

ring, but the striking similarity in the spectral characteristics of **2** and **3** suggests that it is highly probable that **3** also exist in a chair conformation (**4b**). It is very tempting to carry this analogy over to **1** for which no spectral change was observed but caution is suggested in light of the recently observed change from a twist-boat conformation for cyclohexane-1,4-dione to a chair for 1,4-dimethylenecyclohexane.⁸ On the other hand, the negative results for **1** and 2,2-dibenzyl-5,5-dimethylcyclohexane-1,3-dione⁸ do not necessarily rule out a chair conformation since cyclohexanone, which exists as a chair, does not give rise to a spectral change down to -170° .⁹

Our work certainly indicates that more information is necessary in this area of chemistry and our objective will now be a systematic study of various derivatives of cyclohexane-1,3-dione in an attempt to determine all the relevant factors influencing conformation.

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(9) F. R. Jensen and B. H. Beck, *J. Amer. Chem. Soc.*, **90**, 1066 (1968).

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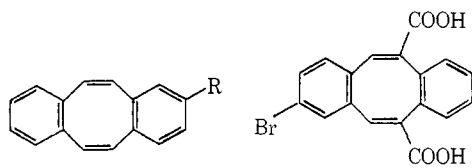
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Received September 7, 1972

Ring Inversion in Di- and Tetrabenzocyclooctatetraenes

Sir:

Recent studies have dealt with the effect of fused benzene rings on the inversion barrier of cyclooctatetraene.¹⁻³ In this connection, we wish to report that the barrier (ΔG^\ddagger) to ring inversion for **1a**, 12.3 ± 0.2 kcal/mol at -5° , is substantially lower than the racemization barrier of 27 kcal/mol earlier reported by us for **2**,⁴ a finding which is consistent with the failure of our attempts to resolve **1c**.⁵



1a, R = CF_2H

b, R = Br

c, R = COOH

d, R = CHO

Decarboxylation of **2** with copper-chromium oxide catalyst⁶ in quinoline at 205° yielded **1b**, mp $78-79^\circ$, which was converted to **1c** by the Grignard synthesis (gaseous carbon dioxide). The acid, mp $264-268^\circ$ dec, on treatment with thionyl chloride gave the acid chloride, mp $140-142^\circ$, which, upon reduction with lithium tri-*tert*-butoxyaluminum hydride,⁷ yielded **1d**, mp $127-129^\circ$; $\delta_{\text{CDCl}_3}^{\text{TMS}}$ 9.87 (s, CHO), 7.78-6.95 (m, aro-

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(2) G. W. Buchanan, *ibid.*, 665 (1972).

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(4) K. Mislow and H. D. Perlmutter, *ibid.*, **84**, 3591 (1962).

(5) P. X. Riccobono, Ph.D. Dissertation, New York University, 1964.

(6) H. Adkins, E. E. Burgoyne, and H. J. Schneider, *J. Amer. Chem. Soc.*, **72**, 2626 (1950).

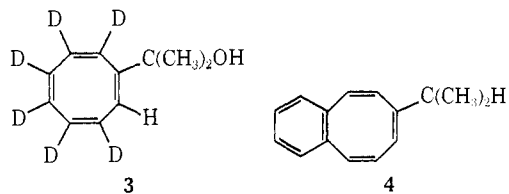
(7) H. C. Brown and R. F. McFarlin, *ibid.*, **80**, 5372 (1958).

matic H), 6.76 (br s, olefinic H). An excess of sulfur tetrafluoride was condensed into a stainless steel bomb containing a methylene chloride solution of **1d** and a catalytic amount of water. Reaction at room temperature for 22 hr gave **1a**, mp $71-72^\circ$; $\delta_{\text{CDCl}_3}^{\text{TMS}}$ 7.50-6.92 (m, aromatic H), 6.75 (s, olefinic H), 6.52 (t, $^2J_{\text{FH}} = 56.4$ Hz, CF_2H).⁸

