Electron-Transfer Processes. XIII. Coupling Reactions of Tertiary Carbanions with α-Substituted Nitroalkanes[1]
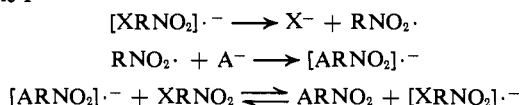
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Abstract: A free-radical chain process has been demonstrated in the reaction of 2-bromo-2-nitropropane with the anions derived from 2-nitropropane, ethylmalononitrile, ethyl 2-cyanopropionate, or 2-cyano-4,4-dimethyl-3-pentanone to yield, respectively, 2,3-dinitro-2,3-dimethylbutane, ethyl(2-nitro-2-propyl)malononitrile, ethyl 2-cyano-2-(2-nitro-2-propyl)propionate, and 2-cyano-2-(2-nitro-2-propyl)-4,4-dimethyl-3-pentanone. With the anions of diethyl ethylmalonate or ethyl 2-ethyl-3-ketobutyrate the predominant reaction of 2-bromo-2-nitropropane was bromine atom transfer. Use of 2,2-dinitropropane gave a free-radical alkylation reaction not only with the anion of 2-nitropropane but with diethyl ethylmalonate, ethyl 2-ethyl-3-ketobutyrate, and 3-methyl-2,4-pentanedione to yield, respectively, diethyl ethyl(2-nitro-2-propyl)malonate, 2-ethyl-2-(2-nitro-2-propyl)-3-ketobutyrate, and 3-methyl-3-(2-nitro-2-propyl)-2,4-pentanedione. 2-Cyano-2-nitropropane reacts with the lithium salt of 2-nitropropane to yield 2-cyano-3-nitro-2,3-dimethylbutane while ethyl 2-cyano-2-nitropropionate or the α-nitro derivative of diethyl ethylmalonate reacts with the anion to yield, respectively, ethyl 2-cyano-2-(2-nitro-2-propyl)propionate and diethyl ethyl(2-nitro-2-propyl)malonate. Catalysis of these reactions by light or by radical anions, such as sodium naphthenide or potassium nitrobenzenide, is particularly noteworthy. These processes are believed to involve radical and radical anion intermediates. Attempts to bring about aromatic alkylation reaction by electron transfer in the reaction of the anion of 2-nitropropane with *m*- or *p*-iodonitrobenzene, or *p*-nitrobenzenediazonium ion, were unsuccessful, apparently because the nitrophenyl radicals failed to add to the anion of 2-nitropropane. In DMSO solution 2,4-dinitrochlorobenzene reacts readily with nitrite ion to yield 2,4-dinitrophenol and with the anion of 2-nitropropane to give a low yield of α, 2,4-trinitrocumene.

The mechanism of Scheme I has been demonstrated for the reactions of the anion of 2-nitro-

Scheme I[a]

$$[XRNO_2] \cdot^- \longrightarrow X^- + RNO_2 \cdot$$

$$RNO_2 \cdot + A^- \longrightarrow [ARNO_2] \cdot^-$$

$$[ARNO_2] \cdot^- + XRNO_2 \rightleftharpoons ARNO_2 + [XRNO_2] \cdot^-$$

[a] R = $(CH_3)_2C$, p-$C_6H_4CH_2$, p-$C_6H_4C(CH_3)_2$; X = Cl.

propane with 2-halo-2-nitropropanes,[3,4] *o*- or *p*-nitrobenzyl chloride,[3–5] or *p*-nitrocumyl chloride.[6] The use of a variety of other anions (A⁻) has been reported for the reactions of the *p*-nitrobenzyl chloride and *p*-nitrocumyl chloride. Enolate anions will react with *p*-nitrobenzyl chloride in DMF solution[6] as well as with 2-chloro-2-nitropropane in ethanol.[3,4] α-Chloro-*p*-nitrocumene readily couples with anions such as the salts of malonic esters, l-methyl-2-naphthol, thiophenol, phenol, methanol, or hydrazoic acid.[7,8]

Other leaving groups besides chloride have been observed in Scheme I. In the para nitrobenzyl system the chain process has been observed for the dimethylsulfonium salt,[4] the trimethylammonium salt,[4,9] or the pentachlorobenzoate[6] while in the para nitro-

cumyl system numerous reactions of α,*p*-dinitrocumene have been described which follow Scheme I.[7,8]

Compounds that react *via* Scheme I (XRNO₂) readily form radical anions by one-electron reduction. However, in general the radical anions are so unstable that they cannot be observed by ordinary esr techniques, *i.e.*, in a static system. Thus, 2-chloro-2-nitropropane,[10] 2,2-dinitropropane,[10] 2-cyano-2-nitropropane,[10] *p*-iodonitrobenzene, *p*-nitrobenzyl chloride, *p*-nitrocumyl chloride, or *p*-nitrobenzyldimethylsulfonium salts all fail to form a radical anion (or dipolar radical) capable of esr detection at room temperature.[4,11]

We have, therefore, studied the reactions of 2,2-dinitropropane,[14] 2-cyano-2-nitropropane,[15] 2-ethyl-2-nitromalonic ester,[16] and several nitrohalobenzenes with the anion of 2-nitropropane and other anions in a manner similar to that employed previously for 2-chloro-2-nitropropane.[4]

Results and Discussion

Reaction of the lithium salt of 2-nitropropane (0.256 *M*) with 2-bromo-2-nitropropane (0.256 *M*) in DMF at 30 or 60°, in the dark or with illumination, produced a near quantitative yield of 2,3-dinitro-2,3-

(1) Reactions of Resonance Stabilized Anions. XXXII. Supported by a grant from the National Science Foundation.

(2) National Institutes of Health Postdoctoral Fellow, 1968–1969.

(3) G. A. Russell and W. C. Danen, *J. Amer. Chem. Soc.*, 88, 5663 (1966).

(4) G. A. Russell and W. C. Danen, *ibid.*, 90, 347 (1968).

(5) N. Kornblum, R. E. Michel, and R. C. Kerber, *ibid.*, 88, 5662 (1966).

(6) N. Kornblum, R. E. Michel, and R. C. Kerber, *ibid.*, 88, 5660 (1966).

(7) N. Kornblum, T. M. Davies, G. W. Earl, N. L. Holy, R. C. Kerber, M. T. Musser, and D. H. Snow, *ibid.*, 89, 725 (1967).

(8) N. Kornblum, T. M. Davies, G. W. Earl, G. S. Greene, N. L. Holy, R. C. Kerber, J. W. Manthey, M. T. Musser, and D. H. Snow, *ibid.*, 89, 5714 (1967).

(9) H. Shechter and R. B. Kaplan, *ibid.*, 73, 1883 (1951).

(10) L. H. Piette, P. Ludwig, and R. N. Adams, *ibid.*, 84, 4212 (1962).

(11) Trinito- or tetranitromethane radical anions are also unstable and decompose by loss of a nitro group.[12] By inference the radical anion of 1,1,1-trinitroethane must also have a short lifetime.[4,13]

(12) C. Lagercrantz and M. Yland, *Acta Chem. Scand.*, 16, 1807 (1962); C. Lagercrantz, *ibid.*, 18, 382, 1384 (1964).

(13) L. Zeldin and H. Shechter, *J. Amer. Chem. Soc.*, 79, 4708 (1957).

(14) For a preliminary report see G. A. Russell, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, 11, 100 (1970).

(15) For a preliminary report see G. A. Russell, *Chem. Soc., Spec. Publ.*, No. 24, 273 (1970); see also N. Kornblum, S. D. Boyd, and F. W. Stuchal, *J. Amer. Chem. Soc.*, 92, 5783 (1970).

