

oxygen atoms in phosphates (but presumably particularly the phosphoryl oxygen atoms) contribute to shielding by partial bonding with the d-orbitals of phosphorus. However, the greater double-bond character in the P-O bonds of phosphates, as compared to those of phosphites, should also be apparent in infrared spectra, but here the situation is confused. No agreement has even been reached as to the correct assignments of individual frequencies to C-O and to P-O stretching motions.<sup>64</sup> Simple inspection, however, does not reveal much difference between the P-O-C vibrations in phosphates and phosphites.

If, indeed, p-d double-bonding is greater in the ester bonds of phosphates as compared to phosphites (and of sulfates as compared to sulfites), then such double-bonding could stiffen the P-O or S-O bonds, with concomitant stabilization of the esters. Since the bond lengths and angles do not exactly fit the five-membered rings of ethylene phosphate and sulfate, the stiffening and flattening of the rings caused by partial double-bonding might produce strain in excess of that previously<sup>6</sup> estimated. At the same time, the resistance of the ring could result in less double-bond character for the P-O and S-O bonds of the cyclic compounds. To the extent that double-bonding is diminished, the five-membered cyclic esters are less stabilized than their open-chain analogs; to the extent that the P-O and S-O bonds are stiffened, they increase the strain in the ring. This explanation places more emphasis on the stabilization of the non-cyclic esters, and less emphasis on ring strain than did our earlier discussions,<sup>6,9</sup> and perhaps makes it easier to understand why ethylene phosphate undergoes oxygen exchange with the solvent at a rate comparable to that of ring opening.<sup>8</sup> If the

(54) L. J. Bellamy, "The Infra-Red Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1958, p. 316.

present view is correct, then the formation of the transition state for either hydrolysis or exchange of five-membered cyclic esters is preferred over that for the non-cyclic esters in part because less energy is required to overcome the stabilization supplied by the partial double bonds. The difference in heat of saponification between the cyclic and non-cyclic esters is of course unaffected by this somewhat different division of the energy, but perhaps this thermochemical quantity should not be regarded exclusively as strain. Presumably the double bond character of the S-O or P-O bonds is lost in the pentacovalent transition state<sup>8</sup> when attack occurs at sulfur or phosphorus, but not when it occurs at carbon. In this way, it may be possible to account for the major part of the kinetic acceleration in the hydrolysis of five-membered cyclic sulfates and phosphates, and to understand why this acceleration is largely absent in the six-membered rings or when attack occurs at carbon. However, it must still be noted that on the one hand the thermochemical "strain" which has been measured (see Table VIII) is inadequate to account fully for the kinetic acceleration in phosphates, and on the other that kinetic acceleration, in alkaline solution, is moderately large for sulfites, where no thermochemical strain has been found. Further, although kinetic acceleration at sulfur may be very large in the cyclic sulfates, this point has not been proved, and at present one can only say that the factor exceeds 300. The difficulties with infrared spectra, noted above, also stand in the way of a complete understanding of the problem. Nevertheless, the role of p-d double-bonding in the kinetic acceleration seems reasonably probable.

**Acknowledgment.**—The authors gratefully acknowledge the support of the National Science Foundation for the work herein reported.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK 27, N. Y.]

## Organic Reactions under High Pressure. VII. Volumes of Activation for Some Diels-Alder Reactions<sup>1</sup>

BY CHEVES WALLING AND HARVEY J. SCHUGAR

RECEIVED JULY 18, 1962

The effect of pressure on the dimerization of cyclopentadiene has been reinvestigated, yielding values of  $\Delta V^*$  near atmospheric pressure of  $-20.2$  to  $-22.5$  cc./mole at  $20-40^\circ$ . Similarly, a value of  $\Delta V^* = -22.6$  cc./mole at  $80^\circ$  has been obtained for the reaction of 2,3-dimethylbutadiene with butyl acrylate. The rearrangement of  $\beta$ -1-hydroxydicyclopentadiene is pressure retarded, consistent with its representing a partial retro-Diels-Alder reaction. These results further support the idea that Diels-Alder reactions of non-cyclic dienes are probably two-step processes involving an open chain intermediate, and that the transition states in reactions of cyclopentadiene are at least highly unsymmetric.

The pronounced increase in rate of Diels-Alder reactions at high pressure was first noted by Raistrick, Sapiro and Newitt in the dimerization of cyclopentadiene,<sup>2</sup> and the phenomenon has been studied further by Walling and Peisach for the case of isoprene dimerization.<sup>3</sup> Since the pressure coefficient of the reaction provides a criterion of mechanism, we have been interested in examining additional systems, particularly since the cyclopentadiene data appear dubious, and the isoprene results have recently been questioned.<sup>4</sup> This paper reports a reinvestigation of the cyclopentadiene dimerization, a study of the reaction between 2,3-dimethylbutadiene and butyl acrylate, and an investi-

gation of the effect of pressure on the rearrangement of  $\beta$ -1-hydroxydicyclopentadiene to *anti*-8-hydroxydicyclopentadiene which has been interpreted by Woodward and Katz<sup>5</sup> as a partial retro-Diels-Alder reaction.

