Electrophilic Substitution in a Tricyclic [10]Annulene

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Electrophilic aromatic substitution reactions of the [10]annulene (**4**) are reported, together with an improved method for its preparation.

We have recently described the preparation of 7b-methyl-7b*H*-cyclopent[*cd*]indene (**4**), an unsubstituted tricyclic aromatic [10]annulene, by bisdecarbonylation of the dialdehyde (**3**) prepared as shown in Scheme 1.[1] The key step in establishing the tricyclic system is the [8+2]cycloaddition of dimethyl acetylenedicarboxylate to the highly reactive 3-methoxy-3a-methyl-3a*H*-indene (**2**).[2,3] We now report an improved synthesis of (**4**), which again involves cycloaddition to (**2**), but is more versatile and amenable to large-scale working,† together with the first results of its aromatic electrophilic substitution reactions.

The 3a*H*-indene (**2**) was generated as before from the trienone (**1**),[3] and treated with 2-chloroacryloyl chloride, a reactive dienophile and useful keten equivalent.[5] Cycloaddition

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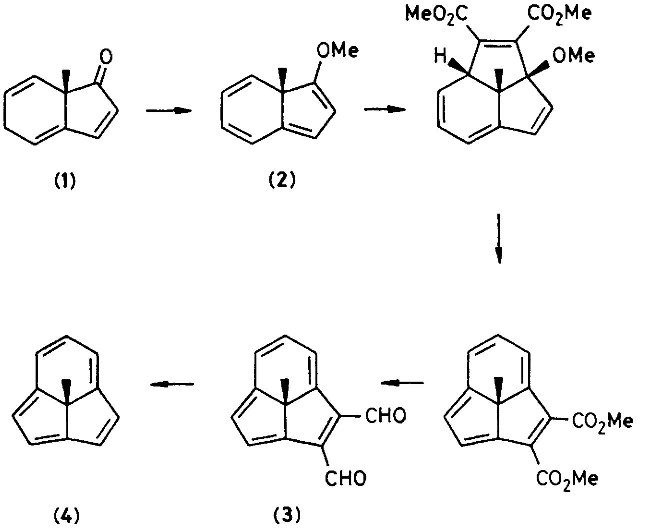
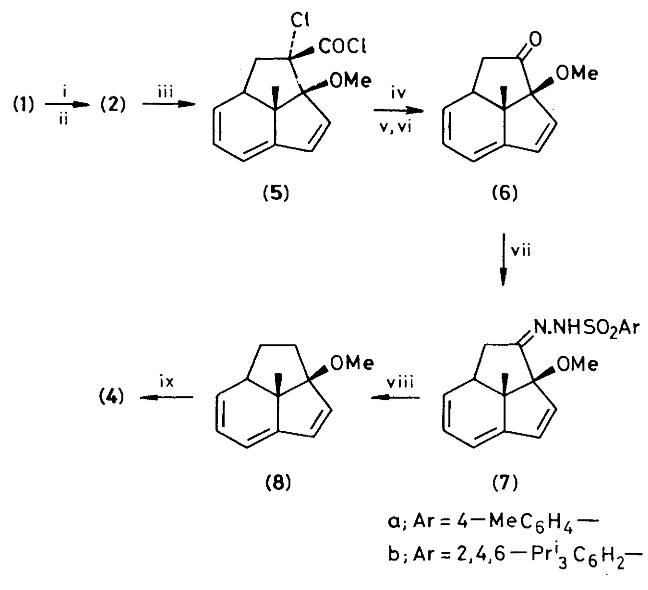
† An alternative synthesis of (**4**) has also been developed, in which the ring closure to the tricyclic system is effected by an intramolecular aldol condensation.[4]



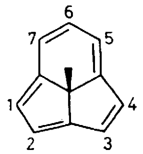
Scheme 1

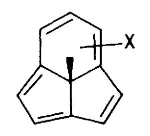


Scheme 2. Reagents: i, KH, 18-crown-6, 1,2-dimethoxyethane (DME), −20 °C; ii, $MeOSO_2F$, DME, −20 °C; iii, $CH_2{=}C(Cl)\text{-}COCl$, DME, −10 °C; iv, NaN_3; v, Heat, DME, 80 °C; vi, AcOH, H_2O, 60 °C; vii, $ArSO_2NHNH_2$; viii, MeLi, C_6H_6, 20 °C; ix, MeLi, C_6H_6, 45 °C or $4\text{-}MeC_6H_4SO_3H$, CH_2Cl_2, 20 °C.

occurred readily to give the expected adduct regiospecifically.‡ The adduct is not isolated but converted directly into the ketone (**6**) under standard conditions.[5] The ketone (**6**) [48% overall from (**1**)], an oil, ν_{max} 1732 cm^{-1}, obviously has considerable potential as a precursor to several annulenes.

