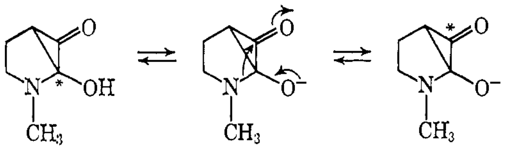
Work is continuing on the application of this rearrangement to other systems.

(22) Another mechanism consistent with the observed scrambling of label is equilibration in **18** *via* **18′** and **18″**. Further data that reflect



18 18′ 18″

on these mechanisms and further applications of this reaction will be presented in our full paper.

(23) National Science Foundation Predoctoral Fellow, 1967–1970.

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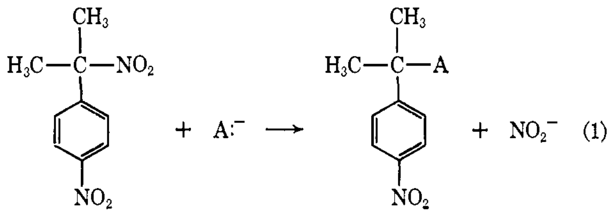
Received June 22, 1970

A New Reaction of α-Nitro Esters, Ketones, and Nitriles and α,α-Dinitro Compounds

Sir:

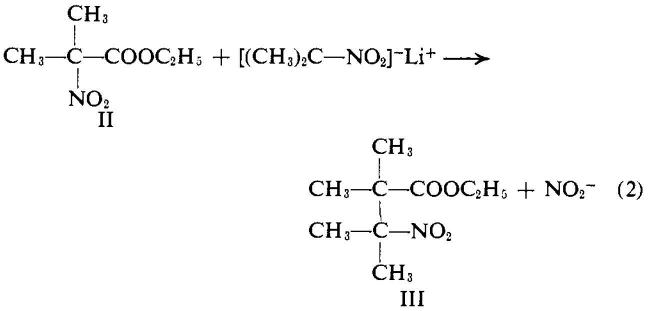
The aliphatic nitro group of α,*p*-dinitrocumene (I) is readily replaced by a variety of anions (eq 1).[1] We



I

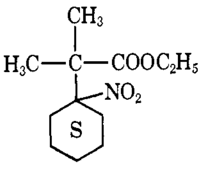
now report a new set of reactions in which displacement of a nitro group is observed in purely aliphatic systems. These reactions take place readily at room temperature and give excellent yields of pure products. They are noteworthy for providing very highly branched compounds which, at best, would be exceedingly difficult to prepare by any other means.

For example, the reaction of eq 2 takes place at room temperature and gives a 95% yield of pure product. Significantly, ethyl α-chloroisobutyrate, $(CH_3)_2C(Cl)COOC_2H_5$, reacts far less rapidly than the α-nitro ester and, what little reaction does occur, does not follow the pattern of eq 2. With ethyl α-bromoisobutyrate, $(CH_3)_2CBrCOOC_2H_5$, the reaction with the lithium salt of 2-nitropropane is again slower than with the α-nitro ester and, again, the reaction pattern of eq 2 is not followed; instead, a complex set of products is formed. Clearly, the displacement of the nitro group of ethyl α-nitroisobutyrate (II) by the 2-nitropropane anion is not an SN2 process.[2]

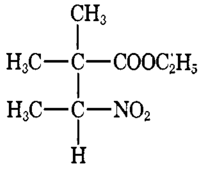


$$CH_3-\underset{\underset{\text{II}}{NO_2}}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-COOC_2H_5 + [(CH_3)_2C-NO_2]^-Li^+ \longrightarrow \begin{array}{l} \quad CH_3 \\ CH_3-C-COOC_2H_5 \\ CH_3-C-NO_2 \\ \quad CH_3 \\ \quad \text{III} \end{array} + NO_2^- \quad (2)$$

The reaction of α-nitro esters with nitroparaffin salts appears to have wide applicability; when II is treated with the salt of nitrocyclohexane the corresponding alkylate IV is obtained in 82% yield. The salts of primary nitroparaffins may also be employed and, indeed, it is easy to isolate the monoalkylate; thus, with the lithium salt of nitroethane, V is obtained in 88% yield. In the same way, the reaction of the ethyl ester of α-nitrocyclohexanecarboxylic acid (VI) with the salt of nitrocyclohexane gives VII in 96% yield, while the salt of 2-nitropropane produces the pure β-nitro ester VIII in 94% yield.

