(C) The Cyanoethylation of Methanol.—Similarly, the experimental data suggest the mechanism

$$CH_3O^- + CH_2{=}CHCN \longrightarrow CH_3OCH_2\bar{C}HCN \text{ (slow)} \quad (14)$$

$$CH_3OCH_2\bar{C}HCN + CH_3OH \longrightarrow CH_3OCH_2CH_2CN + CH_3O^- \text{ (fast)} \quad (15)$$

Therefore

$$dx/dt = k_{14}[CH_2CHCN][CH_3O^-] \equiv k'(a - x)c \quad (16)$$

It is not possible to estimate the concentration of methoxide ion in equation 16. However, it was found that the observed rate constants k' at various alkaline concentrations hold constancy, hence the dissociation of sodium methoxide seems to be almost complete in such a dilute solution.

Acknowledgments.—The authors thank Prof. R. Oda for his advice and Teikoku Jinken Co. for their material assistance.

KYOTO, JAPAN

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, AEROJET-GENERAL CORP.]

Derivatives of 4-Nitrazapentanonitrile

BY MILTON B. FRANKEL AND KARL KLAGER

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4-Nitrazapentanonitrile has been prepared and converted to 4-nitrazapentanoyl chloride, 3-nitrazabutyl isocyanate and 3-nitrazabutylamine. Derivatives of these compounds are reported.

The preparation of aliphatic *gem*-dinitro dinitriles, such as 4,4-dinitroheptanedinitrile,[1] and monoesters, such as methyl 4,4-dinitropentanoate,[2] has been reported recently. Aliphatic secondary nitraza dinitriles such as nitrimino-bis-acetonitrile[3] and nitrimino-bis-propionitrile[4] have also been synthesized, but the secondary nitraza aliphatic mononitriles have not been reported. Because of the desire for comparing the physical properties and chemical reactions of the aliphatic *gem*-dinitro compounds and the nitramino analogs, it was of interest to study the chemistry of a simple aliphatic secondary nitramine containing a mononitrile group.

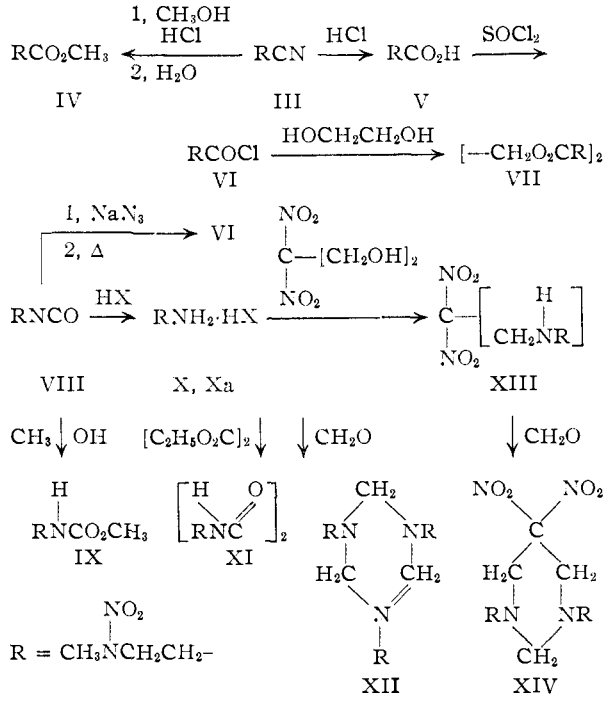
For this purpose 4-nitrazapentanonitrile (III) was chosen since 4-azapentanonitrile (I) was readily available from the Michael reaction of methylamine and acrylonitrile.[5] Using the Wright procedure[4] for the nitration of secondary amines, Compound I was converted *via* the nitric acid salt II into III.

$$CH_3NH_2 + CH_2{=}CHCN \longrightarrow \underset{\text{I}}{CH_3\overset{H}{\overset{|}{N}}CH_2CH_2CN} \xrightarrow{HNO_3} \underset{\text{II}}{CH_3\overset{H\cdot HNO_3}{\overset{|}{N}}CH_2CH_2CN} \xrightarrow[HCl]{Ac_2O} \underset{\text{III}}{CH_3\overset{NO_2}{\overset{|}{N}}CH_2CH_2CN}$$

The chemical reactions of 4-nitrazapentanonitrile (III) are summarized in Chart I.

