containing two and three atoms of phosphorus. These reactions, as well as the ion chemistry observed in mixtures of phosphine with other molecules, will be the subject of a forthcoming publication.

(16) Alfred P. Sloan Fellow, 1968–1970.

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Rearrangement of Protonated Cyclopropyl Ketones to 1-Oxacyclopent-1-enyl Cations[1]

Sir:

Primary, secondary, and tertiary oxonium ions have been prepared by a variety of methods[2] since the pioneering work of Meerwein. We now describe a novel and mechanistically interesting method—the synthesis of 1-oxacyclopent-1-enyl cations from cyclopropyl ketones on heating in strong acids.

The protonation of ketones in acidic media has been studied extensively.[3] Pittman and Olah,[3f,g] in particular, have studied protonated cyclopropyl ketones in strong acids, but no further reactions beyond O-protonation were observed. When cyclopropyl methyl ketone (Ia) was added to 90% H_2SO_4 at room temperature, quantitative O-protonation occurred. On heating the solution to 81° complete conversion to 2-methyl-1-oxacyclopent-1-enyl cation (IIa) occurred in 3000 sec. Ion IIa was identified by its nmr spectrum (Figure 1), which exhibited a singlet at 3.48 ppm (three protons), a triplet
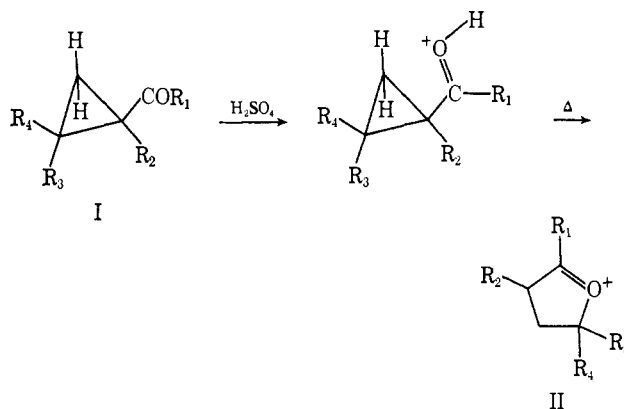
a, $R_1 = CH_3$; $R_2, R_3, R_4 = H$
b, $R_1, R_2 = CH_3$; $R_3, R_4 = H$
c, $R_1, R_2, R_3 = CH_3$; $R_4 = H$
d, $R_1, R_3, R_4 = CH_3$; $R_2 = H$
e, $R_1 = CH_3$; $R_2, R_4 = H$; $R_3 = C_6H_5$
f, $R_1 = C_6H_5$; $R_2, R_3, R_4 = H$
g, $R_1, R_3 = C_6H_5$; $R_2, R_4 = H$
h, $R_1 = c\text{-}C_3H_5$; $R_2, R_3, R_4 = H$

at 4.28 ppm, $J = 7.8$ Hz (two protons), a pentet at 3.03 ppm, $J = 7.8$ Hz (two protons), and a triplet at 6.13 ppm, $J = 7.8$ Hz (two protons).[4] Drowning of ion IIa in excess dilute NaOH solution generated only 5-hydroxy-2-pentanone.[5,6] Oxonium ion formation proved
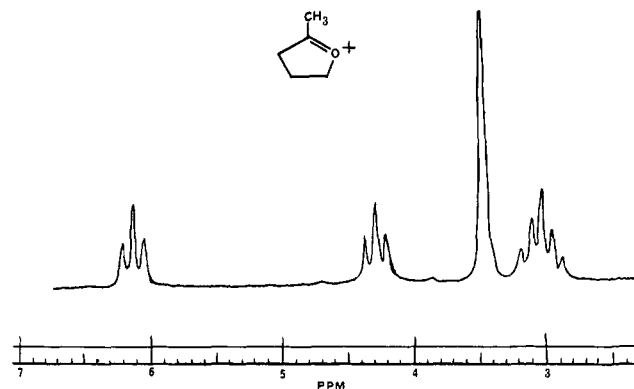

Figure 1.

to be general as illustrated by the rearrangement, in acid solution, of ketones Ia–h[7] to the respective oxonium ions IIa–h. Ions IIa–g were each formed quantitatively,[8] while IIh was obtained in only 45% yield. In the latter example, ring opening of the second cyclo-

(1) (a) Acid-Catalyzed Cyclization Reactions. VI. For paper V, see S. P. McManus and C. U. Pittman, Jr., in press; (b) this work was supported by a University of Alabama Research Committee Grant and at Huntsville by Grant 3501-B from the Petroleum Research Fund, administered by the American Chemical Society, and by NASA Grant NGL 01-002-001.

