448. *Sulphonyl and Sulphinyl Derivatives of β-Keto-esters.*

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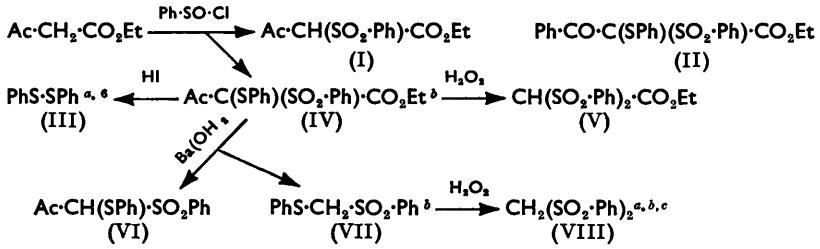
Ethyl *O*-methanesulphonylacetoacetate is rearranged by basic and acidic catalysts to the corresponding *C*-methylsulphonyl ester. Benzenesulphinyl chloride reacts with ethyl acetoacetate to give the *C*-sulphenylsulphonyl ester (IV), reactions of which are described. The benzoylacetate analogue of (IV) was similarly prepared.

Claisen and Haase [1] and Kästner [2] observed that ethyl (*O*-acyl)acylacetates rearranged in presence of acids or bases to the corresponding *C*-acyl esters. It has now been found that ethyl *O*-methanesulphonylacetoacetate undergoes a similar acid–base-catalysed rearrangement. Although ethyl *C*-benzylsulphonylacetoacetate, ethyl *C*-methylsulphonylbenzoylacetate, and ethyl *C*-benzylsulphonylbenzoylacetate were readily prepared, the corresponding *O*-derivatives could not be obtained. Arenesulphonyl halides do not condense with ethyl sodioacetoacetate.[3]

Condensation of benzenesulphinyl chloride with ethyl acetoacetate gave mainly ethyl α-phenylsulphenyl-α-phenylsulphonylacetoacetate (IV), and an oil which formed a cupro-derivative with analytical figures corresponding to the cupro-derivative of ethyl phenylsulphonylacetoacetate (I). Compound (II), the benzoylacetate analogue of (IV), was similarly prepared.



[a] Confirmed by m. p. with authentic samples: other numbered compounds are new. [b] SO_2 bands present in infrared spectrum (see Table). [c] Shriner, Struck, and Jorison, *J. Amer. Chem. Soc.*, 1930, **52**, 2060.

The structure of (IV) was established by its reactions (see diagram) and by infrared measurements (Table). The disproportionation of sulphinyl compounds to give sulphenylsulphonyl derivatives has been frequently discussed.[4] The production of diphenyl

Infrared spectra (cm.$^{-1}$) in chloroform.

Compound	SO_2 bands [12] 1160—1140 (s) and 1350—1300 (s)	SO bands [12] 1060—1040 (s)
(IV)	1142, 1150, 1309, 1321	
(VII)	1150, 1302, 1309	
(VIII) (authentic sample) [10]	1148, 1166, 1332, 1340	
$CH_2(SO·Ph)_2$ (authentic sample) [11]		1043

disulphide (III) by the action of hydriodic acid on the ester (IV) adds to numerous instances of its formation in reactions in which the phenylsulphenyl group is present.[3, 5, 6]

[1] Claisen and Haase, *Ber.*, 1900, **33**, 3778; see Michael and Carlson, *J. Amer. Chem. Soc.*, 1935, **57**, 165.

[2] Kästner, Thesis, Marburg, 1937; "Newer Methods of Preparative Organic Chemistry," p. 289, Interscience Publ., Ltd., London, 1948.

[3] Kohler and MacDonald, *Amer. Chem. J.*, 1899, **22**, 227; Findeisen, *J. prakt. Chem.*, 1902, **65**, 529.

[4] See, for example Cymerman and Willis, *J.*, 1951, 1332; Kurzer, *J.*, 1953, 549; Houben-Weyl, "Methoden der Organischen Chemie," Georg Thieme Verlag, Stuttgart, 1955, Vol. IX, p. 687.

