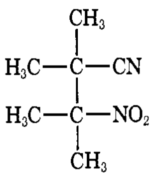
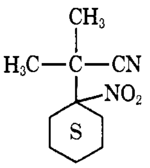
of nitrocyclohexane, XIV is produced in 92% yield after 2 hr.



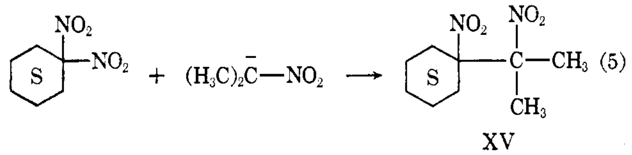
$$\begin{array}{c} \mathrm{CH_3} \\ | \\ \mathrm{H_3C-C-CN} \\ | \\ \mathrm{H_3C-C-NO_2} \\ | \\ \mathrm{CH_3} \end{array}$$

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); $n^{20}\mathrm{D}$ 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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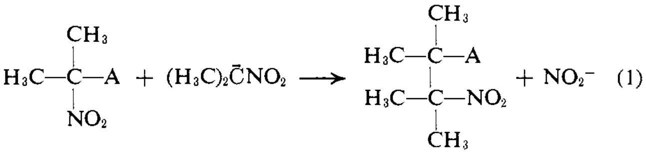
Concerning the Mechanism of Displacement of a Nitro Group from α-Nitro Esters, Ketones, and Nitriles and from α,α-Dinitro Compounds by Nitroparaffin Salts

Sir:

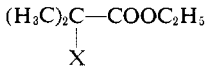
The accompanying communication[1] describes a new and general reaction—the displacement of a nitro group from α-nitro esters, ketones, and nitriles and α,α-dinitro compounds by nitroparaffin salts. We now discuss the matter of mechanism; specifically, the reactions of eq 1 have been studied.



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

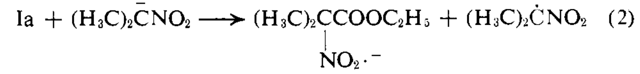
Ia, A = $COOC_2H_5$	IIa, A = $COOC_2H_5$
b, A = COC_6H_5	b, A = COC_6H_5
c, A = CN	c, A = CN
d, A = NO_2	d, A = NO_2

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.



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

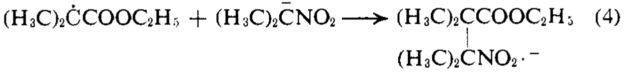
IIIa, X = Cl
b, X = Br



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

IV

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



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

V

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

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).

benzene (*p*-DNB) completely inhibits the reaction of ethyl α-nitroisobutyrate with the lithium salt of 2-nitropropane.[2] Only after 4.5 hr does the reaction begin, and by this time a parallel reaction conducted in the absence of *p*-DNB is 98% complete.

Evidence for the involvement of free-radical intermediates has been obtained by using galvinoxyl, which is known to be an efficient scavenger for free radicals.[3] Five mole per cent of galvinoxyl completely stops the reaction of ethyl α-nitroisobutyrate with the lithium salt of 2-nitropropane for 2.5 hr, after which the reaction slowly starts up; even after 5 hr the reaction has gone only 10%. In contrast, without galvinoxyl, the reaction proceeds 84% in 2.5 hr and is complete in 5 hr.[3a]

In the same way, the reaction of α-nitroisobutyrophenone (Ib) with the salt of 2-nitropropane (eq 1) is completely inhibited for 30 min by either 5 mol % *p*-DNB or 5 mol % galvinoxyl; in the absence of these inhibitors the reaction proceeds 35% to completion in 30 min.[3a] We conclude that the displacement of a nitro group from the α-nitro ketone proceeds by a chain sequence completely analogous to that of eq 2–5.

The reaction of 2-cyano-2-nitropropane (Ic) with the 2-nitropropane anion exhibits the same characteristics as those employing the α-nitro ester Ia and the α-nitro ketone Ib; at the 5 mol % level the presence of *p*-DNB results in a dead period of 2.5 hr after which the reaction begins. With 5 mol % of galvinoxyl the reaction is completely inhibited for 1 hr. In the absence of *p*-DNB and galvinoxyl the reaction proceeds 23% in 1 hr and 47% in 2.5 hr.[3a] Clearly, displacement of a nitro group from the α-nitro nitrile is a chain process. A mechanism analogous to that of eq 2–5, involving the $(H_3C)_2C(CN)NO_2\cdot^-$ radical anion and the $(H_3C)_2\dot{C}CN$ radical, is easily envisioned.

When conducted in DMSO the reaction between 2,2-dinitropropane (Id) and the lithium salt of 2-nitropropane is complete in 2 min but, if 5 mol % *p*-DNB is present, it proceeds only 10% in this time. In DMF, galvinoxyl at the 5 mol % level completely stops the reaction for 90 min, and even after 210 min the reaction goes only 8%.[3a] In contrast, the reaction in DMF is 99% complete after 90 min. As in the preceding cases, it is apparent that we deal with a chain reaction. Here again it is reasonable to presume that a radical-anion free-radical mechanism, fully analogous to that of eq 2–5, is involved.

