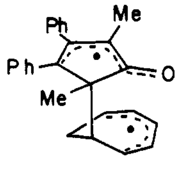
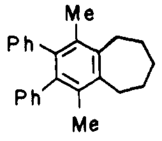
on change in solvent polarity rules out a dipolar intermediate, while the potential diradical intermediate XIII is ruled out by the pyrolysis of II, which must proceed through XIII to IV without formation of I or III.



XIII



XIV

Since this is the first set of addends which give both [6 + 4] and [4 + 2] adducts simultaneously, it is of interest to note that, in this case, the Diels–Alder addition proceeds stereospecifically *endo*, while the [6 + 4] addition proceeds stereospecifically *exo*. This result is in agreement with considerations of secondary orbital interactions made by Hoffman and Woodward; that is, for [4 + 2] cycloadditions, secondary orbital interactions stabilize the *endo* transition state, while for [6 + 4] cycloadditions, secondary orbital interactions destabilize the *endo* transition state.[12,3f]

These results, combined with the nonselective [4 + 2] cycloaddition of VII to cyclopentene and cycloheptene,[8,13] appear to rule out the dominant influence of inductive forces[14] or angular dependence of overlap[15] on the stabilization of the *endo* transition state in Diels–Alder reactions and suggest that secondary orbital interactions are the primary influence in determination of product stereochemistry.

Acknowledgment. The financial support of the National Institutes of Health and the National Science Foundation (Harvard) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (L. S. U.), is gratefully acknowledged.

(12) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, 87, 4388 (1965).

(13) K. N. Houk, *Tetrahedron Lett.*, in press.

(14) A. Wasserman, "Diels-Alder Reactions," Elsevier, London, 1965, and references therein.

(15) W. C. Herndon and L. H. Hall, *Tetrahedron Lett.*, 3095 (1967).

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Received March 7, 1970

Cycloaddition Reactions of Tropone and 2,5-Dimethyl-3,4-diphenylcyclopentadienone[1]

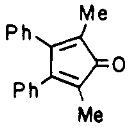
Sir:

In the accompanying communication, competition between *exo* [6 + 4] and *endo* [4 + 2] cycloadditions has been reported for the reaction of cycloheptatriene and 2,5-dimethyl-3,4-diphenylcyclopentadienone (I).[2] Tropone reacts readily with I to give an equally complex sequence of events, the preliminary studies of which are reported herein.[3]

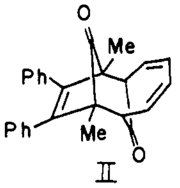
When tropone and I (as the dimer[4]) were heated together in a small amount of acetone or tetrahydrofuran at 60°, the [6 + 4] adduct II, mp 148–150°, crystallized in 95% yield after 8 hr.[5,6] The ir of II (CCl_4, 5.64, 5.77 μ) indicated the presence of two bridged carbonyl groups while the nmr ($CDCl_3$; 1.15 ppm (6 H); $A_2X_2Y_2$ spin system; A_2, 3.6 ppm, X_2Y_2, 5.9 ppm) demonstrated the symmetrical nature of the adduct and corresponded closely to the nmr of the [6 + 6] photodimer of tropone.[7]

Sodium borohydride reduction of II gave a single keto alcohol, III, mp 180.5–181.5° (ir (CCl_4) 5.77 μ), which underwent retro-[6 + 4] reaction to give tropone and 2,5-dimethyl-3,4-diphenylcyclopent-2-enone[8] upon pyrolysis at 200°. Bromination of III gave a mixture of bromo ethers IVa (ir (CCl_4) 5.81, 9.28 μ) and IVb (ir (CCl_4) 5.81, 9.41 μ) in a ratio of 2:1. While IVa was inert to zinc in hot acetic acid or sodium iodide in acetone, IVb was rapidly converted to III under these conditions, as was observed in the cycloheptatriene series.[2] Nmr spin-decoupling experiments confirmed the structures of IVa and IVb, and, therefore, the *exo* nature of [6 + 4] adduct II.

