We should note that the formal positive charge on the chlorine atom in pure $ClOSO_2F$ is somewhat greater than on the chlorine atom for mixtures of $ClOSO_2F$ with HSO_3F and HSO_3F/SbF_5. On the other hand, the available experimental data indicate a significantly greater reactivity of $ClOSO_2F$ in the presence of HSO_3F [4] and even greater reactivity in the presence of HSO_3F/SbF_5 [5, 6]. This finding is apparently a consequence of finer details in these chemical reactions not related to the intramolecular charge distribution in $ClOSO_2F$.

CONCLUSIONS

NQR spectroscopy was used to find the localization of formal positive charge on the chlorine and bromine atoms in $ClOSO_2F$ and $BrOSO_2F$.

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NITROSOALKANE STRUCTURE OF THE PRODUCTS OF THE THERMOLYSIS OF β-(N-NITROSOHYDROXYLAMINO)HYDROCINNAMIC ACID DERIVATIVES

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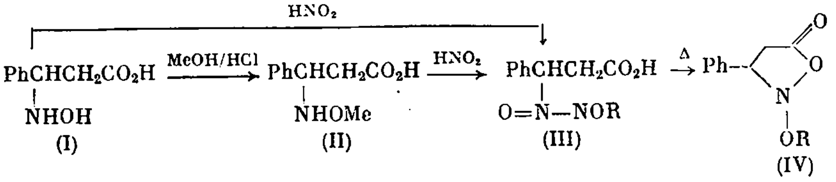
Compounds with the $O-\overset{|}{N}-O$ fragment have been studied in sufficient detail to undertake a critical evaluation of the early studies on synthesis of these compounds and proof of their structure. For example, Sokolov et al. [1] showed that the adducts of isoxazoles with HCl do not correspond in their properties to the previously postulated 2-hydroxy-3-chloro-Δ^4-isoxazoline structure containing the $O-\overset{|}{N}-O$ agment [2] and are actually Δ^2-isoxazolines.

In the present work, we restudied the conversions of derivatives of β-hydroxylaminohydrocinnamic acid (I), whose products were described in 1906 as the first compounds with the $O-\overset{|}{N}-O$ fragment, 2-hydroxy- and 2-alkoxy-1,2-oxazolidin-5-ones (IV) [3].



R = H (a), Me (b).

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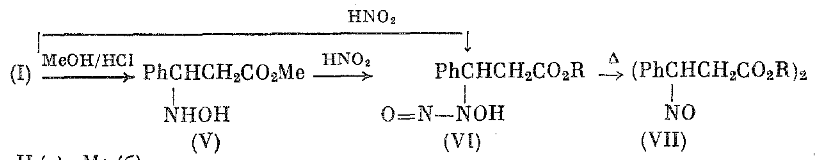
0568-5230/86/3501-0228$12.50

The results of Posner [3] raised doubts since products (IV) are cyclic analogs of N-acyloxy-N-alkoxyamines, which are thermally unstable [4]. In addition, the most characteristic property of N-nitrosohydroxylamines is their spontaneous or acid-catalyzed conversion to C-nitro derivatives. This is one of the preparative methods for the preparation of these C-nitro derivatives [5].

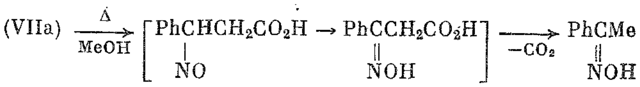
We have found that the treatment of (I) by HCl/MeOH, as expected, does not give methoxyamine (II) proposed by Posner [3] but rather methyl β-hydroxylaminohydrocinnamate (V). The IR spectrum of (V) has bands characteristic for the MeO_2C group [6]. We then carried out the nitrosylation of (I) and (V) according to Posner [3] and obtained N-nitrosohydroxylamines (VI) which were identical to the samples described by Posner [3] relative to their melting points and elemental analysis. The thermolysis of (VI) by heating at reflux for 15 min in benzene gave products which were also identical to those described by Posner [3] as (IV). However, PMR, IR, and mass spectroscopy indicated that these compounds are dimers of C-nitroso compounds (VII) and not their isomers with the $O{-}\overset{|}{N}{-}O$ fragment (IV). Thus, the IR spectra of (VII) have strong bands characteristic for the N–O bond of the trans dimers of aliphatic C-nitroso compounds [5]. The mass spectrum of (VIIb) shows a molecular ion peak for the monomeric nitroso compound and an $[M - NO]^+$ ion peak characteristic for nitroso compounds.



$$\text{(I)} \xrightarrow{MeOH/HCl} \underset{\text{(V)}}{\underset{NHOH}{PhCHCH_2CO_2Me}} \xrightarrow{HNO_2} \underset{\text{(VI)}}{\underset{O{=}N{-}NOH}{PhCHCH_2CO_2R}} \xrightarrow{\Delta} \underset{\text{(VII)}}{(\underset{NO}{PhCHCH_2CO_2R})_2} \qquad \text{(I)} \xrightarrow{HNO_2} \text{(VI)}$$

R = H (a), Me (б).

