


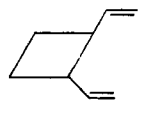


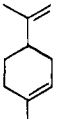

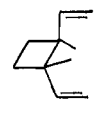
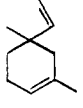

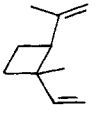


TABLE IV
 PRODUCT DISTRIBUTIONS

Starting material	Temp., °C.	Products, %				
						
	210.3	7.0	67.5	26.3		
	187.3	6.1	68.2	25.6		
	175.2	4.8	69.3	25.8		
	153.9	3.8	70.4	25.7		
	139.3	3.5	71.3	25.2		
		[X] (probably <i>cis</i> -, <i>trans</i> -1,5-cyclooctadiene)				
	65.4	1.5			98.5	
	79.8	2.0			98.0	
	96.8	2.5			97.5	
	108.5	3.0			97.0	
						
	Temp., °C.					
	92.4	14.5	72.9	5.4	7.2	
	109.2	16.0	71.9	5.0	7.1	
	121.9	17.1	70.0	4.3	8.6	
	135.7	18.0	69.5	3.9	8.6	
						
	135.7	11.1	1.3	45.7	32.1	9.8
	149.2	12.2	0.7	41.0	33.8	12.3
	161.3	12.5	1.2	39.1	31.4	15.8
	176.8	14.0	1.05	35.4	30.7	18.8

of the tube was changed from Pyrex to soft glass to investigate possible wall effects. None was found. Another test for wall effects involved addition of cyclohexane to the early runs. The cyclohexane was also used as an internal standard to check the possibility that material was destroyed in side reactions such as polymerization since nonvolatile materials would not be detected. No loss of material was indicated. The material in the tubes

was frozen in liquid nitrogen, a vacuum was applied, and the tubes were sealed while frozen. All tubes were stored in the cold before use.

A thermostated oil bath with $\pm 0.1^\circ$ temperature control was used for the rate studies. Because small, thin-walled tubes were used, the error due to equilibration time was less than 1% of the total time of the shortest run. The tubes were all quenched by swirling in a water bath at room temperature.

Analyses were carried out with a Loenco Model 15-B-2 gas chromatograph with a 6-ft. column of 10% Carbowax 20M on firebrick at a temperature of 75° with 10 p.s.i. of helium pressure. Integrations were done with an automatic disk integrater.

Optically Active *trans*-1,2-Divinylcyclobutane.—Brown's method of partial asymmetric hydroboration of divinylcyclobutane was used.⁸ α -Pinene (43.7 g., $[\alpha]^{25}_D -23.0^\circ$, distilled from balsam fir oil) was placed in a 500-ml., round-bottomed flask with 120 ml. of diglyme which had been distilled from lithium aluminum hydride. Sodium borohydride (4.35 g.) was added and the mixture was cooled in ice water and stirred with a magnetic stirrer. When cool, 22 g. of freshly distilled boron trifluoride etherate was added and the reaction mixture stirred in ice water for 4 hr. *trans*-1,2-Divinylcyclobutane (35 g.) was added and the mixture stirred in an ice bath for 4 more hours. Then 10 ml. of water was added to destroy the excess sodium borohydride and the mixture was distilled under vacuum into a Dry Ice condenser until the volume of the pot was reduced by one half. The distillate was dried and redistilled through a spinning-band column. This distillate was purified further by preparative gas chromatography on a Carbowax column and finally a bulb-to-bulb distillation gave 9.7 g. of *trans*-1,2-divinylcyclobutane having $[\alpha]^{25}_D 2.0^\circ$. This material was diluted with pure racemic divinylcyclobutane to give material with a full-scale deflection on the 0.1° scale of a Bendix Ericsson Type 143 A automatic polarimeter with a 4 cm. path length in the polarimeter cell.

Racemization Kinetics.—The optically active divinylcyclobutane was then sealed in 1-ml. portions into 13×125 mm. test tubes. These were heated in the oil bath to effect racemization. Since large tubes were used, time zero was taken at 200 sec. After quenching, the activity of the contents of the tube was measured with the same polarimeter.