(16) G. A. Russell, Abstracts, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, Div. Org. Chem., Paper No. 5.
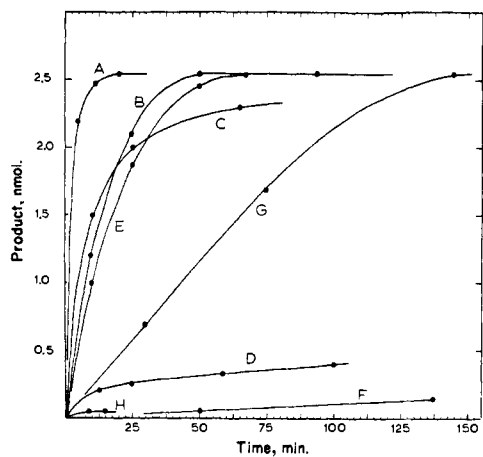
Figure 1. Coupling products isolated from the reaction of 2.56 mmol of 2-lithio-2-nitropropane in 10 ml of DMF under nitrogen with 2.56 mmol of (A) 2-bromo-2-nitropropane, 60°, dark; (B) 2-bromo-2-nitropropane, 30°, dark; (C) 2,2-dinitropropane, 60°, dark; (D) 2,2-dinitropropane, 30°, dark; (E) 2,2-dinitropropane, 30°, illuminated; (F) 2-cyano-2-nitropropane, 30°, dark; (G) 2-cyano-2-nitropropane, 30°, illuminated; (H) 2-bromo-2-nitropropane or 2,2-dinitropropane, 30°, illuminated in the presence of oxygen.
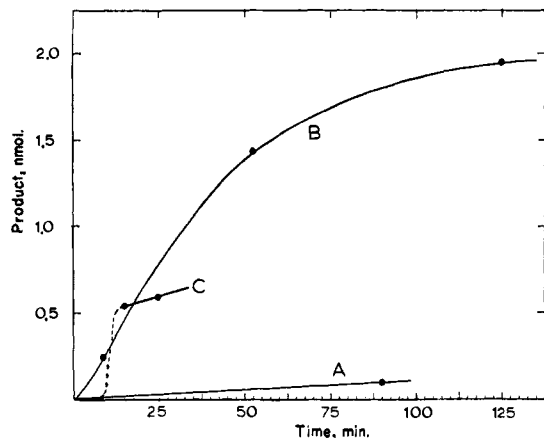

Figure 2. Formation of 2-nitro-2-methyl-3,3-dicarboethoxypentane from the reaction of 2.56 mmol of the sodium salt of diethyl ethylmalonate with 2.56 mmol of 2,2-dinitropropane in 10 ml of DMF at 30°: (A) dark; (B) illuminated; (C) dark, 0.15 mmol of potassium nitrobenzenide added between 7 and 10 min.

dimethylbutane. Reaction of the lithium salt with 2,2-dinitropropane at 30° in the dark gave a very low yield of the coupled product even after a long reaction period (Figure 1). At 60° in the dark the coupled product was formed readily. A quantitative yield of the dimer was formed when the solutions were illuminated in the absence of oxygen at 30 or 60° (Figure 1). No dimer was formed when oxygen was bubbled through the solutions.

Reaction of the lithium salt of diethyl ethylmalonate with 2-chloro-2-nitropropane will yield the mixed dimer via Scheme I.[4,17] With 2-bromo-2-nitropropane the sodium salt of the diester yields a gel which when illuminated forms a mixture of ~2 parts of 2,3-dimethyl-2,3-dinitrobutane to 1 part of the mixed dimer, 2-nitro-2-methyl-3,3-dicarboethoxypentane. Little re-

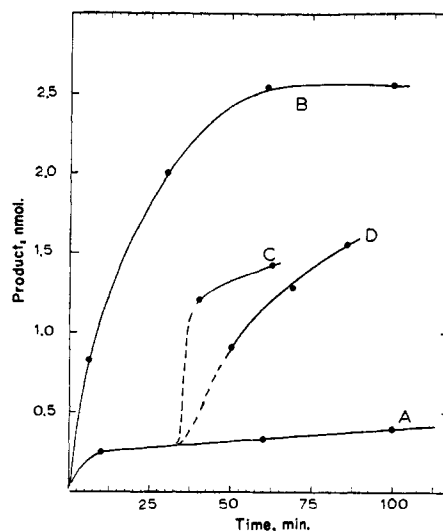(17) E. E. van Tamelen and G. van Zyl, J. Amer. Chem. Soc., 71, 835 (1949).
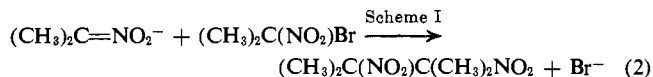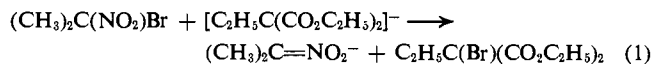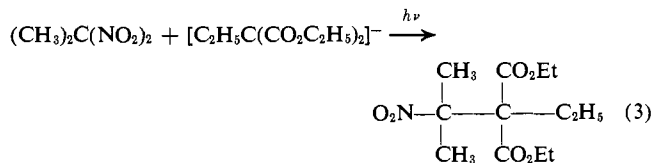

Figure 3. Formation of 2,3-dimethyl-2,3-dinitrobutane by the reaction of 2.56 mmol of 2,2-dinitropropane with 2.56 mmol of lithio-2-nitropropane in 10 ml of DMF at 30°: (A) dark; (B) illuminated; (C) dark, 1 mmol of sodium naphthalenide added after 35 min; (D) dark, 1 mmol of sodium naphthalenide added at a constant rate between 35 and 85 min.

action occurs in the dark. The failure of 2-bromo-2-nitropropane to give a high yield of coupled product with diethyl ethylmalonate is the result of bromine atom transfer[17] between the malonate anion and the bromonitro compound (reactions 1 and 2).

$$(CH_3)_2C(NO_2)Br + [C_2H_5C(CO_2C_2H_5)_2]^- \longrightarrow$$
$$(CH_3)_2C{=}NO_2^- + C_2H_5C(Br)(CO_2C_2H_5)_2 \quad (1)$$

$$(CH_3)_2C{=}NO_2^- + (CH_3)_2C(NO_2)Br \xrightarrow{\text{Scheme I}}$$
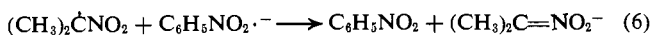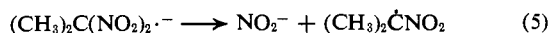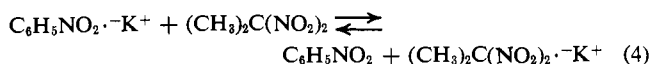$$(CH_3)_2C(NO_2)C(CH_3)_2NO_2 + Br^- \quad (2)$$

The diethyl 2-bromo-2-ethylmalonate can be isolated as a reaction intermediate. This complication is avoided by use of 2,2-dinitropropane where an atom transfer does not occur.

2,2-Dinitropropane reacts with the anion of diethyl ethylmalonate to yield only the mixed dimer (reaction 3). Again, little reaction occurs in the dark but a

$$(CH_3)_2C(NO_2)_2 + [C_2H_5C(CO_2C_2H_5)_2]^- \xrightarrow{h\nu}$$

$$O_2N-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\overset{\overset{\displaystyle CO_2Et}{|}}{\underset{\underset{\displaystyle CO_2Et}{|}}{C}}-C_2H_5 \quad (3)$$

facile coupling is observed when the reaction mixture is illuminated (Figure 2). In Figure 2 additional evidence for the chain mechanism of Scheme I is given in terms of catalysis of the dark reaction by potassium nitrobenzenide.[18] In the experiment reported the sudden addition of 0.15 mmol of potassium nitrobenzenide to a mixture of 2.56 mmol of 2,2-dinitropropane and 2.56 mmol of the anion of the diester resulted in the rapid formation of 0.55 mmol of the mixed dimer. Unfortunately, a radical anion such as nitrobenzene can both initiate and terminate the chain sequence of Scheme I, e.g., reactions 4 and 6.

(18) G. A. Russell and A. G. Bemis, Inorg. Chem., 6, 403 (1967).

$C_6H_5NO_2\cdot^-K^+ + (CH_3)_2C(NO_2)_2 \rightleftharpoons$

$$C_6H_5NO_2 + (CH_3)_2C(NO_2)_2\cdot^-K^+ \quad (4)$$

$$(CH_3)_2C(NO_2)_2\cdot^- \longrightarrow NO_2^- + (CH_3)_2\dot{C}NO_2 \quad (5)$$

$$(CH_3)_2\dot{C}NO_2 + C_6H_5NO_2\cdot^- \longrightarrow C_6H_5NO_2 + (CH_3)_2C{=}NO_2^- \quad (6)$$

Sodium naphthenide also is effective in promoting the coupling reaction between 2,2-dinitropropane and the anion of 2-nitropropane. Figure 3 shows that the addition of 1 mmol of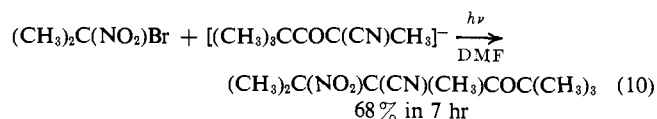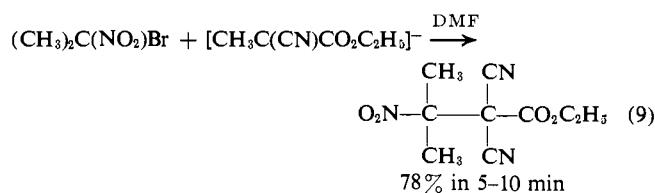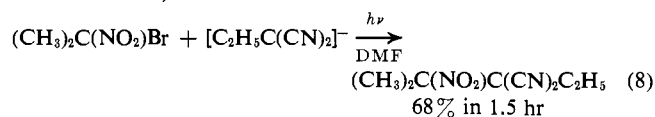 the naphthalene radical anion to a mixture of 2.56 mmol of the dinitropropane and the salt of 2-nitropropane results in the immediate formation of approximately 1 mmol of the dimer as well as the initiation of further reaction. Attempts to catalyze the reaction of azide ion or 2,6-dimethylphenoxide ion with 2-bromo-2-nitropropane by traces of the anion of 2-nitropropane failed. The salt of 2-nitropropane was consumed to yield the dimer and the other anions were not consumed to an appreciable extent.

