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A New Reaction of α-Nitro Nitriles: Conversion to β-Nitro Nitriles[1]

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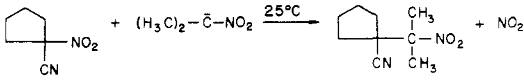
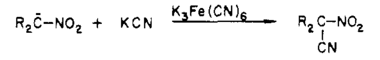
At room temperature the nitro group of an α-nitro nitrile is readily displaced by nitroparaffin anions with the result that β-nitro nitriles are produced in excellent yields. Evidence is presented for the view that these reactions are electron-transfer chain processes.

A new reaction, illustrated by eq 1, was reported in 1970.[2] Because of the difficulty of preparing α-nitro nitriles, the preliminary report was based on the reactions of just two α-nitro nitriles. The recently discovered oxidative substitution reaction of eq 2[3,1] has made α-nitro nitriles readily available, and the study of their chemistry has now become feasible.



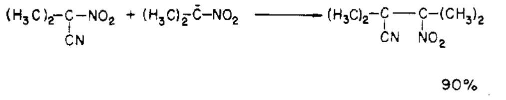
(1)



$$R_2\bar{C}-NO_2 + KCN \xrightarrow{K_3Fe(CN)_6} R_2\underset{CN}{C}-NO_2 \tag{2}$$

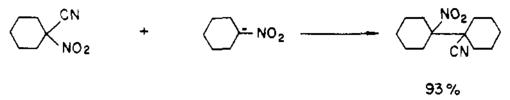
The studies herein reported leave no room for doubting that the transformation of eq 1 is but one example of a general reaction in which the nitro group of an α-nitro nitrile is displaced by a nitroparaffin anion at room temperature with the formation of a β-nitro nitrile. The yields of pure products are excellent; our results are summarized in Table I.[4]

The reactions of nitroparaffin salts with α-nitro nitriles exhibit the characteristics[9] of radical anion–free radical chain processes. Thus, the transformation of eq 3 is complete in 60 min when the reaction mixture is exposed to two 20-W ordinary fluorescent lights; but if di-*tert*-butyl nitroxide is present at the 5 mol % level, there is no reaction whatsoever for at least 6 h. Inhibition, albeit less dramatic, is also observed with 5 mol % of *p*-benzoquinone or 5 mol % of galvinoxyl. Although the reaction of eq 3 proceeds in the dark, it does so at a distinctly slower rate than the light reaction—a fact that is consonant with the assignment of an electron-transfer chain mechanism;[9] and, here too, the reaction is inhibited by 5 mol % of galvinoxyl or *p*-dinitrobenzene.



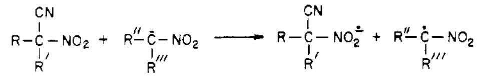
$$(H_3C)_2-\underset{CN}{C}-NO_2 + (H_3C)_2\bar{C}-NO_2 \longrightarrow \underset{90\%}{(H_3C)_2-\underset{CN}{C}-\underset{NO_2}{C}-(CH_3)_2} \tag{3}$$

In the same way, the transformation of eq 4 is speeded up by exposure to two 20-W fluorescent lights and is strongly inhibited by di-*tert*-butyl nitroxide (10 mol %) or by *m*-dinitrobenzene (10 mol %).



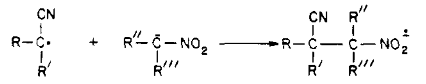
(4)

The electron-transfer chain mechanism of eq 5–8 provides a simple basis for understanding these facts.

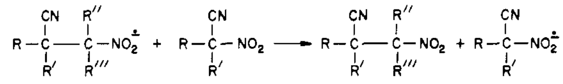


$$R-\overset{CN}{\underset{R'}{C}}-NO_2 + R''-\underset{R'''}{\bar{C}}-NO_2 \longrightarrow R-\overset{CN}{\underset{R'}{C}}-NO_2^{\cdot-} + R''-\underset{R'''}{\dot{C}}-NO_2 \tag{5}$$

$$R-\overset{CN}{\underset{R'}{C}}-NO_2^{\cdot-} \longrightarrow R-\overset{CN}{\underset{R'}{C}}\cdot + NO_2^- \tag{6}$$



$$R-\overset{CN}{\underset{R'}{C}}\cdot + R''-\underset{R'''}{\bar{C}}-NO_2 \longrightarrow R-\overset{CN}{\underset{R'}{C}}-\overset{R''}{\underset{R'''}{C}}-NO_2^{\cdot-} \tag{7}$$



$$R-\overset{CN}{\underset{R'}{C}}-\overset{R''}{\underset{R'''}{C}}-NO_2^{\cdot-} + R-\overset{CN}{\underset{R'}{C}}-NO_2 \longrightarrow R-\overset{CN}{\underset{R'}{C}}-\overset{R''}{\underset{R'''}{C}}-NO_2 + R-\overset{CN}{\underset{R'}{C}}-NO_2^{\cdot-} \tag{8}$$

Experimental Section

Infrared spectra (IR) were recorded on a Beckman IR-33 spectrometer. Nuclear magnetic resonance spectra (NMR) were obtained on a Perkin-Elmer R-32 90-MHz spectrometer.

