analysis (Me_4Si) to give spectra as that depicted in Figure 2C. A fourth sample of the crude ozonolysis product was kept at room temperature. ^1H NMR analysis (Me_4Si) after 24 h showed the spectrum depicted in Figure 2D and GLC analysis showed the peaks of **11**, **12**, and **13**. GC/MS *m/e* (relative intensity): **11**, 60 (100, M^+), 45 (4, $M - CH_3)^+$); **12**, 60 (69, M^+), 45 (100, $(COOH)^+$], 43 (92, $(CH_3CO)^+$); **13**, 74 (42, M^+), 59 (16, $M - CH_3)^+$), 43 (100, $(CH_3CO)^+$). A fifth sample of the crude ozonolysis product was admixed with an excess of Me_2S-d_6 and warmed up to room temperature. The sample turned yellow, and ^1H NMR analysis (Me_4Si) showed the most intensive signal at δ 2.30 for compound **15**. GLC analysis showed the peaks of **12**, **13**, **15**, and **16**. GC/MS *m/e* (relative intensity): **12**, 60 (69, M^+); **13**, 74 (42, M^+); **15**, 86 (14, M^+), 43 (100, $(CH_3CO)^+$); **16**, 76 (7, M^+), 75 (100, $M - H)^+$), 45 (73, $M - OCH_3)^+$).

Quantitative ^1H NMR Analysis of Reaction Products from the Ozonolysis of 3 in CD_2Cl_2. A solution of 376.0 mg (2.85 mmol) of **3**[14] and 397.0 mg (2.98 mmol) of 1,1,1-trichloroethane in 3 mL of CD_2Cl_2 was ozonized to completion at −78 °C. A sample was kept at room temperature for 24 h. Quantitative ^1H NMR analysis (Me_4Si) showed the presence of **9** [δ 8.03 (1 H); 40%[16]], **11** [δ 3.73 (3 H); 10%], **12** [δ 2.08 (3 H); 50%], and **13** [δ 2.02 and 3.65 (3 H each); 50%]. The quantitative analysis is based on a comparison of the intensities of the signals of the individual components with that of 1,1,1-trichloroethane at δ 2.74.

Acknowledgment. Support of this research by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie is gratefully acknowledged.

Registry No. **1**, 513-81-5; **3**, 85526-22-3; **5**, 50-00-0; **6**, 4461-52-3; **7**, 10027-72-2; **8**, 98218-20-3; **9**, 64-18-6; **10**, 87742-47-0; **11**, 107-31-3; **12**, 64-19-7; **13**, 79-20-9; **14**, 108-24-7; **15**, 431-03-8; **16**, 109-87-5; **18**, 98218-21-4.

Stereochemical and Regiochemical Course of Isodicyclopentadiene–Tropone Cycloaddition Reactions[1]

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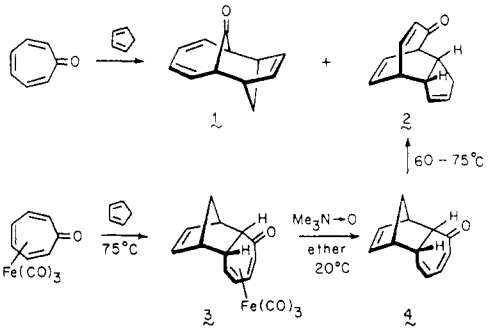
The reactions of isodicyclopentadiene and two spirocyclic derivatives with tropone, 2-methyltropone, and 2-methoxytropone have been investigated. Cycloaddition of the two parent molecules occurred predominantly by a [6 + 4] bonding pathway with a marked above-plane selectivity. The presence of a 2-substituent on the tropone rendered this process inoperative. Instead, capture of the [1,5] sigmatropic diene isomers **15** and **30** was seen. In the latter instance, a Diels–Alder mode was kinetically favored, with the tropones functioning as 4π donors. The regioselectivity that distinguishes the methyl and methoxyl examples was accountable in terms of frontier molecular orbital theory. When the pure spirocyclic systems were heated with tropone in benzene solution, no reaction occurred. However, condensations with isomeric contaminants were seen to occur. The various phenomena are discussed at the mechanistic level.

Tropone is well recognized to undergo cycloaddition with cyclopentadiene. Whereas a reaction temperature of 80 °C provides **1**, heating of the reactants to 145 °C delivers **2**.[2] Formation of these adducts has been attributed to the operation of concerted exo [6 + 4] and endo [4 + 2] pathways, respectively.[3] An alternative mechanistic formulation that would lead with equal stereospecificity to **1** and **2** involves initial formation of the simple Diels–Alder adduct **4**, followed by thermally allowed [1,5] and [3,3] sigmatropic carbon migration.[4] Franck–Neumann and Martina have recently found it possible to prepare **4** by an independent method.[5] Through condensation of tropone–iron tricarbonyl with cyclopentadiene, access to **3** was realized. Subsequent to decomplexation of **3** under mild conditions, the thermally labile **4** was obtained and shown to undergo only the Cope rearrangement to **2** at 60–75 °C (E_a = 28.5 kcal/mol). Consequently, ketone **1** probably results directly from [6 + 4] cycloaddition.



Although tropone is reported to react similarly with other dienes,[6-10] several other processes can compete effectively with the [6 + 4] bonding scheme. In particular, successful operation of the latter pathway is especially sensitive to substitution in either addend. 2-Chlorotropone

(1) Electronic Control of Stereoselectivity. 29. For Part 28, see: Paquette, L. A.; Kravetz, T. M. *J. Org. Chem.*, in press.

(2) (a) Cookson, R. C.; Drake, B. V.; Hudec, J.; Morrison, A. *Chem. Commun.* **1966**, 15. (b) Itô, S.; Fujise, Y.; Okuda, T.; Inoue, Y. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1351. (c) Itô, S.; Sakan, Y.; Fujise, Y. *Tetrahedron Lett.* **1970**, 2873. (d) Tanida, H.; Pfaendler, H. R. *Helv. Chim. Acta* **1972**, *55*, 3062. (e) Haywood-Farmer, J.; Friedlauder, B. T.; Hammond, L. M. *J. Org. Chem.* **1973**, *38*, 3145.

(3) Woodward, R. B.; Hoffmann, R. *Angew. Chem.* **1969**, *81*, 797.

(4) The ability of tropone to function as the 4 π component in the Diels–Alder reaction is signaled most convincingly by its capture of ethylene at elevated temperatures: (a) Uyehara, T.; Yamada, J.-T.; Kato, T. *Tetrahedron Lett.* **1983**, *4445*. (b) Uyehara, T.; Kitahara, Y. *Chem. Ind. (London)* **1971**, 354.

(5) Franck-Neumann, M.; Martina, D. *Tetrahedron Lett.* **1977**, 2293.