(2) (a) H. Meerwein, K. Bodenbenner, P. Borner, F. Kunert, and K. Wunderlich, *Ann.*, 632, 38 (1960); (b) H. Meerwein, V. Hederich, H. Morschel, and K. Wunderlich, *ibid.*, 635, 1 (1960); (c) C. B. Anderson, E. C. Friedrich, and S. Winstein, *Tetrahedron Letters*, 2037 (1963); (d) R. W. Taft, R. H. Martin, and F. W. Lampe, *J. Am. Chem. Soc.*, 87, 2490 (1965); (e) R. H. Martin, F. W. Lampe, and R. W. Taft, *ibid.*, 88, 1353 (1966); (f) K. Dimroth and P. Heinrich, *Angew. Chem.*, 78, 714 (1966); (g) B. G. Ramsey and R. W. Taft, *J. Am. Chem. Soc.*, 88, 3058 (1966); (h) S. Kabuss, *Angew. Chem.*, 78, 714 (1966); (i) H. Hart and D. A. Tomalia, *Tetrahedron Letters*, 5385 (1966); (j) D. A. Tomalia and H. Hart, *ibid.*, 3389 (1966); (k) H. Hart and D. A. Tomalia, *ibid.*, 1347 (1967); (l) F. M. Beringer and S. A. Gatton, *J. Org. Chem.*, 32, 2630 (1967); (m) G. A. Olah and J. M. Bollinger, *J. Am. Chem. Soc.*, 89, 2993 (1967); (n) H. P. Ward and D. D. Sherman, *ibid.*, 89, 4222 (1967); (o) G. A. Olah and J. Sommer, *ibid.*, 90, 4323 (1968); (p) P. E. Peterson and F. J. Slama, *ibid.*, 90, 6516 (1968); (q) S. Kabuss, *Angew. Chem. Intern. Ed. Engl.*, 7, 64 (1968); (r) K. Dimroth and W. Mach, *ibid.*, 7, 461 (1968); (s) C. U. Pittman, Jr., and S. P. McManus, *Chem. Commun.*, 1479 (1968); (t) R. F. Borch, *J. Am. Chem. Soc.*, 90, 5303 (1968); (u) C. H. V. Dusseau, S. E. Schaafsma, H. Steinberg, and T. J. deBoer, *Tetrahedron Letters*, 467 (1969); (v) R. J. Gargiulo and D. S. Tarbell, *Proc. Natl. Acad. Sci. U. S.*, 62, 53 (1969).

(3) (a) S. Nagakwa, A. Minegishi, and K. Stanfield, *J. Am. Chem. Soc.*, 79, 1033 (1957); (b) R. Stewart and K. Yates, *ibid.*, 80, 6355 (1958); (c) H. J. Campbell and J. T. Edward, *Can. J. Chem.*, 38, 2109 (1960); (d) R. Stewart, M. R. Granger, R. B. Moodie, and J. J. Muenster, *ibid.*, 41, 1065 (1963); (e) T. Birchall and R. J. Gillespie, *ibid.*, 43, 1045 (1965); (f) C. U. Pittman, Jr., and G. A. Olah, *J. Am. Chem. Soc.*, 87, 2998 (1965); (g) C. U. Pittman, Jr., and G. A. Olah, *ibid.*, 87, 5123 (1965); (h) T. J. Sekur, *Tetrahedron Letters*, 4793 (1966); (i) T. G. Bonner and J. Phillips, *J. Chem. Soc., B*, 650 (1966); (j) T. D. J. D'Silva and H. Ringold, *Tetrahedron Letters*, 1505 (1967); (k) M. Brookhart, G. C. Levy, and S. Winstein, *J. Am. Chem. Soc.*, 89, 1735 (1967); (l) G. A. Olah, M. Calin, and D. H. O'Brien, *ibid.*, 89, 3586 (1967); (m) G. A. Olah and M. Calin, *ibid.*, 90, 938 (1968); (n) G. A. Olah and M. Calin, *ibid.*, 90, 4672 (1968).

