Rearrangement of 2,4-Diphenylthietan Dioxides to 3,5-Diphenyl-1,2-oxathiolan 2-Oxides

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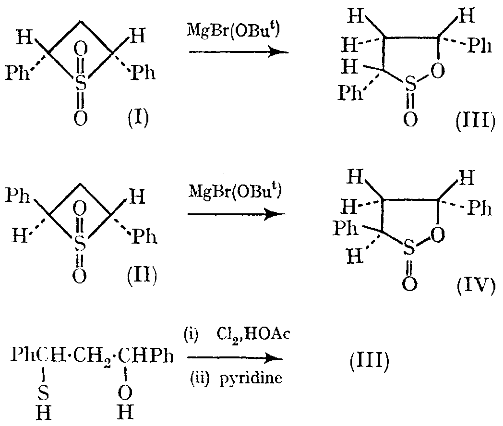
WE had shown previously that treatment of either *cis*- or *trans*-2,4-diphenylthietan dioxide[1] [(I) and (II) respectively] with ethylmagnesium bromide in ether–benzene gave *trans*-1,2-diphenylcyclopropanesulphinic acid (74% yield). More recently we found that reaction of either *cis*- or *trans*†-2,4-diphenylthietan oxide with potassium t-butoxide in dimethylformamide yielded *cis*-1,2-diphenylcyclopropanesulphinic acid (*ca.* 23% yield) and *cis*-1,2-diphenylcyclopropanethiol (22–33% yield).[2] Here, we report the rearrangement of (I) and (II) to the corresponding *cis*- and *trans*-3,5-diphenyl-1,2-oxathiolan 2-oxides [(III) and (IV) respectively].[3] Unlike the previous stereoconvergent rearrangements of (I) and (II), the rearrangements to (III) and (IV) seem to be stereospecific, at least for the initially formed product. These rearrangements are the reverse of the recently described rearrangements of sulphinic esters to sulphones.[4]

Reaction of *cis*-2,4-diphenylthietan dioxide (I) with magnesium t-butoxide‡ in ether under reflux for 23 hr. yielded *cis*-3,5-diphenyl-1,2-oxathiolan 2-oxide (III), m.p. 121·5—122·5° (70% yield); ν_{max} (KBr) 1115 (–O–C–), 1149, 1157 (–SO·O–) cm.$^{-1}$; n.m.r.§ (C_6H_6):[5] ν_A 133·6, ν_B 151·0, ν_P 224·1, ν_X 310·6, $J_{AB} = -13·0$, $J_{AP} = +5·8$, $J_{AX} = +5·8$, $J_{BP} = +13·8$, $J_{BX} = +10·6$ c./sec.; n.m.r. ($CDCl_3$): ν_A 164·5, ν_B 168·3, ν_P 257·3, ν_X 334·2, $J_{AB} = -13·2$, $J_{AP} = 6·1$, $J_{AX} = 5·6$, $J_{BP} = 13·7$, $J_{BX} = 10·9$. The structure of (III) was established by its synthesis from 3-hydroxy-1,3-diphenylpropane-1-thiol[1] (V) by reaction with chlorine[6] and acetic acid in methylene chloride, treatment of the product with pyridine, then chromatography of the resulting material.

Reaction of *trans*-2,4-diphenylthietan dioxide (II) for 44 hr. under conditions similar to those given above yielded *trans*-3,5-diphenyl-1,2-oxathiolan 2-oxide (IV), m.p. 73–74·5°; ν_{max} (KBr) 1108 (–C–O–), 1138 (–SO·O–) cm.$^{-1}$; n.m.r. ($CDCl_3$): ν_A 154, ν_K 199, ν_P 262, ν_X 372, $J_{AK} = -12·8$, $J_{AB} = 7·4$, $J_{AP} = 2·6$, $J_{AX} = 12·4$, $J_{BP} = 8·4$ c./sec. Since the chemical shifts of all of the protons were well separated in this spectrum, a first-order analysis of the spectrum was performed.



The structure and the stereochemistry of compounds (III) and (IV) followed directly from the analyses of the n.m.r. spectra. In both cases

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† Of the three possible isomeric, optically inactive, 2,4-diphenylthietan oxides, only two are known to us. Throughout this Communication, *cis*- and *trans* refer to the configurations of the phenyl groups.

‡ The structure of the reagent is not known. It was prepared by the addition of one mole of t-butyl alcohol to ethylmagnesium bromide in ether.

§ The n.m.r. spectra were determined with a Varian Associates A–60 spectrometer and are recorded in c./sec. downfield from tetramethylsilane.

the two upfield protons were strongly coupled ($J = ca.\ -13$ c./sec.), and both, in turn, were coupled to both downfield protons. The coupling constant between the two downfield protons was very small, and could not be determined from spectra of the precision used here. This led to the following sequence of atoms $-CH-CH_2-CH-$ with the downfield protons on carbon atoms attached to oxygen and sulphur. With compound (IV), $J_{AX} = 2{\cdot}6$ c./sec. was small. The dihedral angle between H_X and H_Y should be between 60° and 120°; thus H_A and H_X should be *trans* to each other. This makes H_K *cis* to H_X ($J_{KX} = 8{\cdot}4$) and *trans* to H_P ($J_{KX} = 12{\cdot}4$); H_A is *cis* to H_X ($J_{AP} = 7{\cdot}4$). The phenyl groups must be *trans* to each other in compound (IV). A similar analysis of the n.m.r. spectra of compound (III) necessitated a *cis*-relationship for the phenyl groups. N.m.r. spectra on the total isolated after 18 and 23 hr. reactions of (I) and (II) respectively, with magnesium t-butoxide indicated a high degree of stereospecificity for this rearrangement. However, any discussion of mechanism must await a definitive determination of the configuration of the oxygen atom on sulphur $(-\underset{\substack{\| \\ O}}{S}-O-)$.

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[1] R. M. Dodson and G. Klose, *Chem. and Ind.*, 1963, 450, 1203.

[2] R. M. Dodson, J. T. Yu, P. D. Hammen, and E. H. Jancis, unpublished results.

[3] Recently two examples of the conversion of thietan dioxides to cyclic sulphinates have appeared in the literature (D. C. Dittmer, R. S. Henion, and N. Takashina, 153rd National Meeting of the American Chemical Society, Miami, Florida, April 1967, Abstract O 101; R. W. Hoffmann and W. Sieber, *Annalen*, 1967, **703**, 96). Both examples involved the heating of relatively stable thietan dioxides to temperatures of 300—400° and undoubtedly, proceeded *via* free-radical intermediates. E. K. Fields and S. Meyerson (*J. Amer. Chem. Soc.*, 1966, **88**, 2836) had previously postulated the rearrangement of dibenzothiophen dioxide to a cyclic sulphinate from its mass spectrum.

[4] C. J. M. Stirling, *Chem. Comm.*, 1967, 131; S. Braverman and Y. Stabinsky, *ibid.*, 1967, 270.

[5] These spectra were calculated as ABPX systems using the energy levels given by C. A. Reilly and J. D. Swalen, *J. Chem. Phys.*, 1961, **34**, 980. The sign of the geminal coupling constant was not experimentally determined. Coupling constants should be accurate to $\pm 0{\cdot}2$ c./sec.

[6] Since completion of this synthesis, a related synthesis of a cyclic sulphinate ester has been described by E. N. Givens and L. A. Hamilton, *J. Org. Chem.*, 1967, **32**, 2857.