

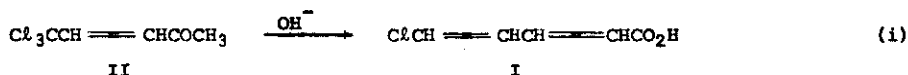
The Mechanism of the Alkaline Rearrangement of 1,1,1-Trichloro-2-penten-4-one

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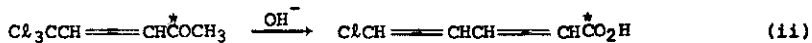
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The formation of the carboxylic acid, 5-chloro-2, 4-pentadienoic acid (trans-2, cis-4) (I), by the alkaline hydrolysis of 1,1,1-trichloro-2-penten-4-one (II) has been reported.<sup>1-3</sup>



Two mechanistic pathways for such reactions have been offered. The first required a 1,5-migration of chlorine in an enolate anion.<sup>1</sup> The second involves cyclisation of the enolate anion to form a cyclopropanone.<sup>2</sup> Our studies have enabled us to establish the pathway for this reaction. The alkaline hydrolysis of (II), either 4-<sup>14</sup>C or 1-<sup>14</sup>C labelled, have been carried out and the product degraded to give the result shown in (ii) and (iii).



These results exclude the migration of chlorine<sup>1</sup> 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.*<sup>2</sup> We favour the direct formation of a cyclopropanone. A recent report<sup>4</sup> by Takeda of the related synthesis of a cyclobutenecarboxylic acid from  $\alpha$ -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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