

1205, 1180, 1050 cm^{-1} ($\text{S}=\text{O}$). PMR spectrum (CF_3COOH , TMS): 2.33 (2H, m, CH_2); 3.13 m, (2H, m, CH_2N); 3.87 (2H, m, CH_2SO_2); 5.17 (2H, s, $\text{CH}_2\text{C}=\text{O}$); 7.50 ppm (14H, m, aromatic protons).

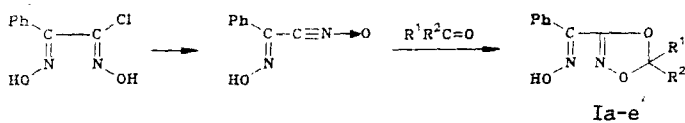
NONCATALYTIC ADDITION OF NONACTIVATED CARBONYL DERIVATIVES TO
 α -OXIMINOPHENYLACETONITRILE OXIDE

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Nitrile N-oxides undergo a cycloaddition reaction with carbonyl compounds, activated by electron-acceptor substituents. Nonactivated aldehydes and ketones react only in the presence of a boron trifluoride etherate catalyst [1].

We studied the properties of α -oximinophenylacetonitrile oxide, formed by the dehydrochlorination of phenylchloroglyoxime, and found that in contrast to other nitrile oxides, this compound reacts readily with nonactivated aldehydes and ketones with the formation of the corresponding 1,4,2-dioxazoles:



a $\text{R}^1=\text{R}^2=\text{H}$; b $\text{R}^1=\text{H}$, $\text{R}^2=\text{CH}_3$; c $\text{R}^1=\text{R}^2=\text{CH}_3$; d $\text{R}^1=\text{CH}_3$, $\text{R}^2=\text{C}_2\text{H}_5$; e $\text{R}^1\text{R}^2=(\text{CH}_2)_5$

Even formaldehyde undergoes this reaction, but its cycloaddition products could not be obtained previously. In the reaction with cyclic ketone - cyclohexanone, the corresponding spiro-derivative **Ie** is formed.

The reaction is carried out at room temperature by adding a dehydrochlorinating agent (a solution of sodium bicarbonate or triethylamine) to a solution of chlorophenylglyoxime and the carbonyl derivative in alcohol (compounds **Ia,b,e**) or in an excess of the same carbonyl derivative (compounds **Ic,d**).

Oxime of 3-Benzoyl-1,4,2-dioxazole (Ia). mp 215...216°C (from alcohol). PMR spectrum (here and below in DMSO-D_6): 5.75 (2H, s, CH_2); 7.47 (3H, m, m-, p-H); 8.44 (2H, m, o-H); 10.78 ppm (1H, s, OH).

Oxime of 3-Benzoyl-5-methyl-1,4,2-dioxazole (Ib). mp 164...165°C (from benzene). PMR spectrum: 1.62 (3H, d, CH_3); 5.96 (1H, q, CH); 7.47 (3H, m, m-, p-H); 8.46 (2H, m, o-H); 10.73 ppm (1H, s, OH).

Oxime of 3-Benzoyl-5,5-dimethyl-1,4,2-dioxazole (Ic). mp 189...191°C (from benzene). PMR spectrum: 1.69 (6H, s, CH_3); 7.44 (3H, m, m-, p-H); 8.44 (2H, m, o-H); 10.73 ppm (1H, s, OH).

Oxime of 3-Benzoyl-5-methyl-5-ethyl-1,4,2-dioxazole (Id). mp 159...161°C (from alcohol). PMR spectrum: 0.73 (3H, t, CH_3); 1.67 (3H, s, CH_3), 2.04 (2H, q, CH_2); 7.48 (3H, m, m-, p-H); 8.49 (2H, m, o-H); 10.79 ppm (1H, s, OH).

Oxime of 3-Benzoyl-1,4,2-dioxazole-5-spirocyclohexane (Ie). mp 246...248°C (from alcohol). PMR spectrum: 1.80 (10H, m, C_5H_{10}); 7.48 (3H, m, m-, p-H); 8.50 (2H, m, o-H); 10.80 ppm (1H, s, OH).

LITERATURE CITED

1. C. Grundman and P. Grunanger, *The Nitrile Oxides*, Springer-Verlag, Berlin (1971), p. 120.

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