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THE REACTION OF 2-CHLOROTROPONE WITH CYCLOPENTADIENE

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The formation of exo-tricyclo[4.4.1.$1^{2,5}$]dodeca-3,7,9-triene-11-one (I), the first example of a thermal [6+4] cycloaddition (1), has been reported by Cookson et al (2) and us (3) starting from tropone and cyclopentadiene. However, upon the extention of the reaction to 2-chlorotropone, we have found that the major course of the reaction is completely altered. The result is reported herein.

2-Chlorotropone (II) (4) was heated with cyclopentadiene (III) under nitrogen at 105° (sealed tube) for 3 hrs to give a mixture of at least four products in 73% yield. Extensive SiO_2 chromatography separated the mixture into four 1 : 1 adducts with the following physical properties (in the order of elution):

Adduct (IV) with the αβ-unsaturated carbonyl group (5), m.p. 77-78.5°, λmax 237 (ε 3470), 271 mμ (3010), ν 1670 cm^{-1}, MS. m/e 208, 206 (M^+), 141, 143 (base peak, C_7H_6OCl), 66 (C_5H_6), 11% yield.

Adduct (V) with saturated carbonyl group, m.p. 63.5-65°, λmax 252 (ε 3070), 261 (4100), 270 mμ (4040), ν 1730, 1740 cm^{-1}, MS. m/e 208, 206 (M^+), 171 (base peak, M-Cl), 66 (C_5H_6), 11% yield.

Adduct (VI) with αβ-unsaturated carbonyl group, m.p. 82-83°, λmax 225 (ε 4920), 255 mμ (1280), ν 1670 cm^{-1}, 2% yield.

Adduct (VII) with αβ-unsaturated carbonyl group, m.p. 116-117°, λmax 231 mμ (ε 3940), ν 1670 cm^{-1} MS. m/e 208, 206 (M^+), 171 (base peak, M-Cl), 66 (C_5H_6) in 19% yield.

Structure of the major product VII, was elucidated by, in addition to the above spectroscopic evidence, the extensive NMDR study on VII (NMR spectrum of VII is shown in FIGURE) and its trideuterio compound, VII-d_3, m.p. 115-117°, obtained from 2-chlorotropone-3,5,7-d_3 (6). NMR parameters obtained

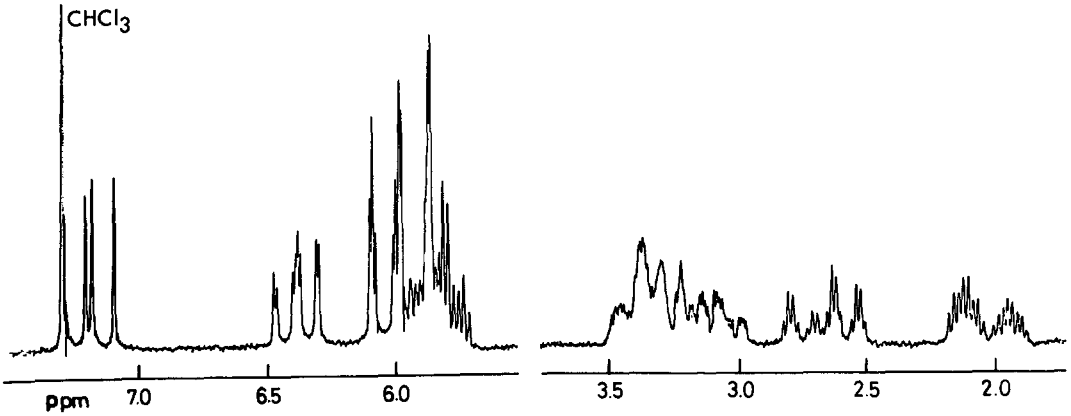
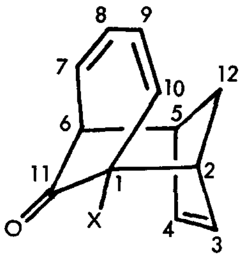


FIGURE. NMR Spectrum of VII in $CDCl_3$

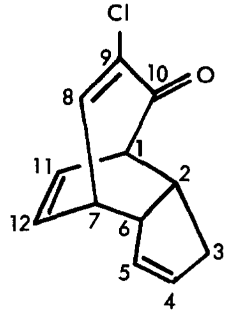
are as follows: δ_2: 3.40, δ_3,δ_4: 5.77, 5.92, $\delta_{5\beta}$: 2.66, $\delta_{5\alpha}$: 2.04, δ_6: 3.11, δ_7: 3.2-3.4, δ_8: 7.18, δ_9: 5.93, δ_{11}: 6.05, δ_{12}: 6.39, $J_{5\alpha,5\beta}$: 16.5, $J_{5\alpha,6}$: 5.5, $J_{5\beta,6}$: 9.1, $J_{5\alpha,4}$: 1.7, $J_{5\beta,4}$: 1.5, $J_{2,3}$: 1.5, $J_{2,6}$: 9.1, $J_{3,4}$: 6.0, $J_{5\alpha,2}$: 3.5, $J_{5\beta,2}$: 1.5, $J_{5\alpha,3}$: 1.7, $J_{5\beta,3}$: 1.5, $J_{2,4}$: 1.5, $J_{6,12}$: 1.0, $J_{11,12}$: 9.0, $J_{7,12}$: 6.5, $J_{7,8}$: 8.5, $J_{8,9}$: 11.0, $J_{6,7}$: 1.0-1.5, $J_{7,9}$: 1.0, $J_{7,11}$: 1.0. The small magnitude of $J_{6,7}$ reveals the endo configurations for VII.

