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SELECTIVE TRAPPING OF REARRANGED SPIROCYCLIC ISODICYCLOPENTADIENES BY TROPONE[1]

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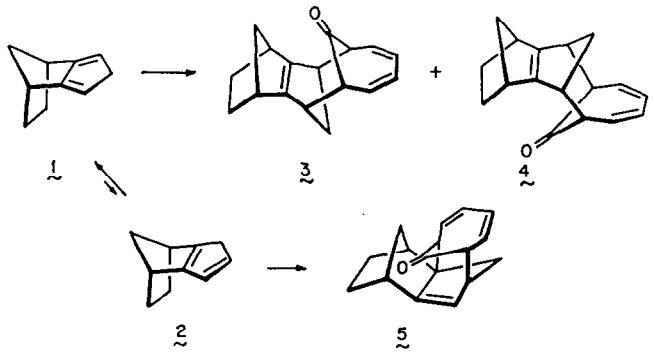
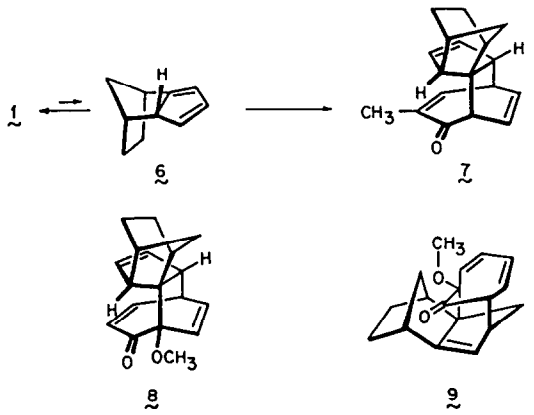
Summary: The unparalleled substituent-dependent regulation of the course of cycloaddition reactions between isodicyclopentadienes and tropones is described.

[6+4] and [3+4] cycloadditions to isodicyclopentadiene (1) are now recognized to proceed with predominant exo face selectivity,[3] in contrast to Diels-Alder reactions which normally occur from the endo face.[4] A showcase example is the condensation with tropone (C_6H_6, RT, 9 days) that leads predominantly to 3 (71%) and 4 (15%). The companion formation of 5 (10%) arises from



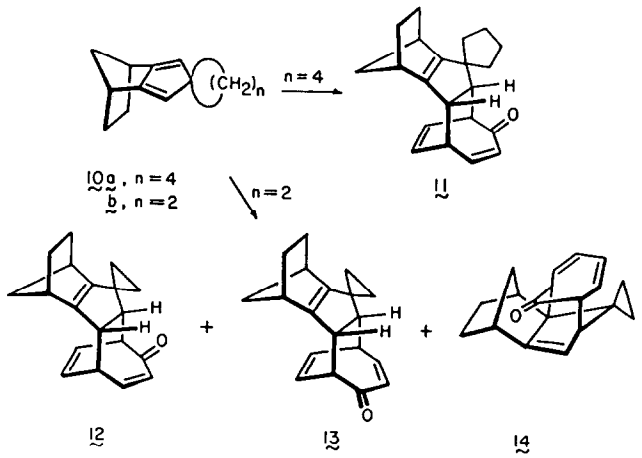
[6+4] capture of the [1,5] hydrogen shifted diene isomer 2. Since the concentration of 2 at 20°C is known to be very low,[5] its relative reactivity toward tropone must be greater than that of 1. This conclusion is supported by results which materialize at higher temperatures where the 1 ⇄ 2 interconversion rate is accelerated. For example, 5 constitutes the major product (78%) in refluxing benzene.[6,7]

Past experimental studies have shown the intermolecular tropone-cyclopentadiene reaction to be sensitive to steric factors present in either reaction partner. The present system is no exception. Thus, heating 1 with 2-methyltropone in refluxing benzene for 6 days provided 7 as the only detectable adduct. The structure and stereochemistry of this ketone were established by X-ray analysis (Figure 1). Its characterization requires that 6 be the reactive diene partner,



with [4+2] cycloaddition to the methylenenorbornane double bond proceeding in anti-Alder fashion. Under identical conditions, 2-methoxytropone gave rise to 8 (75%) and 9 (25%). The obvious reversal in regioselectivity is consistent with expectations based on molecular orbital considerations.[8] Structural assignments to this pair of adducts were made on the basis of detailed ^{1}H NMR comparisons with the spectra of 7 and 5, respectively.

