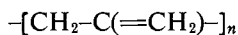


the repeating sequence is



Substantiating evidence for the correctness of the structure outlined above is available from X-ray analysis. An oriented sample showed a highly crystalline X-ray fiber diagram.<sup>11</sup> Results of the X-ray studies indicate that the molecular structure is a succession of nearly gauche conformations, *i.e.*, a  $2_1$  helix<sup>11</sup> as shown in Figure 2.

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### The Valence Isomerization of 1,2,3,4-Tetraphenylcyclobutene and Its Anion

Sir:

As part of our program on small ring compounds accessible *via* tetraphenylcyclobutadiene, we have prepared *cis*- and *trans*-1,2,3,4-tetraphenylcyclobutene and have investigated the stereospecificity and kinetics of their valence isomerization.<sup>1</sup> A novel finding is that the tetraphenylcyclobutenyl anion can also undergo an extremely facile cyclobutene-butadiene valence isomerization.

Reduction of tetraphenylcyclobutadiene-nickel bromide complex<sup>2</sup> with  $\text{LiAlH}_4$  yields (90%) a single isomer of 1,2,3,4-tetraphenylcyclobutene<sup>3</sup> (I) whose geometry was demonstrated as *cis* by catalytic hydrogenation to 1,2,3,4-tetraphenylcyclobutane.<sup>4</sup> *cis*-I undergoes ring opening at 50° to yield exclusively the expected<sup>5</sup> product, *cis,trans*-1,2,3,4-tetraphenylbutadiene (*cis,trans*-II), whose identity and absence of *cis,cis*- and *trans,trans*-II was demonstrated by n.m.r. characterization of all three butadiene isomers. The chemical shift of the olefinic protons (Table I) correlate well with the deshielding influence of the  $\beta$ -phenyl groups.<sup>6</sup> The solvent-independent, first-order isomerization of *cis*-I has rate constants of  $8 \times 10^{-5} \text{ sec.}^{-1}$  at 50° and  $2.5 \times 10^{-6}$  at 25°, with  $E_a = 25 \text{ kcal./mole}$ .

Addition of butyllithium to *cis*-I in THF generates the stable, deep-green tetraphenylcyclobutenyl monoanion (III), which incorporates 1 deuterium atom on

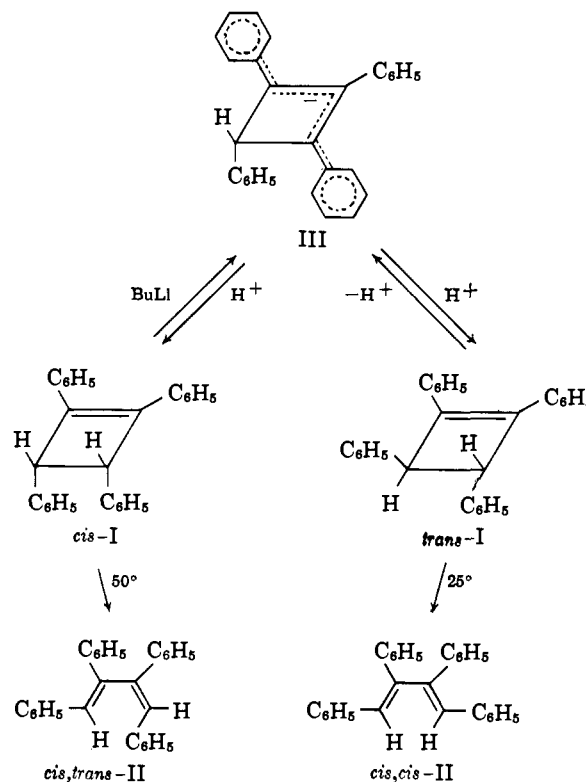
Table I. Properties of 1,2,3,4-Tetraphenylbutadiene Isomers (II)

Isomer	M.p., °C.	$\lambda_{\text{max}}$ , (log $\epsilon$ ) <sup>a</sup>	N.m.r. <sup>b</sup> ( $\delta$ )
<i>cis,cis</i> <sup>7</sup>	185-186	312 <sup>c</sup> (4.57)	6.32 <sup>d</sup>
<i>cis,trans</i>	82-83	285 (4.43)	6.72, <sup>e</sup> 6.98 <sup>e</sup>
<i>trans,trans</i>	148-149	292 (4.6)	>7.0 <sup>f</sup>

<sup>a</sup> In ethanol. <sup>b</sup> In  $\text{CDCl}_3$ . <sup>c</sup> Center of doublet. <sup>d</sup> Two-proton singlet. <sup>e</sup> One-proton singlet. <sup>f</sup> Hidden by phenyl protons.