Since the 4-vinylcyclohexene produced was only slightly active, a new batch of undiluted active divinylcyclobutane was prepared and rearranged. The 4-vinylcyclohexene was separated from the other products by preparative gas chromatography and the activity measured to give a nearly full-scale deflection on the polarimeter. The rotation of the recovered starting material was also measured and found to have decreased from 2.0 to 1.2°.

Since the amount of activity of the 4-vinylcyclohexene depended on the temperature of the rearrangement, active 4-vinylcyclohexene was sealed in a tube and left for 11 hr. at 200° . At the end of this time its activity was found to be unchanged. The racemization rates are all corrected for the activity of the product.

Acknowledgment.—This work was partially supported by both the Petroleum Research Fund of the American Chemical Society and the National Science Foundation.

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, UNION CARBIDE CORP., CHEMICALS DIVISION, SOUTH CHARLESTON 3, W. VA.]

Cumulative Effects in Small Ring Cleavage Reactions. A Novel Cyclobutane Rearrangement

By DAVID J. TRECKER AND JOSEPH P. HENRY

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trans-1,2-Divinyl-1,2-dimethylcyclobutane (I) undergoes a novel rearrangement at moderately elevated temperatures to 1,4-dimethyl-4-vinyl-1-cyclohexene (II) and 1,6-dimethyl-1,5-cyclooctadiene (III). The activation energy (32.2 kcal./mole) suggests that the driving force for the rearrangement stems from cumulative diallylic stabilization of the biradical intermediate IV. Cleanly first order over the temperature range 101 – 128° , the reaction is represented by the Arrhenius expression $k = 2.3 \times 10^{14} \exp(-32,200/RT)$.

Facility of small ring cleavage reactions has been attributed to (a) relief of ring strain^{1,2} and (b) stabilization of the reaction intermediate—generally considered to be a short-lived biradical.^{2,3} Thus, where

(1) B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958).

(2) W. von E. Doering and W. R. Roth, *Angew. Chem. Intern. Ed. Engl.*, **2**, 115 (1963).

(3) P. Nangia and S. W. Benson, *J. Am. Chem. Soc.*, **84**, 3411 (1962).

ethane requires 84 kcal./mole for homolysis of the carbon-carbon bond,⁴ a similar cleavage is accomplished in cyclopropane⁵ with the expenditure of 64.2 kcal./mole. Addition of a vinyl group to the cyclopropane ring further facilitates bond breaking, presumably be-

(4) T. L. Cottrell, "The Strength of Chemical Bonds," Academic Press, Inc., New York, N. Y., 1958, p. 194.

(5) S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961).

cause of the added stability gained through the intermediacy of an allylic radical.^{2,6,7} The resulting rearrangement to cyclopentene⁸ requires an activation energy of 49.6 kcal./mole. While such cyclopropane rearrangements are well documented,⁹ analogous reactions involving the cyclobutane ring have not been



reported to date.¹⁰ We now offer an example of such a ring expansion, here energetically enhanced by apparent diallyl participation in the initial ring cleavage.

trans-1,2-Divinyl-1,2-dimethylcyclobutane (I), obtained from the photosensitized dimerization of isoprene,¹¹ rearranges with some facility at temperatures above 90°. The resulting products, suitably isolated and identified, were found to be 1,4-dimethyl-4-vinyl-1-cyclohexene (II, 72%), isoprene (18%), and 1,6-dimethyl-1,5-cyclooctadiene (III, 7%). Trace amounts of other products were also formed. Exact product distributions at various temperatures are compiled in Table I. Structures of II and III were assigned on the basis of infrared and n.m.r. spectra, comparison with authentic samples, and degradation to known compounds. Details are given in the Experimental section.

TABLE I
DISTRIBUTION OF REARRANGEMENT PRODUCTS^a

Temp., °C.	Isoprene, %	II, %	III, %	Others, ^b %
98	13.2	76.9	6.4	3.5
102	13.8	76.4	6.3	3.5
108	15.2	74.9	6.5	3.4
113	17.8	72.7	6.1	3.4
115	18.7	71.7	6.2	3.5
120	18.9	70.4	7.0	3.7
130	19.1	70.2	7.1	3.6

^a Values represent averages of v.p.c. analyses³¹ made after 1-2 hr. of reaction. ^b The unidentified products, apparently isomeric to I, do not correspond to any thermal^{14,15} or photodimers¹¹ of isoprene.

