PERIODIC CHANGE IN THE REACTIVITY OF THE 2-ALKOXYTETRAHYDRO-2-PYRANYL RADICAL DURING HOMOLYTIC TRANSFORMATIONS OF 2-ALKOXYTETRAHYDROPYRANS AT PRESSURES UP TO 1000 MPa

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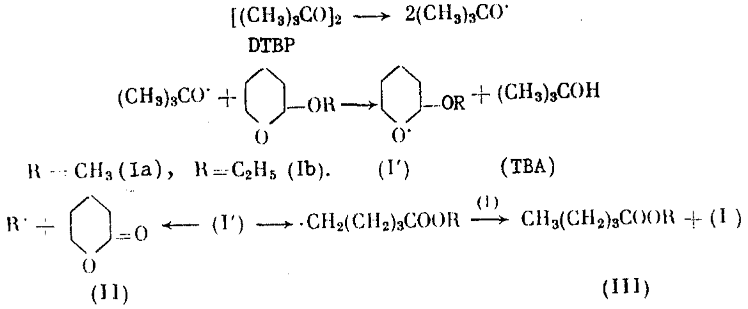
It has been observed that the relative rates of formation of lactone II and ester III, d[II; III]/d[TBA], depend in an undulatory manner on the degree of transformation of I, measured by [TBA].



The corresponding curves for Ia obtained by spline approximation [1] of the experimental dependences of [II] and [III] on [TBA] (32 points each) are presented in Fig. 1.

In conformity with this, the [II]/[III] ratio is determined not by the magnitude of pressure p, as proposed in [2], but rather by the amplitudes and phase shift of the d[II]/d[TBA] and d[III]/d[TBA] vibrations.

For pure Ia the [II]/[III] ratio decreases sharply up to [TBA] = 0.1 M, after which little change is observed (Fig. 1). A qualitatively similar pattern is observed for Ia and Ib in benzene (70 mole %). For pure Ib the [II]/[III] ratio depends only slightly on [TBA] because of the coherence of the d[II]/d[TBA] and d[III]/d[TBA] vibrations.

These results are explained by a periodic change in the ratio of the reactivities of radical I' with respect to cleavage of the endo- and exocyclic C–O bonds and to chain-termination reactions as the reaction products accumulate.

The methods used to carry out the experiments and the analysis of the products were given in [3].

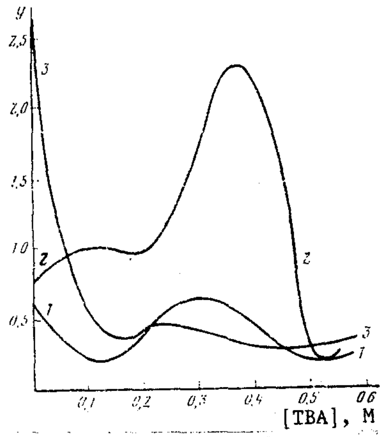


Fig. 1. Relative rates of formation of II and III and [II]/[III] ratio as a function of [TBA] for Ia (130°C, $[DTBP]_0$ = 0.30 and 0.65 M, p = 20-500 MPa): 1) y = d[II]/d[TBA]; 2) y = d[III]/d[TBA]; 3) y = [II]/[III].

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SYNTHESIS OF NEW TYPES OF ORGANOSULFUR NITRO COMPOUNDS

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We have synthesized for the first time analogs of sulfoxides and sulfones of the I-III type in which the oxygen atoms are replaced by N-nitroimido groups: $R_2\overset{+}{S}-\overset{-}{N}-NO_2$ (I), $R_2\overset{+}{S}(O)\overset{-}{N}-NO_2$ (II), and $R\,\overset{++}{S}(\overset{-}{N}-NO_2)_2$ (III).

N-Nitrosulfylimides I were obtained by direct replacement of the oxygen atom by a nitroimido group by reaction of the sulfoxides with nitroamide in the presence of acetic anhydride or by an exchange reaction of iodonium N-nitroimides with dialkyl sulfides:

$$R^1R^2S \rightarrow O + H_2N-NO_2 \xrightarrow{(CH_3CO)_2O} \underset{(I)}{R^1R^2\overset{+}{S}-\overset{-}{N}-NO_2}$$

$R^1 = R^2 = Me$ (Ia), $R^1 = R^2 = Et$ (Ib), $R^1 = Me$, $R^2 = Ph$ (Ic), $R^1 = R^2 = Ph$ (Id).

$$o\text{-}NO_2C_6H_4IO + NH_2NO_2 \rightarrow o\text{-}NO_2C_6H_4\overset{+}{I}-\overset{-}{N}-NO_2 \xrightarrow{(CH_3)_2S} o\text{-}NO_2C_6H_4I + (CH_3)_2\overset{+}{S}-\overset{-}{N}-NO_2.$$

N-Nitrosulfoximides II were synthesized by oxidation of I with $KMnO_4$ or H_2O_2:

$$R^1R^2\overset{+}{S}-\overset{-}{N}-NO_2 \xrightarrow{KMnO_4 \text{ or } H_2O_2)} \underset{(II)}{R^1R^2\overset{+}{S}(O)\overset{-}{N}-NO_2}$$

$R^1 = R^2 = Me$ (IIa), $R^1 = Me$, $R^2 = Ph$(IIb), $R^1 = R^2 = Ph$(IIc).

N,N'-Dinitrosulfodiimides III were obtained by nitration of unsubstituted sulfodiimides or their N,N'-bis(trimethylsilyl) derivatives with nitronium tetrafluoroborate or dinitrogen pentoxide in acetonitrile:

$$R^1R^2S(NR')_2 + NO_2X \rightarrow R^1R^2\overset{++}{S}(\overset{-}{N} - NO_2)_2 + RX$$

$R^1 = R^2 = Me$ (IIIa), $R^1 = R^2 = Ph$ (IIIb); $R' = H$, $Si(CH_3)_3$; $X = BF_4$, NO_3.

Compounds I-III are stable crystalline substances, the structures of which were confirmed by the results of elemental analysis and data from the IR, UV, and PMR spectra and x-ray diffraction analysis.

N-Nitro-S,S-dimethylsulfylimide (Ia). This compound was obtained in 64.8% yield and had mp 56°C. PMR spectrum (CH_2Cl_2, δ, ppm): 2.82 (6H, CH_3). IR spectrum (ν, cm^{-1}): 1402, 1273 ($N-NO_2$). UV spectrum (CH_3OH, λ, nm, log ε): 255/3.99.

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