$\text{D}_2\text{O}$  quenching.<sup>8</sup> The assumption that the stability of III is due to charge delocalization over the planar, 1,3-diphenylallylic system is supported by its n.m.r. spectrum, which parallels that of the diphenylmethyl anion.<sup>9</sup> While steric considerations predict *trans*-I to be thermodynamically favored, protonation of III by oxy acids leads entirely to the kinetically controlled product, *cis*-I.

Dramatically different results are realized when *cis*-I is equilibrated by means of lithium cyclohexylamide or potassium *t*-butoxide in THF; within minutes the 2-proton singlet of *cis*-I at  $\delta$  4.67 is replaced by a similar resonance at  $\delta$  4.02. The lability of this new product has precluded isolation in a pure state, but it is assumed to be *trans*-I from n.m.r. data<sup>10</sup> and its chlorination to 3,4-dichlorotetraphenylcyclobutene.<sup>11</sup>



*trans*-I isomerizes significantly faster than *cis*-I and, as expected from analogy with *trans*-tetramethylcyclo-

(1) For leading references in this active field see: R. Criegee, D. Seebach, R. Winter, B. Borretzen, and H. Brune, *Ber.*, in press. We thank Professor Criegee and Dr. Winter for a copy of the manuscript prior to publication.

(2) H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2194 (1961).

(3) This compound is identical with the product obtained from the hydride transfer process between cycloheptatriene and tetraphenylcyclobutenyl cation [H. H. Freedman and A. M. Frantz, Jr., *ibid.*, **84**, 4165 (1962)].

(4) (a) J. D. Dunitz, *Acta Cryst.*, **2**, 1 (1949); (b) H. Shechter, W. J. Link, and G. V. D. Tiers, *J. Am. Chem. Soc.*, **85**, 1601 (1963).

(5) (a) *Cf. cis*-1,2,3,4-tetramethylcyclobutene to *cis,trans*-1,2,3,4-tetramethylbutadiene [R. Criegee and K. Noll, *Ann.*, **627**, 1 (1959)]; (b) *cis*-3,4-dicarboxycyclobutene to *cis,trans*-muconic acid [E. Vogel, *ibid.*, **615**, 14 (1958)].

(6) D. Curtin, H. Gruen, and B. Shoulders, *Chem. Ind. (London)*, 1205 (1958).

(7) H. H. Freedman, *J. Org. Chem.*, **27**, 2298 (1962).

(8) The potential Hückel aromatic dianion cannot be prepared by this technique. However, other approaches have proved more rewarding (to be published).

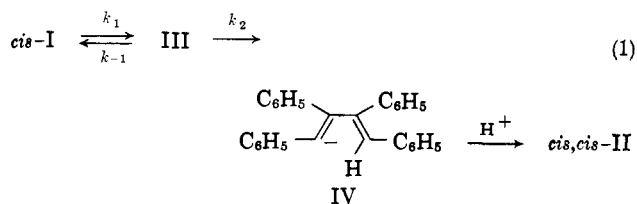
(9) V. R. Sandel and H. H. Freedman, *J. Am. Chem. Soc.*, **85**, 2328 (1963).

(10) The chemical shift difference of the allylic protons of *cis*- and *trans*-I parallels that for *cis*- and *trans*-1,2-diphenylbenzocyclobutene [L. A. Carpino, *ibid.*, **84**, 2196 (1962)] and *cis*- and *trans*-1,2-diphenyl-naphtho[b]cyclobutene [M. P. Cava, B. Hwang, and J. P. Van Meter, *ibid.*, **85**, 4031 (1963)].