(6) Garst, M. E.; Roberts, V. A.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 3882. (b) Garst, M. E.; Roberts, V. A.; Prussin, C. *Tetrahedron* **1978**, *39*, 581. (c) Mukerjee, D.; Watts, C. R.; Houk, K. N. *J. Org. Chem.* **1983**, *43*, 817. (d) Itô, S.; Ohtani, H.; Narita, S.; Honma, H. *Tetrahedron Lett.* **1972**, 2223.

(7) 1,3-Cyclohexadiene: Mukai, T.; Akasaki, Y.; Hagiwara, T. *J. Am. Chem. Soc.* **1972**, *94*, 675.

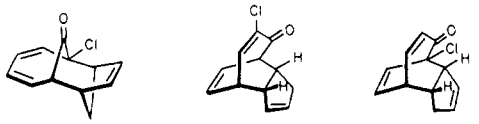
(8) Cyclopentadienones: Houk, K. N.; Woodward, R. B. *J. Am. Chem. Soc.* **1970**, *92*, 4145.

(9) Pyrones: Sasaki, T.; Kanematsu, K.; Iizuka, K. *J. Org. Chem.* **1976**, *41*, 1105.

(10) Isobenzofurans: (a) Paddon-Row, M. N.; Warrener, R. N. *Tetrahedron Lett.* **1974**, 3797. (b) Takeshita, H.; Wada, Y.; Mori, A.; Hatsui, T. *Chem. Lett.* **1973**, 335. (c) Jones, D. W.; Kneen, G. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1647.

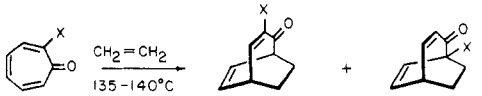
0022-3263/85/1950-4199$01.50/0

is an informative example. Heating with cyclopentadiene at 105 °C for 3 h produced **5** (11%), **6** (11%), **7** (19%), and exo isomers of **7** (2%).[11] The regioselectivity witnessed



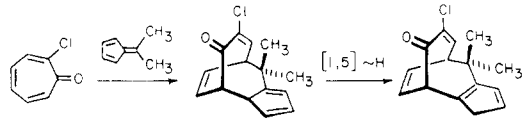
5 **6** **7**

for preferential attachment of the chlorine atom to a bonding center also surfaces during Diels–Alder reaction with ethylene. The weighting in favor of **9**, the more highly accentuated regioselectivity in the 2-methoxy example, and the product distribution crossovers encountered in the methyl, benzoyloxy, and phenyl cases can be rationalized on theoretical grounds, provided that closed-shell repulsion terms are included.[12] Consequently, electron-density alterations within the tropone can play an important product-determinative role.[11-13]



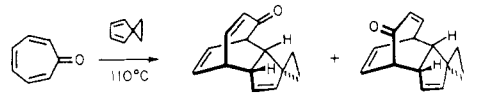
	8	**9**
a, X = Cl	41%	59%
b, X = OCH_3	12%	88%
c, X = Ph	100%	
d, X = CH	58%	42%
e, X = OCOPh	60%	40%

Structural changes in the cyclopentadiene partner are likewise not inconsequential. Where methylfulvenes are concerned, addition initially proceeds across positions 2 and 6, *with the ketone now serving as the 4π component.*[14] An ensuing rapid [1,5] hydrogen shift is followed by capture of a second tropone molecule.[15] In the cycloaddition of 2-chlorotropone with 6,6-dimethylfulvene, **11** can be isolated because further reaction is kinetically slowed.[16] With 2,7-dichlorotropone, no observable cycloaddition takes place, assumedly for steric reasons.[16]



10 **11**

Evidence that [6 + 4] cycloadditions are easily bypassed in favor of other thermally allowed processes if a modicum of steric impedance is encountered comes from studies involving tropone and spiro[2.4]hepta-2,6-diene. Heating equimolar amounts of these reagents at 110 °C for 6 days gives rise to **12** and **13** as major products (79% and 13%,



12 **13**

respectively).[17] Evidently, the steric congestion offered by the quaternary carbon of the diene is adequate to compel it to react as a 2π partner, despite the higher activation energy customarily associated with this reaction channel.

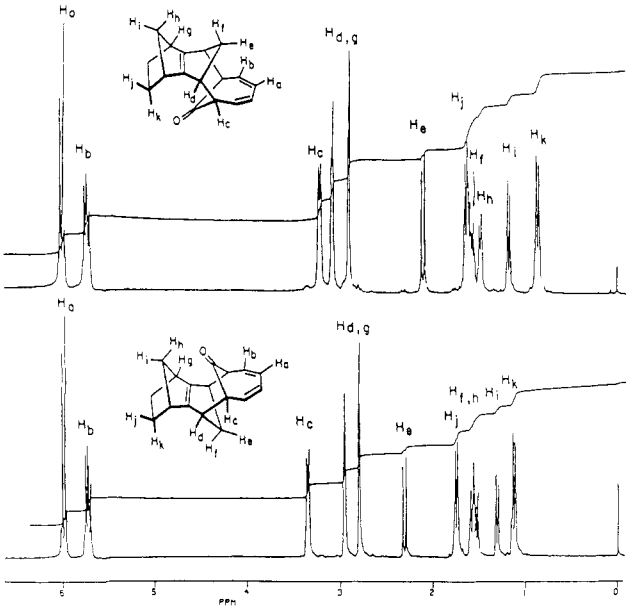


Figure 1. 300-MHz ^1H NMR spectra of the stereoisomeric [6 + 4] tropone–isodicyclopentadiene adducts **16** (top) and **17** (bottom) recorded in $CDCl_3$ solution.

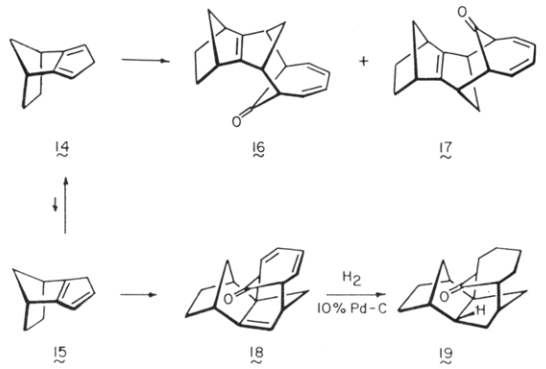
In this paper, an extension of tropone cycloaddition chemistry to encompass the new area of π-facial stereoselectivity[18] is reported.[19] Our objectives were fourfold: (a) to ascertain whether expanding the distance between reacting centers (for tropone, the C_2–C_7 gap is 2.55 Å)[20] relative to those customarily found in cyclopentadiene rings (C_1–C_4 = 2.19–2.32 Å)[21] and typical dienophiles (1.30 Å for maleic anhydride)[22] would, as in [3 + 4] cycloadditions to isodicyclopentadiene,[1,19] result in a stereoselectivity crossover during [6 + 4] bonding; (b) to determine if 2-substituted tropones engage in parallel chemistry;[23] (c) to uncover the impact of steric blockade within the isodicyclopentadiene on the course of the cycloaddition process;[23] (d) to utilize the findings in a–c for advancing the present level of theoretical understanding of the electronic character of isodicyclopentadienes and its practical consequences.