At -50° the 94.1-MHz ^{19}F nmr spectrum of **1a** (CFCl_3) consists of the AB portion of an ABX system (ν_A 50.39, ν_B 49.80 ppm downfield from C_6F_6 as internal reference; $^2J_{\text{HFA}} \cong ^2J_{\text{HFB}} = 56.4$ Hz, $^2J_{\text{FF}} = 296$ Hz).⁹ Upon warming the sample, the ABX spectrum collapses to an A_2X pattern. The temperature-dependent spectrum was analyzed as two overlapping AB systems,¹⁰ and rates were determined by line-shape analysis, which yielded the value for the ring inversion barrier of **1a** reported above.

The present work fully bears out our conjecture of 10 years ago⁴ that "nonbonded interaction of carboxyl groups and benzene hydrogens in the transition state [for the racemization of **2**] is likely to contribute significantly to the destabilization of the transition state." Although the mechanism of enantiomerization is still in doubt,¹¹ the observed barrier for **2** must be a lower limit to the ring inversion process. The very much higher value of this barrier, as compared to that of **1a**, is a consequence of repulsive interactions in the transition state.¹³

The barriers observed for ring inversion in the cyclooctatetraene derivative **3**, $\Delta G^\ddagger_{-2} = 14.7$ kcal/mol,¹⁵ and the benzocyclooctatetraene derivative **4**, ΔG^\ddagger_{-30}



$= 13.4$ kcal/mol,² differ but slightly from that of **1a**. It thus appears that in the absence of substitution patterns which are capable of giving rise to strong non-bonded interactions, the overall effect of benzene fusion on the structural rigidity of the cyclooctatetraene ring is quite minor.¹⁶ Where steric factors are operative,

(8) Acceptable elemental analyses were obtained for all new compounds. Mass spectra were likewise consistent with the assigned structures.

(9) Since only the four central lines of the spectrum were observed, $^2J_{\text{FF}}$ was obtained from the proton-decoupled AB spectrum. Such behavior for the CF_2H group has been previously noted. See, for example, J. W. Rakshys, Jr., S. V. McKinley, and H. H. Freedman, *J. Amer. Chem. Soc.*, **93**, 6522 (1971).

(10) G. M. Whitesides and J. D. Roberts, *ibid.*, **87**, 4878 (1965).

(11) Originally, the racemization of **2** was simply viewed⁴ as proceeding through a conformational tub inversion, by way of a planar transition state. Subsequently, Stiles and Burckhardt¹² suggested an alternative mechanism by way of an intermediate [2 + 2] cycloaddition product.

(12) M. Stiles and U. Burckhardt, *J. Amer. Chem. Soc.*, **86**, 3396 (1964).

(13) Ground-state stabilization of **2** by, for example, intramolecular H-bonding interactions between the two carboxyl groups, may be ruled out by the observation¹⁴ that the barriers to racemization of the sodium salt and the dimethyl ester of **2** differ by no more than 1 kcal/mol from that of the parent compound.

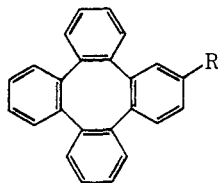
(14) H. D. Perlmutter, Ph.D. Dissertation, New York University, 1963.

(15) F. A. L. Anet, A. J. R. Bourn, and Y. S. Lin, *J. Amer. Chem. Soc.*, **86**, 3576 (1964).