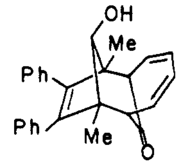
When a solution of tropone and I[4] in benzene was heated at 70° for 1 hr, II (46%) and Va (24%) were detected by nmr. After heating this solution 1 day at 70°, preparative layer chromatography gave II (53%) and light yellow Va, mp 123.5–124.0° (30%), along with recovered I-dimer. The [8 + 2] nature of Va was shown by ir (CCl_4; 5.84 μ) and nmr ($CDCl_3$; 0.75 (3 H, s), 2.00 (3 H, s), 2.5 (1 H, bd; J = 4.5 Hz), 4.9 (1 H, dd; J = 4.5 Hz, J = 9.0 Hz), 5.9–6.4 ppm (4 H, mm). The nmr of the tropone moiety is nearly identical with that of VI, obtained from diphenylketene and tropone.[9] The relative orientation of the addend fragments in the adduct has not been established as yet.



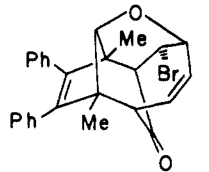
I



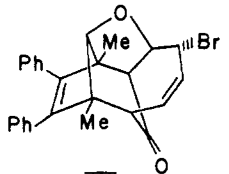
II



III



IVa



IVb

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(1) Taken in part from K. N. Houk, Ph.D. Dissertation, Harvard University, 1968.

(2) K. N. Houk and R. B. Woodward, *J. Amer. Chem. Soc.*, 92, 4143 (1970).

(3) References to the [6 + 4] cycloaddition reported herein have been made; see ref 2, footnotes 3e and 4.

(4) C. F. H Allen and J. Van Allan, *J. Amer. Chem. Soc.*, 64, 1260 (1942); C. F. H. Allen and J. A. Van Allan, *ibid.*, 72, 5165 (1950).

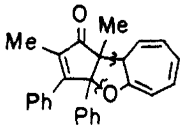
(5) All new compounds gave elemental and spectral analyses compatible with the assigned structures.

(6) The high yield of II obtained depends on the low solubility of II relative to Va and I-dimer.

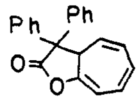
(7) T. Mukai, T. Tezuka, and Y. Akasaki, *J. Amer. Chem. Soc.*, 88, 5025 (1966).

(8) Rearrangement of the initially formed dienol is perhaps quite common in the reduction of cyclopentadienones, although the literature on the latter subject is moderately confused: M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, 65, 261 (1965).

(9) C. Jutz, I. Rommel, I. Lengyel, and J. Feeney, *Tetrahedron*, 22, 1809 (1966); R. Gompper, A. Studeneer, and W. Elser, *Tetrahedron Lett.*, 1019 (1968).

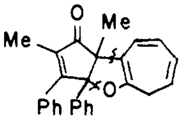


Va

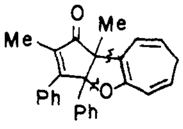


VI

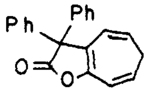
Va was quantitatively converted to Vb, mp 149–150°, in 24 hr at 36° with 10^{-6} *M* CF_3CO_2H in CCl_4, while heating Vb at 65° in the same acidic medium produced a 50:50 mixture of Vb and Vc. Both Va and Vb were stable under these conditions in the absence of acid. The mixture of Vb and Vc was unchanged upon solution in concentrated H_2SO_4 or upon thermolysis at 100°. Separation of Vb and Vc was not accomplished with a variety of chromatographic methods, and the mixture formed beautiful yellow mixed crystals, mp 153°. The structures of Vb and Vc were shown by nmr, by comparison with the established order of thermodynamic stability of alkyl- and alkoxycycloheptatrienes,[10,11] and by formation of VII upon thermolysis of VI.[9,12] Catalytic hydrogenation of Vb or the Vb,c mixture produced VIII, mp 144.5–145.5°, while catalytic hydrogenation of Va gave VIII (32%) and epimeric mixture IX, mp 112–122° (39%). All the isomers of V produced the same tropylium salt X upon treatment with trityl fluoroborate in SO_2 or CH_2Cl_2.



