control the formation of the single olefin, VII, from the dehydration of VI.

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Dimerization and Cycloadditions of Tetra-*t*-butylhexapentaene

Sir:

Di-*t*-butylpropargyl acetate (1) was prepared as a possible generator of di-*t*-butylvinylidenecarbene (2) by γ-elimination reactions.[1] Such a carbene would be expected to react with nucleophiles at the terminal carbon atom.[2] The ester 1 was prepared from the alcohol[3] by reaction with methyllithium followed by acetic anhydride.

Reactions of 1 with potassium *t*-butoxide and olefins gave moderate yields of di-*t*-butylvinylidenecyclopropanes[4] (Table I). In the absence of olefins, 1 was allowed to react with potassium *t*-butoxide to give the allenic ether 3 and the hexapentaene 4 in yields of 19 and 20%. The products probably arose from reactions of 2 with the alkoxide and acetylide ions, respectively, rather than SN2′ displacements on 1 because 3 and 4 were essentially absent in the reactions of 1 in the presence of olefins.

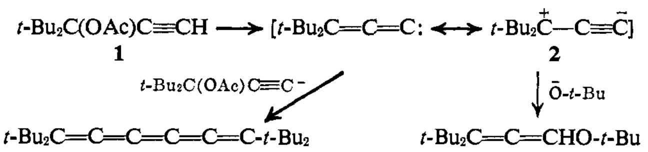
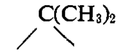
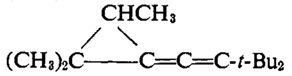
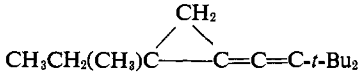
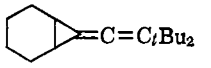
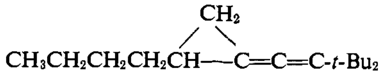
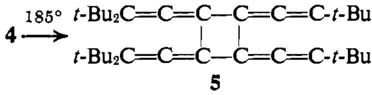


Table I. Di-*t*-butylvinylidenecyclopropanes

Olefin	Product	Bp, °C (mm)	Yield, %
$(CH_3)_2C{=}C(CH_3)_2$		Mp 69–70°	52
$(CH_3)_2C{=}CHCH_3$		48 (0.4)	10
$CH_3CH_2(CH_3)C{=}CH_2$		54 (0.5)	10
		89 (0.35)	22
$CH_3CH_2CH_2CH_2CH{=}CH_2$		75 (0.5)	22

The ether 3 had infrared absorption at 1935 and 1955 cm^{-1}, indicating the presence of the allenic system. The nmr spectrum of 3 showed absorption at δ 6.25 (vinyl hydrogen), 8.74 (alkoxy methyls), and 8.80 (*t*-butyl methyls). The intensity ratio of vinyl to methyl hydrogens was 1:28. The hexapentaene 4 had electronic absorption maxima at 237 (ϵ 185,000), 308 (28,900), and 336 mμ (33,000), in agreement with previously synthesized aliphatic hexapentaenes.[5,6] In addition, there was a weak (ϵ 870) absorption at 417 mμ which was present after repeated crystallizations and sublimations. The nmr spectrum of 4 showed a single unsplit resonance at δ 1.28. The infrared spectrum of 4 showed absorption at 2020 and 1990 cm^{-1} which may be attributed to stretching of the double bonds of the cumulative system.

The cumulene 4 was inert to oxygen at room temperature and showed no tendency to polymerize. Upon melting (185°), however, 4 dimerized in 95% yield to tetrakis(di-*t*-butylvinylidene)cyclobutane (5). The symmetry of the dimer was deduced from the single, unsplit nmr signal (δ 1.20). Structure 5 is also consistent with the infrared allene absorption at 1950 and 1925 cm^{-1} the absence of isolated or conjugated double bond absorptions, and the electronic absorption maxima at 316 (ϵ 2040), 298 (1720), 268 (13,200), 258 (16,300), and 250 mμ (15,800). The spectrum is very similar to that reported for tetramethylenecyclobutane.[7] The dimer 5 melted without decomposition at 361°. Unlike the photodimer of tetraphenylbutatriene,[8] dimer 5 has shown no tendency to revert to monomer.



5

The dimerization 4 → 5 occurred to only a slight extent in solution in decahydronaphthalene at 200°, even though 4 was completely consumed. The major product was the bisallene formed by the addition of hydrogen to the central bond of 4. This material was not obtained analytically pure. A possible explanation for the reactions of 4 is that 4 is thermally converted to a triplet which can react with solvent or with 4 to give dimer. Such a species should be reactive in other cycloaddition reactions.

At 200°, 4 added tetrafluoroethylene to give 6 in

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[1] H. D. Hartzler, *J. Am. Chem. Soc.*, **83**, 4990 (1961).