Results

The Tropone–Isodicyclopentadiene Case Study. Because of high-lying σ orbitals within its norbornyl unit,

(11) Itô, S.; Sakan, K.; Fujise, Y. *Tetrahedron Lett.* **1969**, 775.
(12) Uyehara, T.; Kitahara, Y. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3335.
(13) (a) Takeshita, H.; Hatsui, T.; Iwabuchi, R.; Itoh, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1257. (b) Sasaki, T.; Manabe, T.; Wakabayashi, E. *Tetrahedron* **1980**, *36*, 2119.
(14) (a) Houk, K. N.; Luskus, L. J.; Bhacca, N. S. *J. Am. Chem. Soc.* **1970**, *92*, 6392. (b) Bhacca, N. S.; Luskus, L. J.; Houk, K. N. *J. Chem. Soc., Chem. Commun.* **1971**, 109.
(15) Pfaendler, H. R.; Tanida, H. *Helv. Chim. Acta* **1973**, *56*, 543.
(16) Pfaendler, H. R.; Tanida, H. *Helv. Chim. Acta* **1973**, *56*, 545.
(17) Tanida, H.; Yano, T.; Ueyama, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 946.
(18) (a) Gleiter, R.; Paquette, L. A. *Acc. Chem. Res.* **1983**, *16*, 328. (b) Paquette, L. A. In "Stereochemistry and Reactivity Pi Systems", Watson, W. H., Ed.; Verlag Chemie International: Deerfield Beach, FL, 1983; pp 41–73. (c) Gleiter, R.; Böhm, M. C. In ref 18b, pp 105–146.
(19) (a) Paquette, L. A.; Hathaway, S. J.; Kravetz, T. M.; Hsu, L.-Y. *J. Am. Chem. Soc.* **1984**, *106*, 5741. (b) Paquette, L. A.; Hsu, L.-Y.; Gallucci, J. C.; Korp, J. D.; Bernal, I.; Kravetz, T. M.; Hathaway, S. J. *Ibid.* **1984**, *106*, 5743.
(20) Barrow, M. S.; Mills, O. S.; Filippini, G. *J. Chem. Soc., Chem. Commun.* **1973**, 66.
(21) (a) Zerger, R.; Stucky, G. *J. Organomet. Chem.* **1974**, *80*, 7. (b) Einstein, F. W. B.; Gilbert, M. M.; Tuck, D. G. *Inorg. Chem.* **1972**, *11*, 2832. (c) Barrow, M. J.; Ebsworth, E. A. V.; Harding, M. M.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1980**, 603. (d) Birkhahn, M.; Krommes, P.; Massa, W.; Lorberth, J. *J. Organomet. Chem.* **1981**, *208*, 161.
(22) Marsh, R. E.; Ubell, E.; Wilcox, H. E. *Acta Crystallogr.* **1962**, *15*, 35.
(23) For a preliminary report, see: Paquette, L. A.; Hathaway, S. J.; Galluci, J. C. *Tetrahedron Lett.* **1984**, 2659.

isodicyclopentadiene (**14**) possesses a conjugated π system perceived to be significantly influenced by prevailing σ/π interactions.[18] A strong predilection for Diels–Alder addition from below-plane is recognized to exist.[24-27] The π-face stereoselection exhibited by **14** toward tropone is contrastingly different. Thus, dissolution of equimolar amounts of these reactants in benzene at 20 °C for 9 days resulted in 50% consumption of the hydrocarbon. The resulting three adducts (**16–18**) were readily separated by silica gel chromatography. That the two more prevalent



ketones **16** (15%) and **17** (75%) were [6 + 4] addends was clearly indicated by their ^{1}H NMR spectra (Figure 1). The simplification seen in both instances as a result of the existence of an internal plane of symmetry was also apparent by ^{13}C NMR spectroscopy. While **16** and **17** are nearly indistinguishable below δ 2.5, important differences appear at higher field. Most notably affected by the change in stereostructure are the endo ethano protons H_k. Whereas their characteristic double doublet pattern appears at δ 1.13 in **17**, their proximity to the carbonyl group in **16** leads to significant shielding[28] (δ 0.86). Interestingly, the apical methylene proton H_h is less responsive to its proximity to the carbonyl (Figure 1) because of its differing spatial relationship to the C=O plane.

Ultimately, these stereochemical assignments were confirmed by X-ray structure analysis of both isomers.[19b] The central double bond in **16** is distorted by 11.4° from planarity, with the bending occuring in the downward direction customarily found for *syn*-sesquinorbornenes.[25h,i,26,27a] For **17**, the interplanar angle was determined to be 178.9°; thus, its internal olefinic bond constitutes an essentially planar system.

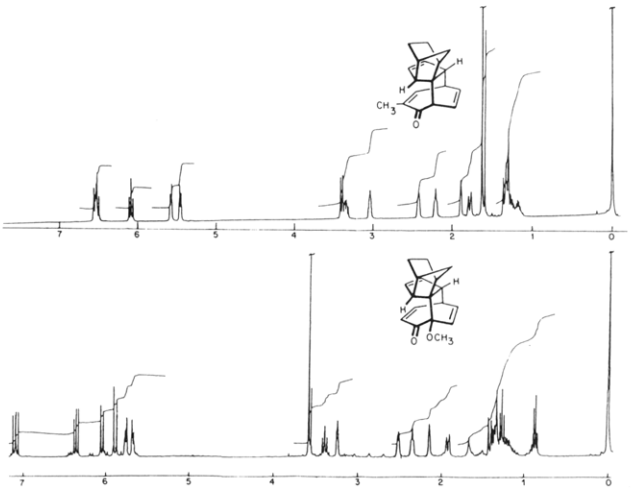


Figure 2. 300-MHz ^{1}H NMR spectra (in $CDCl_3$ solution) of **20** (top) and **21** (bottom). The acidic nature of this solvent induces the decomposition of **21**; the appearance of a methoxyl-containing degradation product is evident in the lower spectrum.

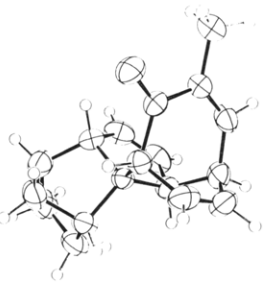


Figure 3. ORTEP drawing of **20**. The non-hydrogen atoms are drawn with 50% probability ellipsoids. Hydrogen atoms have been drawn artifically small.

The third adduct, isolated as a viscous oil (10%), exhibited five olefinic protons in its 300-MHz ^{1}H NMR spectrum. This observation and the associated signals to higher field were compatible with an addend arising from [6 + 4] bonding to **15**, the [1,5] hydrogen shifted isomer of isodicyclopentadiene.[29,30] To establish this point unequivocally, **18** was exhaustively hydrogenated to yield the crystalline hexahydro derivative **19** whose structural features were fully corroborated by X-ray analysis.[19a] Since the equilibrium concentration of **15** at room temperature is recognized to be very low,[29,30] the rate of its conversion to **18** has to compare closely with that leading to **17** and to be faster than that which ultimately delivers **16**.

