OXIDATION OF ETHYL (DIMETHYLSULFURANYLIDENE)ACETATE

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Little is known on the action of oxidizing agents on stabilized sulfur ylids. We were the first to study the oxidation of the stabilized sulfur ylid, $(CH_3)_2\overset{+}{S}\overset{-}{C}HCO_2C_2H_5$ (I) by $(C_6H_5O)_3P{\cdot}O_3$ (II), $(o\text{-}CH_3C_6H_4O)_3P{\cdot}O_3$ (III), $(CH_3)_2C(OH)OOOH$ (IV), and ozone.

Ozonides (II) and (III) were obtained in CH_2Cl_2 according to Tompson [1]. A solution of (IV) in 2-propanol was obtained by analogy to our previous procedure [2]. A sample of cooled (I) (1-8 mmoles) in 1 ml CH_2Cl_2 was added to 20 ml of a solution of (II)-(IV) (4-12 mmoles) at from −78 to −60°C in an argon atmosphere. The mixture was maintained for 3 h at from −78 to −60°C and then warmed to about 20°C. The ozone oxidation was carried out in a bubbler at −50°C in $CDCl_3$.

The reaction products were identified and analyzed by ^1H and ^{13}C NMR spectroscopy.

The oxidation of (I) by (II)-(IV) gave ethyl (dimethyloxosulfuranylidene)acetate, $(CH_3)_2\overset{+}{S}(O)\bar{C}HCO_2C_2H_5$ (V) (PMR spectrum in $(CD_3)_2CO$ (δ, ppm): 1.14 t (CH_3), 3.07 s ($(CH_3)_2\overset{+}{S}O$), 3.97 q (CH_2)), dimethylsulfoxide (VI), dimethylsulfone (VII), and ethyl glyoxalate (VIII). Thus, these products were obtained upon the reaction of 2.18 mmoles (I) with 10 mmoles (II) in the ratio (V):(VI):(VII):(VIII) = 1.5:0.8:1.0:3.5. The oxidation of 0.95 mmole (I) by 4.32 mmoles (IV) leads to (V)-(VII) in the ratio 2.1:1.8:1.0:4.5. Treatment of (I) by a two-fold excess of ozone gives largely (VII) and the monoethyl ester of oxalic acid in approximately equal amounts.

LITERATURE CITED

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