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Synthesis of 3a,8a-Dihydrocyclopent[*a*]inden-3(8*H*)-one[1)]

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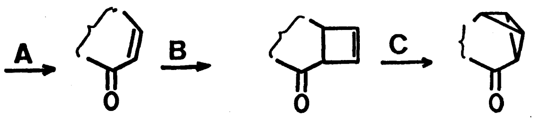
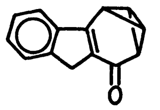
Synopsis. 3a,8a-Dihydrocyclopent[*a*]inden-3(8*H*)-one (**6**) was prepared from a known compound, 2,2-dichloro-2,2a,7,7a-tetrahydro-1*H*-cyclobut[*a*]inden-1-one, by a simple ketone 1,2-transposition followed by introduction of a double bond. The photochemical behavior of **6** was also examined.

The reaction sequence which involves the preparation of the appropriate enone (step-A), its photoannelation with acetylene (or its equivalents) (step-B), and photochemical construction of bicyclobutane (step-C), is our strategy for the synthesis of valene-type isomers of cyclic conjugated systems.[2)]



As already reported, enones **5** and **4** proved to be useful intermediates for our synthesis of **1**[2c)] and **2**,[2d)] respectively. 3a,8a-Dihydrocyclopent[*a*]inden-3(8*H*)-one (**6**) corresponds to the precursor for the synthesis of a benzazulvalene derivative **3** on the line of our methodology. Although the β,γ-unsaturated ketone chromophore in **6** is presumed to disturb the desired photochemical transformations,[3)] synthesis and efficiency of photocycloaddition of **6** were pursued.

Enone **6** was prepared from the known compound **7**[4)] by a simple ketone 1,2-transposition[5)] followed by introduction of a double bond. Thus cyclobutanone **7** was subjected to ring enlargement[6)] with diazomethane to afford **8** (87%), which was reduced with sodium borohydride in methanol to yield epimeric alcohols **9** as a colorless solid. Vinyl chloride **10** obtained from **9** through reduction with zinc dust in acetic acid was transformed to cyclopentanone **11** by hydrolysis with 90% sulfuric acid at room temperature for 30 min, in 40.6% yield based on **8**. Alcohol **9** and vinyl chloride **10** could be used without purification during the above transformations.



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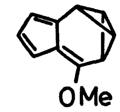

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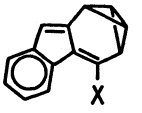

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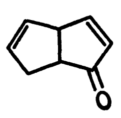

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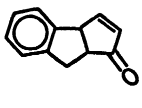

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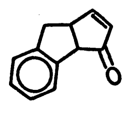

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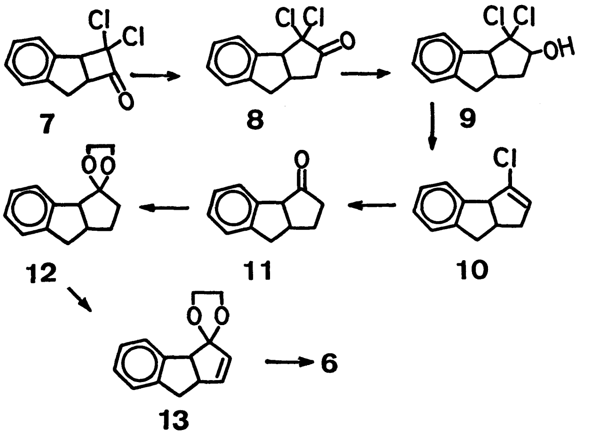
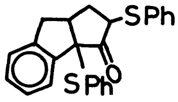
Because of the easy deprotonation at angular position α to carbonyl group of **11**, routine sulfenylation[7)] (LDA 2 equiv., diphenyl disulfide 2 equiv.) afforded bissulfenylated ketone **14** as a sole product. However, a similar method used in the synthesis of **5**[2c,8)] was applicable to regiospecific introduction of a double bond to **11** in a yield of 80.4%. While the formation of enone **5** was accompanied with the formation of **15** (15%), none of the isomeric enone was produced during the formation of **6**.



Photoannelations of **6** with acetylene, 1,2-dichloroethylene or bis(trimethylsilyl)acetylene were unsatisfactory. In all cases, the yields of the desired adducts were less than 5% and reaction mixtures showed several spots on TLC and strong absorption band at 1820 cm^{-1} in their IR spectra. Upon photolysis in KBr disk, **6** showed infrared absorption band characteristic of a ketene at 2120 cm^{-1}. Furthermore, irradiation of **6** in a mixture of acetone–methanol afforded methyl ester **16** in 80% yield. Apparently, a Norrish-type I reaction of **6**, followed by formation of ketene **17**, overcomes photocycloaddition.



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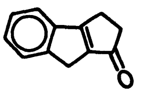

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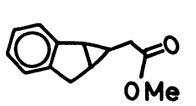

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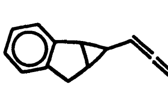

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In conclusion, the synthetic method involving ketone 1,2-transposition is useful for the preparation of related cyclopentenones. Enone **6** is not appropriate to our purpose. The benzene ring must be masked. Studies in this line are in progress.

Experimental

^{1}H NMR (100 MHz) spectra were recorded on a Varian XL-100 spectrometer. Chemical shifts are reported in ppm (δ) downfield from TMS as internal standard and coupling constants are given in Hz. IR spectra were recorded on a JASCO A-100 instrument and mass spectra were obtained on a JEOL JMS-01SG-2 spectrometer.

