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REDUCTIVE ELIMINATION REACTION OF β-NITROSULFONES VIA ONE ELECTRON TRANSFER PROCESS. A NEW SYNTHETIC METHOD FOR THE PREPARATION OF α,β-UNSATURATED NITRILES AND ESTERS

Noboru Ono*, Rui Tamura, Jun-ichi Hayami, and Aritsune Kaji
Department of Chemistry, Faculty of Science, Kyoto University,
Kyoto 606, Japan

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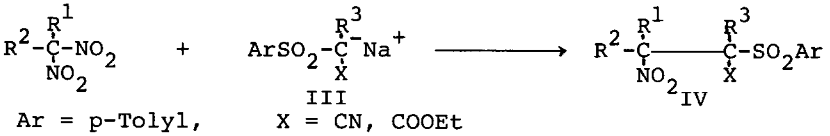
Reductive elimination of nitro groups from the vicinal dinitro compounds is a useful procedure for the olefin synthesis, in which olefins are obtained in good yields by the action of mild reducing agents such as sodium sulfide,[1)] stannous chloride,[2)] or calcium amalgam.[3)] We have tried to extend this procedure to the preparation of α,β-unsaturated nitriles or esters(II), but the difficulties have been encountered in the preparation of the requisite starting materials, compound I in eq 1. We therefore devised a new reductive elimination reaction to afford II from the easily available starting materials.

$$R^2-\underset{NO_2}{\overset{R^1}{C}}-\underset{NO_2}{\overset{R^3}{C}}-X \longrightarrow (R^1)(R^2)C{=}C(R^3)(X)$$

I II

X = CN, COOEt (1)

The procedure of this new olefin synthesis consists of the preparation of α-cyano- or α-ethoxycarbonyl-β-nitrosulfones(IV) and the subsequent reaction of IV with a mild reducing agent. Compound IV was prepared by the reaction of an anion(III) of α-cyanosulfones or α-ethoxycarbonylsulfones with α,α-dinitro compounds in DMF at room temperature in about 50-70% yields. This coupling reaction proceeds by way of the radical chain pathway and now this type of reaction is well documented.[4)] The conversion of IV to II proceeded smoothly when a solution of IV in DMF was treated with sodium sulfide at room temperature.



$$R^2-\underset{NO_2}{\overset{R^1}{C}}-NO_2 + ArSO_2-\underset{X}{\overset{R^3}{C^-}}Na^+ \longrightarrow R^2-\underset{NO_2}{\overset{R^1}{C}}-\underset{X}{\overset{R^3}{C}}-SO_2Ar \quad (2)$$

III IV

Ar = p-Tolyl, X = CN, COOEt

$$IV + Na_2S \longrightarrow II + NaNO_2 + ArSO_2Na + S \quad (3)$$

In a typical example, a mixture of IIIa(8.7g,40mmol) and 2,2-dinitropropane(6.03g,45mmol) in DMF(60ml) was stirred for 4 hr at room temperature. After the usual work up, recrystallization of the crude product from ethanol gave 6.8g(66% yield) of analytically pure IVa; mp 118.5-119.5°. A mixture of IVa

(5.33g,15mmol) and $Na_2S \cdot 9H_2O$(5.0g,18mmol) in DMF(30ml) was stirred under nitrogen for 3 hr at room temperature. Working up in the usual manner followed by distillation gave pure IIa(1.18g,69% yield); bp 60°/35mmHg. Thus, the conjugated olefins(II) were prepared in good yields from readily available starting materials.$^{5)}$ Some typical examples are presented in the table.

Table Conjugated Olefins(II) Prepared by Reductive Elimination of IV

II, III or IV	R^1	R^2	R^3	X	Isolated Yield of II(%)
a	CH_3	CH_3	CH_3	CN	69(95)*
b	CH_3	C_2H_5	CH_3	CN	62(E/Z = 1.2)
c	$-(CH_2)_4-$		CH_3	CN	70
d	$-(CH_2)_5-$		CH_3	CN	70
e	CH_3	CH_3	C_2H_5	CN	62
f	CH_3	CH_3	n-C_4H_9	CN	71
g	CH_3	CH_3	n-C_8H_{17}	CN	74(91)*
h	CH_3	CH_3	CH_3	COOEt	79
i	CH_3	n-C_5H_{11}	CH_3	COOEt	62(E/Z = 1.2)

* Yield determined by VPC using an internal standard.

The yields in this table refer to pure, isolated products starting from pure IV. The preparation of II could also be achieved by a one-pot process without isolation of the intermediate IV. For example, IIb and IIg were prepared in 74% and 77% overall yield, respectively, by a one-pot process.(These yields were determined by VPC.) The advantage of the present procedure is that the C-alkylation of α-sulfonyl carbanions allows the introduction of a wide variety of R^3 in the final products. In this regard, the present method may find wider appliciability in olefin synthesis than the reductive elimination of the vicinal dinitro compounds.(Alkylation of α-nitrocarbanions gives mainly O-alkylated products.) Other good one electron transfer agents were also effective for this elimination reaction; for example, the reaction of IVa with sodium thiophenoxide or lithium salt of 2-nitropropane gave IIa in 70% or 53% yield, respectively. But a strong base such as sodium methoxide was not effective. Furthermore, this elimination reaction was completely inhibited by the addition of 5 mole% of di-tert-butyl nitroxide. These facts suggest that the present reaction is not a usual E_2, but it proceeds by way of a radical chain mechanism involving one electron transfer processes. The precise nature of the chain process will be discussed elsewhere.

References 1) N. Kornblum, S. D. Boyd, H. W. Pinick, and R. G. Smith, J. Am. Chem. Soc., 93, 4316(1971). 2) K. Fukunaga, Synthesis, 442(1975).
3) N. Kornblum and L. Cheng, J. Org. Chem., 42, 2945(1977). 4) N. Kornblum, Angew. Chem. Int. Edit., 14, 734(1975). 5) The preparation of α,α-dinitro compounds was carried out by the method described in ref. 1.