The anion of ethyl 2-ethyl-3-ketobutyrate also gave a low yield of coupled product with 2-bromo-2-nitropropane because of bromine atom transfer. However, a good yield of coupled product was obtained by use of 2,2-dinitropropane. 3-Methyl-2,4-pentanedione also gave a good yield of coupled product with 2,2-dinitropropane when illuminated in DMF or DMSO solution (reaction 7).

$$(CH_3)_2C(NO_2)_2 + RC(X){=}C(O^-)CH_3 \xrightarrow[h\nu]{DMF}$$

$$\underset{X}{\underset{|}{(CH_3)_2C}}\overset{NO_2\ \ COCH_3}{\underset{|\quad\quad |}{-C-}}R \quad (7)$$

1a, X = CO₂C₂H₅; R = C₂H₅
b, X = COCH₃; R = CH₃
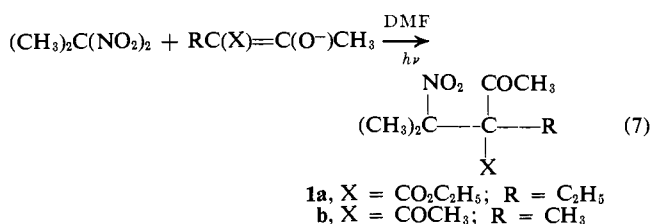
A variety of cyano-substituted anions reacted with 2-bromo-2-nitropropane without extensive bromine atom transfer. The coupled products were formed from the anions of ethylmalononitrile, ethyl α-cyanopropionate, and 2-cyano-4,4-dimethyl-3-pentanone (reactions 8–10).
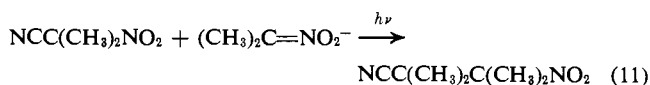
$$(CH_3)_2C(NO_2)Br + [C_2H_5C(CN)_2]^- \xrightarrow[DMF]{h\nu}$$

$$(CH_3)_2C(NO_2)C(CN)_2C_2H_5 \quad (8)$$

68% in 1.5 hr

$$(CH_3)_2C(NO_2)Br + [CH_3C(CN)CO_2C_2H_5]^- \xrightarrow{DMF}$$

$$\underset{\underset{CN}{|}}{\underset{\underset{CH_3}{|}}{O_2N{-}C}}{-}\underset{\underset{CN}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}CO_2C_2H_5 \quad (9)$$

78% in 5–10 min

$$(CH_3)_2C(NO_2)Br + [(CH_3)_3CCOC(CN)CH_3]^- \xrightarrow[DMF]{h\nu}$$

$$(CH_3)_2C(NO_2)C(CN)(CH_3)COC(CH_3)_3 \quad (10)$$

68% in 7 hr

Reactions 8–10 are presumed to occur via Scheme I. Reaction 9 yielded 78% of the coupled product in 5 min in the dark or light. However, in the presence of 5 mol % of p-dinitrobenzene only 18% of the cou-
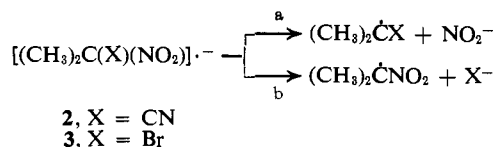
$$(CH_3)_2\dot{C}NO_2 + C_2H_5C(CO_2C_2H_5)_2]_2^-$$

$$C_2H_5\dot{C}(CO_2Et)_2 + [(CH_3)_2CNO_2]^-$$
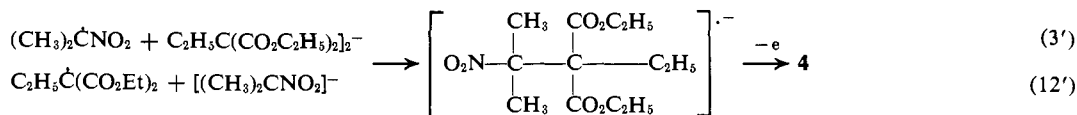
pled product could be detected in 1 hr.

2-Cyano-2-nitropropane (0.256 M) reacted with the lithium salt of 2-nitropropane (0.256 M) when illuminated to give a quantitative yield (glpc) of 2-cyano-2-nitro-2,3-dimethylbutane (isolated yield = 77%) (reaction 11). Apparently radical ion **2** decom-
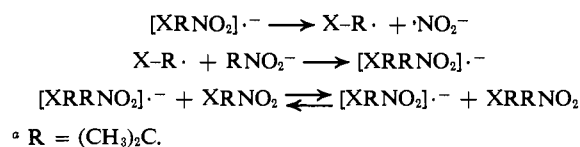
$$NCC(CH_3)_2NO_2 + (CH_3)_2C{=}NO_2^- \xrightarrow{h\nu}$$

$$NCC(CH_3)_2C(CH_3)_2NO_2 \quad (11)$$

poses solely by path a, the overall reaction sequence

$$[(CH_3)_2C(X)(NO_2)]\cdot^-\ \begin{cases} \xrightarrow{a} (CH_3)_2\dot{C}X + NO_2^- \\ \xrightarrow{b} (CH_3)_2\dot{C}NO_2 + X^- \end{cases}$$

2, X = CN
3, X = Br

being given in Scheme II.

Scheme II[a]

$$[XRNO_2]\cdot^- \longrightarrow X{-}R\cdot + \cdot NO_2^-$$

$$X{-}R\cdot + RNO_2^- \longrightarrow [XRRNO_2]\cdot^-$$

$$[XRRNO_2]\cdot^- + XRNO_2 \rightleftharpoons [XRNO_2]\cdot^- + XRRNO_2$$

[a] R = (CH₃)₂C.
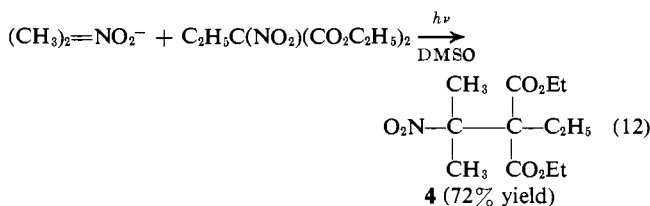
The key to successful utilization of the reactions of Schemes I or II involves the formation of an intermediate radical anion by the trapping of a radical by an anion. The presence of a nitro group in the radical anion greatly stabilizes the intermediate and facilitates its formation. Scheme II is unique in that in this process the intermediate radical does not contain the nitro substituent. In all other examples of alkylation (Scheme I) the intermediate radical has contained the nitro substituent. Moreover, process a is not restricted to the cyano substituent. The nitrocarboethoxy derivatives work well and give a good yield of coupled product with the anion of 2-nitropropane (e.g., reaction 12).

$$(CH_3)_2{=}NO_2^- + C_2H_5C(NO_2)(CO_2C_2H_5)_2 \xrightarrow[DMSO]{h\nu}$$

$$\underset{\underset{CO_2Et}{|}\ \underset{CH_3}{|}}{\underset{\underset{CH_3}{|}\ \underset{CO_2Et}{|}}{O_2N{-}C}}\quad\underset{}{\underset{}{-C{-}C_2H_5}} \quad (12)$$

4 (72% yield)

We note that **4** can be formed by either reaction 3 or 12. The key steps of Scheme I or II involved are eq 3' and 12'.

As expected, ethyl 2-cyano-2-nitropropionate (0.25 M) reacted with the anion of 2-nitropropane (0.25 M) to yield the coupled product formed by loss of nitrite from the ester in 75% yield (5 min in DMF at 25° with illumination), reaction 13. The reaction was essentially completely inhibited by 5 mol % of p-dinitrobenzene. We conclude that in Scheme II radical anions **5** and **6** react by loss of nitrite exclusively.

