

Benzoyl-substituted Thiirans and Oxathioles. The Synthesis and Properties of 2-Benzoyl-5-phenyl-1,3-oxathiole

By Ulla Jacobsson Kempe, Tomas Kempe, and Torbjörn Norin,* Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm 70, Sweden

2-Benzoyl-5-phenyl-1,3-oxathiole (8) has been prepared and characterized. The chemical and spectral properties of this compound confirm our previous assignment of the structure of 2-benzoyl-2,4,5-triphenyl-1,3-oxathiole (2a) which had earlier been reported to be 2,3-dibenzoyl-2,3-diphenylthiiran (1a). Deuterium-labelling experiments have shown that no equilibrium occurs under mild conditions (120 °C) between the 2-benzoyl-5-phenyl-1,3-oxathiole (8) and the corresponding thiiran (15). At higher temperatures decomposition occurs. Upon rapid pyrolysis at 275 °C 1,2-dibenzoyl-ethylene is formed.

THE structural assignments^{1,2} for the compounds previously thought to be 2,3-dibenzoyl-2,3-diphenylthiiran (1a) and the corresponding thiiran 1-oxide (1b) and 1,1-dioxide (1c) have been revised³ and shown to be the corresponding oxathiole derivatives (2a—c). These thiiran derivatives appear not to be stable compounds and seem to rearrange spontaneously to the corresponding oxathiole derivatives.³ Such a rearrangement will be analogous to the vinyl cyclopropane rearrangement⁴ and is thus reversible. However, it has not been possible to detect by deuterium labelling any equilibration between 2-benzoyl-5-phenyl-1,3-oxathiole 3,3-dioxide (3) and the corresponding thiiran 1,1-dioxide (4) under the experimental conditions used (<150 °C).³

¹ D. C. Dittmer and G. C. Levy, *J. Org. Chem.*, 1965, **30**, 636; D. C. Dittmer, G. C. Levy, and G. E. Kuhlmann, *J. Amer. Chem. Soc.*, 1969, **91**, 2097; D. C. Dittmer, G. E. Kuhlmann, and G. C. Levy, *J. Org. Chem.*, 1970, **35**, 3676; D. C. Dittmer, G. C. Levy, and G. E. Kuhlmann, *J. Amer. Chem. Soc.*, 1967, **89**, 2793.

² C. J. Ireland and J. S. Pizey, *J.C.S. Chem. Comm.*, 1972, 4; G. Kresze and W. Wucherpfennig, *Angew. Chem. Internat. Edn.*, 1967, **6**, 149.

In order to gain more information on the properties of oxathioles and their possible rearrangement to thiirans we have now studied 2-benzoyl-5-phenyl-1,3-oxathiole (8). This compound has been briefly described by Ollis and his co-workers,⁵ however, without any experimental details of its preparation or its properties.

The oxathiole (8) was prepared according to the route previously outlined.⁵ The starting material, 2,5-dihydrothiophen (5) was synthesized *via* the reduction of thiophen according to Birch and McAllan.⁶ Attempts to prepare (5) from *cis*-1,4-dibromobut-2-ene or the corresponding 1,4-dichloride or 1,4-dimesylate by treatment with hydrogen sulphide-sodium ethoxide or sodium

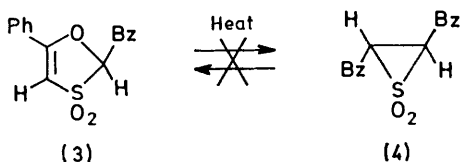
³ U. Jacobsson, T. Kempe, and T. Norin, *J. Org. Chem.*, 1974, **39**, 2722.

⁴ J.-C. Paladini and J. Chucho, *Bull. Soc. chim. France*, 1974, 197; W. Eberbach and B. Burchardt, *Tetrahedron Letters*, 1976, 3887.

