[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

Organic Reactions Under High Pressure. IV. The Dimerization of Isoprene[1]

BY CHEVES WALLING AND JACK PEISACH[2]

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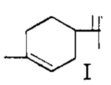
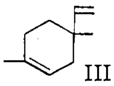
The dimerization of isoprene is strongly accelerated by pressure, results indicating values of $\Delta V^{\ddagger}$ of −24.3 and −25.6 cc./mole at 60 and 75°. The corresponding values for the over-all volume change in the reaction are almost twice as great, −45.5 and −48.7 cc./mole, respectively. From this it is concluded that the transition state is non-cyclic, but rather one leading to an open-chain diradical. The dimerization leads to some six different isomeric products of which 1-methyl-4-isopropenylcyclohexene (I), 2-methyl-4-isopropenylcyclohexene (II) and 4-ethenyl-2,4-dimethylcyclohexene (III) are present in the largest quantity. At lower temperatures yields of I increase, while pressure favors II. It is concluded that at ordinary pressures the intermediate diradical has a head-to-tail structure, while pressure increases the amount of symmetric tail-to-tail intermediate.

The dimerization of isoprene at elevated temperatures has been known for many years, although the structures of the products of the reaction have only recently been partially clarified. The reaction was first described by Bouchardat[3] and Tilden[4] who heated isoprene at 250–290° and obtained a terpenic product, b.p. 170–180°, subsequently identified by Wallach[5] as dipentene (*d,l*-limonene) (I) *via* its tetrabromide, m.p. 125°.


I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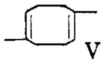
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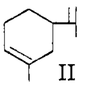
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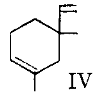
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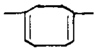
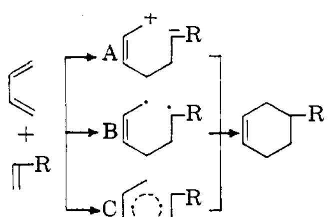

VI

In 1913, Lebedev[6] isolated a product, b.p. 64–66° (12 mm.), from the dimerization at 150° which he identified as 2,4-dimethyl-4-ethenylcyclohexene (IV), while, in 1924, Aschan[7] reported the product prepared below 100° as II.

In 1932, Whitby and Crozier[8] reinvestigated the reaction and concluded that dipentene (I) was the sole product formed under a variety of conditions, although Wagner–Jauregg,[9] in 1931, reported that while compound I was the product formed at above 200°, at below 100° the reaction led to II.

Recently Binder, Eberly and Smith,[10] applying modern fractionation techniques to the problem, have concluded that, although I and II are the major products of the dimerization (60% at 240°, almost 100% at 60°) both III and IV (30%) and V and VI (10%) are formed as well at the higher temperature.

The dimerization of isoprene represents a typical Diels–Alder condensation, and the mechanisms of such processes have received a great deal of discussion. Essentially three types of transition state have been proposed for the process: an open-chain polar structure (A), an open-chain diradical (B) and a cyclic delocalized structure (C). Structure A is now generally considered unlikely as inconsistent with the observation that Diels–Alder reactions proceed at essentially the same rate in the gas phase and in a variety of polar and non-polar solvents. Structure B, first proposed by Harkness, Kistiakowsky and Mears,[11] is energetically plausible and consistent, as far as we are aware, with all known facts concerning the reaction. Thus the structures of Diels–Alder products are generally consistent with the postulate of the formation of the most stable intermediate diradical, and the facilitation of the process by electron-withdrawing groups on the dienophile is to be expected from the well recognized role of polar effects in radical processes. Further, the stereospecificity generally observed in the reaction simply requires that the final ring closure from B be rapid compared to the time required for rotation around a carbon–carbon single bond.



In spite of this, the consensus of most workers in the field[12] at present is to favor the cyclic delocalized structure C, first proposed in somewhat different forms, by Wassermann and by Evans and Warhurst.[13] This formulation as a typical "4-center" reaction is also consistent with the facts cited above and accounts nicely for the endo configuration observed in the formation of bridged rings from cyclopentadiene and similar molecules. Presumably this cyclic transition state is stabilized by the contributions of polar structures, and could conceivably be a diradical structure as well.[14]

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(1) Taken from a portion of the dissertation of Jack Peisach submitted in partial fulfillment of the requirements of Ph.D. degree, 1958. This work was supported by both the Office of Naval Research and the National Science Foundation.

(2) Socony Vacuum Fellow, 1955–1956.

(3) G. Bouchardat, *Bull. soc. chim.*, **24** [2], 111 (1875).

(4) W. A. Tilden, *J. Chem. Soc.*, **45**, 410 (1884).