### Results

**Cyclopentadiene.**—The dimerization of cyclopentadiene was studied by Raistrick, *et al.*,<sup>2</sup> at pressures up to 3000 kg./cm.<sup>2</sup> and temperatures from  $0-40^\circ$  in the absence of solvent. Although the reaction was accelerated by pressure over the whole range studied, their results are peculiar in that  $\Delta V^*$ , defined by the equation

$$d \ln k/dP = -\Delta V^*/RT \quad (1)$$

changes markedly with temperature.<sup>6</sup> In fact, a moderate extrapolation indicates that at higher temperatures  $\Delta V^*$  would become larger than  $\Delta V$  for the

(1) Taken from the Ph.D. thesis of Harvey J. Schugar, Columbia University, 1962. Support of this work by a grant from the Petroleum Research Fund of the American Chemical Society is gratefully acknowledged.

(2) B. Raistrick, R. H. Sapiro and D. M. Newitt, *J. Chem. Soc.*, 1761 (1939).

(3) C. Walling and J. Peisach, *J. Am. Chem. Soc.*, **80**, 5819 (1958).

(4) S. W. Benson and J. A. Berson, *ibid.*, **84**, 152 (1962).

(5) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

(6) This peculiarity was pointed out to us by M. G. Gonikberg in 1960.

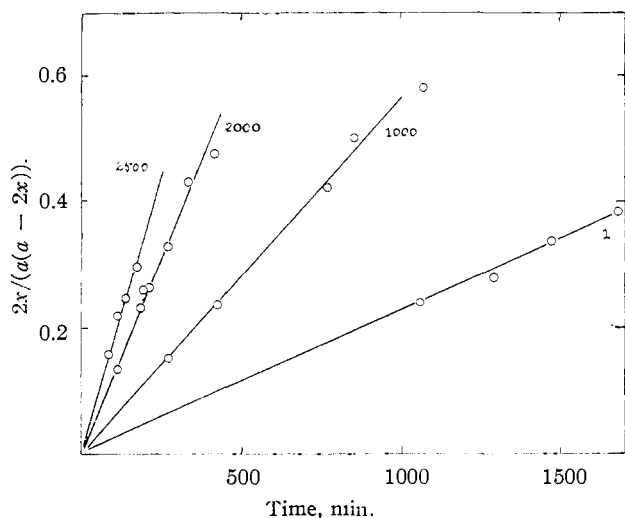


Fig. 1.—Effect of pressure (kg./cm.<sup>2</sup>) on the dimerization of cyclopentadiene at 40°;  $a$  = initial concentration,  $x$  = concentration of dimer.

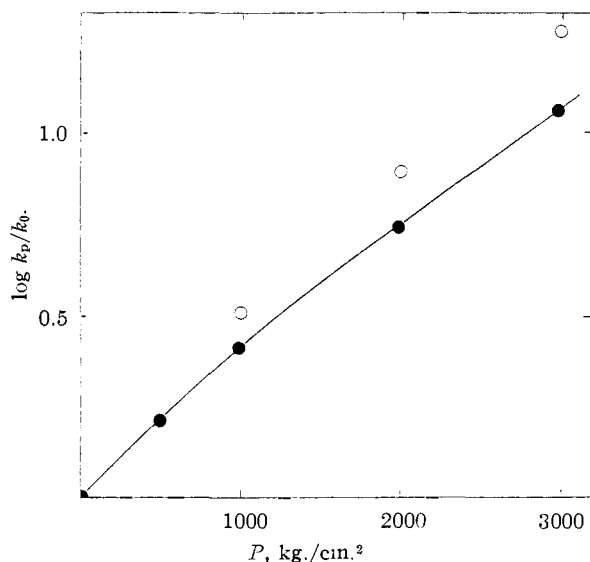


Fig. 2.—Effect of pressure on cyclopentadiene dimerization at 30°: open circles, data of Raistrick, *et al.*<sup>2</sup>

over-all reaction. Since it is hard to rationalize such behavior, we suspected that their data were in error, either because of the formation of higher polymers, or through their failure to obtain isothermal conditions in their reaction vessel. Either supposition was plausible since they followed reaction simply by change in index of refraction, and also reported that at slightly higher pressures and temperatures cyclopentadiene underwent violent decomposition to carbonaceous products.<sup>7</sup>

Accordingly, we have reinvestigated the dimerization in dilute solution in *n*-butyl chloride (an inert solvent of known compressibility) at 20, 30 and 40°, following the reaction by gas chromatographic (G.L.C.) determination of dimer. Under these conditions no detectable higher products are formed, the reaction is cleanly bimolecular, and it is slow enough (reaction times 1–150 hr.) to insure isothermal reaction conditions. Typical rate data are plotted in Fig. 1, while Fig. 2 gives a plot of  $\log k$  vs.  $P$ , compared with results reported by Raistrick, *et al.*<sup>2</sup> Experiments at other temperatures showed similar consistency, and values of  $\Delta V^*$ , extrapolated to atmospheric pressure, are listed in Table I,

(7) B. Raistrick, R. H. Sapiro and D. M. Newitt, *J. Chem. Soc.*, 1770 (1939).