Unless otherwise specified, reactions were carried out at room temperature, under nitrogen, with the reaction vessel held under two 20-W ordinary fluorescent lights. Magnetic stirring was always employed. The Me_2SO (Crown Zellerbach Corp.) was vacuum distilled over CaH_2 and kept over type 4A molecular sieves under nitrogen.[10]

I. Preparation of 1-Nitro-2-cyano-2-methylheptane. Approximately 1 mL of a 22.2% suspension of potassium hydride in oil[11] was placed in a 50-mL, nitrogen-filled flask and washed twice with 15–20-mL portions of pentane. After removal of residual pentane with a stream of N_2 the dry KH (0.165 g, 4.13 mmol) was treated with 5 mL of Me_2SO; this produced a colorless

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[1] This is paper 27 in the series "Substitution Reactions which Proceed via Radical Anion Intermediates". For the preceding paper, see: Kornblum, N.; Singh, H. K.; Kelly, W. J. *J. Org. Chem.* **1983**, *48*, 332. For a recent review, see: Kornblum, N. "The Chemistry of Functional Groups, Supplement F: The Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives"; Patai, S., Ed.; Wiley: New York, 1982; p 361.

[2] Kornblum, N.; Boyd, S. D.; Stuchal, F. W. *J. Am. Chem. Soc.* **1970**, *92*, 5783.

[3] Matacz, Z.; Piotrowska, H.; Urbanski, T. *Pol. J. Chem.* **1979**, *53*, 187.

[4] The reaction of α-nitro nitriles with nitroparaffin salts has considerable synthetic value. It not only provides highly branched compounds containing a quaternary carbon atom—compounds that would be exceedingly difficult to prepare by any other means—but, in addition, these quaternary carbon compounds possess functional groups that lend themselves to a variety of transformations. Thus, the β-nitro nitriles obtained from secondary nitroparaffin salts are tertiary nitro compounds; such compounds readily undergo electron-transfer reactions in which the tertiary nitro group is selectively replaced by hydrogen,[5] by thiol,[6] and by CH_2NO_2.[7] The β-nitro nitriles that derive from the reaction of α-nitro nitriles with the salts of nitromethane and higher primary nitroparaffins contain primary or secondary nitro groups and, consequently, they can, in turn, undergo the numerous ionic and electron-transfer reactions of nitroparaffin salts.[8]

[5] Kornblum, N.; Carlson, S. D.; Smith, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 647.

[6] Kornblum, N.; Widmer, J. *J. Am. Chem. Soc.* **1978**, *100*, 7086.

[7] Kornblum, N.; Erickson, A. S. *J. Org. Chem.* **1981**, *46*, 1037.

[8] The recently described conversion of CH_2NO_2 to an aldehyde group is of special interest [Kornblum, N.; Erickson, A. S.; Kelly, W. J.; Henggeler, B. *J. Org. Chem.* **1982**, *47*, 4534].

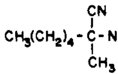
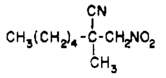
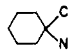
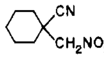
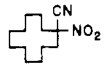
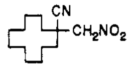
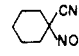
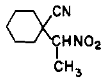
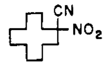
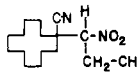
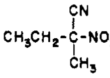
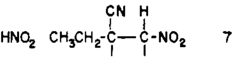
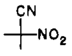
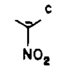
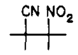
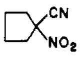
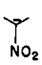
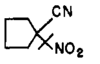
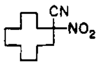
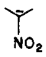
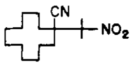
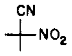
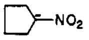
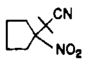
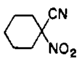
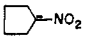
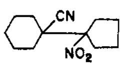
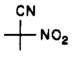
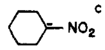
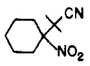
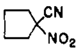
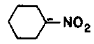
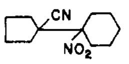
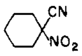
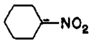
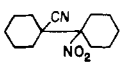
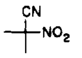
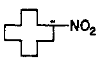
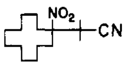
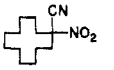
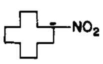
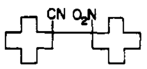
[9] Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734.

[10] We are indebted to the Crown Zellerbach Corp. for a generous supply of Me_2SO.

[11] Alfa Products.

0022-3263/84/1949-0358$01.50/0

Table I. Conversion of α-Nitro Nitriles to β-Nitro Nitriles

	α-nitro nitrile	nitroparaffin anion[a]	β-nitro nitrile	yield,[b] %
I	 $CH_3(CH_2)_4\text{-}\overset{CN}{\underset{CH_3}{C}}\text{-}NO_2$	$\bar{C}H_2NO_2$	 $CH_3(CH_2)_4\text{-}\overset{CN}{\underset{CH_3}{C}}\text{-}CH_2NO_2$	77
II		$\bar{C}H_2NO_2$		80
III		$\bar{C}H_2NO_2$		83
IV		$CH_3\bar{C}HNO_2$		80
V		$CH_3CH_2\bar{C}HNO_2$		71
VI	 $CH_3CH_2\text{-}\overset{CN}{\underset{CH_3}{C}}\text{-}NO_2$	$CH_3(CH_2)_5\bar{C}HNO_2$	 $CH_3CH_2\text{-}\overset{CN}{\underset{CH_3}{C}}\text{—}\overset{H}{\underset{(CH_2)_5\text{-}CH_3}{C}}\text{-}NO_2$	77
VII		 [c]		90
VIII				74
IX				75
X				81
XI				81
XII		 [c]		92
XIII				77
XIV				93
XV				71
XVI				54

[a] Except where otherwise stated, the K^+ salt was employed. [b] Pure, isolated product. [c] Li^+ salt used.