⁵ S. Mageswaran, W. D. Ollis, and I. O. Sutherland, *J.C.S. Chem. Comm.*, 1973, 656.

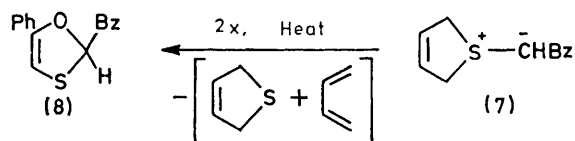
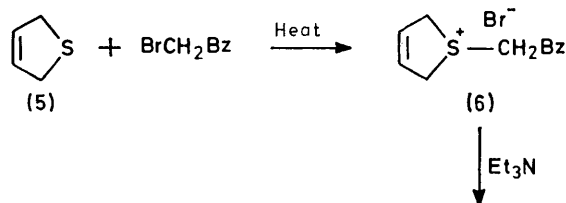
⁶ S. F. Birch and D. T. McAllan, *J. Chem. Soc.*, 1951, 2556.

sulphide in ethanol gave poor yields. Phenacyl-2,5-dihydrothiophenium bromide (6) was obtained by the



a; X = S
b; SO
c; SO₂

treatment of (5) with α -bromoacetophenone. Dehydrobromination of (6) gives the 2,5-dihydrothiophenium phenacylide (7), which when heated gives 2-benzoyl-5-phenyl-1,3-oxathiole (8). Possible routes for the transformation of (7) into (8) are *via* the dihydrothiopyran (9)⁷ and subsequently 2-phenylthioglyoxal (10) [reaction (a)] or by direct conversion into 2-phenylthioglyoxal (10) [reaction (b)]; these mechanisms differ from the one suggested previously.⁵ On storage over-



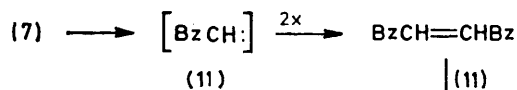
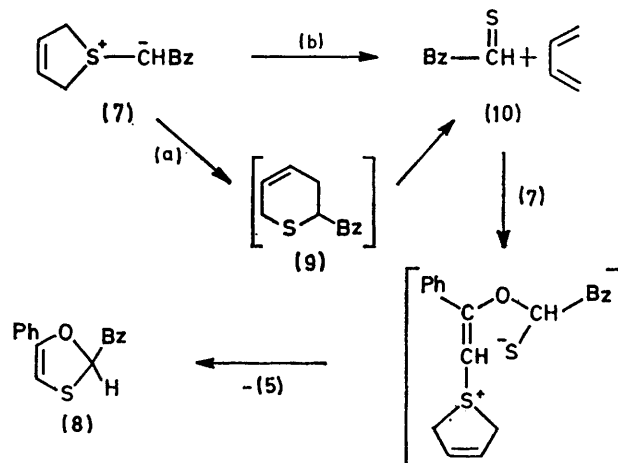
night the sulphonium ylide (7) is transformed into *trans*-1,2,3-tribenzoylcyclopropane (12) probably *via* the carbenoid intermediate (11). Sulphonium ylides are known to undergo such a reaction.⁸

The structure of the oxathiole (8) has been settled by a consideration of its spectroscopic properties. The ¹³C n.m.r. spectrum which exhibits signals for the three ring carbons at δ 84.5 (C-2), 92.1 (C-4), and 151.3 (C-5) and for the carbonyl carbon at δ 189.6, is fully in accord with the previously reported³ ¹³C n.m.r. chemical shifts of several oxathiole derivatives. The ¹H n.m.r. spectrum shows the phenyl protons as a multiplet at δ ca. 7–8 and

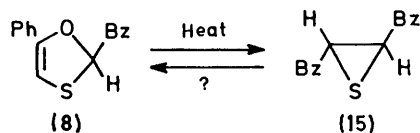
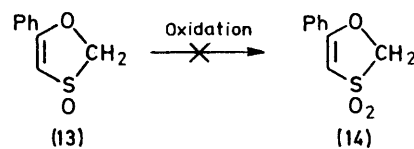
⁷ W. Ando, S. Kondo, K. Nakayama, K. Ichibori, H. Kohoda, H. Yamato, I. Imai, S. Nakaido, and T. Migita, *J. Amer. Chem. Soc.*, 1972, **94**, 3870; E. Vedejs and J. P. Hagen, *ibid.*, 1975, **97**, 6878.

