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REACTION OF TROPONE WITH DIMETHYL QUADRICYCLENE-2,3-DICARBOXYLATE. A THERMAL[$_{\pi}6 + _{\sigma}2 + _{\sigma}2$]CYCLOADDITION CONCURRED WITH A RADICAL ADDITION

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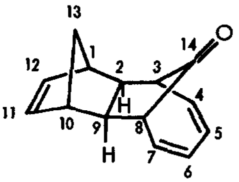
In an accompanying communication the reaction of tropone (1) with quadricyclene (2) leading to 2,9-exo,cis-quadricyclo[8.2.1.1$^{3,8(exo)}$.0^{2,9}]tetradeca-4,6,11-trien-14-one (3) was presented as the first example of thermal[$_{\pi}6 + _{\sigma}2 + _{\sigma}2$]cycloaddition.[1] This finding prompted us to extend this reaction to derivatives of 1 and 2 and we wish to report here the reaction of 1 with dimethyl quadricyclene-2,3-dicarboxylate (4). The effect of the electron-withdrawing carboxylate groups is of interest, particularly from a mechanistic viewpoint.



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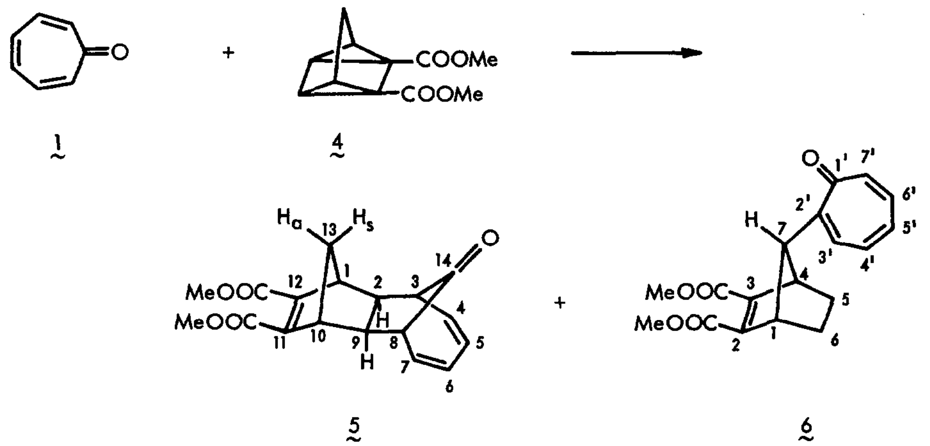
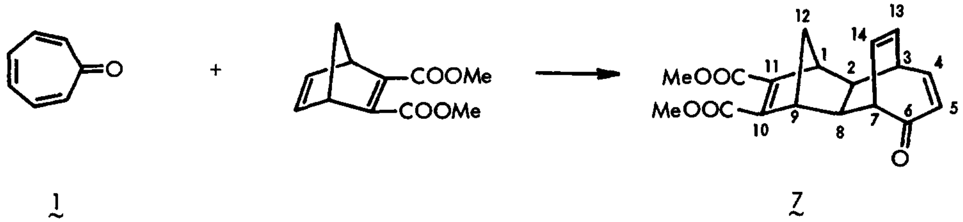
A mixture of 1 and 4 in a mole ratio of 5 to 1 was heated at 80° in the dark under nitrogen atmosphere for 4 days. Although the reaction products were more complex than those from the reaction of 1 with 2, chromatography of the reaction mixture on silica gel followed by thin layer chromatography on KGF$_{254}$ (Merck) separated three crystalline products; 5, mp 116°, 7% yield; 6, mp 112-114°, 7% yield; and 7, mp 128-129°, 5% yield; each of which was shown to be a 1 : 1 adduct by its elementary analysis and mass spectrum. However, 7 was shown to be almost certainly not a direct product from 1 and 4.[2] On catalytic reduction, both 5 and 7 absorbed 2 moles of hydrogen in ethanol and 3 moles in acetic acid, while 6 absorbed 4 moles in acetic acid. For 5; uv max (cyclohexane) 220 mμ (ε 9500), 279 (sh, 2950), and 310 (sh, 448); ir ($CHCl_3$) 1740 (C=O) and 1720 cm^{-1} (ester C=O); nmr ($CDCl_3$) with addition of 0.4 mole ratio of Eu(DPM)$_3$ as a shift reagent, δ 2.00 (d-m, 1, H_{13a}, $J_{13a,13s}$ = 11.0Hz), 2.37 (d-t, 1, H_{13s}, $J_{13a,13s}$ = 11.0, $J_{1,13s}$ = 1.4), 3.60-3.95 (m, 2, H_3 and H_8), 4.14 (d, 2, H_2 and H_9, $J_{2,13a}$ = 1.7), 4.55 (t, 2, H_1 and