4-Nitrazapentanonitrile (III) was converted *via* the imino ester hydrochloride to methyl 4-nitrazapentanoate (IV). The ethyl ester was prepared in the same manner. Hydrolysis of III or IV with concentrated hydrochloric acid gave 4-nitrazapentanoic acid (V), which was refluxed with thionyl chloride to yield 4-nitrazapentanoyl chloride (VI). Ethylene bis-4-nitrazapentanoate (VII) was prepared from VI and ethylene glycol. Compound VI was converted to the corresponding azide which was decomposed *in situ* to give 3-nitrazabutyl isocyanate (VIII). The methyl carbamate (IX) of VIII was prepared. Treatment of VIII with 35% nitric acid and concentrated hydrochloric acid gave 3-nitrazabutylammonium nitrate (X) and 3-nitrazabutylammonium chloride (Xa), respectively. The condensation of 3-nitrazabutylamine with ethyl oxalate gave N,N'-bis-(3-nitrazabutyl)-oxamide (XI), and with formaldehyde yielded 1,3,5-tris-(3'-nitrazabutyl)-hexahydro-1,3,5-triazine (XII). The Mannich reaction of X and 2,2-

CHART I



(1) L. Herzog, M. H. Gold and R. D. Geckler, THIS JOURNAL, **73**, 749 (1951).

(2) H. Shechter and L. Zeldin, *ibid.*, **73**, 1276 (1951).

(3) A. P. N. Franchimont and J. V. Dubsky, *Rec. trav. chim.*, **36**, 80 (1916).

(4) G. F. Wright, *et al.*, *Can. J. Research*, [B] **26**, 114 (1948).

(5) A. H. Cook and K. J. Reed, *J. Chem. Soc.*, 399 (1945).

dinitro-1,3-propanediol[6] gave 2,7,7,12-tetranitro-2,5,9,12-tetraazatridecane (XIII). Treatment of XIII with formaldehyde yielded 1,3-bis-(3′-nitrazabutyl)-5,5-dinitrohexahydro-1,3-diazine (XIV).

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Experimental[7,8]

Nitric Acid Salt of 4-Azapentanonitrile (II).—Nitric acid (1485 g., 16.5 moles, 70%) was cooled to 0–5° and 1260 g. (15 moles) of 4-azapentanonitrile[5] was added with vigorous stirring, while the temperature was held at 0–5° by external cooling. The white solid was collected in a sintered glass funnel, washed with ether, and dried *in vacuo* over potassium hydroxide, 1200 g. (54.4%), m.p. 70–71°.

4-Nitrazapentanonitrile (III).—To 840 ml. of acetic anhydride, at 15–20°, were added dropwise with stirring 13.8 ml. of concentrated hydrochloric acid and 42 ml. of technical grade 100% nitric acid, successively. At 20–25°,[9] 735 g. (5 moles) of the nitric acid salt of 4-azapentanonitrile was added portionwise in 30 minutes. After the addition was completed, the temperature was allowed to rise to 30° and the reaction mixture became homogeneous. After stirring for an additional 2 hours, the solution was cooled to 5° and diluted with 2 liters of ice-water. The oil was separated and the aqueous phase was extracted with three 600-ml. portions of methylene chloride. The oil and methylene chloride extracts were combined, washed once with 300 ml. of water and dried over sodium sulfate. The solvent was removed *in vacuo* and the residue was distilled from a claisen flask to give 600 g. (93.0%) of a light yellow liquid, b.p. 60–70° (40 μ), $n^{25}D$ 1.4863.

Anal. Calcd. for $C_4H_7N_3O_2$: C, 37.21; H, 5.46; N, 32.54. Found: C, 37.13; H, 5.20; N, 32.76.

Methyl 4-Nitrazapentanoate (IV).—Anhydrous hydrogen chloride gas was bubbled into a stirred solution of 129.0 g. (1 mole) of 4-nitrazapentanonitrile, 130 ml. of methanol and 130 ml. of absolute ether until the solution was saturated. Considerable heat was evolved and the white crystalline imino ester hydrochloride precipitated. After stirring for 2.5 hours longer at 0–5°, the white solid was collected, washed with ether, and transferred to a beaker containing 130 ml. of water. The mixture was neutralized with a saturated solution of sodium bicarbonate and heated to 50° for 30 minutes to complete the hydrolysis. The oily layer was separated and the aqueous phase was extracted with three 80-ml. portions of methylene chloride. The oil and extracts were combined, washed with 30 ml. of water, 30 ml. of 3% sodium bicarbonate solution and 30 ml. of water. The methylene chloride solution was dried over sodium sulfate, concentrated, and distilled to give 100 g. (61.7%) of colorless liquid, b.p. 107° (1 mm.), $n^{25}D$ 1.4694.

