Synthesis and Tautomerization of 2-Nitro-1-nitrosoethylbenzene in Acetone†

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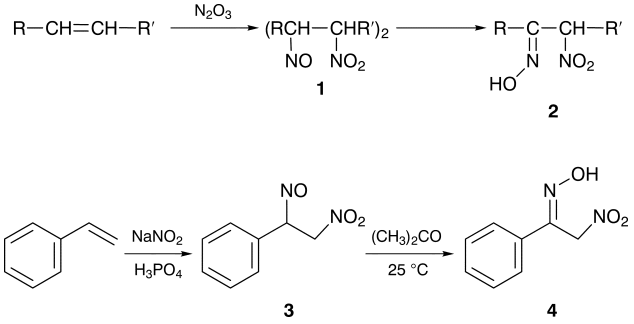
2-Nitro-1-nitrosoethylbenzene has been synthesized in fairly high yield and its tautomerization studied by ^{1}H NMR spectroscopy.

The reaction of dinitrogen trioxide with olefins affords 1-nitro-2-nitroso derivatives, commonly referred to as pseudo-nitrosites **1**.[1] These adducts can be converted into the more soluble isomers, the corresponding 1,2-nitroximes **2**.[1,2] Reaction of styrene with arsenic[3] and concentrated nitric acid or dinitrogen trioxide[1b] produces 2-nitro-1-nitrosoethylbenzene **3**. Compound **3** is transformed easily into the more stable isomer 2-isonitroso-1-nitro-2-phenylethane **4** by boiling in ethanol.[4] The structure of compounds **3** and **4** were earlier deduced only from their elemental analyses and for compound **4** ^{1}H NMR data were also reported.[5]



2-Nitro-1-nitrosoethylbenzene **3** and 2-isonitroso-1-nitrophenylethane **4** are frequently used as useful products[6] and as versatile intermediates in organic synthesis.[7] In addition **4** is used in analytical chemistry for indirect determination of styrene.[8] Various approaches can lead to these compounds.[9] However, much demand still exists for their preparation in high yields and free of compound **4** under mild and safe conditions.

We now report a new method for the preparation of compound **3** in high yields under easy and safe conditions and deduce the essential structure of compounds **3** and **4** from their IR, ^{1}H, ^{13}C NMR and mass spectra. In addition, the tautomerization of **3** to **4** was studied by using ^{1}H NMR spectroscopy in acetone at 25–40 °C.

For the tautomerization study a fresh sample of compound **3** was dissolved in $(CD_3)_2CO$ [0.01 g in 0.4 ml $(CD_3)_2CO$ in a 5 mm NMR tube] and equilibrated at the required temperature. The progress of the tautomerization was monitored by recording the appearance and disappearance of the methylene signals of **3** and **4** (Fig. 1). Integration of the area under the methylene signal of **4** with respect to that of the methylene signals of **3** gave the concentration of the species present. The rate of the reaction is given by rate $= k[\mathbf{3}]^x$ or $k[\mathbf{4}]^y$, where x or y is the reaction order. The integrated rate equation for a first order reaction is $\ln[\mathbf{4}]_t = -kt + \ln[\mathbf{3}]_0$.

The concentration of compound **4** at time t was found by setting the peak area for **3** equal to one and measuring the peak area of **4** relative to it. Typical data are presented in

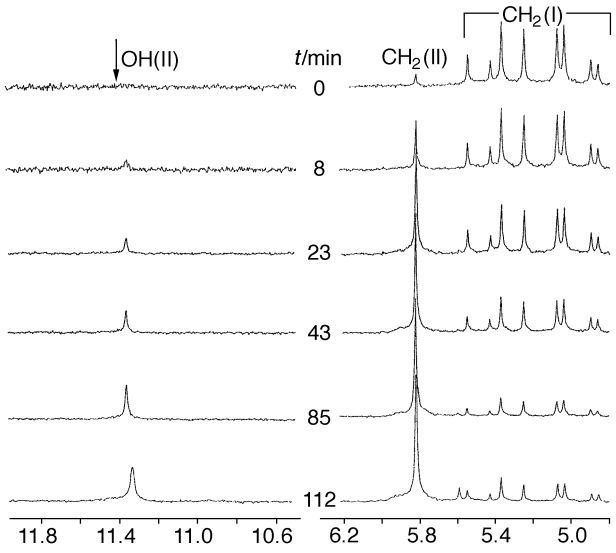


Fig. 1

Table 1. A plot of $\ln[\mathbf{4}]_t$ *versus* time should yield a straight line if the reaction is first order [see Fig. 2(a)]. The slope of this line is equal to k. The rate constants were obtained at several temperatures (298, 303 and 313 K) [Fig. 2(a)–2(d), Table 2].

