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CYCLOADDITION REACTION OF TROPONE AND CYCLOPENTADIENE

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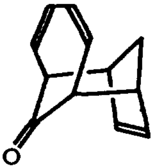
The sharp contrast in the behaviour of tropone (I) and 2-chlorotropone toward the cycloaddition reaction with cyclopentadiene (II) (1,2) prompted us to investigate further the reaction of the former, and the behaviour of tricyclo[4.4.1.$1^{2,5}$]dodeca-3,7,9-trien-11-one (III), the [6+4] cycloaddition product from I (1), toward heat or acids.

When I and II were kept at room temperature for 24 hours in the presence of p-toluenesulfonic acid, a mixture of products was obtained in 80% yield. The mixture was separated by chromatography using silver nitrate-impregnated silica gel to give, in addition to III (65%), four new oily adducts, IV, V, VI and VII in 6%, 4%, 4% and <1% yield, respectively.

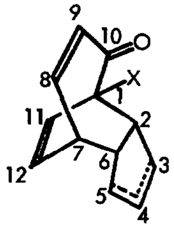
The structures of these adducts were determined in the following ways. All of these adducts (3) contain α,β-unsaturated carbonyl system as shown by UV[λ 230 (ε 5650), 252 (3070 sh), 340 nm (120) for IV ; λ 222 (5310), 255 (2530 sh), 335 nm (150) for V ; λ 224 (5960), 255 (1910 sh), 264 nm (1750 sh) for VI ; λ 228 (4690), 255 (1950 sh), 265 nm (1350 sh) for VII], IR[ν 1663, 1633 cm^{-1} for IV, V and VII; 1663, 1630 cm^{-1} for VI] and NMR spectra (Table). Over all NMR patterns of these compounds are also very similar with each other.

Upon zinc amalgam reduction in acetic acid, IV yielded a liquid dihydro compound VIII, ν1700 cm^{-1}, in which the double bond conjugated with the carbonyl group had been reduced. VIII was identical (TLC, IR, NMR) with the compound obtained by a similar reduction of the 2-chlorotropone-cyclopentadiene adduct IX (2) thus establishing the structure.

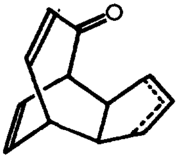
Catalytic hydrogenation of V yielded a fully-saturated hexahydro compound X, liq. ν 1700 cm^{-1}



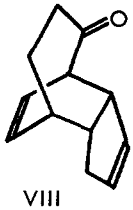
III



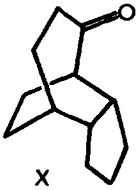
IV, X=H, Δ^3
V, X=H, Δ^4
IX, X=Cl, Δ^3



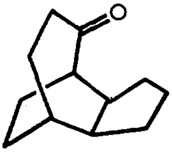
VI, Δ^3
VII, Δ^4



VIII



X



XI

[2,4-dinitrophenylhydrazone, m.p. 130-131°], which was identical (VPC, IR, NMR) with the hexahydro derivative of IV, thus proving the identity of the carbon skeleton in IV and V. Since only one double bond isomer of IV is possible, the structure V is established.

The identity of the carbon skeleton in VI and VII was verified by their catalytic hydrogenation to give the identical hexahydro compound XI, liq. ν 1699 cm^{-1} [2,4-dinitrophenylhydrazone, m.p. 171.5-173.5°] which is different from X. The structure assignment of VI and VII was based on the detailed NMR analyses. NMDR experiments on VI disclosed the presence of methylene group (δ 2.10, J=15.5, 3.5, 3.5, 1.7, 1.7, δ 2.63, J=15.5, 9.8, 2.0, 2.0, 2.0) next to a double bond, thus eliminating the [4+4] type of structures. The NMDR experiments also disclosed that H_1 was coupled to H_2 with the large coupling constant (J=6.0) in addition to H_9 (J=2.0), H_{11} (J=7.0) and H_{12} (J=1.0). This large coupling constant (J_{12}) is only compatible with an exo orientation of the five-membered ring (2,4,5).

TABLE Chemical Shifts of Olefinic Protons in the Adducts

	H_3	H_4	H_5	H_8	H_9	H_{11}	H_{12}
IV	~5.5(2H)			7.11	5.70	6.04	6.38
V		5.41	~5.65	7.11	5.74	6.04	6.38
VI	5.61(2H)			6.90	5.70	6.06	6.48
VII		5.45	~5.65	6.79	5.75	6.06	6.48

For the location of the double bond in five-membered ring we have the following evidence. Although NMR patterns of VI and VII are very similar, H_8 signal in VII appears in a higher field than that in VI (Table). This means that the hydrogen receives the diamagnetic anisotropy of the double bond in the five-membered ring more effectively in VII and therefore suggests the double bond facing to the hydrogen in VII (Δ^4) and the alternative position in VI (Δ^3) (6).