The tropone–isodicyclopentadiene reaction was also carried out in refluxing benzene until the tropone was completely consumed (51 h). Expectedly, the amount of **18** that was isolated from the dark reaction mixture rose to 18%. Below-plane adduct **16** was also obtained, although in inferior yield. Significantly, no **17** was found. In control experiments, it was ascertained that although **16** was stable for prolonged periods in benzene at 80 °C, **17** was not. Decomposition to a noncharacterizable tarry substance was noted.

The Course of 2-Methyl- and 2-Methoxytropone Additions. No observable reaction occurred when solu-

(24) (a) Alder, K.; Flock, F. H.; Janssen, P. *Chem. Ber.* **1956**, *89*, 2689. (b) Kobuke, Y.; Sugimoto, T.; Furukawa, J. *J. Org. Chem.* **1976**, *41*, 1457.

(25) (a) Paquette, L. A.; Carr, R. V. C.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1970**, *102*, 1186. (b) Böhm, M. C.; Carr, R. V. C.; Gleiter, R.; Paquette, L. A. *Ibid.* **1980**, *102*, 7218. (c) Paquette, L. A.; Carr, R. V. C.; Arnold, E.; Clardy, J. *J. Org. Chem.* **1980**, *45*, 4907. (d) Paquette, L. A.; Carr, R. V. C.; Charumilind, P.; Blount, J. F. *Ibid.* **1980**, *45*, 4922. (e) Paquette, L. A.; Carr, R. V. C. *J. Am. Chem. Soc.* **1980**, *102*, 7553. (f) Paquette, L. A.; Charumilind, P. *Ibid.* **1982**, *104*, 3749. (g) Paquette, L. A.; Charumilind, P.; Kravetz, T. M.; Böhm, M. C.; Gleiter, R. *Ibid.* **1983**, *105*, 3126. (h) Paquette, L. A.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Bass, L. S.; Clardy, J. *Ibid.* **1983**, *105*, 3136. (i) Paquette, L. A.; Hayes, P. C.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Blount, J. F. *Ibid.* **1983**, *105*, 3148. (j) Paquette, L. A.; Schaefer, A. G.; Blount, J. F. *Ibid.* **1983**, *105*, 3642. (k) Paquette, L. A.; Kravetz, T. M.; Böhm, M. C.; Gleiter, R. *J. Org. Chem.* **1983**, *48*, 1250. (l) Paquette, L. A.; Browne, A. R.; Doecke, C. W.; Williams, R. V. *J. Am. Chem. Soc.* **1983**, *105*, 4113. (m) Paquette, L. A.; Charumilind, P.; Gallucci, J. C. *Ibid.* **1983**, *105*, 7364. (n) Hathaway, S. J.; Paquette, L. A. *Tetrahedron* **1985**, *41*, 2037. (o) Paquette, L. A.; Green, K. E.; Hsu, L.-Y. *J. Org. Chem.* **1984**, *49*, 3650. (p) Charumilind, P.; Paquette, L. A. *J. Am. Chem. Soc.* **1984**, *49*, 3650. (q) Paquette, L. A.; Green, K. E.; Gleiter, R.; Schafer, W.; Gallucci, J. C. *Ibid.* **1984**, *106*, 8232.

(26) Watson, W. H.; Galloy, J.; Bartlett, P. D.; Roof, A. A. M. *J. Am. Chem. Soc.* **1981**, *103*, 2022.

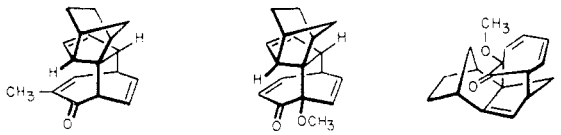
(27) (a) Hagenbuch, J.-P.; Vogel, P.; Pinkerton, A. A.; Schwarzenbach, D. *Helv. Chim. Acta* **1981**, *64*, 1818. (b) Avenati, M.; Vogel, P. *Ibid.* **1982**, *65*, 204. (c) Mahaim, C.; Vogel, P. *Ibid.* **1982**, *65*, 866.

(28) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: New York, 1969; pp 88–92.

(29) Subramanyam, R.; Bartlett, P. D.; Iglesias, G. Y. M.; Watson, W. H.; Galloy, J. *J. Org. Chem.* **1982**, *47*, 4491.

(30) Paquette, L. A.; Williams, R. V.; Carr, R. V. C.; Blount, J. F. *J. Org. Chem.* **1982**, *47*, 4566.

tions containing isodicyclopentadiene and 2-methyltropone or 2-methoxytropone were kept at room temperature for extended periods of time. In the first instance, heating in refluxing benzene resulted in 32% consumption of the hydrocarbon during 6 days. The only detectable adduct, isolated in 81% yield, was initially formulated as **20** on the basis of its distinctive 300-MHz ^{1}H NMR spectrum (Figure 2). Of the five vinyl protons present, two are rather deshielded and appear as a complex multiplet centered at δ 6.56. A triplet of area 1 (J = 8 Hz) at δ 6.10 and a second two-proton AB pattern centered at δ 5.52 round out this region. Although many of the remaining protons are nonoverlapping in their chemical shift, the next most informative piece of information was the location of the narrowly split (J = 1.4 Hz) methyl doublet at δ 1.66. This substituent must consequently be positioned on a trigonal carbon atom; that is, the regiochemistry must be as illustrated and result from exclusive capture of yet another isodicyclopentadiene tautomer. X-ray analysis was again utilized to establish convincingly the structural assignment to **20** (Figure 3).



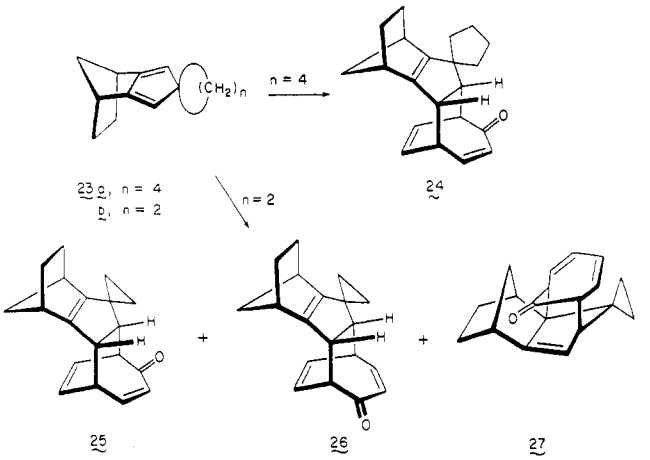
20 **21** **22**

Under identical conditions, 2-methoxytropone reacted to the extent of 44% and gave rise with low recovery to a chromatographically separable 3:1 mixture of **21** and **22**. Although adduct **21** exhibits six olefinic protons, the relatively close correspondence of many of the remaining protons (Figure 2) indicates that this adduct is structurally related to **20**. The reversal in regioselectivity apparent in **21** is accountable in terms of expectations based on molecular orbital theory.[12]