The idea that an aliphatic nitro group is capable of accepting one electron and that the resulting radical anion, by loss of nitrite ion, gives a free radical (eq 2 and 3) is derived from the pioneering work of Hoffmann, *et al.*[4] However, where the earlier workers employed metallic sodium, or electrochemical reduction, as the source of electrons, the present study uses nitroparaffin salts. It is quite remarkable that such a "low-pressure" source of electrons as a nitroparaffin anion is able to bring about the transformations of eq 1 and of the accompanying communication.[1]

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(3) P. D. Bartlett and T. Funahashi, *J. Amer. Chem. Soc.*, **84**, 2600 (1962).

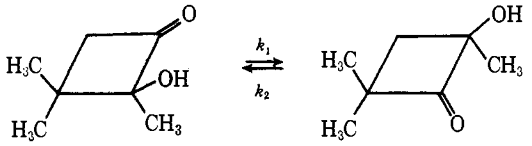
(3a) NOTE ADDED IN PROOF. It has now been found that 5 mol % of di-*tert*-butylnitroxide (or 5 mol % of *p*-benzoquinone) also inhibits these reactions.

(4) A. K. Hoffmann, W. G. Hodgson, D. L. Maricle, and W. H. Jura, *ibid.*, **86**, 631 (1964); also see H. Sayo, Y. Tsukitani, and M. Masui, *Tetrahedron*, **24**, 1717 (1968).

Ketol Rearrangements of 2-Hydroxy-2-methylcyclobutanones

Sir:

Secondary reactions have made the study of the photocyclization of 2,3-alkanediones difficult. In the presence of acids,[1a,2a] bases,[1b,c] and some metal salts,[1b,2] the product 2-hydroxy-2-methylcyclobutanones rearrange. These catalysts are so effective that as adventitious impurities they cause interconversion during photolysis and product isolation. Hence, this rearrangement is much more facile than those of cyclobutanones[3] and other tertiary ketols[1,2] previously reported. The two-component system (**1** ⇄ **2**) was convenient for the study of catalysis. The compositions at equilibrium (also with four-component systems involving 3- and 4-alkyl-2-hydroxy-2-methylcyclobutanones) permit calculation of the differences in free energy between isomers.



1 **2** (1)

Irradiation (three GE sunlamps at 6 cm, 2.5 hr, 25°, N_2, in a water-cooled Pyrex cell) of 5-methyl-2,3-hexanedione (0.1 *M* in benzene) gave nearly pure **1** (nmr) after evaporation of the solvent. Simple distillation gave a mixture of **1** (90%, nmr) and **2** (10%, bp 38–42° (0.4 mm)). Pure **1** (mp 11–14°; ir 1786 and 3400 cm^{-1}; parent mass 128; nmr (CCl_4) δ 1.12 (s, 3), 1.27 (s, 3), 1.30 (s, 3), 2.41 and 2.69 (AB m, 2, J = 16.8 Hz), 3.5–4.3 concentration dependent (s, 1); *p*-nitrophenylhydrazone, mp 215–217°) was obtained by recrystallization (pentane, −78°). Slow spinning-band distillation of a mixture of **1** and **2** gave *only* pure **2**: bp 38–39° (0.4 mm); ir 1784 and 3400 cm^{-1}; nmr (CCl_4) δ 1.21 (s, 3) 1.24 (s, 3), 1.41 (s, 3), 2.00 (s, 2), 3.5–4.3 ppm concentration dependent (s, 1); in benzene, ring methylene gives δ 1.68 and 1.88 (AB, m, 2, J = 11.3 Hz); *p*-nitrophenylhydrazone mp 142–145°. Periodic acid oxidation of **1** gave 4-oxo-3,3-

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(1) (a) A. E. Favorskii, V. Vasil'ev, A. I. Umnova, E. Kochergina, and E. Venus-Danilova, *Zh. Russ. Fiz.-Khim. Obshchest., Chast Khim.*, **60**, 369 (1928); *Bull. Soc. Chim. Fr.*, **43**, 551, 568, 571 (1928); (b) I. Elphimoff-Felkin, *et al.*, *ibid.*, 1845 (1956); 522 (1958); 1052 (1967); (c) A. Nickon, T. Nishida, and Y.-i Lin, *J. Amer. Chem. Soc.*, 91, 6860 (1969).

(2) (a) S. N. Danilov and E. Venus-Danilova, *Zh. Obshch. Khim.*, **3**, 559 (1933); *Ber.*, **67**, 24 (1934); (b) L. L. Smith, M. Marx, J. J. Garbarini, T. Foell, V. E. Origoni, and J. J. Goodman, *J. Amer. Chem. Soc.*, **82**, 4616 (1960); (c) H. Köller, *Tetrahedron Lett.*, 4317 (1968); (d) C. A. Brown and C. Djerassi, *J. Chem. Soc. C*, 2550 (1969).

(3) (a) W. T. Erman, *J. Amer. Chem. Soc.*, **91**, 779 (1969); (b) P. Yates and A. G. Fallis, *Tetrahedron Lett.*, 2493 (1968).