[2] Evidence has recently been presented to demonstrate that the position of attack by nucleophiles on vinylidene carbenes is markedly influenced by steric effects: G. F. Hennion and C. V. DiGiovanna, *J. Org. Chem.*, 30, 3696 (1965).

[3] W. J. Hickenbottom, A. A. Hyatt, and M. B. Sparke, *J. Chem. Soc.*, 2529 (1954).

[4] Accurate analytical data were obtained for all new compounds.

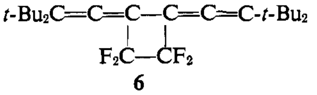
[5] F. Bohlmann and K. Kieslich, *Ber.*, **87**, 1363 (1954).

[6] L. Skattebøl, *Tetrahedron*, **21**, 1357 (1965).

[7] G. W. Griffin and L. I. Peterson, *J. Am. Chem. Soc.*, **85**, 2268 (1963).

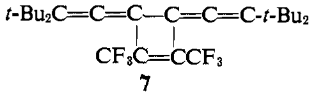
[8] R. O. Uhler, H. Shechter, and G. V. D. Tiers, *ibid.*, **84**, 3397 (1962); K. Brand, *Ber.*, **54**, 1947 (1921).

70% yield. With hexafluoro-2-butyne, **4** gave the cycloadduct **7** as well as its valence bond isomer **8**. It was shown that **7** isomerized to **8** at this temperature (200°).



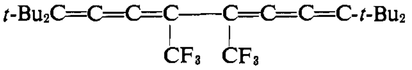
$$\begin{array}{c} t\text{-}Bu_2C{=}C{=}C{-}C{=}C{=}C\text{-}t\text{-}Bu_2 \\ F_2C{-}CF_2 \end{array}$$

6



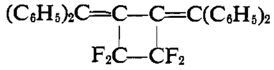
$$\begin{array}{c} t\text{-}Bu_2C{=}C{=}C{-}C{=}C{=}C\text{-}t\text{-}Bu_2 \\ CF_3C{=}CCF_3 \end{array}$$

7



$$\begin{array}{c} t\text{-}Bu_2C{=}C{=}C{=}C{-}C{=}C{=}C{=}C\text{-}t\text{-}Bu_2 \\ CF_3 \quad CF_3 \end{array}$$

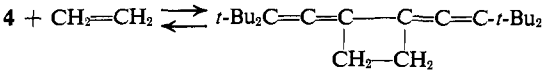
8



$$\begin{array}{c} (C_6H_5)_2C{=}C{-}C{=}C(C_6H_5)_2 \\ F_2C{-}CF_2 \end{array}$$

9

The reaction of **4** with ethylene in ethyl acetate at 200° returned **4** even though the cumulene in ethyl acetate dimerized rapidly at 200°. A possible explanation for the preservation of **4** in the presence of ethylene is that the cycloadduct **10** is formed but reverts to starting materials. Opening of **10** to 1,1-di-*t*-butylbutatriene is not observed, and such a reaction of **10** would be expected to be energetically less favorable than the return to starting materials.



$$4 + CH_2{=}CH_2 \rightleftarrows \begin{array}{c} t\text{-}Bu_2C{=}C{=}C{-}C{=}C{=}C\text{-}t\text{-}Bu_2 \\ CH_2{-}CH_2 \end{array}$$

10

Although we were unable to isolate the dimer of tetraphenylbutatriene from its thermal reactions, this cumulene also gave cycloadditions. With tetrafluoroethylene at 200°, a low yield of the adduct **9** was obtained.

The symmetry of the cycloadducts **6**–**9** was determined by single, unsplit absorption signals in both the fluorine and proton nmr.

In all cases where cycloaddition to cumulenes has been observed, addition has occurred at the central bond. This is to be expected if the triplet states of the cumulenes are intermediates.

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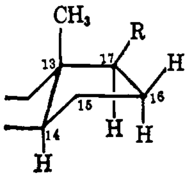
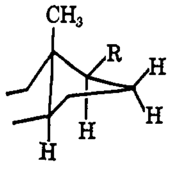
Steroid Ring D Torsional Angles and Conformations from X-Ray Data

Sir:

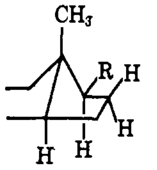
One of the subtlest problems extant in molecular geometry is that of determining the conformations adopted by ring D of the steroids. Thus, for the three symmetrical conformations (I, II, and III),[1] the C_{16},C_{17} torsional angle ($\theta_{16,17}$, IV) only varies from 0° in I to about −30° in III.[2] This is approximately one-half the staggered (60°) to eclipsed (0°) value normally found in cyclohexane conformations.[3,4] While important ring D data have been obtained by some physical methods[1,5–9] it has become apparent that the precision of X-ray crystallography would be definitive here. In particular scrutiny of the five torsional angles of ring D would readily reveal the subtlest aspects of its symmetry.[10] Unfortunately it is the present X-ray practice to report bond angles (ω_a) and bond lengths (d_{ab}) but not the vitally necessary torsional angles.



