(in mμ) 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 mono-annelated cyclopropenylidenecyclopentadiene IIb were quite similar to the diannelated material IIa. The ultraviolet and visible spectra of IIa and IIb 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 mμ longer wave length in the monoannelated material IIb than in its diannelated analog IIa. This effect of annelation is analogous to that in the sesquifulvalene system.[10] The most pronounced difference between IIa and IIb appeared in their stabilities. Although IIb 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 nonannelated diphenylcyclopropenylidenecyclopentadiene failed. The necessary cyclopentadienylcyclopropene precursor was isolated and characterized as its maleic anhydride adduct (m.p. 148.5–149.5 from benzene–cyclohexene)[5,6] but we have not yet succeeded in the hydride abstraction step.

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(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 (Cyclopropenylidenecyclopentadiene) Derivatives

Sir:

The calicene[1] nucleus (I), like its vinylogous counterpart sesquifulvalene (II), is predicted to possess the stability associated with high delocalization energy[2] and a closed-shell configuration. Whereas a few sesquifulvalene derivatives have recently been prepared,[3,4] 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[5] has prompted us to explore the use of suitable derivatives of cyclopenta-

(1) Calicene (*calix,* cup) is the evocative trivial name assigned the cyclopropenylidenecyclopentadiene 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 0.37β per π-electron for calicene, as compared with 0.33β per π-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. Agranat, *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.

I   II
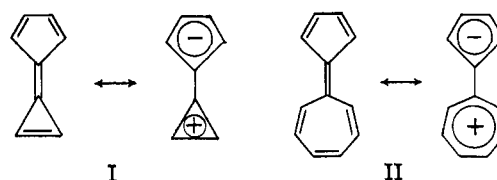
Reaction of freshly distilled methyl 1-indenecarboxylate with di-*n*-propylcyclopropenone at 120° in acetic anhydride under nitrogen led on cooling to a crystalline condensation product, m.p. 157–158°, in 15% yield. Analytical data (*Anal.* Found: C, 81.71; H, 7.88; mol. wt. [vapor-pressure thermistor], 293) and spectroscopic characterization [infrared: λ_{max}^{KBr} (in μ): 5.36, 5.91, 6.25, 6.49, and 6.68; ultraviolet: $\lambda_{max}^{CH_3OH}$ (in mμ) (log ϵ) 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 CDCl$_3$ showed two nearly equivalent propyl groups; a methoxyl singlet at τ 6.12 and, standing amid the 4-proton benzenoid multiplet, a sharp singlet at τ 2.43 corresponding to the single vinyl proton. Consistent with the high reactivity toward electrophiles predicted[6] 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 [$\lambda_{max}^{CH_3OH}$ (in mμ) (log ϵ) 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,[7] to display a spectrum having in addition to the two propyls and one methoxyl group the τ 4.80 one-proton singlet and the rather narrow four-proton aromatic peak at τ 2.30 demanded by a structure such as IV.


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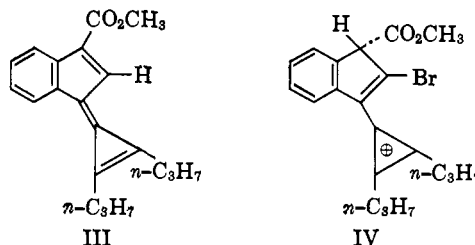
Employment of a suitable fulvene such as V[8] in the condensation with di-*n*-propylcyclopropenone gave a mixture from which cream-colored needles of the dibenzoylcalicene VI, m.p. 111–112°, could be isolated by careful chromatography over silica gel. Structure VI was supported by analysis [*Anal.* Found: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

protons and the two equivalent propyl groups, a two-proton *singlet* at τ 3.25. The ultraviolet spectrum of the diketone VI in either cyclohexane or acetonitrile showed maxima at 346 mμ (log ϵ 4.34) and 255 mμ (log ϵ 4.25), but in hydrogen-bonding solvents (*e.g.*, methanol) there was observed a moderate bathochromic shift to 361 mμ (log ϵ 4.35) and 260 mμ (log ϵ 4.32). As a vinylogous cyclopropenone the diketone VI was reversibly converted by aqueous acid to a yellow cation [λ_{max}^{12NHCl} 430 mμ (log ϵ 4.36) and 402 mμ (log ϵ 4.37)], provisionally represented as VII on the basis of its simple n.m.r. spectrum which showed a symmetrical molecule lacking new carbon-bound hydrogen. Spectrophotometric determination of the base strength of VI in aqueous hydrochloric acid (isosbestic point at 385 mμ (log ϵ 4.32)) showed that half-protonation occurred at $H_0 = -2.0 \pm 0.3$, which makes this substance slightly more basic than diphenylcyclopropenone.[9]

V VI VII
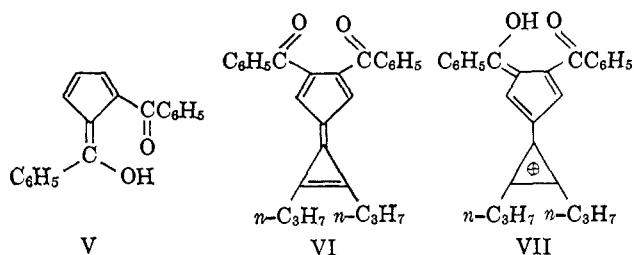
Preliminary studies indicate that the present synthesis can be extended to utilize still simpler cyclopentadiene nucleophiles. Details of this work and further observations bearing on the "aromaticity" of the calicene system will be presented shortly.