We have previously noted a limitation to Scheme I when the intermediate radical becomes a powerful

$$\longrightarrow \left[\underset{\underset{CH_3}{|}\ \underset{CO_2C_2H_5}{|}}{\overset{CH_3\quad CO_2C_2H_5}{\underset{}{O_2N{-}C{-}C{-}C_2H_5}}}\right]\cdot^- \xrightarrow{-e} \mathbf{4} \quad (3')$$

$$(12')$$

electron acceptor.[4] Thus, the 1,1-dinitroethyl radical prefers to undergo electron transfer with anions such as the anion of 2-nitropropane or the butylthiyl anion (Scheme III).

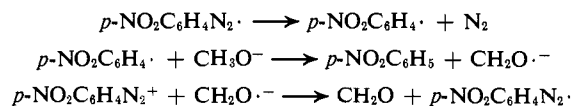Halonitroaromatic substrates might be expected to enter into alkylation reaction by the electron-transfer process (ETP) of Scheme I. The intermediacy of iodoaryl radical anions in certain aromatic sub-

$$(CH_3)_2C\!\!=\!\!NO_2^- + CH_3C(NO_2)(CN)(CO_2C_2H_5) \xrightarrow[h\nu]{DMF}$$

$$O_2N\!\!-\!\!\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\!\!-\!\!\overset{\overset{\displaystyle CN}{|}}{\underset{\underset{\displaystyle CO_2C_2H_5}{|}}{C}}\!\!-\!\!CH_3 \quad (75\%) \quad (13)$$

$$\left[R\!\!-\!\!\overset{\overset{\displaystyle CO_2C_2H_5}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}\!\!-\!\!NO_2 \right]^{\cdot-} \longrightarrow R\!\!-\!\!\overset{\overset{\displaystyle CO_2C_2H_5}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}\!\cdot \ + NO_2^-$$

5, X = $CO_2C_2H_5$; R = C_2H_5
6, X = CN; R = CH_3

Scheme III[a]

$$CH_3C(NO_2)_3 + Y^- \longrightarrow Y\cdot + [CH_3C(NO_2)_3]^{\cdot-} \longrightarrow$$
$$NO_2^- + CH_3\dot{C}(NO_2)_2$$

$$CH_3C(NO_2)_2\cdot + Y^- \longrightarrow Y\cdot + [CH_3C(NO_2)_2]^-$$

$$2Y\cdot \longrightarrow Y\text{-}Y$$

$$[CH_3C(NO_2)_2]^- + H^+ \longrightarrow CH_3C(NO_2)_2H$$
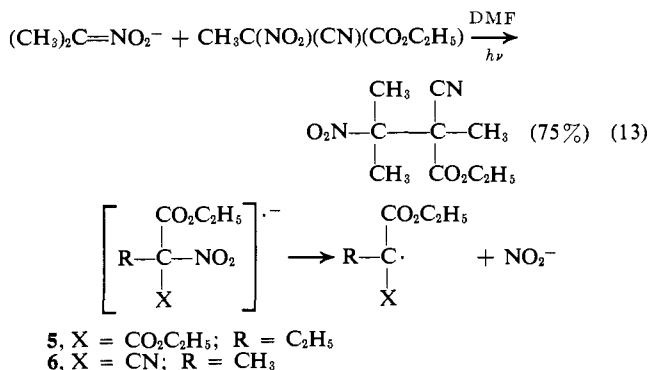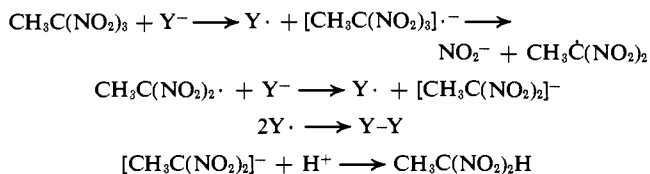
[a] $Y^- = n\text{-}C_4H_9S^-$.

stitutions has been suggested recently by Kim and Bunnett.[19] In addition the decomposition of the p-iodonitrobenzene radical anion to the para nitrophenyl radical upon electrolytic reduction has been documented as well as the facile trapping of the para nitrophenyl radical by cyanide ion.[20] However, reaction of the anion of 2-nitropropane in the dark or with illumination with p-iodonitrobenzene produced the dimer of the nitroalkane. Moreover, the para nitrophenyl radical is not trapped by nitroalkyl carbanions in aqueous solution as judged by esr spectroscopy although the phenyl radical itself is readily trapped.[21] m-Nitroiodobenzene also failed to yield the alkylation product when illuminated in the presence of the anion of 2-nitropropane. p-Nitrobenzenediazonium fluoroborate was also examined as a possible reactant in ETP similar to Scheme I. With methoxide ion a dediazonization reaction is known to occur via the para nitrophenyl radical intermediate (Scheme IV).[22]

Scheme IV

$$p\text{-}NO_2C_6H_4N_2\cdot \longrightarrow p\text{-}NO_2C_6H_4\cdot + N_2$$

$$p\text{-}NO_2C_6H_4\cdot + CH_3O^- \longrightarrow p\text{-}NO_2C_6H_5 + CH_2O\cdot^-$$

$$p\text{-}NO_2C_6H_4N_2^+ + CH_2O\cdot^- \longrightarrow CH_2O + p\text{-}NO_2C_6H_4N_2\cdot$$

In the presence of 2 M sodium nitrite in DMSO solution the diazonium ion reacted vigorously to produce 15% of p-dinitrobenzene, possibly by an

(19) J. K. Kim and J. F. Bunnett, *J. Amer. Chem. Soc.*, **92**, 7643, 7644 (1970).

(20) J. G. Lawless and M. D. Hawley, *J. Electroanal. Chem.*, **21**, 365 (1969); D. E. Bartok, W. C. Danen, and M. D. Hawley, *J. Org. Chem.*, **35**, 1206 (1970).

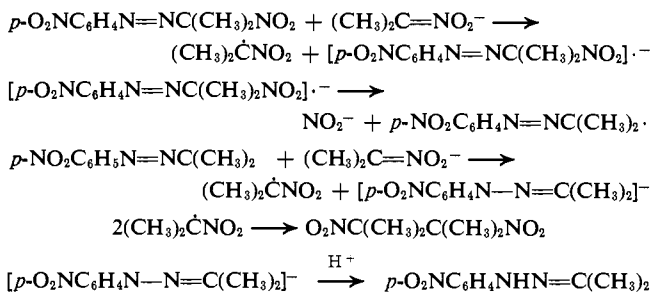(21) Unpublished results with Dr. A. R. Metcalfe.

(22) J. R. Bunnett and H. Takayama, *J. Amer. Chem. Soc.*, **90**, 5173 (1968).

ETP. The reaction of p-nitrobenzenediazonium fluoroborate with the anion of 2-nitropropane in DMSO occurs extremely rapidly to produce the 1:1 adduct, reaction 14. The adduct will react with 2
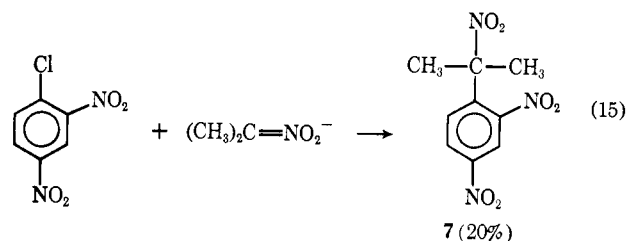
$$p\text{-}O_2NC_6H_4N_2^+ + (CH_3)_2C\!\!=\!\!NO_2^- \longrightarrow$$
$$p\text{-}O_2NC_6H_4N_2C(CH_3)_2NO_2 \quad (14)$$
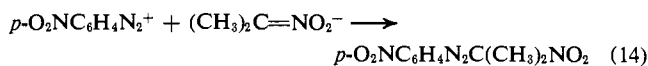
more equiv of the 2-nitro-2-propyl anion to yield acetone p-nitrophenylhydrazone and 2,3-dinitro-2,3-dimethylbutane, apparently via Scheme III'.