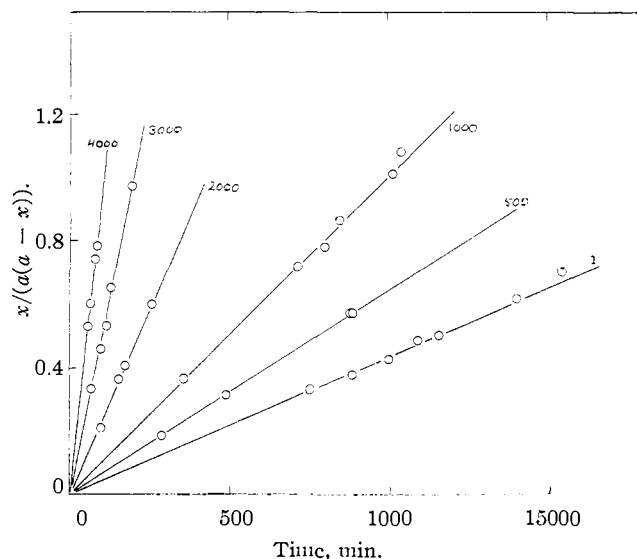


Fig. 3.—Effect of pressure (kg./cm.<sup>2</sup>) on the reaction of 2,3-dimethylbutadiene and *n*-butyl acrylate at 80°; initial concentration of reactants,  $a$ , are equal;  $x$  = concentration of product.

together with Raistrick's results and the corresponding over-all volume changes for the reaction. From our results,  $\Delta V^*$  increases only slightly with temperature, paralleling the increase in  $\Delta V$ , so that their difference,  $\Delta V^* - \Delta V$ , remains sensibly constant.

TABLE I  
ACTIVATION VOLUMES FOR CYCLOPENTADIENE DIMERIZATION  
(CC./MOLE)

$T$ , °C.	$\Delta V^{*a}$	$\Delta V^{*b}$	$\Delta V^c$
0	....	-14.3	....
20	-20.2	-17.7	-31.4
30	-22.3	-21.9	-32.2
40	-22.5	-25.7	-33.0

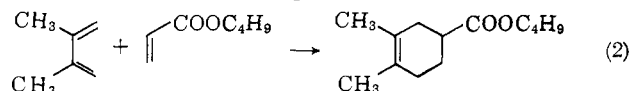
<sup>a</sup> This paper. <sup>b</sup> Raistrick, *et al.*<sup>2</sup> <sup>c</sup> Over-all volume change for dimerization.

The effect of pressure on the quasi-thermodynamic quantities  $\Delta H^*$  and  $\Delta S^*$  can also be calculated from our data, and are listed in Table II. Their significance is discussed further below, and we merely note here that their smooth variation with pressure supports the internal consistency of the data.

TABLE II  
 $\Delta H^*$  AND  $\Delta S^*$  FOR CYCLOPENTADIENE DIMERIZATION AT 30°

$P$ , kg./cm. <sup>2</sup>	$\Delta H^*$ , kcal./mole	$\Delta S^*$ , cal./deg. mole
1	17.0	-29.0
1000	17.3	-27.0
2000	17.5	-23.9
3000	18.3	-19.8

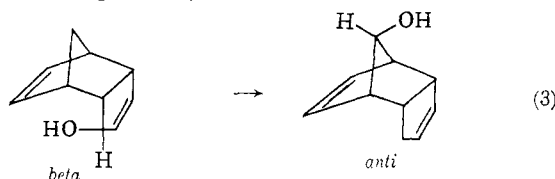
**2,3-Dimethylbutadiene-Butyl Acrylate.**—The reaction of this pair of compounds is typical of a Diels-



Alder reaction between a diene and a dienophile possessing a strong electron-withdrawing group, and was selected because it proceeds cleanly at a convenient rate with no possibility of complications due to isomeric products. At 70 and 80° in bromobenzene as solvent, second-order rate constants were found to be  $3.47 \times 10^{-6}$  and  $7.59 \times 10^{-6}$  l./mole sec., respectively, giving  $\Delta H^*$  17.7 kcal./mole and  $\Delta S^*$  -30.8 cal./degree mole. The molar volume change for the reaction is -42 cc., calculated from bulk densities of products and

reactants. The possibility that it is significantly different in bromobenzene solution was rendered unlikely by showing that a mixture of bromobenzene, reactants and products had very closely (within 0.2%) the volume predicted from simple addition of the volumes of the components. Plots of kinetic runs at 80° and varying pressures are shown in Fig. 3, and the plot of  $\log k$  vs. pressure in Fig. 4. The slope of the curve in Fig. 4 corresponds to  $\Delta V^* = -22.6$  cc./mole, and its linear form makes the extrapolation to atmospheric pressure particularly straightforward.

**1-Hydroxydicyclopentadiene.**—Woodward and Katz have shown that  $\alpha$ - and  $\beta$ -1-hydroxydicyclopentadiene rearrange smoothly to *syn*- and *anti*-8-hydroxydicyclopentadiene, respectively,<sup>5</sup> e.g.



Further, since optically active starting materials yield optically active products, they conclude that the rearrangement is truly intramolecular with only one bond between the cyclopentadiene units being broken in the process. Similar stereospecificity has subsequently been observed in the rearrangements of 1-ketodicyclopentadiene<sup>8a</sup> and methacrolein dimer,<sup>8b</sup> but is not unique for all Diels-Alder type products.

*A priori*, the Woodward and Katz rearrangements might be regarded as partial retro-Diels-Alder reactions or as unrelated Cope rearrangements. Since the former should be pressure retarded, and since Cope rearrangements in open-chain systems are pressure accelerated,<sup>9,10</sup> we have investigated the effect of pressure on the rearrangement of the  $\beta$ -alcohol (chosen because the equilibrium lies far on the side of the rearranged product) following the process by infrared analysis. The reaction at 105–125° (no solvent) was found to be cleanly unimolecular, and results are listed in Table III.

