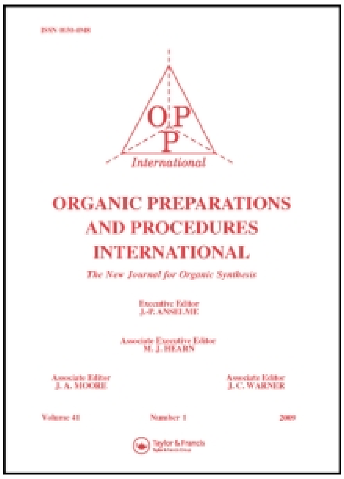

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BROMINE OXIDATION OF THE DIPOTASSIUM SALT OF α,α'-DINITROSUCCINONITRILE INTO THE POTASSIUM SALT OF NITROKETOSUCCINONITRILE

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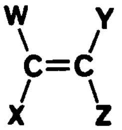
Comparable electronic effects for cyano and nitro groups permit the projection of many of the useful properties of tetracyanoethylene (TCNE)[1] to the other six derivatives in which ethylene is tetrasubstituted by combinations of these two groups. Tetranitroethylene **1**, apparently highly reactive,[2] has not been isolated but has been trapped as its Diels-Alder adducts with anthracene and cyclopentadiene.[3] Tricyanonitro-, trinitrocyano- and 1,1-dicyano-2,2-dinitroethylene and dinitromaleo- and dinitrofumaronitrile (**2a**,**2b**) remain unknown.



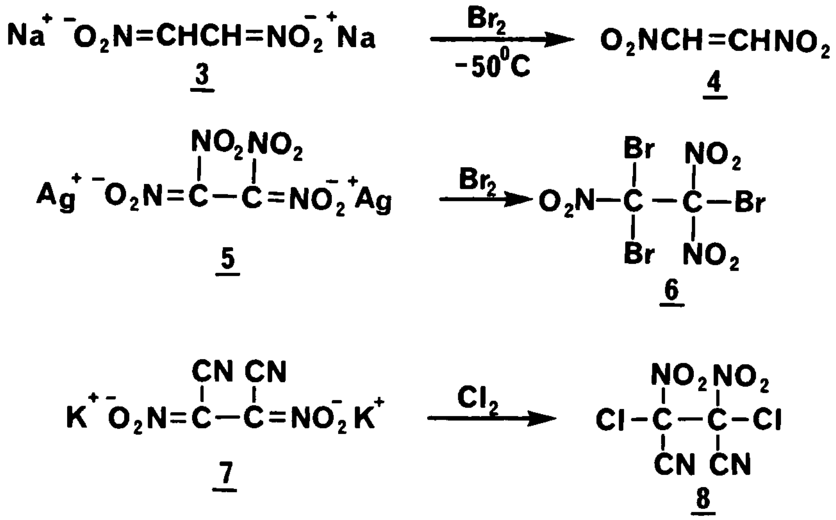
1, $W = X = Y = Z = NO_2$

2a, $W = Y = CN$, $X = Z = NO_2$

2b, $W = Z = CN$, $X = Y = NO_2$

Unsuccessful attempts to produce olefins **1** or **2** have included a) coupling from methylene derivatives, e.g., dihalodinitromethane $X_2C(NO_2)_2$,[4,5] dihalonitroacetonitrile $X_2C(NO_2)CN$,[4,6] or nitroacetonitrile, O_2NCH_2CN;[6,7] b) elimination reactions from hexasubstituted ethanes, e. g., 1,2-dichlorotetranitroethane, [Cl$(O_2N)_2C]_2$;[8] c) oxidation of the nitrogen of certain derivatives of the NCCN moiety.[9]

Halogen oxidation of dinitronate salts has been erratic. Bromine oxidized the disodium salt of dinitroethane (3) into 1,2-dinitroethylene (4) but transformed the disilver salt of tetranitroethane (5) into 1,1,2-tribromo-1,2,2-trinitroethane (6).[8,10] Chlorine and the dipotassium salt of α,α'-dinitrosuccinonitrile (7) gave 1,2-dichloro-1,2-dicyano-1,2-dinitroethane (8).[11]