(5) O. Wallach, *Ann.*, **227**, (1885).

(6) S. V. Lebedev, *J. Russ. Phys. Chem. Soc.*, **45**, 1249 (1913).

(7) O. Aschan, *Ann.*, **439**, 221 (1924); **461**, 1 (1928); *Ber.*, **57**, 1959 (1924).

(8) G. S. Whitby and R. N. Crozier, *Can. J. Res.*, **6**, 203 (1932).

(9) T. Wagner-Jauregg, *Ann.*, **488**, 176 (1931).

(10) J. L. Binder, K. C. Eberly and G. E. Smith, *Am. Chem. Soc. Meeting Abstracts*, **131**, 5 (1957); also private communication.

(11) J. B. Harkness, G. B. Kistiakowsky and W. H. Mears, *J. Chem. Phys.*, **5**, 682 (1937).

(12) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 711–721.

(13) A. Wassermann, *J. Chem. Soc.*, 338, 1511 (1935); M. G. Evans and E. Warhurst, *Trans. Faraday Soc.*, **34**, 614 (1938). The Wassermann (non-planar) conformation of the transition state is that generally favored today.[12]

(14) *Cf.* C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 186–189.

Measurement of the effect of high pressures on the rate of Diels–Alder reactions should provide a means of distinguishing between paths B and C, since through the relation

$$d \ln k/dP = -\Delta V^{\ddagger}/RT$$

the volume of the transition state may be determined. The accelerating effect of pressure on the dimerization of cyclopentadiene already has been noted by Raistrick, Newitt and Sapiro,[15] and this paper describes a similar study of isoprene. In addition, because of the uncertainties mentioned earlier, we also have made a detailed study of the products formed both at atmospheric and high pressures.

Experimental

High Pressure Experiments.—All runs were carried out in the high pressure equipment described previously,[16] using as an internal vessel a collapsible Teflon (polytetrafluoroethylene) tube supported by an external steel sleeve so that it could withstand the internal pressure due to the vapor pressure of isoprene at 75°.[17] Rate measurements were made at 60 and 75°, and the competing free radical polymerization of isoprene to a rubbery polymer (which is also greatly pressure accelerated[18]) was satisfactorily suppressed by a small amount of trinitrobenzene.

Runs were prepared by introducing a degassed TNB-isoprene solution into a Teflon reaction vessel with a hypodermic syringe. Care was taken not to agitate the solution to any great extent to prevent oxygen introduction. After closing the vessel and wrenching it tight, it was placed in the high pressure bomb for approximately 15 minutes in order to obtain thermal equilibrium. After this time, the required pressure was applied *very slowly* (three minutes for 3,000 kg./cm.^{2}) in order to dissipate heat produced by the compression of hydraulic fluid.

After the time desired for a particular run, the pressure was released slowly with the dump valve and the sample was removed and cooled. The contents of the reaction vessel were transferred and weighed into a tared 20-cc. pear-shaped flask.

The bulk of isoprene in the sample was fractionally distilled from the flask with a semi-micro Vigreux column, adaptor and cow. The remaining isoprene, which was tenaciously retained by the dimer, was removed with the aspirator at room temperature. The flask and contents were then weighed in order to obtain the weight of unreacted monomer. Successive fractional distillation at 10 mm. and further weighings gave the weights of dimer and polymer produced. From these, the percentage conversion and the rate of dimerization were determined. Even for 60% dimer conversion, the yield of polymer rarely exceeded 0.1%.

Runs under no external pressure were carried out on degassed solutions in thick walled test-tubes in a thermostat (60–90°) or in heavy-walled bomb tubes in an oven (120–185°). Yields were determined and products isolated as in the pressure experiments.

Fractionation of Products.—Our isoprene dimers boiled from 160–185° and gas chromatography using a Perkin-Elmer model 154 vapor fractometer (best with A and C columns in series at 150° and 30 lb. helium pressure) showed three sharply separated peaks. The components comprising these peaks were separated by careful fractional distillation through a good fractionating column (or alternatively by using a Wilkens Instrument Co. Aerograph gas chromatograph as a fractionating device). Physical constants of the fractions were in good agreement with those reported by Binder, Eberly and Smith[10] and also the earlier literature, and were evidently mixtures of I and II, III and IV, and V and VI, Table I.

In gas chromatography the fractions appeared in order of increasing boiling points on all columns employed.

