

Les deux signaux se trouvant à 172,2 ppm et à 185,7 ppm peuvent être attribués au carbone du groupement lactonique (C-8) et à celui du groupement cétonique (C-4) respectivement. La distinction entre ces signaux est basée sur les données de la littérature (cf. p. ex. Réf. 2 p. 119 (β -propiolactone; 171,2 ppm) et Réf. 3 (*p*-benzoquinone; 187,0 ppm)).

Les signaux observés à 167,0 ppm et à 102,9 ppm représentent chacun deux carbones. Leur intensité relative indique deux carbones non protonés et deux carbones protonés respectivement.

La théorie du déplacement chimique du carbone² permet de prévoir dans le cas des cétones α,β -éthyléniques une différence sensible entre l' α -carbone et le β -carbone, ce dernier apparaissant à champ nettement plus faible. On en déduit aisément que la structure correcte du produit β -lactonique correspond à la formule 1 puisque les α -carbones du composé étudié absorbant à 102,9 ppm se trouvent protonés.

Le spectre de RMN du ¹³C a été mesuré en solution dans le CDCl₃ à 22,63 MHz sur un spectromètre Bruker Spectrospin muni d'une transformée de Fourier. Les déplacements chimiques sont donnés par rapport au tétraméthylsilane (TMS=0).

Nous remercions vivement Monsieur le Docteur G. Lukacs, Institut de Chimie des Substances Naturelles, Gif-sur-Yvette, France, pour une discussion fructueuse.

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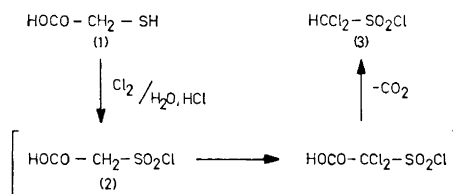
Reçu le 16 avril 1973.

A Convenient Method for the Preparation of Dichloromethanesulphonyl Chloride

TOMAS KEMPE and TORBJÖRN NORIN

Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm 70, Sweden

Previously reported methods for the preparation of dichloromethanesulphonyl chloride (3) require several steps and the over-all yields are low.¹⁻⁴ During the course of a study of halosulphinic acids, a new method for the preparation of dichloromethanesulphonyl chloride (3) has been developed. It is known that chlorosulphonylacetic acid (2) can be prepared from thioglycolic acid (1) by chlorination in aqueous solution.⁵ We have found that chlorination of thioglycolic acid in concentrated aqueous hydrochloric acid gives dichloromethanesulphonyl chloride (3) in one step without isolation of intermediates, e.g. chlorosulphonylacetic acid (2). The formation of the product (3) may proceed *via* decarboxylation of dichlorinated chlorosulphonylacetic acid as indicated in the tentative reaction scheme.



Experimental. Thioglycolic acid (92 g, 1 mol) was dissolved in 300 ml of concentrated aqueous hydrochloric acid (37 % w/v) and treated with a slow stream of chlorine during 2 days at about 10°. The dichloromethanesulphonyl chloride (3) separated during the reaction as a heavy oil. This oil was recovered, washed with water, dried over anhydrous sodium sulphate, and distilled under vacuum to give the pure dichloromethanesulphonyl chloride (82 g; b.p. 56°/6 mm; n_D^{25} = 1.4954; lit.³ b.p. 60–62°/9 mm, n_D^{20} 1.4949) in 45 % of the theoretical yield. The product was characterized as the dichloromethanesulphonyl anilide, m.p. 76° (lit.³ m.p. 76°).

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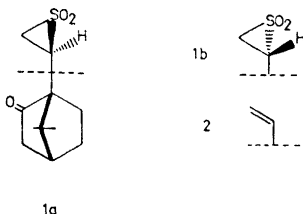
Received April 28, 1973.

Epimeric 2-[(1S)-7,7-Dimethyl-2-oxo-1-norbornanyl]-thiirane-1,1-dioxides

TOMAS KEMPE and TORBJÖRN NORIN

Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm 70, Sweden

The reaction between diazomethane and the intermediate sulphene produced by treatment of (1S)-camphor-10-sulphonyl chloride with triethylamine has been reported to give a thiiranedioxide (m.p. 83–85°).^{1,2} We have repeated this experiment. The two epimeric thiiranedioxides (*1a* and *1b*) thus formed have now been separated by thin layer and column chromatography on silica gel. The mixture of epimers as well as each of the two pure isomers decomposed when heated above their melting points yielding the known (1S)-7,7-dimethyl-1-vinyl-2-norbornanone (*2*).^{1,2}



Experimental. 2-[(1S)-7,7-dimethyl-2-oxo-1-norbornanyl]-thiirane-1,1-dioxides (*1a* and *1b*). The mixture of the epimeric thiiranedioxides (*1a* and *1b*) was prepared from (1S)-camphor-10-sulphonyl chloride (m.p. 67–68°; $[\alpha]_D^{21} + 30^\circ$, *c* 2.0 in CHCl_3) according to the procedure of Opitz and Fischer.^{1,2} The two compounds could be separated by TLC (Merck Silica gel HF₂₅₄), e.g. when eluted with ethyl ether, R_F values were 0.55 and 0.77. The epimers were separated on preparative scale by column chromatography (silica gel/ethyl ether) to yield a low-melting isomer (R_F 0.77; m.p. 81–86° dec.; approximate yield 70%; $[\alpha]_D^{21} - 5.6^\circ$, *c* 3.1 in CHCl_3) and a high-melting isomer (R_F 0.55; m.p. 100–106° dec.; approximate yield 15%; $[\alpha]_D^{21} - 58.6^\circ$, *c* 0.8 in CHCl_3). The two isomers exhibited similar IR spectra: ν (CHCl_3) 1735 (C=O), 1320 and 1160 (SO_2) cm^{-1} .^{1,2} The compounds were insufficiently stable at room temperature for meaningful elemental analysis. However, they could readily be characterized by heating to yield (1S)-7,7-dimethyl-1-vinyl-2-norbornanone (*2*) (m.p. 65–66°; $[\alpha]_D^{21} + 16^\circ$, *c* 3.3 in CHCl_3).^{1,2}

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Received April 28, 1973.

On the Electrical Properties of $\text{Pd}_{17}\text{Se}_{15}$, Pt_5Se_4 , and PtTe

ARNE KJEKSHUS

Kjemisk Institutt, Universitetet i Oslo, Blindern, Oslo 3, Norway

Only sparse information is available on the low temperature electrical behaviours of transition metal pnictides and chalcogenides. Moreover, the few investigations hitherto have been concerned with phases having relatively simple compositions and crystal structures. Therefore, it was considered worthwhile to study a few phases which do not satisfy the above