

CYCLOPROPENES AS DIENOPHILES. THE STEREOCHEMISTRY AND NUCLEAR MAGNETIC  
RESONANCE SPECTRA OF SOME DIENE ADDUCTS OF TRIPHENYLCYCLOPROPENE AND  
DIPHENYLCYCLOPROPENECARBOXYLIC ACID.\*

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The facility with which cyclopropenes undergo Diels-Alder additions with 1,3-dienes has been briefly noted in earlier reports of the reaction of cyclopropene with cyclopentadiene and 1,3-butadiene<sup>(1)</sup> and of triphenylcyclopropene and diphenylcyclopropenecarboxylic acid with tetraarylcyclopentadienones.<sup>(2)</sup> Our continuing interest in the utility of cyclopropenes in synthesis prompted the further investigation of these adductions with primary concern for the stereochemistry of reaction and the effect of structural changes on dienophilic reactivity. We now report observations that unambiguously establish the stereochemistry for the adduction of triphenylcyclopropene and diphenylcyclopropenecarboxylic acid derivatives with cyclopentadiene and 2,3-dimethylbutadiene. A remarkable effect of geminal substitution on dienophile reactivity of cyclopropenes is also described.

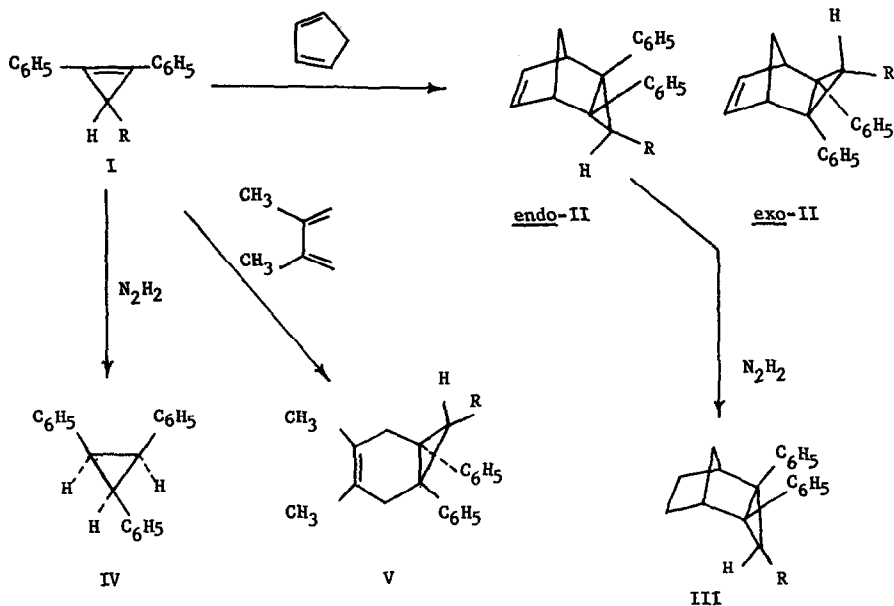
Triphenylcyclopropene (Ia) reacted readily with an excess of cyclopentadiene at room temperature to produce a single crystalline adduct

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IIa, <sup>(3)</sup> m.p. 160-162°, in high yield (70-85%). This adduct instantly decolorized bromine-carbon tetrachloride and dilute potassium permanganate solutions, and its infrared and ultraviolet spectra were in complete accord with the assigned tricyclic structure. Treatment of IIa with diimide generated in situ from potassium azodicarboxylate-acetic acid <sup>(4)</sup> in dimethoxyethane-methanol solution afforded the saturated hydrocarbon IIIa, <sup>(3)</sup> m.p. 149-150.5°. A similar reduction of triphenylcyclopropene gave cis-1,2,3-triphenylcyclopropane (IV), <sup>(3,5)</sup> m.p. 87-89°, in good yield without contamination by products of possible ring opening. In accord with the assigned all cis structure, V showed a simple n.m.r. spectrum in carbon tetrachloride with sharp singlets at 3.05 and 7.14 $\tau$  with an area ratio of 5:1 respectively. The n.m.r. spectra of IIa and IIIa are summarized in Table I.

Wiberg and Bartley <sup>(1)</sup> have shown the tricyclo[2.2.1.0<sup>2,4</sup>]oct-6-ene obtained by addition of cyclopropene with cyclopentadiene not to be identical with the isomeric hydrocarbon prepared from norbornadiene by the Simmons-Smith method. <sup>(7)</sup> Since the exo configuration is preferred for the latter on the basis of stereochemical arguments, <sup>(1,7)</sup> the configuration of the former isomer is presumed to be endo. <sup>(8)</sup> In the addition of cyclopentadiene to triphenylcyclopropene steric control of the approaching diene (vide infra) favors formation of either endo-IIa or exo-IIa, and only these isomers need be considered for the structure of IIa. A choice between the two possibilities may be made in the n.m.r. since the lone cyclopropyl proton of endo-IIa should be strongly shielded by the double bond and accordingly shifted to a higher field compared to that for the same proton of the saturated adduct IIIa. Table I reveals a shielding of 0.5 p.p.m. for the cyclopropyl proton of IIa clearly establishing the endo configuration for this adduct.



