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ON THE FAVORSKII REARRANGEMENT OF DICHLOROMETHYLKETONES.

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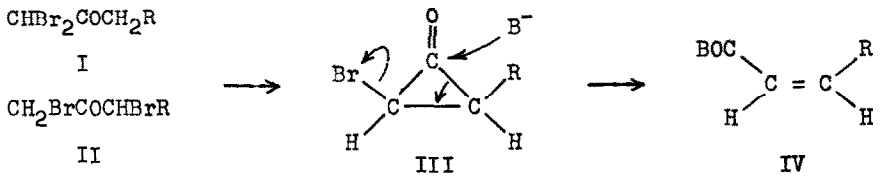
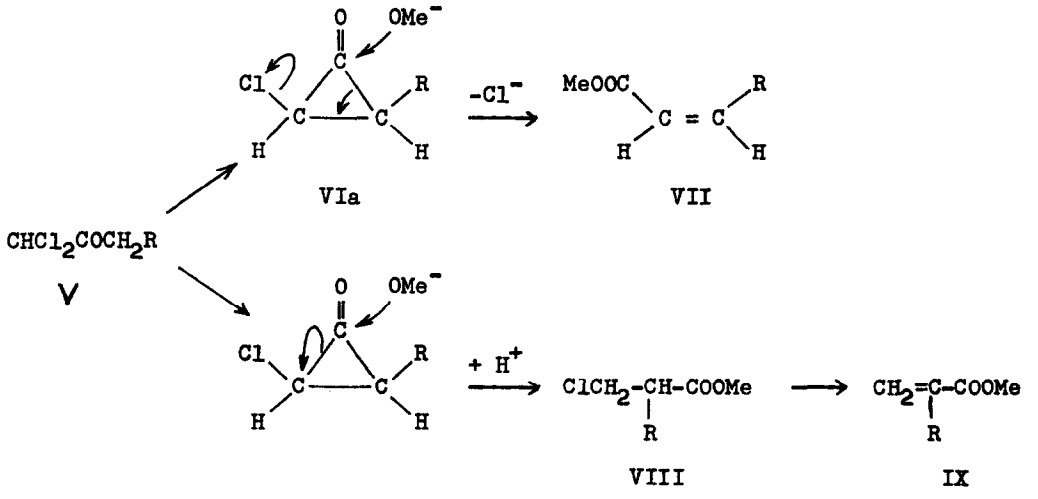
By treatment with sodium methoxide 2,2-dichloro-1,3-cyclohexanediones (1,2,3), are methanolysed to give methyl 4-dichloroacetylbutyrates, which further undergo a Favorskii rearrangement (3). In some aspects this Favorskii rearrangement proved different from the normal reaction. This now was further examined with dichloromethylketones of the type $Cl_2CHCOCH_2R$.

All α,α- and α,α' dibromomethylketones (I, II) mentioned so far in the literature give cis β-substituted acrylic acids or derivatives (IV)(4,5). The eventual intermediate monobromo-acids could not be isolated. This has been explained by a trans-antiparallel 1,3-elimination forming a 2-alkyl-3-bromocyclopropanone (III), which is specifically cis due to steric hindrance. This intermediate then is opened by the base with concerted elimination of a bromine anion and conservation of stereospecificity (4).



In opposition to this the Favorskii rearrangement of dichloromethylketones (V) by sodium methylate in methanol as investigated by us proceeds in two competitive reaction ways. By successive additions of small amounts of base, equivalent amounts of dichloromethylketone are converted into a mixture of cis β-substituted methyl acrylate (VII) - normally expected product - and α-chloromethyl-substituted methyl ester (VIII). The formation of the latter substance

is unexpected and the first example of a new reaction way in Favorskii rearrangement conditions. When more base is added after all starting material has disappeared the α-chloromethyl-ester (VIII) eliminates hydrogen chloride yielding α-substituted methyl acrylates (IX)



The ratio of β-substituted acrylate to chloromethyl-ester depends strongly on the branching of the alkyl group as is seen from the table.

TABLE

$RCH_2COCHCl_2$		cis RCH=CHCOOMe	$ClCH_2CHRCOOMe$
R = Pr	(Va)	100 %	-
R = i.Bu	(Vb)	100 %	-
R = i.Pr	(Vc)	67 %	33 %
R = t.Bu	(Vd)	25 %	75 %
R = $MeOOC.CH_2C(CH_3)_2$	(Ve)	50 %	50 %

Thus for primary alkyl groups only the "normal" cis β-substituted acrylates are obtained, but for dichloromethyl-neopentylketones (Vd) (tertiary alkyl group) the "abnormal" product is three times as abundant as the "normal" one. Methyl 4-dichloroacetyl-3,3-dimethylbutyrate (Ve) is the methanolysis

product of 2,2-dichlorodimedone.

The "normal" reaction giving cis β-substituted methyl acrylates probably proceeds in the same way as for dibromoketones (4) via a 2-alkyl-3-chlorocyclopropanone, which then is opened with concerted elimination of a chlorine anion (VIa). The "abnormal" reaction could be explained by the same intermediate cyclopropanone, which however is opened now at the opposite side (VIb). Concerted elimination of a chlorine anion then is impossible, which results in the formation of 2-chloromethyl-substituted esters.

It is known that cyclopropanones can be opened at either side, depending on the structure (6). Why α-chloromethyl-esters are favoured in the case of branched alkyl dichloromethylketones however is an open question.

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