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On the Interesting Course of Dichloroketene Addition to 1,5-Dimethyl-1,5-cyclooctadiene

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ON THE INTERESTING COURSE OF DICHLOROKETENE
ADDITION TO 1,5-DIMETHYL-1,5-CYCLOOCTADIENE

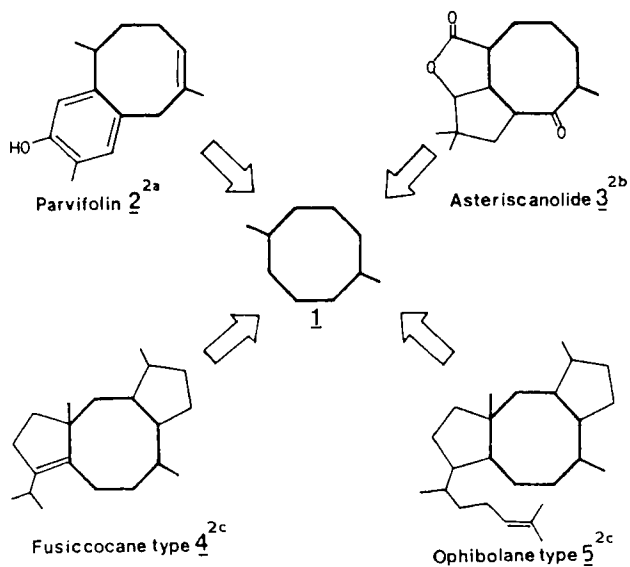
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Abstract: Reaction of dichloroketene with 1,5-dimethyl-1,5 COD 6 charters an eventful course to furnish novel tricyclic ketone 10, through the intermediacy of tricyclic hydroxy olefin 9, in which the two carbon atoms of dichloroketene form a bridge across the eight membered ring.

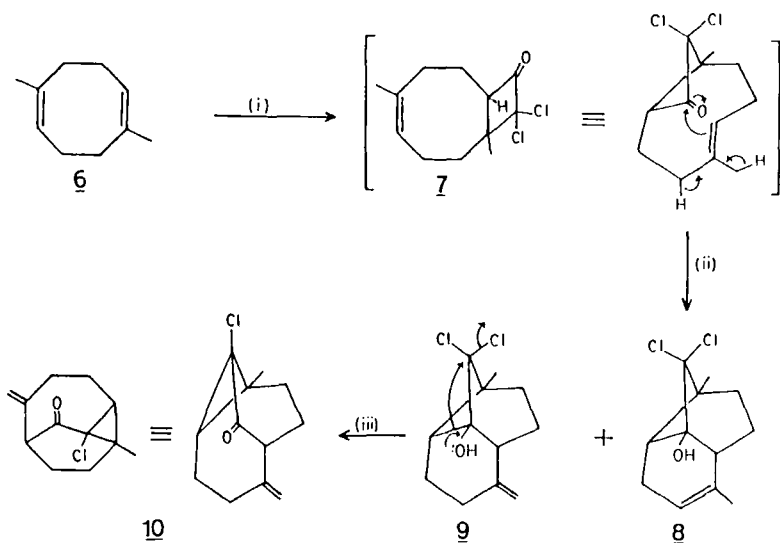
There is a great deal of current interest in the synthesis of complex cyclooctanoid natural products on account of their novel structural features and biological activity.¹ As a part of our synthetic interest in the area,^{1a,b} we recognised the ubiquitous presence of a 1,5-dimethylcyclooctane core in the majority of cyclooctanoid natural products (heavy line in 2-5,² Scheme 1). This led us to identify 1,5-dimethyl-1,5-cyclooctadiene 6, the commercially available dimer of isoprene, as a building-block for this class of com-

Scheme 1



pounds through site-selective cyclopentannulations. In this context, we attempted cyclopentannulation of 6 through the Greene methodology³ of dichloroketene addition. However, the reaction of 6 with dichloroketene took an eventful and interesting course and this potentially useful observation is disclosed here.

Exposure of 6 to *in situ* generated dichloroketene under ultrasound irradiation⁴ led to a labile reaction mixture in which the presence of the required 2+2-adduct 7 could be detected on the basis of spectral data. Attempted purification of this material on

Scheme 2

silica gel column or exposure to Lewis acids resulted in the formation of two tricyclic products **8** and **9** (1:5, 63%). While the major product **9** could be purified and fully characterised, the presence of the minor

Reagents & Yields: (i) Cl_3CCOCl , Zn-Cu, ether, ultrasound, 20-25°C; (ii) Silica gel 63%; (iii) Alumina, 3h, 85%.