TABLE I

PHYSICAL CONSTANTS OF DIMER FRACTIONS

Fraction	B.p.	Mm.	$n^{20}D$
III + IV	83.2– 84.1	58	1.4658
I + II	95.0– 95.8	60	1.4737
V + VI	98.8–100.0	60	1.4848

Analysis of Dimer Fractions.—Since no further resolution of the dimer fractions of Table I could be achieved, those containing six-membered rings were identified by dehydrogenation to aromatic systems, oxidation to phthalic acids, and conversion to methyl esters. In a pilot experiment limonene vapor was passed over 30% palladium–charcoal at 300° and was dehydrogenated in 75% yield to give a mixture of *p*-cymene and *p*-methylisopropylbenzene. This was oxidized by chromic acid to the phthalic acid (65% yield) and was converted in better than 95% yield to the corresponding methyl ester *via* the acyl halide from PCl_5 and the acid, followed by methanol addition.

The melting point of dimethyl terephthalate is 141–142°, and dimethyl isophthalate, 64–65°. The product resulting from *d*-limonene dehydrogenation yielded an ester melting sharply at 141–142° and no 64–65° ester. This showed that our dehydrogenation and oxidation technique did not give any rearranged product. Repeating this procedure for the diprene fraction resulted in an ester, insoluble in base, having a melting point over the range 60–122°. By careful fractional crystallization of this ester from a methanol-water mixture, two distinct crystalline fractions were separated. The first was pure white and had a melting point of 142°, and the other was off-white and had a melting point of 63–64° when recrystallized and vacuum-dried. Mixed melting points of the 142° ester with authentic dimethyl terephthalate prepared from *p*-cymene, and the 63–64° ester with authentic dimethyl isophthalate showed no depression.

When this technique was repeated for the dimethyl ethenyl compound, dehydrogenation was found to be more difficult, but by increasing the dehydrogenation temperature to 360°, and following the same oxidation and esterification techniques, enough ester could be produced to indicate that this lower boiling fraction consists of a mixture.[19]

A spectrophotometric technique was employed to analyze ester mixtures more precisely. In 95% ethanol, the terephthalic ester has a peak in the ultraviolet at 241.6 mμ, and the *meta* exhibits a shoulder at 222.0 mμ. They have extinction coefficients of 2080 and 1277 l./mole. Solutions of either compound and mixtures follow Beer's law.

Solutions were made up of known concentrations of *meta* and *para* esters, and the percentage *para* ester in the mixtures were plotted against their extinction coefficients. It was found that the peak at 241.6 mμ in the spectrum of dimethyl terephthalate was shifted down as the concentration of isophthalate ester was increased.

Solutions of unknowns were then prepared and, from their extinction coefficients, their *para/meta* ratios were calculated. Density measurements on isoprene and limonene (the major product at low temperatures) were carried out at 60° and 75°. In the case of isoprene a sealed pycnometer was used since the material was above its boiling point. Results were

	Isoprene	Limonene
d_{30}	0.6703	0.8378
d_{60}	.6396	.8134
d_{70}	.6240	.8031

Results

Results of a typical series of rate measurements at 4570 kg./cm.^{2} and 75° appear in Fig. 1 and give good straight lines when plotted as a second-order reaction. Second-order rate constants at pressures up to 8000 kg./cm.^{2} appear in Table II and are

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

(16) C. Walling and J. Pellon, THIS JOURNAL, **79**, 4776 (1957).

(17) C. Walling and J. Pellon, *ibid.*, **79**, 4787 (1957). The vessel is that illustrated in Fig. 1B.

(18) J. B. Conant and C. O. Tongberg, *ibid.*, **52**, 1659 (1930).

(19) The higher temperatures required and the necessity of eliminating a geminate alkyl group makes our identification of isomer distribution in this case somewhat less certain. However, even in such circumstances, alkyl group migration generally is rare. *Cf.* P. A. Plattner and E. C. Armstrong in "Newer Methods of Preparative Organic Chemistry," Interscience Publishers Inc., New York, N. Y., 1948, pp. 36–41.