Scheme III'

$$p\text{-}O_2NC_6H_4N\!\!=\!\!NC(CH_3)_2NO_2 + (CH_3)_2C\!\!=\!\!NO_2^- \longrightarrow$$
$$(CH_3)_2\dot{C}NO_2 + [p\text{-}O_2NC_6H_4N\!\!=\!\!NC(CH_3)_2NO_2]\cdot^-$$

$$[p\text{-}O_2NC_6H_4N\!\!=\!\!NC(CH_3)_2NO_2]\cdot^- \longrightarrow$$
$$NO_2^- + p\text{-}NO_2C_6H_4N\!\!=\!\!NC(CH_3)_2\cdot$$

$$p\text{-}NO_2C_6H_5N\!\!=\!\!NC(CH_3)_2 + (CH_3)_2C\!\!=\!\!NO_2^- \longrightarrow$$
$$(CH_3)_2\dot{C}NO_2 + [p\text{-}O_2NC_6H_4N\!\!-\!\!N\!\!=\!\!C(CH_3)_2]^-$$

$$2(CH_3)_2\dot{C}NO_2 \longrightarrow O_2NC(CH_3)_2C(CH_3)_2NO_2$$

$$[p\text{-}O_2NC_6H_4N\!\!-\!\!N\!\!=\!\!C(CH_3)_2]^- \xrightarrow{H^+} p\text{-}O_2NC_6H_4NHN\!\!=\!\!C(CH_3)_2$$

2,4-Dinitrochlorobenzene and 2,4-dinitroanisole form radical anions upon electrolytic reduction at 25 or −70° in DMF. The radical anions decay rapidly when the electrolysis is halted. However, from the hyperfine splitting constants the radical anions are not simple one-electron reduction products. Thus 2,4-dinitrochlorobenzene appears to be a good candidate for ETP via Scheme I or III. The anion of 2-nitropropane reacted with the dinitro compound extremely rapidly in either DMF or DMSO to give a complex reaction mixture containing 2,4-dinitrophenol, 2,3-dinitro-2,3-dimethylbutane, and 16–20% of α,-2,4-trinitrocumene (reaction 15). It is hard to imagine

$$\underset{NO_2}{\underset{|}{\overset{Cl}{\overset{|}{\bigcirc}}}}\!\!NO_2 + (CH_3)_2C\!\!=\!\!NO_2^- \longrightarrow \underset{NO_2}{\overset{CH_3\!\!-\!\!\overset{NO_2}{\overset{|}{C}}\!\!-\!\!CH_3}{\bigcirc}}\!\!NO_2 \quad (15)$$

7 (20%)

reaction 15 occuring except via trapping of the 2,4-dinitrophenyl radical by the 2-nitro-2-propyl anion.

The trinitrocumene **7** failed to react with the anion of 2-nitropropane under conditions where α,p-dinitrocumene is converted into 2-(4-nitrophenyl)-1,1,2-trimethyl-1-nitropropane.[7,8] Instead, α,2,4-trinitrocumene oxidizes the anion of 2-nitropropane into its dimer. Apparently the radical anion of the α,2,4-trinitrocumene does not readily decompose to the cumyl radical. In fact, the radical anion can be detected by esr and appears to be stable in DMF at −70°. Oxidation of the anion of 2-nitropropane to the dimer also occurs with m-dinitrobenzene, 2,4-dinitroaniline, 2,4-dinitroanisole, and 2,4-dinitrophenatole via an ETP.[23]
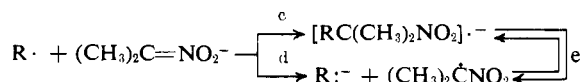
Nitrite ion also reacts readily with 2,4-dinitrochlorobenzene in DMSO solution, to yield after hydrolysis 2,4-dinitrophenol in 80% yield, apparently via ionic substitution.[24]

(23) G. A. Russell, E. G. Janzen, and E. T. Strom, *ibid.*, **86**, 1807 (1964).

$$\text{(structure)} + 2NO_2^- \xrightarrow{DMSO}$$

$$\text{(structure)} + NO + NO_2 + Cl^- \quad (16)$$
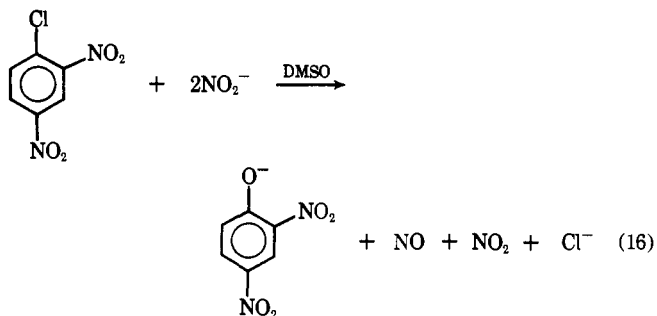
Radical attack on the nitrite ion by the 2,4-dinitrophenyl radical would have been expected to occur at the nitrogen atom[20,25] and would not have led to the phenol.

In summary, the course of an ETP between a substituted nitroalkane and an anion depends not only on the competition between steps a and b but also c and d, illustrated for the case where the anion is the

$$R\cdot + (CH_3)_2C{=}NO_2^- \xrightarrow{\begin{array}{c} c \\ d \end{array}} \begin{array}{c} [RC(CH_3)_2NO_2]\cdot^- \\ R{:}^- + (CH_3)_2\dot{C}NO_2 \end{array} \Bigg] e$$

2-nitro-2-propyl system. Step c predominates over d when R = 2-cyano-2-propyl, 2-carboethoxy-2-propyl, 2-nitro-2-propyl, para nitrobenzyl, or para nitrocumyl. However, for R = para nitrophenyl or 1,1-dinitroethyl, process d is dominant. Of course, process d cannot be easily distinguished from c followed by e or vice versa.

Experimental Section[26]

General Reaction Conditions. The coupling reactions that were performed using light catalysis were carried out in a reaction vessel which was cooled by an external water jacket (reaction volumes 10–20 ml) or an internal cooling coil (reaction volumes 50–100 ml) connected to a Haake circulating pump to maintain temperature control that was placed 6–12 in. from a 500-W GE sunlamp. Dark reactions were conducted in flasks wrapped with aluminum foil. All reactions were performed under an atmosphere of nitrogen, unless otherwise stated.

Preparation of Reactants. The following compounds were prepared by published procedures: 2-lithio-2-nitropropane,[27] 2-bromo-2-nitropropane,[28] 2,2-dinitropropane,[29] diethyl ethylmalonate,[30] ethyl 2-ethyl-3-ketobutyrate,[31] 3-methyl-2,4-pentanedione,[32] ethylmalononitrile,[33] ethyl 2-cyanopropionate,[34] 2-cyano-2-nitro-

propane,[35] m-iodonitrobenzene,[36] and p-nitrobenzenediazonium tetrafluoroborate.[37] p-Iodonitrobenzene and 2,4-dinitrochlorobenzene were commercial products.

2-Cyano-4,4-dimethyl-3-pentanone. 2-Bromo-4,4-dimethyl-5-pentanone (52.0 g) was dissolved in ethanol (200 ml) containing sodium cyanide (14.5 g) and the mixture was refluxed for 1 hr. Working up by dilution with water (500 ml) followed by ether extraction, drying of the ether layer (MgSO₄), and evaporation of the ether gave a yellow oil (37 g). Distillation of the oil gave three fractions: 24.5 g; bp 64–65° (13 mm), 9.1 g; bp 66–81° (13 mm) and 2.2 g; bp 81–88° (13 mm). The material bp 64–65° (13 mm) was found to be 1-cyano-1-tert-butyl-2-methyloxirane: ir (liquid film) no C=O absorption, 2245 (CN extremely weak), 1082, and 900 cm⁻¹; nmr (CCl₄) δ 3.18 (q, 1, J = 5.5 Hz), 1.50 (d, 3, J = 5.5 Hz), 1.08 (s, 9); mass spectrum (70 eV) m/e (relative intensity) 139 (12.4), 124 (48.7), 111 (9.6), 95 (81.0), 80 (100), 68 (93.5).

Anal. Calcd for C₈H₁₃NO: C, 69.06; H, 9.35; N, 10.07. Found: C, 69.25; H, 9.54; N, 9.92.

The middle fraction was a mixture of the above oxirane (7 parts) and the required 2-cyano-4,4-dimethyl-3-pentanone (2 parts). The final fraction was the required cyano ketone in approximately 85% purity. The cyano ketone was prepared in larger quantity from the oxirane (or mixtures of oxirane and cyano ketone) by the following procedure. The 1-cyano-1-tert-butyl-2-methyloxirane (20 g) was heated in DMF (50 ml) containing KCN (10 g) at 100° (steam bath) for 24 hr. Working up in the usual manner followed by distillation gave 14.2 g (71%) of 2-cyano-4,4-dimethyl-3-pentanone: bp 87–90° (13 mm); ir (liquid film) 2242 (C≡N) and 1728 cm⁻¹ (C=O); nmr (CCl₄) δ 3.95 (q, 1, J = 7 Hz), 1.42 (d, 3, J = 7 Hz), 1.25 (s, 9); mass spectrum (70 eV) m/e (rel intensity) 139 (3.1), 122 (12.3), 109 (75.5), 96 (39.1), 85 (100), 80 (61.5), 69 (86.2).

Anal. Calcd for C₈H₁₃NO: C, 69.06; H, 9.35; N, 10.07. Found: C, 69.12; H, 9.49; N, 9.87.

