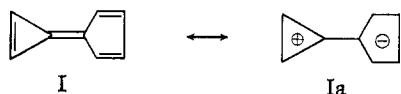


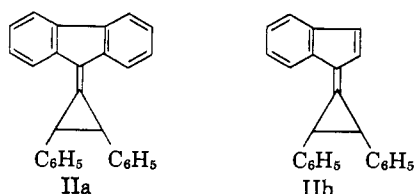
Annulated Cyclopropenylidenecyclopentadienes

Sir:

Although the area of nonbenzenoid aromatic hydrocarbons has been quite extensively explored in recent years,<sup>1</sup> to date no example of a cyclopropenylidenecyclopentadiene<sup>2</sup> (I) has been reported. This type of hydrocarbon would be especially notable<sup>3</sup> because a significant contribution of resonance form Ia would be expected as a result of the well-known tendency of unsaturated three- and five-membered rings to support positive and negative charges, respectively.<sup>3</sup>

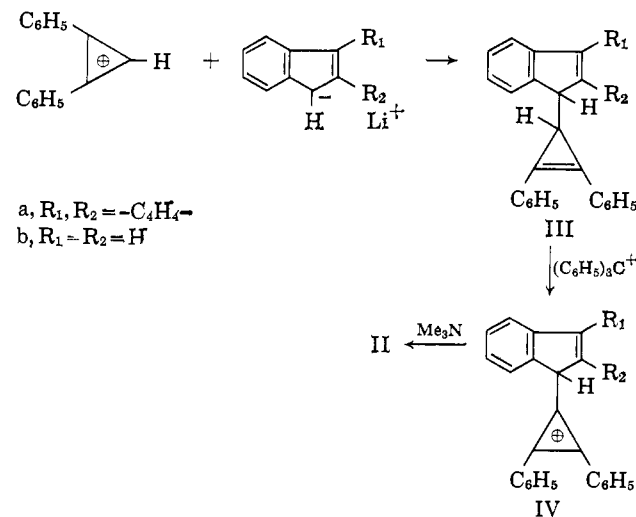


The purpose of this communication is to report the synthesis and some of the properties of the two annulated cyclopropenylidenecyclopentadienes IIa and IIb.



The method of synthesis of both hydrocarbons is outlined in Scheme I. The cation-anion additions<sup>4</sup> were

Scheme I



conducted in ether at  $-78^\circ$  to give 31 and 73% yields of IIIa (m.p.  $98-99^\circ$  from EtOH)<sup>5,6</sup> and IIIb (m.p.  $170.5-171.5^\circ$  from benzene-pentane),<sup>5,6</sup> respectively.

- (1) For a recent review with ample references, see K. Hafner, *Angew. Chem. Intern. Ed. Engl.*, **3**, 165 (1964).
- (2) H. Prinzbach (*ibid.*, **3**, 319 (1964)) has recently coined the trivial name calicene for this type of ring system.
- (3) Cf. J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952).
- (4) See R. Breslow, H. Höve, and H. N. Chang, *ibid.*, **84**, 3168 (1962).
- (5) Spectral and physical properties were all consistent with the proposed structures.
- (6) These compounds gave correct analyses.

Hydride abstractions were effected with triphenylmethyl fluoroborate in methylene chloride at  $0^\circ$  to give triphenylmethane and nearly colorless perchlorate salts<sup>7</sup> of IVa and IVb. Proton abstractions were effected with trimethylamine in ether-methylene chloride mixtures at  $0^\circ$  to give deep red solutions of the cyclopropenylidenecyclopentadienes. Evaporation of the solvent gave IIa (m.p.  $160-161^\circ$  from benzene-cyclohexane. *Anal.* Found: C, 94.51; H, 5.16; mol. wt. by differential vapor pressure osmometer  $355 \pm 13$ ; single spot on t.l.c.) and IIb as an impure material (see below).

A net dehydrogenation in going to IIa was confirmed by the n.m.r. spectrum which showed a loss of the two aliphatic hydrogen resonances at  $\tau$  5.63 (broadened doublet) and 7.12 (sharp doublet) that were present in the spectrum of IIIa.

