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CYCLOPENTA[b]PYRANS

FROM TETRAACETYLETHYLENE AND CYCLOPENTADIENE

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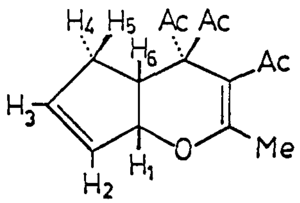
3,4-Diacetyl-3-hexene-2,5-dione (tetraacetylethylene) (I) behaves as an highly activated unsaturated system and undergoes ready addition reactions. With 2,3-dimethylbutadiene it behaves as dienophile to yield the expected Diels-Alder adduct, 4,4,5,5-tetraacetyl-1,2-dimethylcyclohexene-1 (1,2,3).

We now wish to report a novel cycloaddition of tetraacetylethylene to cyclopentadiene.

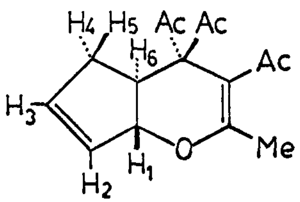
In a typical experiment the tetraketone (I) was refluxed with cyclopentadiene (1:1.5) in chloroform for 2 hours to give a colourless adduct, $C_{15}H_{18}O_4$, m.p. 75-76° (III), in 75% yield after crystallization from light petroleum (75-120°), $\lambda_{max.}$ (CH_3OH) 270 nm (log ε 3.91); $\nu_{max.}$ (KBr) 3060w, 1690s, 1600vs cm^{-1}. Compound (III) was not stable indefinitely, but in a few months it changed into a tarry material, containing (t.l.c.) compound (IV) (see below).

When the adduct (III) was heated at 90° in monoglyme for 48 hours and the resulting brown solution was evaporated, we obtained a resinous material from which the isomer (IV), m.p. 100-101°, was isolated in 30% yield by crystallization from light petroleum (75-120°), $\lambda_{max.}$ (CH_3OH) 268 nm (log ε 4.04); $\nu_{max.}$ (KBr) 3060w, 3045w, 1710s, 1620vs cm^{-1}.

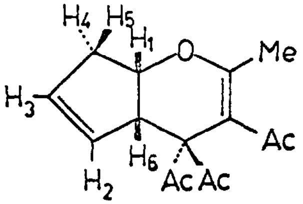
The presence of a very strong band at about 1600 cm^{-1} in the i.r. spectra, which is indicative of a conjugated -CO-C=C-O- system (4,5), and the u.v. absorption at about 270 nm (6) ruled out a norbornene structure for compounds (III) and (IV), and were in full agreement with cyclopenta[b]pyran derivatives.



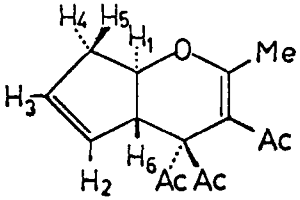
(III)



(IV)



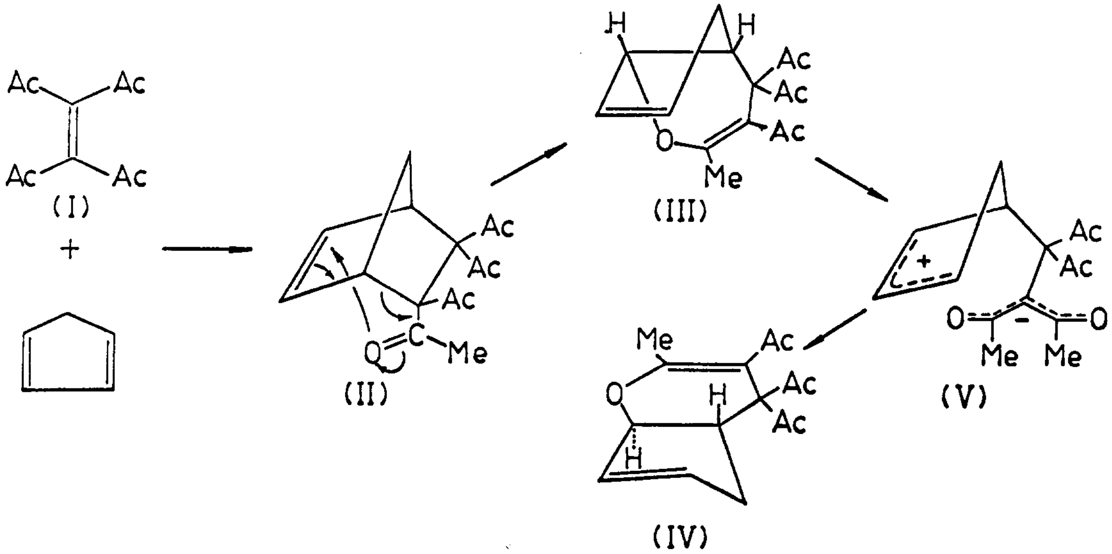
(VI)



