mate,[5] chlorate,[6] nitrate,[7] for example) but not with potassium and ammonium salts,[1,6,8] while the thallous salts form solid solution with corresponding potassium and ammonium salts (sulfate,[2] chlorate,[9] primary orthophosphate,[10] for example) but not, at least in the present case, with the sodium salt.[11] According to the ionic radii usually listed[12] (Na$^+$, 0.95, K$^+$, 1.33; NH$_4^+$, 1.48; Ag$^+$, 1.26; Tl$^+$, 1.44), one would not quite expect this difference between argentous and thallous salts. The values listed by Sidgwick[13] (Na$^+$, 0.98; K$^+$, 1.33; Ag$^+$, 1.13; Tl$^+$, 1.49), on the other hand, would be in better agreement. While the sulfates of all of these five cations are orthorhombic, moreover, the axial ratios (a:b:c) fall into two groups.[14] For Na_2SO_4 and Ag_2SO_4 they are 0.598:1:1.252 and 0.570:1:1.235, respectively. In the other group we have 0.573:1:0.742 for K_2SO_4, 0.563:1:0.732 for $(NH_4)_2SO_4$, and 0.555:1:0.733 for Tl_2SO_4.

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Formylation during Nitrolysis in Chloroform

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It has been shown[2] that the nitrolysis of N,N′-dicyclohexylimidazolidine in acetic anhydride–nitric acid yields mainly N-nitro-N,N′-dicyclohexyl-1,2-diaminoethane mononitrate (I), although some N-nitro-N′-aceto-N,N′-dicyclohexyl-1,2-diaminoethane is also formed, presumably by acetylation of I. When chloroform is included in the nitrolysis medium neither of these products can be isolated. Instead a mixture is obtained which, when partially purified, shows by its X-ray diffraction powder pattern that it contains N-nitro-N′-nitroso-N,N′-dicyclohexyl-1,2-diaminoethane (II). Destruction of this component by potassium persulfate–absolute nitric acid mixture leaves a compound for which analysis indicates the formula $C_{15}H_{27}N_3O_3$. This substance gives a positive Franchimont nitramine test and a negative lanthanum nitrate test for an aceto group. It has been proven to be N-nitro-N′-formyl-N,N′-dicyclohexyl-1,2-diaminoethane (III) by its synthesis *via* formylation of I.

The presence of a formyl group in III may be ascribed either to oxidation of the methylene linkage of the imidazolidine or to formylation of I by mixed formic–acetic anhydride. Such an anhydride might arise from formic acid produced by decomposition of chloroform in the nitrolysis medium. The latter interpretation is preferred because none of III was formed when chloroform was absent. Furthermore a small yield of III could be obtained when formic acid rather than chloroform was used in the reaction mixture. This meager yield was not unexpected in consideration of the instability of formic acid in the nitrolysis medium. Indeed the stability of the disubstituted formamide (III) in this medium was unexpected and is being investigated further.

Experimental[3]

N-Nitro-N′-formyl-N,N′-dicyclohexyl-1,2-diaminoethane (III).—To 21.0 ml. (0.5 mole) of absolute nitric acid at −2 to 0° was added dropwise with stirring, a solution of 5.9 g. (0.025 mole) of N,N′-dicyclohexylimidazolidine in 25 ml. of chloroform (ethanol-free and dry). Then 100 ml. of distilled acetic anhydride was added at 0–5° and the stirred suspension maintained at 35–45° for seven hours. All volatile solvents were removed under reduced pressure. The residual oily solid was thrice-crystallized from ethanol to yield 2.0 g., m.p. 147–148°. This material did not depress the melting point of authentic N-nitro-N′-nitroso-N,N′-dicyclohexyl-1,2-diaminoethane (m.p. 147–148°) and the X-ray (Cu,Kα; Ni filtered) diffraction powder pattern included spacings (Å.) characteristic of pure II. Thus intensities [I/I_0] and spacings for II are: [10] 4.62; [7] 3.12; [6] 5.67, 4.03, 3.70; [5] 8.34, 2.81, 2.38; [4] 2.71, 1.90; [3] 2.59, 2.19; [2] 6.70, 5.15, 2.00, 1.77; [1] 2.27, 2.06, 1.72, 1.65, 1.48, 1.26. The impure 2.0 g. portion gave a comparable pattern: [10] 4.66; [6] 5.67, 3.86, 2.84; [5] 3.12; [4] 4.07, 2.39; [3] 8.18, 3.70, 2.13; [2] 5.15, 3.45, 2.71; [1] 2.55, 2.21, 1.96, 1.92, 1.79, 1.76, 1.51. In order to demonstrate the non-identity with N-nitro-N′-aceto-N,N′-dicyclohexyl-1,2-diaminoethane the powder pattern for the latter substance was also determined: [10] 5.03, 4.57; [7] 5.71; [6] 4.23, 3.42; [5] 3.66, 3.10; [4] 8.42, 2.42; [3] 2.76; [2] 2.26, 2.08; [1] 2.59, 2.23.

Furthermore purification of the 2-g. portion was accomplished firstly by treatment with 7.2 g. of ammonium persulfate in 7.2 g. of absolute nitric acid at 0–5° for four hours to yield a semi-solid oil after drowning in ice. This oil was treated five minutes with 15 ml. of hot 70% nitric acid, the mixture drowned in ice, and the resulting solid crystallized from ethanol or diisopropyl ether to yield 0.94 g. (13%) of III, m.p. 163–164°.

Anal. Calcd. for $C_{15}H_{27}N_3O_3$: C, 60.6; H, 9.17; N, 14.2. Found: C, 60.5; H, 9.05; N, 14.3.

The X-ray diffraction pattern with CuKα (Ni filtered) radiation included spacings in Å. with intensities [I/I_0] as follows: [10] 4.97; [7] 4.15; [6] 3.86; [5] 5.60, 2.83; [3] 3.45, 2.99; [2] 3.23, 2.32, 2.14, 1.79; [1] 2.62, 2.49, 1.76.

If the chloroform was eliminated from the preparative procedure and 10 ml. of formic acid was, instead, added at 0° subsequent to addition of the acetic anhydride, the otherwise identical method gave a 13% yield of I and a 2% yield of III.

When 1.50 g. (0.0047 mole) of I was dissolved in 7 ml. of 99% formic acid, the solution warmed to 50°, and 2.2 ml. (0.0225 mole) of acetic anhydride added dropwise with stirring at 50–55° over a 45-minute interval, subsequent dilution into ice–water mixture gave 0.67 g., m.p. 130–155°. Crystallization from 70% nitric acid and then from ethanol yielded 0.14 g., (48% crude yield, 10% pure), m.p. 162–164°. A mixed melting point with III obtained by nitrolysis was not depressed.

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(3) All melting points are corrected against reliable standards.