solution in ca. 5 min after which 0.232 g (3.8 mmol) of nitromethane[12] in 5 mL of Me_2SO was added. A white precipitate formed immediately and did not dissolve after stirring for 30 min. This mixture was treated with a solution of 2-cyano-2-nitroheptane[1] (0.340 g, 2 mmol) in 2 mL of Me_2SO and within 5 min a clear yellow solution was produced. After 3 h the solution was poured into a mixture of 50 mL of cold water and 75 mL of pentane and acidified (pH 5) with a solution of urea (0.96 g, 0.016 mol) in 4.8 mL of 20% aqueous acetic acid. The pentane phase was isolated and the aqueous phase was extracted with pentane. The combined pentane solutions were washed with cold water and dried (anhydrous $MgSO_4$). Removal of the pentane followed by Kugelrohr distillation at 40–42 °C (0.08 mm) gave 0.283 g (77% yield) of VPC-pure 1-nitro-2-cyano-2-methylheptane, a colorless liquid: ^1H NMR ($CDCl_3$) δ 0.92 (t, 3 H), 1.50 (s, 3 H), 1.53 (m, 8 H), 4.55 (q, 2 H); IR ($CHCl_3$) 4.43 μm (CN), 6.48 (NO_2).

Anal. Calcd for $C_9H_{16}N_2O_2$: C, 58.70; H, 8.70; N, 15.22. Found: C, 58.82; H, 9.03; N, 15.20.

II. Preparation of 1-(Nitromethyl)-1-cyanocyclohexane. The potassium salt of nitromethane in 10 mL of Me_2SO, prepared as described above with 0.230 g (5.75 mmol) of KH and 0.329 g (5.4 mmol) of nitromethane, was treated with a solution of 0.416 g (2.7 mmol) of 1-cyano-1-nitrocyclohexane[1] in 5 mL of Me_2SO. After 2 h the resulting solution was added to 50 mL of cold water and acidified with 1.32 g (0.022 mol) of urea in 6.6 mL of 20% aqueous acetic acid. The resulting mixture was ether extracted and the ether solution was washed with cold water and dried ($MgSO_4$). Removal of the ether gave a white solid, mp 86–90 °C, which was flash chromatographed on silica gel with hexane–benzene (2:3) and then recrystallized from hexane–benzene (6:1). This gave 0.363 g (80% yield) of white crystals: mp 90.5–92 °C; ^1H NMR ($CDCl_3$) δ 1.60 (m, 10 H), 4.50 (s, 2 H); IR ($CHCl_3$) 4.43 μm (CN), 6.49 (NO_2).

Anal. Calcd for $C_8H_{12}N_2O_2$: C, 57.14; H, 7.14; N, 16.66. Found: C, 57.31; H, 7.29; N, 16.73.

III. Preparation of 1-(Nitromethyl)-1-cyanocyclododecane. Nitromethane (0.318 g, 5.2 mmol) was converted to its potassium salt with 0.225 g (5.6 mmol) of KH and 15 mL of Me_2SO. Treatment with a solution of 0.619 g (2.6 mmol) of 1-cyano-1-nitrocyclododecane[1] in 5 mL of Me_2SO for 2 h gave a mixture, which was worked up in the usual way with use of ether for extraction. The crude product was a white solid, mp 75–79 °C. Flash chromatography on silica gel using benzene–hexane (1:1) yielded 0.580 g of crystals, mp 81–83 °C. This, on recrystallization from hexane–benzene (9:1), gave 0.543 g (83% yield) of white crystals: mp 82–83 °C; ^1H NMR ($CDCl_3$) δ 1.36 (s, 18 H), 1.76 (m, 4 H), 4.46 (s, 2 H); IR ($CHCl_3$) 4.43 μm (CN), 6.48 (NO_2).

Anal. Calcd for $C_{14}H_{24}N_2O_2$: C, 66.67; H, 9.52; N, 11.11. Found: C, 66.61; H, 9.87; N, 11.11.

IV. Preparation of 1-(α-Nitroethyl)-1-cyanocyclohexane. Pentane-washed KH (0.250 g, 6.25 mmol) was dissolved in 3 mL of Me_2SO and treated with a solution of 0.450 g (6.0 mmol) of nitroethane[12] in 14 mL of Me_2SO. The resulting white precipitate did not dissolve after stirring for 30 min, but on addition of 0.462 g (3.0 mmol) of 1-cyano-1-nitrocyclohexane[1] in 3 mL of Me_2SO, a yellow solution was produced within 5 min. After 15 min the solution was cooled to 5 °C and acidified (pH 6) with urea (1.08 g, 0.018 mol) in 5.4 mL of 20% aqueous acetic acid. After the addition of 50 mL of cold water, the mixture was ether extracted, washed with cold water, and dried ($MgSO_4$). Removal of the ether gave a light yellow solid, mp 81–84 °C. Flash chromatography on silica gel using hexane–benzene (9:1) produced a colorless solid, mp 82–85 °C, which on recrystallization from hexane–ethyl acetate (9:1) gave 0.435 g (80% yield) of the analytically pure β-nitro nitrile: mp 83.5–85 °C; ^1H NMR ($CDCl_3$) δ 1.55 (m, 10 H), 1.75 (d, 3 H), 4.50 (q, 1 H); IR ($CHCl_3$) 4.43 μm (CN), 6.48 (NO_2).

Anal. Calcd for $C_9H_{14}N_2O_2$: C, 59.34; H, 7.69; N, 15.38. Found: C, 59.54; H, 7.89; N, 15.16.

