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Rearrangement of 1-Methylcyclopentyl Hypochlorite

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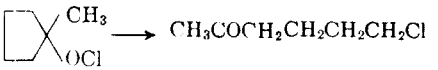
1-Methylcyclopentyl hypochlorite has been found to rearrange readily to 6-chlorohexan-2-one as the sole product.

A series of tertiary alkyl hypochlorites was studied by Chattaway and Backeberg,[1] who showed the reaction for their facile decomposition to be

$$R_3C—OCl \rightarrow R_2CO + RCl$$

The reaction occurs spontaneously at temperatures slightly above room temperature and is accelerated by ultraviolet light.

We have prepared 1-methylcyclopentyl hypochlorite,[2] I, and have observed that it rearranges readily to give an open-chain haloketone, 6-chlorohexan-2-one (II), as the sole product.[3] No cleavage to cyclopentanone and methyl chloride was observed.



I II

This rearrangement of tertiary cycloaliphatic hypohalites provides a new synthetic approach to ω-haloketones, compounds often difficulty accessible by other means.

EXPERIMENTAL

Preparation of 1-methylcyclopentyl hypochlorite.[4] A nearly homogeneous solution of 37.5 g. (0.39 mole) 1-methylcyclopentanol[5] and 30 g. of sodium hydroxide (0.75 mole) in 700 ml. of water was stirred in an ice-bath and saturated with chlorine during two hours. The yellow oil which separated to the bottom was extracted from the aqueous solution with three 100-ml. portions of methylene chloride. The extracts were washed with a saturated aqueous sodium bicarbonate solution and with water, then dried over magnesium sulfate. Removal of solvent at reduced pressure left a residue of 40 g. crude 1-methylcyclopentyl hypochlorite (76% of theory).

This material had a strong hypochlorite odor, and gave a strong positive chlorine test. Attempts to effect a careful distillation failed because of the instability of the product, but in one attempt, some material was distilled at 32°/8 mm., which can only be regarded as an approximate boiling point.

Rearrangement of I to II. The rearrangement of 1-methylcyclopentyl hypochlorite to 6-chlorohexan-2-one was observed during attempted distillations of I. At temperatures as low as 40° the rearrangement was essentially quantitative and was accompanied by a color change from yellow to pale green. The rearranged product was fractionally distilled to give a colorless liquid, b.p. 85.5–86.5°/16 mm. This showed no active chlorine, formed a precipitate with 2,4-dinitrophenylhydrazine solution, gave a positive iodoform test, and gave no precipitate with cold alcoholic silver nitrate, but did yield silver chloride when heated with alcoholic silver nitrate. These properties are in accordance with the structure shown for II.

Anal. Calc'd for $C_6H_{11}ClO$: Cl, 26.37. Found: Cl, 26.45, 26.52.

(1) Chattaway and Backeberg, *J. Chem. Soc.*, **123**, 2999 (1923).

(2) Englund, U. S. Patent 2,675,402 (1954).

(3) Englund, U. S. Patent 2,691,682 (1954).

(4) Teeter, Bachmann, Bell, and Cowan, *Ind. Eng. Chem.*, **41**, 849 (1949).

(5) Zelinsky and Namjetkin, *Ber.*, **35**, 2683 (1902).