Vb

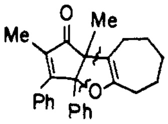


Vc

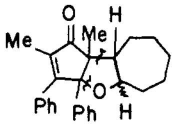


VII

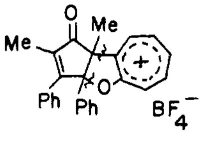
When tropone and I were heated above 100°, a third adduct, XI, mp 252°, was formed along with II and Va. Since II and Va were in equilibrium with tropone and I above 60° and XI was stable above 150°, XI could be prepared in high yield by prolonged heating of the addends above 100°. The ir (CCl_4; 5.84, 5.98 μ), the nmr ($CDCl_3$, 1.15 (3 H, s), 1.75 (3 H, s), 3.5 (2 H, m), 5.5–7.0 ppm (4 H, m), and spin-decoupling experiments proved the [4 + 2] nature of XI. Sodium borohydride reduction of XI gave a mixture of alcohols XII and XIII, the latter the result of reduction of both the α,β unsaturation and the carbonyl group. Photolysis of this mixture gave a mixture of caged alcohols, XIV, mp 185°, and XV, 196–201°, which were separated by preparative layer chromatography. Jones oxidation of XIV gave the α,β-unsaturated ketone XVI, mp 238–240°, proving that XI was an *endo* [4 + 2] adduct. XVI was identical with the caged ketone produced in the cycloheptatriene series.[2]



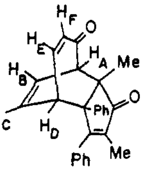
VIII



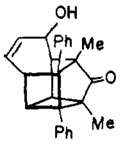
IX



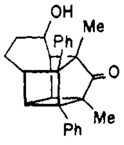
X



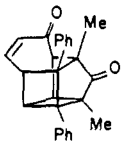
XI



XIV



XV

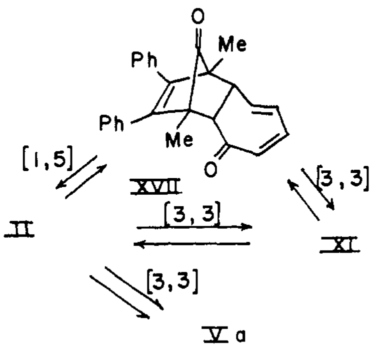


XVI

While no chemical evidence exists as to the *syn* or *anti* nature of the carbonyl groups in XI, nmr spin-decoupling experiments favor the *syn* orientation. In particular, irradiation of the high-field methyl resonance results in sharpening of the broad H_A resonance to a sharp eight-line multiplet while the H_D resonance is unaffected by irradiation of the high-field methyl. The small coupling (~0.2 Hz) between H_A and the saturated methyl group hydrogens is compatible with the presence of a small coupling through four bonds.

It has thus been firmly established that the reaction of tropone and I leads to *exo* [6 + 4] and [8 + 2] and *endo* [4 + 2] cycloadducts. It is interesting to note that all of these thermally allowed cycloadducts[13] lie on thermally allowed conversion pathways (Scheme I). In spite of this formal possibility, however, the following evidence strongly indicates the occurrence of three separate concerted cycloadditions.

SCHEME I



In preliminary investigations concerning the mechanism of formation of II, Va, and XI, the reaction of tropone and I was monitored by nmr. It was found that [II]/[Va] = 2 from 1 min to 10 hr, at which time equilibrium was attained. This implies that the direct interconversion II ⇄ Va was either extremely rapid or occurred only by dissociation–recombination of II or Va. The rates of formation of II and Va were unchanged in acetone, tetrahydrofuran, or benzene, which implies that a dipolar intermediate does not intervene in these reactions, even though the dipolar intermediate, XVIII, is an attractive intermediate in the formation of Va.

