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REVISION OF THE STRUCTURE OF THE REACTION PRODUCT OF CHLORAL WITH α-ACETYLCYCLOPENTANONE IN THE PRESENCE OF BASE

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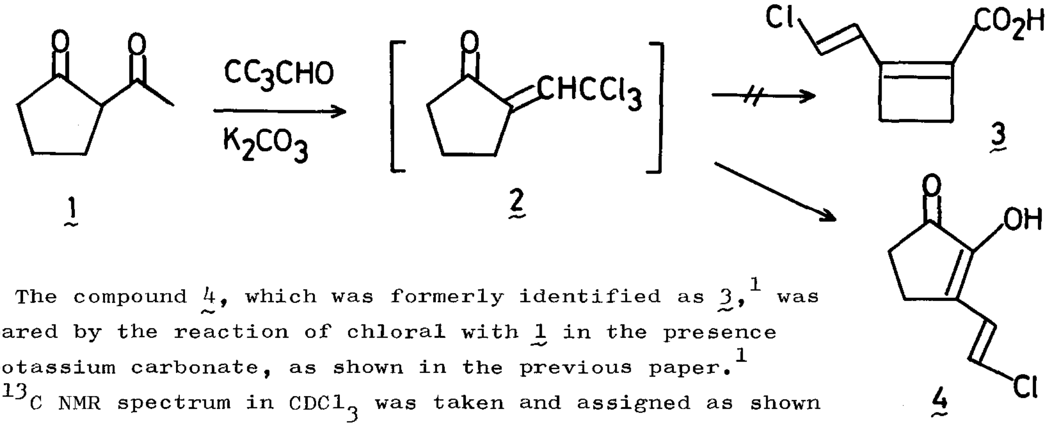
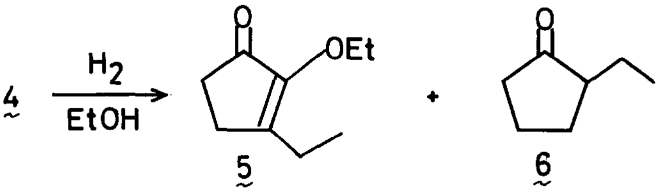
Summary: The structure of the product from the title reaction has been revised by means of ^{13}C NMR, X-ray crystallographic analysis as well as additional chemical transformations.

In 1973 and 1974, two (S. T. and A. T.) of the present authors reported that the reaction of chloral with α-acetylcyclopentanone (1) in the presence of potassium carbonate gave 2-(2′-chlorovinyl)cyclobutenecarboxylic acid (3),[1] which was thought to be derived from the intermediate compound 2 by a Favorskii type rearrangement. The structure of 3 was assigned based on IR, ^{1}H NMR, and mass spectral data, elemental analyses as well as the results of permanganate oxidation. We recently reinvestigated the structure of this compound by means of ^{13}C NMR and X-ray crystallographic analysis as well as additional chemical transformations. We wish to report in this communication the correction of the formerly assigned structure 3 to 3-(2′-chlorovinyl)-2-hydroxy-2-cyclopentenone (4), which is not a product by a Favorskii-type rearrangement.[2]



The compound 4, which was formerly identified as 3,[1] was prepared by the reaction of chloral with 1 in the presence of potassium carbonate, as shown in the previous paper.[1] Its ^{13}C NMR spectrum in $CDCl_3$ was taken and assigned as shown in Fig. 1. The spectral data, in which the signal at 202.5 ppm appeared at too down field for that of the carboxyl group,[3] ruled out the structure 3.

The hydrogenation of 4 conducted in ethanol at 30°C ($PdCl_2$-gum arabic, 2 h) gave a mixture of 2-ethoxy-3-ethyl-2-cyclopentenone (5)(17%) and 2-ethylcyclopentanone (6)(53%).[4] The structure of 5 has been confirmed by the independent synthesis through the O-ethylation of 3-ethyl-2-hydroxy-2-cyclopentenone (7).[5]



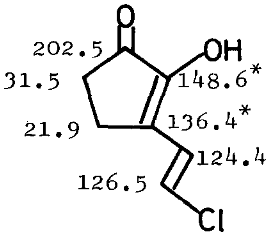


Fig. 1.(*Assignment may be interchangeable.)

The structure of 4 was absolutely verified with X-ray crystallographic analysis.[6] ORTEP drawing in Fig. 2 illustrates the geometrical aspect of the molecule and explains the chemical structure reasonably.

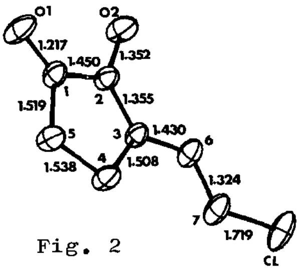
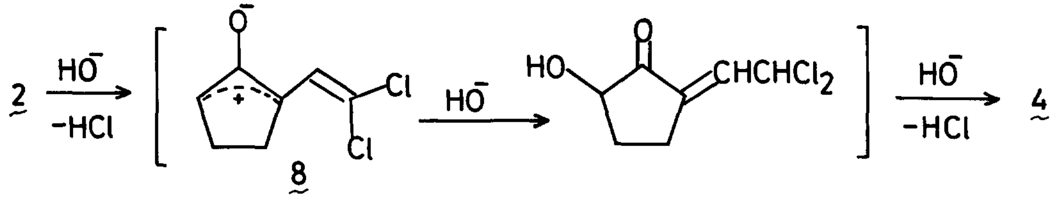


Fig. 2

The mechanism of the present reaction is considered as follows. The formation of α-trichloroethylidenecyclopentanone (2) is reasonably anticipated by analogy of the base-catalyzed deacylative condensation of aldehydes with 1,3-dicarbonyl compounds.[7] The transient intermediate 2 may undergo the rearrangement to produce 4 in alkaline media via a zwitterion 8, which has been suggested to be involved in Favorskii rearrangement.[8]



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