⁸ (a) B. M. Trost, *J. Amer. Chem. Soc.*, 1967, **89**, 138; (b) A. W. Johnson and R. T. Amel, *J. Org. Chem.*, 1969, **34**, 1240.

two singlets at δ 6.98 and 5.83. The singlet at δ 6.98 disappears on base-promoted deuteration of (8), thus indicating that it is due to the C-2 proton while the singlet at δ 5.83 is assigned to the C-4 proton. The u.v. spectrum indicates an extended conjugated system (see Experimental section), as expected for a styrene chromophore with polar oxygen and sulphur substituents.



The oxidation of (8) to obtain the corresponding sulphone (3) failed although the oxidation product (3) is known³ to be stable. Acetophenone was formed during



the reaction. Johnson and Rogers have reported⁹ several attempts to oxidize 5-phenyl-1,3-oxathiole 3-oxide (13). The corresponding sulphone (14) which is also a stable compound^{3,10,11} was not obtained.

⁹ C. R. Johnson and P. E. Rogers, *J. Org. Chem.*, 1973, **38**, 1798.

¹⁰ K. Dickoré, *Annalen*, 1964, **671**, 135.

¹¹ H. Nozaki, M. Takaku, Y. Hayasi, and K. Kondô, *Tetrahedron*, 1968, **24**, 6563.

Previous studies have shown that there is no thermal equilibration between 2-benzoyl-5-phenyl-1,3-oxathiole 3,3-dioxide (3) and the thiiran 1,1-dioxide (4) at temperatures below 150 °C. The C-C bond of this thiiran 1,1-dioxide is expected to be rather weak^{3,12} and should thus favour the formation of oxathiole 3,3-dioxide (3) in such an equilibrium reaction. The C-C bond of the thiiran (15) is expected to be much stronger. It was, therefore, of interest to investigate the possibility of rearranging the oxathiole (8) to the thiiran (15) or to investigate the existence of a thermal equilibration by deuterium labelling. The oxathiole (8), deuteriated in the 2-position was, therefore, prepared by a base-induced deuterium exchange reaction. Deuterium scrambling was not observed, either during the exchange reaction or upon heating the specifically deuteriated compound in refluxing benzene for 2 h. Furthermore, scrambling was not observed upon heating the deuteriated compound (neat) above its melting point (120 °C). At this temperature slight decomposition was observed. N.m.r. measurements also showed that the decomposition was complete in 0.5 h at *ca.* 140 °C. On pyrolysis of the oxathiole (8) at 275 °C 1,2-dibenzoyl ethylene is formed as the sole volatile product. It is difficult to account for this decomposition without proposing a mechanism involving the thiiran (15) as an intermediate which would then yield the olefin by extrusion of sulphur.¹³

The intermediate thiiran (15) seems to decompose at a higher rate than it is converted back into the oxathiole (8). This explains why no deuterium scrambling is observed.

The results of the present investigation give further evidence for the oxathiole nature of the compounds (2a-c), (3), and (8). Recently Pizey and his co-workers¹⁴ have claimed that they obtained the thiiran (1a) upon treatment of deoxybenzoin with thionyl chloride. The product exhibited the same m.p. and spectroscopic properties as those of a compound previously described by Dittmer and his co-workers and later shown³ by us to be the oxathiole (2a).