Diethyl 2-Ethyl-2-nitromalonate. Diethyl 2-ethylmalonate[30] (30 g) was stirred with fuming nitric acid (sp gr 1.5; 65 ml) for 4 days as described in the literature[38] and worked up by dilution with ice water followed by ether extraction, drying (MgSO₄), and concentration *in vacuo*. The crude product which was not purified in the literature procedure[38] was found to be stable to distillation giving 8.2 g (22%) of diethyl 2-ethyl-2-nitromalonate: bp 118–119° (4 mm); ir (liquid film) 1760 (C=O), 1571 (NO₂), and 1257 cm⁻¹ (C–O); nmr (CCl₄) δ 4.33 (q, 4, J = 7 Hz (CH₃CH₂OCO)₂), 2.25 (q, 2, J = 7 Hz, CH₃CH₂C), 1.33 (t, 6, J = 7 Hz (CH₃CH₂OCO)₂), 1.16 (t, 3, J = 7 Hz, CH₃CH₂C).

Anal. Calcd for C₉H₁₅NO₆: C, 46.35; H, 6.44; N, 6.01. Found: C, 46.50; H, 6.66; N, 6.05.

This compound could also be prepared in better yield from treatment of diethyl 2-bromo-2-ethylmalonate[39] (20 g) in DMSO (50 ml) with sodium nitrite (10.0 g) at 80–90° for 4 hr. Working up in the usual manner gave 7.1 g (40%) of diethyl 2-ethyl-2-nitromalonate, bp 119° (4 mm).

Ethyl 2-Cyano-2-nitropropionate. Ethyl 2-cyanopropionate[34] (12.4 g) was dissolved in a mixture of glacial acetic acid (40 ml) and anhydrous sodium acetate (10.0 g) cooled to 20°. Bromine (16.5 g) was added with vigorous stirring and the mixture stirred at 20–30° for 1 hr. The reaction mixture was worked up in the usual way to give on distillation 16.4 g (82%) of ethyl 2-bromo-2-cyanopropionate: bp 86–88° (13 mm); ir (liquid film) 2247 (C≡N, very weak), 1755 (C=O), and 1255 cm⁻¹ (C–O); nmr (CCl₄) δ 4.37 (q, 2, J = 7 Hz), 2.20 (s, 3), 1.42 (t, 3, J = 7 Hz); mass spectrum (70 eV) m/e (rel intensity) 207 (1.0), 205 (1.0), 192 (0.5), 190 (0.5), 180 (0.5), 178 (0.5), 162 (4.2), 160 (4.2), 135 (94), 134 (19.0), 133 (100), 132 (15.8), 108 (2.0), 107 (1.9), 106 (2.0), 105 (1.9).

Anal. Calcd for C₆H₈BrNO₂: C, 34.97; H, 3.91; N, 6.80. Found: C, 35.18; H, 3.97; N, 6.81.

Ethyl 2-bromo-2-cyanopropionate (12 g) was added dropwise to a solution of sodium nitrite (4.5 g) in DMSO (100 ml) and the temperature was maintained at 20° by external cooling. After

(24) For a pertinent discussion see A. J. Parker, *Quart. Rev., Chem. Soc.*, 16, 163 (1962).

(25) W. A. Waters, *J. Chem. Soc.*, 266 (1942).

(26) Melting points were determined in open capillary tubes using a Thomas Hoover melting point apparatus and are uncorrected. Infrared spectra were taken with a Beckman IR-12 spectrometer using sodium chloride cells. Mass spectra were determined on an Atlas Model CH4 spectrometer. Proton magnetic resonance spectra were determined with a Varian Associates Model A60 spectrometer using tetramethylsilane as an internal standard. Microanalyses were performed by Galbraith Laboratories. Gas chromatography (glpc) was performed using Aerograph Model A-90-P and A-350-B instruments and the columns used were 20% DEGS on Chromosorb W, 5% SE-52 on Chromosorb W, and 5% SF-1150 on Chromosorb W at 110–190° using helium as carrier gas. Either p-tolyl phenyl ether was used as an internal standard or m-dinitrobenzene was added in known amount to crude reaction mixtures prior to glpc for the determination of yields in those cases where indicated in experimental by "yield (glpc)" or for the data presented in Figures 1, 2, and 3.

(27) R. C. Kerber, G. W. Urry, and N. Kornblum, *J. Amer. Chem. Soc.*, 87, 4520 (1965).

(28) V. Meyer and J. Tscherniak, *Ann.*, 180, 118 (1876).

(29) R. B. Kaplan and H. Schecter, *J. Amer. Chem. Soc.*, 83, 3535 (1961).

(30) A. Michael, *J. Prakt. Chem.*, 72, 537 (1905).

(31) M. Conrad and L. Limpach, *Ann.*, 192, 153 (1878).

(32) R. G. Kelso, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Amer. Chem. Soc.*, 77, 1751 (1955).

(33) P. B. Russell and G. H. Hitchings, *ibid.*, 74, 3443 (1952).

(34) N. Zelinsky, *Ber.*, 21, 3160 (1888).

(35) J. R. Tilney-Bassett and W. A. Waters, *J. Chem. Soc.*, 3129 (1957).

(36) H. G. Dennett and E. E. Turner, *ibid.*, 476 (1926).

(37) E. B. Starkey in "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 225.

(38) C. Ulpiana, *Gazz. Chim. Ital.*, 35I, 273 (1905).

(39) C. S. Palmer and D. W. McWherter, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1944, p 245.

stirring for 1 hr the reaction mixture was worked up in the usual manner to give on distillation 5.2 g (55%) of ethyl 2-cyano-2-nitropropionate: bp 99–101° (13 mm); ir (liquid film) 2240 (C≡N, extremely weak), 1775 (C=O), 1590 (NO₂), and 1263 cm⁻¹ (C—O); nmr (CCl₄) δ 4.43 (q, 2, J = 7 Hz), 2.20 (s, 3), 1.40 (t, 3, J = 7 Hz).

Anal. Calcd for C₆H₈N₂O₄: C, 41.85; H, 4.68; N, 16.27. Found: C, 41.66; H, 4.83; N, 16.05.

The methylation of the potassium salt of ethyl cyanonitroacetate has been reported[40] to give ethyl 2-cyano-2-nitropropionate, mp 80°, and an oily material which exploded on attempted distillation and hence was assigned as methyl cyanoethoxycarbonylmethanenitronate (7).

7
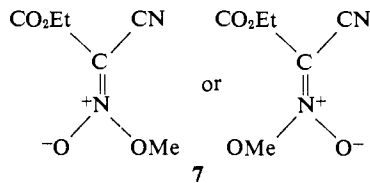
The nmr of the mp 80° solid was found to be that of one of the isomers of 7, *viz.*, in CDCl₃: δ 4.38 (q, 2, J = 7 Hz), 4.02 (s, 3, OCH₃), and 1.37 (t, 3, J = 7 Hz). The oily material (formed in equal weight amount as the solid) was determined by nmr to be a mixture of 20% of the mp 80° isomer (methoxyl at δ 4.02), 20% of ethyl 2-cyano-2-nitropropionate, and 60% of the other isomer of 7 (same chemical shifts for the ethyl protons, methoxyl at δ 4.09). No attempt was made to purify the oily material because of its explosive nature.[40]

Coupling Reactions. Reaction of the Lithium Salt of Nitropropane and Bromonitropropane or Dinitropropane. The reaction of the lithium salt of 2-nitropropane (2.56 mmol) in DME (5 ml) and either bromonitropropane (2.56 mmol) or dinitropropane (2.56 mmol) in DMF was followed by glpc giving the results shown in Figures 1 and 3. Working up these reaction mixtures in the usual way gave near quantitative yields (90–95%) of 2,3-dimethyl-2,3-dinitrobutane: mp 215–216° [lit.[17] 215.5–216°]; nmr (CDCl₃) δ 1.72 (s).

Reaction of the Sodium Salt of Diethyl 2-Ethylmalonate with Bromonitropropane. A mixture of diethyl 2-ethylmalonate (5 mmol; 9.4 g) and sodium methoxide (3.0 g) in DMF (100 ml) was deoxygenated using nitrogen for 30 min and then added to a stirred solution of bromonitropropane (5 mmol; 8.4 g) in DMF (100 ml) which had also been deoxygenated, and the resulting mixture was irradiated under the general reaction conditions at 25° for 24 hr. The initial gel formed, dissolved, leaving a clear solution. Working up by dilution with water, ether extraction, followed by aqueous washing of the ether layer, drying (MgSO₄), and concentration gave a yellow oil containing much solid material. The crude material was stirred with pentane (50 ml) at 0° and the white precipitate of 2,3-dimethyl-2,3-dinitrobutane, mp 215°, filtered off. The yield was 2.9 g. The pentane layer was concentrated and distilled to give 3.3 g of diethyl 2-ethylmalonate: bp 98–104° (13 mm) [lit.[30] 92° (10 mm)] a 3.2-g fraction, bp 104–118° (13 mm), consisting of a mixture of the malonic ester and the bromomalonic ester (glpc, nmr), a 2.5-g fraction, bp 119–125° (13 mm), which was shown by nmr and glpc to be diethyl 2-bromo-2-ethylmalonate [lit.[17] bp 121–124° (12 mm)], and a 1.5-g fraction of diethyl ethyl(2-nitro-2-propyl)malonate, bp 160–167° (13 mm) [lit.[17] bp 161–165° (14 mm)] which is further characterized below.