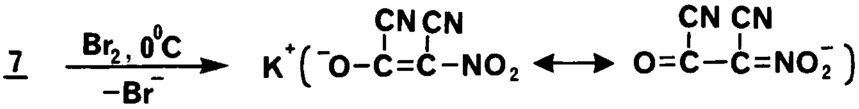


$$\underset{3}{Na^+\,{}^-O_2N{=}CHCH{=}NO_2^-\,{}^+Na} \xrightarrow[-50^0C]{Br_2} \underset{4}{O_2NCH{=}CHNO_2}$$

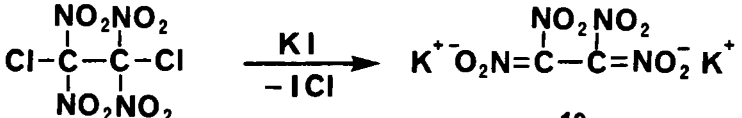
$$\underset{5}{Ag^+\,{}^-O_2N{=}C(NO_2){-}C(NO_2){=}NO_2^-\,{}^+Ag} \xrightarrow{Br_2} \underset{6}{O_2N{-}CBr_2{-}C(NO_2)_2{-}Br}$$

$$\underset{7}{K^+\,{}^-O_2N{=}C(CN){-}C(CN){=}NO_2^-\,K^+} \xrightarrow{Cl_2} \underset{8}{Cl{-}C(NO_2)(CN){-}C(NO_2)(CN){-}Cl}$$

In contrast with the chlorination reaction 7 → 8, bromine and the dipotassium salt 7 gave a 21% yield of the potassium salt of nitroketosuccinonitrile (9) along with potassium bromide (77%). The structure for the salt 9 was supported by elemental analysis and by infrared absorption at 2200 (w, cyano group) and 1645 cm^{-1} (m, carbonyl group in a salt of an α-nitroketone).[12] Other IR absorption at 1590 (s) and 1380 cm^{-1} (s) is characteristic of a nitro group. The salt 9 resisted attack by halogen, a property previously reported for the dipotassium salt 10 of tetranitroethane (prepared along with a mixed halogen from 1,2-dichlorotetranitroethane and potassium iodide).[8] In concentrated sulfuric acid at -40°, the salt 9 gave an intractable mixture, and in methanol it was slowly converted into an unidentified solid, $C_6H_5N_3O_5K_2$, mp. 276-277° (dec.).



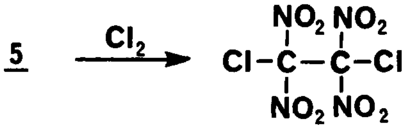
9



10

Electrophilic attack by halogen on a mononitronate salt is known to produce a *gem*-halonitro compound.[13] Apparently, similar reactions gave the dichloride 8 and 1,2-dichlorotetranitroethane 11 from the dinitronates 7 and 5.[8,11] An electron transfer from a nitronate anion to halogen can initiate these as well as similar reactions, i.e., 3 → 4, 5 → 6, 7 → 8 and 7 → 9 by the formation of intermediate radical anions.[14] The intermediate 12 from the dinitronate 3 can afford the olefin 4 by an additional electron transfer and account for the formation of 1,4-dinitrobutadiene[14] by coupling of intermediate 12 followed by an additional electron transfer and 1,2-elimination of dinitrogen tetroxide.

$$R_2C=NO_2^- \xrightarrow{X_2} R_2CXNO_2\ ,\quad X = Cl,Br$$

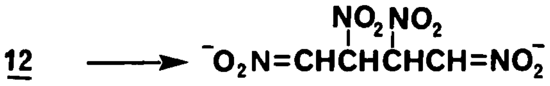


$$\underline{5} \xrightarrow{Cl_2} Cl-\overset{NO_2}{\underset{NO_2}{C}}-\overset{NO_2}{\underset{NO_2}{C}}-Cl$$

