethyl ether. The ether extracts were combined, neutralized, washed with water, dried over sodium sulfate and then evaporated. Distillation of the dark product under nitrogen at reduced pressure yielded nitrocyclopropane as a slightly yellow liquid (13.5 g., 0.155 mole, 3.6% conversion based on nitric acid injected, very little nitric acid was consumed under these conditions); only trace amounts of high boiling residues were obtained. Redistillation of the nitrocyclopropane yielded a colorless product almost identical with that obtained from the experiments with dinitrogen tetroxide: b.p. 65–67° (58 mm.), 141.5–143.5° (742 mm.), $n^{20}D$ 1.4398, d^{20}_4 1.1346; *MR*D (found) 20.15, *MR*D (calcd.) 20.18.

Anal. Calcd. for $C_3H_5NO_2$: C, 41.38; H, 5.75; N, 16.09. Found: C, 41.69; H, 5.64; N, 15.85.

Reduction of Nitrocyclopropane to Cyclopropylamine.—(a) Concentrated hydrochloric acid (16 ml. of 35% HCl) was added dropwise in 10 hours to a stirred suspension of nitrocyclopropane (2.2 g., 0.0253 mole), powdered iron (4 g., 0.072 mole) and water (25 ml.) at 90–100°. The mixture was cooled, made strongly alkaline with concentrated sodium hydroxide, and then extracted with cold ethyl ether. Benzoyl chloride (3.56 g., 0.0253 mole) and concentrated sodium hydroxide (5 ml. of 20% solution) were added to the ether extract, and the mixture was stirred for 3 hours. The ether solution was separated, washed with dilute sodium hydroxide and water, and dried; evaporation of the extract yielded N-cyclopropylbenzamide (white needles). After being recrystallized twice from benzene-methylcyclohexane and twice from water-ethanol, the amide melted at 100.6–101.0°, lit.[8] 98.5°; yield 0.65 g., 0.0038 mole, 12.2%. The melting point of the amide was not depressed by an authentic sample, m.p. 97.0–98.5°.

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[10] (a) L. Henry, *Bull. acad. roy. Belg.*, [3] **34**, 547 (1897); *Chem. Zentr.*, **69**, I, 193 (1898); (b) V. Meyer and P. Askenasy, *Ber.*, **23**, 1701 (1892); (c) E. Schmidt and G. Rutz, *ibid.*, **61**, 2142 (1928); (d) A. G. Suzie, Ph.D. thesis, Purdue University, 1939.

[11] H. C. Brown and M. Gerstein, THIS JOURNAL, **72**, 2926 (1950); H. C. Brown, R. S. Fletcher and R. B. Johannesen, *ibid.*, **73**, 212 (1951).

[12] P. Lipp, J. Buchkremer and H. Seeles, *Ann.*, **499**, 1 (1932).

[13] N. Kornblum, N. N. Lichtin, J. T. Patton and D. C. Iffland, THIS JOURNAL, **69**, 313 (1947). *Cf.* W. Theilacker and G. Wendtland, *Ann.*, **570**, 33 (1950), and R. L. Shriner, R. Adams and C. S. Marvel in H. Gilman, "Organic Chemistry," John Wiley and Sons, New York, N. Y., 2nd Ed., 1943, Vol. I, p. 388 ff.

[14] H. B. Hass, J. Dorsky and E. B. Hodge, *Ind. Eng. Chem.*, **33**, 1138 (1941); H. B. Hass and J. A. Patterson, *ibid.*, **30**, 67 (1938).

[15] The conversion of dinitrogen tetroxide to nitrocyclopropane (mole ratio of cyclopropane and nitrogen dioxide 2:1) at 360–390° and an exposure time of 59–62 seconds ranged from 4.0–4.9%; however, little oxidation and decomposition of the reaction mixture occurred under these conditions. At 335–360°, the conversion to nitrocyclopropane was from 2–4%.

Anal. Calcd. for $C_{10}H_{11}ON$: C, 74.50; H, 6.83; N, 8.70. Found: C, 74.68; H, 6.78; N, 8.44.

(b) Nitrocyclopropane (2.0 g., 0.023 mole) in anhydrous methanol (32 ml.) was hydrogenated over W-6 Raney nickel[16] at 40 p.s.i. in a Parr apparatus at 25–30°. After the theoretical quantity of hydrogen had been absorbed (4 hours), the catalyst was removed by filtration and phenyl isothiocyanate (3.15 g., 0.023 mole) was added to the reduction mixture. The mixture, after having been stored for 24 hours at 25–30°, was refluxed for 2 hours and then concentrated by partial distillation. Water was added to the residual oil, and the mixture was crystallized at 0°. The solid product was decolorized and recrystallized from water–methanol and from benzene–cyclohexane to give crude N-cyclopropyl-N′-phenylthiourea (3.1 g., 70.2%, m.p. 90–110°). The white derivative, after recrystallization from water–methanol and from benzene–cyclohexane (twice) melted at 123.4–124.2° (0.88 g., 19.9%), lit.[8] 123.0–123.5°; the melting point of the thiourea was not depressed by an authentic sample.