V. Preparation of 1-(α-Nitro-*n*-propyl)-1-cyanocyclododecane. Oil-free KH (0.204 g, 5.1 mmol) was dissolved in 3 mL of Me_2SO, and then 0.427 g (4.8 mmol) of 1-nitropropane[12] in 14 mL of Me_2SO was added; this produced a white precipitate. A solution of 0.571 g (2.4 mmol) of 1-cyano-1-nitrocyclododecane in 4 mL of Me_2SO (obtained by warming to 40 °C) was then introduced. The resulting reaction mixture became a clear solution within 20 min; it was then worked up as in the preceding preparation. The crude product was a liquid that solidified at 0 °C. Flash chromatography on silica gel using hexane–ethyl acetate (19:1) yielded white crystals, mp 79–83 °C, which after several recrystallizations from hexane gave 0.480 g (71% yield) of the pure

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[12] Our thanks are due to the Commercial Solvents Corp. for generous gifts of nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane.

β-nitro nitrile: mp 84.5–85.5 °C; ^{1}H NMR (CDCl$_3$) δ 1.02 (t, 3 H), 1.35 (s, 18 H), 2.00 (m, 6 H), 4.30 (q, 1 H); IR (CHCl$_3$) 4.43 μm (CN), 6.48 (NO$_2$).

Anal. Calcd for C$_{16}$H$_{28}$N$_2$O$_2$: C, 68.57; H, 10.00; N, 10.00. Found: C, 68.35; H, 10.24; N, 9.83.

VI. Preparation of 4-Nitro-3-cyano-3-methyldecane. A solution of 0.225 g (5.6 mmol) of oil-free KH in 3 mL of Me$_2$SO was treated with 0.754 g (5.2 mmol) of 1-nitroheptane[1] in 14 mL of Me$_2$SO. The white precipitate that formed did not dissolve after 30 min of stirring, but the addition of 0.333 g (2.6 mmol) of 2-cyano-2-nitrobutane[1] in 3 mL of Me$_2$SO produced a clear solution in 10 min. After an additional 10 min, the solution was colled in an ice bath and acidified to pH 6 with 0.936 g (0.0156 mol) of urea in 4.6 mL of 20% acetic acid, cold water (50 mL) was added, and the mixture was extracted with ether. The extracts were washed with cold water and dried (MgSO$_4$), and the solvent was removed. The residual yellow liquid was flash chromatographed on silica gel, first using hexane to remove some unreacted 1-nitroheptane and then using hexane–benzene (7:3). This gave 0.450 g (77% yield) of a colorless liquid whose VPC exhibited two peaks corresponding to the two racemates of this β-nitro nitrile. For analysis this liquid was Kugelrohr distilled at 80 °C (0.08 mm). ^{1}H NMR (CDCl$_3$) δ 0.90 (t, 3 H), 1.65 (m, 18 H), 4.45 (d of t, 1 H); IR (neat) 4.43 μm (CN), 6.48 (NO$_2$).

Anal. Calcd for C$_{12}$H$_{22}$N$_2$O$_2$: C, 63.71; H, 9.74; N, 12.39. Found: C, 63.87; H, 9.97; N, 12.28.

VII. Preparation of 2-Nitro-3-cyano-2,3-dimethylbutane. The lithium salt of 2-nitropropane[13] (1.90 g, 20 mmol) and 1.10 g (10.1 mmol) of 2-cyano-2-nitropropane[1] in 50 mL of Me$_2$SO were allowed to react in the usual way (exposure to two 20-W fluorescent lights, under N$_2$, stirring). After 50 min the mixture became homogeneous, and after 1 h the solution was poured into 250 mL of cold water and extracted with dichloromethane. The extracts were washed with cold water and dried (MgSO$_4$), and the solvent was removed. This gave 1.457 g (90% yield) of VPC-pure 2-nitro-3-cyano-2,3-dimethylbutane: white crystals, mp 195–196 °C (lit.[14] mp 194 °C); ^{1}H NMR (CDCl$_3$) δ 1.45 (s, 6 H), 1.73 (s, 6 H); IR (CCl$_4$) 4.43 μm (CN), 6.42 (NO$_2$).

VIII. Preparation of 1-(α-Nitroisopropyl)-1-cyanocyclopentane. Oil-free KH (0.276 g, 6.9 mmol) was dissolved in 3 mL of Me$_2$SO and then 2-nitropropane[12] (0.587 g, 6.6 mmol) in 14 mL of Me$_2$SO was added. A white precipitate formed immediately; 20 min later a solution of 1-cyano-1-nitrocyclopentane (0.462 g, 3.3 mmol) in 3 mL of Me$_2$SO was added and then the reaction was allowed to proceed for 1$^3/_4$ h. The reaction mixture was poured into cold water and ether extracted, and after washing with cold water the ether solution was dried (Na$_2$SO$_4$). The ether was removed and the residual liquid was cooled in ice, whereupon it crystallized to a white solid melting at 40–43 °C. Purification by flash chromatography on silica gel using hexane–benzene (1:1) followed by recrystallization from hexane gave 0.445 g (74% yield) of white crystals: mp 44–45 °C; ^{1}H NMR (CDCl$_3$) δ 1.73 (s), 1.70–2.30 (broad absorption); IR (Cl$_4$) 4.48 μm (CN), 6.47 (NO$_2$).

Anal. Calcd for C$_9$H$_{14}$N$_2$O$_2$: C, 59.32; H, 7.74; N, 15.38 (mol wt 182). Found: C, 59.26; H, 7.83; N, 15.55 (mol wt 185).

