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[3,2]-Sigmatropic Rearrangement of Acyloxy Nitronic Acids into Geminal Acyloxy Nitroso Compounds*

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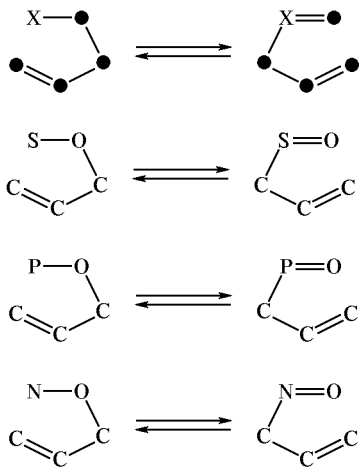
Abstract—Acylation of secondary nitroalkanes is accompanied by [3,2]-sigmatropic rearrangement of acyloxy nitronic acids into geminal acyloxy nitroso compounds which are formed in preparative yields.

Since 1975, N.S. Zefirov and S.S. Trach perform systematic studies aimed at developing a formally logical approach to description of organic reactions. The goals of these studies are (1) creation of a hierarchical classification of organic reactions and a strict mathematical model for their description [1], (2) search for unknown reactions and reaction types [2, 7, 8], (3) description of transformations of heterocycles [4], (4) development of a methodology for nonempirical computer synthesis [5], and (5) computer-aided study of mechanisms of organic reactions [9].

Let us consider a symbolic representation of a five-center [3,2]-sigmatropic rearrangement [Eq. (1) in Scheme 1] [2, 7].** Design of unknown reactions on the basis of this symbolic equation implies combinatorial replacement of common (dark circles) and specific reaction centers by symbols of the corresponding elements [1, 3, 6]. At present, a fairly large number of reactions are known, which conform to Eq. (1). Examples are processes described by Eq. (1a) [8, 10],*** (1b) [11], and (1c) [12] (Scheme 1). The goal of the present study was to analyze the process described by Eqs. (2a) and (2b) (Scheme 2). This process is accompanied by change in the degree of oxidation of nitrogen by two units, i.e., by the transformation $N^{+1} \rightarrow N^{+3}$ (which is hardly probable) or $N^{+3} \rightarrow N^{+5}$, which is more probable for a branched skeleton, especially when methyl groups are present and when the process is directed from the right to the left. This is illustrated by Eq. (2b) which describes

Scheme 1.



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** Analysis of monocyclic five-center processes with a single specific center (additional constraints: bond order variation equal to ±1 and the absence of triple bond or allene fragment in the five-membered ring) with the use of SIMBEQ program [6] gives 21 symbolic equations, but only two of them refer to sigmatropic rearrangements. Strictly speaking [3], the process should be regarded as [3,2β-3,2α]-sigmatropic rearrangement (here, the Greek letters denote the position of specific reaction centers in the initial and final structures).

*** It should be noted that the sulfenate–sulfoxide rearrangement was discovered almost simultaneously by four different research teams [8, 10] on the basis of different starting points. Our considerations [8] are based completely on the formally logical approach (see Scheme 1).

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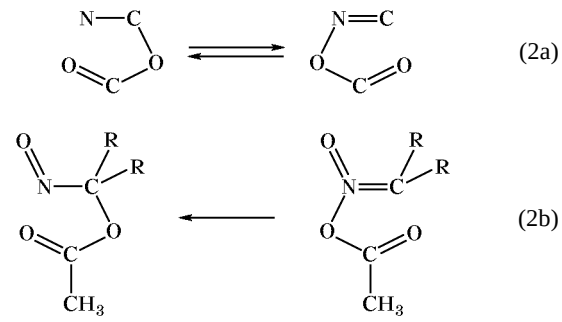
the rearrangement from acyloxy nitro compounds to α-acyloxy nitroso compounds.

Scheme 2.

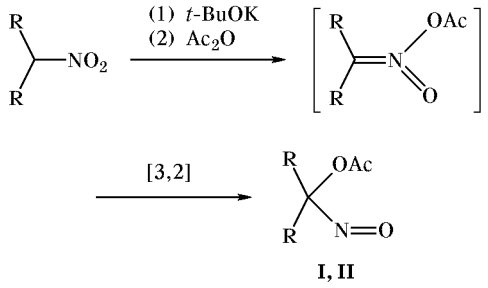


(2a)

(2b)

Thus, in the first step of our study we tried to effect acylation of secondary nitro compounds in the *aci* form. Such transformation was reported in 1958 by White and Considine [13] for aryl-substituted nitro compounds. In order to elucidate the scope of its application, we examined the acylation of nitroalkanes (Scheme 3).