The Effect of Spiroalkylation. Because of the recognized sensitivity of the tropone–cyclopentadiene reaction to steric factors in either reaction partner, predictions concerning the outcome of cycloadditions involving spirocyclic hydrocarbons **23a** and **23b**[25g] could not be reliably made a priori. It was anticipated that heating for prolonged periods of time would be required. In actuality, when equimolar amounts of **23a** and tropone were heated at 80 °C in benzene for 4 days, a single product was isolated in low yield (6%) following silica gel chromatography. The rather complex ^{1}H NMR spectrum of this substance indicated not only that a 1:1 cycloaddition had occurred but also that tropone had functioned specifically as a 4π donor. Particularly evident was the pattern characteristic for an α,β-unsaturated ketone [δ 7.13 and 5.71 (J = 11 Hz)]. Both ^{1}H and ^{13}C NMR determinations indicated the substance to lack symmetry. Ultimate identification of the adduct as **24** was realized by X-ray analysis.[23]

We next focused our attention on the behavior of **23b**. Heating in this case required 6 days in benzene at 80 °C to achieve a modicum of reaction. Although considerable darkening and resinification were in evidence after this time, it proved possible to isolate in low yield the isomeric products **25**, **26**, and **27** in relative amounts of 66%, 17%, and 17%.

Particularly helpful in our structural assignments to these ketones was knowledge of the ^{1}H NMR spectra of **18** and **24**. As concerns **27**, for example, all of its proton resonances below δ 2.0 are virtually superimposable upon those of **18** (see Experimental Section). The replacement of one apical methylene group by a spirocyclopropane moiety was, of course, evident at higher field. Similarly,



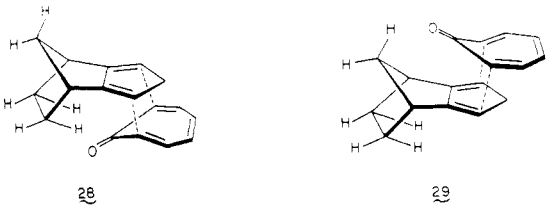
23 a, n = 4; b, n = 2 **24** **25** **26** **27**

the spectral features of **25** and **26** compare closely to those exhibited by **24**. The chemical shifts and multiplicities of the four olefinic protons in each of the three compounds play a particularly diagnostic role. The distinction between **25** and **26** was also arrived at from chemical shift considerations, with isomers **12** and **13** now serving as points of reference.

These experiments reveal that **23a** and **23b** are not reactive per se toward tropone. In both instances, the adduct structures disclose that a nonsymmetric isodicyclopentadiene tautomer has been trapped. In the case of **24–26**, these isomeric hydrocarbons have made available one of their double bonds for Diels–Alder condensation. In all four adducts, tropone has entered from the exo surface. The relative orientation of the carbonyl group and cyclopentane ring in **24** is noteworthy in relation to the relative distribution of **12** and **13** uncovered by Tanida and co-workers.[17]

Discussion

Stereochemical Selectivity of the [6 + 4] Cycloaddition. The intermolecular [6 + 4] cycloaddition of tropone to isodicyclopentadienes has been found to be limited to the parent system in either component. Nevertheless, the resulting reaction provides important evidence of a face selectivity preference (above plane) opposite to that (below plane) observed for the majority of [4 + 2] processes involving diene **14**. The major recognized stereoelectronic feature of [6 + 4] addition reactions is an overriding adherence to exo bonding because of repulsive secondary frontier molecular orbital interactions.[2,3] We can consequently limit the energetically accessible transition states to those represented by **28** and **29**. These



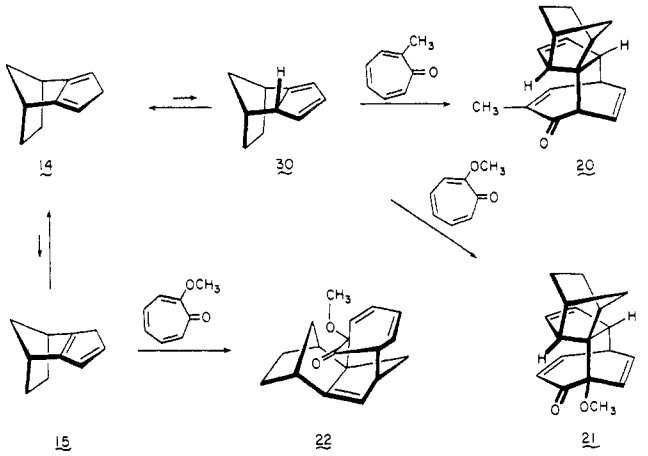
28 **29**

formalisms are distinguished only by the presence of a relatively remote methano or ethano norbornyl bridge syn facial to the approaching tropone. Since attempted equilibration of adducts **16** and **17** was not successful, adduct formation probably occurs under kinetic control. On this basis, "concerted" bonding option **29** can be construed to occur at a rate significantly faster than that associated with alternative **28**.

As will be discussed below, this observation is entirely consistent with, although not limited to, the π-orbital

tilting and closed-shell repulsion arguments previously advanced.[18,25]

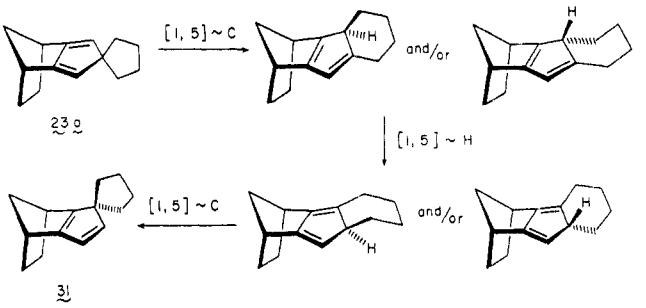
Consequences of Tropone Substitution at C-2. The inability of 2-methyl and 2-methoxytropone to enter into [6 + 4] condensation with isodicyclopentadiene conforms to the known sensitivity of this cycloaddition process to substituent perturbation, particularly at a bonding site.[11-13] The steric nature and electronic character of 2-methyltropone also appear nonconducive to the capture of **15**, the sigmatropic tautomer selectively captured by dienophiles of low reactivity.[29-31] Instead, it is the yet more fleeting [1,5] hydrogen shift isomer **30**[32,33] that is singled out from the equilibrating diene mixture. This result was unexpected, since Sasaki had previously shown that 2-substituted tropones are capable of Diels–Alder reaction (as 4π donors) with norbornene-type double bonds.[13b] The unreceptiveness of **15** may have a steric origin; however, the observation that 2-methoxytropone adds in [6 + 4] fashion to this diene to give **22** requires that electronic factors be involved as well.



