Silyl Alkenyl Ethers as the Synthetic Equivalent of Enols. A New Synthesis of αβ-Unsaturated Ketones

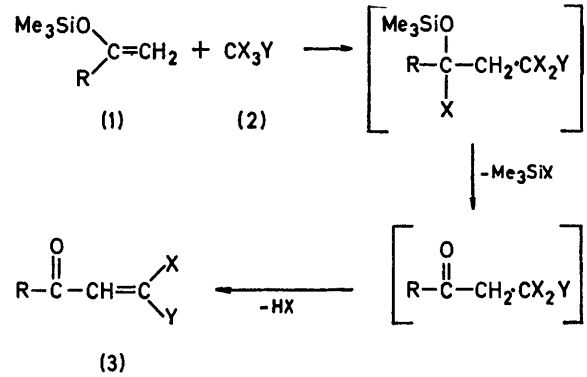
By SHINJI MURAI,* YOSHIAKI KUROKI, TOMOYUKI AYA, NOBORU SONODA, and SHIGERU TSUTSUMI
(*Department of Petroleum Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka, Japan*)

Summary A new synthesis of αβ-unsaturated ketones *via* the addition of polyhalogeno compounds to trimethylsilyl enol ethers is described.

ADDITION of a carbon–halogen bond across the double bond of an enol would be expected to give rise to a ketone with a new carbon–carbon double bond. However, such a reaction is difficult because the enol is generally the less stable part of a keto–enol tautomer.

We report the synthesis of β-halogeno-αβ-unsaturated ketones,[2] by the addition of polyhalogeno compounds to trimethylsilyl alkenyl ethers (Scheme). The synthesis is based on the fact that suitably substituted organosilanes readily undergo β-elimination.[3]

Trimethylsilyl alkenyl ethers (**1**) were prepared by reaction of the corresponding ketones with trimethylsilyl chloride and triethylamine in dimethylformamide.[1b] A mixture of the trimethylsily alkenyl ether, the polyhalogeno compound, and a catalytic amount of cuprous chloride[4] was refluxed for 2—15 h in a mixture of PhCl and $HCONMe_2$. The products were isolated in high purity (40—80%) by distillation, and showed typical i.r. absorptions for αβ-unsaturated ketones at 1700—1670 and 1605—1555 cm^{-1}.



SCHEME. R = Ph, Bu^t, or neopentyl; CX_3Y = CCl_4, CBr_4, CCl_3CN, CCl_3CO_2Et, CBr_3CO_2Et.

We are grateful to Shin-Etsu Chemical Industry Co., Ltd. for providing the trimethylsilyl chloride.

(*Received, 17th April* 1972; *Com.* 638.)

[1] (a) Yu. I. Baukov and I. F. Lutsenko, *Organometallic Chem. Rev. A*, 1970, **6**, 355; (b) H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, 1969, **34**, 2324.
[2] R. V. Kausbick, *J. Org. Chem.*, 1970, **35**, 1211.
[3] A. W. P. Jarvie, *Organometallic Chem. Rev. A*, 1970, **6**, 153.
[4] S. Murai and S. Tsutsumi, *J. Org. Chem.*, 1966, **31**, 3000.