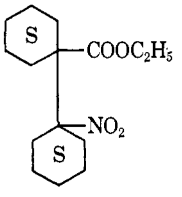


IV

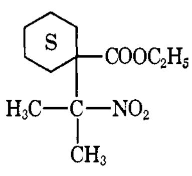


$$\begin{array}{l} \qquad\quad CH_3 \\ H_3C-C-COOC_2H_5 \\ H_3C-C-NO_2 \\ \qquad\quad H \end{array}$$

V

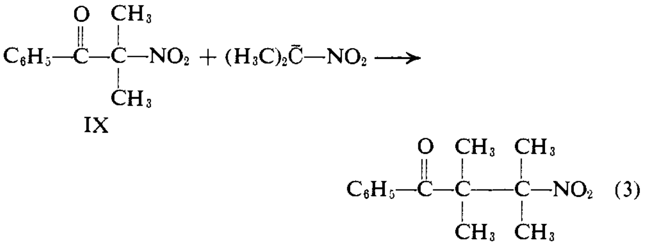


VII



VIII

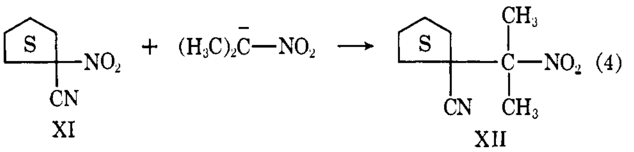
The nitro group of α-nitro ketones is also readily replaced. The reaction of eq 3 takes place in 30 hr in DMSO but requires only 3 hr in hexamethylphosphoramide; the yield of β-nitro ketone X is 80–85%. Here again it is significant that α-bromoisobutyrophenone gives a complex mixture of products and that α-chloroisobutyrophenone reacts less rapidly than α-nitroisobutyrophenone (IX).[2]



$$C_6H_5-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-NO_2 + (H_3C)_2\bar{C}-NO_2 \longrightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-NO_2 \quad (3)$$

IX X

α-Nitro nitriles also react cleanly. For example, the reaction of nitro nitrile XI is complete after 4 hr and gives an 84% yield of the pure product (eq 4). Treatment of α-nitroisobutyronitrile with the salt of 2-nitropropane gives XIII (90% yield in 1 hr); with the salt



XI XII

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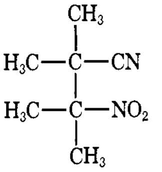
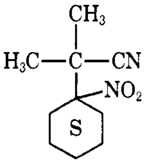
(1) N. Kornblum, T. M. Davies, G. W. Earl, G. S. Greene, N. L. Holy, R. C. Kerber, J. W. Manthey, M. T. Musser, and D. H. Snow, *J. Amer. Chem. Soc.*, **89**, 5714 (1967).

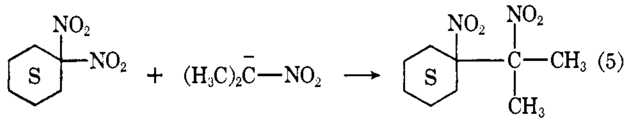
(2) The matter of mechanism is discussed in the accompanying communication: N. Kornblum and S. D. Boyd, *ibid.*, **92**, 5784 (1970).

of nitrocyclohexane, XIV is produced in 92% yield after 2 hr.


XIII


XIV

The displacement of a nitro group from α,α-dinitro compounds is an especially facile process. In DMSO the reaction of eq 5 is complete after 15 min and provides a 91% yield of XV. In DMSO (or in DMF) the salts of 2-nitropropane and nitrocyclohexane react rapidly with 2,2-dinitropropane to give the corresponding dinitro compounds, 2,3-dinitro-2,3-dimethylbutane and XV, in 82–85% yields.


XV

As a typical example: the lithium salt of 2-nitropropane[3] (14.3 g) is placed in a dry flask fitted with a stirrer and a rubber stopple. The system is swept with nitrogen for 0.5 hr and then 375 ml of DMSO (distilled from calcium hydride and stored under nitrogen) is introduced through the stopple using a hypodermic syringe. This is followed by the addition of 12.43 g of ethyl α-nitroisobutyrate[4] and then the nitrogen flow is terminated. The stirred mixture is exposed to two 20-W ordinary fluorescent lights[5] for 11 hr, after which time the resulting yellow solution is poured into ice water and extracted with ethyl ether. The ether solution is washed with water, dried, and evaporated. Distillation of the residue gives 14.87 g (95% yield) of pure III: bp 69.5–70° (1 mm); $n^{20}D$ 1.4456. *Anal.* Calcd for $C_9H_{17}NO_4$: C,53.20; H, 8.37; N, 6.89; mol wt, 203. Found: C, 53.36; H, 8.56; N, 7.12; mol wt, 205.[6]

Acknowledgment. We thank Eli Lilly and Company and the Purdue Research Foundation for generous support. We are also indebted to the Commercial Solvents Corporation, Crown Zellerbach Corporation, and Dow Chemical Company for gifts of nitroparaffins, DMSO, and HMPA, respectively.

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(3) R. C. Kerber, G. W. Urry, and N. Kornblum, *J. Amer. Chem. Soc.*, **87**, 4525 (1965).

(4) N. Kornblum, R. K. Blackwood, and J. W. Powers, *ibid.*, **79**, 2507 (1957).

