

Generation and Pyrolysis of a Cyclopropyl Substituted Cyclopentadiene: a Potential Source of Unsaturated Annelated Cyclopentanones

By ROBERT D. MILLER

(I.B.M. Research Laboratory, San Jose, CA 95193)

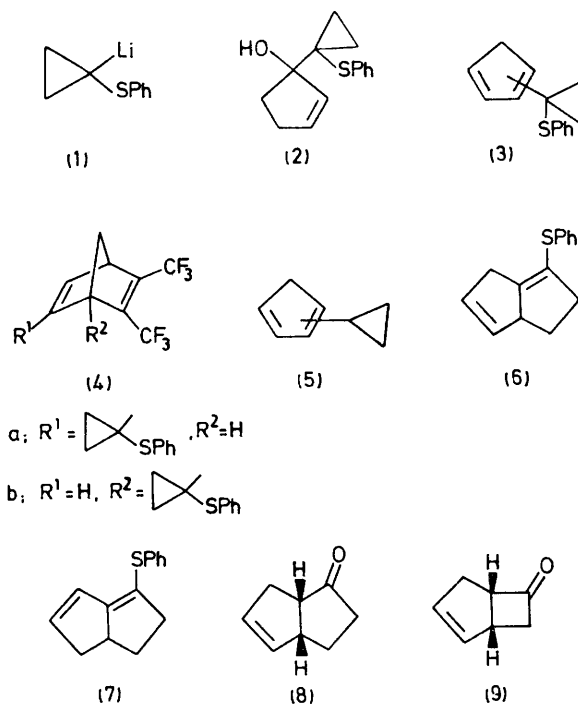
Summary The tertiary allylic alcohol (**2**) is readily dehydrated by catalytic amounts of non-aqueous acid to the cyclopentadiene derivative (**3**), which is subsequently regiospecifically transformed to the vinyl sulphide (**6**) by pyrolysis.

THE addition of cyclopent-2-en-1-one to a solution of (**1**)^{1a} in tetrahydrofuran (THF) at 0 °C produced the expected

adduct (**2**). Subsequent treatment of (**2**) with a catalytic amount of toluene-*p*-sulphonic acid in benzene (25 °C; 3 h) led to rapid dehydration to the cyclopentadiene derivative (**3**) in nearly quantitative yield. Under these conditions, there was no evidence of expansion of the cyclopropane ring to produce a spiroannulated product.¹ The diene (**3**) reacted in a Diels-Alder fashion with excess of hexafluorobut-2-yne (Et₂O; 10 °C; 6 h) to produce a mixture of two

adducts (4a) and (4b) in a ratio of 4:1. Benzenethiol was readily eliminated from (3) by treatment with Na-NH₃ or with LiAlH₄ in refluxing THF (2 h) yielding cyclopropylcyclopentadiene (5) as a mixture of positional isomers (66%).

When (3) was dropped into a hot conditioned quartz tube packed with Pyrex beads (500 °C; 0.2 mmHg), it underwent a surprisingly smooth vinylcyclopropane rearrangement² (80%) to yield a vinyl sulphide predominantly as a single regioisomer: ¹H n.m.r. τ (CCl₄) 2.88 (m, 5H), 4.17 (br s, 2H), 6.34 (m, 1H), 7.0–7.9 (m, 5H), and 8.25–8.77 (m, 1H); i.r. (neat) 3040, 2940, 2840, 2820, 1660w, 1585, 1480, 1440, 1130, 750, 700, and 680 cm⁻¹; u.v. (C₆H₁₄) λ 248 (ϵ 9670) and 266 (8170) nm. Since the spectral data did not unambiguously distinguish between the isomeric vinyl sulphides (6) and (7) each formally accessible from different positional isomers of (3), the product was hydrolysed to produce the corresponding ketone (65%).³ The ketone isolated from the hydrolysis was subsequently identified as (8) by its spectral data and by comparison with an authentic sample prepared by ring expansion of (9).⁴ The isolation of (8) firmly established (6) as the major product from the pyrolysis of (3) and represents a simple synthetic route to the *cis*-bicyclo[3.3.0]octane skeleton containing different functional groups, which is not readily accessible. The isolation of a single vinyl sulphide from the pyrolysis of (3) is interesting as the positional isomers of the cyclopentadiene should be in mobile equilibrium *via* 1,5-sigmatropic hydrogen migration under the reaction conditions.⁵ Since (6) is most simply viewed as arising from the 1-substituted cyclopentadiene derivative, apparently the extended cyclopropyl conjugation (*vs.* cross-conjugation



for the 2-isomer) favourably influences the energy of the transition state.

(Received, 19th January 1976; Com. 040.)

† Spectral data in accord with the proposed structures have been obtained.

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² H. M. Frey and R. Walsh, *Chem. Rev.*, 1969, **69**, 103; M. R. Willcott, III, R. L. Cargill, and A. B. Sears, *Progr. Phys. Org. Chem.*, 1972, **9**, 25.

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⁴ J. D. Roberts and W. F. Gorham, *J. Amer. Chem. Soc.*, 1954, **74**, 2278.

⁵ S. McLean and P. Haynes, *Tetrahedron*, 1965, **21**, 2329; S. McLean, C. J. Webster, and R. J. D. Rutherford, *Canad. J. Chem.*, 1969, **47**, 1555.