[5] See Miller and Smiles, *J.*, 1925, **127**, 224; Gibson, Miller, and Smiles, *ibid.*, p. 1821; Houben-Weyl, *op. cit.*, p. 55.

[6] Stenhouse, *Proc. Roy. Soc.*, 1868, **17**, 64, who gives m. p. 61°.

Gibson [7] considered that he had obtained compound (VI) by the condensation of phenylsulphonylacetone and *S*-phenylsulphonylthiophenol (phenyl benzenethiolsulphonate, $Ph{\cdot}SO_2{\cdot}SPh$) in presence of sodium ethoxide. His product has now been found to be compound (VII). The acetyl group in compound (VI) is readily removed by alkaline hydrolysis.

Experimental

Crystallisation was from ethanol unless otherwise stated.

Preparation of Sulphonylacylacetates.—Ethyl *C*-methylsulphonylacetoacetate (Found: C, 40·7; H, 6·1; S, 15·7. Calc. for $C_7H_{12}O_5S$: C, 40·4; H, 5·8; S, 15·4%) and ethyl *O*-methanesulphonylacetoacetate (Found: C, 40·1; H, 6·0; S, 14·8%. Calc. as for the *C*-derivative) were obtained as oils.[8] The *C*-ester gave a red colour with ferric chloride; the reaction of the *O*-ester was negative.

Ethyl C-Benzylsulphonylacetoacetate.—Toluene-ω-sulphonyl chloride (10 g.) and a suspension in ether (100 ml.) of ethyl sodioacetoacetate [from sodium (1·2 g.) and the ester (6·4 g.)] were refluxed together for 6 hr., and the resulting ethereal solution was extracted with ice-cold aqueous sodium hydroxide (7·5%) [giving extract (A)] and was washed with water and dried ($MgSO_4$). The light yellow oil obtained on evaporation of the solvent had b. p. 154—156°/1 mm. The analytical figures differed from those required for ethyl *O*-toluene-ω-sulphonylacetoacetate.

The alkaline extract, (A) above, on acidification yielded to ether a yellow-brown viscous oil; *ethyl C-benzylsulphonylacetoacetate*, b. p. 172—176°/1 mm. (distillate, 4·6 g.) (Found: C, 54·4; H, 5·6; S, 11·4. $C_{13}H_{16}O_5S$ requires C, 54·9; H, 5·7; S, 11·3%). The ethanolic ferric colour was red. The *cupro-derivative*, obtained when an ethereal solution of the *C*-benzylsulphonyl ester was shaken with aqueous cupric acetate, separated in blue prisms, m. p. 232—234° (Found: C, 49·3; H, 5·0; S, 10·6; Cu, 10·7. $C_{26}H_{30}O_{10}S_2Cu$ requires C, 49·6; H, 4·8; S, 10·2; Cu, 10·1%).

Repetition of Böhme and Fischer's experiment [8] confirmed that the interaction of ethyl sodiobenzoylacetate and methanesulphonyl chloride gives ethyl *C*-methylsulphonylbenzoylacetate (Found: C, 52·9; H, 5·1; S, 12·2. Calc. for $C_{12}H_{14}O_5S$: C, 53·3; H, 5·2; S, 11·8%) with no trace of the *O*-derivative.

Ethyl C-Benzylsulphonylbenzoylacetate.—This preparation was carried out as described for ethyl *C*-benzylsulphonylacetoacetate (above) using ethyl benzoylacetate (2·7 g.), sodium (0·3 g.), anhydrous ether (150 ml.) and toluene-ω-sulphonyl chloride (5 g.). The mixture was refluxed for 2 hr. The alkali-insoluble portion of the product gave analytical figures which did not correspond to those required for ethyl *O*-toluene-ω-sulphonylbenzoylacetate. The fraction soluble in alkali was *ethyl C-benzylsulphonylbenzoylacetate* (Found: C, 62·5; H, 5·5; S, 9·4. $C_{18}H_{18}O_5S$ requires C, 62·4; H, 5·2; S, 9·2%) which separated in plates (0·9 g.), m. p. 126—128°. The ethanolic ferric colour was red. The compound did not give a cupro-derivative. Böhme and Fischer [8] could not obtain a cupro-derivative from ethyl *C*-methylsulphonylbenzoylacetate which they showed existed mainly in the keto-form.

