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Silyl Alkenyl Ethers as the Synthetic Equivalent of Enols. New Syntheses of β-Keto-sulphides and 1,3-Diketones

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Summary New syntheses of β -keto-sulphides and 1,3diketones via the addition of a sulphenyl chloride and polychloroacetyl chlorides to trimethylsilyl alkenyl ethers are described.

RECENTLY we have shown that silvl alkenyl ethers can be used as the synthetic equivalent of enols.^{1,2} We report here that electrophilic addition of a sulphur-halogen bond, as well as a carbon-halogen bond, can also provide new synthetic methods *via* readily available silvl alkenyl ethers³ (Schemes 1 and 2).



The β -keto sulphides⁴ (Scheme 1) were synthesised as ollows. Phenylsulphenyl chloride (25 mmol) in CH₂Cl₂ 20 ml) was added slowly to a stirred solution of the tri-

methylsilyl alkenyl ethers⁵ (1; 25 mmol) in CH_2Cl_2 (15 ml) at -40 to -60°. The red colour (PhSCl) disappeared instantly. The solution was then stirred at a room temperature for 1 h. Distillation gave the β -keto-sulphides (2a), (2b), and (2c) in 78, 60, and 68% yields respectively.



1,3-Diketones were synthesised (Scheme 2) as follows. To a solution of the trimethylsilyl alkenyl ether⁵ (1; 25 mmol in CH₂Cl₂ (25 ml) was added the polychloroacetyl chloride (3; 25 mmol) in CH₂Cl₂ (25 ml) at 25° and the mixture was stirred for 24 h at this temperature. Methanol (20 ml) was then added and the solution was refluxed for 1 h. Distillation gave pure polychloromethyl 1,3-diketones (4) (a, 67%; b, 47%; c, 41%; and d, 40%) showing i.r. absorptions at *ca*. 1600 br, s cm⁻¹ typical of 1,3-diketones. Methanolysis



Preliminary experiments show that (4c) forms a europium complex⁶ having high solubility in nonpolar solvents.

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- S. Murai, Y. Kuroki, T. Aya, N. Sonoda, and S. Tsutsumi, J.C.S. Chem. Comm., 1972, 741.
 Y. Kuroki, S. Murai, N. Sonoda, and S. Tsutsumi, Organometallics in Chemical Synthesis, in the press.
 Yu. I. Baukov and I. F. Lutsenko, Organometallic Chem. Rev. (A), 1970, 6, 355.

(5)

- ⁴ D. N. Harpp and P. Mathiaparanam, J. Org. Chem., 1971, 36, 2540.
 ⁵ H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, J. Org. Chem., 1969, 34, 2342.
 ⁶ W. DeW. Horrocks, jun., and J. P. Sipe, tert., J. Amer. Chem. Soc., 1971, 93, 6800.