When this reaction was carried out with the *lithium* salt of 2-nitropropane in Me$_2$SO for 4$^1/_2$ h (with the usual exposure to two 20-W fluorescent light under N$_2$, with magnetic stirring), the crude 1-(α-nitroisopropyl)-1-cyanocyclopentane was contaminated with about 4% of an impurity, which, by VPC and NMR, appeared to be 2-nitro-3-cyano-2,3-dimethylbutane. Presumably a small amount of transcyanation from α-nitro-α-cyanocyclopentane to the 2-nitropropane anion occurred and the resulting 2-nitro-2-cyano-propane reacted with the 2-nitropropane anions, which are abundant (cf. preceding preparation).

It has not been established whether or not the side reaction is fostered by the use of lithium salt. As will be seen from the sequel, this side reaction is more of a problem when α-nitro-α-cyanocyclopentane is treated with the lithium salt of nitrocyclohexane.

IX. Preparation of 1-(α-Nitroisopropyl)-1-cyanocyclododecane. To the salt obtained by treating a solution of 0.230 g (5.75 mmol) of KH in 3 mL of Me$_2$SO with 0.489 g (5.5 mmol) of 2-nitropropane[12] in 14 mL of Me$_2$SO was added a solution of 0.536 g (2.25 mmol) of 1-cyano-1-nitrocyclododecane[1] in 3 mL of Me$_2$SO. The mixture was allowed to react for 18 h and the resulting clear yellow solution was poured into 60 mL of cold water. Ether extraction was followed by back-washing with cold water and drying (Na$_2$SO$_4$). Removal of the ether left an oil that crystallized at 0 °C, mp 55–63 °C. Flash chromatography on silica gel using benzene–hexane (2:3) gave a colorless oil, which at 0 °C on treatment with ca. 2 mL of hexane crystallized, mp 68–70 °C. Recrystallization from hexane gave 0.472 g (75% yield) of analytically pure 1-(α-nitroisopropyl)-1-cyanocyclododecane: mp 69–70 °C; IR (CHCl$_3$) 4.43 μm (CN), 6.48 (NO$_2$).

Anal. Calcd for C$_{16}$H$_{28}$N$_2$O$_2$: C, 68.57; H, 10.00; N, 10.00. Found: C, 68.63; H, 10.08; N, 9.82.

X. Preparation of 1-(α-Cyanoisopropyl)-1-nitrocyclopentane. This reaction was carried out as described for the preceding preparation, using 0.260 g (6.5 mmol) of KH, 0.713 g (6.2 mmol) of nitrocyclopentane,[15] and 0.354 g (3.1 mmol) of 2-cyano-2-nitropropane[1] in a total of 20 mL of Me$_2$SO. After a 1-h reaction time and the usual workup, a white solid, mp 56–58 °C, was obtained. Flash chromatography on silica gel using hexane–benzene (3:2) gave 0.550 g of a white solid, mp 57–58.5 °C. When this was again flash chromatographed, using hexane–benzene (3:2), 0.454 g (81% yield) of the pure β-nitro nitrile was obtained; white crystals, mp 58.5–60 °C. For analysis a sample was recrystallized from hexane: mp 58.5–60 °C; IR (CHCl$_3$) 4.43 μm (CN), 6.49 (NO$_2$).

Anal. Calcd for C$_9$H$_{14}$N$_2$O$_2$: C, 59.34; H, 7.69; N, 15.38. Found: C, 59.58; H, 7.54; N, 15.21.

XI. Preparation of 1-(α-Nitrocyclopentyl)-1-cyanocyclohexane. This was prepared in the usual way, using 0.170 g (4.37 mmol) of KH, 0.460 g (4.0 mmol) of nitrocyclopentane,[15] 3.08 g (2.0 mmol) of 1-cyano-1-nitrocyclohexane,[1] 20 mL of Me$_2$SO, and a reaction time of 1 h. The usual workup produced a white solid with a melting range of 95–102 °C. Repeated recrystallization from 95% ethanol gave 0.360 g (81% yield) of white crystals: mp 110–111 °C; IR (CHCl$_3$) 4.46 μm (CN), 6.50 (NO$_2$).

Anal. Calcd for C$_{12}$H$_{18}$N$_2$O$_2$: C, 64.86; H, 8.10; N, 12.61. Found: C, 64.60; H, 8.18; N, 12.72.

XII. Preparation of 1-(α-Cyanoisopropyl)-1-nitrocyclohexane. The lithium salt of nitrocyclohexane[13] (2.03 g, 15 mmol) and 1.111 g (10.2 mmol) of 2-cyano-2-nitropropane[1] in 50 mL of Me$_2$SO were allowed to react for 2 h as in experiment VII. The usual workup using benzene for extraction gave 1.984 g of crude product as a white solid. This, on recrystallization from hexane, gave 1.819 g (92% yield) of pure β-nitro nitrile: mp 108–109 °C; ^{1}H NMR (CDCl$_3$) δ 1.42 (s, 6 H), 1.0–2.0 (br, 8 H), 2.5–2.9 (br d, 2 H); IR (CHCl$_3$) 4.39 μm (CN), 6.46 (NO$_2$).

Anal. Calcd for C$_{10}$H$_{16}$N$_2$O$_2$: C, 61.19; H, 8.21; N, 14.28 (mol wt 196). Found: C, 61.33; H, 8.06; N, 14.07 (mol wt 195).