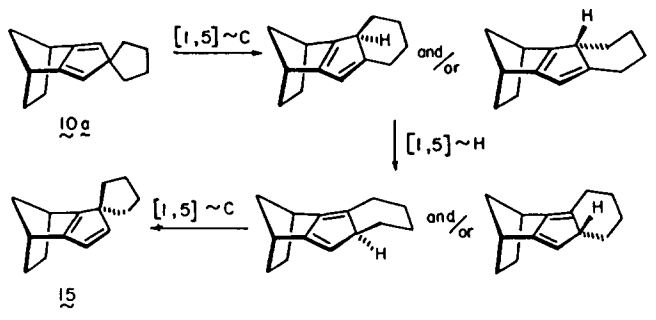
Additional intriguing results were encountered when the spirocyclic derivatives 10a and 10b[9] were heated to 80°C with tropone (C_6H_6, 4 and 6 days, respectively). In the first instance, a single product was isolated following chromatography and identified by X-ray analysis as 11



(Figure 2). The relative orientation of the carbonyl group and spirocyclopentane ring is noteworthy.[10] With 10b, the isomeric products 12 (66%), 13 (17%), and 14 (17%) were formed. Knowledge of the ^{1}H NMR spectra of 5 and 11 proved invaluable in deducing the carbon skeletons of these molecules. The syn/anti distinction between 12 and 13 was arrived at from chemical shift considerations.[10]

These findings signal that 10a and 10b are not particularly reactive toward tropone. More significantly, the adduct structures reveal that extensive carbon and hydrogen [1,5] sigmatropy has occurred to gain access to isomer 15 (Scheme I). The closest literature analogies of which we are aware are the thermal interconversion of 4- and 5-methylspiro[2.4]hepta-4,6-dienes at 240-270°C,[11] and gas phase isomerization of *cis*- and *trans*-6,9-dimethylspiro[4.4]-nona-1,3-diene at 230-280°C.[12] However, no isomer specific trapping experiments have previously come to light. One notable feature of the cycloadditive behavior of 15 is the regioselectivity of its cycloaddition chemistry. Steric factors undoubtedly contribute to the minor involvement of its expectedly more reactive norbornene double bond.

SCHEME I



In summary, isodicyclopentadiene (1) reacts with 2-substituted tropones via its bond shift isomer 6 to give principally Diels-Alder adducts of the type 7 and 8. The involvement of 6 is particularly notable since its reactivity in the Diels-Alder reaction is recognized to be the lowest of the three isomeric dienes.[5c] Spiroalkylation of 1 as in 10 results in steric retardation of the [6+4] pathways normally available to 1. Instead, skeletal isomerization to 15 (and the corresponding spirocyclopropane) occurs as low as 80°C and precedes cycloadditive capture.[13]

REFERENCES AND NOTES

(1) Electronic Control of Stereoselectivity. 25. For Part 24, see Paquette, L. A.; Hsu, L.-Y.; Gallucci, J. C.; Korp, J. D.; Bernal, I.; Kravetz, T. M.; Hathaway, S. J. submitted for publication.

(2) Author to whom inquiries concerning the X-ray crystal structure analyses should be addressed.

(3) Paquette, L. A.; Hathaway, S. J.; Kravetz, T. M.; Hsu, L-Y. submitted for publication.

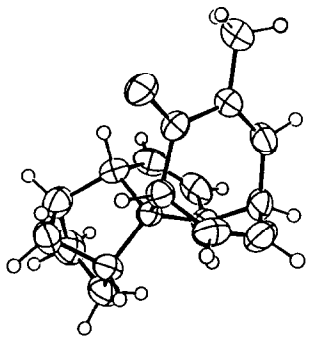


Figure 1. ORTEP diagram of 7.

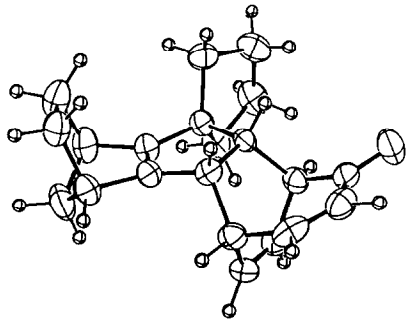


Figure 2. ORTEP diagram of 11.

Non-hydrogen atoms are drawn with 50% probability ellipsoids. Hydrogen atoms have been drawn artificially small.

(4) (a) Gleiter, R.; Paquette, L. A. *Accounts Chem. Res.* 1983, *16*, 328. (b) Paquette, L. A. in "Stereochemistry and Reactivity of Pi Systems," Watson, W. H., Ed., Verlag Chemie, 1983, 41-73.

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(6) Control experiments have shown that 3 decomposes at these more elevated temperatures. Ketones 4 and 5 do not share this property.

(7) All of the cycloadditions reported herein proceed with low to moderate conversion. The percentage values cited reflect the relative amounts of substance in the cycloadduct mixture.

(8) Uyehara, T.; Kitahara, Y. *Bull. Chem. Soc. Japan* 1979, *52*, 3355.

(9) Paquette, L. A.; Charumilind, P.; Kravetz, T. M.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* 1983, *105*, 3126.

(10) The cycloaddition of spiro[2.4]hepta-4,6-diene to tropone affords a 79:16 mixture of proximal and distal Diels-Alder adducts: Tanida, H.; Yano, H.; Ueyama, M. *Bull. Chem. Soc. Japan* 1972, *45*, 946.

(11) Clark, R. A.; Hayles, W. J.; Youngs, D. S. *J. Am. Chem. Soc.* 1975, *97*, 1966.

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(13) We thank the National Institutes of Health for support of this work through Grant CA-12115.

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