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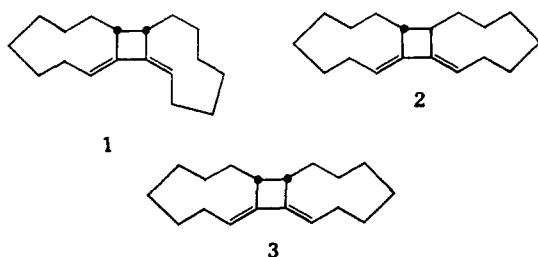
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## The Dimerization of Racemic and Optically Active 1,2-Cyclononadiene<sup>1</sup>

Sir:

The mechanism of the thermal dimerization of allenes to form 1,2-dimethylenecyclobutane derivatives has generally been discussed in terms of some type of diradical intermediate or some form of four-center addition.<sup>2</sup> In order to shed new light on this (2 + 2) cycloaddition<sup>3</sup> we have examined the course of dimerization of both racemic and optically active 1,2-cyclononadiene. Although this allene is undoubtedly somewhat strained, we suggest that it is sufficiently normal to serve as a general, if simplified, model for dimerization of allenes devoid of activating substituents.

Dimerization of neat racemic 1,2-cyclononadiene at 125° affords an essentially quantitative yield of a mixture of three isomers: 6.3% **1**, 62.5% **2**, and 31.2% **3**.<sup>4</sup> The nmr spectra of **2** and **3** show identical broad triplets at  $\delta$  5.52 for the two vinyl protons. The two *syn* tertiary allylic protons of **3** appear as a multiplet at  $\delta$  2.9 (*trans* C-C deshielding), whereas in **2** the corresponding signal for the *anti* protons is at *ca.*  $\delta$  2.2 (*cis* C-C shielding). We have not been able to isolate pure **1**, but nmr analysis of mixtures of **1** (40%) and **2** (60%) has established that **1** has two nonequivalent vinyl protons (*ca.*  $\delta$  5.5 and 5.8) indicating one *cis* and one *trans* double bond and a *syn* ring fusion ( $\delta$  2.9).



The stereochemistry assigned is supported<sup>6</sup> by the relative thermal stabilities of the cyclobutenes obtained

(1) Supported in part by the National Science Foundation (GP-8181).  
(2) For reviews see (a) J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, 1 (1962); (b) D. R. Taylor, *Chem. Rev.*, **67**, 317 (1967).

(3) For pertinent information and references on related (2 + 2) cycloadditions see (a) R. Huisgen, L. Feiler, and G. Binsch, *Angew. Chem.*, **76**, 892 (1964); (b) R. Montaigne and L. G. Ghosez, *ibid.*, **80**, 194 (1968); (c) E. F. Kiefer and M. Y. Okamura, *J. Am. Chem. Soc.*, **90**, 4187 (1968); (d) W. R. Dolbier, Jr., and S.-H. Dai, *ibid.*, **90**, 5028 (1968); (e) J. E. Baldwin and J. A. Kapecki, *ibid.*, **91**, 3106 (1969).

(4) (a) Diene **2** is the lower and **3** is the higher melting compound isolated by Skattebøl and Solomon<sup>6</sup> who established the general structure but not the stereochemistry. (b) The compounds can be separated analytically on lightly loaded glpc columns employing SE-30 or Versamid 400.

(5) L. Skattebøl and S. Solomon, *J. Amer. Chem. Soc.*, **87**, 4506 (1965).

(6) The reactivity toward maleic anhydride is **3** > **1** > **2**.

from **2** and **3** by 1,4 reduction with sodium in liquid ammonia. As predicted,<sup>7</sup> the *anti* compound from **2** opens more rapidly than the *syn* isomer<sup>8</sup> from **3**.