XIII. Preparation of 1-(α-Nitrocyclohexyl)-1-cyanocyclopentane. In the usual way 2.10 g (5.25 mmol) of KH, 0.645 g (5.0 mmol) of nitrocyclohexane, and 0.350 g (2.5 mmol) of 1-cyano-1-nitrocyclopentane[1] were allowed to react for 1 h with a total of 20 mL of Me$_2$SO, and the product was isolated and purified on silica gel, using hexane–benzene (1:1). This gave 0.475 g of a solid, mp 91–95 °C. Recrystallization from hexane produced 0.425 g of white crystals (77% yield): mp 97–97.5 °C; ^{1}H NMR (CDCl$_3$) δ 1–2.3 (br, 16 H), 2.6 and 2.8 (br peaks, 2 H); IR (CHCl$_3$) 4.46 μm (CN), 6.49 (NO$_2$).

Anal. Calcd for C$_{12}$H$_{18}$N$_2$O$_2$: C, 64.74; H, 8.16; N, 12.60 (mol wt 222). Found: C, 65.13; H, 8.13; N, 12.60 (mol wt 221).

When this reaction was carried out with the *lithium* salt of nitrocyclohexane (as described in experiment VIII above), the crude product, after a 17-h reaction time, was a mixture of the desired β-nitro nitrile (ca. 94%) and a second β-nitro nitrile (ca. 6%). This second β-nitro nitrile was shown to be 1-nitro-1′-cyanobicyclohexyl. Since it differs by just one CH$_2$ from the desired 1-(α-nitrocyclohexyl)-1-cyanocyclopentane, the isolation of this compound was attended by substantial losses. The 1-nitro-1′-cyanobicyclohexyl presumably arises from transfer of a cyano group to the nitrocyclohexane anion[16] and reaction of the

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(13) Kornblum, N.; Boyd, S. D.; Ono, N. *J. Am. Chem. Soc.* **1974**, *96*, 2580.

(14) Tilney-Bassett, J. F.; Waters, W. A. *J. Chem. Soc.* **1957**, 3129.

(15) Kornblum, N.; Powers, J. W. *J. Org. Chem.* **1957**, *22*, 455.

1-cyano-1-nitrocyclohexane with the nitrocyclohexane anion, which is present in large amount. As noted above it has not been fully established whether or not this side reaction is fostered by the use of lithium salts. In any event, the use of potassium salts of nitroparaffins appears to prevent any significant incursion of side reactions.

XIV. Preparation of 1-Nitro-1′-cyanobicyclohexyl. Nitrocyclohexane (0.645 g, 5.0 mmol), KH (0.210 g, 5.25 mmol), 1-cyano-1-nitrocyclohexane[1] (0.385 g, 2.5 mmol), and 20 mL of Me_2SO were employed. The reaction was allowed to proceed for 1 h after which the usual workup employing ether for extraction gave a crude product, mp 174–178 °C. Recrystallization from methanol yielded 0.560 g (95% yield) of white crystals: mp 176–178 °C; IR ($CHCl_3$) 4.43 μm (CN), 6.49 (NO_2).

Anal. Calcd for $C_{13}H_{20}N_2O_2$: C, 66.10; H, 8.47; N, 11.81 (mol wt 236). Found: C, 66.30; H, 8.21; N, 11.98 (mol wt 237).

XV. Preparation of 1-(α-Cyanoisopropyl)-1-nitrocyclododecane. In the usual way 0.210 g (5.25 mmol) of KH was dissolved in 3 mL of Me_2SO and then 1.065 g (5.0 mmol) nitrocyclododecane[1] in 14 mL of Me_2SO was added. The resulting mixture was stirred for 20 min and then 0.285 g (2.5 mmol) of 2-cyano-2-nitropropane[1] in 3 mL of Me_2SO was introduced. After 26 h the resulting solution was worked up in the usual way with use of ether for extraction. The crude product (mp 55–69 °C) was flash chromatographed on silica gel, using benzene–hexane (2:3), whereupon a white solid, mp 72–76 °C, was obtained. Recrystallization from methanol gave 0.494 g (71% yield) of analytically pure 1-(α-cyanoisopropyl)-1-nitrocyclododecane: mp 75–76 °C; IR ($CHCl_3$) 4.43 μm (CN), 6.49 (NO_2).

Anal. Calcd for $C_{16}H_{28}N_2O_2$: C, 68.57; H, 10.00; N, 10.00. Found: C, 68.65; H, 10.08; N, 9.73.

XVI. Preparation of 1-Nitro-1′-cyanobicyclododecane. The potassium salt of nitrocyclododecane[1] (1.193 g, 5.6 mmol) in 17 mL of Me_2SO was prepared as in the preceding preparation, using 0.237 g (5.9 mmol) of KH. To this mixture was added a solution of 0.66 g (2.8 mmol) of 1-cyano-1-nitrocyclododecane[1] in 3 mL of Me_2SO. Not only was the reaction flask exposed, as usual, to two 20-W fluorescent lights but, in addition, a 60-W incandescent bulb was held about 10 cm from the flask. As a consequence, the temperature of the reaction flask was ca. 40 °C. After 96 h the yellow reaction mixture was poured into 75 mL of water and extracted with ether and then with dichloromethane. After drying ($MgSO_4$) and removal of solvents, the residue was flash chromatographed on silica gel, using hexane–benzene (7:3). The impure β-nitro nitrile so obtained was recrystallized from 2-propanol. In this way 0.610 g (54% yield) of analytically pure 1-nitro-1′-cyano-bicyclododecane was obtained as a white solid: mp 176–178 °C; IR ($CHCl_3$) 4.44 μm (CN), 6.49 (NO_2).

Anal. Calcd for $C_{25}H_{44}N_2O_2$: C, 74.26; H, 10.89; N, 6.93. Found: C, 74.06; H, 10.66; N, 6.74.

