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The Configurations of *N*-Methyl- and *N*-*t*-Butyl-α-methoxycarbonylmethanimine *N*-Oxides

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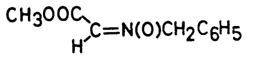
Synopsis. *N*-Methyl-α-methoxycarbonylmethanimine *N*-oxide, *Z* configuration in crystal, was found to exhibit a facile equilibration with its *E*-isomer in solution. The configuration of *N*-*t*-butyl derivative was always *Z*.

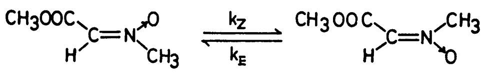
Recently, we found that *N*-benzyl-α-methoxycarbonylmethanimine *N*-oxide (**1**) and its analogues exist in one configuration in the crystalline state but, in solution, exhibit a facile isomerization to give a mixture of *E*- and *Z*-isomers.1) The configuration of **1** in the crystalline state have been proved to be *Z* by X-ray crystal analysis.2)

In this paper, we wish report the geometrical structures of *N*-methyl- (**2**) and *N*-*t*-butyl-α-methoxycarbonylmethanimine *N*-oxides (**3**) in order to clarify the influence of a substituent on the nitrogen atom.

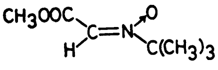


$$\overset{CH_3OOC}{\underset{H}{}}C{=}N(O)CH_2C_6H_5$$

1



2Z **2E**



3

Experimental

*Preparation of **2** and **3**.* According to the procedure of Winterfeldt and co-workers,3) **2** and **3** were prepared from *N*-alkylhydroxylamine hydrochloride and methyl glyoxylate4) in the presence of sodium acetate and calcium chloride.

2, Mp 69—71 °C (from benzene, lit,3) mp 71 °C); ν (KBr): 1710 and 1230 cm^{-1}; $\lambda_{\max}$(MeOH): 268 nm. Found: C, 40.98; H, 6.03; N, 11.96%. Calcd for $C_4H_7NO_3$: C, 41.02; H, 6.03; N, 11.96%.

3, Bath temp 110—120 °C/0.55 mmHg (1 mmHg≈133.322 Pa) (Kugelrohr dist): ν(film): 1720 and 1180 br cm^{-1}; $\lambda_{\max}$ (MeOH): 270 nm. Found: C, 52.98; H, 8.42; N, 8.66%. Calcd for $C_7H_{13}NO_3$: C, 52.81; H, 8.23; N, 8.79%.

^{1}H-NMR Measurements. ^{1}H-NMR spectra were obtained on a JEOL JNM-PMX60SI spectrophotometer and δ-values were calculated from the TMS as an internal standard (35 °C).

Discussion

The *N*-methyl derivative **2** had been already prepared in 1969 by Winterfeldt and co-workers3) and the ^{1}H-NMR spectrum (CDCl$_3$) reported showed only three signals at δ 7.39, 3.82, and 3.66. These results suggested the absence of a geometrical isomer.

However, as shown clearly in Fig. 1, the spectra of **2** changed gradually with the elapse of time. The signal at δ 3.81 decreased, while a new peak appeared at δ 4.14 increased. The relative intensities of these two peaks remain constant after 40 min.

The signal at δ 4.14 is assignable to the *N*-CH$_3$ group in *E*-nitrone (**2E**) as the result of the deshielding effect of the neighboring methoxycarbonyl group.1) Thus, the phenomena in Fig. 1 are explained by arguing that an initial *Z*-nitrone (**2Z**), which determines the crystal structure, isomerizes to the *E*-isomer (**2E**) when it dissolves in CDCl$_3$ and that, after 40 min, the system reaches the equilibrium mixture of both isomers. The *E*/*Z* ratio at equilibrium was calculated from the peak areas of δ 4.14 and 3.81 and the rate constant of isomerization was obtained from the *E*/*Z* ratios at different time. The results are summarized in Table 1.

From the Table, it is clear that the solvent polarity is significant in determining the *E*/*Z* ratio at equilibrium: the less polar the solvent polarity, the more predominant the *E*-isomer. Although the detailed mechanism of the stabilizing the two geometrical isomers in a given solvent is still unclear, the *Z*-isomer, which is anticipated5) to have a larger dipole moment than the *E*-isomer, is thought to be more stabilized

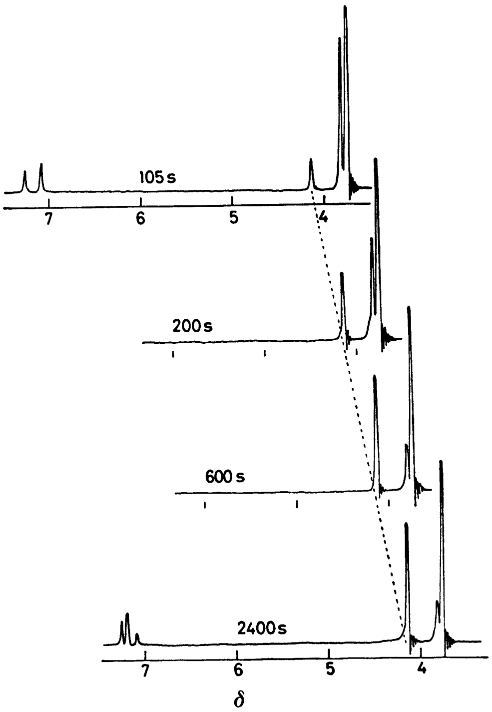


Fig. 1. Time-dependence of the intensities of methyl protons in the ^{1}H-NMR spectra of **2** in CDCl$_3$.

Table 1. The E/Z ratio and the rate constant of isomerization of **2**[a)]

Solvent	E/Z	k_Z/s^{-1}	k_E/s^{-1}
C_6D_6	6.0		
$CDCl_3$	3.8	2.4×10^{-3}	6.2×10^{-4}
CD_3OD	0.83	3.3×10^{-5}	4.0×10^{-5}
DMSO-d_6	0.67		

a) Measured at 0.08 mmol of 2 in 0.3 ml of each solvent.

in more polar solvents.

The rate constant in CD_3OD is smaller than that in $CDCl_3$. This can be partially explained by considering the hydrogen bonding between the nitrone oxygen and the solvent hydrogen (=N→O···H–O–R).

In the case of *N*-*t*-butyl derivative **3**, both ^{1}H-NMR (δ in $CDCl_3$: 7.25, 3.76, and 1.49) and ^{13}C-NMR (δ in $CDCl_3$: 161.3, 121.1, 74.8, 51.8, and 28.2) were simple and no changes were observed even when the temperature was raised to 62 °C. This shows that only one configurational isomer is present in solution. As a large NOE (35%) was observed between the olefinic proton and *t*-butyl protons,[6)] the configuration of the nitrone **3** was proved to be *Z*.

Various derivatives have been investigated; among these, *N*-alkyl-α-methoxycarbonylmethanimine *N*-oxides which have at least one hydrogen at the carbon attached to the nitrogen of the nitrone chromophore are apt to equilibrate into *E*- and *Z*-isomers in solution at room temperature.

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