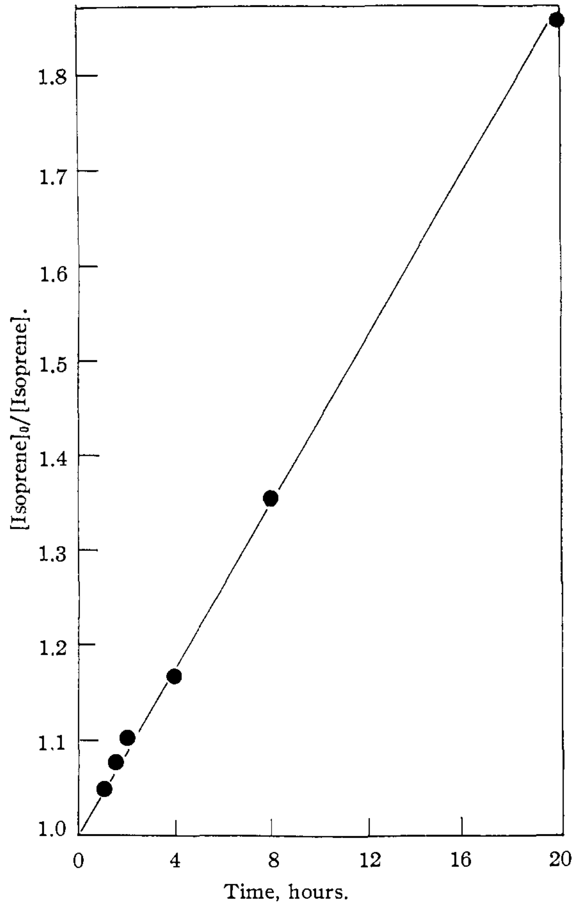

Fig. 1.—Dimerization of isoprene at 75° and 4570 kg./cm.²

plotted in Fig. 2. A linear relation between log k and pressure is observed up to 5000 kg./cm.² from which ΔV may be calculated in this range as −24.3 and −25.6 cc./mole at 60 and 75°, respectively.

TABLE II

EFFECT OF PRESSURE ON THE RATE OF DIMERIZATION OF ISOPRENE

60°		75°	
Pressure, kg./cm.²	$k \times 10^6$, l./mole sec.	Pressure, kg./cm.²	$k \times 10^6$, l./mole sec.
1	0.00457	1	0.0212
1055	.0118	1019	.0527
2109	.0290	1758	.0953
3164	.0705	3164	.380
3375	.0770	3768	.522
4218	.208	4218	.771
5132	.385	4570	.981
5343	.332	5597	1.793
5765	.429	6046	2.053
6749	.711	7593	3.306
7382	.876		
8085	1.175		

Measurements of the rate of dimerization under no external pressure between 60 and 185° are summarized in Table III. The data give a good Arrhenius plot, and the rate constant over this range is given by the equation

$$k = 7.9 \times 10^7 \exp 24{,}900/RT$$

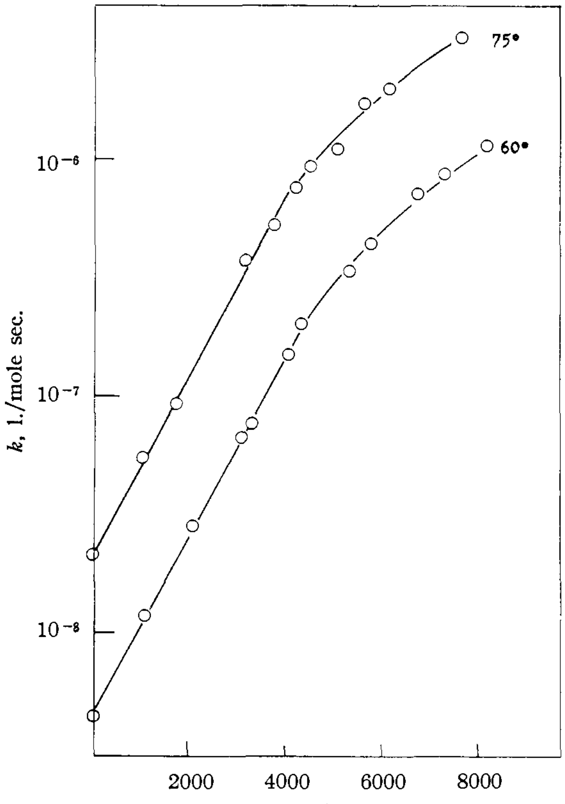

Fig. 2.—Variation in rate of dimerization of isoprene with pressure.

For the gas phase reaction Vaughan[20] reports

$$k = 5.3 \times 10^8 \exp 28{,}900/RT$$

Variation of product composition with pressure and temperature in terms of the separable fractions of Table I appear in Figs. 3 and 4, while our data on ratios of *meta* and *para* isomers in the major fractions are listed in Table IV.

TABLE III

DIMERIZATION OF ISOPRENE

T, °C.	$1/T$, °K.	k, l./mole sec.
60	3.00×10^{-3}	4.57×10^{-9}
75	2.87	2.12×10^{-8}
90	2.75	7.92×10^{-8}
120	2.54	1.05×10^{-6}
140	2.42	3.73×10^{-6}
175	2.23	2.46×10^{-5}
185	2.18	3.38×10^{-5}

TABLE IV

PERCENTAGE, *para* ISOMER IN MIXED DIMER FRACTIONS

Conditions	Fractions, %.	
	I and III	III and IV
1 kg.,cm.², 140°	75	
1 kg./cm.², 175°	74	17.5
6328 kg.,cm.², 75°	42	
7030 kg./cm.², 60°	44	

Unfortunately the data of this table are somewhat limited, chiefly because only small amounts of product were available from the high pressure

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(20) W. E. Vaughan, THIS JOURNAL, 55, 4109 (1933).

