

## KINETICS OF THE COPE REARRANGEMENT OF 1,1-DIDEUTERIOHEXA-1,5-DIENE\*†

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**Abstract**—The degenerate Cope rearrangement of 1,1-dideuteriohexa-1,5-diene to 3,3-dideuteriohexa-1,5-diene was studied kinetically at four temp. 207·1, 217·8, 237·1 and 258·2°. The rate constant is given by the expression  $\log k_1 = 10.36 - 34.3/\theta$  where  $\theta = 4.575 T \times 10^{-3}$ ;  $\Delta H^\ddagger = 33.5 \pm 0.5$  kcal/mole and  $\Delta S^\ddagger = -13.8 \pm 1$  e.u. The kinetics of the formation of propylene and phenylbut-1-ene from hexa-1,5-diene and toluene at five temperatures over the range 387·1–437·1° are given by  $\log k_1 = 12.03 - 51.0/\theta$ .

THE Cope rearrangement<sup>1,2</sup> has been the subject of such extensive structural, mechanistic<sup>3</sup> and theoretical investigation<sup>4–6</sup> since its discovery by the late Arthur C. Cope that no justification for the determination of the kinetic parameters of the structurally unperturbed parent seems necessary. These parameters are the required standards against which those of substituted hexa-1,5-dienes may be compared to reveal the effects of substituents, steric factors and incorporation into rings. They are as indispensable for estimation of the magnitude of the concert in the Cope rearrangement as are reliable values for the cleavage of hexa-1,5-diene to a pair of allyl radicals.

From a number of appropriately labelled hexadienes, 1,1-dideuteriohexa-1,5-diene was selected. Its preparation<sup>7</sup> proceeds from hexa-1,5-diene, through 1,2-dibromohex-5-ene, hex-5-en-1-yne, 1-deuteriohex-5-en-1-yne, and tri-n-butyl-(1-deuteriohexa-1,5-dien-1-yl)tin. The resulting 1,1-dideuteriohexa-1,5-diene shows less than 1% of impurities on a number of gas chromatographic columns.

Thermal rearrangements were effected in ampoules sealed under vacuum and heated in the vapors of boiling liquids: tetrahydronaphthalene, 207·1°; naphthalene, 217·8°; quinoline, 237·1°; diphenyl ether, 258·2°. Analysis of the extent of rearrangement was effected by IR spectroscopic monitoring of the absorption band in 3,3-dideuteriohexa-1,5-diene at 2090 cm<sup>-1</sup>. Calibration was effected on known mixtures of unrearranged

\* Preliminary announcement of these results has been made *inter alios* by J. A. Berson and M. Jones, Jr., *J. Am. Chem. Soc.* **86**, 5017 (1964), footnote 9, and by W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin and M. Saunders, *Tetrahedron* **23**, 3943 (1967), footnote 12.

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TABLE 1. REACTION OF 1,1-DIDEUTERIOHEXA-1,5-DIENE AT DIFFERENT TEMPERATURES

Temp. [°C]	Rec. temp. [°K <sup>-1</sup> × 10 <sup>-3</sup> ]	Time [sec.]	x <sup>a</sup>	log (1 - x) <sup>-1</sup>	Rate const. [sec <sup>-1</sup> × 10 <sup>6</sup> ]	Stand. dev.
207.1°	2.0821	23700	0.2393	0.11878	5.709 <sup>b</sup>	±0.207
		43210	0.4136	0.23180	5.733 <sup>c</sup>	±0.202
		60660	0.5086	0.30856		
		81300	0.5754	0.37202		
217.8°	2.0369	10860	0.2276	0.11216	11.866 <sup>b</sup>	±0.230
		24840	0.4618	0.26905	11.885 <sup>c</sup>	±0.232
		34560	0.5468	0.34371		
		62100	0.7686	0.63563		
237.1°	1.9598	1980	0.1823	0.08740	48.504 <sup>b</sup>	±2.09
		5640	0.4362	0.24887	48.815 <sup>c</sup>	±2.01
		10920	0.6730	0.48545		
		14520	0.7174	0.54882		
258.2°	1.8820	2700	0.6254	0.42643	177.97 <sup>b</sup>	±6.51
		5100	0.8517	0.82885	178.35 <sup>c</sup>	±6.29
		6900	0.8853	0.94043		
		8400	0.9424	1.23957		

<sup>a</sup> Fractional approach to equilibrium

<sup>b</sup> Unweighted

<sup>c</sup> Weighted

material and the equilibrium mixture obtained by heating 1,1-dideuteriohexa-1,5-diene at 258° until no further change in the IR or NMR spectrum was observed. The accuracy lay within 1-2 percentage units over the range 20-80% of reaction. The experimental data and the calculated first-order rate constants are given in Table 1.