Dimerization (125°, 70 min) of optically active 1,2-cyclononadiene,<sup>9</sup>  $[\alpha]^{25}_D +163^\circ$  ( $\text{CH}_2\text{Cl}_2$ ), gave 0.4% **1**, 11.8% **2**, and 79.8% **3**. Clearly, at least for the most part, dimerization stemming from the combination of *d*-allene with *d*-allene (or *l* with *l*) gives **3** (which is *meso*), while combination of *d*-allene with *l*-allene gives **2** and **1** (which are not *meso*).<sup>10</sup> Because the rotation of optically pure allene is not known, at this time the degree of stereospecificity cannot be determined, but we believe it is close to 100%.<sup>11</sup>

The net stereochemical effect of this cycloaddition is that of *cis* addition to one allene (suprafacial) and *trans* addition to the other (antarafacial). This surprising finding definitely is not predicted by earlier theories,<sup>2</sup> but it is exactly the result predicted by Hoffmann and Woodward<sup>12</sup> for a thermal (2 + 2) cycloaddition. If the dimerization is a one-step reaction, then it is another striking example of the remarkable predictive powers of the Woodward-Hoffmann rules. However, because of the additional  $\pi$  electrons, this cycloaddition may be more complex than is implied for a concerted (2 + 2) addition, and we consider it worthwhile to consider whether or not any nonconcerted mechanism could give the above stereochemical results.

An alternative possibility is that the dimerization results from a multistep process, each step of which is stereospecific. One such process is outlined in Scheme I for both *dl* and active allene. In each case the transition state **4** is meant to indicate that the allenes have come together in a "crossed" configuration (which steric factors appear to require)<sup>13</sup> and that the start of bonding of the central carbon atoms is accompanied by simultaneous conrotatory twisting (in the sense that will minimize steric interactions and strain) leading to a "perpendicular" 2,2'-diallylene, **5**. Rotation about the central bond of **5** gives the planar, or nearly planar, 2,2'-diallylene **6**. Disrotatory closure of the latter clearly leads to dimers having the stereochemistry observed. Reversing the order of the rotatory motions,

(7) (a) R. E. K. Winter, *Tetrahedron Letters*, 1207 (1965); (b) R. Criegee and H. J. Reinhardt, *Chem. Ber.*, **101**, 102 (1968).

(8) Conrotatory opening of the *syn* isomer gives *cis,trans*-1,1'-bicyclonononyl, which at somewhat higher temperatures undergoes 1,5-sigmatropic rearrangement to 3-cyclononylidene cyclononene.

(9) A. C. Cope, W. R. Moore, R. D. Bach, and H. J. S. Winkler, *J. Am. Chem. Soc.*, in press.

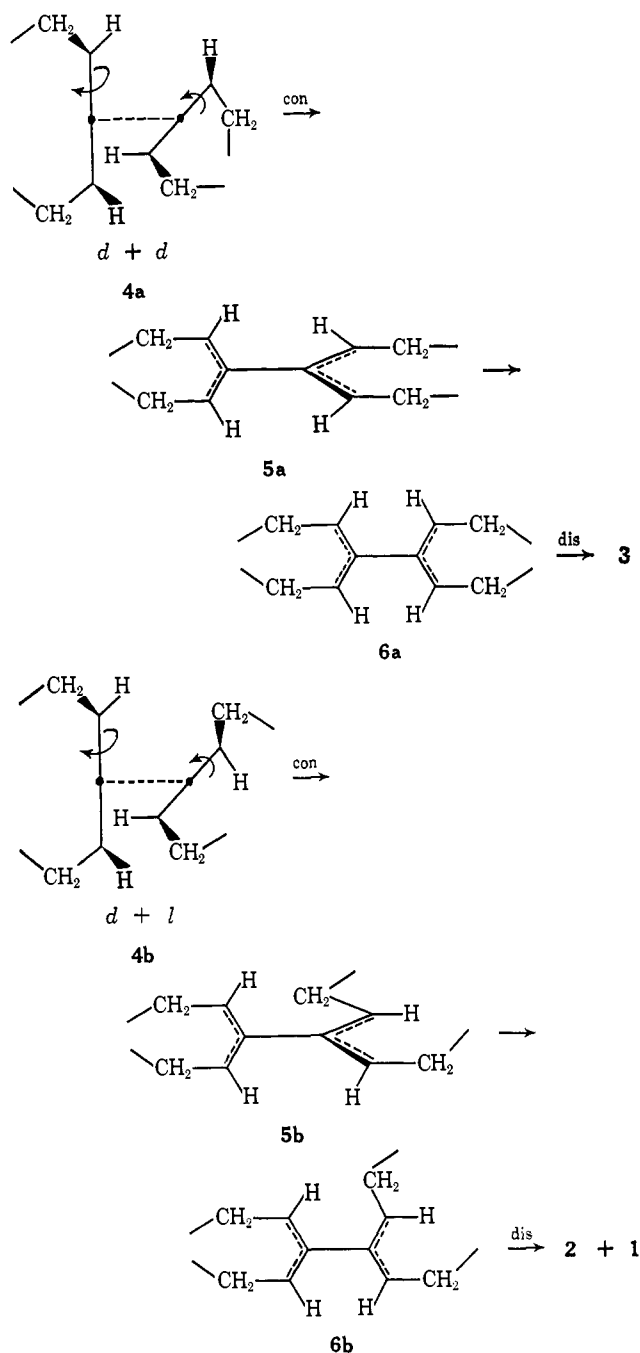
(10) (a) The mixtures of dimers have rotations close to zero indicating that nearly racemic **2** must be formed. Some activity is expected because the dimerization occurs in an optically active solvent (the allene). Dimerization of racemic allene in optically active solvents has led to comparable low rotations. (b) The product ratios obtained from dimerization of racemic allene thus indicate that *d* + *l* react nearly four times as fast as *d* + *d* (hence nearly twice as fast as *d* + *d* and *l* + *l* combined).