Reaction of Cyclopropanecarboxylic Acid and Hydrazoic Acid.—A solution (700 ml.) of hydrazoic acid (26.2 g., 0.61 mole) in chloroform was added dropwise to a stirred mixture of cyclopropanecarboxylic acid[17] (48.3 g., 0.56 mole) in concentrated sulfuric acid (210 ml., 95.5% H_2SO_4) at 40°. After evolution of nitrogen had ceased, the chloroform layer was separated. The aqueous mixture was cooled to 0° and concentrated sodium hydroxide was added slowly until the solution became very alkaline. Distillation of the mixture yielded a volatile amine, b.p. 45–60°; the product was dried over solid potassium hydroxide and then fractionated to yield cyclopropylamine (10 g., 32.5% yield), b.p. 48–50° (752 mm.), lit.[8] 49.5–50°. Cyclopropylamine was converted to N-cyclopropylbenzamide (95% yield) by reaction with benzoyl chloride according to the procedure described by Shriner and Fuson[18]; the amide, after recrystallization from benzene–methylcyclohexane and from ethanol, melted at 97.0–98.5°, lit.[8] 98.5°. Reaction of cyclopropylamine with phenyl isothiocyanate occurred vigorously to give N-cyclopropyl-N′-phenylthiourea, m.p. 124.5–124.9° (from ethanol–water), lit.[8] 123.0–123.5°.

Properties of Nitrocyclopropane and Its Isomeric Nitroolefins.—The properties of nitrocyclopropane have been compared with those of 1-,[19a] 2-,[19a] and 3-nitropropene,[19b] respectively. Nitrocyclopropane, a colorless liquid having a mild, sweet odor, may be stored at room temperature for months or distilled at atmospheric pressure with only slight decomposition. It is not decomposed or polymerized appreciably by continued exposure to light, air, dilute hydrochloric acid, aqueous sodium bicarbonate, or concentrated aqueous sodium hydroxide. The nitrocycloalkane (0.2 g.) in carbon tetrachloride (2 ml.) at 25° absorbs bromine (5%) in carbon tetrachloride (0.2 ml.) very slowly in ordinary light; it (0.2 g.) does not decolorize aqueous potassium permanganate (2%, 1 ml.) in water-dioxane (50:50 by volume, 3 ml.) at 25° in 2 hours. Nitrocyclopropane (0.3 g., 0.034 mole) was only slightly dissolved by a stirred solution of sodium hydroxide (0.45 g., 0.112 mole) in water (4.05 g.) at 25° in 24 hours[20,21] (the aqueous and the nitrocyclopropane layers remained colorless throughout this experiment); after cooling the reaction mixture to 0°, the nitrocyclopropane was recovered in high yield. Reactions of aliquot portions of a solution of nitrocyclopropane (0.3 g., 0.034 mole), sodium hydroxide (0.65 g., 0.163 mole), water (4.2 g.) and ethanol (2.3 g.), after intervals of 0.2, 0.5, 2, 6, 24 and 48 hours at 25°, with aqueous sodium nitrite and then dilute hydrochloric acid failed to give a characteristic pseudonitrole test for a secondary nitro compound.[22]

1- and 2-nitropropenes are pale yellow lachrymatory oils which absorb bromine (5%) in carbon tetrachloride (> 0.6 ml.) rapidly (0.2 g. of nitroölefin in 2 ml. of carbon tetrachloride, 2-nitropropene reacts more rapidly than 1-nitropropene) at 25°. In dioxane-water (50:50 by volume, 3 ml.) at 25°, the nitroölefins (0.2 g.) are almost instantaneously oxidized by aqueous potassium permanganate (2%, > 8 ml.). 2-Nitropropene polymerizes to dark colored products upon storage at 0° or when heated to boiling at atmospheric pressure; 1-nitropropene may be stored for long periods (> 2 years) at 0° or heated at 140–150° (0.5 hours) without undergoing extensive reaction. The nitropropenes (0.3 g.) dissolve (< 10 minutes) in stirred aqueous sodium hydroxide (10%, 4.5 ml.) at 25° to give yellow-red solutions; in the presence of sodium bicarbonate or sodium hydroxide at room temperature, 2-nitropropene is converted to a white-yellow polymer.

3-Nitropropene (b.p. 68–69° (98–100 mm.), $n^{20}\text{D}$ 1.4270, d^{20}_4 1.056) is a colorless irritating liquid which on storage at 0–5° slowly becomes yellow colored. At 25° the nitropropene (0.2 g.) rapidly decolorizes aqueous potassium permanganate (2%, > 8 ml.) in dioxane-water (50:50 by volume, 3 ml.) and bromine (5%) in carbon tetrachloride (2 ml.). 3-Nitropropene (0.3 g.) dissolves in less than 2 minutes in stirred aqueous sodium hydroxide (10%, 4.5 ml.) at 25° to give a colorless solution; addition of sodium nitrite and dilute hydrochloric acid to this mixture followed by neutralization of the solution with aqueous sodium hydroxide gave a characteristic nitrolate test[10b] (red color) for primary mononitroalkanes.

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(16) H. Adkins and H. R. Billica, THIS JOURNAL, **70**, 695 (1948); the catalyst had been stored for 2 weeks at −10° after preparation before being used.

(17) C. M. McCloskey and G. Coleman, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., Vol. 24, 1944, p. 36.

(18) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 178.

(19) (a) Obtained from H. L. Cates, Jr.; prepared by the method of G. D. Buckley and C. W. Scaife, *J. Chem. Soc.*, 1471 (1947); (b) obtained from R. B. Kaplan; prepared by the method of reference 10a.

(20) Under comparable conditions, 2-nitropropane was dissolved in less than 5 minutes.

(21) H. Stone, Ph.D. Dissertation, The Ohio State University, Columbus, Ohio, 1950, in a study of the kinetics of neutralization of nitrocycloalkanes, reports that the conductivities of dilute solutions of nitrocyclopropane and sodium hydroxide in dioxane–water at 24.75° are essentially unchanged during the time interval one minute to 3 days, and that the ultraviolet spectrum of a nitrocyclopropane solution with an equivalent of base is identical, within experimental error, with that obtained in the absence of base. The results of this investigation will be reported in a future communication.

(22) O. Piloty and A. Stock, *Ber.*, **35**, 3093 (1902).