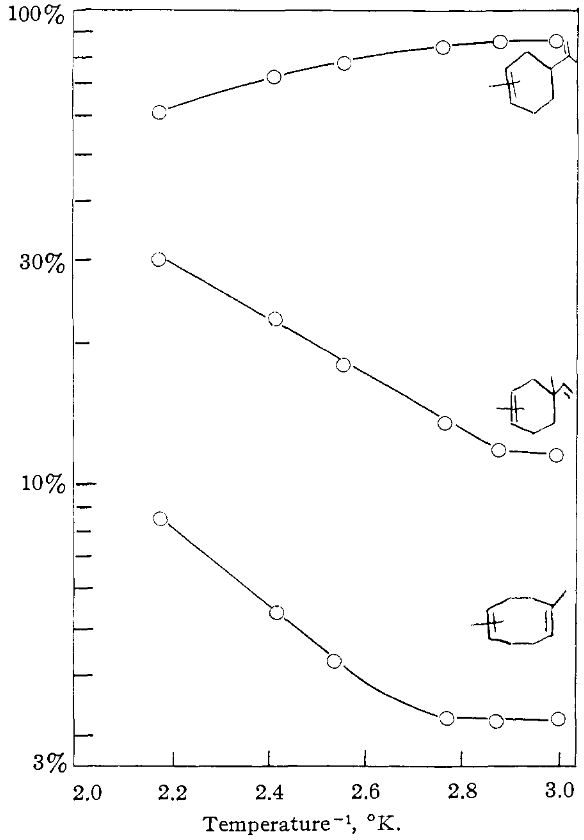

Fig. 3.—Isoprene dimer composition *vs.* 1/T (°K.).

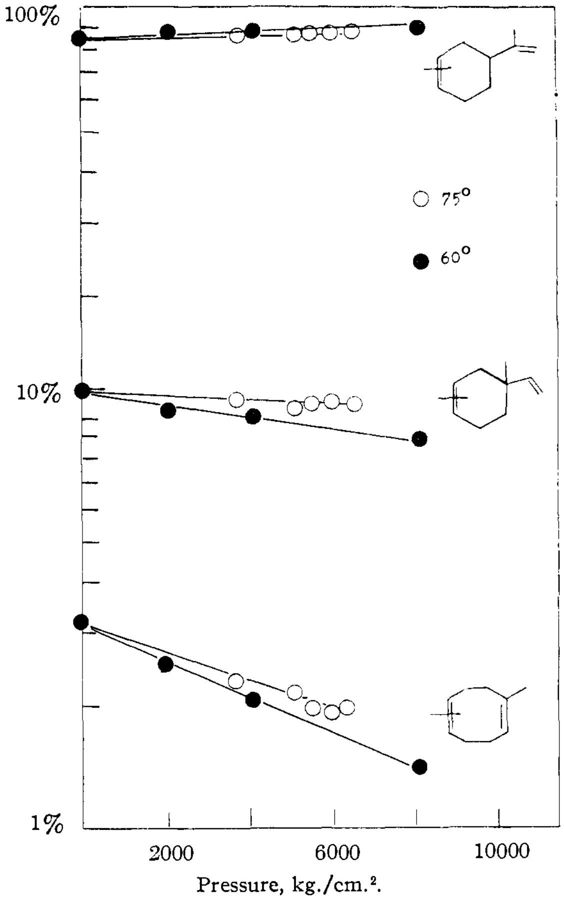

Fig. 4.—Isoprene dimer composition *vs.* pressure.

and low temperature experiments. Nevertheless, it appears that, at 175°, the product is approximately 45% I, 25% IV, 15% II, and 15% of a mixture of the remaining isomers. At lower temperatures the yield of methylisopropenylcyclohexenes, I and II, increases and we believe that the increase in the *meta/para* isomer ratio formed under high pressure at 60–75° probably is due to the change in pressure rather than temperature since no significant change in this ratio was noted between 140–175°.