(4) (a) The simplicity of this spectrum results from the equivalence of the *cis* and *trans* vicinal coupling constants between the 3,4 and the 4,5 positions. This was expected in analogy with the 2,3-dihydrofuran system (*cf.* L. M. Jackman, "Applications of NMR Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p 87) and the previously reported 1-oxacyclopent-1-enyl cations.[2n,8] (b) All spectra were taken on a Varian HA-100 instrument and positions are reported relative to TMS (internal capillary).

(5) L. Joris and P. von R. Schleyer, *J. Am. Chem. Soc.*, 90, 4599 (1968).

(6) Addition of authentic 5-hydroxy-2-pentanone[5] to 90% H_2SO_4 generated ion IIa quantitatively.

(7) Ketones were prepared by standard methods [*cf.* J. M. Conia, *Angew. Chem. Intern. Ed. Engl.*, 7, 570 (1968)] or were purchased. All compounds reported here were fully characterized.

(8) The nmr bands of protonated ketones disappear completely and are replaced by bands completely attributable to the corresponding oxonium ion. With the exception of IIh, no other bands are found in the spectra and the total number of protons measured by integration agrees with quantitative generation of cations IIa–g. The rates of rearrangement were monitored by observing both the disappearance and the appearance of characteristic bands.

Table I. Nmr Assignments of 1-Oxacyclopent-1-enyl Cations[a]

Ion	R₁	CH, CH₂ at C-3	CH₂ at C-4	CH, CH₂ at C-5	CH₃ at C-3	CH₃ or C₆H₅ at C-5
IIa	CH₃	4.28 (tr)	3.03 (p)	6.13 (t)		
	3.48 (s)	[7.8]	[7.8]	[7.8]		
IIb	CH₃	4.37 (m)	2.73 (t)	6.04 (t)	2.08 (d)	
	3.48 (s)		[7.7]	[7.7]	[7]	
			3.24 (t)			
			[7.7]			
IIc	CH₃	4.29 (m)	2.86 (t)	6.29 (m)	2.05 (d)	2.31 (d)
	3.43 (s)		[7.4]		[6.9]	[6.5]
			2.27 (t)			
			[7.4]			
IId	CH₃	4.38 (tr)	2.91 (t)			2.32 (s)
	3.44 (s)	[7.1]	[7]			
IIe	CH₃	4.31 (tr)	3.06 (t)	7.03 (t)		7.78 (m)
	3.40 (s)	[7.7]	[7.7]	[7.7]		
			2.47 (t)			
			[7.7]			
IIf	C₆H₅	4.50 (tr)	3.03 (p)	6.00 (t)		
	ortho 8.72 (d)	[7.8]	[7.8]	[7.8]		
	meta 8.08 (tr)					
	para 8.44 (tr)					
IIg	ortho 8.51[c]	4.49 (tr)[b]	3.19 (t)[d]	6.91 (t)[b]		7.69 (m)
	meta 7.84 (m)		[8]			
	para 8.27	[8]	2.92 (t)	[~8]		
			[8]			
IIh	c-C₃H₅	4.36 (tr)[b]		6.22 (t)[b]		
	α 3.07 (m)	[7.2]	e	[7.2]		
	β 2.87 (m)					

[a] Chemical shifts are given in parts per million below TMS (internal capillary) in 90% H_2SO_4 at 32°; coupling constants (in brackets) are measured in hertz. The integrated areas were in agreement with structure. [b] Broadened. [c] meta protons are partially overlapped by the C-5 phenyl hydrogen bands. [d] Partially overlapped. [e] Not clearly resolved from the cyclopropyl hydrogens. Abbreviations: s, singlet; d, doublet; t, triplet; p, pentet; m, multiplet.