11

$$\underline{3} + Br_2 \xrightarrow{-50^0C} {}^-O_2N=CH\overset{\bullet}{C}HNO_2 \xrightarrow{Br_2} \underline{4}$$

12



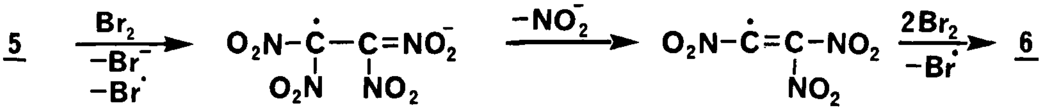
$$\underline{12} \longrightarrow {}^-O_2N=CH\overset{NO_2}{C}H\overset{NO_2}{C}HCH=NO_2^-$$

13

$$\underline{13} + Br_2 \longrightarrow O_2NCH=CHCH=CHNO_2 + N_2O_4 + \overset{\bullet}{Br} + Br^-$$

14

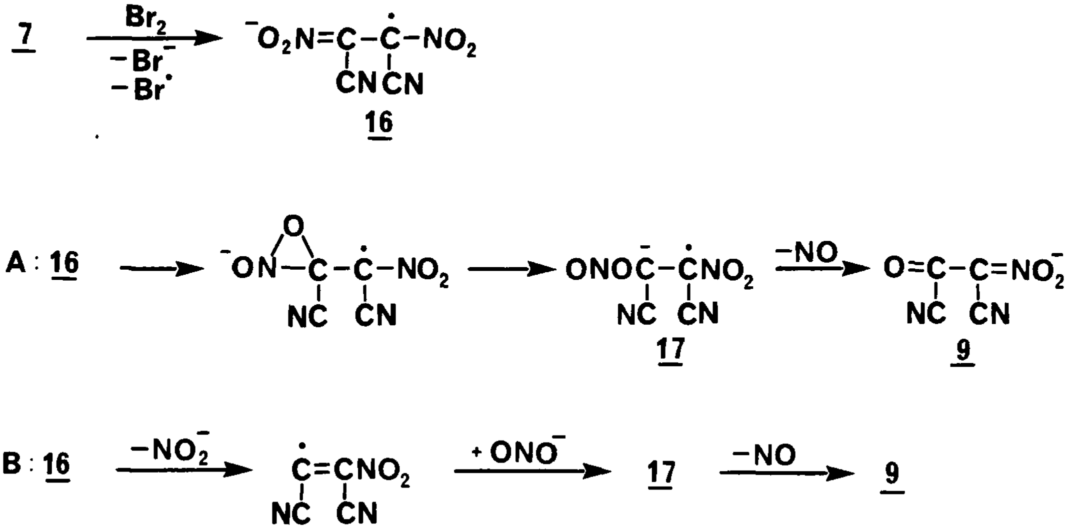
Ejection of nitrite ion[15] from the intermediate radical anion 15 (generated from the dinitronate 5) can lead to the formation of the tribromotrinitroethane 6 on further reaction with bromine. An expected evolution of nitrogen oxides was not reported in the abstract.[8]



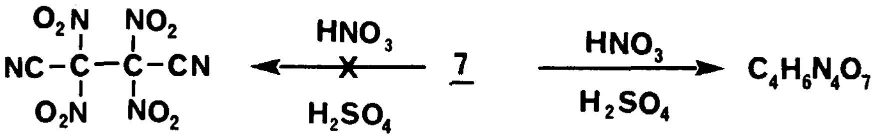
$$\underline{5} \xrightarrow[-Br^-\ -Br^\bullet]{Br_2} O_2N-\underset{O_2N}{\overset{\bullet}{C}}-\underset{NO_2}{C}=NO_2^- \xrightarrow{-NO_2^-} O_2N-\overset{\bullet}{C}=\underset{NO_2}{C}-NO_2 \xrightarrow[-Br^\bullet]{2Br_2} \underline{6}$$

15

In the conversion of an intermediate radical anion 16 from the dinitronate 7 into the ketonitronate 9 a nitro group was the presumed source of the keto oxygen atom.[16] A differentiation between intramolecular and intermolecular creation of new carbon-oxygen bonding cannot be made at this time; however, it was assumed that in either event, isomerization of a nitro derivative into a nitrite ester occurred. There is precedent for both the thermal isomerization (path A)[17] and also for expulsion of a nitrite anion followed by recombination and expulsion of nitric oxide (path B)[3] to give an -oxonitronate salt.