(9) Half-protonation of diphenylcyclopropenone occurs at $H_0 = -2.5 \pm 0.3$ (unpublished observations from this laboratory).

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Stereochemistry of the Eight-Coordinate Bisnitrilotriacetatozirconate(IV) Ion[1]

Sir:

Stability of the bisnitrilotriacetatozirconate(IV) ion (to be written ZrA_2^{2-}) clearly is dependent upon a mutual accommodation of the joint requirements of multidentate chelation and eight-coordination. Of the several constraints imposed upon branching glycinate ring formation which emerge from studies of ethylenediaminetetraacetato chelates,[2] we cite just two: the ring span, defined as the separation of the complexed nitrogen and oxygen atoms in the ring (or as the edge of the coordination polyhedron thereby spanned), should lie in the range 2.66 $\pm$ 0.06 Å.; and the bond angles at nitrogen should be 109.5 $\pm$ 4°. Experience further indicates that only the square (D_{4d}) antiprism and the tetragonal (D_{2d}) dodecahedron of $Mo(CN)_8^{4-}$

type are acceptable eight-coordination polyhedra.[3] For ZrA_2^{2-}, nonetheless, an apparently strong *a priori* case for quasi-cubic coordination can be put together from individually plausible considerations.

Maintenance of threefold symmetry in the disposition of the three glycinate rings branching from each nitrogen atom would lead quite naturally to the simplest possible configuration for a ZrA_2^{2-} complex—a configuration of C_{3i}-$\bar{3}$ symmetry[4] observing the required ring constraints while based upon a quasi-cubic coordination group. Chemical experience, in contrast with approximate bonding theory, would suggest very weak and, consequently, very long Zr–N bonds; a flattened octahedral ZrO_6 group would become the heart of the configuration, and neither the practical availability nor the doubtful merits of f-orbitals for bonding[5] would be of real concern.

Structure determination for the crystalline potassium salt by means of the three-dimensional X-ray analysis described briefly in the final paragraph provides an unequivocal answer to the question of coordination type. The configuration of ZrA_2^{2-}, as indicated by Figure 1, is firmly based upon the dodecahedral coordination group[3]; the symmetry of C_2-2, allowed by the pattern of ring connexities, is required in the crystal. In rather surprisingly close agreement with expectations[3] listed for the case of monodentate ligands, the Zr–O_A bonds (2.251 Å.) are significantly longer than the Zr–O_B links (2.124, 2.136 Å.), and the eight g edges (averaging 2.785 Å.) are significantly longer than the four m edges (averaging 2.62 Å.) and the two a edges (2.68 Å.). By far the largest distortion of the coordination group from an effectively higher symmetry is that produced by the extraordinarily long Zr–N bonds (2.439 Å.). (Standard deviations of 0.007–0.008 Å. for individual Zr–O and Zr–N bond lengths and 0.010–0.013 Å. for individual polyhedron edges, *i.e.*, ring spans, apply in the noncentrosymmetric crystalline arrangement.) Ring spans are 2.62, 2.68, and 2.75 Å., of which the last corresponds to a naturally long g edge of the coordination polyhedron. The observed configuration is unique among the possible stereoisomeric types in its maximal use of short ring spans. Averaged angles, with accompanying mean deviations, at nitrogen are 108.1 $\pm$ 0.4° within rings and 110.8 $\pm$ 0.1° between rings.

With the full panoply of 4d and 5sp^3 orbitals of Zr(IV) available for bonding, it is not at all apparent from present approximate theory why the interaction of Zr(IV) with amino nitrogen should be so weak. Although the hypothetical quasi-cubic configuration for ZrA_2^{2-} would seem to gain relatively by virtue of the weak Zr–N interactions, it remains definitely inferior to the dodecahedral configuration in respect to steric repulsions—a property nearly independent of the assumed bonding type. Using methods outlined earlier,[3] we estimate that it would cost the ZrA_2^{2-} ion an additional 9–10 kcal./mole in ligand repulsive energy to transform from dodecahedral to quasi-cubic coordination. With each definitive study of the mat-

(2) *Cf.* M. D. Lind, M. J. Hamor, T. A. Hamor, and J. L. Hoard, *Inorg. Chem.*, **3**, 34 (1964), and earlier papers cited therein.

(3) J. L. Hoard and J. V. Silverton, *ibid.*, **2**, 235 (1963), give complete descriptions and a critical comparison of the eight-coordination polyhedra.

(4) It is readily demonstrable that for so large a central atom the glycinate ring must be nonplanar, thus precluding the higher symmetry of D_{3d}-$\bar{3}m$.

(5) *Cf.* G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940).