propyl group competed with the generation of IIh at 90–100°. The nmr spectra of the ions are summarized in Table I. The products of drowning the ions into aqueous NaOH at 5–10° as well as the rates of rearrangement[8] of some of the protonated ketones are listed in Table II.
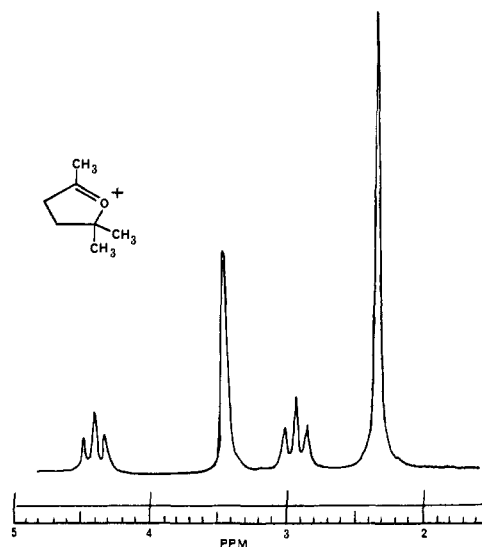

Figure 2.

The rearrangement rates were first order over 85% of the reaction. The rates increased with decreasing acidity from 96 to 75% H_2SO_4 and were greatly increased by ring substitution at the β position. For example, 2,2-

Table II. Selected First-Order Rate Constants for Oxonium Ion Generation

Ion	H_2SO_4, %	Temp, °C	k_1, sec⁻¹	Product from drowning
IIa	96	81	7.93 × 10⁻⁴	5-Hydroxy-2-pentanone
	90	81	1.32 × 10⁻³	
	85	81	1.62 × 10⁻³	
	80	81	1.85 × 10⁻³	
	75	81	2.43 × 10⁻³	
IIb	96	98	1.84 × 10⁻³	5-Hydroxy-3-methyl-2-pentanone
	80	98	4.30 × 10⁻³	
	80	76	1.31 × 10⁻³	
IIf	90	81	3.3 × 10⁻³	3-Hydroxypropyl phenyl ketone
	75	81	6.77 × 10⁻³	
IIh[a]	90	94	5.16 × 10⁻⁴	
IIc	90	30	2.25 × 10⁻⁴	5-Hydroxy-3-methyl-2-hexanone
IId	90	15	Very rapid	5-Hydroxy-5-methyl-2-hexanone

[a] Based on measurements over the first 25% conversion.

dimethyl-1-acetylcyclopropane (Id) rearranged quantitatively to ion IId (Figure 2) at 10° faster than the ketone could be added to an acid-filled nmr tube. Substitution of methyl for hydrogen at the α position (Ib,c) does not increase the rate of rearrangement. The increase in rate with decreasing acidity could be explained by irreversible electrophilic attack on the ring competing more effectively at lower acidity with reversible O-protonation.[9] Electrophilic ring attack could lead to (1) ring opening to a classical carbonium ion which then

(9) Though the rate of ring protonation should decrease with decreasing acidity, this might be offset by the greater availability of unprotonated ketone.
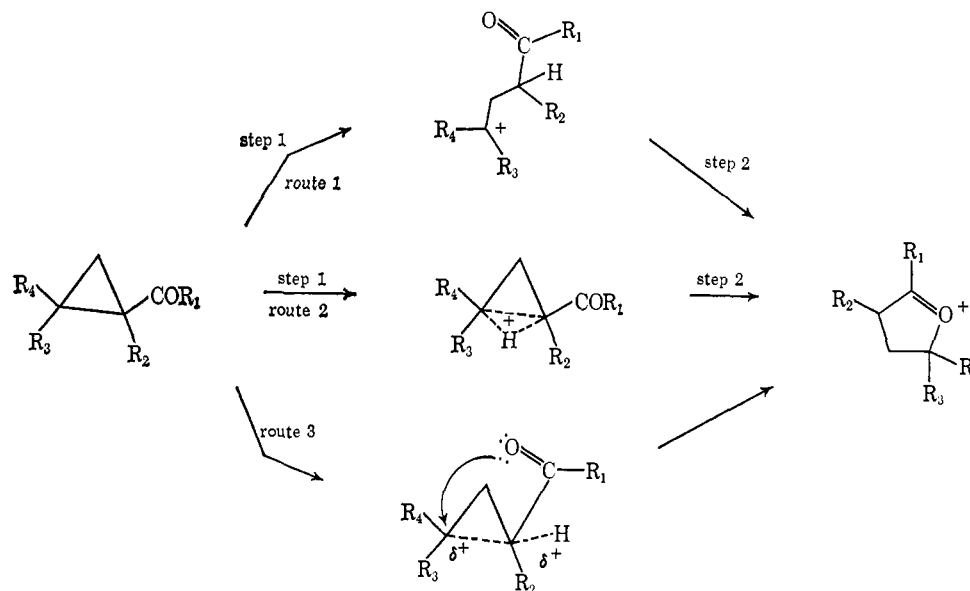
quickly cyclizes by carbonyl oxygen attack, (2) formation of protonated cyclopropane which then proceeds to II with carbonyl oxygen participation, or (3) a concerted C-protonation ring opening with neighboring group participation by carbonyl oxygen.