The rate constants were calculated from the equation

$$k_a = (2.303/2 T) \log(1 - x)^{-1}$$

which was derived in neglect of a thermodynamic isotope effect; that is,  $k_1 + k_{-1}$  was set equal to  $2k_a$  on the assumption that  $K = 1$ . In a recent study of secondary isotope effects in the Cope rearrangement, an equilibrium constant of 1.24 at 200° was found for 3,3,4,4- and 1,1,6,6-tetradeuteriohexa-1,5-diene.<sup>8</sup> For the dideuterio analogue  $K = 1.12$  might be expected. Although we had observed a small isotope effect we did not attempt to dissect the average rate constant reported here into its components. In this same work,<sup>8</sup> forward rate constants at 200° and 150° based on single determinations are reported and are considerably higher than those calculated from our expression: 12.3 and  $0.188 \times 10^{-6} \text{ sec}^{-1}$  vs 3.10 and  $0.0409 \times 10^{-6} \text{ sec}^{-1}$ , respectively.

These data have been treated anew recently by Professor Melvin J. Goldstein and Mr. Melvyn Benzon of Cornell University. Values of the rate constants were obtained by a non-linear least squares program which found the value of  $k_a$  at each of the four temperatures and which minimized the sums of squares of the deviations between  $f_{\text{obs}}$  and  $f_{\text{calc}}$ , where  $f = 1 - e^{-(2k_a t)}$ . Although calculations were made with both unweighted and weighted  $f_{\text{obs}}$  and are reported in Table 1, the unweighted values are

the more valid in view of the essentially constant experimental error. The best values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were calculated by a program which minimized the very same sums of squares of deviations in  $f_{\text{obs}}$  concurrently at all temperatures. The activation parameters are  $\Delta H^\ddagger = 33.5 \pm 0.5$  kcal/mole and  $\Delta S^\ddagger = -13.8 \pm 1$  e.u. The rate constant for the reaction is given by  $\log k_1 = 10.36 - 34.3/\theta$  where  $\theta = 2.303 RT \times 10^{-3}$ . This value of  $\log A$  compares favourably with that calculated by Benson and O'Neal (10.6).<sup>9</sup>

These values may be compared with those for 3-methylhexa-1.5-diene [ $\log k_1 = 10.85 - 34.95/\theta$ ]<sup>10</sup>, 3,3-dimethylhexa-1.5-diene [ $\log k_1 = 11.13 - 34.62/\theta$ ],<sup>2</sup> *meso*-3,4-dimethylhexa-1.5-diene to *cis, trans*-octa-2.6-diene [ $\Delta H^\ddagger + 33.1$  kcal/mole,  $\Delta S^\ddagger - 11.2$  e.u.], *rac* to *trans, trans* [ $\Delta H^\ddagger + 35.2$  kcal/mole,  $\Delta S^\ddagger - 5.9$  e.u.] and *rac* to *cis, cis* [ $\Delta H^\ddagger + 35.3$  kcal/mole,  $\Delta S^\ddagger - 10.1$  e.u.],<sup>11</sup> 1-methyl-3,3-dicyano hexa-1.5-diene [ $\log k_1 = 10.97 - 25.8/\theta$ ],<sup>12</sup> 1-isopropyl-2-methyl-3-cyano-3-alkoxycarbonylhexa-1.5-diene [ $\log k_1 = 10.58 - 28.6/\theta$ ],<sup>12</sup> and 1,2-tetramethylene-3,3-dicyano-hexa-1.5-diene [ $\log k_1 = 10.90 - 26.2/\theta$ ].<sup>12</sup> From this collection of data, the rearrangement appears to be moderately responsive to radical stabilizing substituents, but a more incisive insight awaits the systematic study of the effects of substituents and a comparison with their effects on the free carbon radical.