Additional evidence for the correctness of the assignment of structure (VII) is the conversion of (VIIa) upon heating in methanol at reflux for 3 h to acetophenone oxime [7]



$$\text{(VIIa)} \xrightarrow[MeOH]{\Delta} \left[\underset{NO}{PhCHCH_2CO_2H} \to \underset{NOH}{\overset{}{PhCCH_2CO_2H}}\right] \xrightarrow{-CO_2} \underset{NOH}{PhCMe}$$

Thus, the conclusions of Posner [3] are incorrect. Therefore, the 2-alkoxy-1,2-oxazolidines and 2,8-dioxa-1-azabicyclo[3.3.0]octanes obtained by V. A. Tartakovskii in 1964 by the 1,3-dipolar cycloaddition of nitrone ethers to olefins [8] should be considered the first example of compounds with the $O{-}\overset{|}{N}{-}O$ fragment.

EXPERIMENTAL

The PMR spectra were obtained on Jeol C-60-HL, Bruker WP-80-SY, and Bruker WM-400 spectrometers. The IR spectra were obtained for KBr pellets on a UR-20 spectrometer. The mass spectra were taken on a Hitachi M-80A mass spectrometer (peaks with relative intensity >10% are given).

A sample of β-hydroxylaminohydrocinnamic acid (I) was obtained according to Posner [3] in 75% yield, bp 163-165°C.

Methyl β-hydroxylaminohydrocinnamate (V) was obtained according to the method for the synthesis of (II) [3] in 37% yield, mp 99-100°C. IR spectrum (ν, cm^{-1}): 1735 (CO), 1350 (δ_{as} Me). PMR spectrum (60 MHz, CD_3OD, δ, ppm, J, Hz): 2.52, 2.68 (CH_2, $J_{AB} = -8.2$, $J_{AX} = J_{BX} = 6.7$), 3.40 (MeO_2C), 4.15 (CH), 7.12 (Ph).

The dimer of β-nitrosohydrocinnamic acid (VIIa) was obtained according to the method for the synthesis of (IVa) [3]. A solution of 1.6 g (23 mmoles) $NaNO_2$ in 5 ml water was added dropwise to a solution of 3.8 g (20.9 mmoles) (I) in 30 ml 20% H_2SO_4 at 0°C. The mixture was extracted by six 20-ml portions of ether, and the extract was evaporated. The residue was dissolved in 13 ml benzene, and the solution obtained was heated at reflux for 15 min. The residue was separated, washed with benzene, and dried in vacuum to yield 1.5 g (40%) (VIIa), mp 125-127°C (126-129°C [3]). IR spectrum (ν, cm^{-1}): 1710 (CO), 1198 (NO). PMR spectrum (400 MHz, CD_3OD, δ, ppm, J, Hz); 2.81, 3.29 (CH_2, $J_{AB} = -17.3$, $J_{AX} = 11.0$, $J_{BX} = 3.9$), 6.52 (CH), 7.3 (Ph). Found: C 60.31; H 4.94; N 7.71%. Calculated for $C_9H_9NO_3$: C 60.33; H 5.06; N 7.28%.

The dimer of methyl β-nitrosohydrocinnamate (VIIb) was obtained according to the procedure for the synthesis of (IVb) [3] by analogy to (VIIa). The yield was 18%, mp 125-126°C (from benzene). IR spectrum (ν, cm^{-1}): 1744 (CO), 1198 (NO). PMR spectrum (80 MHz, C_5D_5N, δ, ppm, J, Hz): 2.85, 3.54 (CH_2, $J_{AB} = -17.2$, $J_{AX} = 11.0$ $J_{BX} = 4.1$), 3.14 (MeO_2C), 6.81 (CH), 7.3 (Ph). Mass spectrum, 70 eV, m/z (rel. intensity, %): 193 (5.2) M^+ (monomer), 192 (3.6), 163 (12.0) $[M - NO]^+$, 162 (22.5), 161 (28.9), 131 (57.1), 121 (66.9), 105 (15.2), 104 (52.1), 103 (100) $[M - HNO - MeO_2C]^+$, 91 (22.5), 78 (15.5), 63 (15.5), 59 (10.3) $[MeO_2C]^+$, 51 (30), 50 (10.7). Found: C 62.55; H 5.84; N 7.4%. Calculated for $C_{10}H_{11}NO_3$: C 62.16; H 5.73; N 7.24%.

Thermolysis of (VIIa). A solution of 0.45 g (2.53 mmoles) (VIIa) in 10 ml methanol was heated at reflux for 3 h and ethanol was removed in vacuum. The residue was subjected to chromatography on a silica gel column using 2:3 benzene–isopropyl ether as the eluent to yield 0.28 g (81%) acetophenone oxime identical to an authentic sample relative to melting point and PMR spectrum (60 MHz, CD_3OD, δ, ppm): 2.11 (Me), 7.3 (Ph).

CONCLUSIONS

The thermolysis of β-(N-nitrosohydroxylamino)hydrocinnamic acid and its methyl ester gives examples of β-nitrosohydrocinnamic acid and its methyl ester, respectively, and not 2-hydroxy- or 2-methoxy-1,2-oxazolidine-5-ones as incorrectly considered previously.

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