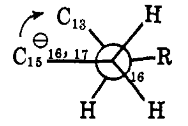
I



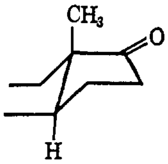
II



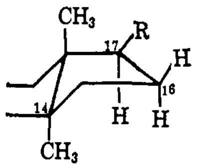
III



IV



V



VIII

In this communication, the requisite torsional angles have been calculated[11] from all accurate reported fractional atomic coordinate data of steroids,[12–17] and these values were used to solve the ring D conformational problem.

In Table I, the value of $\theta_{16,17}$ of 1° 52′ calculated from the excellent Norton, Kartha, and Lu data[12] on 4-bromoestrone (V) is significant since a value of 0° means that C_{13}, C_{15}, C_{16}, and C_{17} are in one plane and ring D is α envelope. Since 1° 52′ is within experimental error of zero,[18] the biologically important estrone type prefers the α envelope (V). Presumably the angle strain for the ketone at C_{17} is minimized in this conformation. The reduction product of V, however, 4-bromoestradiol (VI), has undergone a ring D conformational change since $\theta_{15,16}$ derived from

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(1) F. V. Brutcher, Jr., and W. Bauer, *J. Am. Chem. Soc.*, **84**, 2233, 2236 (1962). Conformation I is termed the α envelope since the C_{14} atom is below the plane of C_{13}, C_{15}, C_{16}, C_{17}. III then represents the β envelope, while II is the half-chair.

(2) In IV, from the nearer to the farther ring valence bond the motion is clockwise and as in a standard mathematics handbook, the torsional angle ($\theta_{16,17}$) is defined as a negative angle.

(3) M. Hanack, "Conformation Theory," Academic Press, New York, N. Y., 1965.

(4) E. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," John Wiley and Sons, Inc., New York, N. Y., 1965.

(5) J. Fishman and C. Djerassi, *Experientia*, **16**, 138 (1960).

(6) A. D. Cross and P. Crabbé, *J. Am. Chem. Soc.*, **86**, 1221 (1964).

(7) A. D. Cross and C. Beard, *ibid.*, **86**, 5317 (1964).

(8) J. Fishman, *ibid.*, **87**, 3455 (1965).

(9) W. Klyne, *Bull. Soc. Chim. France*, 1396 (1960).

(10) While inspection of the stacking diagram may rule out the other envelope, it does not differentiate between a particular envelope, a distorted envelope, or a half-chair.

(11) This involves proper multiplication of the fractional atomic coordinates by the dimensions of the unit cell. These atomic coordinates lead to the relevant C–C bond vectors. Derivation of the proper θ's is standard (see E. B. Wilson, "Vector Analysis," Dover Publications, Inc., New York, N. Y., 1901, and also E. J. Corey and R. Sneen, *J. Am. Chem. Soc.*, 77, 2505 (1954)). By recalculating ω and d to avoid round-off and using our θ's we have shown that these internal coordinates lead to mathematically closed five-membered rings.

(12) D. A. Norton, G. Kartha, and C. T. Lu, *Acta Cryst.*, **16**, 89 (1963).

(13) D. A. Norton, G. Kartha, and C. T. Lu, *ibid.*, **17**, 77 (1964).

(14) H. Bürki and W. Nowacki, *Z. Krist.*, **108**, 206 (1956).

(15) J. Fridrichsons and A. McL. Mathieson, *J. Chem. Soc.*, 2159 (1953).

(16) H. J. Geise, C. Romers, and E. W. M. Rutten, *Acta Cryst.*, **20**, 249 (1966). We calculate that the 2α,3β-dibromo- and the 2α,3β-dichloro-5α-cholestanes reported by H. J. Geise and C. Romers (*ibid.*, **20**, 257 (1966)) have smaller $\theta_{15,16}$'s of −7° 35′ and −8° 18′. They are not included in Table I.

(17) C. Romers, B. Hesper, E. VanHeijkoop, and H. J. Geise, *ibid.*, **20**, 363 (1966).

(18) In Table I, $\Delta\theta$ is the column average of the probable error in each θ calculated by propagation of the standard deviations of the atomic coordinates where reported (see L. G. Parratt, "Probability and Experimental Errors in Science," John Wiley and Sons, Inc., New York, N. Y., 1961).