Concert in the Cope rearrangement, as in any reaction, is defined by the difference between the observed energy of activation and that energy reasonably inferred for a non-concerted model. Since the original work of Cope *et al.*, dissociation of the 3,4-bond into a pair of allylic radicals has been accepted as the model of non-concert. Failure to observe the predicted cross-products of recombination has been taken as convincing invalidation of this mechanism.



est.  $\Delta H_f^\circ \sim 55$  kcal/mole



$\Delta H_f^\circ = +20.2$  kcal/mole<sup>14</sup>



$\Delta H_f^\circ = 77.8$  kcal/mole<sup>10</sup>

The magnitude of the concert is given by the difference in the heats of formation of the transition state<sup>3</sup> and a pair of allylic radicals. By the Pitzer-Franklin method of group equivalents<sup>13</sup> as most recently modernized by Benson *et al.*,<sup>14</sup> a heat of formation of hexa-1.5-diene can be calculated to be +20.2 kcal/mole.\*

It follows that  $\Delta H_f^\ddagger$ , the heat of formation of the rate-determining transition state in this Cope rearrangement is 54.5 kcal/mole. Although there are several values of the heat of formation of the allylic radical,<sup>15</sup> a recent investigation by Tsang<sup>16</sup> leads to a value of 38.9 kcal/mole, or 77.8 kcal/mole for a pair of allylic radicals. The size of the concert of the Cope rearrangement is therefore 23.3 kcal/mole when measured against this model.

The geometry to be assigned to this "concerted" transition state has remained undecided between the familiar four-centered  $\pi$ -complex, in which the 3,4-bond can be described as having been transformed from  $sp^3-sp^3$  to half p-half p and the 1,6 no-bond has become half p-half p, and the cyclohexane-2,5-diyl diradical in which the 3,4 bond

\* This value compares with that of +19.76 kcal/mole calculated by us from the reported heat of combustion [ $\Delta H_R - 918.44$  kcal/mole: J. Coops, D. Mulder, J. W. Diske and J. Smittenberg, *Rec. Trav. Chim.* **65**, 128 (1946)] and heat of vaporization ( $\Delta H_{\text{vap}} + 7.22$  kcal/mole: R. J. Akers and J. J. Throssell, *Trans. Faraday Soc.* **63**, 124 (1967), who derive  $\Delta H_f^\circ + 17.8$  kcal/mole from these data].

is essentially unchanged and the 1.6-bond is now an equally fully formed  $sp^3-sp^3$  bond. Like the  $\pi$ -complex, but for different reasons, this diradical would also be expected to be more stable in the chair conformation and would accommodate the experimental findings of Doering and Roth.<sup>3</sup> Although this hypothetical transition state does not appear capable of accommodating the effect of ring strain in lowering the activation energy of rearrangement of molecules like *cis*-1.2-divinylcyclopropane or homotropilidene,<sup>17</sup> it should be considered for the unperturbed parent or for specially substituted derivatives.

The heat of formation of such a diradical can be estimated from the heat of formation of the isopropyl radical (+16.7)<sup>16</sup> and group corrections. From the resultant calculated heat of formation, +53.9 kcal/mole, a minimum activation energy for the conversion of hexa-1.5-diene to the chair conformation of the cyclohexa-1.4-diyl diradical of 33.7 kcal/mole is obtained. The diradical is thus an energetically acceptable intermediate provided the activation energy for its cleavage to hexa-1.5-diene be negligible.

The most direct way to estimate the concert of the Cope rearrangement appeared to involve the determination of the activation energy for the cleavage of hexa-1.5-diene to a pair of allylic radicals. We had hoped to be able to develop a trapping system which, by transfer of an H atom, would have brought each allylic radical to analysis in the form of propylene. In the event, we did not find this reagent among cumene, cyclohexane, toluene, aniline or indene, but wish to report one set of experimental data involving toluene as the trapping reagent.

Four other attempts on this activation energy are reported in the literature. The first by Ruzicka and Bryce<sup>18</sup> afforded an equation for the first-order rate constant,  $\log k_1 = 7.0 - 31.3/\theta$ , the value of which must be severely restricted by the many unseparated side-reactions encountered under the experimental conditions. Our first attempt involving determination of the rate of disappearance of hexa-1.5-diene in the presence of excess cyclohexane left us with reservations and was mentioned only in passing:  $\log k_1 = 11.2 - 44.9/\theta$ .<sup>19</sup> Homer and Lossing have examined the direct decomposition of hexa-1.5-diene at very low pressures and were unable reliably to extrapolate to high pressures:  $\log k_1 = 10.2 - 44.1/\theta$ .<sup>20</sup> Akers and Throssell attempted to correct for back reactions but, among assumptions, are obliged to assign a zero activation energy for the recombination of two allyl radicals.<sup>21</sup> More recently, Golden, Gac and Benson have reported in preliminary fashion an experimental determination of the equilibrium constant for the system, hexa-1.5-diene—two allylic radicals:  $\log k_1 = 15.6 - 62.6/\theta$ .<sup>15</sup>