Rate studies demonstrate that over the temperature range studied (101-128°) the reaction follows first-order kinetics in disappearance of I. The kinetic data are summarized in Table II. Reactions run under identical conditions with saturated solutions of oxygen, nitric oxide, and nitrogen (control) showed no detectable variations in rate, suggesting that there is no radical chain component in the process. The possibility of an equilibrium¹² or stepwise interconversion between I and any of the rearrangement products was ruled out on the basis that II and IV do not equilibrate or revert to I when heated separately under similar reaction conditions.¹³

(6) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 3547 (1961).

(7) H. M. Frey and D. C. Marshall, *ibid.*, 3981 (1962); H. M. Frey, *Trans. Faraday Soc.*, **58**, 516 (1962).

(8) C. O. Overberger and A. E. Borchert, *J. Am. Chem. Soc.*, **82**, 1007, 4891 (1960).

(9) For a review, see E. Vogel, *Angew. Chem. Intern. Ed. Engl.*, **2**, 1 (1963).

(10) Rearrangements similar to those reported in this paper have been investigated by G. S. Hammond and C. D. DeBoer. We are indebted to them for making their data available to us prior to publication.

(11) D. J. Trecker, R. L. Brandon, and J. P. Henry, *Chem. Ind. (London)*, 652 (1963).

(12) Cf. C. L. Wilson, *J. Am. Chem. Soc.*, **69**, 3002 (1947).

(13) The possibility that I cracks to isoprene, which then thermally dimerizes to II and III, is rejected on the grounds that 1- and 2-methyl-4-isopropenyl-1-cyclohexene, rather than the observed rearrangement products, are the major thermal dimers of isoprene.^{14,15}

(14) N. Nazarov, A. I. Kuznetsova, and N. V. Kuznetsov, *Zh. Obshch. Khim.*, **25**, 291 (1955).

(15) J. L. Binder, K. C. Eberly, and G. E. P. Smith, Jr., *J. Polymer Sci.*, **38**, 229 (1959).

TABLE II
KINETIC DATA FOR FIRST-ORDER DISAPPEARANCE OF I^a

Run	Temp., °C.	<i>k</i> , sec. ⁻¹	ln <i>k</i>
1	128.2 ± 0.3	6.55 ± 0.09 × 10 ⁻⁴	-7.323
2	121.7 ± .3	3.23 ± .02 × 10 ⁻⁴	-8.029
3	114.9 ± .3	1.66 ± .10 × 10 ⁻⁴	-8.694
4	113.1 ± .2	1.20 ± .07 × 10 ⁻⁴	-9.018
5	106.6 ± .2	6.67 ± .18 × 10 ⁻⁵	-9.605
6	101.0 ± .2	3.48 ± .14 × 10 ⁻⁵	-10.254

^a Procedure and method of analysis are described in the Experimental section.

The energy of activation associated with the disappearance of I was determined from the Arrhenius plot shown in Fig. 1. With an uncertainty of ± 0.7 kcal./