(VII)

The ^{1}H-n.m.r. spectrum of III in $CDCl_3$ exhibits three singlets (integral ratio 8:3:3) at δ 2.1, 2.31, and 2.43 for the methyl groups (the signal at highest field partially overlaps a structured resonance at about δ 2.2 attributable to the methylene ring protons), and four single-proton multiplets at δ 3.28, 5.02, 5.92, and 6.08 which were assigned to the H-6, H-1, H-2, and H-3 protons respectively, on the basis of chemical shifts and double resonance experiments. Such experiments ruled out the structures (VI) and (VII) and prompted us to formulate compound (III) as cis-3,4,4-triacetyl-2-methyl-4,4a,5,7a-tetrahydrocyclopenta[b]pyran. Irradiation at δ 5.02 (H-1) has a very little effect on the signal at lowest field (H-3) which appears as a doublet of triplets ($J_{2,3} = 5.75$; $J_{3,4} = J_{3,5} = 2$ Hz), but reduces the multiplet at δ 5.92 (H-2) to a structured doublet; at the same time it causes the multiplet at δ 3.28 (H-6) to change into a triplet ($J_{4,6} = J_{5,6} = 7.7$ Hz). The same values for the coupling constants $J_{3,4}$, $J_{3,5}$ and $J_{4,6}$, $J_{5,6}$ were fully consistent with the cis-configuration (III) for which, as it results from the Dreiding model,. a conformational equilibrium can be taken into consideration. The olefinic resonances do not change by irradiation at δ 3.28 (H-6), whereas the multiplet at δ 5.02 (H-1) collapses to a structured singlet under the same conditions, but it gives rise to a broad doublet ($J_{1,6} = 6.7$ Hz) by irradiation at δ 6.08 and 5.92. Irradiation at δ 2.2 reduces the complex pattern of H-3 and H-2 to a doublet ($J_{2,3} = 5.75$ Hz) and a doublet of doublets ($J_{2,3} = 5.75$; $J_{1,2} = 2.35$ Hz) respectively. Furthermore, it causes the H-1 and H-6 resonances to turn into a doublet of doublets ($J_{1,6} = 6.7$; $J_{1,2} = 2.35$ Hz) and a weakly structured doublet ($J_{1,6} = 6.7$ Hz).

The spectrum of the higher melting isomer (IV), in the same solvent, shows four three-protons singlets at δ 1.51, 2.12, 2.29, and 2.35 for the methyl groups and five multiplets (integral ratio 2:1:1:1:1) at δ 2.75, 3.1, 4.87, 5.85, and 6.14, which were assigned to the methylene ring protons and to the H-6, H-1, H-2, and H-3 protons, respectively. Spin decoupling experiments were in full agreement with this assignment ($J_{1,2}$ = 2.2; $J_{2,3}$ = 5.7; $J_{2,4}$ = $J_{2,5}$ = 1.5; $J_{3,4}$ = $J_{3,5}$ = 2.1; $J_{1,6}$ = 4.9 Hz) and the structures (VI) and (VII) were again discarded on the basis of the lack of detectable interaction of the H-6 and H-1 protons with the olefine and the methylene protons, respectively. Irradiation at δ 4.87 (H-1) gave different results for the H-6 resonance with respect to those previously observed for compound (III); in fact the eight-components pattern now changes into a well resolved doublet of doublets ($J_{4,6}$ = 6.2; $J_{5,6}$ = 8.4 Hz). The two values for the coupling constants could be rationalized on the basis of the rigid <u>trans</u>-configuration of compound (IV), whose Dreiding model clearly shows different dihedral angles between H-6 and the methylene protons.



The resonances of the tertiary and quaternary carbon atoms adiacent to the oxygen in the dihydropyran ring were easily identified in the ^{13}C-n.m.r. spectra (in $CDCl_3$) of compounds (III) and (IV) at δ 82.0, 88.5 and 163.7, 168.1, respectively.

While the mechanism of the cycloaddition of the tetraketone (I) to cyclopentadiene has not been established, the formation of compound (III) may involve the Diels-Alder adduct

(II); such a highly hindered intermediate, having two exo carbonyl groups, easily undergoes a [3, 3]-sigmatropic (oxo-Cope) rearrangement, as previously reported in the literature for similar rearrangements (7, 8, 9). This interpretation well accounts for the regio- and stereospecificity of the reaction.

The dipolar species (V), highly stabilized in both the anion and cation portions, may represent a plausible intermediate for the thermal irreversible isomerization of III into IV.

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