CONCLUSIONS

The reaction of triphenyl phosphite and di- and tribromoacetaldehydes proceeds through initial halophilic attack with subsequent formation of triphenyl phosphate and tetraphenylphosphonium bromide.

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SYNTHESIS OF ESTERS OF OXATHIINECARBOXYLIC AND DITHIINECARBOXYLIC ACIDS AND THEIR DERIVATIVES

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In previous work [1], we showed that the methyl ester of 3-phenyl-3-chloro-2-ketopropionic acid (I) reacts with thiourea to form 5-phenyl-4-carbomethoxy-2-aminothiazoles. In the present study, we established that the reaction of (I) with mercaptoethanol (II) and 1,2-dithioglycol (III) in the presence of base gives the corresponding chlorine substitution products, which, in the presence of p-toluenesulfonic acid, dehydrate to give oxathiine (IV) and dithiine (V), respectively, which hold interest for the preparation of biologically active compounds [2].



Sulfones (VI) and (VII) are obtained upon the oxidation of (IV) and (V) by the action of H_2O_2 in acetic acid.

The structure of the compounds obtained was confirmed by IR and PMR spectroscopy and elemental analysis. Thus, the PMR spectrum of (IV) has triplets for the OCH_2 and SCH_2 group protons at 4.33 and 3.10 ppm, respectively. The singlet at 3.46 ppm is related to the carbomethoxy group protons. An analogous pattern is found in the PMR spectrum of (VI), although

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we should note that the oxidation of the sulfide sulfur to a sulfone sulfur leads to downfield shift in the signals of the OCH_2 and SCH_2 (4.90 and 3.66 ppm, respectively), while the shielding of the carbomethoxy group protons is not altered. A broad signal for the CH_2CH_2 group is found for (V) and (VII) at 3.16 and 4.46 ppm, respectively. The shielding of the carbomethoxy group in going from (V) to (VII) is only slightly altered [3.33 ppm in (V) and 3.53 ppm in (VII)].

The IR spectra of (IV)-(VII) have a strong band at $1710-1730 \text{ cm}^{-1}$ characteristic for ester C=0 stretching vibrations. The IR spectrum of (VI) and (VII) has a band for the SO₂ group at 1330 cm⁻¹.

EXPERIMENTAL

The IR spectra were taken for vaseline mulls on a UR-20 spectrometer, while the PMR spectra were taken on a Varian T-60 spectrometer with TMS as the internal standard.

<u>2-Carbomethoxy-3-phenyl-5,6-dihydro-1,4-oxathiine (IV)</u>. A solution of 22 g NaHCO₃ in 150 ml water was added with stirring over 1 h to a solution of 7.8 g (0.1 mole) (I) and 21.2 g (0.1 mole) (II) in 150 ml benzene. The solution was stirred for an additional 40 min. The benzene layer was separated and dried over Na₂SO₄. A sample of 0.5 g p-toluenesulfonic acid was added to the solution. The reaction solution was heated at reflux for 48 h with a Dean-Stark trap until 1.8 ml (0.1 mole) water was eliminated. The mixture was cooled to ~20°C and dried over Na₂SO₄. After evaporation, the residue was crystallized from hexane to give 67% (IV), mp l16-l17°C. IR spectrum (ν , cm⁻¹): 1710 (C=0). PMR spectrum, in CDCl₃ (δ , ppm): 3.10 t (SCH₂), 3.46 s (C(0)OCH₃), 4.33 t (OCH₂), 7.16 s (C₆H₅). Found, %: C 61.24; H 5.31; S 13.53. C₁₂H₁₂O₃S. Calculated, %: C 62.02; H 5.08; S 13.57.

<u>2-Carbomethoxy-3-phenyl-5,6-dihydro-1,4-dithiine (V)</u>. Analogously, a sample of (IV) obtained from (I) and (III) gave (V) in 72% yield, mp 63-64°C. IR spectrum (ν , cm⁻¹): 1700 (C=O). PMR spectrum in CCl₄ (δ , ppm): 3.16 br. s (CH₂CH₂), 3.33 s (C(O)OCH₃), 7.23 s (C₆H₅). Found, %: C 57.41; H 4.70; S 25.24. C₁₂H₁₂O₂S₂. Calculated, %: C 57.13; H 4.75; S 25.42.

<u>2-Carbomethoxy-3-phenyl-4,4-dioxido-5,6-dihydro-1,4-oxathiine (VI)</u>. A sample of 24 ml 30% H₂O₂ was added to a solution of 5 g (0.02 mole) (IV) in 40 ml acetic acid. The mixture was maintained at ~20°C for three weeks. The crystalline precipitate was washed with hexane to give (VI) in 91% yield, mp 149-150°C. IR spectrum (v, cm⁻¹): 1730 (C=O), 1325 (SO₂). PMR spectrum in (CD₃)₂SO (δ , ppm): 3.46 s (C(O)OCH₃), 3.66 t (SCH₂), 4.90 t (OCH₂), 7.30 s (C₆H₅). Found, %: C 52.01; H 4.55; S 11.72. C₁₂H₁₂O₅S. Calculated, %: C 51.80; H 4.31; S 11.52.

<u>2-Carbomethoxy-3-phenyl-5,6-dihydro-1,1,4,4-tetraoxido-1,4-dithiine (VII)</u>. A sample of 30 ml 30% H_2O_2 was added to a solution of 5 g (0.02 mole) (V) in acetic acid at ~20°C, heated to 80°C, and stirred for an additional 2 h. The crystalline precipitate was filtered off and recrystallized from acetone to give (VII) in 70% yield, mp 256°C. IR spectrum (v, cm⁻¹): 1730 (C=O), 1330 (SO₂). PMR spectrum in (CD₃)₂SO (δ , ppm): 4.46 br. s (CH₂CH₂), 3.53 s (C(O)OCH₃), 7.16-7.66 m (C₆H₅). Found, % C 44.40; H 3.61; S 19.19. C₁₂H₁₂O₆S₂. Calculated, %: C 44.17; H 3.67; S 19.65.

CONCLUSIONS

The reaction of the methyl ester of 3-phenyl-3-chloro-2-ketopropionic acid with mercaptoethanol and 1,2-dithioglycol gives derivatives of oxathiine and dithiine. The oxidation of these products gives the corresponding sulfones.

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