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SYNTHESIS OF ISOXAZOLINE-N-OXIDES BY THE REACTION OF SULFONIUM YLIDES WITH α,β-UNSATURATED NITRO COMPOUNDS

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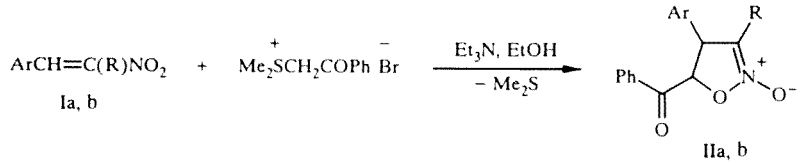
Sulfonium ylides of the type $Me_2S^+C^-HZ$ (Z = COR, COOR) are known to react with electron deficient alkenes to give substituted cyclopropanes [1]. We have shown for the first time that this rule is broken for unsaturated nitro compounds which give 5-membered heterocycles, isoxazoline-N-oxides, in place of the 3-membered carbocycles. (A similar reaction is already known for selenonium ylides [2]).

Dimethylsulfoniophenacylide, $Me_2S^+C^-HCOPh$ (generated in the reaction mixture by treatment of dimethylphenacylsulfonium bromide with triethylamine), reacted with the unsaturated nitro compounds (I a and I b) to give the isoxazoline-N-oxides IIa and IIb respectively:



a Ar = 3-$NO_2C_6H_4$, R = COOEt; b Ar = Ph, R = Me

Compound Ia reacted with the ylide at 30-40°C in 2 min whereas the less reactive compound Ib required 30 min and the yield of compound II was halved (in both cases the crystalline product was formed from the solution). The sulfonium ylide, unlike its less reactive selenonium analog, did not interphase catalysis, and this decreased the reaction considerably and considerably eased isolation of the products (see [2]).

^{1}H NMR Spectroscopy showed that the reaction was stereospecific to give the *trans*-isomer of product II: for compound IIa $J_{4,5}$ = 3.6 Hz and for compound IIb 4.5 Hz (see [2, 3]).

The ^{1}H NMR spectra were taken in $(CD_3)_2CO$ solution and the IR spectra in KBr disks.

5-Benzoyl-4-(3-nitrophenyl)-3-ethoxycarbonyl-4,5-dihydroisoxazole-2-oxide (IIa). Yield 85%. mp 135-136°C. IR Spectrum: 1730 (ester CO), 1700 (ketone CO), 1630 (C=N), 1535, 1355 cm^{-1} (NO_2). ^{1}H NMR Spectrum: 1.12 (3H, t, CH_3), 4.1-4.2 (2H, m, OCH_2), 5.45 (1H, d, J = 3.6 Hz, 4-H), 6.31 (1H, d, J = 3.6 Hz, 5-H), 7.60 (2H, t, H_{arom}), 7.70-7.90 (2 H, m, H_{arom}), 8.00-8.10 (3H, m, H_{arom}), 8.20 (1H, d, H_{arom}), 8.29 ppm (1H, s, H_{arom}). Found, %: C 59.22, H 4.14, N 7.40. Calculated for $C_{19}H_{16}N_2O_7$, %: C 59.37, H 4.20, N 7.29.

5-Benzoyl-3-methyl-4-phenyl-4,5-dihydroisoxazole-2-oxide (IIb). Yield 41%. mp 124-125°C. Lit. 123-124°C [2]. IR Spectrum: 1705 (ketone CO), 1670 cm^{-1} (C=N). ^{1}H NMR Spectrum: 1.81 (3 H, d, J = 1.5 Hz, CH_3), 4.90 (1 H, m, 4-H), 5.89 (1H, d, j = 4.5 Hz, 5-H), 7.4-7.6 (7H, m, H_{arom}), 7.70 (2H, t, H_{arom}), 7.99 ppm (2H, d, H_{arom}). Found, %: C 72.49, H 5.52, N 5.17. Calculated for $C_{17}H_{15}NO_3$, %: C 72.58, H 5.38, N 4.98.

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