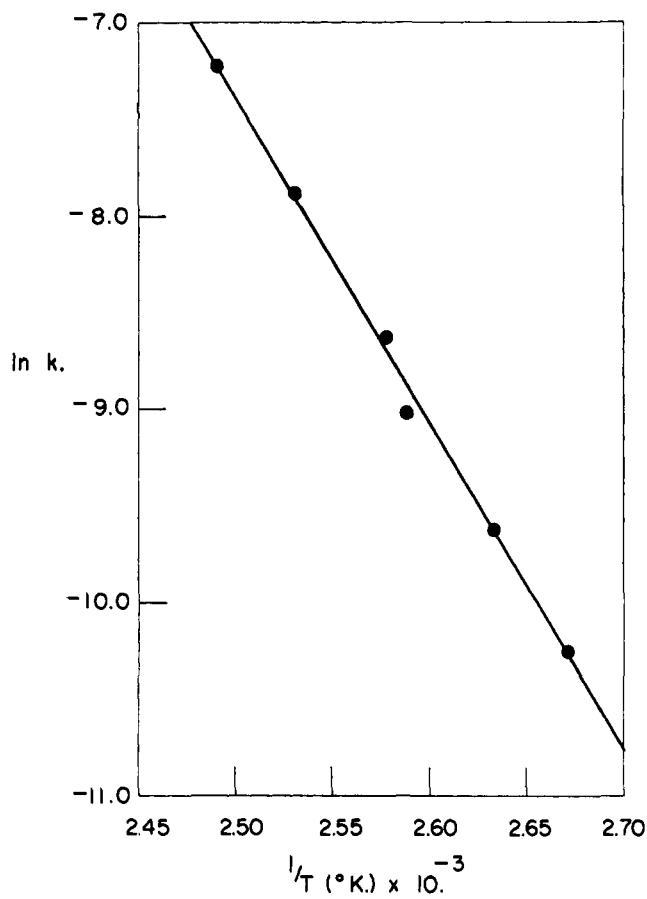


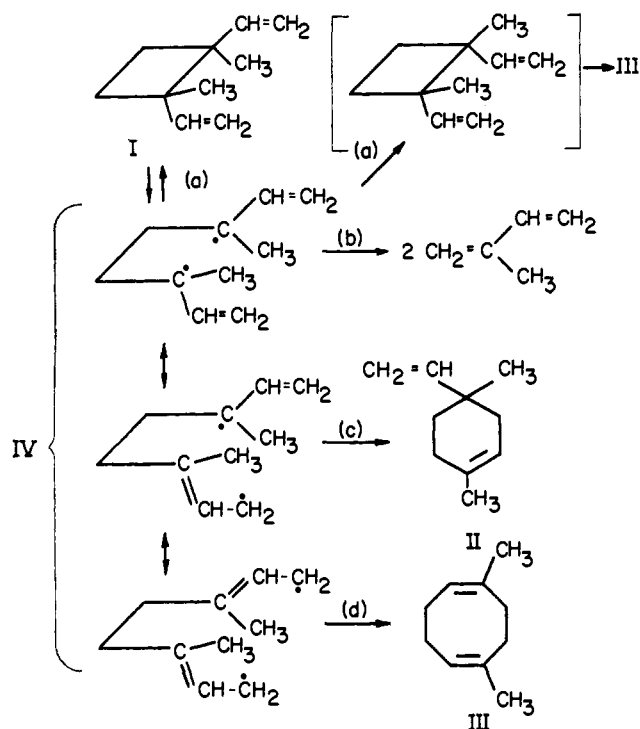
Figure 1.

mole, the activation energy was taken as 32.2 kcal./mole. The over-all rate equation for the reaction may be expressed as $k = 2.3 \times 10^{14} \exp(-32,200/RT)$ sec.⁻¹. The apparent entropy of activation at 128.2°, estimated from the expression $A = \kappa e(kT/h) \exp(\Delta S^\ddagger/R)$,¹⁶ was found to be +11.0 e.u.

The rearrangement products and composite kinetic data are accommodated most readily in terms of a two-step mechanism involving a biradical intermediate.^{2,3,7} In such a scheme the initial homolytic cleavage would afford intermediate IV, which might then: (a) reclose to the *cis* or *trans* form of I, (b) undergo further homolysis to yield two molecules of isoprene, (c) rotate and collapse to the cyclohexene product (II), or (d) close to III, as indicated.¹⁷ Alternatively, III might arise

(16) The transmission coefficient, κ , was assumed to be unity.

(17) The number of rotations necessary to bring IV into proper alignment for ring closure will depend on the conformation of I at the moment of bond cleavage, since allyl radicals largely retain their stereochemical integrity; cf. C. Walling and W. Thaler, *J. Am. Chem. Soc.*, **83**, 3877 (1961).



from a Cope-like rearrangement¹⁸ involving the *cis* form of I, formed from reclosure step a.