(11) From product ratios determined after a few per cent reaction (to avoid racemization), assuming that the reaction is 100% stereospecific and that the relative rates of *d* + *d* and *d* + *l* combinations are the same as in racemic allene, we estimate that optically pure allene has  $[\alpha]^{25}_D$  170-175° ( $\text{CH}_2\text{Cl}_2$ ).

(12) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968). Professor Hoffmann has elaborated this view in private discussions and at the Twenty-first Organic Chemistry Symposium of the American Chemical Society, Salt Lake City, Utah, June 1969, Abstracts, pp 110-129.

(13) Molecular models indicate that the hexamethylene chain effectively screens one side of each double bond of 1,2-cyclononadiene. Two of the four remaining possible ways to effect the *d* + *d* combination suffer an unfavorable  $\text{CH}_2 \cdots \text{CH}_2$  interaction which is absent in the *d* + *l* combinations, suggesting a steric basis for the higher rate<sup>10b</sup> of the latter reaction.

Scheme I



*i.e.*, having a disrotatory "joining" followed by a conrotatory closure from either 5 or 6 (e.g., **4a**  $\rightarrow$  **5b**  $\rightarrow$  **3**), will not change the stereochemical predictions. However, the conrotatory "joining" shown in Scheme I may follow if the transition state **4** is stabilized by the equivalent of spiroconjugation.<sup>14</sup> While such interaction probably is very small in **5**, it could be significant in **4** if twisting is much farther advanced than bending. Disrotatory closure of **6** is predicted from orbital symmetry arguments if one assumes a singlet state for this species.

Granting that the success of the Woodward-Hoffmann predictions argues strongly for a concerted reaction in this case, we suggest that in general one must

(14) (a) H. E. Simmons and T. Fukunaga, *J. Am. Chem. Soc.*, **89**, 5208 (1967); (b) R. Hoffmann, A. Imamura, and G. D. Zeiss, *ibid.*, **89**, 5215 (1967).

consider the possibility that intermediates both appear and react stereospecifically.

(15) (a) National Institutes of Health Predoctoral Fellow, 1964-1967; (b) National Science Foundation Trainee, 1967-1968.