EXPERIMENTAL

The u.v. spectrum was recorded on a Beckman DK-2 spectrophotometer and the i.r. spectra on a Perkin-Elmer model 257 i.r. spectrophotometer. N.m.r. spectra were obtained using Varian model EM360 (60 MHz) and XL-100A (25.2 MHz, ¹³C n.m.r. spectrum) instruments. The samples were dissolved in CDCl₃ unless otherwise stated. Mass spectra were obtained using an LKB model 9000 mass spectrometer (direct inlet, 70 eV).

Phenacyl-2,5-dihydrothiophenium Bromide (6).—A mixture of 2,5-dihydrothiophen (4.95 g, 0.058 mol) and phenacyl bromide (12 g, 0.060 mol) in anhydrous benzene (40 ml) was stirred at room temperature for 7 days (*cf.* ref. 15). A white solid crystallized from the reaction mixture. A first

crop of the solid was collected after 3 days and the rest at the end of the reaction. After rinsing with ether the total yield of the white solid was 10.7 g (65%), $\delta[(\text{CD}_3)_2\text{SO}]$ 4.46 (s, 4 H), 5.38 (s, 2 H), 6.06 (s, 2 H), and 7.34–8.18 (m, 5 H).

2,5-Dihydrothiophenium Phenacylide (7).—Triethylamine (2.84 g, 0.028 mol) was added to a stirred suspension of the sulphonium bromide (6) (4 g, 0.014 mol) in ethanol (60 ml), cooled in an ice-bath (*cf.* ref. 8b). Stirring was continued at low temperature for 2 h after which the reaction was quenched with water. After extraction with chloroform the organic phase was washed with water and brine, dried, and evaporated *in vacuo* to give 2.1 g (73.5%) of the yellow ylide. The ylide was used immediately, due to its instability, $\delta[(\text{CD}_3)_2\text{SO}]$ 4.03 (s, 4 H), 4.52br (s, 1 H), 6.03 (s, 2 H), and 7.16–7.80 (m, 5 H).

2-Benzoyl-5-phenyl-1,3-oxathiole (8).—A solution of the sulphonium ylide (7) (2.1 g, 0.010 mol) in benzene (50 ml) was refluxed overnight. Evaporation *in vacuo* gave an oil which solidified on cooling. After rinsing the solid with isopentane it was recrystallized from a minimal amount of methanol to give 0.73 g (54.5%) of orange needles, m.p. 109–110 °C, λ_{max} (95% EtOH) 241 (ϵ 16 300), 283sh (6 800), 313 (8 800), 325sh (7 200), and 400 nm (1 370); ν_{max} (KBr) 1 685 (s, C=O) and 1 240 cm⁻¹ (s, C=C-O); δ_{H} 5.83 (s, 1 H, =CH), 6.98 (s, 1 H, CH), and 7.16–8.03 (m, 10 H, aromatic); δ_{C} 189.6 (C=O), 151.3 (C-5), 133.7, 132.8, 129.3, 128.8, 128.5, 125.1 (all aromatic), 92.1 (C-4), and 84.5 (C-2), *J* (C-2, H-2) 166.3, (C-2, H-4) 4.8, (C-4, H-4) 189.5, and (C-4, H-2) 1.4 Hz; *m/e* 268 (*M*⁺, 7%), 164 (11) 163 (*M*⁺ - 105, 100), 135 (23), 134 (12), 105 (16), 102 (6), 91 (40), 89 (6), and 77 (30).

The Instability of the Ylide (7).—If the reaction mixture of the ylide preparation was stored in a refrigerator overnight, pale yellow crystals were isolated after recrystallization from methanol, m.p. 218–219 °C [reported^{8b} m.p. for *trans*-1,2,3-tribenzoylcyclopropane (12): 219–220 °C]. The ¹H n.m.r. spectrum agreed with that reported¹⁶ for *trans*-1,2,3-tribenzoylcyclopropane (12), *m/e* 354 (*M*⁺, 1%), 277 (*M*⁺ - 77, 2), 250 (5), 249 (*M*⁺ - 105, 27), 234 (1), 233 (7), 115 (2), 106 (8), 105 (100), 78 (3), and 77 (35).