There was no evidence of formation of ethyl *O*-benzenesulphonylacetoacetate when ethyl acetoacetate and benzenesulphonyl chloride were heated in presence of pyridine at 150° for 1 hr. Similar negative results were obtained when the pyridine–acid chloride method was applied under a variety of conditions to prepare ethyl *O*-toluene-ω-sulphonylacetoacetate and ethyl *O*-methanesulphonylbenzoylacetate.

Transformation of Ethyl O-Methanesulphonylacetoacetate into the Corresponding C-Derivative.—(*a*) A mixture of ethyl *O*-methanesulphonylacetoacetate (0·6 g.), dry pyridine (10 ml.), and hot-powdered sodium hydroxide (0·5 g.) was shaken at room temperature for 12 hr. and acidified. The ethereal extract of the product was washed with ice-cold aqueous sodium hydroxide (7·5%), and the alkaline solution was acidified and extracted with ether. The oil (0·3 g.) which remained on evaporation of the solvent was ethyl *C*-methylsulphonylacetoacetate. It gave a red colour with ethanolic ferric chloride and with phenylhydrazine yielded *N*-acetyl-*N'*-phenylhydrazine (Found: N, 18·3. Calc. for $C_8H_{10}ON_2$: N, 18·7%), m. p. 124—126°, not depressed by addition of samples of similar m. p., prepared from authentic ethyl *C*-methylsulphonylacetoacetate,[8] and from phenylhydrazine and acetic anhydride.[9]

[7] Gibson, *J.*, 1932, 1824.
[8] Böhme and Fischer, *Ber.*, 1943, **76**, 92.
[9] Fischer, *Annalen*, 1878, **190**, 129.

(*b*) When in the above experiment sodium hydroxide was replaced by potassium cyanide, and the mixture was heated at the b. p. of pyridine for 2 hr., the yield of *C*-methylsulphonyl ester was 15%.

(*c*) Boron trifluoride was passed through an anhydrous ethereal solution (5%) of ethyl *O*-methanesulphonylacetoacetate until absorption was complete (40 min.). The product was shaken with 30% aqueous sodium acetate, and the ethereal solution was washed with aqueous sodium hydrogen carbonate and with water, and dried ($MgSO_4$). Evaporation of the solvent gave ethyl *C*-methylsulphonylacetoacetate (30% yield) which was identified as described at (*a*).

Reaction of Benzenesulphinyl Chloride with Ethyl Acetoacetate.—The chloride (12 g.) was added dropwise to a mixture of ethyl acetoacetate (6·5 g.) and pyridine (8 g.) at 0° and the product extracted with ether after 12 hr. The ethereal solution was washed with dilute acid and alkali. Removal of the solvent gave *ethyl α-phenylsulphenyl-α-phenylsulphonylacetoacetate* (IV), which crystallised in prisms (11·7 g.), m. p. 83—84° (Found : C, 56·9; H, 4·6; S, 16·8. $C_{18}H_{18}O_5S_2$ requires C, 57·1; H, 4·8; S, 16·9%).

Acidification of the alkaline extract of the ethereal solution yielded a yellowish-brown oil (1·1 g.) which could not be distilled. The *cupro-derivative*, which separated in blue-green needles, m. p. 242—243°, gave analytical figures corresponding to ethyl cuprophenylsulphonylacetoacetate (cf. I) (Found : C, 48·2; H, 4·4; S, 10·0; Cu, 10·0. $C_{24}H_{26}O_{10}S_2Cu$ requires C, 47·9; H, 4·3; S, 10·6; Cu, 10·5%).