- a; R = C<sub>6</sub>H<sub>5</sub>  
 b; R = CO<sub>2</sub>CH<sub>3</sub>  
 c; R = CO<sub>2</sub>H

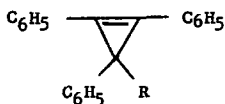
The addition of methyl 2,3-diphenylcycloprop-2-enecarboxylate (Ib) <sup>(9)</sup> with excess cyclopentadiene in benzene or neat solution proceeded smoothly at room temperature to yield 70-80% of a crystalline adduct I Ib, <sup>(3)</sup> m.p. 172-173°. Infrared, ultraviolet and n.m.r. (Table I) spectral data supported the tricyclic structure. Reduction with diimide as above gave the saturated adduct IIIb, <sup>(3)</sup> m.p. 101-102°. Comparison of the n.m.r. spectra of I Ib and IIIb (Table I) revealed the identical relationship for the cyclopropyl proton resonance of the unsaturated and saturated adduct

that was observed in the triphenylcyclopropene case. Thus the stereochemistry is again clearly endo.<sup>(10)</sup> Cyclopentadiene likewise added to the acid Ic to give an analogous adduct (IIc),<sup>(3)</sup> m.p. 230-231.5°, which was converted to its methyl ester by treatment with diazomethane in ether. This material melted slightly lower than IIb although the infrared and n.m.r. spectra of the two esters were virtually identical.

The reaction of triphenylcyclopropene with 2,3-dimethylbutadiene in neat solution was somewhat sluggish as expected requiring a 24 hour reflux period to produce 43% of crystalline Va,<sup>(3)</sup> m.p. 202-204°. Infrared and n.m.r. spectra indicated the material was homogeneous. The cyclopropyl proton of Va was shifted upfield in the n.m.r. as compared to the similar proton for IIIa or IV. Although the magnitude of the shift is admittedly small, its direction is consistent with possible shielding of this proton by the double bond in the syn isomer Va. The proposed structure is further supported on steric grounds by results obtained with the tetrasubstituted cyclopropenes discussed below. The similar adduction of Ib or Ic with 2,3-dimethylbutadiene required longer reflux periods to obtain somewhat lower yields of the corresponding adducts. These adducts have not as yet been fully characterized.

The stereoselectivity of the above diene reactions suggested that, for steric reasons, geminally disubstituted cyclopropenes should be very poor dienophiles. The failure of tetraphenylcyclopentadienone to react with triphenylcyclopropenyl methyl ether (VIa) under a variety of forcing conditions had been previously noted in our polyaryltropilidene studies; however, the instability of the cyclopropenyl ether at elevated temperatures prevented these experiments from being conclusive. We accordingly prepared the hydrocarbons methyltriphenylcyclopropene (VIb)<sup>(3)</sup> and tetraphenylcyclopropene (VIc)<sup>(3)</sup> from triphenylcyclopropenyl bromide<sup>(11)</sup> and the requisite

Grignard reagent and found them to be moderately stable at 150-200°C.<sup>(12)</sup> An attempt to prepare diene adducts of VIb and VIc was made using the following



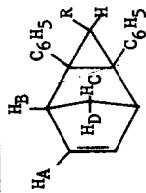
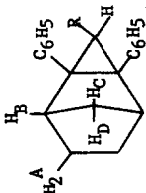
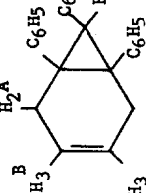
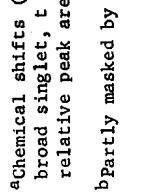

VI a; R = OCH<sub>3</sub>  
 b; R = CH<sub>3</sub>  
 c; R = C<sub>6</sub>H<sub>5</sub>

dienes and reaction conditions: (i) 2,3-dimethylbutadiene in refluxing neat solution for 7 days; (ii) tetraphenylcyclopentadienone in refluxing xylene solution for 3 days and in the solid melt at 200-235° for 1 hour; (iii) 1,4-diphenyl-2,3-benzofuran in refluxing xylene solution for 3 days.<sup>(13)</sup> No trace of adduct could be detected in any of the reactions with tetraphenylcyclopropene, and the recovery of starting materials was greater than 50% in each case. Similar results were obtained with VIb except in the reaction with the diphenylbenzofuran where an 8% yield of a crystalline adduct,<sup>(3)</sup> m.p. 270.5-272.5°, was obtained. The structure of this adduct is still under investigation.

