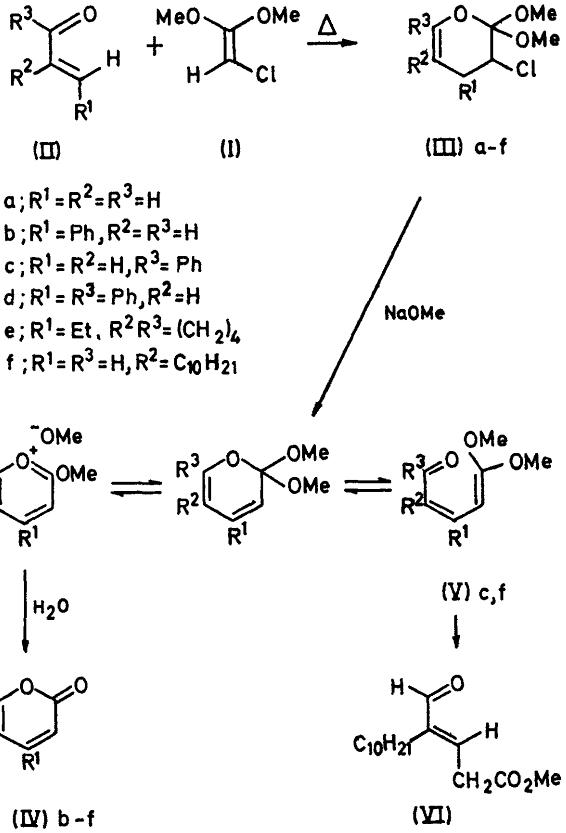
A New Synthesis of α-Pyrones

By Alain Bélanger and Paul Brassard*
(*Départment de Chimie, Université Laval, Québec, Canada*)

Summary A simple two-step synthesis of α-pyrones from αβ-unsaturated carbonyl compounds has been devised.

The reaction of keten acetals with αβ-unsaturated carbonyl compounds has been known for some time to give dihydropyrans.[1] Analogous products have now been prepared using chloroketen dimethyl acetal[2] (I) and acraldehyde (IIa), cinnamaldehyde (IIb), phenyl vinyl ketone (IIc), chalcone (IId), 2-propylidenecyclohexanone (IIe), and 2-methylenedodecanal (IIf). The expected 3-chloro-3,4-dihydro-2,2-dimethoxypyrans (IIIa—f) were obtained in all cases and the assigned structures confirmed by i.r. and n.m.r. spectroscopy. The condensations were effected by heating the two components at 150° for 72 h, usually in the presence of small amounts of hydroquinone (IIc reacts at 120° in 10 min.). The reaction seems to reach an equilibrium and appreciable amounts of starting materials can be recovered along with a 30—70% yield of the dihydropyran: (IIIa) 56%, b.p.$_{12\,\text{mm}}$ 90—92°; (IIIb) (*trans* only 42%, b.p.$_{1\,\text{mm}}$ 94—96°, m.p. 106—107° (ether); (IIId) (*trans*) 36%, m.p. 125—126° (ether–petroleum) and (IIId) (*cis*) 21%, m.p. 79—80° (ether–petroleum); (IIIe) (*cis* only) 32%, b.p.$_{0\cdot01\,\text{mm}}$ 80—85°; (IIIf) 52%, b.p.$_{0\cdot05\,\text{mm}}$ 125—130°.

Compounds (IIIa—f) are readily hydrolysed to the corresponding aldehydo- or keto-esters and attempts to dehydrohalogenate the latter by various reagents yielded only starting material, cyclopropane derivatives, or unidentified products. However, when the dihydropyrans (IIIb—f) are treated with about 4 equiv. of sodium methoxide in dimethyl sulphoxide or, in some cases, dimethylformamide at room temperature, the corresponding α-pyrones (IVb—f) are obtained directly within a few hours: (IVb) 85%, m.p. 75—76°; (IVc) 64%, m.p. 63—64° (lit.[3] m.p. 63—64°); (IVd) 72%, m.p. and mixture m.p. 136—137° (authentic compound);[4] (IVe) 78%, m.p. 80—81°; (IVf)



Scheme

52%: *vide infra*, m.p. 9·5—11·5° [α-pyrone (IVa) decomposes under these conditions].

A somewhat more complex process is observed with dihydropyrans unsubstituted in the 4-position (IIIc,f). The reaction of (IIIc) with base (*ca.* 4 equiv) leads to a mixture of the pyrone (IVc), the acetal (Vc), and an unidentified ester, while (IIIf) always gives the by-product (VI) (*ca.* 25%) (comparison of the n.m.r. spectrum with those of tiglaldehyde and methyl 4-formylbut-3-en-1-oate[5] indicates that it is probably the *trans*-isomer) and an oxidation product which is probably methyl *trans*-tetradec-2-en-4-on-1-oate, m.p. 61·5—62·0°. With a large excess of base (*ca.* 7 equiv.), (IIIf) is converted mainly into the acetal (Vf) (55%). This compound, after isolation from the reaction medium rearranges spontaneously to the α-pyrone within a few hours. These observations indicate that the reaction probably proceeds through the pyrilium salt (Scheme).

Applications of this method to the synthesis of steroidal and other natural dienolides are being investigated.

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