product was inferred on the basis of IR, ^1H NMR data. The structure of the major product **9** followed from its characteristic ^{13}C NMR signal at δ 98.5 ($-\overset{|}{\text{C}}-\text{OH}$) and ^1H NMR resonances at 4.78 (m, $\text{C}=\overset{\text{H}}{\text{C}}-\overset{\text{H}}{\text{H}}$) and δ 1.16 (s, quaternary methyl group). We envision the formation of

8 and 9 from 7 via a catalysed transannular ene reaction between the strained carbonyl group and the proximal cyclooctene double bond.⁵

The tricyclic hydroxy-olefin 9 on treatment with base or more conveniently basic alumina readily rearranged to the ring contracted cyclopropyl ketone 10. Structure of 10 follows from its mass spectral data, presence of carbonyl absorption (IR : 1695 cm⁻¹, ¹³C NMR: δ 201.4) and a deshielded β-methyl (δ 1.44, s) on the cyclopropyl ketone moiety in the ¹H NMR spectrum. Thus, an interesting C₁₀-bridged tricyclic system became available in just two steps from 6.

Experimental Section⁶

Dichloroketene addition to 1,5-dimethyl-1,5-cyclooctadiene 6:

A two necked 100 mL RB flask fitted with a reflux condenser, pressure equalising addition funnel and nitrogen inlet was charged with 6 (500 mg, 3.6 mmol), Zn-Cu couple (360 mg, 5.6 mmol) and anhydrous ether (60 mL). The flask was then partially submerged in a sonicator and positioned to produce maximum agitation. To this suspension, trichloroacetylchloride (830 mg, 4.5 mmol) in anhydrous ether (25 mL) was added (30 min) and

the temperature was carefully maintained around 20-25°C. Sonication was continued for further 20 min. Then the reaction mixture was diluted with ether (25 mL). The ethereal layer was decanted and the residue was washed with ether (2 x 25 mL). The combined ethereal solution was successively washed with water (2 x 20 mL) sat. sodium bicarbonate (2 x 20 mL), brine (2 x 20 mL) and dried over anhydrous Na₂SO₄. Removal of solvent over rotary evaporator gave 750 mg of an oily residue. The spectral data recorded on this sample indicated the presence of 7. IR (neat): 1800 cm.⁻¹ ¹H NMR (100 MHz, CDCl₃): δ 5.36 (1H, t, -CH=C-CH₃), 1.66 (3H, s, -CH=C-CH₃), 1.32 (3H, s, -Cl₂-C-CH₃). 500 mg of the above reaction mixture was charged on a silica gel (20 g) column. Elution with 70% benzene-hexane furnished the unreacted 1,5-dimethyl cyclooctadiene (160 mg). Further elution with the same solvent gave a mixture (1 : 5) of tricyclic hydroxy compounds 8 and 9, 200 mg (63% based on recovered 6). Repeated chromatography on silica gel led to a further enriched sample of 9 bp.: 135°/0.6 torr (bath). IR(neat): 3600-3300, 3070 cm.⁻¹ ¹H NMR (100 MHz, CDCl₃): δ 4.78 (2H, m), 3.9-1.5 (11H series of m), 1.16 (3H, s). ¹³C NMR (25 MHz, CDCl₃): δ 149.2, 109.4, 98.5, 80.5, 45.9, 45.2, 43.9, 30.3, 26.2, 23.8, 19.8, 18.7. Mass: M/Z: 246 (M⁺), 248 (M⁺ +2), 250 (M⁺ +4). Anal. Calcd. for

$C_{12}H_{16}Cl_2O$: C, 58.31; H, 6.52. Found: C, 58.49; H, 6.43.

Rearrangement of tricyclic hydroxy compound 9 on alumina:

96 mg of 9 was charged on alumina (10 g) column. The material was allowed to be adsorbed for 3h. Elution of the column with 80% benzene-hexane furnished tricyclic ketone 10 (70 mg, 85%). bp.: 140°C/0.3 torr (bath). IR(neat): 3060, 1696, 890 cm^{-1} . 1H NMR (100 MHz, $CDCl_3$): δ 4.96 (1H, br s), 4.8 (1H, br s), 3.46 (1H, br s), 2.66-1.58 (9H, series of m), 1.44 (3H, s). ^{13}C NMR (25 MHz, $CDCl_3$): δ 201.4(s), 144.3(s), 113.6(t), 58.5(s), 53.2(d), 43.7(d), 39.5(s), 34.6(t), 33.0(t), 25.9(q), 23.9(t), 23.0(t). Mass: 210 (M^+), 212 ($M^+ + 2$). Anal. Calcd. for $C_{12}H_{15}ClO$: C, 68.08; H, 7.60. Found: C, 67.88; H, 7.58.

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