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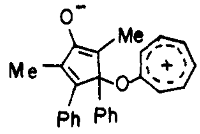
(10) Equilibration of methoxy- (or ethoxy-) cycloheptatriene yields 77.0% (84.8%) 1-, 18.5% (15.2%) 3-, and 4.6% (0%) 2-methoxy- (ethoxy-) cycloheptatriene, while equilibration of ethyl- (or methyl-) cycloheptatriene gives 37% (70%) 1-, 25% (16%) 3-, 31% (9%) 2-, and 6% (5%) 7-ethyl- (methyl-) cycloheptatriene.[11]

(11) T. Nozoe and K. Takahashi, *Bull. Soc. Chem. Jap.*, 38, 665 (1965); E. Weth and A. S. Dreiding, *Proc. Chem. Soc., London*, 59 (1964); K. Conrow, *J. Amer. Chem. Soc.*, 83, 2343 (1961).

(12) A. S. Kende, *Tetrahedron Lett.*, 2661 (1967).

(13) It is assumed that Va is the *endo* [8 + 2] adduct, although the subtleties of stereochemistry and orientation are still being investigated.



XVIII

When II or Va was heated above 100°, equilibrium between tropone, I, II, and Va was rapidly attained before formation of XI was noted, so that no information is available as to the origin of XI. However, the presence of XVII was never detected by nmr, and the direct Cope rearrangement of II to XI is sterically impossible, so that the concerted formation of XI is implied.

A second example now exists of competing *exo* [6 + 4] and *endo* [4 + 2] cycloadditions, lending further support to the Woodward–Hoffmann explanation of *exo–endo* phenomena.[2,14]

Acknowledgment. The financial support of the National Institutes of Health and the National Science Foundation (Harvard) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (L. S. U.), is gratefully acknowledged.

(14) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 4388 (1965); R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

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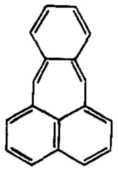
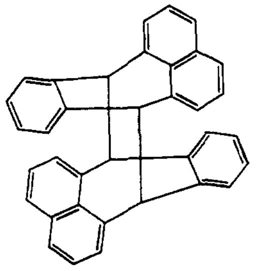
Photochemical Synthesis of Matrix-Isolated Pleiadene

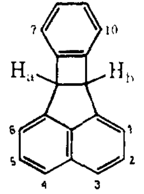
Sir:

Pleiadene[1] (I) has long been a subject of theoretical[2] and experimental[3] interest but has never been directly observed. Cava and Schlessinger[3b] succeeded in generating I which could be trapped with N-phenylmaleimide but otherwise dimerized immediately to II; identical results were obtained for simple derivatives.[3c]

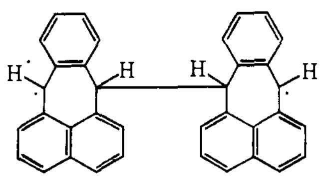
We wish to report a photochemical preparation and spectral characterization of stable matrix-isolated I using a novel precursor, 6b,10b-dihydrobenzo[1,2]cyclobut[3,4-*a*]acenaphthylene (III). The unusual path followed in the photochemical process is discussed in the following communication.[4]