In the present series of experiments toluene was used in large excess (200:1) as the trapping agent for the allylic radicals with good effect, 95% of the product consisting of propylene and 4-phenyl-but-1-ene. First-order rate constants were unchanged over the entire reaction and were obtained at five temperatures over the range, 387.1–437.1°. An Arrhenius plot gave a good straight line from which the following equation was obtained by the method of least squares:  $\log k_1 = 12.03 \pm 0.26 - 51.0 \pm 0.8/\theta$  where  $\theta = 0.004575 T$ . It follows that  $\Delta H^\ddagger = 49.6 \pm 0.8$  kcal/mole and  $\Delta S^\ddagger = -4.8 \pm 1.2$  e.u.

As an afterthought, a sample of 1.1-dideuteriohexa-1.5-diene was partially rearranged at 383° for 915 min to give a sample of recovered hexa-1.5-diene which now consisted of approximately 30%  $d_0$ , 50%  $d_2$  and 20%  $d_4$ . Clearly toluene had not trapped the

TABLE 2. FIRST-ORDER RATE CONSTANTS FOR THE FORMATION OF PROPYLENE AND PHENYLBUT-1-ENE FROM HEXA-1,5-DIENE

Temp in °C	Time 10 <sup>-3</sup> sec	(W <sub>H</sub> ) <sup>°a</sup> in mg	Extent reaction (%)	(W <sub>H</sub> ) <sup>°b</sup> in mg	W <sub>CH</sub> <sup>c</sup> in mg	A <sub>P</sub> / A <sub>CH</sub> <sup>d</sup>	A <sub>B</sub> <sup>°</sup> / A <sub>CH</sub> <sup>d</sup>	(W <sub>H</sub> ) <sub>eq</sub> <sup>e</sup> in mg	k <sub>1</sub> <sup>f</sup> sec <sup>-1</sup> 10 <sup>5</sup>	k <sub>1</sub> sec <sup>-1</sup> 10 <sup>5</sup>
387.1°	30.00	2.416	33.1	2.381	2.832	0.479	0.295	0.751	1.27	
	37.00	1.506	36.0	1.481	2.360	0.389	0.239	0.507	1.14	
	43.20	2.605	46.6	2.536	2.564	0.818	0.486	1.143	1.39	1.30
	50.40	2.400	51.4	2.327	1.943	1.07	0.638	1.134	1.33	
	58.40	1.988	46.6	1.922	1.908	0.969	0.589	1.017	1.31	
400.1°	6.09	2.347	14.8	2.339	3.084	0.197	0.125	0.340	2.58	
	10.80	2.529	27.3	2.500	2.752	0.437	0.281	0.678	2.96	
	17.40	2.743	41.8	2.685	2.478	0.804	0.501	1.108	3.06	3.01
	27.20	2.590	57.4	2.509	3.243	1.191	0.673	1.425	3.10	
	34.20	2.383	66.4	2.294	2.026	1.398	0.754	1.483	3.04	
412.7°	6.24	2.061	27.9	2.041	2.450	0.401	0.278	0.572	5.33	
	7.80	2.584	38.2	2.544	2.922	0.575	0.376	0.954	6.07	
	9.78	2.343	44.1	2.298	2.543	0.715	0.445	1.011	5.95	5.67
	12.10	1.845	46.7	1.805	2.634	0.576	0.347	0.831	5.10	
	15.90	1.977	60.7	1.917	2.093	1.021	0.586	1.147	5.75	
427.0°	3.60	2.174	34.4	2.141	3.093	0.401	0.269	0.712	11.3	
	3.60	3.260	41.2	3.201	3.570	0.668	0.403	1.308	14.6	
	5.58	1.655	53.8	1.616	2.964	0.536	0.321	0.868	13.8	
	7.20	2.442	59.6	2.379	3.196	0.792	0.454	1.359	11.8	13.1
	7.20	2.046	58.5	1.994	2.700	0.781	0.454	1.138	11.8	
	10.80	2.361	78.2	2.282	2.514	1.42	0.671	1.777	14.0	
	14.40	2.537	86.5	2.443	3.536	1.327	0.471	2.124	14.2	
437.1°	3.00	2.435	47.7	2.406	2.938	0.696	0.423	1.124	21.0	
	3.60	1.899	48.2	1.875	2.742	0.582	0.352	0.876	17.5	
	4.44	2.252	55.0	2.218	2.876	0.765	0.426	1.163	16.7	19.9
	4.92	2.477	66.5	2.415	2.654	1.151	0.614	1.592	21.9	
	5.58	2.217	70.4	2.153	2.803	1.029	0.543	1.497	21.3	