Discussion

Our results on product distribution are in at least qualitative agreement with those of Binder, Eberly and Smith[10] while our rate data indicate no large difference in reaction rate in the liquid and gas phase.[19] Our pressure measurements show a large increase in rate of dimerization with pressure, corresponding to values of $\Delta V^{\ddagger}$ of -24.3 and -25.6 cc./mole at 60 and 75°. The significant point, however, is a comparison of these values with those for the over-all volume changes in the reaction which amount to -45.5 and -48.7 cc./mole at 60 and 75°, respectively. *This large difference of 21–23 cc./mole we consider to be quite inconsistent with a cyclic transition state for the reaction and strong evidence for an open-chain diradical intermediate.*

The basis of this conclusion is as follows. The proposed cyclic transition state for the Diels–Alder reaction is sometimes mentioned as resembling a molecular addition compound of π-complex, and in such species intermolecular distances are only slightly less than van der Waals radii.[21] Strong dienophiles such as maleic anhydride indeed form colored π-complexes with dienes (and also with aromatic molecules with which they do not react). However, such complexes are formed exothermically (if they are to exist in appreciable concentration), while the transition state under consideration is endothermic in respect to reactants by 25 kcal./mole. Since this additional energy arises from bond bending and compression of the reacting molecules, a π-complex seems a very poor model for the detailed structure of the transition state, and contributions of polar structures resembling those of π-complexes[22] should simply permit the reactants to approach each other more closely for the same expenditure of energy.

A better approach to the cyclic structure seems to be from the point of the reverse reaction, dissociation of the Diels–Alder adduct. Here the best models should be homolytic dissociation processes, since interpretation of $\Delta V^{\ddagger}$'s for ion-producing processes are complicated by electrostriction of the surrounding solvent during ion solvation. Here, typically, $\Delta V^{\ddagger}$ for the decomposition of benzoyl peroxide in acetophenone is 4.8 cc./mole,[17] and 3.8 cc./mole for the decomposition of azobisisobutyronitrile (where two bonds may be breaking simul-

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[21] Thus, in the chloranil-hexamethylbenzene complex the minimum intermolecular C–C separation is 3.30 Å.; T. T. Harding and S. C. Wallwork, *Acta Cryst.*, **8**, 787 (1955).

[22] R. B. Woodward, This Journal, **64**, 3058 (1942).

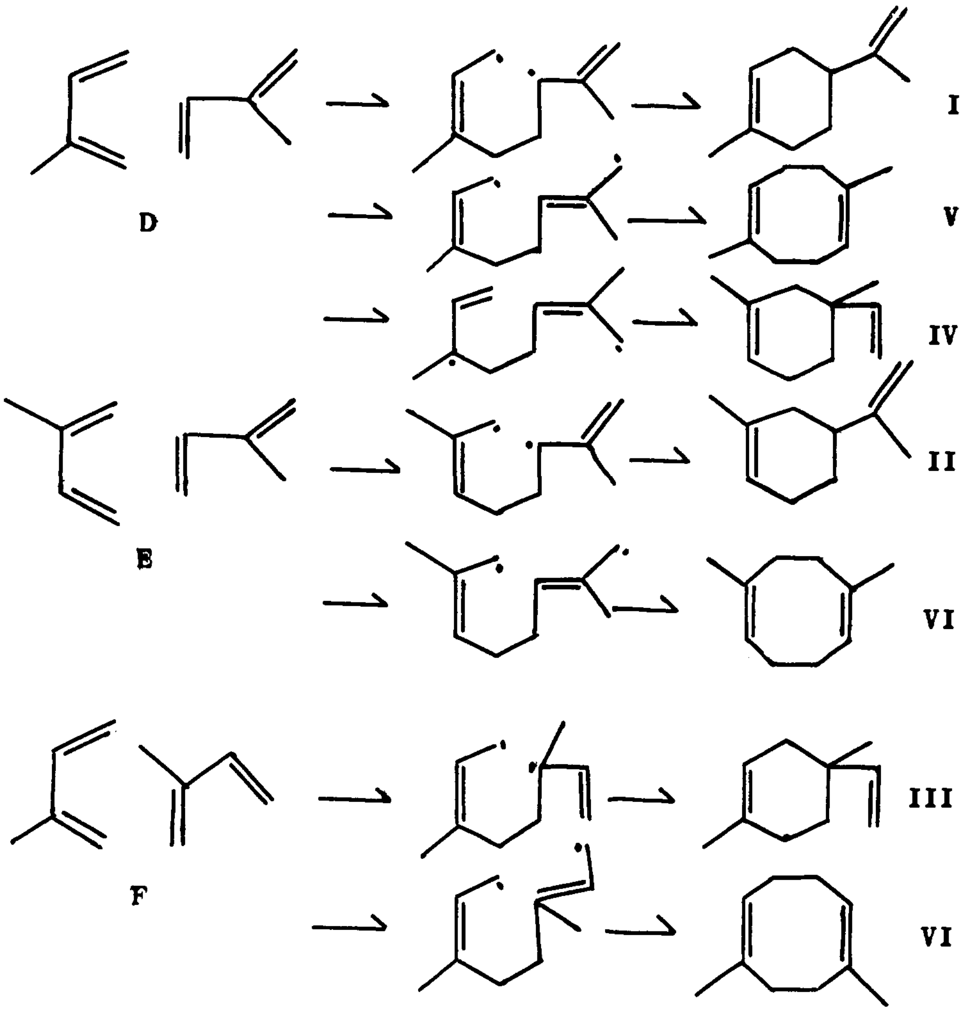

Fig. 5.—Possible diradical intermediates in the dimerization of isoprene.