The infrared spectrum not only confirmed loss of the aliphatic hydrogens (disappearance of a peak at  $3.41 \mu$ ) but also presented strong evidence for the methylenecyclopropene type of structure. Whereas the fluorenylcyclopropene IIIa showed a rather weak cyclopropene absorption at  $5.55 \mu$  and nothing but typical aromatic absorption between 6.0 and  $6.8 \mu$  the cyclopropenylidenecyclopentadiene IIa showed a strong doublet with maxima at 5.42 and  $5.56 \mu$  and a very intense peak (as intense as any peak in the spectrum) at  $6.43 \mu$ . Intensification of absorption and splitting into a doublet in the  $5.5 \mu$  region is a property that we have found in other methylenecyclopropenes. An intense absorption about  $6.5 \mu$  also appears to be characteristic of methylenecyclopropenes.<sup>7,8</sup>

The effect of solvent on the ultraviolet and visible spectrum of IIa [ $\lambda_{max}$  acetonitrile (in  $m\mu$ ): 238 sh (55,100), 242 (59,500), 262 sh (30,700), 296 sh (10,760), 363 sh (29,900), 375 (31,800), and 437 (4000)] furnished strong evidence for a significant contribution of an ionic form such as Ia to the ground state of this cyclopropenylidenecyclopentadiene. The most notable solvent effect was on the long wave-length absorption where it was found that a shift to longer wave lengths accompanied a decrease in solvent polarity. For example, a change from acetonitrile to cyclohexane caused a bathochromic shift of 41  $m\mu$ . A solvent effect of this type can only be interpreted as resulting from a transition to an excited state that is less polar (or, possibly, of reversed polarity) than the ground state.<sup>9</sup> This leads to the unavoidable conclusion that the ground state of IIa must be dipolar. Evaluation of the degree of polarity must await dipole moment studies. The effect of fluoroboric acid on the spectrum of IIa [ $\lambda_{max}$  acetonitrile

- (7) A. S. Kende and P. T. Izzo, *J. Am. Chem. Soc.*, **86**, 3587 (1964); E. D. Bergmann and I. Agranat, *ibid.*, **86**, 3587 (1964); M. A. Battiste, *ibid.*, **86**, 942 (1964); W. M. Jones and J. M. Denham, *ibid.*, **86**, 944 (1964).
- (8) If the absorption around  $6.5 \mu$  is due to C=C stretch of the exocyclic double bond, its intensity (see K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p. 3) in the cyclopropenylidenecyclopentadiene system would indicate appreciable contribution of an ionic resonance form to the ground state. Unfortunately, the origin of this peak must await assignment by a qualified spectroscopist.
- (9) N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954); also see E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).

(in  $m\mu$ ) 252 (33,500), 262 (31,600), 273 sh (29,200), 296 (31,800), and 309 (31,600)] further confirmed the suggested structure.

In the areas significant to structure assignment, the n.m.r. and infrared spectra of a solution of the monoannulated cyclopropenyldenecyclopentadiene I**b** were quite similar to the diannulated material I**a**. The ultraviolet and visible spectra of I**a** and I**b** were also quite similar. Perhaps the most interesting difference was in the position of the long wave-length maximum which appeared in cyclohexane at 12  $m\mu$  longer wave length in the monoannulated material I**b** than in its diannulated analog I**a**. This effect of annelation is analogous to that in the sesquifulvalene system.<sup>10</sup> The most pronounced difference between I**a** and I**b** appeared in their stabilities. Although I**b** was reasonably stable in solution under an inert atmosphere, it rapidly decomposed when it was subjected to air or evaporated to dryness. Low-temperature precipitation also led to its decomposition, and we were unable to isolate this material as a pure substance.

Finally, attempts to obtain the nonannulated diphenylcyclopropenyldenecyclopentadiene failed. The necessary cyclopentadienylcyclopropene precursor was isolated and characterized as its maleic anhydride adduct (m.p. 148.5–149.5 from benzene–cyclohexene)<sup>5,6</sup> but we have not yet succeeded in the hydride abstraction step.

**Acknowledgment.** The authors are most grateful to the U. S. Army Research Office (Durham) and to the National Science Foundation for their generous support of this work. They are also especially appreciative of the many helpful discussions of this work with Dr. Merle A. Battiste.

(10) H. Prinzbach and W. Rosswog, *Tetrahedron Letters*, 1212 (1963).

(11) Alfred P. Sloan Fellow.

(12) Danforth Fellow, 1960–1964.

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## The Synthesis of Calicene (Cyclopropenyldenecyclopentadiene) Derivatives

Sir:

The calicene<sup>1</sup> nucleus (I), like its vinylogous counterpart sesquifulvalene (II), is predicted to possess the stability associated with high delocalization energy<sup>2</sup> and a closed-shell configuration. Whereas a few sesquifulvalene derivatives have recently been prepared,<sup>3,4</sup> the highly strained calicene system has defied synthesis to date. The recent observation that malononitrile undergoes condensation with di-*n*-propylcyclopropenone to give a substituted triafulvene<sup>5</sup> has prompted us to explore the use of suitable derivatives of cyclopenta-

(1) Calicene (*calix*, cup) is the evocative trivial name assigned the cyclopropenyldenecyclopentadiene system by H. Prinzbach, *Angew. Chem.*, **76**, 235 (1964).

