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REACTION OF TROPONE WITH QUADRICYCLENE.
AN EXAMPLE OF $[_{\pi}6 + _{\sigma}2 + _{\sigma}2]$ CYCLOADDITION

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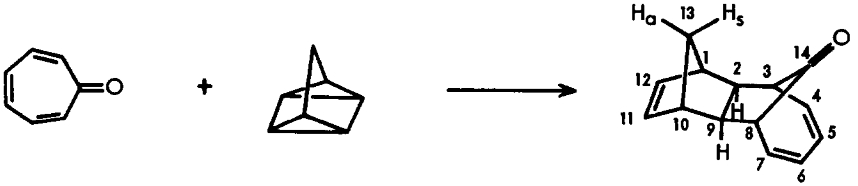
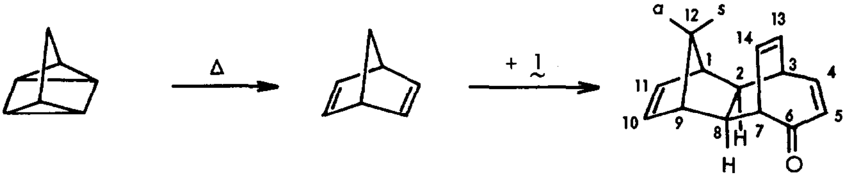
Cycloaddition between 6π and 4π addends ($[_{\pi}6 + _{\pi}4]$ cycloaddition) was theoretically predicted[1] and was shortly after demonstrated by the reaction of tropone with cyclopentadiene.[2] We have investigated a reaction between tropone (1) and quadricyclene (2) and thereby found the first example of cycloaddition between a 6π system and a pair of strained σ bonds ($[_{\pi}6 + _{\sigma}2 + _{\sigma}2]$ by the terminology of Woodward and Hoffmann[1]).



1 2 3

Equivalent amounts of 1 and 2 were heated together in the dark at 70° for 5 days to yield a complex mixture consisting mainly of polymeric substances. Chromatography of this mixture on silica gel followed by thin layer chromatography on KGF$_{254}$ (Merck) separated a 1 : 1 adduct (3), mp 82.5-84°, in 9% yield; and a mixture of crystals of another 1 : 1 adduct (4), mp 52°, and a compound of unknown structure in 6% yield. When the reaction was traced by vpc, the formation of 3 was shown to be initially predominant over the other two products. The elementary analysis and mass spectrum (70 eV m/e 198 (M$^+$)) of 3 were in agreement with the formula $C_{14}H_{14}O$. An ir carbonyl absorption at 1740 cm^{-1} in CCl_4 and uv absorption maxima in cyclohexane at 221 mμ (ϵ 12900), 268 (4820), and 279 (4800) are compatible with the presence of a cyclohepta-3,5-dienone moiety[2] but not a CH=CH·C=O chromophore.[3] The nmr spectrum of 3 in $CDCl_3$

when 0.5 equivalent amounts of Eu(DPM)$_3$ were added as a shift reagent revealed signals at δ 2.10 (d-qui,[4] 1, $J_{13a,13s} = 10$ Hz, $J_{13a,2} = 1.7$, anti-H_{13}), 4.26 (m, 2, H_1 and H_{10}), 4.63 (d, 2, $J_{2,13a} = 1.7$, H_2 and H_9), 5.92 (d-m, 1, H_{13s}), 6.86 (t, 2, olefinic H_{11} and H_{12}), 7.31 (six, 2, olefinic H_5 and H_6), 8.10 (t-d, 2, H_4 and H_7), and 9.09 (broad d, 2, $J_{3,4} = 9$, H_3 and H_8). That 3 is a norbornene derivative is immediately suggested by comparing these nmr data with the many available data and references obtained from norbornene derivatives.[5] The appearance of the six olefinic protons as three pairs and the six protons (H_1, H_{10}, H_2, H_9, H_3, and H_8) as three pairs is indicative of the presence of a plane of symmetry in the molecule. The absence of coupling between H_1 and H_2 (or H_{10} and H_9) and the presence of long range coupling between H_{13a} and H_2 (or H_9) *indicate the endo orientations of H_2 and H_9 hydrogens to the norbornene ring.* Orientation of the carbonyl group — whether the structure is 3 or 5 — was determined by the difference between the pseudo contact shifts of H_{13a} and H_{13s} with varying amounts of Eu(DPM)$_3$. It was found that the shift of H_{13s} was significantly larger than that of H_{13a} (Figure 1). The molecular model of 3 can rationalize this difference, but that of 5 can not.



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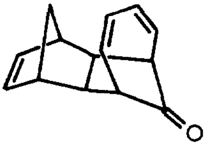

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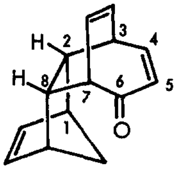

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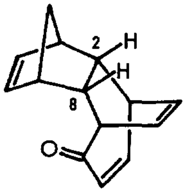

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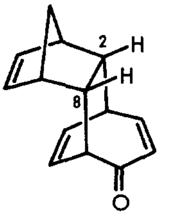

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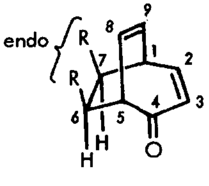