By insisting that **30** be its reaction partner, the 2-alkyltropone must settle for the somewhat lessened dienophilic reactivity of a 2-methylenenorbornane double bond. Cycloaddition occurs regiospecifically in anti-Alder fashion across C-4/C-7 of this tropone to deliver **20**. The alkyl-substituted double bond does not become involved because the donor properties of methyl promote a slower rate of reaction toward an electron-rich diene. The acceptor 2-methoxyl group, on the other hand, polarizes the tropone LUMO, lowers all orbital energies, and gives rise to an opposite regioselectivity (see **21**). Indeed, all of the cycloadditions described herein occur preferentially along those reaction channels where the stabilizing interactions of the tropone LUMO and diene HOMO are maximized and steric contributions are minimized. The regioselectivity encountered in **21** is anticipated, since C-2 of 2-methoxytropone is the more electrophilic 4π terminus.

Preequilibration within the Spiroalkylated Isodicyclopentadienes. When the methylene group in **14** is dialkylated as in **23**, the steric repulsions to above-plane and below-plane approach by tropone become appreciably enhanced. Conservative estimates place the added energy requirements at 1–1.5 kcal/mol from either direction.[34] Because of these repulsions, direct bonding between these reagents is kinetically retarded. The structures of adducts **24–27** suggested that extensive carbon and hydrogen sigmatropy might have occurred to generate diene **31** and its cyclopropyl analogue in situ prior to cyclization (see Scheme I). The closest literature analogies are the thermal interconversion of 4- and 5-methylspiro[2.4]hepta-4,6-dienes at 240–270 °C[35] and gas-phase isomerization of *cis*- and *trans*-6,9-dimethylspiro[4.4]nona-1,3-diene at 230–280 °C.[36] The parent spiro[4.4]nona-1,3-diene is apparently thermally labile and undergoes [1,5] sigmatropic rearrangement readily.[37] However, no isomer-specific trapping experiments have previously come to light. Nor was any hint of structural isomerization in evidence during Diels–Alder cycloadditions to **23a** and **23b**.[25h] Consequently, the purity of **23a** and **23b** was first assessed by VPC (thermal conductivity detection), MPLC, and ^{1}H NMR spectroscopy (^{1}H and ^{13}C). By all these measures, the two hydrocarbons appeared to possess >98% purity. However, when flash vacuum pyrolysis of **23a** up to 500 °C and of **23b** at 300 °C failed to give indication of rearrangement, suspicion arose about the actual operability of the illustrated **23** → **31** transformation under the considerably milder cycloaddition conditions. Accordingly, recourse was subsequently made to capillary VPC techniques for analysis of homogeneity. This tool revealed that both **23a** and **23b** contained nontrivial amounts of a second isomeric substance having a very similiar retention time. The relative percentage concentration of each impurity proved to be somewhat variable (5–10%) and dependent upon the precise fraction cut during distillation. Although it was not possible to isolate these minor isomers preparatively and consequently to identify them spectroscopically, the inference capable of being drawn from the cycloaddition results is that they are **31** and the cyclopropyl analogue, respectively. By means of gas-phase thermolysis at 400 °C, it was possible to decompose **31** selectively. The sample of **23a** purified in this manner proved completely unreactive to tropone when heated together with it in the original manner. Thus, **31** is *not* produced in situ but is present at the outset, having arisen from competing spiroalkylation of the cyclopentadienide anion at one of the two available sites α to the norbornane ring.

Scheme I

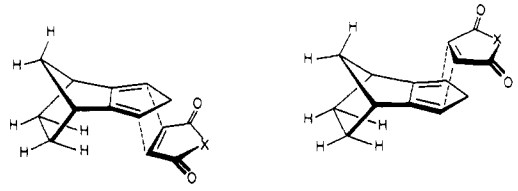


The regiochemistry that prevails during Diels–Alder addition of tropone to **31** is observed in the lone adduct **24**. The drop-off in regioselectivity that occurs in the spirocyclopropyl example (**25**:**26** = 3.9) compares closely to the relative distribution of **12** and **13** (4.9:1) noted earlier by Tanida for the structurally simpler diene. The spiroconjugation known to be present uniquely in the spirocyclopropane systems[25h,38] may prove to be one possible

(31) Paquette, L. A.; Charumilind, P.; Gallucci, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 7364.
(32) Bartlett, P. D.; Wu, C. *J. Am. Chem. Soc.* **1983**, *105*, 100.
(33) Washburn, W. N.; Hillson, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 4575.
(34) Brown, F. K.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 1971–1978.
(35) Clark, R. A.; Hayles, W. J.; Youngs, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 1966.
(36) Boersma, M. A. M.; de Haan, J. W.; Kloosterziel; van de Ven, L. J. M. *J. Chem. Soc., Chem. Commun.* **1976**, 1168.
(37) Marchand, A. P.; Wu, A. *J. Org. Chem.* **1985**, *50*, 396.
(38) Gleiter, R.; Heilbronner, E.; de Meijere, A. *Helv. Chim. Acta* **1971**, *54*, 1029.

contributor to this state of affairs.

Theoretical Considerations. To account for the preferential bonding of those dienophiles that undergo anti-Alder [4 + 2] cycloaddition to **14** from below-plane, i.e., as in **32** instead of **33**, we have invoked σ/π interaction entailing subjacent orbital control.[18] Admixture of the norbornane σ orbitals with the π orbitals of the diene operates in ψ_1 to tilt the terminal π orbitals disrotatorily inward on top and outward at the bottom (see **34** and **35**).

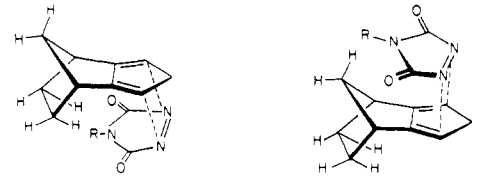


32 **33**

34 **35**

Consequently, as a dienophile approaches from below, the mismatch in orbital alignment (**34**) leads to a reduction in antibonding destabilization. In contrast, above-plane approach generates the maximum closed shell repulsion (**35**) that the distorted π ensemble can offer.