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## Nuclear Magnetic Resonance of Phosphorus Compounds. V. Signs of Geminal Coupling Constants between Protons on Phosphorus<sup>1</sup>

Sir:

We wish to report measurements of the magnitudes and multiple resonance determinations of the signs of the geminal nmr coupling constants,  $J_{\text{HPH}}$ , between protons bonded to phosphorus of different coordinations.<sup>2</sup> These results are important in light of the observed changes of the corresponding coupling between protons on carbon<sup>3</sup> and a recent approximate theoretical treatment of the latter couplings.<sup>4</sup>

Our results are presented in Table I.<sup>5</sup> The magni-

Table I. Signs and Magnitudes of Geminal Proton-Proton Coupling Constants in Some Phosphorus Compounds

Compound	$J_{\text{HPD}}^a$	$J_{\text{HPH}}^{a,b}$	H-P-H bond angle, deg
$\text{CH}_3\text{PHD}$	-2.04	-13.4	93.4 <sup>c</sup>
$\text{PH}_2\text{D}$	-2.03	-13.3	93.3 <sup>d</sup>
$\text{C}_6\text{H}_5\text{PHD}$	-2.00	-13.1	...
$\text{CF}_3\text{PHD}$	-1.90	-12.5	97.4 $\pm$ 1.5 <sup>e</sup>
$\text{PH}_3\text{D}^+$	< 0.2	< 1.3	109.47 <sup>f</sup>
$(\text{CH}_3)_2\text{PHD}^+$	+0.51	+3.3	...
$\text{O}_2\text{PHD}^-$	+5.35	+35.1	92 <sup>g</sup>

<sup>a</sup> In Hz. <sup>b</sup> Calculated from  $J_{\text{HPD}}$  taking  $\gamma_{\text{H}}/\gamma_{\text{D}} = 6.55$ . <sup>c</sup> E. L. Breig and C. C. Liu, *J. Chem. Phys.*, **35**, 2139 (1961). <sup>d</sup> C. C. Loomis and M. W. P. Standberg, *Phys. Rev.*, **81**, 798 (1951). <sup>e</sup> I. Y. M. Wang, C. O. Britt, A. H. Cowley, and J. E. Boggs, *J. Chem. Phys.*, **48**, 812 (1968). <sup>f</sup> Assumed. <sup>g</sup> Reference 11.

tudes of the  $J_{\text{HPD}}$ 's (and hence  $J_{\text{HPH}}$ 's) were obtained from the <sup>1</sup>H spectra. The signs of  $J_{\text{HPD}}$  relative to  $J_{\text{PD}}$  and  $J_{\text{PH}}$  were established by a variety of multiple resonance experiments. These included selective irradiation of single lines that gave rise to Overhauser effects<sup>6</sup> and/or splittings<sup>7</sup> and indor experiments where either a <sup>1</sup>H or <sup>31</sup>P line was continuously observed while an irradiating frequency was swept through an appropriate portion of the rest of the spectrum.<sup>8,9</sup>

(1) Previous paper in this series: S. L. Manatt, D. D. Elleman, A. H. Cowley, and A. B. Burg, *J. Am. Chem. Soc.*, **89**, 4544 (1967).

(2) Previous data on the sign of  $J_{\text{HPH}}$  were from the analysis of the biphosphine spectrum which could only be accommodated if  $J_{\text{HPH}}$  is the same sign as  $J_{\text{PP}}$  which is a different sign from the  $J_{\text{HPH}}$ 's [R. M. Lynden-Bell, *Trans. Faraday Soc.*, **57**, 888 (1961)], and from preliminary analysis of the spectra of chloromethylphosphine and ethylphosphine whose spectra are best fitted if  $J_{\text{HPH}}$  and  $J_{\text{CH}}$  are both the same sign and negative (unpublished work of S. L. Manatt).

(3) See A. A. Bothner-By, *Advan. Magnetic Resonance*, **1**, 149 (1965); R. C. Cookson, T. A. Grabb, J. J. Frankel, and J. Hudes, *Tetrahedron, Suppl.*, **7**, 355 (1966).

(4) J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, **42**, 1339 (1965).

(5) We are grateful to Dr. W. D. White for the synthesis of  $\text{C}_6\text{H}_5\text{PHD}$ .

(6) K. Kuhlman and J. D. Baldeschwieler, *J. Am. Chem. Soc.*, **85**, 1010 (1963).

(7) R. Freeman and W. A. Anderson, *J. Chem. Phys.*, **37**, 2053 (1962).