(11) First reported in reference cited in ref. 3.

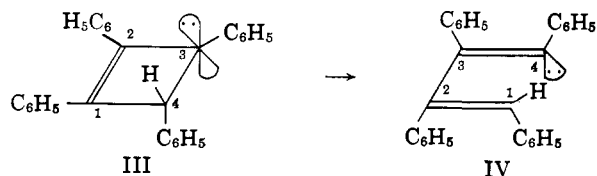
butene,<sup>5a</sup> affords only *cis,cis*-II.<sup>12</sup> The rate constant at 24° in THF is  $5 \times 10^{-5} \text{ sec.}^{-1}$ , and  $E_a = 21 \text{ kcal./mole.}^{13}$

It can now be demonstrated that, when *cis*-I undergoes reversible anion formation in dimethyl sulfoxide (DMSO), anion isomerization is competitive with anion protonation. A DMSO solution, 0.1 M in both *cis*-I and potassium *t*-butoxide, is completely isomerized to *cis,cis*-II in 15 min. at 24°. Since the rate of isomerization of *trans*-I is approximately the same in both DMSO and in THF (with or without added base) and is considerably slower than *cis*-I in DMSO with base, it is clear that the source of *cis,cis*-II is the anion III and not *trans*-I. In DMSO-*d*<sub>6</sub>, *cis*-I with butoxide affords a mixture of approximately equivalent amounts of *cis*-I (*-d*<sub>1</sub> and *-d*<sub>2</sub>) and *cis,cis*-II (*-d*<sub>1</sub> and *-d*<sub>2</sub>) after 5 min., suggesting that  $k_{-1}$  and  $k_2$  of eq. 1 are of comparable magnitude.<sup>14</sup> To explain the absence of anion isom-



erization in THF (*i.e.*,  $k_2$  is negligible) we propose that DMSO, with its unique ability to solvate cations, produces solvent-separated ion pairs of greatly increased reactivity relative to the stabilized ion pairs present in THF.

The conrotatory mechanism for cyclobutene isomerization<sup>15</sup> is not readily applied in predicting the stereospecific isomerization of anion III, with its single  $sp_3$ -hybridized center. The *cis* geometry at the butadienyl 1,2-bond is predictable from preferred eclipsing in the transition state of hydrogen, rather than phenyl, with the adjacent anionic  $\pi$ -lobe. The *cis* geometry at the 3,4-bond is less clear, but may be due to the minimum



movement necessary for the phenyl at C-3 in III to attain the configuration at C-4 in IV. Alternatively, the formation of *cis,cis*-II may be due to the stability of anion IV, which can exist in a quasi-five-membered ring sustained

(12) This rapid isomerization may explain why both Shechter<sup>4b</sup> and Baker [W. Baker, J. W. Hilpern, and J. F. W. McOmie, *J. Chem. Soc.*, 479 (1961)] could only isolate *cis,cis*-II from reactions in which *trans*-I is a likely intermediate.

(13) The similarity between the rates and activation energies for I (*cis* and *trans*) and the *cis* and *trans* isomers of 1,2-diphenylbenzocyclobutene [R. Huisgen and H. Seidl, *Tetrahedron Letters*, 3381 (1964)] suggests that the rate of isomerization is primarily dependent on the allylic substituents.

(14) It is evident that solvent DMSO is serving as the proton source and that protonation is kinetically controlled. Cf. C. F. Price and W. H. Snyder, *J. Am. Chem. Soc.*, 83, 1773 (1961), who report kinetic control in the rearrangement of allylic ethers *via* their anions generated from butoxide in DMSO, and A. Schriesheim, J. E. Hofmann, and C. A. Rowe, Jr., *ibid.*, 83, 3731 (1961), who demonstrate both kinetic control and solvent exchange with allylic olefins in this solvent-base system.

(15) R. B. Woodward and R. Hofmann, *ibid.*, 87, 395 (1965).