Anal. Calcd. for $C_5H_{10}N_2O_4$: C, 37.03; H, 6.22; N, 17.28. Found: C, 37.67; H, 6.69; N, 17.85.

Ethyl 4-nitrazapentanoate, b.p. 112° (1 mm.), $n^{25}D$ 1.4644, was prepared in the same manner as the methyl ester.

4-Nitrazapentanoic Acid (V).—A mixture of 812 g. (6.3 moles) of 4-nitrazapentanonitrile and 2436 ml. of concentrated hydrochloric acid was heated on the steam-bath for 8 hours and cooled. The solution was extracted with six 300-ml. portions of methylene chloride. The combined extracts were dried over sodium sulfate and concentrated *in vacuo* to give 463.5 g. (50.0%) of white solid, m.p. 51–53°. Recrystallization from ethylene dichloride raised the melting point to 53–54°.

Anal. Calcd. for $C_4H_8N_2O_4$: C, 32.43; H, 5.44; N, 18.92. Found: C, 32.49; H, 5.47; N, 18.70.

A mixture of 162.0 g. (1 mole) of methyl 4-nitrazapentanoate and 325 ml. of concentrated hydrochloric acid was heated to reflux for three hours and concentrated *in vacuo*. The residue was recrystallized from isopropyl ether to give 102.0 g. (69%) of white solid, m.p. 53–54°.

4-Nitrazapentanoyl Chloride (VI).—In a flask fitted with a condenser and an attached water-trap, was placed 240 ml. of thionyl chloride, and 148 g. (1 mole) of 4-nitrazapentanoic acid was added portionwise. The mixture was warmed gently on a steam-bath to initiate the reaction and then the steam removed until the evolution of gas had subsided. The solution was then refluxed for 2 hours, cooled, and concentrated *in vacuo* leaving a quantitative yield of a dark red oil. This crude acid chloride was used for the subsequent reactions. A sample was distilled from a bulb tube to give a light yellow liquid, b.p. 100–107° (10 μ), $n^{25}D$ 1.4997.

Ethylene Bis-4-nitrazapentanoate (VII).—A mixture of 12.0 g. (0.194 mole) of ethylene glycol, 84.0 g. (0.50 mole) of 4-nitrazapentanoyl chloride and 200 ml. of chloroform was refluxed for 20 hours. The solution was cooled, and washed with 150 ml. of water, 150 ml. of 1% sodium hydroxide solution and 150 ml. of water. The chloroform extract was separated, dried and concentrated *in vacuo* leaving 66.0 g. of brown oil. The oil was crystallized from methanol, using charcoal, to give 43.0 g. (68.8%) of white solid, m.p. 58–58.5°.

Anal. Calcd. for $C_{10}H_{18}N_4O_8$: C, 37.27; H, 5.63; N, 17.39. Found: C, 37.63; H, 5.32; N, 17.96.

3-Nitrazabutyl Isocyanate (VIII).—A solution of 167.0 g. (1 mole) of 4-nitrazapentanoyl chloride in 150 ml. of chloroform was added slowly with vigorous stirring to a solution of 130.0 g. (2 moles) of sodium azide in 390 ml. of water while the temperature was maintained at 10–15°. The mixture was stirred for an additional 30 minutes at 10° and the two phases were separated. The aqueous layer was extracted with an additional 150 ml. of chloroform. The combined chloroform solution was washed with water, dried over anhydrous sodium sulfate, and filtered. The azide was decomposed by refluxing the filtrate on a steam-bath until the evolution of nitrogen had ceased. The solution was concentrated *in vacuo* leaving 133 g. (91.8%) of a viscous residue, which crystallized on standing at −10°. Recrystallization from absolute ether gave white crystals, m.p. 25–26°.

Anal. Calcd. for $C_4H_7N_3O_3$: C, 33.10; H, 4.86; N, 28.96. Found: C, 32.85; H, 4.53; N, 29.69.

