

## Additive Pummerer Rearrangement of Methyl Cyclopentylidene(phenylsulphinyl)-acetate Induced by Acetyl Chloride, Trifluoroacetic Anhydride, or Thionyl Chloride

By HIROSHI KOSUGI, HISASHI UDA,\* and SHŪICHI YAMAGIWA

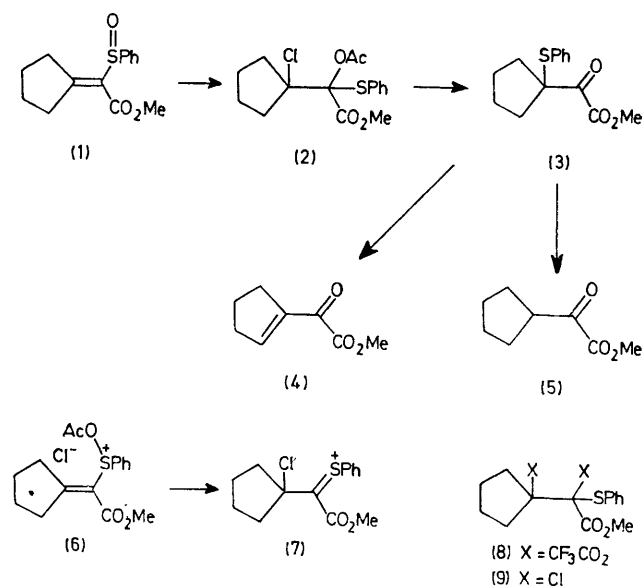
(Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Sendai 980, Japan)

**Summary** Methyl cyclopentylidene(phenylsulphinyl)acetate, on treatment with acetyl chloride, trifluoroacetic anhydride, or thionyl chloride, undergoes an additive-type Pummerer rearrangement to give  $\alpha\beta$ -difunctionalised phenylthio-derivatives.

We have recently reported the vinylogous Pummerer-type and the allylic sulphoxide-sulphenate-type of rearrangement of the methyl ester (**1**) to allylic ( $\gamma$ -position) oxygen-functionalised compounds.<sup>1</sup> We now report another type of rearrangement, the additive Pummerer rearrangement, of (**1**) induced by acetyl chloride, trifluoroacetic anhydride, or thionyl chloride.

Treatment of (**1**) with acetyl chloride in dichloromethane at 0 °C to room temperature for 15 min gave after work-up (evaporation and preparative t.l.c.) the acetoxy-chlorophenylthio-ester (**2**) (90%); positive halogen test;  $\nu_{\max}$  (CCl<sub>4</sub>) 1765 and 1742 cm<sup>-1</sup>;  $\delta$  (CCl<sub>4</sub>) 1.50–2.70 (8H, m, ring H), 1.92 and 3.53 (each 3H, s, COMe), and 7.10–7.80 (5H, m, Ph). Compound (**2**) rearranged further upon heating at reflux for 1 h in dioxan–water (3:1), to give a quantitative yield of the  $\beta$ -phenylthio-glyoxylate (**3**);  $\nu_{\max}$  (CCl<sub>4</sub>) 1745 and 1705 cm<sup>-1</sup>;  $\delta$  (CCl<sub>4</sub>) 1.40–2.40 (8H, m, ring H), 3.86 (3H, s, OMe), and 7.28 (5H, s, Ph).<sup>†</sup> The structure of (**3**) was confirmed by transformation into the unsaturated glyoxylate (**4**) by oxidation (*m*-chloroperoxybenzoic acid)

to the sulphoxide followed by pyrolysis (70 °C in CCl<sub>4</sub>) and into the saturated glyoxylate (**5**) (identical with an authentic sample<sup>2</sup>) by reductive desulphurisation (Raney-Ni). It is



<sup>†</sup> All new compounds except (**2**) and (**8**) had satisfactory microanalyses. Compounds (**2**) and (**8**) were homogeneous spectroscopically and on t.l.c.

significant that the rearrangement of (2) to (3) also takes place thermally; in fact, attempted purification of (2) by distillation at 120 °C and 1.0 mmHg gave almost pure (3). This result indicates that in (2) the acetoxy-group is at the  $\alpha$ -position, and the chloro-group  $\beta$ .

A reasonable pathway for the formation of (2) is through an intermediate (7) formed by the attack of  $\text{Cl}^-$  on the vinyl-acetoxy-sulphonium salt (6); this is formally the additive Pummerer reaction.<sup>3</sup> The exclusive attack of  $\text{Cl}^-$  (or  $\text{CF}_3\text{CO}_2^-$ , see below) on the  $\beta$ -olefinic carbon atom of (6) is probably due to its high nucleophilic character, in contrast to the preferential abstraction of a  $\gamma$ -allylic hydrogen-atom under the conditions (dioxan-dil.  $\text{H}_2\text{SO}_4$  or  $\text{Ac}_2\text{O}$ , heat) suitable for the vinylogous Pummerer rearrangement of (1).<sup>1‡</sup>

‡ The lack of a  $\beta$ -hydrogen atom in (1) prevents the  $\beta$ -hydrogen-participating rearrangement to produce chlorovinylsulphide or  $\beta$ -ketosulphide as observed in the reaction of styryl sulphoxides with thionyl chloride or  $\text{PCl}_5$  (G. A. Russell, E. Sabourin, and G. J. Mikol, *J. Org. Chem.*, 1966, **31**, 2854; N. Miyamoto, D. Fukuoka, K. Utimoto, and H. Nozaki, *Bull. Chem. Soc. Japan*, 1974, **47**, 1817).

§ Analogous rearrangements involving migration of a sulphide group and formation of a carbonyl group were recently reported for  $\alpha\beta$ -epoxy-sulphides and  $\beta$ -amino-vinylsulphoxides (D. F. Tavares and R. E. Estep, *Tetrahedron Letters*, 1973, 1229; see also T. Cohen, D. Kuhn, and J. R. Falck, *J. Amer. Chem. Soc.*, 1975, **97**, 4749; K. Ogura and G. Tsuchihashi, *ibid.*, 1974, **96**, 1960).

<sup>1</sup> H. Kosugi, H. Uda, and S. Yamagiwa, *J.C.S. Chem. Comm.*, 1975, 192.

<sup>2</sup> M. Igarashi and H. Midorikawa, *Bull. Chem. Soc. Japan*, 1961, **34**, 1543; *J. Org. Chem.*, 1967, **32**, 3399.

<sup>3</sup> The intramolecular additive-type Pummerer reaction in cyclic vinyl sulphoxides has been reported: J. Kitchin and R. J. Stoodley, *J.C.S. Chem. Comm.*, 1972, 959.

<sup>4</sup> For the use of trifluoroacetic anhydride in the Pummerer rearrangement see A. K. Sharma and D. Swern, *Tetrahedron Letters*, 1974, 1503.

The transformation of (2) to (3) may take place by elimination of  $\text{AcOH}$  and  $\text{HCl}$ , or  $\text{AcCl}$ , with concomitant migration of the  $\text{PhS}$  group and ketonisation. §

A similar rearrangement of (1) was observed in the reaction with trifluoroacetic anhydride<sup>4</sup> or thionyl chloride (0 °C; 30 min); the di-trifluoroacetoxy- (8) and dichloro-compound (9), respectively, were obtained quantitatively. When treated with refluxing aqueous dioxan for 30 min, compound (8) was quantitatively converted into (3), whereas compound (9) was recovered unchanged.

The present reactions provide a useful method for preparation of the  $\beta$ -phenylthioglyoxylate derivatives.

(Received, 21st November 1975; Com. 1304.)