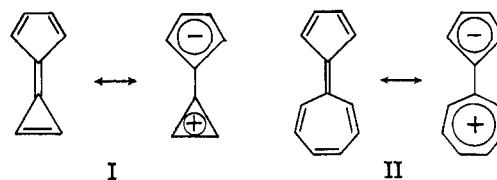
(2) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952), calculate a Hückel DE value of 0.37 $\beta$  per  $\pi$ -electron for calicene, as compared with 0.33 $\beta$  per  $\pi$ -electron for sesquifulvalene or benzene.

(3) H. Prinzbach and D. Seip, *Angew. Chem.*, **73**, 169 (1961).

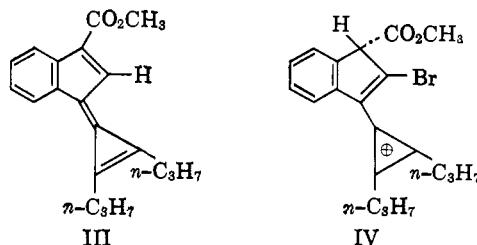
(4) H. Prinzbach and W. Rosswog, *Tetrahedron Letters*, **19**, 1217 (1963).

(5) E. D. Bergmann and I. Agrat, *J. Am. Chem. Soc.*, **86**, 3587 (1964); A. S. Kende and P. T. Izzo, *ibid.*, **86**, 3587 (1964).

diene in this condensation. The applications of this principle to the synthesis of a benzocalicene ester and a calicene diketone are described.



Reaction of freshly distilled methyl 1-indenecarboxylate with di-*n*-propylcyclopropenone at 120° in acetic anhydride under nitrogen led on cooling to a crystalline condensation product, m.p. 157–158°, in 15% yield. Analytical data (*Anal.* Found: C, 81.71; H, 7.88; mol. wt. [vapor-pressure thermistor], 293) and spectroscopic characterization [infrared:  $\lambda_{\text{max}}^{\text{KBr}}$  (in  $\mu$ ): 5.36, 5.91, 6.25, 6.49, and 6.68; ultraviolet:  $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$  (in  $m\mu$ ) (log  $\epsilon$ ) 363 (4.56), 275 (4.09), sh 248 (4.41), and 234 (4.55)] of this product pointed to the benzocalicene structure III. The 60-Mc. nuclear magnetic resonance (n.m.r.) spectrum of III in  $\text{CDCl}_3$  showed two nearly equivalent propyl groups; a methoxyl singlet at  $\tau$  6.12 and, standing amid the 4-proton benzenoid multiplet, a sharp singlet at  $\tau$  2.43 corresponding to the single vinyl proton. Consistent with the high reactivity toward electrophiles predicted<sup>6</sup> for the calicene system, the ester III reacted “instantaneously” with bromine or (preferably) N-bromosuccinimide in chloroform at room temperature to give a crystalline *monosubstitution* product, m.p. 189–190° (*Anal.* Found: Br, 21.18), having an infrared and ultraviolet spectrum [ $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$  (in  $m\mu$ ) (log  $\epsilon$ ) 365 (4.51), 281 (4.06), and 234 (4.57)] very similar to that of the precursor, III. This bromo derivative was too insoluble for direct n.m.r. study but did dissolve readily in trifluoroacetic acid, apparently by protonation on carbon,<sup>7</sup> to display a spectrum having in addition to the two propyls and one methoxyl group the  $\tau$  4.80 one-proton singlet and the rather narrow four-proton aromatic peak at  $\tau$  2.30 demanded by a structure such as IV.



Employment of a suitable fulvene such as V<sup>8</sup> in the condensation with di-*n*-propylcyclopropenone gave a mixture from which cream-colored needles of the dibenzoylcalicene VI, m.p. 111–112°, could be isolated by careful chromatography over silica gel. Structure VI was supported by analysis [*Anal.* Found: C, 85.58; H, 6.81; mol. wt. (vapor pressure thermistor), 420], by the characteristic acylcalicene infrared [ $\lambda_{\text{max}}^{\text{KBr}}$  (in  $\mu$ ) at 5.40, 6.14, 6.57, and 6.75], and by the n.m.r. spectrum in  $\text{CDCl}_3$  which showed, in addition to the ten benzenoid

(6) O. Chalvet, R. Daudel, and J. J. Kaufman, *J. Phys. Chem.*, **68**, 490 (1964).

(7) The analogous protonation of a methylenecyclopropene ester has been described by M. A. Battiste, *J. Am. Chem. Soc.*, **86**, 942 (1964).

(8) W. J. Linn and W. H. Sharkey, *ibid.*, **79**, 4970 (1957).