Reaction of Sodio Diethyl Ethylmalonate with Dinitropropane. The reaction of the sodium salt of diethyl ethylmalonate (2.56 mmol), prepared either by the reaction of sodium hydride or sodium methoxide on the malonic ester in DMF (5 ml) and dinitropropane (2.56 mmol) in DMF (5 ml), was followed by glpc and gave the results shown in Figure 2. Larger scale reactions proceeded more slowly and in slightly poorer yield. A typical example is given below. All reactions were conducted in deoxygenated DMF under nitrogen.

Diethyl ethylmalonate (4.7 g) was deoxygenated in DMF (50 ml) and added to a deoxygenated solution of dinitropropane (3.5 g) in DMF (50 ml) and the resulting solution was irradiated (lamp at 6 in. from reaction flask) at 25° for 24 hr. Working up in the usual manner followed by distillation gave a small amount of low boiling material followed by 4.4 g (65%) of ethyl ethy(2-nitro-2-propyl)malonate: bp 160–162° (13 mm) [lit.[17] 161–165° (14

mm)]; ir (liquid film) 1737 (C=O), 1558 (NO₂), and 1255 cm⁻¹ (C—O); nmr (CCl₄) δ 4.20 (q, 4, J = 7 Hz), 1.93 (q of m, 2, J ≈ 7 Hz), 1.70 (s, 6), 1.28 (t, 6, J = 7 Hz), 1.03 (t, 3, J = 7 Hz).

Reaction of the Sodium Salt of Ethyl 2-Ethyl-3-ketobutyrate with Bromonitropropane. Ethyl 2-ethyl-3-ketobutyrate (7.8 g) and sodium methoxide (2.8 g) in DMF (100 ml) were allowed to react under the usual conditions (see above) with bromonitropropane (9 g) in DMF (100 ml) for 24 hr (lamp at 6 in., 25°). The reaction mixture was worked up in the usual way and the resulting product was treated with pentane (100 ml) at 0°. The precipitated 2,3-dimethyl-2,3-dinitrobutane (2.8 g, mp 215–216) was filtered off and the filtrate was concentrated and distilled. Four products were obtained: 3.3 g of ethyl 2-ethyl-3-ketobutyrate, bp 80–85° (13 mm); 1.4 g of the above keto ester and ethyl 2-ethyl-2-bromo-3-ketobutyrate, bp range 86–95° (13 mm); 1.4 g of near pure (nmr) ethyl 2-ethyl-2-bromo-3-ketobutyrate, bp 96–105° (13 mm) [lit.[41] bp 100–102° (11 mm)], whose nmr and ir were identical with an authentic sample;[41] and 0.7 g of 2-ethyl-2(2-nitro-2-propyl)-3-ketobutyrate, bp ≈ 155° (13 mm), which was contaminated with small amounts of 2,3-dimethyl-2,3-dinitrobutane. The nitro keto ester is prepared in good yield and characterized below.

Reaction of the Sodium Salt of Ethyl 2-Ethyl-3-ketobutyrate with Dinitropropane. Ethyl 2-ethyl-3-ketobutyrate (790 mg) and sodium methoxide (290 mg) DMF (10 ml) were allowed to react under the usual conditions with dinitropropane (700 mg) in DMF (10 ml) for 10 hr (lamp at 6 in., temperature 25°). The reaction mixture was worked up as usual and the crude product purified by glpc to give 810 mg (66%) of ethyl 2-ethyl-2-(2-nitro-2-propyl)-3-ketobutyrate which was identical in all respects with the material prepared below.

The coupling reaction on ten times the above scale was much slower and gave only 4.5 g (37%) of product after 24 hr in DMF. The use of DMSO instead of DMF gave a better yield. Ethyl 2-ethyl-3-ketobutyrate (5.7 g) in DMSO (72 ml) and sodium methoxide (2.2 g) were treated under the usual conditions (lamp at 6 in., temp 25°) with dinitropropane (5.0 g) in DMSO (72 ml) for 24 hr (addition of a further quantity of sodium methoxide (0.5 g) after 5 hr increases the yield by 15–20%). The reaction mixture was worked up in the usual way and the crude product distilled to give 5.7 g (65% yield) of ethyl 2-ethyl-2-(2-nitro-2-propyl)-3-ketobutyrate: bp 153–155° (13 mm); ir (liquid film) 1747 (C=O, ester), 1724 (C=O, ketone), 1560 (NO₂), 1362 (NO₂), and 1255 cm⁻¹ (C–O); nmr (CCl₄) δ 4.25 (q, 2, J = 7 Hz), 2.2 (s, 3), 1.78 (q of m, 2, J ≈ 7 Hz), 1.67 (s, 6), 1.31 (t, 3, J = 7 Hz), 0.95 (t, 3, J ≈ 7 Hz); mass spectrum (70 eV) m/e (rel intensity) 199 (3.8), 198 (3.8), 157 (100), 156 (44.4), 129 (51.1), 111 (57.5), 95 (7.3), 87 (6.2), 83 (38).

Anal. Calcd for C₁₁H₁₉NO₅: C, 53.88; H, 7.75; N, 5.71. Found: C, 54.07; H, 8.07; N, 5.48.

Reaction of the Sodium Salt of 3-Methyl-2,4-pentanedione with Dinitropropane. Sodium methoxide (290 mg) and 3-methyl-2,4-pentanedione (570 mg) in DMF (10 ml) were treated with dinitropropane (700 mg) under the usual conditions for 24 hr. Working up in the usual manner gave, after recrystallization from carbon tetrachloride–pentane, 460 mg (45%) of 3-methyl-3-(2-nitro-2-propyl)-2,4-pentanedione: mp 78°; ir (Nujol mull) 1722 (C=O), 1700 (C=O), and 1545 cm⁻¹ (NO₂); nmr (CCl₄) δ 2.17 (s, 6, [COCH₃]₂), 1.68 (s, 6, –C(CH₃)₂NO₂), 1.58 (s, 3, CCH₃); mass spectrum (70 eV) m/e (rel intensity) 155 (9.4), 129 (2.1), 144 (8.5), 113 (100), 112 (11.9), 111 (15.2), 97 (26.2), 95 (28.7).

Anal. Calcd for C₉H₁₅NO₄: C, 53.73; H, 7.46; N, 6.97. Found: C, 53.94; H, 7.60; N, 6.87.

The use of DMSO instead of DMF raised the yield to 63% (24 hr).

Reaction of the Sodium Salt of Ethylmalononitrile with Bromonitropropane. Ethylmalononitrile (470 mg) and sodium methoxide (300 mg) were allowed to react under the usual conditions with 2-bromo-2-nitropropane (840 mg) in DMF (10 ml) for 1.5 hr. Working up in the usual way, followed by recrystallization from pentane gave 610 mg (68% yield) of ethyl (2-nitro-2-propyl)malonitrile: mp 58°; ir (Nujol mull) 2257 (C≡N extremely weak), and 1552 cm⁻¹ (NO₂); nmr (CCl₄) δ 2.00 (m, 2, J ≈ 7 Hz), 1.92 (s, 6), 1.24 (m, 3, J ≈ 7 Hz); mass spectrum (70 eV) m/e (rel intensity) 135 (13.4), 107 (100), 93 (10.1), 79 (5.2).

Anal. Calcd for C₈H₁₁N₃O₂: C, 53.04; H, 6.08; N, 23.20. Found: C, 52.81; H, 5.97; N, 22.95.

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Reaction of the Sodium Salt of Ethyl 2-Cyanopropionate and Bromonitropropane. Ethyl 2-cyanopropionate (6.4 g) and sodium methoxide (2.8 g) in DMF (100 ml) were treated under the usual conditions with 2-bromo-2-nitropropane (8.4 g) in DMF (100 ml) for 5–10 min. Working up in the usual way followed by distillation gave 7.8 g (72% yield) of ethyl 2-cyano-2-(2-nitro-2-propyl)propionate: bp 170–173° (13 mm) or 155° (4 mm); ir (liquid film) 2245 (C≡N), 1753 (C=O), 1564 (NO₂) and 1257 cm⁻¹ (C–O); nmr (CCl₄) δ 4.30 (q, 2, J = 7 Hz), 1.85 (s, 3), 1.80 (s, 3), 1.67 (s, 3), 1.37 (t, 3, J = 7 Hz); mass spectrum (70 eV) m/e (rel intensity) 214 (0.3), 168 (4.8), 140 (0.6), 124 (10.4), 113 (2.3), 96 (100), 95 (34.7), 80 (4.7), 69 (18.0).

