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REACTIVITY OF DIALKENYLOXYMETHYL CARBOXYLATES TOWARDS CARBOXYLIC ACIDS

A SYNTHESIS OF ISOPROPENYL FORMATE AND OF ACYLALS

by

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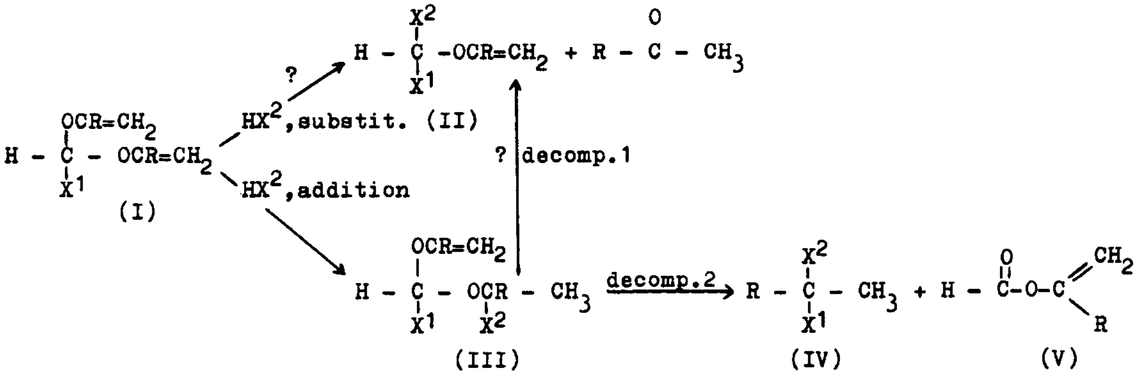
Investigating the reactivity of dialkenyloxymethyl carboxylates, obtained from alkenyl orthoformates and carboxylic acids[1], we found a rather simple procedure for the preparation of isopropenyl formate, which seems ready for further generalization.

In the scheme two possibilities for the conversion of dialkenyloxymethyl carboxylates (I) with carboxylic acids have been given.



R=H or Me; X^1, X^2=OCOH, $OCOCH_3$, $OCOCH_2Cl$, $OCOCCl_3$

Our experiments clearly indicated that the reaction proceeds mainly via the addition step followed by a fast decomposition of III according to the second pathway; diacyloxy ethers (II) were only incidentally isolated in very small amounts.

In the synthetic procedure a carboxylic acid (HX^2) is added dropwise to a dialkenyloxymethyl carboxylate (I) at room temperature. Only with acetic acid the temperature of the reaction mixture had to be raised to about 80°C. The alkenyl formate (V) is immediately removed from the reaction mixture at low pressure and collected in a dry ice cooled vessel. The highest yields (75%) were obtained with the high boiling mono- or trichloroacetic acid from which it could be rapidly and completely separated. Isopropenyl formate decomposes into acetone and carbon monoxide in the presence of acids. Preparation from propyn and formic acid must be therefore very difficult, which might explain its absence in the literature.

Isopropenyl formate, bp.80-81°C, n_D^{20}=1.3990, was identified by NMR measurements: δ =1.88, 4.61 and 7.92 ppm relative to TMS intern ($\sim$10% solution in CCl_4) for the methyl, the methylene and the formyl proton, respectively. The mass spectrum showed peaks at m/e = 86, 58 and 43.

Acylals (IV) are obtained as second products from the reaction mixtures. Ketone acylals (R=Me), even with different acid residues ($X^1 \neq X^2$), have not been described before. They could be isolated in yields from 50-80% (see table I) and have been identified after distillation through a vigreux column (25 x 1 cm) by NMR (Varian HA100) and mass spectrometry (Varian-Mat SM1-B).

Table I

Physical data and yields of acetone acylals

Compound	Bp	n_D^{20}	Yield
$(CH_3)_2C(OCOH)_2$	56°/16 mm	1.4140	75%
$(CH_3)_2C(OCOCH_3)_2$	62°/25 mm	1.4090	60%
$(CH_3)_2C(OCOCCl_3)_2$	110°/1.4 mm	(mp.41°C)	80%
$(CH_3)_2C(OCOCH_2Cl)_2$	116°/4.5 mm	1.4475	75%
$(CH_3)_2C(OCOH)(OCOCH_2Cl)$	86°/5 mm	1.4442	50%

Preliminary results indicate that isopropenyl formate easily formylates weakly basic amino compounds. It seems especially valuable for formylations which are only possible in neutral medium. Investigations about a generalization of the synthetic method and reactivity of the compounds IV and V are in progress.

References: 1) J.W. Scheeren, J.E.W. van Melick and R.J.F. Nivard,
accepted for publication in Rec.Trav.Chim. 1971.