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SYNCHRONOUS ELIMINATION OF THE NITRO AND ESTER GROUPS OR THE NITRO AND KETO GROUPS VIA ONE ELECTRON TRANSFER REACTION

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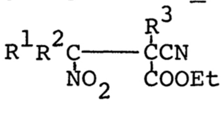
The nitro and ester groups are eliminated from α-cyano-β-nitroesters(1)on treatment with one electron transfer reagents. Similarly, the nitro and acetyl groups are eliminated from α-acetyl-β-nitroesters(2)or α-acetyl-β-nitroketones(3).

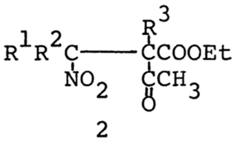
α-Halonitroalkanes or α,α-dinitroalkanes couple with the sodium salt of α-cyanoesters, β-ketoesters, or β-diketones to give 1, 2, or 3, respectively.[1)] α,β-Unsaturated nitriles or α,β-unsaturated carbonyl compounds are obtained by heating 1 or 2 with sodium bromide in HMPA, respectively.[2)] The usefulness of these coupling reactions will be further enhanced if a procedure to remove the nitro, ester, or acetyl groups from 1, 2, or 3 under mild conditions is found.

In this paper we wish to report a novel reductive elimination of the nitro and ester groups from 1, and the elimination of the nitro and acetyl groups from 2 and 3.



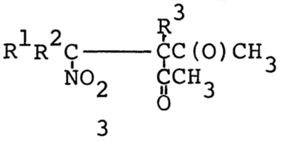
$R^1R^2\underset{NO_2}{C}-\overset{R^3}{\underset{COOEt}{C}}CN$

1



$R^1R^2\underset{NO_2}{C}-\overset{R^3}{\underset{\underset{O}{\|}{C}CH_3}{C}}COOEt$

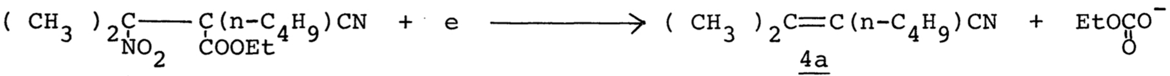
2



$R^1R^2\underset{NO_2}{C}-\overset{R^3}{\underset{\underset{O}{\|}{C}CH_3}{C}}C(O)CH_3$

3

For example, the nitro and ester groups are eliminated from 1a($R^1=R^2=CH_3$, $R^3=n\text{-}C_4H_9$)on treatment with Na-naphthalene, Na-dispersion in THF or Li in ethylenediamine(EDA) to give α,β-unsaturated nitriles(4a)and ethyl carbonate ion.[3)]



$$(CH_3)_2\underset{NO_2}{C}-\underset{COOEt}{C}(n\text{-}C_4H_9)CN + e \longrightarrow (CH_3)_2C{=}C(n\text{-}C_4H_9)CN + EtO\underset{O}{\overset{\|}{C}}O^-$$

1a 4a

The conversion of 1a to 4a can be also accomplished on treatment with $NaNO_2$ or the lithium salt of 2-nitropropane. The reactions induced by anions are accelerated by exposure to a 150 W tungsten lamp. Results are summarized in Table 1 and 2.

The nitro and acetyl groups are eliminated from 2 or 3 by the similar procedure to give acetate ion and α,β-unsaturated carbonyl compounds.[4)] Our understanding of the mechanism of the present reductive elimination is meager. Results in Table 1 and 2 suggest that the reaction proceeds via one electron transfer reaction. Various pathways are envisioned for the loss of the nitro, ester, or acetyl groups. The stereochemistry and mechanism of the present reaction is under investigation. For the purpose of the preparation of olefins, the methods shown in Table 2 are very attractive, for they do not require strong reducing agents nor strong bases. Some typical examples of the preparation of olefins by the method shown in Table 1 or 2 are summarized in Table 3.

Table 1. Conversion of 1a to 4a by Reducing Agents

Reducing Agents(equiv.)	Solvent	Temp. °C	Time	Yield of 4a
Na-naphthalene(1. 1)	THF	0	5 min	64%
Na-dispersion(1.1)	THF	65	4 h	73
Li(1.1)	EDA	25	4 h	83(56%)*

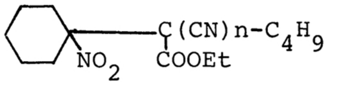
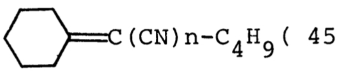
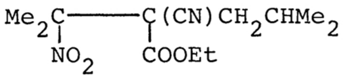
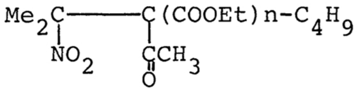
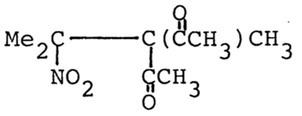
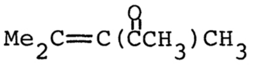
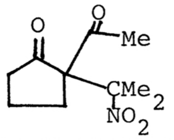
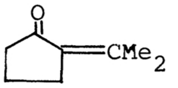
Yields were determined by GLPC using an internal standard. * Isolated yield.

Table 2. Conversion of 1a to 4a by Certain Anions under Irradiation

Anions	Solvent	Light	Temp. °C	Time h	Yield of 4a
NaBr	HMPA	150W	25	24	0%
$NaNO_2$	HMPA	150W	25	90	66
$NaNO_2$	HMPA	dark	25	90	20
$Li^+(Me)_2\bar{C}NO_2$	HMPA	150W	25	24	80
$Li^+(Me)_2\bar{C}NO_2$	HMPA	dark	25	24	38

150W : Tungsten lamp.

Table 3. Preparation of Olefins from 1, 2, or 3

Starting materials	Reaction conditions	Product(Isolated Yield)
	Li-EDA, 25°C, 4 h (Temp), (Time)	 (45%)
 $Me_2C(NO_2)-C(CN)(COOEt)CH_2CHMe_2$	$NaNO_2$-HMPA, 80°C, 150W, 3 h (Solvent), (Light)	$Me_2C{=}C(CN)CH_2CHMe_2$ (83%)
 $Me_2C(NO_2)-C(COOEt)(COCH_3)n\text{-}C_4H_9$	Li-EDA, 25°C, 4 h	$Me_2C{=}C(COOEt)n\text{-}C_4H_9$ (58%)
 $Me_2C(NO_2)-C(COCH_3)_2CH_3$	$Li^+(Me)_2\bar{C}NO_2$-HMPA, 35°C, 150W, 4 h	 $Me_2C{=}C(COCH_3)CH_3$ (62%)
	$Li^+(Me)_2\bar{C}NO_2$-HMPA, 35°C 150W, 4 h	 (78%)

References 1) N. Kornblum, Angew. Chem. Int. Ed., 14, 734 (1975). 2) N. Ono, R. Tamura, J. Hayami, and A. Kaji, Chem. Lett., 189 (1977). 3) Diethyl carbonate was obtained on treatment of the reaction mixture with ethyl iodide. 4) The nitro and ester groups are preferentially eliminated from 2 on treatment with a soft nucleophile.[2] In the present case, certain hard nucleophiles are formed and they attack the carbonyl carbon. Acetate ion was trapped as p-bromophenacyl ester.

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