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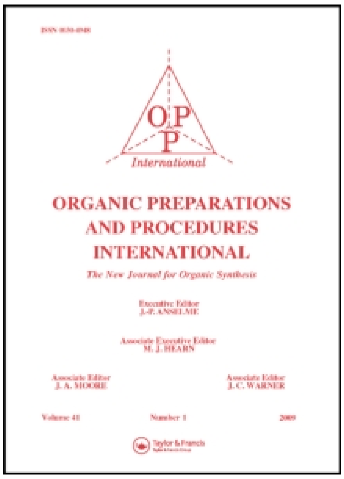

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DINITRONATE SALTS OF SUCCINONITRILE

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DINITRONATE SALTS OF SUCCINONITRILE

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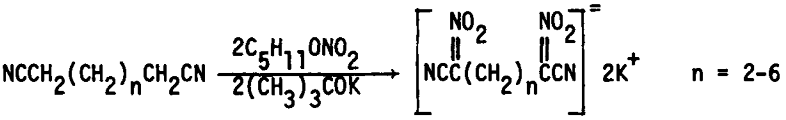
Feuer and Savides have reported the nitration of aliphatic dinitriles with amyl nitrate in the presence of strong base,[1] and prepared the α,α′-dinitrodinitrile salts of the corresponding α,ω-dinitriles in the series $NCCH_2(CH_2)_nCH_2CN$ where n = 2-6. However, only the dipotassium salt of adiponitrile was isolated; the nitration products of the higher homologues were identified through their dibromo derivatives. We wanted to prepare the nitration product of the first member in the series, starting with succinonitrile where n = 0. The use of the conditions of Feuer and Savides, namely, very low temperature reactions (below -35°) with potassium *t*-butoxide in tetrahydrofuran[1] or potassium amide in liquid ammonia[2], did not afford the desired product, dipotassium 2,3-dinitrosuccinonitrile (I). However, after numerous unsuccessful attempts and with several modifications, we were able to prepare and characterize this compound; the disodium, disilver and dichloro derivatives of 2,3-dinitrosuccinonitrile have also been prepared. The reactants and conditions which proved successful involved the use of *n*-propyl nitrate and potassium ethoxide in reaction with succinonitrile at 0°. The use of potassium *t*-butoxide or potassium amide yielded chiefly potassium nitrite. Apparently, these bases are too strong and react with the nitrate instead of



$$NCCH_2(CH_2)_nCH_2CN \xrightarrow[2(CH_3)_3COK]{2C_5H_{11}ONO_2} \left[NC\overset{NO_2}{\overset{\|}{C}}(CH_2)_n\overset{NO_2}{\overset{\|}{C}}CN \right]^{=} 2K^+ \qquad n = 2\text{-}6$$

the active methylene compound. Amyl nitrate and methyl nitrate were also investigated in this reaction. Amyl nitrate gave very low yields whereas methyl nitrate did not give the desired product.

The crude product (I) is a hygroscopic black material which is purified to a yellow crystalline solid by methanol wash followed by recrystallization from water/isopropyl alcohol. Characterization was accomplished by complete elemental analyses of both the dipotassium and disilver salts of I. The disodium salt was prepared by passing the dipotassium salt through an ion exchange column. The direct preparation of the disodium salt using sodium ethoxide in the synthesis was not successful. The dichloro compound was prepared by the direct chlorination of I; it was also obtained as a by-product of the attempted nitration of I with $ClNO_2$. The dichloro compound is a low melting hygroscopic solid. The dinitronate salts (potassium, sodium, and silver) are yellow to orange solids. They do not exhibit the characteristic nitro absorption in the 6.0-6.4μ region of the infrared but have six major absorptions in the regions 4.4-4.6μ, 6.8-7.2μ, 7.5-7.9μ, 8.5-8.7μ, 10.0-10.3μ and 13.7-14.0μ. Ultraviolet spectra of the salts exhibit a major peak in the range of 325-350mμ.

The stability of these salts is interesting. Although they burn very energetically, particularly the disilver salt, they appear to be quite stable both to heat and shock. The disilver salt explodes at 162° while the dipotassium and disodium salts melt at 274° and 290° respectively with decomposition.

EXPERIMENTAL

Succinonitrile, propyl nitrate and amyl nitrate were obtained commercially. Methyl nitrate was prepared in this laboratory according to the method of Desseigne.[3] Melting points are uncorrected. Infrared spectra were run on a Perkin-Elmer 137 Infracord Spectrophotometer and Ultraviolet spectra were obtained on a Cary 14 UV-Visible Spectrophotometer.

Dipotassium-α,α′-Dinitrosuccinonitrile.- Potassium ethoxide (0.256 mole) was formed *in situ* from 10g (0.256g atom) of potassium and 75 ml of ethanol. Ether (120 ml) was added during this step to help solubilize the ethoxide. To this solution at 0° was added dropwise a mixture of 10.2g (0.128 mole) of succinonitrile and 29.4g (0.28 mole) of propyl nitrate in 100 ml of benzene. The reaction mixture was maintained at 0° during this addition and then stirred at 0° overnight. The resulting brown slurry was filtered and the solid was dried *in vacuo* over phosphorous pentoxide to yield 8g of crude dipotassium-α,α′-dinitrosuccinonitrile. Addition of ether to the filtrate yielded an additional 3g of crude material. All operations were carried out in a nitrogen atmosphere. The crude material, which is hygroscopic, was purified by washing with about 30 mls of methanol and then 20 mls of acetone followed by decolorization from a 40° aqueous solution and finally recrystallization from water/isopropyl alcohol. The purified material was a yellow solid, mp. 274°(dec.). The total overall yield of purified material was 4.7g (15%).

Anal. Calcd for $C_4N_4O_4K_2$: C, 19.51; N, 22.76; O, 26.02; K, 31.71
Found: C, 19.73; N, 22.71; O, 25.85; K, 31.21

Disilver-α,α′-Dinitrosuccinonitrile.- The disilver salt was precipitated from solution when silver nitrate was added to an aqueous solution of the dipotassium salt. The yellow-orange disilver salt was nonhygroscopic; it did not melt but rather exploded at 162°. The yield was quantitative.

Anal. Calcd for $C_4N_4O_4Ag_2$: C, 12.50; N, 14.58; Ag, 56.25; O, 16.67
Found: C, 13.06; N, 14.02; Ag, 55.80; O, 16.02

Disodium-α,α′-Dinitrosuccinonitrile.- The disodium salt was formed by passing an aqueous solution of 1.5g of the dipotassium salt through an ion exchange column 6 inches long and 18mm in dia. (Dowex 50 W-X8 in the sodium form). The disodium salt was isolated by evaporating the eluent and drying *in vacuo* over phosphorous pentoxide. The resulting yellow solid melted at 290° (dec.). The yield was quantitative.

α,α'-Dichloro-α,α'-Dinitrosuccinonitrile.- Dipotassium α,α'-dinitrosuccinonitrile (1g) was suspended in 50 ml anhydrous ether and cooled to 0°. Chlorine was bubbled in slowly until the salt was decolorized and the solution turned yellow. The mixture was filtered and solvent was removed *in vacuo*. There remained a mixture of white solid and yellow oil. The white solid hygroscopic product was removed by sublimation of 40-50°/1mm. The yield was 0.38g (40%).

Anal. Calcd for $C_4N_4O_4Cl_2$: C, 20.1; Cl, 29.7

Found: C, 20.0; Cl, 29.9

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