(5) Reactions employing α-nitro esters and nitriles and α,α-dinitro compounds when conducted in total darkness proceed at a considerably slower rate; with α-nitro ketones no light effect is noted.

(6) Satisfactory elemental analyses and nmr and ir spectra were obtained for all new compounds.

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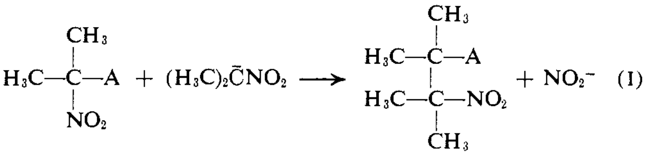
Received July 13, 1970

Concerning the Mechanism of Displacement of a Nitro Group from α-Nitro Esters, Ketones, and Nitriles and from α,α-Dinitro Compounds by Nitroparaffin Salts

Sir:

The accompanying communication[1] describes a new and general reaction—the displacement of a nitro group from α-nitro esters, ketones, and nitriles and α,α-dinitro compounds by nitroparaffin salts. We now discuss the matter of mechanism; specifically, the reactions of eq 1 have been studied.

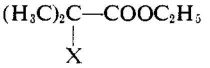


$$H_3C-\underset{NO_2}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-A + (H_3C)_2\bar{C}NO_2 \longrightarrow \begin{matrix} CH_3 \\ | \\ H_3C-C-A \\ | \\ H_3C-C-NO_2 \\ | \\ CH_3 \end{matrix} + NO_2^- \quad (1)$$

Ia, A = $COOC_2H_5$
b, A = COC_6H_5
c, A = CN
d, A = NO_2

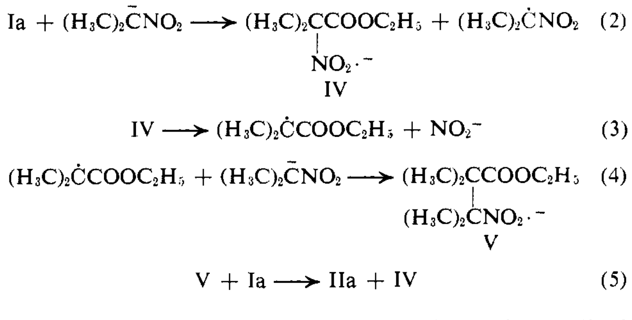
IIa, A = $COOC_2H_5$
b, A = COC_6H_5
c, A = CN
d, A = NO_2

Significantly, ethyl α-chloroisobutyrate (IIIa) and ethyl α-bromoisobutyrate (IIIb) react less rapidly with the lithium salt of 2-nitropropane than does ethyl α-nitroisobutyrate (Ia). Indeed the α-chloro ester hardly reacts at all under conditions which result in complete reaction with the α-nitro ester. Furthermore, whereas the α-nitro ester Ia gives (eq 1) a 95% yield of IIa, treatment of the α-bromo ester IIIb with the lithium salt of 2-nitropropane produces a complex set of products from which a 9% yield of IIa is isolated. It is also of interest that the reaction of ethyl α-nitroisobutyrate (Ia) with the 2-nitropropane anion is greatly accelerated by light.[1] Clearly, the displacement of a nitro group from the tertiary carbon of Ia is not an S_N2 process, a conclusion which accords with the fact that clean C-alkylation, rather than O-alkylation, of the 2-nitropropane anion is observed.[2] These facts, and the evidence presented below, lead us to propose the chain mechanism of eq 2–5.



$$(H_3C)_2\underset{X}{\underset{|}{C}}-COOC_2H_5$$

IIIa, X = Cl
b, X = Br



$$Ia + (H_3C)_2\bar{C}NO_2 \longrightarrow \underset{IV}{(H_3C)_2\underset{NO_2\cdot^-}{\underset{|}{C}}COOC_2H_5} + (H_3C)_2\dot{C}NO_2 \quad (2)$$

$$IV \longrightarrow (H_3C)_2\dot{C}COOC_2H_5 + NO_2^- \quad (3)$$

$$(H_3C)_2\dot{C}COOC_2H_5 + (H_3C)_2\bar{C}NO_2 \longrightarrow \underset{V}{(H_3C)_2\underset{(H_3C)_2CNO_2\cdot^-}{\underset{|}{C}}COOC_2H_5} \quad (4)$$

$$V + Ia \longrightarrow IIa + IV \quad (5)$$

Strong support for a chain reaction involving radical anions is provided by the fact that 5 mol % *p*-dinitro-

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(1) N. Kornblum, S. D. Boyd, and F. W. Stuchal, *J. Amer. Chem Soc.*, **92**, 5783 (1970).

(2) R. C. Kerber, G. W. Urry, and N. Kornblum, *ibid.*, **87**, 4520 (1965).