3,3-Dichloro-3,3a,8,8a-tetrahydrocyclopent[a]*inden-2(1*H*)-one (8).* Ring expansion of **7** with diazomethane was carried out as described in the literature.[6] Yield: 87%; mp: 70—73 °C from ether: IR (KBr): 1761 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ=2.44 (1H, dd, J=19.5 and 5.1 Hz), 2.72—3.44 (4H, m), 4.24 (1H, d, J=7.8 Hz), 7.15—7.35 (3H, m), 7.6 (1H, m). Found: C, 59.77; H, 4.20%. Calcd for $C_{12}H_{10}OCl_2$: C, 59.78; H, 4.18%.

3,3-Dichloro-1,2,3,3a,8,8a-hexahydrocyclopent[a]*inden-2-ol (9).* To a solution of 1.862 g of **8** in 40 ml of methanol was added 302.6 mg of sodium borohydride. After one hour stirring, 250 ml of ether was added. The mixture was washed (H_2O and then brine), dried ($MgSO_4$), and concentrated to yield 1.886 g of crude alcohol **9** as a colorless solid, which was used in a next step without purification.

3-Chloro-1,3a,8,8a-tetrahydrocyclopent[a]*indene (10).* 1.886 g of alcohol **9** was treated with 1.530 g of zinc in 20 ml of acetic acid at 90 °C for 1 h. After cooling, 100 ml of hexane was added. The mixture was washed (H_2O and then brine) and dried ($MgSO_4$). Removal of the solvent afforded an oil which was passed through a short plug of deactivated silica gel (10% water) with hexane to yield 884 mg of **10** as yellow oil, which was used in the next step without further purification.

1,2,8,8a-Tetrahydrocyclopent[a]*inden-3(3a*H*)-one (11).* Sulfuric acid (90%, 3 ml) was slowly added to 884 mg of **10** with stirring at 0 °C. After 30 min the mixture was poured onto ice. After routine treatment, chromatography over 8 g of deactivated silica gel (10% water), eluted with a mixture of hexane–benzene (9:1 v/v) afforded 540 mg of **11** as a colorless oil; bp: 65 °C/0.3 mmHg; IR (neat): 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ=1.58 (1H, m), 2.10—2.40 (3H, m), 3.20 (1H, m), 2.80, 3.24 (2H, AB-part of an ABX_n, J=14.0), 3.73 (1H, dm, J=8.0), 7.10—7.26 (3H, m), 7.43 (1H, m). Found: C, 83.81; H, 7.03%. Calcd for $C_{12}H_{12}O$: C, 83.94; H, 7.00%.

3a,8a-Dihydrocyclopent[a]*inden-3(8*H*)-one (6).* This material was obtained from the ketone **11** by using the general procedure (acetalization, bromination, dehydrobromination and deacetalization) of Eaton *et al.*[8] Yield: 80.4%; mp: 85.5—86.0 °C from hexane–ether, colorless needles; IR (KBr): 1695 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ=2.92 (1H, d, J=16.5 Hz), 3.35 (1H, dd, J=16.5 and 9.0 Hz), 3.82 (1H, m), 3.87 (1H, m), 6.03 (1H, dd, J=5.7 and 1.6 Hz), 7.10—7.25 (3H, m), 7.50 (1H, m), 7.59 (1H, dd, J=5.7 and 2.5 Hz). Found: C, 84.32; H, 5.93%. Calcd for $C_{12}H_{10}O$: C, 84.68; H, 5.92%.

Attempted Photoannelation of 6. In a typical run, 222 mg of **6** was dissolved in 80 ml of dichloroethylene. After nitrogen was bubbled through for 1 h, the solution was irradiated at 0 °C. After **6** was disappeared on TLC examination, the solvent was removed under reduced pressure and the residue was checked by IR and NMR spectra for product analysis. Other conditions examined were: acetylene in acetone at −78 °C and bis(trimethylsilyl)acetylene in acetone or acetonitrile at 0 °C. In all cases, irradiations were conducted with a 100 W high pressure mercury lamp through Pyrex filter.

Photolysis of 6 in KBr Disk. 3 mg of **6** was placed in a KBr disk. The disk was irradiated using a 100 W high pressure mercury lamp through a Pyrex filter. The photolysis was followed by measuring the IR spectrum every 10 min. After 50 min, the absorption band attributable to ketene at 2120 cm^{-1} reached its maximum and then gradually decreased on further irradiation.

Photolysis of 6 in the Presence of Methanol. 100 mg of **6** was dissolved in a mixture (50 ml) of acetone–methanol (2:1 v/v). After nitrogen was bubbled through for 30 min, the solution was irradiated using 100 W high pressure mercury lamp through Pyrex filter. After 1 h, the solvent was removed under reduced pressure and the residue was chromatographed over deactivated silica gel (6% water) with benzene. An epimeric mixture of the methyl ester **16** (94 mg) was obtained as a colorless oil. IR (neat): 1720 cm^{-1}; MS: 202 (M^+, 10%), 143 ($M^+-C_2H_3O_2$, 23%), 142 ($M^+-C_2H_4O_2$, 46%), 141 ($M^+-C_2H_5O_2$, 40%), 129 ($M^+-C_3H_5O_2$, 42%), 128 (naphthalene cation, 100%), 115 (indenium ion, 60%); ^{1}H NMR ($CDCl_3$): δ=0.7 (0.6 H, m), 1.2—2.05 (2.4 H, m), 2.10—2.60 (2H, m), 2.70—3.50 (2H, m), 3.55 (1.2 H, s), 3.65 (1.8 H, s), 6.6—7.4 (4H, m).

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