Oxidation of Compound (8).—An excess of hydrogen peroxide (30%; 5 ml) was added to the oxathiole (8) (200 mg, 0.75 mmol) dissolved in acetic acid (4 ml). The reaction mixture was refluxed for 3 h and was then allowed to cool overnight. After dilution with water the mixture was extracted with chloroform. The organic phase was washed with a saturated sodium hydrogencarbonate solution, water, and then brine, and then dried and evaporated *in vacuo* to give a yellow oil. The ¹H n.m.r. and i.r. spectra of the oil were in accord with those of an authentic sample of acetophenone. *m*-Chloroperbenzoic acid and perphthalic acid were also tried as oxidation reagents. However, the reaction mixtures were complex and no oxathiole 3,3-dioxide (3) could be detected.

2-Benzoyl-2-deuterio-5-phenyl-1,3-oxathiole [²H]-(8).—The oxathiole (8) (200 mg, 0.75 mmol) was dissolved in deuteriochloroform (2 ml) and methan[²H]ol (1 ml). Triethylamine (113 mg, 1.12 mmol) in deuteriochloroform was added and the solution was stirred for 2 h. The solvent was evaporated *in vacuo* and a small amount of methan[²H]ol

¹² R. Hoffmann, H. Fujimoto, J. R. Swenson, and C.-C. Wan, *J. Amer. Chem. Soc.*, 1973, **95**, 7644.

¹³ M. Sander, *Chem. Rev.*, 1966, **66**, 297.

¹⁴ C. J. Ireland, K. Jones, J. S. Pizey, and S. Johnson, *Synthetic Comm.*, 1976, **6**, 185.

¹⁵ K. W. Ratts, *J. Org. Chem.*, 1972, **37**, 848.

¹⁶ J. N. Shoolery, *Svensk kem. Tidskf.*, 1957, **69**, 185; N. Obata and I. Moritani, *Bull. Chem. Soc. Japan*, 1966, **39**, 1975.

was added to the residual oil; 72 mg of a yellow solid separated, δ 5.83 (s, 1 H, =CH) and 7.10—8.10 (m, 10 H, aromatic); *m/e* 269 (M^+ , 9%), 165 (12), 164 ($M^+ - 105$, 100), 163 (8), 136 (19), 135 (7), 134 (7), 105 (10), 92 (33), and 77 (23).

Equilibration of [2- 2 H]-(8).—(a) The oxathiole [2- 2 H]-(8) was heated at 120 °C, which is slightly above its melting point, for 30 min; (b) the oxathiole [2- 2 H]-(8) was heated in refluxing benzene for 2 h. The 1 H n.m.r. spectra of the product from the two runs (a) and (b) showed no scrambling of deuterium between the 2 and 4 positions in the oxathiole system. The n.m.r. spectrum of the sample from run (a) provided evidence for the fact that some decomposition had occurred. Additional experiments, when the oxathiole (8) was heated at various temperatures showed that the decomposition was complete after 30 min at 140 °C. The decom-

position product was a complex mixture, which has not been further investigated.

Pyrolysis of (8).—The oxathiole (8), dissolved in acetone, was injected on g.l.c. (injector and column temperatures were 275 and 200 °C, respectively; column 1.5 m \times 3.2 mm, packed with 5% SE-30 on Varaport 30). The decomposition product, 1,2-dibenzoylene, was the only detectable compound after the solvent peak. The structure was proven by comparison with an authentic sample on g.l.c. and m.s.

Financial support from The Swedish Natural Science Research Council is gratefully acknowledged. We thank Dr. T. Nishida, The Swedish Tobacco Company, for the 13 C n.m.r. spectrum.

8/345 Received 1st March, 1978]