Sodium Hypobromite Oxidation of Certain Cycloalkanones

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The hypohalite oxidation of methyl ketones to carboxylic acids is a well-recognized useful synthetic procedure.[1,2] More recently higher alkylaryl and alkylheterocyclic ketones have been converted to carboxylic acids in good yields by the use of alkaline hypohalite solutions.[3,4] The present work reports the hypohalite oxidation of cyclohexanone and cyclopentanone.

Cyclohexanone was smoothly converted to adipic acid by three equivalents of sodium hypobromite solution at room temperature. The attack of sodium hypobromite on cyclopentanone was considerably more vigorous however, and when the reaction was allowed to proceed at 30–35°, a very small amount of succinic acid was isolated. When conducted at 5–10° a fair yield of glutaric acid along with a smaller amount of succinic acid was isolated. With cyclopentanone the consumption of sodium hypobromite was more than the three moles required according to the stoichiometry as described by Levine and Stephens[4] as evidenced by the disappearance of oxidizing reagent during the course of addition of cyclopentanone.

EXPERIMENTAL

Oxidation of cyclohexanone. A sodium hypobromite solution was prepared according to the directions of Levine and Stephens[4] from 88.0 g. (2.2 moles) of sodium hydroxide and 28 ml. (0.55 mole) of bromine in 300 ml. of water. The solution was allowed to warm to 20° and was stirred rapidly while 14.7 g. (0.15 mole) of cyclohexanone was added over a 15-min. period with ice-bath cooling to maintain the temperature at 20–25°. After all the ketone had been added the solution was stirred 2 hr. longer at room temperature. The mixture was then acidified with concentrated hydrochloric acid, whereupon adipic acid precipitated. The slurry was cooled to 5° and filtered. The adipic acid was washed with ice water and dried at 75–80°. The yield of adipic acid, m.p. 150–152°, amounted to 17.3 g. (82%).

Oxidation of cyclopentanone. Cyclopentanone was added dropwise to a sodium hypobromite solution prepared from 88.0 g. of sodium hydroxide and 28 ml. of bromine in 300 ml. of water. In spite of ice-bath cooling, when the addition was started at 20°, the temperature rose to 30–35°. After 10.6 g. of cyclopentanone had been added during 15 min., the solution became colorless and gave a negative test with starch-potassium iodide test paper. The mixture was stirred 15 min. longer, acidified with hydrochloric acid, and evaporated to dryness in vacuum. The residue was extracted thoroughly with ether, and the ether solution was dried and evaporated. Trituration with ether-benzene induced crystallization, and after recrystallization from water there was obtained 2.5 g. of succinic acid, m.p. 186–188°. The mother liquor from trituration with ether-benzene was examined for glutaric acid but none could be isolated.

When the reaction mixture was maintained at 5–10° and the cyclopentanone (12.6 g.) added dropwise over a 0.5-hr. period, 1.7 g. of succinic acid and 8.8 g. of glutaric acid were obtained.

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Inertness of Tetrachlorofulvenes in the Diels-Alder Reaction

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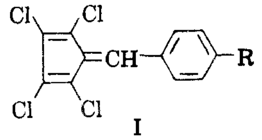
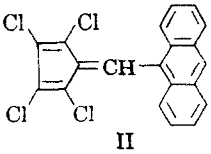
Recently the preparation of tetrachlorofulvenes was disclosed but no mention was made of their being tried in a diene synthesis.[1] It seemed to us that these compounds would be ideal in kinetic studies of the Diels-Alder reaction. Therefore, 1,2,3,4-tetrachloro-6-phenylfulvene (I, R = H) and four of its derivatives (I, R = NO_2, Cl, $N(CH_3)_2$, and OCH_3) were prepared.



I

The fulvenes in preliminary tests gave no evidence of reaction with maleic anhydride in benzene and finally were heated in molten maleic anhydride at 117° for a week. At the end of this time cooling gave colored crystals of the fulvenes in the maleic anhydride and no adduct could be isolated.

When 6-(9-anthryl)-1,2,3,4-tetrachlorofulvene (II) was prepared, treatment with maleic anhydride



II

lead to only a mono adduct. The product still had the color typical of a fulvene and its spectrum indicated the maleic anhydride had reacted with the anthracene moiety.

The color of 1,2,3,4-tetrachloro-6-(2-furyl)fulvene pentadiene did not fade when heated at 100° with maleic anhydride for a week. In addition *p*-[6-(1,2,-

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