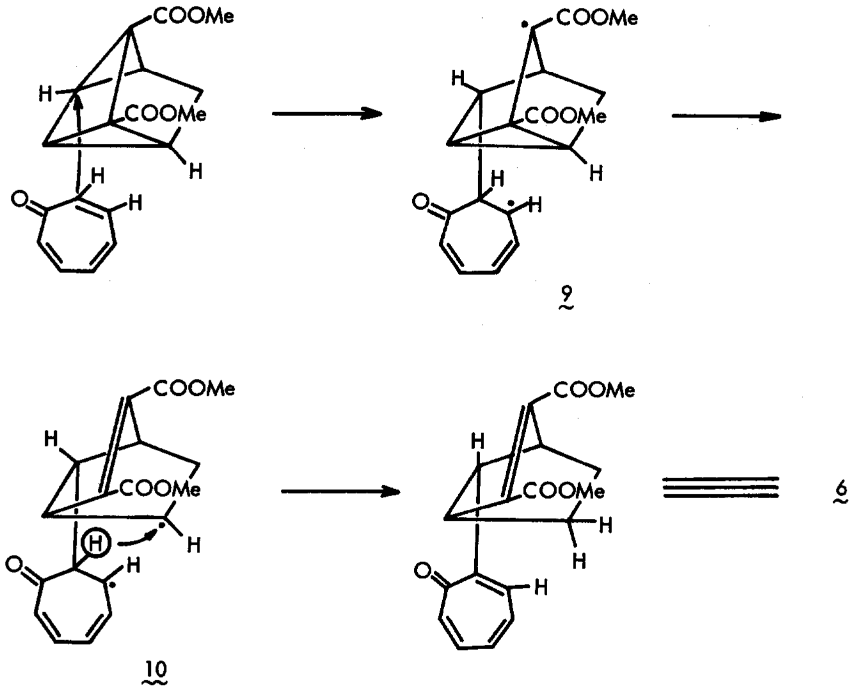




H_{10}, $J_{1,13s} = J_{1,13a} = 1.4$), 5.08 (s, 6, $COOCH_3$), and 5.95-6.20 (m, 4, vinyl). For 6; uv max (cyclohexane) 230 mμ (ε 25600) and 305 (6280); ir ($CHCl_3$) 1720 (ester C=O) 1629, and 1595 cm^{-1}; nmr ($CDCl_3$) δ 1.15-1.83 (m, 4, H_5 and H_6) 3.16 (broad s-like m ($W\frac{1}{2} \simeq 4.5$ Hz), 1, H_7), 3.67 (m, 2, H_1 and H_4), 3.78 (s, 6, $COOCH_3$), and 6.80-7.25 (m, 5, all H in tropone); nmr with addition of 0.7 mole ratio of $Eu(DPM)_3$, δ 7.95 (t-like d-d, 1, $H_{6'}$), 8.17 (t-like d-d, 1, $H_{5'}$), 8.64 (t-like d-d, 1, $H_{4'}$), 9.66 (d, 1, $H_{3'}$), and 13.03 (d, 1, $H_{7'}$), and $J_{3',4'} = 9.2$ Hz, $J_{4',5'} = 10.8$, $J_{5',6'} = 8.2$, and $J_{6',7'} = 11.8$. For 7; uv max (cyclohexane) 226 mμ (ε 11700); ir ($CHCl_3$) 1715 and 1667 cm^{-1} (α,β unsaturated C=O); nmr ($CDCl_3$) δ 1.47 (d-m, 1, H_{12a}, $J_{12a,12s} = 9.5$ Hz), 2.26-2.72 (pair of broad d, 2, H_2 and H_8, $J_{2,8} = 8.7$), 2.67 (d-t, 1, H_{12s}, $J_{12a,12s} = 9.5$, $J_{1,12s} = J_{9,12s} = 1.7$), 2.92-3.23 (overlapping m, 2, H_1 and H_9), 3.23-3.66 (overlapping m, 2, H_3 and H_7), 3.76 (s, 6, $COOCH_3$), 5.64 (d-d, 1, H_5, $J_{4,5} = 11.0$, $J_{5,7} = 2.0$), 5.98-6.67 (pair of broad t-like d-d, 2, H_{13} and H_{14}), and 7.15 (d-d, 1, H_4, $J_{4,5} = 11.0$, $J_{3,4} = 8.0$). These signal assignments were made on the basis of spin-decoupling.

