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THE CYCLOADDITION REACTION OF ISOBENZOFURAN WITH SOME TROPONES

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Isobenzofuran, generated by two different methods, was taken to the reaction with tropone, 2-methoxytropone, and 2-chlorotropone. The [6+4]-adducts were obtained from these three tropones examined, but the [2+4]-adducts were obtained from the former two. The structures of the adducts have been deduced on the basis of the spectroscopic methods of analyses.

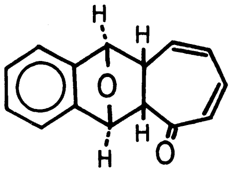
The troponoids have been known to undergo Diels-Alder reaction with dienes to give [6+4]- and [4+2]-adducts and with dienophiles to give [4+2]-adducts.[1,2] But only in a few instances, the troponoids have been allowed to react as a formal 2π-component.[3] Since isobenzofuran (I) should always behave as the 4π-component, the reaction between I and troponoids is expected to yield this rare type of the [2+4]-adducts. The reaction indeed proceeded to give these adducts together with the characteristic [6+4]-adducts as the major products in the most cases.

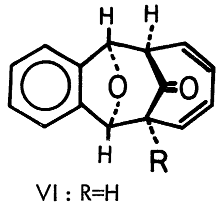
When I, generated at room temperature by the fragmentation of the furan-benzyne adduct (II) in the presence of 3,6-dipyridyltetrazine [method A],[4] was allowed to react with tropone (III), three products, IV (colorless needles, mp 193-195°, 4.5%), V (colorless prisms, mp 179-180°, 12%) and VI (colorless plates, mp 190-191°, 12%) were produced. In parallel, the reaction by I, generated at ca. 160° through the decarbonylative pyrolysis of the adduct of II and tetracyclone [method B],[5] predominantly afforded VI (36%) with some amounts of IV (2%) and V (1%).[6]

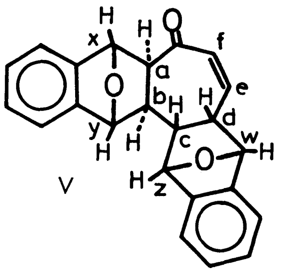
By the reaction with 2-chlorotropone (VII), the single product, VIII (colorless prisms, mp 173-174°) has been obtained (22% by the method A and 25% by the method B).

While, only the method B has been effective in the reaction of 2-methoxytropone (IX) producing two adducts, X (colorless plates, mp 173-174°, 17.5%) and XI (colorless prisms, mp 264-265°, 5.4%).[7]

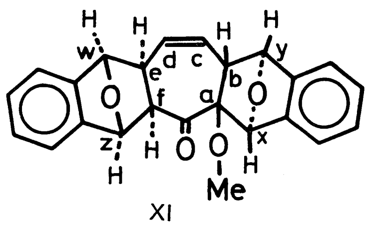
From the NMR spectra, the exo-[6+4]-structures for VI [δ: 3.34(2H, dd, J=6.5, 1.5 Hz), 5.41(2H, d, J=1.5 Hz), 5.60-6.30(4H, m), 7.27(4H, s)], VIII [δ: 3.55(1H, dd, J=6.0, 1.3 Hz), 5.34(1H, s), 5.45(1H, d, J=1.3 Hz), 5.65-6.30(4H, m), 7.17-7.64(4H, m)], and X [δ: 3.26(1H, dd, J=6.5, 1.5 Hz), 3.67(3H, s), 5.08(1H, s), 5.41(1H, d, J=1.5 Hz), 5.60-6.50(4H, m), 7.17-7.45(4H, m)] were evident. Similarly, the structure of IV can be identified as the endo-[2+4]-adduct on the IR ($\nu_{C=O}$: 1680 cm^{-1}) and the NMR [δ: 2.16(1H, m), 3.25(1H, dd, J=10.5, 4.5 Hz),


IV


VI : R=H
VIII : R=Cl
X : R=OMe



V



XI

5.10(1H, d, J=4.5Hz), 5.12(1H, m), 5.42(1H, d, J=4.5Hz), 7.08-7.58(3H, m), 7.38(4H, s)] spectral evidences. IV was the only 1 : 1-adduct with the [2+4]-mode of the reaction in the present investigation (M^+/e : 224).

