A New Olefin Synthesis from α-Halogeno-ketones

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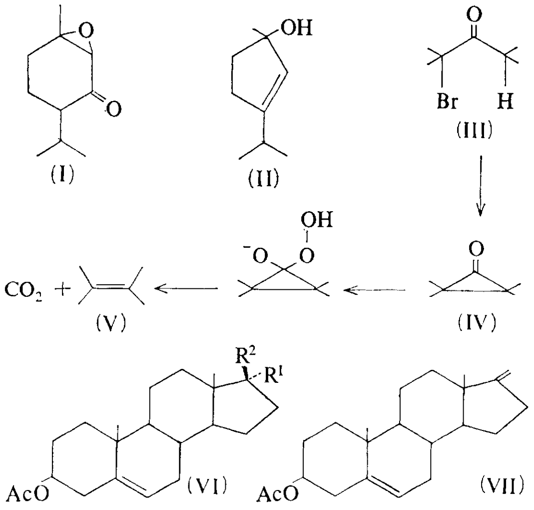
HOPING to develop new synthetic procedures for olefins using readily available starting materials, we have examined the possible direct oxidative decarbonylation† of cyclopropanones, produced *in situ* by the Favorskii rearrangement of α-halogenoketones.[1] There are at least two reactions, which may be interpreted as proceeding by a similar pathway. First the observation of Treibs[2] that the piperitone oxide (I) yields the alcohol (II) when treated with alkaline hydrogen peroxide, and secondly the finding of Volpin[3] that tropylium cation yields benzene with hydrogen peroxide. These reports suggested to us the possibility of trapping an intermediate cyclopropanone (IV), produced in a Favorskii rearrangement of an α-halogenoketone (III), with the nucleophilic hydroperoxide anion and subsequent decomposition of the intermediate species to the olefin (V).



(I) (II) (III) (IV) (V) (VI) (VII)

When the bromoketone[4] (VI; R^1 = Br, R^2 = Ac) was treated, in t-butyl alcohol, with hydrogen peroxide (50%, aqueous) in the presence of either 4N-sodium hydroxide or solid potassium carbonate (reflux), the corresponding 17-methylene compound (VII) resulted in *ca.* 65% yield.‡ This substance was identical in all respects (spectra, mixed m.p.) with an authentic sample prepared from dehydroepiandrosterone acetate according to Sondheimer.[5] The other product was the Favorskii acid[6] (VI; R^1 = Me, R^2 = CO_2H). In order to reduce the amount of acid formed we have used a water-free system, namely potassium t-butyl peroxide (from potassium t-butoxide and t-butylhydroperoxide. However, acid was still obtained and may be the result of a Faworskii-type ring opening of the intermediate hydrated species. It is however the minor product.

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† The formal loss of carbon monoxide is actually achieved by removal of a carbon dioxide molecule.

‡ Some 3β-de-acetylated material was also obtained, which was readily convertible to (VII) by the usual procedure.

Strong support for the intermediacy of the cyclopropanone (IV) has recently been obtained by Greene and his co-workers who have isolated a stable cyclopropanone and observed its conversion, by hydrogen peroxide, to the corresponding olefin.[7]

This then represents a convenient procedure for the formation of olefins, in those cases where a ketone and its α-halogeno-derivative are available.

(*Received, March* 11*th*, 1968; *Com.* 296.)

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[7] Personal communication from Professor F. D. Greene, Massachusetts Institute of Technology.