Structural assignment of **5** was easily made by comparison of the above spectral data with those of **3**. The nmr data of **6** show the spectral features of 2,3-anti-7-trisubstituted norbornene derivatives.[3] The existence of a plane of symmetry in **6** is suggested by the observations that the bridgehead protons, H_1 and H_4, appear at an identical position (δ 3.67) and that addition of $Eu(DPM)_3$ does not result in splitting of the signals due to $COOCH_3$ and the bridgehead protons. Irradiation at the signals due to the bridgehead protons and the C_7 proton (triple resonance) revealed H_5 and H_6 as signals of a symmetrical A_2B_2 type. Irradiation at the signals due to the bridgehead protons alone (double resonance) does not result in signals of a clean A_2B_2 type. These results indicate the presence of a long-range coupling (about 0.7 Hz) between the C_7 proton and the C_5 (or C_6) proton, so that the protons must be in a "W-letter" arrangement; therefore, the C_7 proton is syn to the $COOCH_3$ groups.[4] The uptake of 4 moles on catalytic reduction; the uv max; the ir bands at 1629 and 1595 cm^{-1}; and the presence of 5 vinyl protons by integration of the nmr can be accomodated if **6** is assumed to be a monosubstituted tropone connected with the above norbornene system (for tropone, uv max (n-hexane) 229 mμ (ε 25000) and 305 (~8000)). Then, what position on the tropone ring, α, β, or γ, is connected with the anti-7 position on the norbornene ring? In the presence of $Eu(DPM)_3$, nmr signals due to the tropone protons of **6** appear as two sets of doublets (H_3' and H_7') and three sets of triplet-like doublets of doublets (H_4', H_5', and H_6'), which is a pattern specific for α-monosubstituted tropones, but not for β or γ-monosubstituted tropones.[5] In addition, the vicinal coupling constants obtained are in the same order of magnitude as the corresponding values reported for some α-substituted tropones.[6] Thus, the structure **6** was concluded. The third compound **7** was found to be identical with the major product from the reaction of **1** with dimethyl norbornadiene-2,3-dicarboxylate and the structure was determined as reported in the accompanying communication.

We have not yet obtained any evidence against our proposal that the formation of adducts such as **3** *and* **5** *is due to a concerted* $[{}_{\pi}6 + {}_{\sigma}2 + {}_{\sigma}2]$ *cycloaddition. The formation of* **6** *can be accommodated by* a diradical pathway; addition of **1** to **4** provides a diradical intermediate **9**, the cyclopropane ring of which undergoes ring opening to give **10**, hydrogen shift then leading to **6**.



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REFERENCES

1. H. Tanida and T. Tsushima, Tetrahedron Letters, 1972,

2. Because of technical difficulties, there remain some ambiguities.

3. The best reference compounds are perhaps anti-9-benzonorbornenyl derivatives. The nmr data for these compounds are seen in (a) K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, Tetrahedron Letters 1966, 17; (b) H. Tanida, T. Tsuji, and T. Irie, J. Org. Chem. 31, 3941 (1966).

4. Furthermore, the C_7 proton in 6 appears as a broad singlet-like multiplet which is compatible with the signal pattern of the syn-9 proton in 9-benzonorbornenyl derivatives, but not with that (triplet) of the anti-9 proton.[3]

5. When a sufficient amount of shift reagent is added, the chemical shifts between protons of the tropone ring are enlarged, and the signals are broadened making the small long-range coupling constants vague. Under such conditions the proposed nmr patterns are; for α-substituted tropone, two sets of doublets (H_3 and H_7) and three sets of triplet-like doublets of doublets (H_4, H_5, and H_6); for β-substituted tropone, one broad singlet (H_2), two sets of doublets (H_4 and H_7), and two sets of triplet-like doublets of doublets (H_5 and H_6); for γ-substituted tropone, four sets of doublets (H_2, H_3, H_5, and H_7) and one triplet-like doublet of doublets (H_6).

6. D. J. Bertelli, T. G. Andrews, Jr., and P. O. Crews, J. Amer. Chem. Soc. 91, 5286 (1969). Refer to the data of 2-chlorotropone and 2-methoxytropone.