The Arrhenius data presented above support the proposed mechanism. The positive entropy of activation suggests a lessening of constraints in the transition state, as would be expected in the formation of IV from I.¹⁹ Moreover, the considerable frequency factor is in close accord with those reported for similar thermolysis reactions which involve discrete ring openings.^{6,7,20} Concerted rearrangements, on the other hand, are usually accompanied by significantly negative entropies and somewhat smaller frequency factors.²¹

The composite effects of dimethylallyl stabilization on ring opening may be demonstrated in a qualitative manner by considering the additivity of allyl resonance energies to known bond cleavage energies of similar strained systems.²² The apparent homolysis of *trans*-1,2-dimethylcyclobutane at the 1,2-bond requires an activation energy of 62 kcal./mole.²³ The effect of ring strain is reflected in the deviation of this value from the C-C dissociation energies of linear hydrocarbons.⁴ Addition of the delocalization energies of two allyl radicals (estimated at 12–15 kcal./mole each^{3,24}) to this energy profile should result in a value approximating that required for the formation of IV.

$$E_a = 62 \pm 1 \text{ kcal./mole} - 2(12 \text{ to } 15 \text{ kcal./mole}) = 35 \pm 4 \text{ kcal./mole.}$$

Considering the uncertainty still connected with such approximations, the agreement with the experimental

(18) E. Vogel, *Ann.*, **615**, 1 (1958).

(19) Positive entropies of similar magnitude have been reported for a number of cyclobutane pyrolyses. Cf. R. E. Wellman and W. D. Walters, *J. Am. Chem. Soc.*, **79**, 1542 (1957); C. T. Genaux, F. Kern, and W. D. Walters, *ibid.*, **75**, 6196 (1953).

(20) L. G. Daignault and W. D. Walters, *ibid.*, **80**, 541 (1958); B. C. Roquette and W. D. Walters, *ibid.*, **84**, 4049 (1962).

(21) Pertinent reviews are presented in J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, Chapter 24; and S. J. Rhoads in "Molecular Rearrangements," ed. by P. deMayo, John Wiley and Sons, Inc., New York, N. Y., 1936, Chapter 11.

(22) The validity of such additive effects, although by no means firmly established, has been demonstrated at least semiquantitatively in several instances.^{3,7,9}

(23) H. R. Gerberich and W. D. Walters, *J. Am. Chem. Soc.*, **83**, 4884 (1961).

(24) S. W. Benson, A. N. Bose, and P. Nangia, *ibid.*, **85**, 1388 (1963).

value (32.2 kcal./mole) appears quite satisfactory. We can then conclude that the consequence of combining the delocalization energies of two double bonds on the breaking of a cyclobutane ring is evinced in a predictable lowering of the over-all dissociation energy.

Experimental

Preparation of *trans*-1,2-Divinyl-1,2-dimethylcyclobutane (I).—Isoprene (476 g., 7.0 moles), acetophenone (88 g., 0.7 mole), and *p*-butylcatechol (0.5 g.) were irradiated with a 450-w. Hanovia high-pressure arc in a Pyrex immersion system for 72 hr. Continuous nitrogen ebullition was maintained throughout the reaction period. External cooling held the reaction temperature at $20 \pm 1^\circ$; under such conditions thermal dimerization was negligible. A conversion of 51% to total dimers was obtained at the end of the reaction period. Careful fractionation on a 36-in. Nester and Faust spinning-band column afforded compound I (30.0% yield, based on unrecovered isoprene). The material was redistilled to give isomerically pure I (b.p. $48\text{--}49^\circ$ at 20 mm., n_D^{20} 1.4570, homogeneous to capillary v.p.c.,²⁵ hydrogen uptake of 2.01 equiv.).

Anal. Calcd. for $C_{10}H_{16}$ (I): C, 88.15; H, 11.85; parent mass, 136. Found: C, 87.94; H, 11.66; parent mass, 136.

Other photodimers¹¹ were similarly isolated.