It is obviously required of a dienophile that anti-Alder approach be operative to avoid differential steric control. With highly reactive dienophiles such as triazolinediones, the early timing of the transition states may depend heavily on favorable secondary orbital overlap and the Alder arrangement (**36** and **37**) necessary to its realization.[3]



36 **37**

Under these circumstances, steric contributions from the norbornyl (or norbornenyl) moiety are likely to override the more subtle electronic features of this unusual cyclopentadiene. Our experimental findings are in full agreement with such arguments.[25o]

In tropone, the bonding centers for [6 + 4] cycloaddition reside at distances significantly greater than those present in the usual dienophiles. As a result, it can be expected that the effects operative in **34** and **35** will be reversed since the relevant filled orbitals will now interact more intensely in antibonding fashion during below-plane approach (see **38** and **39**). This resultant preference for above-plane

38 **39**

π-facial selectivity should also occur during [3 + 4] cycloaddition of oxyallyl cations to **14**. The relevant experimental criteria have been successfully applied in a companion study.[1,19a]

Brown and Houk have hypothesized that the stereoselectivity of Diels–Alder reactions involving **14** are controlled instead by torsional and steric factors.[34] The suitability of their model has been weakened by recent X-ray crystallographic studies disclosing that major hybridization changes at the norbornyl apical center make no impact on bridgehead C–H angle deformation.[39] Nonetheless, the resulting long-range through-bond effects of these structural alterations *significantly* perturb the stereoselectivity of dienophile capture.[25q,40]

Interestingly, Brown and Houk also believe that the torsional effects invoked by them for control of π-facial stereoselective capture of **14** by alkenes and alkynes no longer operate in tropone (and oxyallyl cation) cycloadditions.[34] Instead, steric effects alone are thought to be the controlling element. It is more difficult to discount preferential reaction via transition-state **29** because of diminished steric involvement of the carbonyl group. Suitable modeling of both stereochemical options must be carried out to gain a better perspective of prevailing interactions. Perhaps relevant to this question are select metal complexation studies involving **14** wherein its top face appears to offer less steric congestion.[41] Therefore, the present undertaking may not constitute as crystal clear a test of stereoelectronic theory as we had originally hoped. More specifically informative is the remarkably contrasting course of [4 + 2] and [3 + 4] cycloadditions to **14**, which reactions operate in modes fully consistent with the notion that orbital tilting within isodicyclopentadiene is stereochemically determinative.

Experimental Section

Thermal Addition of Tropone to 14. A. Room Temperature. Equimolar amounts (5 mmol) of **14** and tropone were dissolved in dry benzene (10 mL) and stirred magnetically for 9 days at room temperature. The solvent was removed in vacuo, and 1.0 g of the residue was subjected to MPLC on silica gel (elution with 5% ethyl acetate in petroleum ether). There was isolated a total of 740 mg (74%) of purified products. These consisted of **16** (7.6%), **17** (37.4%), **18** (5%), and unreacted isodicyclopentadiene (24%).

16: colorless crystalline solid; mp 112 °C (from methanol–water); 300-MHz ^{1}H NMR ($CDCl_3$) δ 6.04–6.00 (m, 2 H), 5.78–5.72 (m, 2 H), 3.24–3.21 (m, 2 H), 3.10–3.07 (m, 2 H), 2.91 (br s, 2 H), 2.10 (d, J = 11 Hz, 1 H), 1.65–1.46 (m, 4 H), 1.17 (d, J = 8 Hz, 1 H), 0.86 (dd, J = 7.5 and 2.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) 208.89 (s), 152.35 (s), 129.36 (d), 126.61 (d), 56.60 (d), 52.06 (t), 47.97 (d), 41.97 (d), 36.67 (t), 25.81 (t) ppm.

Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.65; H, 7.70.

17: colorless crystalline solid; mp 105.5–107 °C (from methanol–water); 300-MHz ^{1}H NMR ($CDCl_3$) δ 6.01–5.96 (m, 2 H), 5.76–5.69 (m, 2 H), 3.37–3.34 (m, 2 H), 2.97–2.95 (m, 2 H), 2.81 (br s, 2 H), 2.32 (d, J = 12 Hz, 1 H), 1.78–1.73 (m, 2 H), 1.61–1.51 (m, 2 H), 1.32 (d, J = 12 Hz, 1 H), 1.13 (dd, J = 7 and 2.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) 209.21 (s), 154.08 (s), 128.97 (d), 126.55 (d), 58.26 (d), 53.60 (t), 46.89 (d), 40.76 (d), 39.35 (t), 26.32 (t) ppm; mass spectrum, m/z calcd (M^+) 238.1358, found 238.1361.

Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.56; H, 7.69.

18: light tan oil; 300-MHz ^{1}H NMR ($CDCl_3$) δ 6.00–5.93 (m, 2 H), 5.73–5.67 (m, 2 H), 5.36 (d, J = 3 Hz, 1 H), 3.35–3.32 (m, 1 H), 3.30–3.26 (m, 1 H), 3.22–3.19 (m, 1 H), 2.77 (d, J = 3 Hz, 1 H), 2.21–2.14 (m, 3 H), 1.80–1.67 (m, 1 H), 1.65–1.49 (m, 4 H), 1.21 (m, 1 H); ^{13}C NMR ($CDCl_3$) 208.70, 165.83, 128.65, 127.38,

(39) Gallucci, J. C.; Kravetz, T. M.; Green, K. E.; Paquette, L. A. *J. Am. Chem. Soc.*, in press.

(40) Paquette, L. A.; Kravetz, T. M.; Hsu, L.-Y. *J. Am. Chem. Soc.*, in press.

(41) Paquette, L. A.; Schirch, P.; Hathaway, S. J.; Gallucci, J. C., unpublished results.

126.93, 126.42, 118.50, 65.80, 60.69, 58.13, 54.81, 41.52, 40.88, 38.84, 35.90, 34.62, 22.93 ppm; mass spectrum, m/z calcd (M^+) 238.1358, found 238.1360.

B. Refluxing Benzene. Equimolar amounts (5 mmol) of **14** and tropone were combined in dry benzene (10 mL), and this solution was heated at reflux until all the ketone had reacted (51 h). The solvent was removed in vacuo, and the brown oil was subjected to MPLC on silica gel (elution with 5% ethyl acetate in petroleum ether). There was isolated 60 mg (5%) of **16** and 210 mg (18%) of **18**.

Hydrogenation of 18. The oily ketone was hydrogenated over 10% Pd on carbon in ethyl acetate solution at 53 psig for 24 h. The mixture was filtered through Celite, and the filtrate was evaporated. The residue was subjected to MPLC on silica gel (elution with 5% ethyl acetate in petroleum ether). Three crystalline fractions were obtained in a 42:24:34 ratio. The two major components proved to be saturated degradation products, which were not further identified. The minor compound, a colorless crystalline solid, mp 111.5–112 °C (from ether), proved to be **19** (X-ray analysis): mass spectrum, m/z calcd (M^+) 244.1827, found 244.1831.

Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: 83.53; H, 9.96.

Thermal Addition of 2-Methyltropone to 14. Equimolar amounts (5 mmol) of **14** and 2-methyltropone were dissolved in benzene (10 mL), and the solution was heated at the reflux temperature for 6 days. The solvent was removed in vacuo, and the residue was separated into its components by double MPLC on silica gel (elution with 5% ethyl acetate in petroleum ether). Unreacted **14** was recovered to the extent of 68%. The only detectable adduct (**20**) was obtained in 81% yield (corrected for recovered **14**) as a colorless crystalline solid: mp 114–116 °C; 300-MHz ^1H NMR ($CDCl_3$) δ 6.27 (m, 2 H), 5.89 (t, J = 8 Hz, 1 H), 5.42–5.16 (m, 2 H), 3.52 (d, J = 7 Hz, 1 H), 2.80–2.77 (m, 2 H), 2.60 (br s, 1 H), 2.06 (br s, 1 H), 1.77 (s, 4 H), 1.31–1.11 (m, 6 H); ^{13}C NMR ($CDCl_3$) 197.56, 147.51, 138.82, 136.07, 135.82, 132.24, 129.05, 63.70, 57.56, 56.09, 53.92, 47.85, 40.95, 39.49, 39.17, 24.60, 17.96, 15.28 ppm; mass spectrum, m/z calcd (M^+) 252.1514, found 252.1485.

