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The Mechanism of the Alkaline Rearrangement of 1,1,1-Trichloro-2-penten-4-one

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The formation of the carboxylic acid, 5-chloro-2, 4-pentadienoic acid (trans-2, cis-4)

(I), by the alkaline hydrolysis of 1,1,1-trichloro-2-penten-4-one (II) has been reported. 1-3

Cl₃CCH — CHCOCH₃ OH — CLCH — CHCH— CHCO₂H (i)

Two mechanistic pathways for such reactions have been offered. The first required a 1,5-migration of chlorine in an enoiate anion. The second involves cyclisation of the enolate anion to form a cyclopropanone. Our studies have enabled us to establish the pathway for this reaction. The alkaline hydrolysis of (Π) , either $\frac{1}{4}$ - $\frac{1}{4}$ C or $\frac{1}{4}$ - $\frac{1}{4}$ C labelled, have been carried out and the product degraded to give the result shown in (ii) and (iii).

$$\text{Cl}_3\text{CCH} \longrightarrow \text{CH}_3 \xrightarrow{\text{OH}} \text{ClCH} \longrightarrow \text{CHCH} \longrightarrow \text{CHCO}_2\text{H}$$
 (ii)

Cl₃CCH — CHCOCH₃ OH ClCH — CHCO₂H (iii) These results exclude the migration of chlorine¹ and confirm a pathway involving insertion of 5-carbon into the chain. The reaction was also carried out in deuterium oxide, in the presence of excess bromide anions and in the presence of cyclohexene. The acid (I) was found to be completely deuterated in the first case and gave no incorporation of bromide in the second. No products from carbene-type intermediates could be identified in the third.

A Favorskii-type pathway is shown below (iv). This is closely related to that given by Takeda et al.² We favour the direct formation of a cyclopropanone. A recent report by Takeda of the related synthesis of a cyclobutenecarboxylic acid from α-acetylcyclopentanone supports their pathway in terms of the skeletal reorganisation. The pathway (iv) involves intramolecular nucleophilic attack by the carbanion at the double-bond to give, possibly via a carbanion intermediate, the dichloro cyclopropanone shown.

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II
$$\xrightarrow{+OH^-}$$
 Cl_3CCH $CHCOCH_2$ $\xrightarrow{-Cl^-}$ Cl_2C $CHCHCO$ Cl_2C $CHCHCO$ Cl_2C $CHCH_2CO_2$ Cl_2C $CHCH_2CO_2$ $CHCH_2CO_2$ Cl_2CHCH $CHCH_2CO_2$ Cl_2CHCH Cl_2CHCH Cl_2CHCH Cl_2CHCH Cl_2CHCH Cl_2CHCH $CHCHCO_2$ $CHCHCO$ $CHCHCO_2$ CL_2 $CHCH$ $CHCHCO_2$ $CHCHCO$ $CHCHCO$

Takeda² favoured a 1,4-elimination from (IV) to form (I) and also reported the isolation of (III). We have confirmed the latter and submitted (III) to alkaline hydrolysis in water and deuterium oxide. A poor yield of (I) was obtained and was found to be completely deuterated. However (I) is always found with specific configuration as a trans-2-cis-3 diene. The preferred stereochemistry for a base-catalysed 1,4-elimination appears to be syn.⁵ No obvious and simple reason for stereoselectivity in elimination of the conformationally free system (IV) appears to exist. An attractive alternative to account for the stereochemistry would involve the occurrence of the vinyl carbanion (V). Vinyl carbanions are known to possess stereochemical stability in such cis-forms.^{6,7}

An anion, with a contribution from the canonical (V), could be formed by the action of base on either (I) or the allene (VI), formed by base-catalysis from (III) via the acetylene (VII) as in (v) below.

III
$$\xrightarrow{+OH}$$
 Clc \longrightarrow $CCH_2CH_2CO_2$ \longrightarrow $ClcH$ \longrightarrow $CHCH_2CO_2$ (v)

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