Previous work[10] has demonstrated the thermal rearrangement of cyclopropyl ketones to γ,δ-unsaturated ketones. Since γ,δ-unsaturated ketones themselves cyclize to 1-oxacyclopent-1-enyl cations in strong acids,[11] it was necessary to test the possibility of the thermal ring opening of our ketones (I). At temperatures between 80 and 115° in a variety of organic solvents, the cyclopropyl ketones remained unchanged after 3000 sec.

H–D exchange in 96% D_2SO_4 of C-2 methyl hydrogens and C-3 methylene hydrogens in II occurs readily at 80–100° but is slow at 25°. However, when Id was introduced into 96% D_2SO_4 at 15° to give IId, 50% deuterium was immediately incorporated at C-3 *during the rearrangement*. This result rules out a protonated cyclopropane with a sufficient lifetime to give the extensive scrambling characteristic of these intermediates in 57–99% D_2SO_4.[12] After quantitative generation of the ions II, the H–D exchange rate of the C-2 methyl and C-3 methylene hydrogens was studied as a function of acidity. The rate of exchange increased rapidly as the acid concentration was lowered from 96 to 80% D_2SO_4. In 96% D_2SO_4 exchange is slow at 70° but can be conveniently measured by nmr at 100° (35% exchange at the C-2 methyl of IId after 267 sec). In 80% D_2SO_4 the exchange rate is much faster (60% exchange at C-2 methyl in 600 sec at 30°). The increased rate at lower

acid strength suggests water is a base in H–D exchange. The complete lack of exchange at C-4 and C-5 and at C-5 methyl groups, even after heating overnight at 100°, rules out any equilibria between ions II and their corresponding unsaturated ketones. The ratio of C-3 methylene to C-2 methyl H–D exchange rates (1.26 at 24° and 1.20 at 120° for 2,5-dimethyl-1-oxacyclopent-1-enyl cation) illustrates the similarity of transition-state energies for *endo* and *exo* double bond formation during proton loss.[18]

Our results might suggest a duality of mechanisms. The large rate increase of oxonium ion formation with β substitution could signal progressive intervention of mechanism 1 where a tertiary carbonium ion is formed. However, during formation of IId the tertiary ion's lifetime cannot be long enough to permit measurable H–D exchange at the methyl groups. With ketones Ia, b, f, h, intermediate primary carbonium ions would not be easily formed and one would expect mechanisms 2 or 3 to be operative in light of recent studies of protonated cyclopropanes.[12,14]

Finally, attempts to carry out similar reactions with ethyl cyclopropanecarboxylate, ethyl *trans*-2-phenylcyclopropanecarboxylate, and cyclopropanecarboxamide failed. For example, the 2-phenyl ester was recovered in >80% yield after heating at 100° for 600 sec in 90% H_2SO_4.[15]

(10) R. M. Roberts, R. G. Landolt, R. N. Greene, and E. W. Heyer, *J. Am. Chem. Soc.*, **89**, 1404 (1967).