The conversion of (**6**) into the unsubstituted annulene (**4**) (Scheme 2) was readily achieved by means of the Shapiro reaction.[6] Thus, the hydrazone (**7a**) (91%), prepared as a separable mixture of geometric isomers, m.p. 157—150 °C and m.p. 172—175 °C, was treated with a large excess of methyl-lithium in benzene at 20 °C to give the tetraene (**8**), together with some of the annulene (**4**). Elimination of methanol from (**8**) to give (**4**) occurred under the strongly basic reaction conditions, and by heating the reaction mixture to 45 °C, the conversion could be taken to completion. Alternatively, the tetraene (**8**) could be converted into (**4**) (81%) by treatment with a catalytic amount of 4-toluenesulphonic acid in dichloromethane. The yield of the annulene (**4**) was much improved by using the 2,4,6-tri-isopropylbenzenesulphonyl hydrazone (**7b**) formed in 83% yield; trisylhydrazones are known to undergo fragmentation more readily than the corresponding tosylhydrazones.[7] The hydrazone (**7b**), m.p. 174—177 °C, was converted directly into the annulene (**4**) (61%) by treatment with excess of methyl-lithium in benzene at 45 °C. Some tetraene (**8**) (22%) was also formed and converted as above into annulene. The annulene (**4**) can be purified by distillation (bulb-to-bulb) at 60 °C and 0.1 mmHg to give a yellow oil which solidifies to a waxy solid on cooling, m.p. 8.5—11 °C.



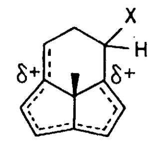


(9)

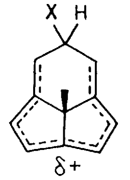
a; X = NO2 b; X = NHCOMe
c; X = COMe d; X = CHO

Table 1. Percentage composition of reaction products.

Isomer	1-	2-	5-	6-
X = NO_2	40	5	40	15
X = COMe	20	0	75	5
X = CHO	4	0	93	3



(10)



(11)

In agreement with its aromatic nature,[1] annulene (**4**) undergoes substitution reactions with electrophilic reagents. Reaction of (**4**) with copper(II) nitrate trihydrate in acetic anhydride[8] at 0 °C gave a mixture of mononitro substitution products (**9a**) (40%). These products could not be completely separated, but n.m.r. spectroscopy clearly established that all four possible mononitro annulenes had been formed in the ratios indicated in Table 1. No dinitroannulenes were observed, and there was no improvement in the positional selectivity of nitration at lower temperatures. In contrast, *trans*-10b,10c-dimethyl-10b,10c-dihydropyrene, a tetracyclic [14]annulene, gives a single mononitro compound under similar conditions.[8] Reduction of the mixture of nitroannulenes (**9a**) with zinc in acetic anhydride gave a corresponding mixture of acetamidoannulenes (**9b**) (55%).

Acetylation of the annulene (**4**) was more selective than nitration; acetic anhydride in dichloromethane in the presence of boron trifluoride–diethyl ether at room temperature gave a mixture of three monoacetyl annulenes (**9c**) (55%) in the ratio

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‡ In a separate experiment, the adduct (**5**) was isolated and the major stereoisomer (25 : 1) was shown to have the stereochemistry indicated.

shown. Formylation with dichloromethyl n-butyl ether and tin(IV) chloride[8] in dichloromethane at −78 °C was much more selective still, giving the aldehyde (**9d**) (28%) with >90% attack at the 5-position. The 5-isomer could be isolated in pure form as its mauve 2,4-dinitrophenylhydrazone, m.p. 202—204 °C.

All substitution products (**9**) show an n.m.r. signal upfield of tetramethylsilane for the central methyl group in the range δ ($CDCl_3$) −1.27 to −1.35 (**9a**), −1.40 to −1.47 (**9b**), −1.42 to −1.47 (**9c**), and −1.36 to −1.42 (**9d**).

The preference for 5- and 1-substitution can be explained by considering the carbocation intermediates involved. For example, the intermediate cation (**10**) for attack of the electrophile, X^+, at the 5-position should be more stable than the cation (**11**) for attack at the 6-position, in spite of the greater symmetry of (**11**), since the positive charge can be delocalised on to two tertiary positions in (**10**) but on to only one in (**11**). 1-Substitution should similarly be favoured over 2- in the five-membered ring. That substitution occurs to a greater extent at the 6- than at the 2-position is possibly due to the enhanced symmetry of intermediate (**11**).

Thus 7b-methyl-7b*H*-cyclopent[*cd*]indene (**4**) exhibits pronounced aromatic reactivity towards electrophiles.

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