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FRAGMENTATION OF A 1-BENZOXEPIN-5-ONE BY POTASSIUM t-BUTOXIDE.

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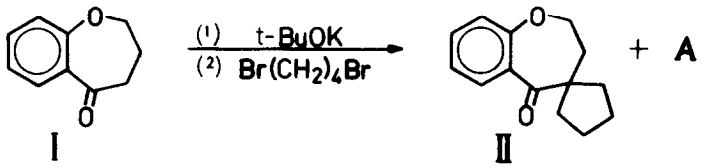
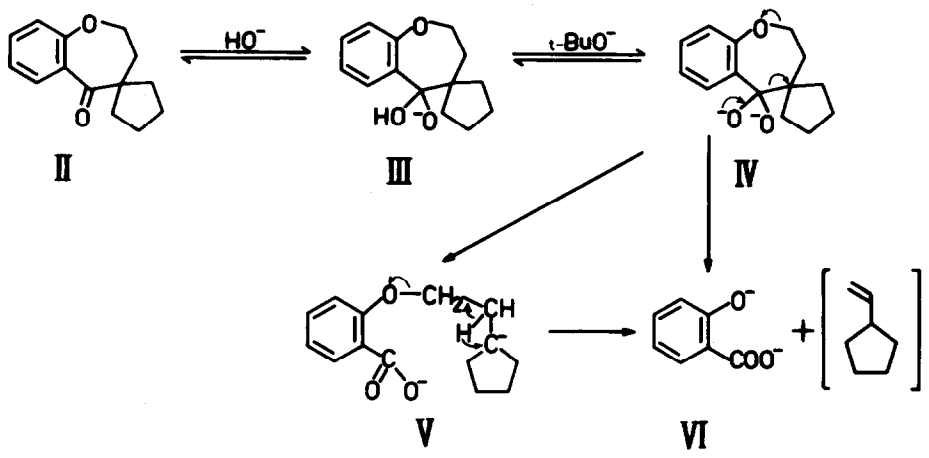
In connection with another work, it became necessary to synthesize a number of substituted 1-benzoxepin-5-ones. The unreported 2,3-dihydro-1-benzoxepin-5-on-4-spirocyclopentane (II) was obtained from the heterocyclic ketone I, with 1,4-dibromobutane in the presence of t-BuOK. Surprisingly, the reaction products proved to be a mixture of parent ketone I, spiro-ketone II, and a solid A. Several recrystallizations of the solid from petroleum ether afforded a



I II

compound m.p. 158.5° which was analyzed. The absence of any methylene protons in the n.m.r. spectrum of this product and the positive reaction with $FeCl_3$ suggested that the compound thus obtained was salicylic acid, and this assumption was confirmed by the mixture melting point withouth depression, and infrared spectrum.

Recent papers dealing with the cleavage of non-enolizable carbonyl compounds by potassium t-butoxide [1-5] lead us to suspect that the salicylic acid originates from a cleavage reaction in which the spiro-ketone II is cleaved by t-BuOK. Consequently, in order to determine whether the actual cleavage was taking place, both ketones, I and II, were treated separately with t-BuOK in similar conditions. When the spiro-ketone II was treated with a benzene solution of potassium t-butoxide (containing a small amount of water) the presence of salicylic acid in the reaction mixture indicated that cleavage of II was taking place, but when the substrate was the parent ketone I, no trace of salicylic acid was found in the reaction mixture.



The result support our assumption and, in addition, it indicates that at least as concerns the $C_{(4)}$-CO bond cleavage, the mechanism must be identical to that proposed for the cleavage of non-enolizable ketones.[1, 4] A possible mechanism of the cleavage reaction might be outlined as follows. The dianion IV formed from II by nucleophilic attack of HO^- and t-BuO^-, affords the salicylate dianion VI (and probably vinyl-cyclopentane which polimerizes) either step by step via the carbanion – carboxylate anion V, or as a concerted reaction IV⟶VI .

Although cleavage reactions of non-enolizable ketones have been observed before under a variety of conditions,[1-5] the fragmentation of II by a double cleavage involving a C-CO and an O-CH_2 bond is unprecedented.

Work is in progress to determine the scope and limitations of this reaction and the result will be reported soon.

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