<sup>a</sup> (W<sub>H</sub>)<sup>°</sup> is weight of hexa-1.5-diene introduced.

<sup>b</sup> An effective weight of starting hexa-1.5-diene obtained by 1) determining independently without added cyclohexane the amount of side-reaction in runs for the shortest and longest times at each temperature (in the runs with toluene, side-products never amounted to more than 7%); 2) interpolating the amount of side-products at intermediate times; and 3) calculating (W<sub>H</sub>)<sup>°</sup><sub>eff</sub> = (W<sub>H</sub>)<sup>°</sup> [1 - 0.6 (F<sub>SR</sub>)]. At the following temperatures the fractions of side-reaction (F<sub>SR</sub>) in runs carried to the given state of completion are given: 387.1°C: 0.023, 32.4%; 0.063, 59.6%; 400.1°: 0.007, 15.5%; 0.061, 65.5%; 412.7°: 0.017, 29.8%; 0.054, 63.2%; 427.0°: 0.024, 32.5%; 0.058, 80.9%; 437.1°: 0.026, 53.4%; 0.044, 67.7%. Interpolations of F<sub>SR</sub> are made from these pairs of data.

<sup>c</sup> The weight of cyclohexane introduced as the reference standard.

<sup>d</sup> The ratio of areas under the gas chromatographic peaks corresponding to propylene (A<sub>P</sub>), phenylbut-1-ene (A<sub>ΦB</sub>) and cyclohexane (A<sub>CH</sub>).

<sup>e</sup> The weight of hexa-1.5-diene equivalent to the amount of propylene and phenylbut-1-ene produced is calculated in the following manner: (W<sub>H</sub>)<sub>eq</sub> = (W<sub>CH</sub>) (MW<sub>H</sub>) [0.324 A<sub>P</sub>/A<sub>CH</sub> (2MW<sub>P</sub>) + 1.24 A<sub>ΦB</sub>/A<sub>CH</sub> (2MW<sub>B</sub>)].

<sup>f</sup> The specific rate constants for the formation of propylene and phenylbut-1-ene are calculated by the expression k<sub>1</sub> = (2.303/t) log [(W<sub>H</sub>)<sup>°</sup><sub>eff</sub> / ((W<sub>H</sub>)<sup>°</sup><sub>eff</sub> - (W<sub>H</sub>)<sub>eq</sub>].

allylic radicals irreversibly upon formation and since we saw no way of legitimately simplifying the complicated set of equations which include the reversible formation of 4-phenyl-but-1-ene and bibenzyl, we were unable to estimate whether the found value of 51.0 kcal/mole is high or low. When aniline and indene gave poor mass balances, the search for a good trapping agent of the type of an H-atom donor was abandoned.

### EXPERIMENTAL

*Hex-5-en-1-yne.* The method of Sondheimer *et al.*<sup>7</sup> was employed with some modifications for the preparation of this molecule from hexa-1.5-diene (Aldrich and Co.).

In a 3-necked, 5-l flask fitted with addition funnel, stirrer and water-cooled condenser, 280 g Br<sub>2</sub> (1.75 mole) was added to 288 g hexa-1.5-diene (3.5 mole) in 1700 ml ether over a 3-hr period. Unreacted hexadiene and solvent were distilled and then retreated with Br<sub>2</sub> (112 g; 0.7 mole). After removal of ether at the aspirator pressure the resultant, combined mixture of products was distilled to give crude, 1,2-dibromohex-5-ene, b.p. 65–77/4 mm, which was redistilled to afford 182 g (21.4% of theory based on hexadiene consumed) of material: b.p. 69–71/2 mm (reported b.p. 54.5°/5 mm [0.5 mm<sup>2</sup>]) from crude material of b.p. 53–93/2 mm;  $n_D^{24}$  1.5188 (reported  $n_D^{27}$  1.5186).