(16) Increased rigidity of the cyclooctatetraene ring on annelation with benzene has been suggested as a possible explanation for the failure to generate dianion species of benzo- and dibenzo[*a,e*]cyclooctatetraene.⁹

however, the effect is likely to be very large, as found by us for **2** and by Allinger, *et al.*, for methyl dibenzo-*[e,g]*[1,4]diazocine-3,10-dicarboxylate ($\Delta G^\ddagger > 48$ kcal/mol).¹⁷

In the light of this conclusion, it is surprising to note that a barrier of 5.7 ± 1 kcal/mol has been reported¹ for the ring inversion of the tetrabenzocyclooctatetraene derivative **5a**, and we were thus led to re-



- 5a**, R = C(CH₃)₂OH
b, R = CHO
c, R = CH(OH)CH₃
d, R = C(CH₃)O
e, R = CF₂H

investigate this claim. Treatment of tetraphenylene¹⁸ with titanium tetrachloride and dichloromethyl methyl ether in methylene chloride¹⁹ gave a mixture of **5b** (mp 206–208°; $\delta_{\text{CDCl}_3}^{\text{TMS}}$ 9.89 (1 H, s, CHO), 7.80–7.60 (2 H, m, aromatic), 7.40–7.00 (13 H, m, aromatic)), and the other positionally isomeric aldehyde (mp 202–203°; $\delta_{\text{CDCl}_3}^{\text{TMS}}$ 9.62 (1 H, s, CHO), 8.00–7.84 (1 H, m, aromatic), 7.45–6.90 (14 H, m, aromatic)), in a ratio of *ca.* 80:20. The aldehydes were separated by fractional crystallization from methylene chloride-hexane. Structural assignments were confirmed by the deshielding of two protons ortho to the carbonyl group in **5b** which thus appear downfield from the other aromatic protons in the ¹H nmr spectrum, whereas the spectrum of the other isomer displays only one such deshielded proton. Reaction of **5b** with methylmagnesium iodide yielded a *ca.* 1:1 mixture of diastereomers, **5c**, mp 195–200°. The 60-MHz nmr spectrum featured resonances at $\delta_{\text{C}_6\text{D}_6\text{CD}_3}^{\text{TMS}}$ 7.29–6.80 (m, aromatic H), 4.40 (q, ³J_{HH} = 6.4 Hz, CHCH₃OH), 1.49 (s, CHCH₃OH), 1.08 (d, CHCH₃OH), 1.05 (d, CHCH₃OH).⁸ Two-phase oxidation of **5c** with chromic acid²⁰ gave **5d** which was then converted with methylmagnesium iodide to **5a**, mp 211–213°. The temperature-dependent spectral characteristics of **5a** agreed with those previously reported.¹

Since **5c** was observed to be a mixture of diastereomers at 40°, ring inversion must be slow on the nmr time scale. The 220-MHz ¹H nmr spectrum (toluene-*d*₈) of **5c** at ambient temperature features two doublets for the methyl signals ($\Delta\nu = 6.8$ Hz) and two quartets for the methine signals ($\Delta\nu = 4.0$ Hz). At 98° the methyl groups still appear as two doublets ($\Delta\nu = 1.8$ Hz); there is no perceptible line broadening, and the decrease in $\Delta\nu$ is due to a temperature-dependent chemical shift. From these data the lower limit for ring inversion of **5c**, and presumably **5a** as well, is 21 kcal/

(17) N. L. Allinger, W. Szkrybalo, and M. A. DaRooge, *J. Org. Chem.*, **28**, 3007 (1963); see also D. M. Hall and J. M. Insole, *J. Chem. Soc.*, 2326 (1964); F. Bell, *ibid.*, 1527 (1952).

(18) Synthesized from biphenylene: D. F. Lindow and L. Friedman, *J. Amer. Chem. Soc.*, **89**, 1271 (1967).

(19) A. Rieche, H. Gross, and E. Höft, *Chem. Ber.*, **93**, 88 (1960).

(20) H. C. Brown and C. P. Garg, *J. Amer. Chem. Soc.*, **83**, 2951 (1961).

mol. Evidently, the persistence of the methyl proton resonance signal of **5a** as a singlet at low temperatures¹ is due to accidental isochrony.²¹

The magnitude of this barrier suggests that resolution of a suitable derivative of **5** should be feasible.²²

Acknowledgment. This work was supported by the National Science Foundation (GP-30257). One of us (K. M.) thanks Professor H. P. Figeys for stimulating discussions which led to a revival of old interests.