By taking the natural logarithm of the Arrhenius equation, the activation energy, $E_a = 65.63$ kJ mol^{-1}, was obtained from a plot ln k *versus* $1/T$. Activation parameters, $\Delta H^{\ddagger} = 57.85$ kJ mol^{-1} and $\Delta S^{\ddagger} = -89.58$ J K^{-1} mol^{-1}, were also determined from a plot of $\ln(k/T)$ *versus* $1/T$. The relatively low enthalpy of activation for this tautomerization suggests a mechanism which is compatible with a cyclic activated complex, in which bond making accompanies bond breaking. In addition, a negative entropy of activation, due to the loss of rotational degrees of freedom associated with the highly ordered transition state, supports this complex formation.

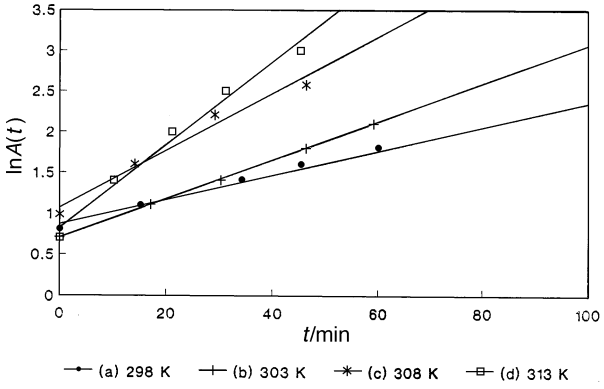


Fig. 2

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Table 1 Integrated area of compound **4** with respect to that of **3** at different temperatures

T/°C	t/min	Integrated area (A_t)	ln A_t
25	0	2.2	0.8
	15	3.0	1.1
	34	4.0	1.4
	45	5.0	1.6
	60	6.0	1.8
	94	9.0	2.2
30	0	2.0	0.7
	17	3.0	1.1
	30	4.0	1.4
	46	6.0	1.8
	59	8.0	2.1
35	0	2.7	1.0
	14	5.0	1.6
	29	9.0	2.2
	46	13.5	2.6
40	0	2.0	0.7
	10	4.0	1.4
	21	7.4	2.0
	31	12.2	2.5
	45	20.1	3.0

Experimental

NMR spectra were recorded on JEOL EX 90-MHz spectrometer using tetramethylsilane as the internal standard. Temperature was calibrated by the shift difference in methanol. The temperature range was 25 to 40 °C. Infrared spectra were taken on a Shimadzu IR-470 spectrophotometer, mass spectra on a Finnigan-Matt 8430 mass spectrometer. Elemental analyses were performed with a CHN Heracus-O-Rapid analyzer.

Preparation of 2-*Nitro*-1-*nitroseothylbenzene* **3**.—Sodium nitrite (34.5 g, 0.5 mol) and styrene (20.8 g, 0.2 mol) were added to chloroform (150 ml) in a 250 cm^3 two-necked round-bottomed flask equipped with condenser and dropping funnel. To this stirred mixture was added phosphoric acid (57.6 g, 85 wt.% solution in water; 0.5 mol) from a dropping funnel over a period of 20 min. After complete addition of phosphoric acid, the mixture was stirred for 4 h at 50 °C, then neutralized with saturated sodium bicarbonate solution. The precipitate was filtered off and washed with water (100 ml) and then *n*-hexane (40 ml). Compound **3** was obtained as a white solid (25.2 g, yield 70%), mp 129 °C; δ_H [90 MHz, $(CD_3)_2CO$] 7.60 (5 H, m, aromatic), 6.90 (1 H, dd, ^3J 9.5, ^3J 2.9, CH), 5.41 (1 H, dd, ^2J 14.0, ^3J 9.5, CH_2), 4.97 (1 H, dd, ^2J 14.0, ^3J 2.9 Hz, CH_2); δ_C [22.5 MHz, $(CD_3)_2CO$], 69.2 (CNO_2), 74.7 (CNO), 127.4, 130.0, 130.9, 135.7 (C_6H_5); $\tilde{\nu}_{max}$/cm^{-1} 2925, 1559, 1373; M^+ at m/z 180, $C_8H_8N_2O_3$ requires 180 (Found: C, 53.6; H, 4.5; N, 15.3. $C_8H_8N_2O_3$ requires C, 53.3; H, 4.4; N, 15.5%).

Preparation of 2-*Isonitroso*-1-*nitro*-2-*phenylethane* **4**.—Compound **3** was completely transformed into **4** in acetone at room temperature after about 24 h. Mp 95–96 °C; δ_H ($CDCl_3$) 5.6 (2 H, s, CH_2) 7.5 (5 H, m, C_6H_5), 9.3 (1 H, s, NOH exchange with D_2O); δ_C ($CDCl_3$) 69.9 (CNO_2), 128.0, 130.6, 131.6, 135.7 (C_6H_5), 149.3 (C═NOH); $\tilde{\nu}_{max}$/cm^{-1} 3279, 1559, 1373.

Table 2 Temperature dependence of rate constants for the tautomerization of **3** → **4** in acetone

T/K	10^2k/min^{-1}	ln(k/T)
298	1.485	−9.907
303	2.381	−9.451
308	3.509	−9.100
313	5.097	−8.800

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