A soln of lithium amide in liquid ammonia was prepared by the method of Vaughn *et al.*<sup>22</sup> Ammonia (2.5 l) was charged from an inverted steel cylinder into a 5-l, 3-necked flask equipped with a stirrer, Dry-Ice condenser and a surrounding Dry-Ice bath. Following the addition of ferric nitrate (2.0 g) and 42 g Li wire (6 g atom) in 3-inch pieces, the mixture was stirred until all Li had reacted. The 1,2-dibromohex-5-ene (182 g) was added dropwise over a 2-hr period, stirred for 3 hr and left standing overnight when most of the ammonia evaporated. The mixture was treated with 175 ml ether cooled in Dry-Ice, treated dropwise with 1-l water and allowed to warm to room temperature. The ether layer was separated, dried (MgSO<sub>4</sub>), filtered and distilled through a fractionating column to give hex-5-en-1-yne; 25.5 g (42.5% of theory); b.p. 70–71°/760 mm; less than 1% impurity by GLPC on several columns.

*1-Deuteriohex-5-en-1-yne.* In a 3-necked, flame-dried, 1-l flask fitted with a stirrer, condenser, addition funnel and stop-cock controlled bottom exit-tube, 9.7 g of Mg turnings (0.4 g-atom) was activated with I<sub>2</sub> vapor and covered with 100 ml of ether under an atmosphere of N<sub>2</sub>. A soln of 43.5 g EtBr (0.4 mole) in 100 ml ether was added dropwise (45 min). After the mixture had been refluxed 45 min, another dry, 1-l, 3-necked flask with condenser and stirrer and containing a soln of hex-5-en-1-yne (25.5 g) in 50 ml ether was attached to the bottom of the Grignard-flask. Slow transfer of the Grignard reagent (20 min) was accompanied by evolution of ethane. After being stirred for 30 min, the mixture was surrounded by an ice-bath and treated dropwise with a soln of AcOH-*d* in deuterium oxide [from 22.5 g Ac<sub>2</sub>O (0.22 mole) and 20 g D<sub>2</sub>O (1.0 mole)]. The mixture was stirred for 2 hr at room temp, filtered, washed with NaHCO<sub>3</sub> aq and H<sub>2</sub>O. The ether layer was separated, dried (MgSO<sub>4</sub>), filtered and fractionally distilled to give 22.5 g 1-deuteriohex-5-en-1-yne (88% of theory); b.p. 70–71°;  $n_D^{24}$  1.4195.

*Tri-n-butyl-(1-deuteriohexa-1.5-dien-1-yl)tin.* A mixture of 12.1 g 1-deuteriohex-5-en-1-yne (0.15 mole) and 48.6 g tri-n-butyl tin hydride, prepared according to Van Der Kerk,<sup>23</sup> was heated for 24 hr at 67° in a 150 ml flask under N<sub>2</sub> (the course of the reaction had been followed by IR). Distillation *in vacuo* afforded 50.5 g of product: b.p. 127–129°/1.3 mm;  $n_D^{22}$  1.4841.

*1.1-Dideuteriohexa-1.5-diene.* Tri-n-butyl-(1-deuteriohexa-1.5-dien-1-yl)tin (48.4 g, 0.13 mole) and 29.5 g (1.48 mole) acetic acid-*d* [from 24.5 g (0.24 mole) acetic anhydride and 6.0 g (0.33 mole) D<sub>2</sub>O] was placed in a 150-ml flask fitted with a distillation head and condenser. As the system was stirred with a magnetic stirrer at 95°, the hexadiene distilled as formed into a receiver cooled in a Dry-Ice bath (4 hr was required). Fractional distillation afforded 8.5 g (78% of theory) of 1.1-dideuteriohexa-1.5-diene: b.p. 57°/760 mm; less than 1% impurity by GLPC. The NMR spectrum:  $\delta$  2.13, pair of d; 4.00 H (allylic CH<sub>2</sub>);  $\delta$  5.10, d and  $\delta$  4.87 m; 2.03 (vinylic CH<sub>2</sub>);  $\delta$  5.75, m; 2.00 H. On the basis of three determinations of relative areas, deuterium content of 98.4% in the terminal methylene was calculated. The absence of any other absorptions places a limit of about 2% on impurities.

