

## Reaction of Dimethylvinylidene with $\gamma\gamma$ -Dimethylallyl Methyl Sulphide. Synthesis of 2,5,5-Trimethylhepta-2,6-dien-4-one (Artemisia Ketone)

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**Summary** The [2,3] sigmatropic rearrangement of the sulphonium ylide derived from the title reaction, followed by hydrolysis of the allenic thioether product affords artemisia ketone (6).

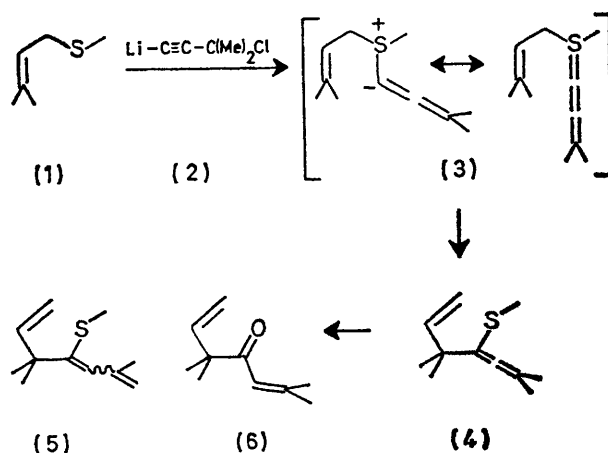
THE synthetic potential of the [2,3] sigmatropic rearrangement of allylic sulphonium ylides has been demonstrated, not only for stereoselective olefin synthesis, but also for binding various isoprenoid units.<sup>1</sup> Recently several types of  $\beta\gamma$ -unsaturated carbonyl compounds have been obtained from carbanions and ylides bearing an auxiliary function on the anionic carbon.<sup>2</sup>

We have now examined the possibility of construction and rearrangement of an allenic ylide of the novel cumulenenic type (3).

Treatment of the lithio-derivative (2)<sup>3</sup> in ether with the sulphide (1) at  $-75$  to  $20^\circ$  gave a mixture (70:15:14:1) of four isomeric compounds [54% or 82% yield based on sulphide (1) consumed]. The major product is the C<sub>11</sub> allenic thioether (4) containing the entire carbon skeleton of artemisia ketone [ $M^+$  182;  $\nu_{\max}$  3080, 1953, 1681, 1635, 1620, 910, and 815  $\text{cm}^{-1}$ ;  $\tau$  (CCl<sub>4</sub>) 8.8 (6H, s), 8.23 (6H, s), 8.05 (3H, s), 5.3—4.9 (2H, m), and 4.20 (1H, dd,  $J$  17 and 10 Hz)].

Prolonged heating during careful distillation causes the allenic thioether (4) to isomerise partially to the dienic

thioether (5), which has been shown by g.l.c. to be the minor of the four isomeric reaction products† [ $M^+$  182;



$\nu_{\max}$  3080, 1635, 915, 895, and 695  $\text{cm}^{-1}$ ;  $\lambda_{\max}$  (cyclohexane) 236 ( $\epsilon$  9500) and 283 nm (2400);  $\tau$  (CCl<sub>4</sub>) 8.75 (6H, s), 8.03br (3H, s), 7.9 (3H, s), 5.3—4.8 (4H, m), 4.15 (1H, dd,  $J$  17.5 and 10.5 Hz), and 3.82br (1H, s)].

† The two other products are: 1-methylthio-3,3,6-trimethylhept-5-en-1-yne and 1-methylthio-3,3,4,4-tetramethylhex-5-en-1-yne.

The thioether (4) is hydrolysed quantitatively in the presence of  $\text{HgCl}_2$  to give artemisia ketone (6) with spectra (i.r., u.v., mass and n.m.r.) identical to those previously reported for the natural product.<sup>4</sup>

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<sup>1</sup> See for example R. B. Bates and D. Feld, *Tetrahedron Letters*, 1968, 417; B. M. Trost and R. LaRochelle, *ibid.*, p. 3327; G. M. Blackburn, W. D. Ollis, C. Smith and I. O. Sutherland, *Chem. Comm.*, 1969, 99; J. E. Baldwin, and R. E. Hackler, *J. Amer. Chem. Soc.*, 1969, 91, 3646.

<sup>2</sup> J. Cast, T. S. Stevens, and J. Holmes, *J. Chem. Soc.*, 1960, 3521; S. Julia, B. Cazes, and C. Huynh, *Compt. rend.*, 1972, 274 C, 2019; J. M. Paton, P. L. Pauson, and T. S. Stevens, *J. Chem. Soc. (C)*, 1969, 2130; A. T. Babayan, A. A. Grigoryan, K. P. Kiramidzhyan, and M. G. Indzhikyan, *Armenian. khim. Zhur.*, 1970, 23, 602; *Chem. Abs.*, 1971, 74, 111,360; L. N. Mander and J. V. Turner, *J. Org. Chem.*, 1973, 38, 2915; C. Huynh, S. Julia, R. Lorne, and D. Michelot, *Bull. Soc. chim. France*, 1972, 4057; J. E. Baldwin and J. A. Walker, *J.C.S. Chem. Comm.*, 1972, 354; E. Hunt and B. Lythgoe, *ibid.*, p. 757; E. J. Corey and S. W. Walinsky, *J. Amer. Chem. Soc.*, 1972, 94, 8932; S. Julia, C. Huynh, and D. Michelot, *Tetrahedron Letters*, 1972, 3587.

<sup>3</sup> J. P. Battioni and W. Chodkiewicz, *Bull. Soc. chim. France*, 1969, 911; to check that the lithium derivative was a carbene precursor, we treated it with styrene and obtained the corresponding cyclopropane in 52% yield.

<sup>4</sup> L. H. Zalkow, D. R. Brannon, and J. W. Uecke, *J. Org. Chem.*, 1964, 29, 2786.