A Ready Route to *cis*-Jasmone *via* 1,3-Dithian-derived 1,4-Diketones

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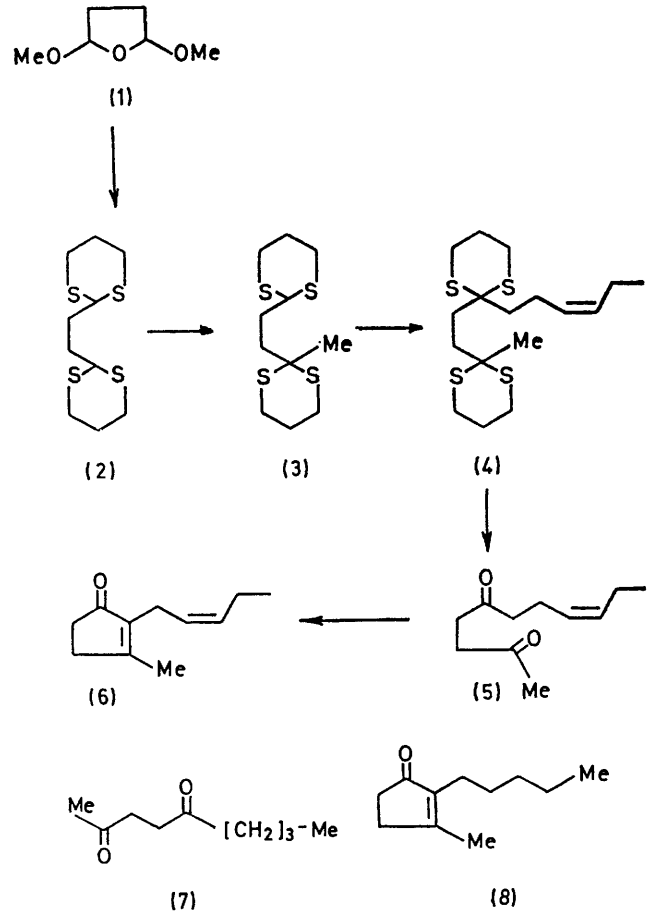
Summary *cis*-Jasmone has been synthesized in high overall yield *via* a bis-dithian derivative.

WE report a synthesis of *cis*-jasmone (**6**) which provides a general route to aliphatic 1,4-diketones,[1] intermediates for several natural products[2] of current interest.

Treatment of (**1**) with propane-1,3-dithiol and hydrogen chloride in chloroform gave the known[3] ethane (**2**) (83%), m.p. 132°. Monometallation of (**2**) (Bu^nLi in THF; −20°; 4 h) followed by reaction with MeI at 0° for 16·5 h gave a quantitative yield of the oily methyl-bisdithian (**3**), δ ($CDCl_3$) 1·52 (3H, s) p.p.m. In turn, (**3**) was similarly treated with Bu^nLi (−20°; 4 h) and 1-bromo-*cis*-hex-3-ene[1c] (0°; 19 h and 25°; 3 h) to give bisdithian (**4**) as an oil (97%), δ ($CDCl_3$) 0·95 (3H, t, *J* 8·0 Hz), 1·54 (3H, s), and 5·37 (2H, m) p.p.m. Compound (**4**) was hydrolysed in water–acetone (1:5) under reflux for 1 h in the presence of mercuric chloride and cadmium carbonate.[4] Stereospecific deoxymercuration[5] of the olefin was accomplished by treatment of the mixture with potassium iodide[4] for 30 min at 25° yielding the oily diketone (**5**) (84·6%); i.r. ($CHCl_3$): 5·88 μm; δ ($CDCl_3$): 0·96 (3H, t, *J* 7·6 Hz) and 2·15 (3H, s). Diketone (**5**) was cyclized (0·5N-NaOH–EtOH reflux; 4·25 h) to yield, together with a small amount of impurity, *cis*-jasmone (**6**) (89·5%) i.r. ($CHCl_3$): 5·93 and 6·05 μm; δ ($CDCl_3$): 0·97 (3H, t, *J* 7·9 Hz), 2·05 (3H, s), and 5·37 (2H, m) p.p.m.; 2,4-dinitrophenylhydrazone, m.p. 112—114°, identical in all respects with a sample kindly provided by Professor G. Büchi. The reported yields are those for crude products. However, in every case these were sufficiently pure for reaction in the next step. On this basis the overall yield of crude *cis*-jasmone was 61% starting from



(**1**). A similar series of reactions produced nonane-2,5-dione (**7**) [70% from (**1**)] and dihydrojasmone (**8**) was also prepared (59% overall), 2,4-dinitrophenylhydrazone, m.p. 120—122°. The crude product was nevertheless very pure.

This work was supported by a contract from the Agency for International Development.

(*Received*, 29*th December* 1971; *Com.* 2189.)

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