taneously) in toluene.[23] Since in the reverse Diels–Alder case two bonds are being stretched simultaneously, a plausible upper limit might be 10 cc./mole, giving a value for $\Delta V^{\ddagger}$ for the dimerization of -35 cc./mole.

The best model for the transition state leading to the non-cyclic diradical is again arrived at by arguing from the reverse reaction and comes from a comparison of molar volumes of cyclic and noncyclic hydrocarbons, Table V. Here two approximations are involved. The transition state should be slightly larger than the diradical to which it leads, and the diradical should be slightly smaller than the corresponding hydrocarbon since it lacks two hydrogens. If these two uncertainties are assumed to cancel, there is an excellent agreement between the molar volume differences of Table V, and the observed differences in $\Delta V^{\ddagger}$ and ΔV overall in our experiments.

If we accept the idea of an open chain intermediate, our product composition studies throw interesting light on its structure. Figure 5 illustrates the different possibilities and it is evident that the major products arise from the head-to-tail structure D which in turn closes chiefly to the dipentene structure I. High temperatures increase the contributions from E and F, while high pressures, which make II an important product, also favor E. *A priori* there seems to be no obvious reason why D should be favored, but it may be that the unsymmetric arrangement permits a larger polar contribution to the transition state leading to the diradical.

TABLE V

MOLECULAR VOLUMES FOR SOME COMPOUNDS RESEMBLING THE TRANSITION STATE AND THE FINAL PRODUCT FOR ISOPRENE DIMERIZATION

Compound	Molec. vol., cc./mole	Compound	Fraction, %, Molec. vol. cc./mole	Diff. cc./mole
Hexene-2	124	Cyclohexene	101	−23
2-Methyl-hexene-2	139	1-Methyl-cyclohexene	118	−21
4-Methyl-hexene-2	140	3-Methyl-cyclohexene	119	−21
3,7-Dimethyl-octene-2	188	Limonene	167	−21

Our conclusions as to mechanism apply of course directly only to the dimerization of isoprene. However, data on the dimerization of cyclopentadiene

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[23] A. H. Ewald, *Disc. Faraday Soc.*, **22**, 97 (1956).

are also consistent with a diradical intermediate. Here $\Delta V^{\ddagger} = -20.0$ cc./mole, compared with -31.6 cc./mole for the over-all change in volume. Again the difference appears too large for a cyclic transition state. At present no data are available to identify the transition state structures in reactions involving strong dienophiles such as maleic anhydride. Here preliminary experiments indicate that such measurements will be difficult because of the great ease with which such systems undergo copolymerization at high pressures.

NEW YORK 27, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI, AND THE WESTINGHOUSE RESEARCH LABORATORIES]

The Constitution of the Grignard Reagent

BY RAYMOND E. DESSY AND GEORGE S. HANDLER

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The magnesium metal plating out at the cathode in the electrolysis of the Grignard reagent prepared by mixing diethylmagnesium with magnesium bromide labeled with radioactive magnesium contains no significant activity. This is further evidence in support of the concept that a solution of ethyl Grignard contains two types of magnesium. It indicates that the positive discharging species contains, as its basic unit, the RMg^+ ion. The equilibria $(C_6H_5)_2Mg \cdot MgBr_2 \rightleftarrows (C_6H_5)_2Mg + MgBr_2 \rightleftarrows 2C_6H_5MgBr$ have also been investigated employing labeled magnesium. The results indicate that phenyl Grignard is better represented by a complex $(C_6H_5)_2Mg \cdot MgBr_2$ than by C_6H_5MgBr. The effect of trace impurities on the exchange reaction is discussed.

The equilibria $Et_2Mg \cdot MgBr_2 \rightleftarrows Et_2Mg + MgBr_2 \rightleftarrows 2EtMgBr$ have been investigated[1] by employing magnesium bromide labeled with radioactive magnesium. Only a small amount of exchange was noted between Et_2Mg and $MgBr_2$ in ether solution over a 36-hour period. These results, in conjunction with the fact[2] that the same species seem to be present in a solution of Et_2Mg and $MgBr_2$ as are present in ethyl Grignard prepared in the normal manner indicated that the ethyl Grignard is better represented by a complex $Et_2Mg \cdot MgBr_2$ than by EtMgBr.