The highly stringent conditions used in these attempted adductions dramatizes the extreme steric sensitivity of Diels-Alder reactions in the cyclopropene series. Certainly the argument of steric control of approaching diene should be an extremely valid one in assessing the stereochemistry of diene additions to cyclopropenes.<sup>(14)</sup>

TABLE I

Proton Magnetic Resonance Spectra of Adducts at 60 Mc.<sup>a</sup>

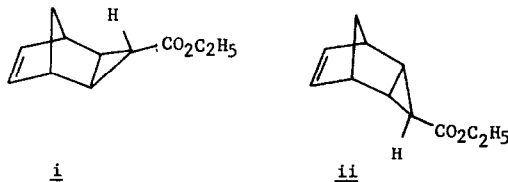
A		B	C	D	Cyclopropyl	Aromatic
	IIa; R = C <sub>6</sub> H <sub>5</sub>	3.77 (m) <sup>b</sup>	7.06 (m)	7.26 (dm)	8.23 (dm)	7.53(s) 2.92(m), 3.23(m), 3.77(m)
	IIb; R = CO <sub>2</sub> CH <sub>3</sub>	3.81 (t)	7.00 (m)	7.38 (dm)	8.32 (dm)	7.72(s) 2.74(m)
	IIIa; R = C <sub>6</sub> H <sub>5</sub>	8.40 (bs)	7.58 (bs)	7.35 (dm)	8.54 (dm)	7.03(s) 2.88(m), 3.32(m), 3.78(m)
	IIIb; R = CO <sub>2</sub> CH <sub>3</sub>	8.50 (bs)	7.54 (bs)	7.47 (dm)	8.63 (dm)	7.27(s) 2.81(m)
	Va	7.34 (m)	8.32 (s)			7.21(s) 2.88(m), 3.04(m), 3.62(m)

<sup>a</sup>Chemical shifts (in  $\tau$ ) measured in CCl<sub>4</sub> relative to tetramethylsilane (10.00  $\tau$ ); s = singlet, bs = broad singlet, t = triplet, m = unresolved multiplet, dm = a doublet of unresolved multiplets; relative peak areas are in accord with assigned structures.

<sup>b</sup>Partly masked by aromatic peak.

## REFERENCES

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2. M. A. Battiste, Chem. Ind. (London), 550 (1961); J. Am. Chem. Soc., 85, 2175 (1963).
3. Satisfactory carbon and hydrogen analyses were obtained for all new compounds prepared in this work.
4. E. E. van Tamelen, R. S. Dewey and R. J. Timmons, J. Am. Chem. Soc., 83, 3725 (1961).
5. A similar preparation of IV by catalytic reduction of I over Lindlar catalyst has been recently reported by R. Breslow and P. Dowd, J. Am. Chem. Soc., 85, 2729 (1963).
6. The utility of diimide in the reduction of unsaturated cyclopropane derivatives (including cyclopropenes) and the remarkable effect of steric bulk on these reductions will be discussed in a separate paper.
7. H. E. Simmons and R. D. Smith, J. Am. Chem. Soc., 81, 4256 (1959); see also H. E. Simmons, E. P. Blanchard and R. D. Smith, ibid., 86, 1347 (1964).
8. In unpublished work Wiberg and coworkers have established the endo configuration for their hydrocarbon by catalytic hydrogenation to endo-2-methylnorbornane; K. B. Wiberg, private communication.
9. R. Breslow, R. Winter, and M. Battiste, J. Org. Chem., 24, 415 (1959).
10. R. R. Sauers and P. E. Sonnet, Chem. Ind. (London), 786 (1963), report the isolation of tricyclooctene esters i and ii from the condensation of ethyl diazoacetate with norbornadiene. Structure assignment was largely based on an observed upfield shift in the n.m.r. for the vinyl hydrogens of ii relative to i. The shift was



attributed to induced shielding of the vinyl protons in ii by the ring current of the endo cyclopropyl group. In the same article the authors report the signal for the lone cyclopropyl proton of i and ii at 7.52 and 8.66  $\tau$  respectively without comment. In view of our n.m.r. results with adducts IIa and IIb it would seem that the large upfield shift for the cyclopropyl proton of ii is of equal or perhaps

greater pertinence to the assignment of the endo configuration to this isomer. Nevertheless the structure assignment of Sauers and Sonnet is well corroborated.

11. R. Breslow and H. W. Chang, J. Am. Chem. Soc., 83, 2367 (1961).
12. Recently, other workers have reported the preparation of these two cyclopropene hydrocarbons subsequent to our preparation and initial studies. Breslow and Dowd (ref. 5) prepared VIb by the identical Grignard method whereas J. A. Berson and M. Pomerantz (J. Am. Chem. Soc., 86, 3896 (1964)) obtained VIc from a novel reaction of benzyne with triphenylcyclopropene.
13. In contrast to these conditions, at room temperature in benzene solution triphenylcyclopropene affords a 94% yield of a crystalline adduct with 1,4-diphenyl-2,3-benzofuran after 4 hours.
14. This argument has been recently used by G. L. Closs, L. E. Closs, and W. A. Boll, J. Am. Chem. Soc., 85, 3796 (1963), in assigning endo stereochemistry to the adduct obtained from cyclopentadiene and 3-methylcyclopropene. These authors also note the failure of 3,3-dimethylcyclopropene to add to cyclopentadiene at elevated temperatures although reaction conditions and recovery of cyclopropene were not reported.