SYNTHESIS OF NITRONES BY REACTION OF ISONITROISOMALONIC ESTERS WITH DIAZOALKANES

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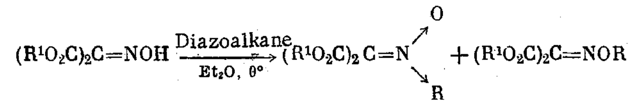
We have observed predominate N-alkylation of activated oximes with diazoalkanes (Table 1).



$$(R^1O_2C)_2C{=}NOH \xrightarrow[Et_2O,\ 0°]{Diazoalkane} (R^1O_2C)_2C{=}\overset{\overset{O}{\nearrow}}{\underset{\underset{R}{\searrow}}{N}} + (R^1O_2C)_2C{=}NOR$$

(Ia-c) (IIa-c)

R = Me, R¹ = Me (a); R = Et, R¹ = Me (b); R = Me, R¹ = Et (c)

The structure of nitrones (Ia-c) was demonstrated by broadening of the MeN signals in PMR spectra and from IR spectra, and also by cycloaddition reactions.

TABLE 1

Compound	Yield*, %	bp, °C (p, mm of Hg)	n_D^{20}	ν, cm⁻¹ (molecular layer)		δ, ppm‡		N, % Found / Calc.
				CO	CN (N→O)	R	R¹	
(Ia)	66,3	112–113 (4) mp 76–77	–	1730†	1559† (1239)	3,56	3.19 and 3.46	7,79 8,00
(IIa)	7,5 (3,7)	88–89 (4)	1,4485	1740 1720	1600	3,64	3,34 » 3,41	7,71 8,00
(Ib)	42,0	111–113 (3) mp 51–52	–	1738†	1555† (1234)	1,01** 4,17	3,25 » 3,51	7,65 7,41
(IIb	11,0 (30,5)	90–91 (4)	1,4454	1740 1720	1600	0,90†† 4,00	3,30 » 3,45	7,55 7,41
(Ic)	56,0	115–116 (3)	1,4730	1730	1553 (1230)	3,65	0,81 » 0,96 3,86 » 4,16	6,86 6,89
(IIc)	11,3 (33,0)	105–107 (5)	1,4432	1735 1710	1600	3,61	0,81 » 0,93 3,92 » 4,10	6,89 6,89
(IIIa)	77,6	Oil‡‡	1,4558	1730	–	1,28 (MeC) 2,83 (MeN)	2,53 (CH_2)*** 3,3 (MeO)	6,11 6,06
(IIIb)	92,0	Oil‡‡	1,4548	1750	–	0,83 and 3,91 (EtO)** 2,85 (MeN) 3,7 (CH_2)	3,3 (MeO)	3,99 4,03

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*The yield of alkylation products of oxime Na Salts by reaction with RI in acetone upon boiling for 5 days is given in parentheses.

†KBr tablets.

‡60 MHz from HMDS, 5 mole % solutions in C_6H_6.

**J = 7.4 Hz.

††J = 7.1 Hz.

‡‡Purified by chromatography on silica gel, $CHCl_3$ as the eluent.

***At −60° in $CHFCl_2$, δ, ppm; 2.63 (CH_2, AB, J_{AB} = 15, Δν = 52 Hz), 1.3 (Me_2C, Δν = 3 Hz).

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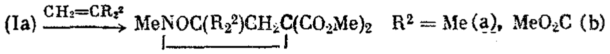

$$\text{(Ia)} \xrightarrow{CH_2{=}CR_2^2} \underbrace{MeNOC(R_2^2)CH_2C}(CO_2Me)_2 \quad R^2 = Me\,(a),\ MeO_2C\ (b)$$

(III a, b

The alternative oxaziridine structure is excluded by the absence of geminal nonequivalence of CH_2N protons in (Ib). In contrast to isomeric O ethers, the mass spectra of (Ia-c) contain peaks of characteristic fragments $(M - R^1OCO_2)^+$ and $(M - R^1OCO_2 - CO_2)^+$.

The O ethers (IIa-c) are identical to the alkylation products of oximes upon reaction with RI (the nitrones formed in this case decompose rapidly in basic medium). In contrast to nitrones, O ethers react with CH_2N_2; for example, 1-methoxyaziridine-2,2-dicarboxylic ester (68%) was obtained from (IIc) [1].

LITERATURE CITED

1. R. G. Kostyanovskii, A. V. Prosyanik, and V. I. Markov, Izv. Akad. Nauk SSSR, Ser. Khim., 482 (1974).

THE REACTION OF ALLENE WITH γ-Al_2O_3 AND NICKEL CARBONYL DEPOSITED ON γ-Al_2O_3

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In a continuation of investigations of catalytic transformations of allene [1] we studied by IR spectroscopy its interaction with γ-Al_2O_3 and $Ni(CO)_4$ deposited on γ-Al_2O_3. In the case of γ-Al_2O_3 isomerization of allene to methacrylate was observed already at 20°C (absorption bands at 2140 and 3350 cm^{-1}). Preliminary adsorption of pyridine on the γ-Al_2O_3 surface suppressed completely the isomerization and the appearance of bands at 1450 cm^{-1} in the spectrum indicated the presence of coordinatively bonded pyridine on the surface. After desorption of pyridine at 250-300° allene again isomerized at ~20°. Evidently isomerization of allene on γ-Al_2O_3 proceeds on Lewis acid centers. Interaction of allene with $Ni(CO)_4$ deposited on γ-Al_2O_3 at a temperature of 0-20° leads to the formation on the γ-Al_2O_3 surface of compounds, characterized by absorption bands at 1150, 1250, 1295, 1340, 1430, 1640, 2850, 2910, 2940, 2990, and 3080 cm^{-1}. The whole set of absorption bands makes it possible to assign the formed compound to the π-allyl complex of Ni on the γ-Al_2O_3 surface can be obtained upon reaction of $Ni(CO)_4$ directly with allene, and not only with allyl halides, as was shown earlier in [1].

LITERATURE CITED

1. Zh. L. Dykh, L. I. Lafer, V. I. Yakerson, A. M. Rubinshtein, Z. M. Taber, I. V. Kalechits, S. S. Zhukovskii, and V. E. Vasserberg, Izv. Akad. Nauk SSSR, Ser. Khim., 299 (1976).
2. B. L. Shaw and A. G. Stringer, Inorg. Chim. Acta, Revs 7, 1 (1973).

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