Methyl 3-Nitrazabutylcarbamate (IX).—A mixture of 29.0 g. (0.20 mole) of 3-nitrazabutyl isocyanate and 30 ml. of methanol was refluxed for 30 minutes and then concentrated *in vacuo*. The residue was recrystallized from a mixture of chloroform and carbon tetrachloride giving 30.1 g. (85%) of white solid, m.p. 87–88°.

Anal. Calcd. for $C_5H_{11}N_3O_4$: C, 33.90; H, 6.26; N, 23.72; OCH_3, 17.52. Found: C, 33.83; H, 6.16; N, 23.49; OCH_3, 16.96.

3-Nitrazabutylammonium Nitrate (X).—The addition of 50 ml. of 35% nitric acid to 29.0 g. (0.20 mole) of 3-nitrazabutyl isocyanate caused a vigorous reaction to occur with the evolution of carbon dioxide gas. The solution was warmed on the steam-bath for one hour and concentrated *in vacuo* to give a quantitative yield of white solid. Recrystallization from methanol gave white needles, m.p. 120–121°.

Anal. Calcd. for $C_3H_{10}N_4O_5$: C, 19.78; H, 5.53. Found: C, 20.02; H, 5.26.

In a similar manner, using concentrated hydrochloric acid, 3-nitrazabutylammonium chloride (Xa) was prepared, m.p. 132–133°.

N,N′-Bis-(3-nitrazabutyl)-oxamide (XI).—To a solution of 11.9 g. (0.10 mole) of 3-nitrazabutylamine in 50 ml. of chloroform was added 7.3 g. (0.05 mole) of ethyl oxalate. An immediate exothermic reaction occurred with the precipitation of a white solid, 9.9 g. (67.8%), m.p. 225–230°.

The oxamide was identified by conversion to the corresponding dinitro derivative. A mixture of 140 ml. of technical 100% nitric acid, 130 ml. of concentrated sulfuric acid and 9.9 g. (0.03 mole) of N,N′-bis-(3-nitrazabutyl)-oxamide was heated at 50–55° with good stirring for 35 minutes. The reaction mixture was cooled and poured on ice. The white solid was collected, washed with water, and dried *in vacuo* over potassium hydroxide; 8.8 g. (67.9%), m.p. 163–165°.

(6) The Mannich reaction of 2,2-dinitro-1,3-propanediol and ethylglycine has been reported; H. Feuer, G. B. Bachman and W. May, THIS JOURNAL, **76**, 5124 (1954).

(7) All melting points are uncorrected.

(8) Microanalyses by Elek Microanalytical Laboratories, Los Angeles, Calif.

(9) It is essential that the temperature be held within this range. If the temperature is too low during the addition, no reaction occurs; however, on warming an uncontrollable reaction may take place.

Recrystallization from acetone raised the melting point to 168–169°.

Anal. Calcd. for $C_8H_{14}N_8O_{10}$: C, 25.13; H, 3.69; N, 29.32. Found: C, 25.22; H, 3.63; N, 29.11.

1,3,5-Tris-(3′-nitrazabutyl)-hexahydro-1,3,5-triazine (XII).—To 15.6 g. (0.10 mole) of 3-nitrazabutylamine hydrochloride, 25 ml. of water and 8.1 g. (0.10 mole) of 37% formalin, a solution of 8.2 g. (0.10 mole) of sodium acetate in 15 ml. of water was added dropwise. After stirring for 30 minutes, a white solid precipitated from the solution. The product was collected, washed with water and dried; 5.9 g. (45.0%), m.p. 88–90°. Recrystallization from ethyl acetate raised the melting point to 97–97.5°.

Anal. Calcd. for $C_{12}H_{27}N_9O_6$: C, 36.63; H, 6.92; N, 32.05. Found: C, 36.98; H, 6.94; N, 31.68.

1,3-Bis-(3′-nitrazabutyl-5,5-dinitrohexahydro-1,3-diazine (XIV).—To 46.5 g. (0.30 mole) of 3-nitrazabutylamine hydrochloride, 24.9 g. (0.15 mole) of 2,2-dinitro-1,3-propanediol[10] and 100 ml. of water, was added dropwise a solution of 24.6 g. (0.30 mole) of sodium acetate in 75 ml. of water. The yellow solid which precipitated was collected, washed with water and dried; 34.6 g. (62.7%), m.p. 110–115°.

A mixture of 3.68 g. (0.01 mole) of the above yellow solid, 0.81 g. (0.01 mole) of 37% formalin and 100 ml. of water was stirred at room temperature for one hour and then at 40–45° for one hour. The tan colored solid was collected and dried; 3.2 g. (84.3%), m.p. 115–120°. Recrystallization from chloroform raised the melting point to 120–121°.