T, °C.	P, kg./cm. <sup>2</sup>	k, sec. <sup>-1</sup> × 10 <sup>3</sup>
105	1	2.54
115	1	8.1
125	1	23.0
115	3500	4.92
115	4900	4.66
115	6900	4.0

At atmospheric pressure,  $\Delta H^* = 32 \pm 2$  kcal./mole,  $\Delta S^* = 2$  e.u., and, calculated from the run at 3,500 kg./cm.<sup>2</sup>,  $\Delta V^* = 6$  cc./mole. However, since a plot of  $\log k$  vs. P is strongly curved and measurements were not made at lower pressures, we can only conclude that  $\Delta V_0^* > 6$  cc./mole and the reaction is significantly pressure retarded.

### Discussion

The mechanism of the Diels-Alder reaction has been the subject of extensive controversy and has generated a formidable literature. As this has received a thorough recent summary by Berson and Remanick,<sup>11</sup> it will not

(8) (a) R. C. Cookson, J. Hudec and R. O. Williams, *Tetrahedron Letters*, **22**, 29 (1960); P. Yates and P. Eaton, *Tetrahedron*, **12**, 13 (1961); (b) R. P. Lutz and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 2198 (1961).

(9) C. Walling and M. Naiman, *ibid.*, **84**, 2628 (1962).

(10) With this said, it must be recognized that there is a close mechanistic similarity between a partial retro-Diels-Alder reaction as Woodward and Katz and we hypothesize, and a Cope rearrangement. In fact, if transition states have the same geometry (as suggested by our results) both names should describe the same process, even though more bond-breaking appears to be involved than in Cope rearrangements in open-chain systems.

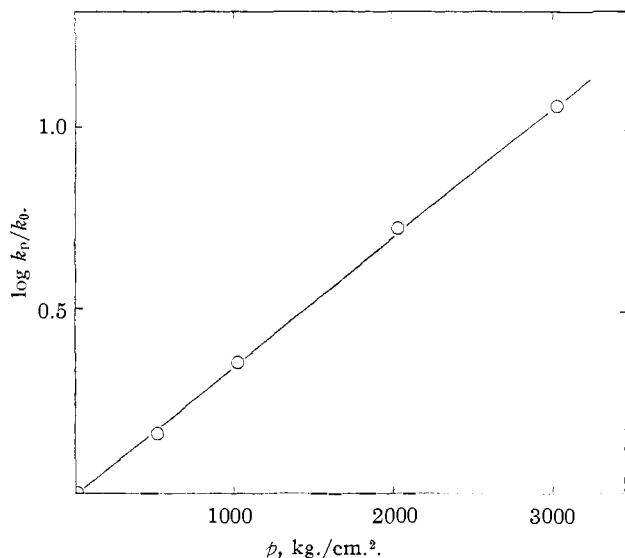
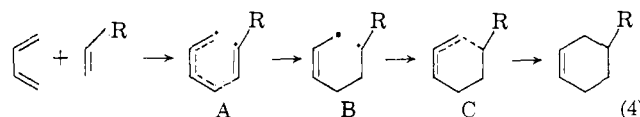
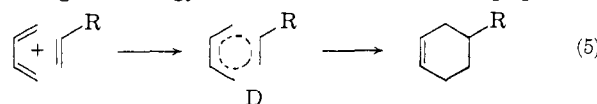


Fig. 4.—Effect of pressure on the reaction of 2,3-dimethylbutadiene with *n*-butyl acrylate at 80°.

be reviewed here. In general, recent interpretations have favored one of two extremes in formulating the reaction path: a two-step process involving a non-cyclic intermediate B in which the transition state A



is of higher energy than C, and a one-step process



with two partial bonds in the transition state D. In the case of path 4, the state of electron pairing in the intermediate B is also of significance and will be mentioned later.

The distinction between the two mechanisms can also be considered in terms of energy changes along the reaction coordinate, illustrated schematically in Fig. 5, which also includes the corresponding volume changes, important in our subsequent discussion.

Unfortunately for this dichotomy, paths 4 and 5 represent extreme examples of possible formulations, and one can easily imagine a sequence of changes in energy profile by which path 4 could pass smoothly over to path 5. This could be accomplished either by successive decreases in the energy of A and increases in the energy of C, or by a dwindling away of C, and a shift of A to the right. As we see it, the Woodward and Katz "new mechanism" encompasses intermediate stages in the second sort of transformation with the driving force provided by "secondary attractive forces." On the other hand, Berson<sup>11</sup> appears to favor path 5, although conceding that different Diels-Alder processes may cover the whole range of energy profiles just described.

Since the large amount of information now available on Diels-Alder reactions, while in part supporting one extreme formulation and in part the other, is, in general, consistent with both, we must now consider whether the data of this paper contribute anything toward a choice. In our previous publication<sup>3</sup> on the dimerization of isoprene it was concluded that the reported value of  $\Delta V^*$  ( $-24$  to  $-26$  cc./mole) was

(11) J. A. Berson and A. Remanick, *J. Am. Chem. Soc.*, **83**, 4947 (1961).

