CHEMISTRY LETTERS, pp. 619-620, 1975. Published by the Chemical Society of Japan

THE REACTION OF CYCLOALKANONES WITH COPPER(II) HALIDES. IV.[1)]
THE OXIDATIVE RING CONTRACTION OF CYCLOHEPTANONES WITH COPPER(II) CHLORIDE IN ACETIC ACID

J. Yasuo SATOH, Kyoko NISHIZAWA*, and Masakatsu HIROSE**
Department of Chemistry, St. Paul's (Rikkyo) University,
Nishi-Ikebukuro, Tokyo 171

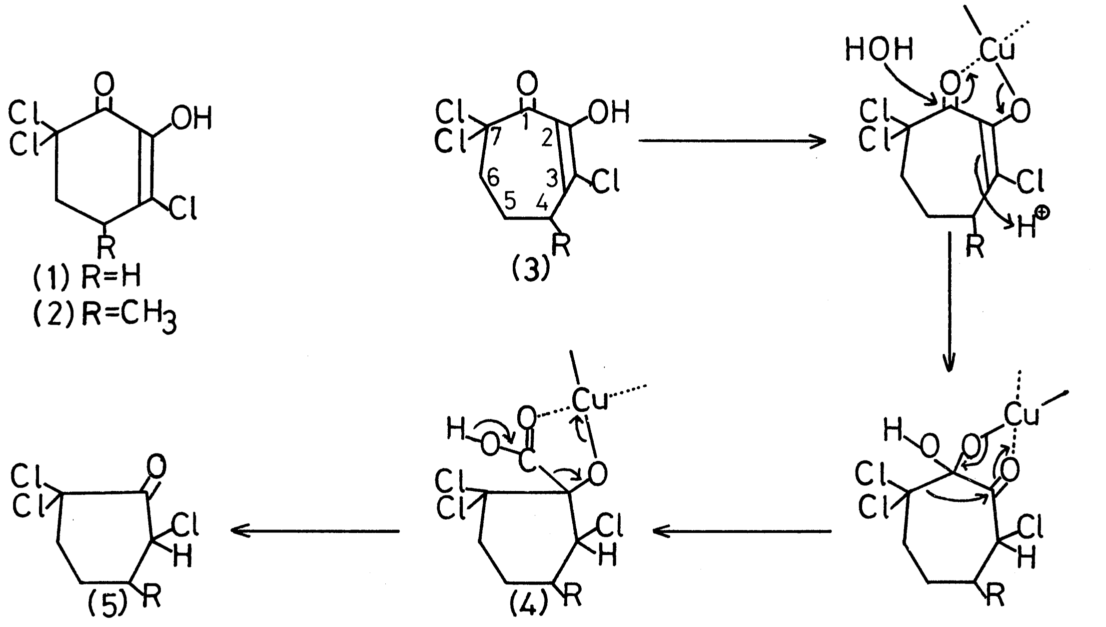
In the reaction of cycloheptanones with copper(II) chloride, it was found that ring contraction accompanying decarbonylation occurred, followed by chlorination, yielding polychlorinated cyclohexane-1,2-diones.

Although many studies have been made on ring contraction of cyclic ketones (e.g., α-diketone and α-haloketone),[2)] in all cases, these were ketones having functional groups at the α-position. Moreover, on ring contraction of α-non-substituted cycloalkanones, reactions with Tl(III) salts[3)] and H_2O_2/SeO_2[4)] were reported. In these reactions, however, decarbonylation was not observed in any case. Previously, the authors reported that the reactions of cyclohexanones with large amounts of copper(II) chloride in 50% dioxane give polychlorinated cyclohexanediones[5)] in good yields. In the present paper, we report that a new oxidative ring contraction occurs in the reaction of cycloheptanones with Cu(II) chloride.

Cycloheptanone (2 g) was treated with 50 molar amounts of $CuCl_2 \cdot 2H_2O$ (163 g) in 50% AcOH (v/v, 200 ml) under reflux conditions for 4 hr. After the usual work-up, 0.74 g (42%) of 3,6,6-trichloro-2-hydroxycyclohex-2-en-1-one (1), mp 119-120°C (lit.,[6)] 115-116°C), was obtained by separation with column chromatography and recrystallization from CCl_4. In the same manner, 4-methylcycloheptanone gave 3,6,6-trichloro-2-hydroxy-4-methylcyclohex-2-en-1-one (2) (41%), mp 119-121°C (lit.,[5)] 119-121°C).

These results denote the new finding that, in the reaction with Cu(II) chloride, ring contraction accompanying decarbonylation occurs, followed by chlorination, the cycloheptanones being converted to the same products as are obtained in the case of cyclohexanones. In this ring contraction, the reaction conditions stated above were superior to using smaller amounts of the reagent and a dioxane medium.

It is considered that this ring contraction would also proceed via the benzilic acid type rearrangement of 1,2,3-triketone.7) That is, the carbon at C_1 in 3,7,7-trichloro-2-hydroxycyclohept-2-en-1-one (3) would be similar to that of the electron poor state in the case of the triketone, because of the inductive effect due to gem-dichloro function at C_7. Compound 3 would be produced by a pathway similar to that for the formation of polychlorinated cyclohexanediones from cyclohexanones described previously.5b) Hence, the reaction would proceed through the pathway shown below. The resulting 4 would be subjected to decarbonylation to give 5, and then 5 would be converted to trichlorocyclohexane-1,2-dione by the pathway described previously.5)



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* Present address: Meiji College of Pharmacy, Yato-machi, Tanashi 188.

** Present address: Department of Management, Senshu University, Tama-ku, Kawasaki 214.

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(Received March 22, 1975)