I

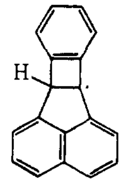

II



III



IV



V

Benzyne (anthranilic acid and amyl nitrite in boiling CH_2Cl_2) adds to acenaphthylene; III was isolated in 8–10% yield by preparative thin-layer chromatography on silica gel with petroleum ether eluent: mp 133–134°, elemental analysis correct for $C_{18}H_{12}$, mass spectrum shows strong peaks at *m/e* 228 (M^+), 226 ($M^+ - 2H$), 114 (M^{2+}), and 113 ($M^{2+} - 2H$), and no higher peaks up to *m/e* 750. The uv absorption spectrum closely resembles a superposition of the spectra of benzocyclobutene[5] and acenaphthene.[6] Proton nmr spectra in acetone-d_6 (60, 100, 220 MHz, TMS internal standard) show an ABC system integrating for 6 H (approximately τ_1 2.45, τ_2 2.53, τ_3 2.37, J_{12} = 7 Hz, J_{23} = 8 Hz), an AA′BB′ system centered at τ 2.84 (4 H), and a broad singlet at 4.67 (2 H, half-width 1.7 Hz). Decoupling showed that the broadening is due to unresolved long-range coupling between the aliphatic protons and both aromatic systems. From measurements of ^{13}C satellites, $J_{H_aH_b} = 3.5 \pm 0.3$ Hz, $J_{^{13}CH_a} = 147.4 \pm 0.5$ Hz. These results compare well with available data for related molecules[7,8a] and leave no doubt about the structure of III.

Benzocyclobutenes open thermally and photochemically to *o*-quinodimethanes.[8] By analogy, we expected III to give I. Although III is thermally quite stable (unchanged after 6 min at 170°), at 230–240° its melt solidifies in *ca.* 5 min and gives II, identified by comparison of the decomposition point and nmr and uv spectra with Cava's values[3b] (good agreement except for a reported uv peak at 214 nm in dioxane solvent, which we believe is spurious).

Irradiation of the colorless rigid solution of III in glass-forming solvents at low temperatures with uv light produces a stable yellow-green coloration, which we assign to I. The change can be followed spectrally: bands of I grow continuously while those of III gradually disappear (several isosbestic points). The spectrum of I is virtually the same in all solvents tested. After complete disappearance of III, further irradiation with uv, visible, or near-ir light produces no change. Thorough attempts to detect an epr signal gave negative results (glycerol–methanol, 9:1, 195°K). When a

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(1) L. F. Fieser and M. Fieser, *J. Amer. Chem. Soc.*, **55**, 3010 (1933).

(2) B. Pullman, A. Pullman, G. Berthier, and J. Pontis, *J. Chim. Phys. Physicochim. Biol.*, **49**, 20 (1952); K. Fukui in "Molecular Orbitals in Chemistry, Physics, and Biology," P.-O. Löwdin and B. Pullman, Ed., Academic Press, New York, N. Y., 1964, ORG 513; G. Binsch and I. Tamir, *J. Amer. Chem. Soc.*, **91**, 2450 (1969).

(3) (a) L. F. Fieser, *ibid.*, **55**, 4977 (1933); (b) M. P. Cava and R. H. Schlessinger, *Tetrahedron*, **21**, 3073 (1965); (c) M. P. Cava and W. S. Lee, *ibid.*, **24**, 837 (1968); M. P. Cava, W. S. Lee, and D. F. Barringer, *ibid.*, **23**, 4557 (1967); M. P. Cava and R. H. Schlessinger, *ibid.*, **21**, 3065 (1965).

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(5) M. P. Cava and D. R. Napier, *ibid.*, **80**, 2255 (1958).

(6) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," Wiley, New York, N. Y., 1951, Spectrum No. 212.

(7) M. J. S. Dewar and R. C. Fahey, *J. Amer. Chem. Soc.*, **84**, 2012 (1962); G. Fraenkel, Y. Asahi, M. J. Mitchell, and M. P. Cava, *Tetrahedron*, **20**, 1179 (1964); E. A. Hill and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 2047 (1967); W. C. Agosta, *ibid.*, **89**, 3505 (1967); R. H. Mitchell and F. Sondheimer, *ibid.*, **90**, 530 (1968); P. R. Houlton and W. Kemp, *Tetrahedron Lett.*, 1045 (1968).

(8) (a) G. Quinkert, K. Opitz, W.-W. Wiersdorff, and M. Finke, *Justus Liebigs Ann. Chem.*, **693**, 44 (1966); (b) G. Quinkert, M. Finke, J. Palmowski, and W.-W. Wiersdorff, *Mol. Photochem.*, **1**, 433 (1969), and references therein.