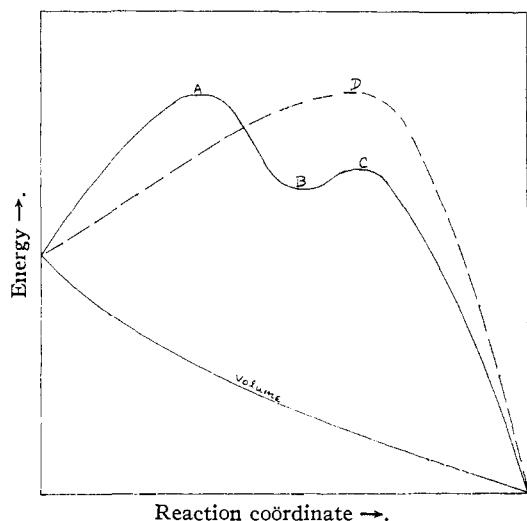


Fig. 5.—Schematic diagram of energy-volume relationships in Diels-Alder reactions: ABC, two-step reaction; D, one step.

approximately that anticipated for transition state A in a two step process, and, since  $\Delta V$  for the dimerization is  $-46$  to  $-49$  cc./mole, indicated a transition state implausibly large for a simple one step cyclic process. We now find essentially the same volume relations for the reaction of 2,3-dimethylbutadiene with butyl acrylate, and must now ask what is their significance.

The experimental validity of the value of  $\Delta V^*$  reported for isoprene dimerization has been questioned by Benson and Berson<sup>4</sup> on the basis that a plot of  $\log k$  vs.  $P$  does not show the curvature which they anticipate from a model which treats the transition state as having the compressibility of an ordinary liquid. They conclude that the actual value of  $\Delta V^*$  is approximately  $-36.5$  cc./mole, and the good, almost linear plot observed below 4000 kg./cm.<sup>2</sup> arises from experimental error. On this basis in turn Berson has rejected our previous value of  $\Delta V^*$  as evidence of mechanism.<sup>11</sup> We do not consider this criticism acceptable: first, because the data; reported here are consistent with the earlier isoprene results; second, because both sets of data require implausible values of transition state compressibility in the Benson-Berson model to obtain "best fits" to the data, and third, because the model itself has serious weaknesses when applied to a system (*cf.* Fig. 5) in which the transition state is neither a volume maximum nor a volume minimum along the reaction coordinate. These latter two points are discussed in detail in the succeeding paper.<sup>12</sup>

If we accordingly accept our values of  $\Delta V^*$  it is easy to show that they are consistent with type A transition states since they are reasonably approximated by the corresponding open-chain molecules in which the two "free valences" have been saturated by hydrogen.<sup>3</sup> Whether they are also consistent with symmetric cyclic transition states (D) is harder to establish. However a calculation using essentially the method of Stearn and Eyring<sup>13</sup> and considering a Diels-Alder product as a cyclohexane ring approximated by a rather flat hexagonal prism which reverts to transition state simply by the stretching of two C-C bonds until the volume has increased 20 cc./mole indicates that the bonds must be stretched some 30% to achieve this expansion. Stearn and Eyring took a 10% increase in bond length to represent the transition state in their calculations for a number of reactions and this value seems to be commonly accepted for simple molecules. While the 10% figure for organic reactions may have become

(12) C. Walling and D. D. Tanner, *J. Am. Chem. Soc.*, **85**, 612 (1963).

(13) A. E. Stearn and H. Eyring, *Chem. Revs.*, **29**, 509 (1941).

established more by repetition than by any direct evidence, our calculation makes our values of  $\Delta V^*$  difficult to reconcile with a cyclic transition state, unless it is somehow assumed that electronic delocalization permits strong bonding at unusually long distances between atoms. If an unsymmetric transition state is chosen in which one bond between the reacting molecules is essentially formed, any interaction through "secondary forces" must be over an even longer distance, and would be relatively weak.

Our results on the dimerization of cyclopentadiene are considerably harder to interpret in terms of any specific transition state structure for the Diels-Alder reaction between *cyclic* molecules. First,  $\Delta V^*$  apparently changes more rapidly with pressure so that extrapolation to atmospheric pressure is more uncertain, and, second, while the difference between  $\Delta V^*$  and  $\Delta V$  (approximately 10 cc./mole) is close to that anticipated for an open intermediate,<sup>14</sup> it seems too small and uncertain to be used by itself as an argument against an essentially cyclic transition state.

Turning now to our measurements on the rearrangement of 1-hydroxydicyclopentadiene, we find  $\Delta H^* = 32 \pm 2$  kcal./mole,  $\Delta V^* > 6$  cc./mole for the reaction. Clearly the reaction differs from a typical Cope rearrangement in which bond forming and bond breaking are concurrent and which is pressure accelerated,<sup>10</sup> and must represent a process in which predominantly bond scission has occurred in the transition state. Such a result is certainly consistent with Woodward and Katz's contention that the rearrangement represents a regression along a Diels-Alder reaction path toward an unsymmetric intermediate such as B in Fig. 5. Because the Diels-Alder reaction between cyclopentadiene and hydroxycyclopentadiene is a hypothetical process, we must take the dimerization of cyclopentadiene itself as a model to investigate the situation further. Here, for the reverse reaction  $\Delta H^* = 33.7$  kcal./mole<sup>15</sup> and  $\Delta V^* = 10$  cc./mole. Volume relations are consistent with a large shift along the reaction coordinate, while a comparison of  $\Delta H^*$ 's indicates that the energy of the transition state for rearrangement must closely approach that of the forward reaction (the same transition state could not, of course, be involved in the two processes, or dissociation would occur in the rearrangement and stereospecificity would be lost).

