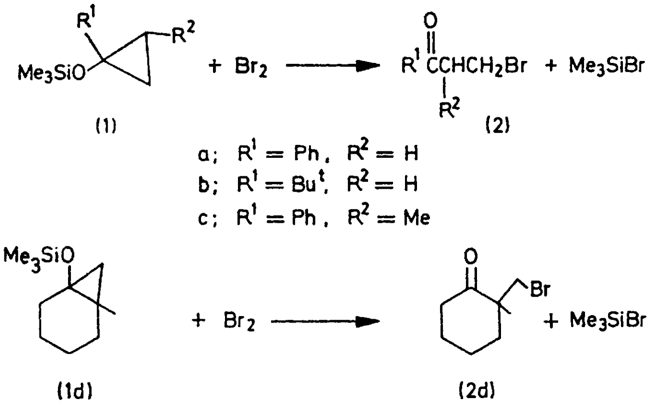
A New Synthesis of β-Bromo Ketones by the Reaction of Silyl Cyclopropyl Ethers with Bromine

By SHINJI MURAI,* YOSHIO SEKI, and NOBORU SONODA

(Department of Petroleum Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka, Japan)

Summary A new synthesis of β-bromo ketones by the reaction of trimethylsilyl cyclopropyl ethers with bromine is described.

REACTION of cyclopropanols with positive halogen is known to give β-halogeno-ketones.[1] This reaction, however, is not synthetically useful because cyclopropanols are fairly unstable and not readily obtainable. Furthermore the hydrogen halide which is formed as one of the reaction products rapidly decomposes the starting material. When a base is used to remove the hydrogen halide formed, dehydrohalogenation from the product, also takes place.[1]



(1) (2)

a; R^1 = Ph, R^2 = H
b; R^1 = Bu^t, R^2 = H
c; R^1 = Ph, R^2 = Me

(1d) (2d)

We now report that trimethylsilyl cyclopropyl ethers (**1**) can be used as the synthetic equivalent[2] of cyclopropanols to give β-bromo ketones (**2**). As we have already shown,[3] (**1**) can be prepared in quantity by reaction of the corresponding silyl alkenyl ethers with Simmons-Smith reagent and are very stable in contrast to cyclopropanols. The only by-product of the bromination of (**1**) is trimethylsilyl bromide which is neutral, does not react with either (**1**) or (**2**), and can be removed without difficulty from the reaction mixture under reduced pressure. The products of the synthesis are shown in the Scheme.

Experimentally, bromine (0·02 mol) in CH_2Cl_2 (10 ml) was added slowly to a solution of the trimethylsilyl cyclopropyl ether (**1**) (0·02 mol) in CH_2Cl_2 (20 ml) at −70°. The solution was stirred at room temperature for 30 min and after removal of the solvent and Me_3SiBr *in vacuo* the practically pure β-bromoketone (**2**) was produced in quantitative yield; (**2a**), m.p. 59—60° (lit.[4] m.p. 57—58°); (**2b**), b.p. 47—49°/0·5 mm; (**2c**), b.p. 92°/1·5 mm (partially decomp.); (**2d**), b.p. 71—75°/0·4 mm.

When two equivalents of bromine were used in the above reactions, the corresponding αβ-dibromo ketones were obtained.

We thank Shin-Etsu Industry Co., Ltd. for the trimethylsilyl chloride.

(*Received*, *7th October* 1974; *Com.* **1250.**)

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