Mechanistic Studies

Reaction of 2-Cyano-2-nitropropane with the Lithium Salt of 2-Nitropropane. A. The Effect of Light. The lithium salt of 2-nitropropane[13] (5.70 g, 60 mmol) and 2-cyano-2-nitropropane (3.29 g, 30.1 mmol) in 150 mL of Me_2SO were allowed to react with exposure to two 20-W fluorescent lights, under N_2, with stirring. After 1 h the reaction mixture was poured into 500 mL of cold water and continuously extracted with pentane for 20 h. Removal of the pentane gave a white solid, which was dissolved in ether and dried ($MgSO_4$). Removal of the ether gave 4.14 g (88% yield) of VPC-pure 2-nitro-3-cyano-2,3-dimethylbutane, mp 195–196 °C.

A duplicate experiment was conducted in total darkness for 1 h and worked up in the same way as the light reaction. Removal of the pentane gave 1.90 g of a colorless liquid, which by VPC and ^{1}H NMR analysis was 86% 2-cyano-2-nitropropane and 14% 2-nitro-3-cyano-2,3-dimethylbutane, i.e., a 6% yield of the β-nitro nitrile.

B. Inhibition Studies. Each experiment of this set employed 0.665 g (7 mmol) of the lithium salt of 2-nitropropane, 0.382 g (3.5 mmol) of 2-cyano-2-nitropropane, and 50 mL of Me_2SO and was conducted with exposure to two 20-W fluorescent lights, under N_2, with stirring. Periodically, 3-mL samples of the reaction solution were worked up and analyzed by VPC. In the absence of inhibitors, the reaction was complete in 25–30 min and when worked up after 1 h gave 2-nitro-3-cyano-2,3-dimethylbutane in 82–86% yield, mp 195–196 °C, and was pure by VPC and ^{1}H NMR.

In a duplicate experiment in which 0.025 g (0.175 mmol, 5 mol %) of di-*tert*-butyl nitroxide was present, there was no reaction whatsoever for at least 6 h. Sometime between 6 and 18 h the reaction started up and proceeded to completion. Workup after 19 h gave a white solid, which by its melting point, NMR, and VPC was the pure β-nitro nitrile.

In another duplicate experiment in which 0.073 g (0.174 mmol, 5 mol%) of galvinoxyl[17] was present, the reaction went 15% to completion in 10 min, as compared with 58% completion for the control. Whereas the control reaction was complete in 30 min, the galvinoxyl-inhibited reaction required 60 min to go to completion. In contrast to the control, the product from the galvinoxyl experiment melted from 192 to 196 °C; VPC and ^{1}H NMR analyses showed that it was at least 95% pure β-nitro nitrile.

Finally, a duplicate experiment in which 0.019 g (0.175 mmol, 5 mol %) of *p*-benzoquinone was present was carried out. Here, there was no reaction whatsoever for 25 min during which time the control reaction went to completion. It started up after 30 min and was complete after a total of 85 min. VPC and ^{1}H NMR analyses showed that the product from the *p*-benzoquinone experiment was at least 95% pure β-nitro nitrile.

Inhibition studies of the dark reaction between the lithium salt of 2-nitropropane and 2-cyano-2-nitropropane were also carried out. In the first of these 5 mol % of galvinoxyl[17] (0.073 g, 0.174 mmol) was present. This reaction (and the control) was conducted in a constant-temperature bath held at 30 °C; periodically 3-mL samples were withdrawn, worked up, and analyzed by VPC. With galvinoxyl present there was no reaction at all after 1 h. In contrast, the control reaction went 24% to completion in 1 h. After 24 h the galvinoxyl reaction was 70% complete, whereas the control was 100% complete. Workup of the control after 26 h gave the pure β-nitro nitrile, mp 195–196 °C, whereas the galvinoxyl-inhibited process yielded a pasty material. VPC and ^{1}H NMR analyses confirmed that the product from the control reaction was pure and that that from the galvinoxyl reaction contained 25–30% of the starting 2-cyano-2-nitropropane and 65–70% of the β-nitro nitrile.

A second pair of reactions was carried out in total darkness at 30 °C. Here 5 mol % (0.028 g, 0.175 mmol) of *p*-dinitrobenzene was used as the inhibitor. The *p*-dinitrobenzene reaction was completely inhibited for $2^1/_2$ h in which time the control had gone 40% to completion. After $8^1/_2$ h the *p*-dinitrobenzene reaction was only 17% complete, whereas the control was 74% complete. After $18^1/_2$ h the control reaction was complete, whereas the one containing *p*-dinitrobenzene was only 52% complete. On work up of the control after 19 h, a white solid was obtained, which by VPC and ^{1}H NMR analyses was shown to be the pure β-nitro nitrile. The experiment in which *p*-dinitrobenzene was present was worked up after 26 h; it gave a pasty white solid, which VPC and ^{1}H NMR

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(16) In this connection ref 14 is of interest.

(17) Bartlett, P. D.; Funahashi, T. *J. Am. Chem. Soc.* **1962**, *84*, 2600.

analyses revealed was 65–75% β-nitro nitrile, 25% starting 2-cyano-2-nitropropane, and a trace of a third component.

Reaction of 1-Cyano-1-nitrocyclohexane with the Potassium Salt of Nitrocyclohexane. A. The Effect of Light. A duplicate of experiment XIV employing 0.374 g (2.43 mmol) of 1-cyano-1-nitrocyclohexane and a 45-min reaction time, rather than 1 h gave 0.531g (93% yield) of the pure β-nitro nitrile, mp 176–178 °C.