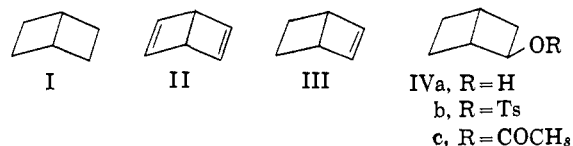
by hydrogen bonding of the relatively acidic proton to the ideally situated lone-pair orbital.

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 Received April 9, 1965

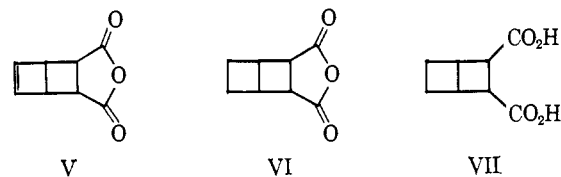
## The Synthesis and Acetolysis of *exo*-Bicyclo[2.2.0]hex-2-yl Tosylate<sup>1</sup>

Sir:

The synthesis of bicyclo[2.2.0]hexane<sup>2</sup> (I) and bicyclo[2.2.0]hexa-2,5-diene<sup>3</sup> (II) have been reported. We now wish to report the synthesis of the remaining hydrocarbon in this series, bicyclo[2.2.0]hex-2-ene (III), its conversion to *exo*-bicyclo[2.2.0]hexan-2-ol (IVa), and the acetolysis of the tosylate of IVa (IVb).



Catalytic hydrogenation of the photoanhydride<sup>3</sup> (V) of *cis*-1,2-dihydrophthalic anhydride gave bicyclo[2.2.0]hexane-2,3-dicarboxylic anhydride (VI),<sup>4</sup> m.p. 84.5–86°, in 90% yield. Hydrolysis of VI gave bicyclo[2.2.0]hexane-2,3-dicarboxylic acid (VII), m.p. 152–156° (89%), which on oxidative bisdecarboxylation with lead tetraacetate in pyridine<sup>5</sup> gave bicyclo[2.2.0]hex-2-ene (III, b.p. 43–48° (277 mm.)) in 30–38%



isolated yield.<sup>6</sup>

Hydrocarbon III gave a mass spectrometric molecular weight of 80 and exhibited a cracking pattern similar to cyclohexadiene. The n.m.r. spectrum of III (CCl<sub>4</sub> solution, TMS internal standard) exhibited olefinic proton resonance at  $\tau$  3.85, methine proton resonance centered at 6.83, and methylene proton resonance as absorption from 7.6 to 8.7, appearing in the expected ratio of 1:1:2.

Hydroboration<sup>7</sup> of III and subsequent oxidation gave mainly *exo*-bicyclo[2.2.0]hexan-2-ol (IVa), b.p. 69–71° (12.5–13 mm.),  $n_D^{20}$  1.4773, in 78% yield. The n.m.r. spectrum of IVa (neat, TMS internal standard)

(1) For the previous paper in this series on strained ring systems see R. N. McDonald and P. A. Schwab, *J. Am. Chem. Soc.*, 86, 4866 (1964).

(2) (a) S. Cremer and R. Srinivasan, *Tetrahedron Letters*, No. 21, 24 (1960); (b) R. Srinivasan, *J. Am. Chem. Soc.*, 83, 4923 (1961); (c) C. E. Griffin, N. F. Hepfinger, and B. L. Shapiro, *ibid.*, 85, 2683 (1963).

(3) E. E. van Tamelen and S. P. Pappas, *ibid.*, 85, 3297 (1963).

(4) All new compounds have given satisfactory analyses.

(5) The conditions for the decarboxylation of VII are similar (reaction temperature 50–53°, time 1.5–2.5 hr.) to those reported for V.<sup>3</sup> Oxidative decarboxylation of VI gives III in approximately 15% yield.

(6) V.p.c. analysis of the mixture before distillation indicated the yield of olefin III was 40–52%. At injection port temperatures above 150° some thermal isomerization of III was observed, and at 330° complete isomerization to 1,3-cyclohexadiene occurred.

(7) G. Zweifel and H. C. Brown, *Org. Reactions*, 13, 1 (1963).