We may also attempt a calculation of the energy relations between the rearrangement transition state and an open-chain (or at least highly unsymmetric) intermediate through which the rearrangement must presumably pass. In going from two molecules of cyclopentadiene to such an intermediate, energy must be supplied to open two carbon-carbon double bonds ( $2 \times 58$  kcal.) and replace the resonance energy of two conjugated dienes ( $2 \times 4$  kcal.), but energy is gained through a new C-C bond (84 kcal.), and the resonance energy of two allylic radicals ( $2 \times 25$  kcal.). Summing these quantities indicates that the intermediate is *more* stable than the starting materials by 10 kcal./mole, and, since  $\Delta H$  for the over-all dimerization is  $-19$  kcal./mole, 9 kcal. less stable than the dimer itself.<sup>16</sup> The result is surprising, but probably reliable to better than 10 kcal./mole. A comparable calculation for the reaction of ethylene and butadiene (the poorest

(14) Volume changes in closing bridged rings appear to be considerably smaller than those involved in cyclizing linear molecules. Comparison of densities of pairs such as 1-cyclophenylcyclopentene-dicyclopentadiene and isopropylcyclopentane-2-methylbicyclopentane indicate a value of 12-14 cc./mole.

(15) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Second Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, Ch. 6.

(16) Values for bond energies and resonance stabilization are those given in C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Ch. 2.

case) indicates that the intermediate would be endothermic by about 10 kcal./mole in relation to starting materials. The figures certainly suggest that open-chain intermediates for Diels-Alder reactions are feasible on purely energetic grounds, since energies are all lower than the activation energies observed. From this calculation we see that the activation energy for the rearrangement (32 kcal./mole) is much larger than the energy required to open one bond of the dimer (presumably <20 kcal.). In short, either the opened intermediate lies in a deep potential valley (*i.e.*, B is much lower than C in Fig. 5) or there are two opened intermediates in fairly rapid equilibrium with starting and rearranged alcohol, respectively, with a considerable barrier to interconversion. The first hypothesis seems most unlikely since it is hard to see how there could be such a large barrier to reclosing the opened bond, and we prefer the second. In either case, however, it is evident that relatively small changes in activation energies for internal rearrangement and complete dissociation of an opened intermediate can give results ranging from the exclusively internal process observed here to the exclusive dissociation observed by Berson and Remanick<sup>11</sup> in the rearrangement of cyclopentadiene-acrylate and methacrylate adducts.

In summary, we believe that the results presented here strongly support the idea of highly unsymmetric transition states in all of the systems studied. While in the Diels-Alder reactions of non-cyclic dienes the data are most consistent with an essentially open-chain intermediate, in the case of cyclopentadiene, close approach between the "open ends" of the transition state and accordingly strong interaction certainly cannot be excluded. However, the pressure retardation of the Woodward-Katz rearrangement suggests that it is indeed a partial regression along the Diels-Alder path and accordingly that here too the reaction is a two-step process with an unsymmetric intermediate. Previously we have referred to such an intermediate (without explicitly considering the electron pairing) as a "diradical," but the term now seems unfortunate, since "diradical" should refer specifically to a triplet species with unpaired electron spins. Although Diels-Alder type reactions brought about energy transfer from photoexcited triplet molecules<sup>17</sup> may well involve triplet intermediates, we agree with Berson<sup>11</sup> that, until the two reactions have been adequately compared, it is simpler and probably more logical to think of any reaction intermediates in the thermal reaction as species with paired spins, even if they are essentially "open-chain" molecules.

Finally we should call attention to the fact that, while the conclusions of this paper are based upon what we consider reliable estimates of  $\Delta V^*$ 's near atmospheric pressure, these quantities, as defined by eq. 1, do not change as expected at higher pressures. Since the products of a typical Diels-Alder reaction are both smaller and less compressible than the reactants,  $\Delta V$  for the over-all reaction decreases markedly with pressure. Because  $\Delta V^*$  is relatively pressure insensitive (*cf.* the small curvature of the plots in Fig. 2 and 4),  $\Delta V^*$  for the reverse reaction must decrease rapidly.<sup>18</sup> Thus at 2000 kg./cm.<sup>2</sup> and 30°,  $\Delta V^*$  for the dimerization of cyclopentadiene is 18.4 cc./mole, while  $\Delta V$  has decreased to approximately 21–22 cc./mole<sup>19</sup>

indicating  $\Delta V^*$  for the back reaction of only about 3 cc./mole. Empirically, this may be thought of as the consequence of an abnormally high "compressibility" of the transition state, but, if the phenomenon is real, it is difficult to explain its physical significance. Actually, as is shown in more detail in the following paper,<sup>12</sup> in systems of this sort it is probably not correct to consider  $\Delta V^*$  as measured as being related to the effect of pressure on the equilibrium between two species which can be treated as normal molecules. In fact, if this were the case, the standard thermodynamic relation  $(\partial\Delta S^*/\partial P)_T = -(\partial\Delta V^*/\partial T)_P$  should hold. These quantities may be calculated for cyclopentadiene dimerization at 30° from the data of Tables II and IV and appear to differ by more than the expected experimental error.