Adduct IV has the same chromophore as VII. The position of the chlorine atom was easily determined by the doublet nature (J=9.5) of H_8 which appears at lowest field (δ 7.41). The position of the double bond in the five-membered ring is assigned from the large chemical shift difference between H_3 and H_4 (7). In order to establish the carbon skeleton, IV was catalytically hydrogenated to give the corresponding hexahydro derivative VIII, liq. ν 1720 cm^{-1}, which was further reduced with zinc amalgam in acetic acid to give a dechlorinated ketone IX, liq. ν 1700 cm^{-1}, 2,4-dinitrophenylhydrazone, m.p. 130-131°. Since the same ketone IX was obtained from VII by the same reaction sequence, both adducts IV and VII have a common carbon skeleton.

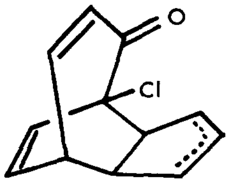
Adduct V has UV and IR properties reminiscent of I (presence of a conjugated diene, saturated six-membered ketone). Its NMR spectrum is also almost identical with that of I, showing well defined C_{12} methylene signals (H_{12a} has J=12, 5, 5, 2, while the other H_{12b} has J=12, 0.7, 0.7). For establishment of the carbon skeleton, V was catalytically reduced to give a hexahydrochloroketone X, liq. ν 1720 cm^{-1}, which was further reduced with zinc-amalgam and acetic acid to give an oily dechloro-



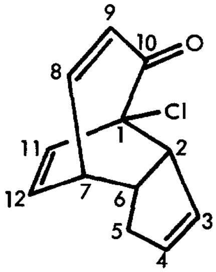
I. X=H
V. X=Cl



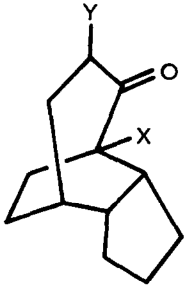
IV



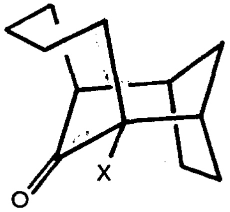
VI



VII



VIII. X=H, Y=Cl
IX. X=Y=H



X. X=Cl
XI. X=H

ketone XI, ν 1709 cm^{-1}, which was also obtained by the catalytic reduction of I, thus proving identity of the carbon skeleton in V and I.

Adduct VI was obtained in a very low yield and was rather unstable so that the structure was assigned from NMR observation: The chemical shifts observed for the vinyl protons are δ_4 and δ_5 ~5.7 (2H), δ_8: 6.95, δ_9: 5.88, δ_{11}: 6.02, δ_{12}: 6.49. When these values are compared with those of VII, it is found that H_8 in VI is more shielded by 0.15 ppm (9). Considering the difference in the shielding effect caused by the double bond in the five-membered ring, the cyclopentene was assigned an exo-orientation, although the exact location of the double bond was not determined.

When II and III were allowed to react for 20 hrs at room temperature in the presence of p-toluenesulfonic acid, the mixture of adducts was obtained in more than 90% yield. However, the presence of the adduct with a saturated carbonyl group (type V) was not detected in IR spectrum of the mixture.

The difference of the behavior of tropone and 2-chlorotropone toward cyclopentadiene is rather remarkable. Although the exact reason for it is not yet clear, the presence of acid is one factor which determine the ratio of the [6+4] adducts and the [4+2] adducts in the present reaction.

References and Footnotes

1) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046, 4388 (1965).

2) R. C. Cookson, B. V. Drake, J. Hudec and A. Morrison, *Chem. Commun.*, 15 (1966).

3) S. Itô, Y. Fujise, T. Okuda and Y. Inoue, *Bull. Chem. Soc. Japan*, **39**, 1351 (1966).

4) B. J. Abadir, J. W. Cook, J. D. Loudon and D. K. V. Steel, *J. Chem. Soc.*, 2350 (1952).

5) All new compounds gave satisfactory elemental analyses. UV and IR spectra were measured for methanol solutions and KBr discs, respectively. NMR spectra were measured at 100 MHz for $CDCl_3$ solution. Chemical shifts (δ) are expressed in ppm from internal TMS and coupling constants (J) in Hz.

6) S. Itô, J. Tsunetsugu, T. Kanno, H. Sugiyama and H. Takeshita, *Tetrahedron Letters*, 3659 (1965).

7) The Δ^3 isomers have a very small difference between δ_3 and δ_4, thus VII and one of the tropone-cyclopentadiene adducts (8) shows signals of H_3 and H_4 almost completely oberlapped in 60 MHz spectra. On the other hand, the Δ^4 isomers (8) show a rather large chemical shift difference for H_4 and H_5, a well separated symmetrical pattern being observed for these signals.

8) S. Itô, K. Sakan and Y. Fujise, to be published.

9) This tendency is observed more clearly in tropone-cyclopentadiene adduct (8).