(11) In addition to our reported[2r,s] work on this topic, we have found that 5-methyl-5-hexen-2-one and 4-methyl-1-phenyl-4-penten-1-one each cyclize rapidly and quantitatively at 15° in 60 to 98% H_2SO_4 to their corresponding 1-oxacyclopent-1-enyl cations. Studies in 96% D_2SO_4 show only a single deuterium is incorporated at the C-5 methyl. Thus cyclization occurs without prior enolization. This does not preclude reversible protonation of oxygen prior to C-protonation; *cf.* G. E. Lienhard and T. C. Wang, *ibid.*, **91**, 1146 (1969).

(12) N. C. Deno, D. LaVietes, J. Mockus, and P. C. Scholl, *ibid.*, **90**, 6457 (1968).

(13) To the degree these transition states resemble their olefinic products, these rates indicate *exo* double bonds are only slightly less stable than *endo* in the dihydrofuran system.

(14) (a) P. S. Skell and I. Starer, *J. Am. Chem. Soc.*, **82**, 2971 (1960); (b) P. S. Skell and I. Starer, *ibid.*, **84**, 3962 (1962); (c) R. L. Baird and A. Aboderin, *ibid.*, **86**, 252 (1964); (d) R. L. Baird and A. Aboderin, *Tetrahedron Letters*, **235** (1963); (e) A. Aboderin and R. L. Baird, *J. Am. Chem. Soc.*, **86**, 2300 (1964); (f) C. C. Lee, J. E. Kruger, and E. W. Wong, *ibid.*, **87**, 3985, 3987 (1965); (g) C. C. Lee and J. E. Kruger, *Can. J. Chem.*, **44**, 2343 (1966); (h) H. Hart and R. H. Schlosberg, *J. Am. Chem. Soc.*, **88**, 5030 (1966); N. Deno and D. N. Lincoln, *ibid.*, **88**, 5357 (1966); H. Hart and R. H. Schlosberg, *ibid.*, **90**, 5189 (1968).

(15) A referee pointed out that it was previously noted that 5-hydroxy-2-pentanone and cyclopropyl methyl ketone gave "identical products" on heating in H_2SO_4 (A. S. Kushner, Ph.D. Thesis, The Pennsylvania State University, 1966). The reaction of cyclopropylcarboxylic acids in H_2SO_4 were investigated in the Ph.D. Thesis of D. LaVietes, The Pennsylvania State University, 1969.

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The Dimerization of Racemic and Optically Active 1,2-Cyclononadiene[1]

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.[2] In order to shed new light on this (2 + 2) cycloaddition[3] 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**.[4] The nmr spectra of **2** and **3** show identical broad triplets at δ 5.52 for the two vinyl protons. The two *syn* tertiary allylic protons of **3** appear as a multiplet at δ 2.9 (*trans* C–C deshielding), whereas in **2** the corresponding signal for the *anti* protons is at *ca.* δ 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.* δ 5.5 and 5.8) indicating one *cis* and one *trans* double bond and a *syn* ring fusion (δ 2.9).
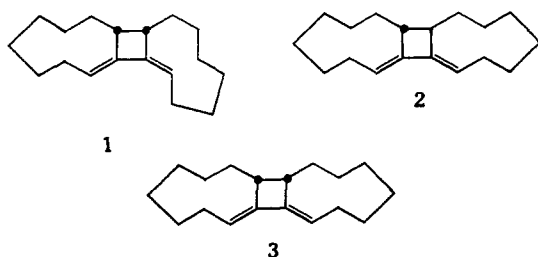
The stereochemistry assigned is supported[6] by the relative thermal stabilities of the cyclobutenes obtained

(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[5] 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,[7] the *anti* compound from **2** opens more rapidly than the *syn* isomer[8] from **3**.

Dimerization (125°, 70 min) of *optically active* 1,2-cyclononadiene,[9] $[\alpha]^{25}$D +163° (CH_2Cl_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*).[10] 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%.[11]

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,[2] but it is exactly the result predicted by Hoffmann and Woodward[12] 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 π 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)[13] 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'-bicyclononenyl, which at somewhat higher temperatures undergoes 1,5-sigmatropic rearrangement to 3-cyclononylidenecyclononene.
(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° (CH_2Cl_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 $CH_2\cdots CH_2$ interaction which is absent in the *d* + *l* combinations, suggesting a steric basis for the higher rate[10b] of the latter reaction.