Thermal Addition of 2-Methoxytropone to 14. Equimolar amounts (5 mmol) of **14** and 2-methoxytropone were dissolved in benzene (10 mL), and the solution was heated at reflux for 6 days. Chromatography of the evaporated reaction mixture in the predescribed manner returned 56% of unreacted **14**. The adducts **21** (3%) and **22** (1%) were subsequently eluted.

21: colorless oil; 300-MHz ^1H NMR ($CDCl_3$) δ 7.09 (dd, J = 9 and 8 Hz, 1 H), 6.36 (dd, J = 9 and 7.5 Hz, 1 H), 6.04 (d, J = 11 Hz, 1 H), 5.88 (d, J = 11 Hz, 1 H), 5.76–5.74 (m, 1 H), 5.68–5.66 (m, 1 H), 3.57 (s, 3 H), 3.39 (m, 1 H), 3.24 (br s, 1 H), 2.35 (br s, 1 H), 2.15 (br s, 1 H), 1.92 (d, J = 10 Hz, 1 H), 1.44–1.23 (m, 3 H), 0.89–0.84 (m, 2 H); ^{13}C NMR ($CDCl_3$) 195.39, 153.63, 136.58, 133.70, 131.47, 131.15, 128.40, 61.76, 60.37, 53.85, 53.40, 46.81, 45.42, 39.73, 38.33, 24.79, 24.27 (one C not observed) ppm; mass spectrum, m/z calcd (M^+) 268.1463, found 268.1504.

22: colorless oil; 300-MHz ^1H NMR ($CDCl_3$) δ 6.03–5.96 (m, 2 H), 5.77–5.73 (m, 2 H), 5.38 (d, J = 3 Hz, 1 H), 3.61 (s, 3 H), 3.28 (m, 1 H), 3.07 (m, 1 H), 2.80 (m, 1 H), 2.5–1.2 (series of m, 9 H); mass spectrum, m/z calcd (M^+) 268.1463, found 268.1472.

Thermal Addition of Tropone to 23a. Equimolar amounts (5 mmol) of **23a** and tropone were heated together at reflux in dry benzene (10 mL) for 4 days under a nitrogen atmosphere. Following the predescribed workup and chromatography, 65% of unreacted **23a** was recovered and 6% of **24** was obtained: white crystalline solid; mp 136 °C (from methanol–water); 300-MHz ^1H NMR ($CDCl_3$) δ 7.13 (dd, J = 11 and 8 Hz, 1 H), 6.23 (t, J = 8 Hz, 1 H), 6.03 (t, J = 8 Hz, 1 H), 5.71 (dd, J = 11 and 2 Hz, 1 H), 3.44–3.36 (m, 2 H), 3.30 (d, J = 10 Hz, 1 H), 2.69 (d, J = 18 Hz, 2 H), 2.60 (d, J = 10 Hz, 1 H), 1.77–1.46 (m, 9 H), 1.40–1.37 (m, 1 H), 1.33–1.25 (m, 1 H), 1.22–1.18 (m, 1 H), 1.03–0.96 (m, 2 H); ^{13}C NMR ($CDCl_3$) 198.16, 154.08, 147.44, 136.32, 129.55, 126.10, 56.53, 54.04, 51.30, 49.00, 41.20, 40.88, 39.99, 39.48, 34.11, 27.40, 25.87, 24.34, 23.83, 23.51 (one C not observed) ppm.

Anal. Calcd for $C_{21}H_{24}O$: C, 86.26; H, 8.27. Found: C, 85.64; H, 8.35.

Thermal Addition of Tropone to 23b. Equimolar amounts (5 mmol) of **23b** and tropone were heated together at reflux in dry benzene (10 mL) for 6 days under a nitrogen atmosphere. Following the predescribed workup and chromatography, there was isolated 50 mg of **25**, 13 mg of **26**, and 13 mg of **27**.

25: 300-MHz ^1H NMR ($CDCl_3$) δ 7.16 (dd, J = 9 and 7 Hz, 1 H), 6.37 (t, J = 8 Hz, 1 H), 6.08 (t, J = 8 Hz, 1 H), 5.73 (dd, J = 11 and 1 Hz, 1 H), 3.45–3.37 (m, 2 H), 3.27 (d, J = 8 Hz, 1 H), 2.77–2.75 (m, 2 H), 2.46 (br s, 1 H), 1.74–0.45 (series of m, 10 H); ^{13}C NMR ($CDCl_3$) 198.00, 154.34, 148.27, 136.97, 129.68, 128.41, 126.23, 65.87, 57.05, 50.92, 50.28, 49.77, 41.02, 39.36, 26.77, 26.33, 15.28, 12.91, 9.14 ppm; mass spectrum, m/z calcd (M^+) 264.1514, found 264.1513.

26: colorless oil; 300-MHz ^1H NMR ($CDCl_3$) δ 6.99 (dd, J = 11 and 8 Hz, 1 H), 6.41 (t, J = 7 Hz, 1 H), 6.02 (t, J = 7 Hz, 1 H), 5.72 (dd, J = 9 and 2 Hz, 1 H), 3.56 (d, J = 9 Hz, 1 H), 3.20 (d, J = 9 Hz, 1 H), 3.00–2.95 (m, 2 H), 2.78 (br s, 1 H), 2.40 (br s, 1 H), 1.69–0.42 (series of m, 10 H); ^{13}C NMR ($CDCl_3$) 169.97, 169.65, 153.26, 135.84, 129.92, 128.36, 127.38, 65.88, 57.68, 55.80, 50.34, 44.36, 39.28, 39.15, 26.74, 26.35, 15.23, 12.50, 9.77 ppm; mass spectrum, m/z calcd (M^+) 264.1514, found 264.1517.

27: colorless oil; 300-MHz ^1H NMR ($CDCl_3$) δ 5.74–5.66 (m, 2 H), 5.36 (d, J = 3 Hz, 1 H), 3.36–3.18 (m, 3 H), 2.76 (d, J = 3 Hz, 1 H), 2.21–2.14 (m, 3 H), 1.80–1.20 (series of m, 8 H); ^{13}C NMR ($CDCl_3$) 208.89, 165.96, 128.72, 127.50, 127.06, 126.55, 118.56, 112.43, 65.86, 60.75, 58.19, 54.87, 41.59, 41.20, 41.01, 38.90, 36.03, 34.69, 23.00 ppm; mass spectrum, m/z calcd (M^+) 264.1514, found 264.1514.

Acknowledgment. We thank the National Institutes of Health for support of this research program through Grant CA-12115.