*Cope rearrangement of 1.1-dideuteriohexa-1.5-diene.* Thermal rearrangement of the hexadiene was effected in the gas-phase in sealed ampoules. The 15-ml ampoule, constructed with a 3–4 inch neck of 6.8 mm O.D. was connected to an oxygen line and heated in a gas-oxygen flame, allowed to cool, disconnected from the oxygen line and connected to a drying tube (CaCl<sub>2</sub>). The assembly was then cooled in a Dewar flask containing Dry-Ice and a 30- $\mu$ l sample of the diene was added to the bottom of the ampoule. The ampoule

was evacuated to 0.2 mm and sealed. By means of a fine wire twisted around its neck, the ampoule, thermometer and thermocouple were suspended into the vapors of the boiling solvent. The apparatus consisted of a 1-1 boiling flask to which a long column 2 inches in width, had been sealed. The lower portion tightly wrapped with glass wool served as the heating chamber, the upper as the reflux condenser.

Temperature was maintained by boiling the following pure liquids under reflux: Tetralin, b.p. 207.1°; naphthalene, b.p. 217.8°; quinoline, b.p. 237.1° and diphenyl ether, b.p. 258.2°. The temp of the vapor was measured periodically during the runs by calibrated Anschutz thermometers and a Chromel-Alumel thermocouple which had been calibrated against a platinum resistance thermometer type 8163, Leeds and Northrup 1321066. Temperature was constant to  $\pm 0.1^\circ$ .

For analysis, the ampoule was removed and the tip of its neck (potentially a narrow test-tube) was placed upside down in a Dry-Ice bath. After the product had condensed, the neck was filed, broken off and sealed with a rubber policeman. The neat sample was transferred to a 0.025-mm I.R. cell.

Of the bands which reflect the development of new C-D bonds, that at  $2090\text{ cm}^{-1}$  was best suited for quantitative use. For purposes of calibration, a sample was brought to equilibrium by heating at 258° until no further change could be seen in the IR or NMR spectrum. The ratio of vinylic methylene to allylic methylene hydrogen atoms as determined from five estimations of relative area in the range  $\delta$  4.7-5.3 and  $\delta$  1.9-2.5 and corrected for 98.4% total deuterium content was 1.059. No effort to elaborate this deuterium isotope effect was made. Calibration was effected with known mixtures of this equilibrated sample and starting material to simulate various stages of completion of the reaction. The composition of the standards, the composition as revealed by examination of the band at  $2090\text{ cm}^{-1}$  and the deviation are given: 23:10, 22:50, -0:60; 33:32, 34:00, +0:68; 44:44, 44:42, -0:12; 50:00, 48:64, -1:36; 57:14, 55:12, -2:00; 66:66, 65:40, -1:26; 76:92, 76:36, -0:56%.

The data presented in Table 1 are obtained by application of Beer's law:  $[\log (SS'/MS')_{\text{equil}} - \log (SS'/MS')_{\text{unk}}] / [\log (SS'/MS')_{\text{equil}}] = [100 - x] / 100$  where SS' is the length of the line separating 0 and 100% absorbance, MS' is the length from the top of  $2090\text{ cm}^{-1}$  absorbance to 100% absorbance and x is the % of the way to equilibrium. The results are given in Table 1.

*Kinetics of the pyrolysis of hexa-1.5-diene.* Pyrolysis was carried out in a 12-1 Pyrex flask heated in an air-thermostat after the design of Clark<sup>24</sup> as modified by Beasley.<sup>25</sup> Vacuum transfer of hexa-1.5-diene, toluene (200/1) and cyclohexane (internal standard) was complete in 1 min. Analysis was effected on a 6 m  $\times$   $\frac{1}{4}$ " gas chromatographic column, 20% SE-30 on 60/80° Chromosorb P with temp and pressure programming (propylene: 67°, 23 ml/min He; hexa-1.5-triene and cyclohexane; 110°, 60 ml/min He; 4-phenyl but-1-ene; 150°, 71 ml/min He). Correction factors *vis-a-vis* cyclohexane as 1.00; hexadiene, 1.09; propylene, 3.09; 4-phenylbut-1-ene, 0.806. It was determined that both toluene and cyclohexane were stable under the conditions and that no one of the more than nine minor products was formed in greater than 1%. The experimental data and the calculated rate constants are given in Table 2.

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