### Experimental

**Materials.**—Except as indicated, all reagents were commercial materials, purified when necessary by conventional methods and purity checked by physical constants and G.L.C. analysis. Cyclopentadiene was prepared by cracking of its dimer at its boiling point; purity by G.L.C., 99.7%. 2,3-Dimethylbutadiene was prepared from pinacol as described in reference 20; b.p. 69°. Its adduct with *n*-butyl acrylate, 4-carbobutoxy-1,2-dimethylcyclohexene, was prepared by heating equimolar quantities of diene and acrylate at 80°. Hydrolysis gave the corresponding acid, m.p. 80.5–81.0°.  $\beta$ -1-Hydroxycyclopentadiene and anti-8-hydroxydicyclopentadiene were prepared as described by Woodward and Katz.<sup>5</sup> Melting points and infrared spectra agreed with those reported.

**High pressure techniques** were essentially those described previously.<sup>8,22</sup> After reaction samples were removed for analysis by methods described below.

**Dimerization of cyclopentadiene** was carried out using 4.40 *M* solutions of monomer in *n*-butyl chloride containing 1.45 *M* *o*-xylene as internal standard. Solutions were stored at –78° until used, and atmospheric pressure runs were carried out in small sealed glass ampoules. Reaction mixtures were analyzed by G.L.C. by comparing peak areas of dimer with those of the *o*-xylene internal standard (after calibration with known mixtures), using a Wilkens Instrument Co. Aerograph with a 10-ft. Carbowax column and an electronic integrator. Second-order rate constants were calculated in the usual manner after correcting concentrations for liquid compressibility (compressibilities of cyclopentadiene<sup>2</sup> and *n*-butyl chloride<sup>23</sup> were taken to be additive). Rate constants are summarized in Table IV

TABLE IV  
DIMERIZATION OF CYCLOPENTADIENE

<i>T</i> , °C.	<i>P</i> , kg./cm. <sup>2</sup>	<i>k</i> , l./mole sec. × 10 <sup>6</sup>	<i>T</i> , °C.	<i>P</i> , kg./cm. <sup>2</sup>	<i>k</i> , l./mole sec. × 10 <sup>6</sup>
20	1	0.625	30	2000	8.76
20	1000	1.45	30	3000	18.0
20	2000	3.19	40	1	3.97
20	3000	6.47	40	1000	9.55
30	1	1.60	40	2000	20.8
30	500	2.42	40	2500	30.5
30	1000	4.09			

(estimated error < 5%) and Fig. 1 gives a good idea of the consistency of the data for individual points. No other product than dimer was detected, and the rate of disappearance of monomer was twice that of dimer formation within the limits of the analytical method. Since the data at 30° indicated an almost linear variation of log *k* with pressure in the range 1–1000 kg./cm.<sup>2</sup>,  $\Delta V^*$  at the other temperatures was calculated from the 1 and 1000 kg./cm.<sup>2</sup> points.

**Reaction of 2-3-dimethylbutadiene-*n*-butyl acrylate** was carried out in essentially the same manner using as solvent bromobenzene containing 0.803 *M* 2-methylnaphthalene as an internal standard and a trace of 1,3,5-trinitrobenzene as an inhibitor for any competing radical polymerization.

Initial diene and acrylate concentrations were 1.14 *M* except in some early atmospheric pressure experiments using 1.39 *M*

(17) G. S. Hammond, N. J. Turro and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961).

(18) The rapid leveling off of rate with pressure in the rearrangement of 1-hydroxydicyclopentadiene (Table III) is quite consistent with this conclusion, and supports the idea that it is indeed a retro-Diels-Alder process.

(19) The compressibility of cyclopentadiene is given by Raistrick,<sup>2</sup> and that of dicyclopentadiene taken as the average between tetralin and limonene; P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **77**, 141 (1948).

(20) "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955.

(21) G. M. Bachman and H. A. Tanner, *J. Org. Chem.*, **4**, 493 (1939), report 80–81°.

(22) C. Walling and J. Pellon, *J. Am. Chem. Soc.*, **79**, 4776, 4786 (1957). An internal Teflon vessel similar to A in Fig. 1 of the second paper was used in most experiments.

(23) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **68**, 8 (1932).

diene. Analysis of reaction products was by G.L.C. using an apiezon column at 200°. Rates were followed (after calibrating the area of the product peak with standard (after calibration with known mixtures), but it was also shown both that the disappearance of acrylate corresponded with the appearance of product, and that the ratio of diene peak to acrylate peak remained constant, indicating that no competing reactions were taking place. Second-order rate constants were calculated assuming that the reaction mixture had the same compressibility as bromobenzene,<sup>24</sup> and are listed in Table V. Densities of diene, acrylate and product were determined at 80° (using a sealed pycnometer for the diene) as:

2,3-Dimethylbutadiene	$d^{80}_4$ 0.6660
<i>n</i> -Butyl acrylate	.8389
Product	.8984

from which  $\Delta V$  for the reaction at 80° = -42 cc./mole.

Calculated and measured volumes for a sample of synthetic mixture corresponding to a reaction mixture at 38% conversion were determined as 26.28 and 26.23 ml., respectively, indicating little volume change on mixing of the components and the validity of using bulk molar volumes in place of partial molar volumes in calculating  $\Delta V$ .

(24) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **66**, 212 (1932).