This experiment was repeated in total darkness with 0.365 g (2.37 mmol) of 1-cyano-1-nitrocyclohexane and after 45 min the reaction mixture was worked up. The crude product was flash chromatographed on silica gel with hexane–benzene (8:2); this eluted 0.180 g (50% recovery) of pure 1-cyano-1-nitrocyclohexane, mp 51–52 °C. Further elution of the column with benzene gave 0.20 g of solid, which, when recrystallized from methanol, gave 0.156 g (26% yield) of the pure β-nitro nitrile, mp 176–178 °C.

B. Inhibition Studies. Each experiment of this set was carried out for 30 min with exposure to two 20-W fluorescent lights, under N_2 with stirring. The control experiment employed 0.188 g KH (4.7 mmol) in 4 mL of Me_2SO and 0.619 g (4.8 mmol) of nitrocyclohexane in 12 mL of Me_2SO. To the resulting mixture was added 0.370 g (2.4 mmol) of 1-cyano-1-nitrocyclohexane in 3 mL of Me_2SO. The usual workup gave ca. 0.7 g of crude product, which was flash chromatographed on silica gel with hexane–benzene (8:2). This resulted in the elution of 0.080 g of a mixture, which by VPC was ca. 50% starting α-nitro nitrile and 50% nitrocyclohexane. Further elution with hexane–benzene (1:1) gave 0.531 g of the β-nitro nitrile, mp 175–178 °C. Recrystallization from methanol afforded 0.471 g (83% yield) of pure 1-nitro-1′-cyanobicyclohexyl, mp 176–178 °C.

A duplicate experiment employing 0.385 g (2.5 mmol) of 1-cyano-1-nitrocyclohexane was carried out in the presence of 0.036 g (0.25 mmol) of di-*tert*-butyl nitroxide. Flash chromatography of the crude product using hexane–benzene (9:1) gave 0.327 g (85% recovery) of pure 1-cyano-1-nitrocyclohexane, mp 51–52 °C. Further elution with ethyl acetate gave none of the β-nitro nitrile.

Another duplicate of the control employed 0.370 g (2.4 mmol) of 1-cyano-1-nitrocyclohexane and was conducted in the presence of 0.040 g (0.24 mmol) of *m*-dinitrobenzene. The pink reaction product was worked up as usual and the crude product flash chromatographed on silica gel with hexane–benzene (9:1). In this way 0.293 g (79%) of the starting α-nitro nitrile (mp 51–52 °C) was recovered. The column was then eluted with ethyl acetate and this gave ca. 90 mg of a yellow solid (mp 90–135 °C), which by thin-layer chromatography consisted of the β-nitro nitrile and *m*-dinitrobenzene.

The experiment of the preceding paragraph was repeated with 0.354 g (2.3 mmol) of 1-cyano-1-nitrocyclohexane and 0.076 g (0.45 mmol) of *m*-dinitrobenzene (20 mol %). Here 0.298 g (84%) of the starting α-nitro nitrile was recovered, mp 51–52 °C. Ethyl acetate elution of the silica gel column gave 67 mg of a yellow solid, mp 76–82 °C, which was slightly impure *m*-dinitrobenzene. Thin-layer chromatography confirmed the presence of *m*-dinitrobenzene, and there was no evidence of any of the β-nitro nitrile.

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Registry No. 1-Nitro-2-cyano-2-methylheptane, 87740-86-1; 1-(nitromethyl)-1-cyanocyclohexane, 87740-87-2; 1-(nitromethyl)-1-cyanocyclododecane, 87740-88-3; 1-(α-nitroethyl)-1-cyanocyclohexane, 87740-89-4; 1-(α-nitro-*n*-propyl)-1-cyanocyclododecane, 87740-90-7; 4-nitro-3-cyano-3-methyldecane, 87740-91-8; 2-nitro-3-cyano-2,3-dimethylbutane, 29770-62-5; 1-(α-nitroisopropyl)-1-cyanocyclopentane, 29770-61-4; 1-(α-nitroisopropyl)-1-cyanocyclododecane, 87740-92-9; 1-(α-cyanoisopropyl)-1-nitrocyclopentane, 87740-93-0; 1-(α-nitrocyclopentyl)-1-cyanocyclohexane, 87740-94-1; 1-(α-cyanoisopropyl)-1-nitrocyclohexane, 29770-63-6; 1-(α-nitrocyclohexyl)-1-cyanocyclopentane, 87740-95-2; 1-nitro-1′-cyanobicyclohexyl, 85690-35-3; 1-(α-cyanoisopropyl)-1-nitrocyclodecane, 87740-96-3; 1-nitro-1′-cyanobicyclododecane, 87740-97-4; 2-cyano-2-nitroheptane, 84065-79-2; 1-cyano-2-nitrocyclohexane, 58102-55-9; 1-cyano-1-nitrocyclododecane, 84065-81-6; 2-cyano-2-nitrobutane, 84065-78-1; 2-cyano-2-nitropropane, 18992-13-7; 1-cyano-1-nitrocyclopentane, 84065-80-5; nitromethane, 75-52-5; nitroethane, 79-24-3; 1-nitropropane, 108-03-2; 1-nitroheptane, 693-39-0; lithium 2-nitropropane, 3958-63-2; 2-nitropropane, 79-46-9; nitrocyclopentane, 2562-38-1; lithium nitrocyclohexane, 51134-38-4; nitrocyclohexane, 1122-60-7; nitrocyclododecane, 1781-70-0.