(21) We have found that the 94.1-MHz ¹⁹F nmr spectrum of **5e** (prepared from **5b** by reaction with SF₆)⁸ exhibits an apparent A₂X pattern, evidently also as the result of accidental isochrony.

(22) NOTE ADDED IN PROOF. The carboxylic acid derived from oxidation of **5b** has been partially resolved, and a lower limit to racemization of 45 kcal/mol has been determined (D. Gust, G. H. Senkler, Jr., and K. Mislow, *J. Chem. Soc., Chem. Commun.*, in press).

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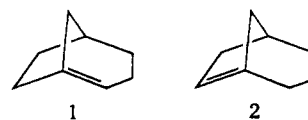
Received August 30, 1972

Bredt's Rule. V. Bicyclo[3.2.1]oct-1-ene^{1,2}

Sir:

Renewed interest^{3,4} in the synthesis and chemistry of bridgehead alkenes in bridged bicyclic ring systems has resulted in the preparation of new isolable and unisolable members of the class. Bridgehead olefins with double bonds endocyclic in eight-membered rings have been isolated and characterized fully,³ while olefins with double bonds endocyclic in rings of seven or fewer members have been too unstable to permit purification and isolation.^{3f,5} Krebs and Keese⁵ have recently reported the generation of 1-norbornene, a highly strained compound which possibly prefers a triplet ground state.

We now report our evidence for the formation of the transient bridgehead olefins **1** and **2** in the bicyclo[3.2.1]-



(1) For previous papers in the series, see ref 3a, 3c, and 3f.

(2) (a) This work was supported by grants from the Petroleum Research Fund, administered by the American Chemical Society, and from the Rackham Fund of the University of Michigan. Mass spectra run on an AEI MS-902 purchased with funds from a NSF equipment grant to the University of Michigan. (b) J. A. C. thanks the Alfred E. Hinsdale Scholarship Fund, the Sun Oil Company, and the Esso Foundation for financial support.

(3) (a) J. R. Wiseman and W. A. Pletcher, *J. Amer. Chem. Soc.*, **92**, 956 (1970); (b) J. A. Marshall and H. Faubl, *ibid.*, **92**, 948 (1970); (c) J. R. Wiseman, H. F. Chan, and C. J. Ahola, *ibid.*, **91**, 2812 (1969); (d) W. Carruthers and M. I. Qureshi, *Chem. Commun.*, 832 (1969); (e) N. M. Weinschenker and F. D. Greene, *J. Amer. Chem. Soc.*, **90**, 506 (1968); (f) J. R. Wiseman and J. A. Chong, *ibid.*, **91**, 7775 (1969); (g) G. L. Buchanan and G. Jamieson, *Tetrahedron*, **28**, 1123 (1972); (h) *ibid.*, **28**, 1129 (1972); (i) P. Warner, R. La Rose, C.-M. Lee, and J. C. Clardy, *J. Amer. Chem. Soc.*, **94**, 7607 (1972); (j) P. G. Gassman, R. L. Cryberg, and K. Shudo, *ibid.*, **94**, 7600 (1972).

(4) For reviews see (a) F. S. Fawcett, *Chem. Rev.*, **47**, 219 (1950); (b) V. Prelog, *J. Chem. Soc.*, 420 (1950); (c) R. C. Fort and P. v. R. Schleyer, *Advan. Alicycl. Chem.*, **1**, 364 (1966).

(5) (a) R. Keese and E. P. Krebs, *Angew. Chem., Int. Ed. Engl.*, **10**, 262 (1971); (b) R. Keese and E. P. Krebs, *Angew. Chem.*, **84**, 540 (1972). See also (c) S. F. Campbell, R. Stephens, and J. C. Tatlow, *Tetrahedron*, **21**, 2997 (1965).