V and XI were shown to be 1 : 2-adducts with the different skeletal arrangement in each other. V(M^+/e : 342) has revealed the presence of an unsaturated carbonyl group ($\nu_{C=O}$: 1668 cm^{-1}) and its NMR spectrum [δ : 1.30(H_b, ddd, J=13, 7, 4Hz), 2.05(H_c, ddd, J=13, 10, 5Hz), 2.13(H_a, d, J=7Hz), 3.30(H_d, m, J=10, 5, 2Hz), 5.23-5.42 (H_y, H_z and H_w, m), 5.72(H_x, s), 5.64(H_f, dd, J=13, 3Hz), 6.13(H_e, dd, J=13, 2Hz), 7.20-7.55(8H, m)] has disclosed four aliphatic protons in a row; thus, together with the identification of the coupling constants, J_{ax}=0, J_{bc}=13, and J_{cz}=J_{dw}=5Hz, the *exo*-*anti*-*endo*-configuration has been deduced. Somewhat large spin-spin splitting, J_{by}=4Hz, in regard to this structure could be interpreted in terms of a twisting of the ring system to reduce the steric interactions caused by a crowded arrangement. The other 1 : 2-adduct, XI (M^+/e : 372), alternatively has a saturated carbonyl group ($\nu_{C=O}$: 1721 cm^{-1}), indicating its gross structure. The NMR spectrum [δ: 2.24(H_f, dd, J=8.3, 2.0Hz), 3.04 (H_e, m, J=8.2, 4.7Hz), 3.17(H_b, dd, J=1.5, 1.2Hz), 3.66(3H, s), 4.82(H_x, s), 5.08(H_y, d, J=1.2Hz), 5.18(H_z, and H_w, overlapped d, J=2.0Hz), 5.86(H_c, dd, J=12.5, 1.5Hz), 6.24(H_d, dd, J=12.5, 4.7Hz), 7.08-7.60(8H, m)] has clearly suggested the *exo*-*anti*-*exo*-structure for XI, since the coupling constants, J_{by}=1.2, J_{ew}=0, and J_{fz}=2.0Hz, are discernible, and since the magnitude of the coupling constants for two olefinic protons with the adjacent methine protons, J_{bc}=1.5, and J_{de}=4.7Hz, are different.

Summarizing the above, only the tropones carrying an electron-attracting group have been reactive towards I. In addition to this, some of the characteristic features of the reaction should be mentioned: At first, IV can not be the precursor of V as the configurations differ. Indeed, all the [2+4]-adducts have the different carbon frame-work, indicating a sort of substituent effect on the course of the reaction. Secondly, since VII has yielded solely the [6+4]-adduct (VIII), and since IV has been isomerized to VI by a thermal treatment in a similar condition with the method B (160-165°, for 2 hours in a benzene solution), the [6+4]-adducts are thermodynamically more stable than the [2+4]-isomers. This should be of interests in regard with the fact that, in general, the reaction of dienes and tropones yields [6+4]- and [4+2]-adducts but no [2+4]-isomers which, in view of the present study, might be thermodynamically unfavorable to survive in their formation conditions. And finally, the chemical shifts for the protons of H_e and H_f of V are unusually high and ascribable, in best, to the anisotropy from the adjacent aromatic ring of the *endo*-orientation.

Studies on other aspects of the reaction are in progress and will be reported elsewhere.

REFERENCES & NOTES

1) There have been numerous reports in this field; the following two described the most recent results. a) S. Itô, H. Ohtani, S. Narita, and H. Honma, Tetrahedron Lett., 2223(1972). b) T. Sasaki, K. Kanematsu, and K. Hayakawa, J. Chem. Soc., Perkin Trans. I, 1951(1972).

2) In this paper, [m+n] expresses the mode of the reaction with mπ-system of troponoids and nπ-system of the other.

3) D. M. Bratby and G. I. Fray, J. Chem. Soc., Perkin Trans. I, 195(1972).

4) R. N. Warrener, J. Amer. Chem. Soc., 93, 2346(1971).

5) L. F. Fieser and M. J. Haddadin, Can. J. Chem., 43, 1599(1965).

6) Fourth compound was isolated in very minute quantity, but no further work was attempted.

7) By the method A, IX has been recovered in quantitatively. On the other hand, 2-(*N*, *N*-dimethylamino)-tropone was failed to give any product by either of the methods.

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