Anal. Calcd for C₉H₁₄N₂O₄: C, 50.43; H, 6.58; N, 13.07. Found: C, 50.21; H, 6.76; N, 12.90.

This reaction was also performed on small scale and yields were estimated by glpc. The reaction of the sodium salt of the cyano ester (0.25 M) and bromonitropropane (0.25 M) in DMF was found to be complete in 5 min at 25° both in dark and using the light source (yield ≈ 78%). In the presence of 0.0125 M p-dinitrobenzene (5 mol %) the yield after 1 hr was only 18%.

Reaction of the Sodium Salt of 2-Cyano-4,4-dimethyl-3-pentanone with Bromonitropropane. Sodium methoxide (280 mg) and 2-cyano-4,4-dimethyl-3-pentanone (700 mg) in DMF (10 ml) were mixed under the usual conditions with 2-bromo-2-nitropropane (900 mg) in DMF (10 ml) and allowed to react for 7 hr. Working up in the usual manner gave a sticky solid which was purified by glpc to give 110 mg of 2,3-dimethyl-2,3-dinitrobutane, mp 215–216°, and 770 mg (68%) of 2-cyano-2-(2-nitro-2-propyl)-4,4-dimethyl-3-pentanone: mp 60° (from hexane); ir (Nujol mull) 2245 (C≡N), 1717 (C=O), and 1552 cm⁻¹ (NO₂); nmr (CCl₄) δ 1.87 (s, 3), 1.78 (s, 3), 1.67 (s, 3), 1.42 (s, 9); mass spectrum (70 eV) m/e (rel intensity) 226 (0.3), 180 (0.7), 162 (5.2), 125 (0.7), 96 (52.1), 85 (20.9), 69 (3.0), 57 (100).

Anal. Calcd for C₁₁H₁₈N₂O₃: C, 58.40; H, 7.96; N, 12.39. Found: C, 58.35; H, 7.98; N, 12.24.

Reaction of the Lithium Salt of 2-Nitropropane and 2-Cyano-2-nitropropane. The lithium salt of nitropropane (285 mg) in DMF (5 ml) was allowed to react with 2-cyano-2-nitropropane (238 mg) in DMF (5 ml) under the usual conditions for 3 hr. Working up in the usual manner gave 300 mg (77%) of 2-cyano-2,3-dimethyl-4-nitrobutane: mp 191–192° (lit.³⁵ mp 194°); nmr (CDCl₃) δ 1.73 (s, 1), 0.70 (s, 1). The results for reactions under other conditions were determined by glpc and are shown in Figure 1.

Reaction of the Lithium Salt of 2-Nitropropane and Diethyl Ethylnitromalonate. The lithium salt of 2-nitropropane (2.5 g) in DMSO (50 ml) was allowed to react under the usual conditions with diethyl ethylnitromalonate (5.8 g) in DMSO (50 ml) for 24 hr. The reaction mixture was worked up in the usual manner to give 2,3-dimethyl-2,3-dinitrobutane (≈300 mg) and 4.9 g (72%) of diethyl ethyl(2-nitro-2-propyl)malonate, bp 159–161° (13 mm), identical with the compound previously described. The use of DMF gave only a 20% yield after 24 hr.

Reaction of the Lithium Salt of 2-Nitropropane with Ethyl 2-Cyano-2-nitropropionate. The lithium salt of 2-nitropropane (240 mg) in DMF (5 ml) was allowed to react with ethyl 2-cyano-2-nitropropionate (430 mg) in DMF (10 ml) under the usual conditions for 5 min. Working up in the usual way followed by glpc gave 540 mg (75%) of ethyl 2-cyano-2-(2-nitro-2-propyl)propionate identical in all respects with the material prepared above. In the presence of 5 mol % (21 mg) of dinitrobenzene the yield (glpc) was only 7% after 1 hr.

Reaction of p-Nitrobenzenediazonium Tetrafluoroborate with Nitrite Ion in DMSO. p-Nitrobenzenediazonium tetrafluoroborate (237 mg, 1 mmol) was added in one portion and with vigorous stirring to 10 ml of 2 M sodium nitrite in DMSO. A vigorous reaction took place, nitrogen being evolved. The reaction was worked up by dilution with water and chloroform extraction. The crude extract was concentrated and 114 mg of trinitrotoluene (0.5 mmol) was added and the yield of p-dinitrobenzene (singlet at δ 8.43) was estimated by nmr. Comparison of the standard TNT peak at δ 8.85 gave a yield of 15% p-dinitrobenzene. Chromatography on alumina of a duplicate reaction gave p-dinitrobenzene, mp 172–173° (lit.³⁷ mp 173°), as the only identifiable product.

Reaction of p-Nitrobenzenediazonium Tetrafluoroborate with the Lithium Salt of 2-Nitropropane. The lithium salt of 2-nitropropane (95 mg; 1 mmol) was added to a solution of p-nitrobenzenediazonium tetrafluoroborate (205 mg; 1 mmol) in DMSO (10 ml). Working up in the usual way followed by recrystallization of the crude product from hexane gave 0.2 g of 2-(p-nitrophenylazo)-2-nitropropane: mp 104° (lit.⁴² 104°).

The above reaction was repeated using 3 mmol of the lithium salt of 2-nitropropane under nitrogen and in light for 3 hr. Working up in the usual manner followed by chromatography on silica gel using benzene–hexane mixtures gave 150 mg of 2,3-dimethyl-2,3-dinitrobutane, mp 215–216°, and 150 mg of acetone p-nitrophenylhydrazone, mp 148–149°, which did not depress the melting point of authentic material prepared from acetone and p-nitrophenylhydrazine hydrochloride.

Reaction of the Lithium Salt of 2-Nitropropane with 2,4-Dinitrochlorobenzene. The lithium salt of 2-nitropropane (1.0 g) in DMF (10 ml) was mixed with 2,4-dinitrochlorobenzene (2.0 g) in DMF (10 ml) and the mixture was stirred at 25° for 15 min. Working up by dilution with water followed by ether extraction gave a dark material which was chromatographed on silica gel using benzene–hexane to give 230 mg of 2,3-dimethyl-2,3-dinitrobutane, mp 215–216° (from ethanol), and 400 mg (16%) of α,2,4-trinitrocumene: mp 95° (ethanol or benzene–pentane); nmr (CDCl₃) δ 8.77 (1, d, J = 2.5 Hz), 8.55 (1, d of d, J = 8.85 and 2.5 Hz), 7.92 (1, d, J = 8.85 Hz), 2.10 (s, 6); mass spectrum (70 eV) m/e (rel intensity) 209 (100), 179 (11.4), 164 (9.3), 149 (7.2), 133 (5.0), 115 (16.2), 91 (12.8).

Anal. Calcd for C₉H₉N₃O₆: C, 42.35; H, 3.53; N, 16.47. Found: C, 42.49; H, 3.52; N, 16.59.

Acidification of the aqueous solution followed by extraction with chloroform gave a dark residue which contained DMF (washing with water removed the phenolic material as well as the DMF). Chromatography on silica gel using 50% benzene–ether gave 310 mg of 2,4-dinitrophenol (recrystallized from benzene–hexane): mp 111–112° (lit.⁴³ 113°).

The reaction proceeded to much the same extent in DMSO (yield of α,2,4-trinitrocumene ≈ 20%). Conducting the reaction in the presence of oxygen (vigorous shaking in an oxygen atmosphere) virtually prevented all α,2,4-trinitrocumene formation.

Reaction of 2,4-Dinitrochlorobenzene with Sodium Nitrite. Sodium nitrite (1.75 g; 22 mmol) was added to a stirred solution of 2,4-dinitrochlorobenzene (2.0 g; 10 mmol) in DMSO (15 ml). The solution warmed spontaneously and a vigorous evolution of nitrogen oxides took place. After 5 min the solution was diluted with water (100 ml) and extracted with ether. The ether layers were found to contain no organic material (other than DMSO). The aqueous layer was acidified with concentrated HCl and the yellow crystalline material was filtered off. Recrystallization from hot water gave 1.34 g (80%) of 2,4-dinitrophenol, mp 112–113° (lit.⁴³ 113°). No 1,2,4-trinitrobenzene was detected.

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