TABLE V

REACTION OF 2,3-DIMETHYLBUTADIENE WITH *n*-BUTYL ACRYLATE AT 80° UNLESS INDICATED

<i>P</i> , kg./cm. <sup>2</sup>	<i>k</i> , l./mole sec. × 10 <sup>6</sup>	<i>P</i> , kg./cm. <sup>2</sup>	<i>k</i> , l./mole sec. × 10 <sup>6</sup>
1 (70°)	0.347	2000	4.04
1	0.757	3000	8.75
500	1.10	4000	17.2
1000	1.73		

Rearrangement of  $\beta$ -1-hydroxycyclopentadiene was studied in decalin solution, and reaction mixtures were analyzed by infrared spectroscopy using a model 221 Perkin-Elmer recording instrument, calibrated with known mixtures. The peaks of interest are (for the  $\beta$ -alcohol) 768(s) and 756(w) cm.<sup>-1</sup> and (for the *anti*-alcohol) 752(s) and 670(w) cm.<sup>-1</sup>. The product (*anti*-alcohol) is stable under the reaction conditions, while the  $\beta$ -alcohol slowly decomposes. Accordingly, appearance of the product peaks was used in calculation of the rate constants of Table III, although material balances were in general 90-98% complete. Initial concentrations were approximately 3 wt. %, and all reactions gave satisfactory first-order plots over the range studied (1-2 half-lives).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK 27, N. Y.]

## Organic Reactions under High Pressure. VIII. The Pressure-Dependence of $\Delta V^*$ and the Compressibility of Transition States<sup>1</sup>

BY CHEVES WALLING AND DENNIS D. TANNER

RECEIVED JULY 18, 1962

The Benson-Berson<sup>3</sup> model for the pressure dependence of  $\Delta V^*$  in which transition states are treated as having compressibility properties similar to ordinary liquids is examined and shown to be plausible only for those systems in which transition states represent volume maxima or minima, since, in others, pressure produces a shift in the transition state along the reaction coordinate. This conclusion is shown to be consistent with the limited amount of data available on the pressure dependence of Cope and Claisen rearrangements and Diels-Alder reactions. Finally, it is suggested that data are best fitted, and  $\Delta V_0^*$ 's determined, by simple power series of the form  $\log k = aP + bP^2 + cP^3 \dots$ , rather than by expressions involving explicit transition-state models.

According to transition-state theory, the effect of pressure on the rate of chemical reaction is given by the well-known expression

$$d \ln k/dP = -\Delta V^*/RT \quad (1)$$

where  $\Delta V^*$ , the "activation volume," represents the difference in volume between reactants and transition state.<sup>2</sup> As several workers have shown, values of  $\Delta V^*$  can in turn provide useful information in reaction mechanism studies by indicating the molar volumes of the transition states involved. Unfortunately, the problem is complicated by the fact that  $\Delta V^*$  is not a pressure-independent quantity, and, since the value at atmospheric pressure is usually that desired, it must be estimated from a curved plot of  $\ln k$  vs.  $P$ . On the other hand, if an adequate theory of the pressure dependence of  $\Delta V^*$  were available, this dependence might be used to gain additional information about transition states. These considerations have recently been pointed out by Benson and Berson<sup>3</sup> in a very interesting and significant paper. Here we will attempt to develop these ideas further and show how our interpretation differs from theirs. Our discussion will be restricted to essentially non-ionic processes, *i.e.*, radical reactions, Diels-Alder type processes and "four-center" reactions such as Cope rearrangements which show no great dependence on solvent polarity or ionizing power, since the interpretation of pressure effects on ionic reactions appears to be even more complex.<sup>3,4</sup>

**The Benson and Berson Model for Transition State Compressibility.**—Benson and Berson<sup>3</sup> have proposed

(1) Support of this work by a grant from the Petroleum Research Fund of the American Chemical Society is gratefully acknowledged.

(2) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **31**, 875 (1935).

(3) S. W. Benson and J. A. Berson, *J. Am. Chem. Soc.*, **84**, 152 (1962).

(4) S. D. Hamann, "Physico-Chemical Effects of Pressure," Academic Press, Inc., New York, N. Y., 1957.

a model for the variation of  $\Delta V^*$  with pressure which assumes that both reactant and transition state in a non-ionic reaction may be treated as normal molecules with equations of state following the Tait equation

$$dV/dP = -J/(K + P) \quad (2)$$

or, in integrated form<sup>5</sup>

$$(V_0 - V_p)/V_0 = C \log(1 + P/B) \quad (3)$$

where  $V_0$  represents molar volume at essentially zero pressure (1 atmosphere) and the parameters in the two forms are related as

$$J = V_0 C/2.303, K = B$$

If an expression similar to 2 is written for a transition state

$$dV^*/dP = -J^*/(K^* + P) \quad (4)$$

and 1, 2 and 4 combined, we obtain

$$RT d^2 \ln k/dP^2 = J^*/(K^* + P) - J/(K + P) \quad (5)$$

Equation 5 now represents a concise expression for the pressure dependence of  $k$ , suitable for machine computation. Its completely integrated form has been given by Benson and Berson, but is too complex to reproduce here. For organic liquids in general,  $C$  is almost constant, having values of 0.205-0.225, while  $B$  ( $=J$ ) varies from 300-1200 kg./cm.<sup>2</sup>. The initial compressibilities of liquids are given by  $J/K$ , and vary considerably. At high pressures,  $P \gg K$ , all liquids show similar compressibilities and 2 is approximated by

$$dV = J \ln P \quad (6)$$

The parameter  $B$  varies in a systematic and predictable manner for different liquids, increasing with molecular weight and density, and decreasing with increasing temperature. It is larger for polar molecules (particularly those held together by hydrogen bonding)

(5) Equation 3 is misstated in ref. 3 and is correct as given here.