In order to clarify the relationship between the [6+4] adduct and the [4+2] adducts, both the cycloaddition reaction of I and II and the thermal reaction of III were investigated under the same conditions. Although stable at room temperature in the presence of p-toluenesulfonic acid, III was completely converted into a mixture of I, IV, V and VI, when the reaction mixture was heated at 80° for 10 hours. After hydrogenation of the mixture, the ratio of X and XI was 72 : 28 (7). When heated at 145° for 4 hours, III yielded a mixture (8) which, after hydrogenation, gave a mixture of X, XI and hexahydro-III (XII) in the ratio of 67 : 14 : 19. A same mixture was obtained by heating tropone and cyclopentadiene under the same conditions followed by an exhaustive hydrogenation. Prolonged heating (145°, 20 hours) of III in xylene afforded a mixture in which V was the predominant component and X : XI : XII was 84 : 13 : 3. IV, V and VI are stable under the conditions they are formed, and interconversion of them did not occur at 145°, although nonspecific decomposition was observed for IV and VI to some extent.

The foregoing results disclosed that 1) the ground state energy of III is higher than those of the [4+2] adducts ; 2) the reaction path leading to III in the cycloaddition reaction has a lower energy barrier compared to those to the [4+2] adducts ; 3) the energy barrier from III to I and II is comparable to those from I and II to the [4+2] adducts. Consequently, III, although formed predominantly under the milder conditions, reverted back to I and II at higher temperatures which in turn recombine to form the [4+2] adducts at the temperatures. Detection of I at higher temperatures, as well as the lack of the rationalization for the stereochemical course of the direct rearrangement from III to the [4+2] adducts, supported the view (9). In the cycloaddition reaction in the presence of acid, the reacting species is presumably hydroxytropylium ion. In fact, tropylium ion undergoes a facile cycloaddition reaction of this type (11). The result will be reported elsewhere.

References and Footnotes

1) a. R.C. Cookson, B.V. Drake, J. Hudec and A. Morrison, Chem. Commun., 15 (1966).
b. S. Itô, Y. Fujise, T. Okuda and Y. Inoue, Bull. Chem. Soc. Japan, 39, 1351 (1966).

2) S. Itô, K. Sakan and Y. Fujise, Tetrahedron Letters, 715 (1969).

3) All new compounds gave satisfactory elemental analyses. UV and IR spectra were taken for methanol solution and liquid film, respectively. NMR spectra were measured 60 MHz and/or 100 MHz for $CDCl_3$ solution.

4) S. Itô, H. Takeshita and Y. Shoji, Tetrahedron Letters, 1815 (1969).

5) The shoulders at 264-5 nm in the UV spectra of VI and VII (*vide supra*), probably due to the transannular interaction of the double bond and enone chromophors, as well as the appearance of H_8 signals in higher fields and H_{12} signals in lower fields in the NMR spectra of VI and VII compared with those in IV and V, can also be explained by the proposed structures.

6) The chemical shift difference of the olefinic hydrogens in the five-membered ring is revealing. As shown in the Table, the difference is small in IV and VI with the double bond at 3 position regardless of the configuration, and H_3 and H_4 appears as a single 2H multiplet, whereas in V and VII with the double bond at 4 position, the difference is large and H_4 and H_5 appear separately. This was effectively used in assigning the structure for one of the 2-chlorotropone-cyclopentadiene adducts (2).

7) The ratio of the hexahydro compounds were determined by VPC (PEG 4000, 175°).

8) Considerable amount of I and a small amount of 1 : 2 adduct (XIII) of unknown structure, m.p. 108-110°, λ 252 (3570), 261 (4960), 270 (4670), ν 1709 cm , m/e 238 (M^+), 172, 107 (base peak), 66, were also isolated from the mixture in addition to III-VII. However, hexahydro-XIII was not detected by VPC.

9) Formation of VI and VII is also unexplicable on the basis of a simple sigmatropic rearrangement of III (10) suggesting them be formed by the direct combination of tropone and cyclopentadiene.

10) R. Hoffmann and R.B. Woodward, J. Am. Chem. Soc., 87, 4389 (1965).

11) S. Itô, I. Itoh and K. Sakan, to be published.