Anal. Calcd. for $C_{10}H_{20}N_8O_8$: C, 31.58; H, 5.30; N, 29.46. Found: C, 31.72; H, 5.36; N, 28.70.

(10) H. Feuer, G. B. Bachman, and J. P. Kispersky, THIS JOURNAL, **73**, 1360 (1951).

AZUSA, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PENNSYLVANIA STATE UNIVERSITY]

Reactions of Bivalent Carbon Compounds. Reactivities in Olefin–Dibromocarbene Reactions

BY PHILIP S. SKELL AND ALBERT Y. GARNER

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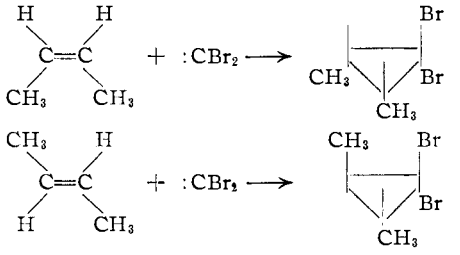
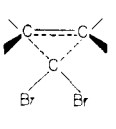
The rate of addition of dibromocarbene, $:CBr_2$, to olefins decreases in the order tetramethylethylene > trimethylethylene > anethole > isobutylene > *asym*-diphenylethylene > butadiene > cyclopentene > cyclohexene = styrene > 1-hexene > allylbenzene > vinyl bromide. Since essentially the same sequences of rates and stereospecificity is observed for bromination and epoxidation of olefins, a common intermediate complex is suggested for these three-center-type addition reactions. It is proposed that the intermediate complex (III) in carbene–olefin reactions is a partially-formed cyclopropane with carbonium ion character developed on one of the carbons of the double bond.

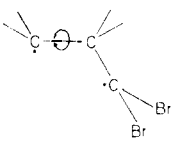
The reaction of dibromocarbene, $:CBr_2$, with *cis*- or *trans*-2-butene is stereospecific and produces the *cis*- or *trans*-1,1-dibromo-2,3-dimethylcyclopropane from the respective olefin.[1] It follows



from these observations that the intermediate had either (a) a cyclopropane structure (I) in which bond formation to both carbons was established simultaneously, or (b) the structure of biradical II, with propane bond angle and bond lengths, which cyclized with a half-life less than 10^{-10} to 10^{-13} second to a cyclopropane. The limits set on the half-life of II resulted from a theoretical consideration of the rates of rotation about the single bond.



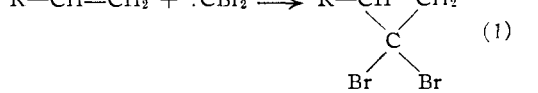
I



II

Relative Rates of Addition of $:CBr_2$ and $\cdot CCl_3$ to Olefins.—With the hope of distinguishing between I and II on experimental grounds we sought evidence for the radical nature of the intermediate. If II has a lifetime longer than a vibration period ($\sim 10^{-13}$ sec.) the interaction of the trivalent carbons over a distance of 2.54 Å. (C_1–C_3 distance in propane) should make a minor contribution to the ground state of II. Thus if II correctly represents the structure of the intermediate in this reaction, the relative rates of reaction of olefins should be essentially the same for $:CBr_2$ and a radical such as $\cdot CCl_3$. Whatever structural factors operate to make one olefin more reactive than another in addition of $\cdot CCl_3$, should operate equally well in the addition of $:CBr_2$, if II is an intermediate.

To ascertain the necessary relative rate constants, $:CBr_2$ was generated in *t*-butyl alcohol solution (from bromoform and potassium *t*-butylate) in the presence of known quantities of two olefins. Preliminary experiments had demonstrated that the olefins were utilized solely in the production of dibromocyclopropanes and that these products were stable. The amounts of the two dibromocyclopropane products were determined and by difference the amounts of unreacted olefin. For two parallel bimolecular reactions (1) the ratio of rate constants is given by equation 4, C and C' be-



(1)

ing the concentrations of the respective olefins and n_i, n_f, n_i' and n_f' being the initial and final molar amounts of the respective olefins. Since the volume of the solution V increased during the reaction

(1) P. S. Skell and A. Y. Garner, THIS JOURNAL, **78**, 3409 (1956).