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It was found that a compound identical with the second adduct 4 is produced in 70% yield by reaction of 1 with a large excess of norbornadiene[6,7] under the above conditions as used for the reaction of 1 with 2. For 4, uv max (cyclohexane) 245 mμ (sh, ε 2150), 360 (92); ir (CCl_4) 1663 cm^{-1}; nmr (CCl_4) δ 1.15 (d-m, 1, $J_{12a,12s}$ = 10 Hz, anti-H_{12}), 1.92-2.43 (AB q, 2, $J_{2,8}$ = 9 Hz, H_2 and H_8), 2.43-3.42 (m, 5, H_1, H_3, H_7, H_9, and syn-H_{12}), 5.46 (d-splitting d, 1, H_5), 5.46-6.60 (m, 4, H_{10}, H_{11}, H_{13}, and H_{14}), 7.01 (q, 1, $J_{4,5}$ = 11 Hz, $J_{3,4}$ = 8 Hz, H_4). In general, cycloaddition of 1 with a 2π olefinic compound proceeds with the formation of a bicyclo[3.2.2]nona-2,6-dien-4-one derivative. The ir carbonyl absorption and the uv max in 4 are consistent with this [3.2.2] structure, but not with the structure of a bicyclo[4.2.1]hepta-2,4-dien-9-one. The presence of the norbornene moiety in 4 is suggested by the nmr data. On the basis of these data, structures 4, 6, 7, and 8 are possible. The H_2 and H_8 bridgehead protons (the C_5 and C_6 protons in norbornene) appear as a clean AB quartet, with no vicinal coupling with either the norbornene bridgehead protons (H_1 and H_9) or with the [3.2.2] bridgehead protons (H_3 and H_7). Therefore, H_2 and H_8 must be endo to the norbornene ring, and structures 7 and 8 are ruled out. The *endo,endo*-6,7 and *exo,exo*-6,7 derivatives of bicyclo[3.2.2]nona-2,6-diene-4-one (9) (substituents on the carbonyl side are defined as exo) are distinguishable by the coupling constants between H_1 and H_7 (or H_5 and H_6) and the presence or absence of long-range coupling between H_6 and H_8 (or H_7 and H_9),[8] and it has been reported that, relative to the endo H_6 and H_7, the exo H_6 and H_7 have much smaller couplings with H_5 and H_1, respectively. Therefore, the clean AB quartet is not consistent with structure 6.

However, it was observed that 2 gradually transformed into norbornadiene under the reaction conditions, that the yield of 4 was very minor at an initial stage of reaction and increased with the reaction period, and also, that 3 did not convert into 4 under the reaction conditions. Consequently, it was concluded that 4 was not a direct product from the reaction of 1 and 2, but was formed after conversion of 2 into norbornadiene.

Addition of hydroquinone as a radical scavenger has no significant effect on the formation of 3. The reaction appears to be stereoselective, since the isomer 5 was not found in the reaction mixture. On the basis of these findings, we favor a concerted cycloaddition mechanism and not a stepwise mechanism for the present reaction. It is of interest to note that the newly-formed butadiene bridge in 3 is located at the endo side of the norbornene ring; but the ethylene bridge in 4 resulting from norbornadiene is located at the exo side.

REFERENCES

1. (a) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.* **87**, 2046, 4388 (1965); (b) R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, Verlag Chemie: GmbH-Academic Press, Inc., pp 83-85 (1970).

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

3. Refer to T. Nozoe, T. Mukai, T. Nagase and Y. Toyooka, *Bull. Chem. Soc. Japan*, **33**, 1247 (1960); A. S. Kende, *J. Amer. Chem. Soc.*, **88**, 5026 (1966).

4. d-qui = doublet of quintets, d-m = doublet of multiplets, six = sixtet, and so on.

5. (a) L. M. Jackman and S. Sternhell, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed, Pergamon Press, New York, N.Y., pp. 230-231, 288-289 (1969); (b) K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Tetrahedron Letters* **1966**, 9; (c) N. Kamezawa, K. Sakashita, and K. Hayamizu, *Organic Mass Resonance* **1**, 405 (1969).

6. Vpc revealed formation of another minor 1 : 1 adduct, whose structure was not determined.

7. An extensive investigation of the reactions of **1** with norbornene and norbornadiene was independently carried out by Y. Kitahara and T. Uehara. Their major adduct from the reaction with the diene was reported to have the structure **4** in agreement with our determination: Y. Kitahara and T. Uehara, Abstracts of the 3rd Symposium of Structural Organic Chemistry, Hiroshima, November, 1970, p. 38.

8. (a) H. Tanida, T. Yano, and M. Ueyama, *Bull. Chem. Soc. Japan* in press (1972); (b) S. Itō, K. Sakan and Y. Fujise, *Tetrahedron Letters*, **1969**, 775.

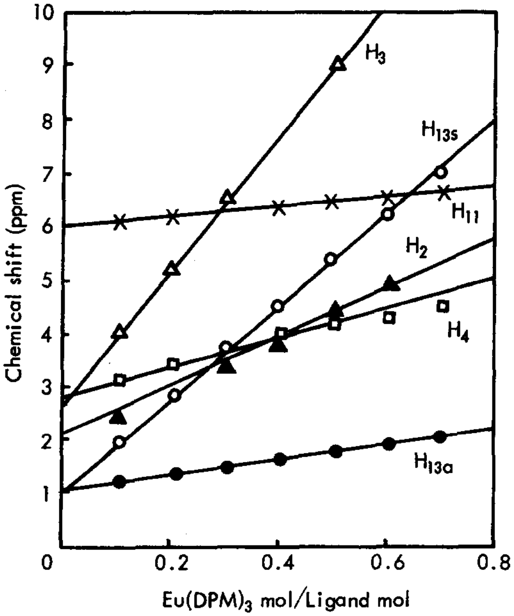

Fig. 1. Pseudo contact shift induced by Eu(DPM)$_3$