In his comprehensive study on the electrolysis of Grignard reagents Evans[3] showed that in the electrolysis of *n*-butylmagnesium bromide in ether solution in addition to magnesium metal plating out at the cathode, there was a net migration of magnesium to the anode compartment, thus indicating that magnesium is present in the anion, as well as the cation. The results with ethylmagnesium bromide indicated a similar dichotomy, but the results were not as clean because of the difficulty in maintaining a true middle compartment during the electrolysis. From this, and a vast amount of other data, Evans arrived at a simplified picture of the Grignard reagent and its electrolysis

$$R_2Mg + MgX_2 \rightleftarrows 2RMgX \qquad (1)$$

$$RMgX \rightleftarrows R^{\ominus} + MgX^{\oplus} \qquad (2a)$$

$$R_2Mg \rightleftarrows R^{\ominus} + MgR^{\oplus} \qquad (2b)$$

$$R^{\ominus} + R_2Mg \rightleftarrows R_3Mg^{\ominus} \qquad (2c)$$

$$R \quad + MgX_2 \rightleftarrows RMgX_2^{\ominus} \qquad (2d)$$

$$MgX_2 \rightleftarrows X^{\ominus} + MgX^{\oplus} \qquad (2e)$$

$$X^{\ominus} + R_2Mg \rightleftarrows R_2MgX^{\ominus} \qquad (2f)$$

$$X^{\ominus} + MgX_2 \rightleftarrows MgX_3^{\ominus} \qquad (2g)$$

$$\text{cathode} \begin{cases} 2RMg^{\oplus} + 2e \longrightarrow Mg + R_2Mg & (3a) \\ 2MgX^{\oplus} + 2e \longrightarrow Mg + MgX_2 & (3b) \end{cases}$$

$$\text{anode} \begin{cases} R_3Mg^{\ominus} \longrightarrow R\cdot + R_2Mg + e & (4a) \\ R_2MgX^{\ominus} \longrightarrow R\cdot + RMgX + e & (4b) \\ RMgX_2^{\ominus} \longrightarrow R\cdot + MgX_2 + e & (4c) \end{cases}$$

In view of the fact that previous work indicated that equation 1 does not apply, and that ionization 2a may therefore be ignored, it was felt that an investigation of the electrolysis of a mixture of Et_2Mg and $MgBr_2$ would prove of value, since it would distinguish processes 3a and 3b, and therefore offer evidence, indirectly, for one of the ionization steps shown in equations 2a-f.

In addition it was felt that an investigation of the equilibria

$$(C_6H_5)_2Mg \cdot MgBr_2 \rightleftarrows (C_6H_5)_2Mg + MgBr_2 \rightleftarrows 2C_6H_5MgBr$$

would also be of value, since aromatic Grignard reagents differ markedly from aliphatic Grignard reagents in reactivity, and appear to be colloidal in nature.

Experimental

Diethylmagnesium.—The diethylmagnesium in ether was prepared by the action of dioxane on an ether solution of ethylmagnesium bromide,[4] with subsequent removal of the solvent, baking at 150° (0.25 mm.) for 3 hours, and dissolution in ether. It contained less than 1 mole % of halogen.

Diphenylmagnesium.—The diphenylmagnesium in ether was prepared in the same manner as the diethylmagnesium except that the final baking temperature was raised to 190° for 5 minutes at the end of the baking period. It contained less than 2 mole % of halogen.

Mg^{28}-Labeled Magnesium Bromide.—Mg^{28} was prepared by a spallation reaction involving proton irradiation of a single crystal of potassium chloride at a radius equivalent to 350 Mev. for one hour in the synchrocyclotron of the Carnegie Institute of Technology. The isolation of the Mg^{28} and the preparation of labeled $MgBr_2$ by reaction of labeled Mg with Br_2 in ether was as previously described.[1] The lower phase of the two phase system, containing 485 mg. $MgBr_2$/ml., was used. It is important to note that the

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(1) R. E. Dessy, G. S. Handler, J. H. Wotiz, and C. A. Hollingsworth, THIS JOURNAL, **79**, 3476 (1957).

(2) R. E. Dessy, J. H. Wotiz and C. A. Hollingsworth, *ibid.*, **79**, 358 (1957).

(3) W. V. Evans and R. Pearson, *ibid.*, **64**, 2865 (1942).

(4) J. H. Wotiz, C. A. Hollingsworth and R. E. Dessy, *ibid.*, **78**, 1221 (1956).