Scheme 3.



I, II

I, R = Me; **II**, RR = $(CH_2)_5$.

In fact, the *aci* forms generated *in situ* from secondary nitroalkanes (2-nitropropane and nitrocyclohexane) are readily acylated with acetic or trifluoroacetic anhydride and acetyl chloride under mild conditions (in diethyl ether). The reaction is accompanied by [3,2]-sigmatropic rearrangement of intermediate acyloxy nitronic acids into geminal acyloxy nitroso compounds. The latter were isolated in 70–75% yield.

EXPERIMENTAL

The electron absorption spectra were measured on a Specord M-40 spectrophotometer. The IR spectra were obtained on a Specord 75IR instrument. The ^{1}H NMR spectra were recorded on a Bruker AC-300 spectrometer (300 MHz) in $CDCl_3$. The mass spectra (70 eV) were run on an HP-5990 (HP-5972) instrument (emission current 1000 mA, vaporizer temperature 70–250°C).

2-Acetoxy-2-nitrosopropane (I). 2-Nitropropane, 10 g (0.11 mol), was added over a period of 30 min to a suspension of 12.32 g (0.11 mol) of potassium *tert*-butoxide in 100 ml of dry diethyl ether under stirring at 0°C. The mixture was stirred for 30 min at 0°C, and 11.22 g (0.11 mol) of acetic anhydride was added over a period of 25 min (the solution turned dark blue). The mixture was stirred for 2 h while cooling and filtered, and the precipitate was washed with diethyl ether on a filter until it became colorless. The blue filtrate was evaporated on a rotary evaporator without heating, and the residue was distilled under reduced pressure to isolate 9.8 g (70%) of compound **I** as an intensely blue oily substance, bp 60–63°C (60 mm). The product is stable at –10°C, and at room temperature it undergoes complete dimerization in 24 h. IR spectrum, ν, cm^{-1}: 1560, 1580 (N=O); 1720 (C=O); 1760 (O–C=O); 2830–1880 (C–H). ^{1}H NMR spectrum, δ, ppm: 1.37 s (6H, CH_3); 2.19 s (3H, $COCH_3$). UV spectrum (CH_3CN): λ_{max} 667 nm (N=O). GC–MS data: retention time 2.66 min; *m*/*z* (I_{rel}, %): 101 (45) $[M-NO]^+$; 59 (100) $[M-NO-CH_2=C=O]^+$. The fragmentation pattern of compound **I** was in a full agreement with published data for 2-acetoxy-2-nitrosopropane [13]. The reaction with acetyl chloride as acylating agent was performed in a similar way. Yield 73%.

1-Acetoxy-1-nitrosocyclohexane (II) was obtained in a similar way from 11.2 g (0.1 mol) of potassium *tert*-butoxide, 12.9 g (0.1 mol) of nitrocyclohexane, and 10.2 g (0.1 mol) of acetic anhydride. Yield 12 g (70%), intensely blue oily substance, bp 50–53°C (0.5 mm); published data [14]: bp 62–78°C (0.3 mm). Compound **II** is stable at room temperature. ^{1}H NMR spectrum, δ, ppm: 2.20 s (3H, $COCH_3$), 1.4–1.9 m (10H, cyclohexane). Mass spectrum, *m*/*z* (I_{rel}, %): 141 (10) $[M-NO]^+$, 99 (100) $[M-NO-CH_2=C=O]^+$, 81 (80) $[M-NO-CH_2=C=O-H_2O]^+$.

1-Nitroso-1-trifluoroacetoxycyclohexane (III). The reaction of nitrocyclohexane with trifluoroacetic anhydride was performed in a similar way. The mixture was evacuated at 10^{-2} mm, 20°C. The residue was a dark blue oily substance. Yield 76%. ^{1}H NMR spectrum, δ, ppm: 1.1–2.8 m (10H, cyclohexane). Found, %: C 42.47; H 4.46; F 25.21; N 6.11. $C_8H_{10}F_3NO_3$. Calculated, %: C 42.67; H 4.48; F 25.31; N 6.22. Compound **III** completely decomposes in 24 h at 20°C.

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