Ethyl α-phenylsulphenyl-α-phenylsulphonylbenzoylacetate (II) was prepared similarly to compound (IV) from benzenesulphinyl chloride (12 g.), ethyl benzoylacetate (9·6 g.), and pyridine (8·4 g.). The product separated in needles (19·6 g.), m. p. 157—158° (Found : C, 62·7; H, 4·5; S, 14·4. $C_{23}H_{20}O_5S_2$ requires C, 62·7; H, 4·5; S, 14·5%).

Reactions of Ester (IV).—Since the ester remained unchanged when refluxed with water for 1 hr., 0·5N-barium hydroxide was employed. The liquid after filtration was extracted with ether. Evaporation of the solvent gave an oil which was diluted with ethanol and kept at 0° for 24 hr. Two solids, (VI) and (VII), separated in succession. *1-Phenylsulphenyl-1-phenylsulphonylacetone* (VI) crystallised in needles (0·4 g.), m. p. 110—111° (Found : C, 59·3; H, 4·6; S, 21·0. $C_{15}H_{14}O_3S_2$ requires C, 58·8; H, 4·6; S, 20·9%). *α-Phenylsulphenyl-α-phenylsulphonylmethane* (VII) separated in needles (0·9 g.), m. p. 61—62° (Found : C, 59·3; H, 4·4; S, 24·2. $C_{13}H_{12}O_2S_2$ requires C, 59·1; H, 4·6; S, 24·2%). Compound (VII) was also obtained (mixed m. p.) by condensation of phenylsulphonylacetone with phenyl benzenethiolsulphonate by Gibson's method [7] [product said to be (VI)], being indistinguishable from (VII) by analysis for carbon and hydrogen.

A mixture of the ester (IV) (2 g.), hydrogen peroxide (4 ml.; 100-vol.), acetic anhydride (10 ml.), and acetic acid (30 ml.) was, after two days, diluted with water, and kept at 0° for 12 hr. The resulting *ethyl di(phenylsulphonyl)acetate* (V) crystallised in needles (0·5 g.), m. p. 134—135° (Found : C, 52·3; H, 4·4; S, 17·1. $C_{16}H_{16}O_6S_2$ requires C, 52·2; H, 4·4; S, 17·4%). Hydrolysis of this ester (V) by boiling 20% aqueous sodium hydroxide for 1½ hr. gave di(phenylsulphonyl)methane [10] (VIII), m. p. and mixed m. p. 117—118° (Found : C, 52·9; H, 4·2; S, 21·9. Calc. for $C_{13}H_{12}O_4S_2$: C, 52·7; H, 4·1; S, 21·6%).

The ester (IV) (1 g.), hydriodic acid (3 ml.; *d* 1·7), and acetic anhydride (6 ml.) were heated on a steam-bath for 30 min., then added to aqueous sodium hydrogen sulphite. The resulting solid crystallised from aqueous ethanol in needles, m. p. and mixed m. p. with diphenyl disulphide [6] (III) 59—60°.

Reactions of α-Phenylsulphenyl-α-phenylsulphonylmethane (VII).—Oxidation of this compound by hydrogen peroxide in glacial acetic acid (see above) gave di(phenylsulphonyl)methane (VIII) (mixed m. p.).[10] Attempts to reduce compound (VII) by zinc dust and acetic acid at the b. p. or by hydriodic acid and acetic anhydride at 150—160° for 45 min. were unsuccessful. On the other hand, both di(phenylsulphinyl)methane [11] and α-phenylsulphinyl-α-phenylsulphonylmethane [11] were reduced to di(phenylsulphenyl)methane [10] by treatment with hydriodic acid and acetic anhydride at room temperature.

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[10] Shriner, Struck, and Jorison, *J. Amer. Chem. Soc.*, 1930, **52**, 2060.
[11] Hinsberg, *J. prakt. Chem.*, 1912, **85**, 337.
[12] Bellamy, "The Infrared Spectra of Complex Molecules," Chapter 22, Methuen & Co., Ltd., London, 1954.