An investigation of the elimination of dinitrogen tetroxide from tetranitrosuccinonitrile 18[18] was thwarted because nitration of the dinitronate salt 7 failed to produce 18 and gave instead an unidentified compound 19.



18

19

Acknowledgement.- Financial assistance was received from ONR.

EXPERIMENTAL SECTION

Instruments included Perkin Elmer 237B and 521 grating IR, Varian A-60, Bruker WP-80 and A.E.I. MS 30 double beam mass spectrometers. Elemental analyses were provided by Micro-Tech Laboratories, Skokie, Illinois.

Potassium Salt of Nitroketosuccinonitrile (**9**).- To a suspension of α,α'-dinitrosuccinonitrile[11] (1.47g, 6 mmol) in anhydrous ether (50 ml) in a three necked round bottom flask equipped with a drying tube filled with Drierite and cooled to -5 $^{\circ}$, bromine (4.0 g, 24 mmol) was added dropwise with vigorous stirring over 45 minutes. After the mixture was stirred at 0° for 16 hrs, a colorless precipitate, 1.68 g, mp. $> 300^{\circ}$, was formed, collected and dissolved in hot methanol (40 ml). Dry ether was added to precipitate potassium bromide (0.54 g, 77%); its identification was confirmed by the precipitation of silver bromide on treatment with a solution of silver nitrate. Concentration of the mother liquor brought about the separation of 0.23g. (21%) of the salt **9**, mp. 193-194° (dec.) after recrystallization from methanol.

IR (KBr): 2220 (w, CN), 1645 (m, CO or C=N), 1590 (s, NO_2), 1460 (m), 1380 (s, NO_2) and 1325 (m).

Anal. Calcd $C_4N_3O_3K$: C, 27.12; N, 23.72; O, 27.12; K, 22.02;

Found: C, 27.27; N, 23.68; O, 28.83; K, 20.14.
27.07 23.59 29.11

Repeated recrystallizations of the salt 9 from methanol gave an unidentified colorless solid, mp. 276-277° (dec.); ir (KBr): 2210 (m, CN), 1710 (s, CO), 1440(w), 1360(s), 1300(m) and 1110(s); nmr(CH_3COCH_3 and DMSO-D_6): δ 2.9(s, 2H) and 3.5 (s, 3H).

Anal. Calcd $C_6H_5N_3O_5K_2$: C, 25.99; H, 1.80; N, 15.16; O, 28.88;

Found: C, 26.45; H, 1.73; N, 15.49; O, 28.15.
26.54 1.69 15.39 28.42

Attempted Nitration of Salt 7.- To a suspension of 7 (0.98 g, 4 mmol)[11] in anhydrous methylene chloride (25 ml) at -35°, concentrated sulfuric acid (5 ml) was added dropwise as a light green paste formed. A solution of concentrated sulfuric acid (2 ml) and fuming nitric acid (2 ml) was then added dropwise and the mixture held for 15 min. at -30° before being warmed gradually to 20°. It was stirred for 30 min. and the separated methylene chloride layer was dried (Na_2SO_4) and concentrated to leave a yellow gum. Trituration with tetrahydrofuran (0.5 ml) gave a yellow solid, 0.42 g (52%), mp. 167-168° (dec.) after recrystallization from acetic acid; IR(KBr): 3345(m), 3240(m), 1670(s), 1620(s), 1380(s), 1265 cm^{-1}(m).

Anal. Calcd $C_4H_6N_4O_7$: C, 21.62; H, 2.70; N, 25.22; O, 50.45.

Found: C, 22.14; H, 2.78; N, 25.59; O, 47.94.
21.96 2.76 25.64 47.76

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