The infrared spectrum of I exhibited bands characteristic of vinyl groups²⁶ at 1640, 998, and 908 cm^{-1} . No absorptions at 888 cm^{-1} (isopropenyl²⁷) or 840–790 cm^{-1} (1-substituted cyclohexene²⁸) were noted. The n.m.r. spectrum²⁹ revealed a typical ABC pattern attributed to vinyl protons (couplings centered at 4.09 τ , J_1 13.7 c.p.s., J_2 9.1 c.p.s.; 5.01 τ , J_2 9.1 c.p.s., J_3 1.7 c.p.s.; 5.10 τ , J_1 13.7 c.p.s., J_3 1.7 c.p.s.), two types of ring methylenes (multiplets centered at 7.80 and 8.15 τ) and one upsplit methyl resonance (8.93 τ). Integrated areas were in the proper ratio.

Ozonolysis of I by conventional techniques, followed by oxidative work-up, afforded *trans*-1,2-dimethylcyclobutane-1,2-dicarboxylic acid. After two sublimations *in vacuo*, the white crystals melted at $236\text{--}237^\circ$ (sealed tube; lit.³⁰ m.p. $237\text{--}238^\circ$).

Anal. Calcd. for $C_8H_{12}O_4$: C, 55.81, H, 6.98; neut. equiv., 86.1. Found: C, 55.77; H, 6.74; neut. equiv., 86.3.

Thermal Rearrangement of I.—Compound I (68 g., 1.0 mole) was stirred in a flask under a brine-cooled reflux condenser at 110° for 25 hr. At the end of this time, v.p.c. analysis³¹ indicated that compound I had been completely converted to II (72%), isoprene (18%), III (7%), and trace amounts of unidentified products.

Compound II, isolated by fractional distillation (b.p. 61° at 20 mm., n_D^{20} 1.4653), was identical in all respects (physical constants, infrared spectrum) with an authentic sample prepared by the thermal dimerization of isoprene (250°)¹⁴ and isolated by preparative-scale gas chromatography.³²

Anal. Calcd. for $C_{10}H_{16}$ (II): C, 88.15; H, 11.85; mol. wt., 136. Found: C, 88.06; H, 12.02; mol. wt., 135.

The nitroso chloride of II (m.p. and mixture m.p. $114\text{--}115^\circ$ ³³) and 2,4-dinitrophenylhydrazine of the corresponding 1,4-dimethyl-4-vinyl-1-cyclohexene-6-one, formed by dehydrochlorination and hydrazine displacement (m.p. and mixture m.p. $117\text{--}118^\circ$ ³³), were identical with authentic samples.

In a similar manner III was isolated (b.p. 45° at 2.5 mm., n_D^{20} 1.4884, uptake of 1.92 equiv. of hydrogen).

Anal. Calcd. for $C_{10}H_{16}$ (III): C, 88.15; H, 11.85. Found: C, 88.29; H, 11.87.

(25) Analyses were carried out on a Barber-Coleman IDS Model 20 chromatograph with flame ionization detector. Capillary columns used were a 200-ft. UCON 5-HB-200 (85°) and a 200-ft. di-*n*-decyl phthalate (100°). Argon (40 p.s.i.) was employed as the carrier gas.

(26) J. A. Anderson, Jr., and W. D. Seyfried, *Anal. Chem.*, **20**, 998 (1948); R. R. Hampton, *ibid.*, **21**, 923 (1949).

(27) H. Sheppard and D. M. Simpson, *Quart. Rev.* (London), **6**, I (1952).

(28) H. L. McMurray and V. Thornton, *Anal. Chem.*, **24**, 318 (1952); L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 51–52.

(29) N.m.r. spectra were taken at 60 Mc. using carbon tetrachloride as solvent, with tetramethylsilane as an internal reference. Chemical shifts are recorded in τ -values; G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(30) C. J. Albisetti, D. C. Englund, M. J. Hogsed, and R. M. Joyce, *J. Am. Chem. Soc.*, **78**, 472 (1956).

(31) An Aerograph Model A-110-C gas chromatograph, employing helium as the carrier gas, was used. Separations were accomplished at 100° on a 10-ft. column of 25% Carbowax 4000, containing 5% silver nitrate, on Chromosorb P.

(32) A Nester and Faust chromatograph, containing a 5-ft. by 0.75-in. column packed with Carbowax 4000 on Chromosorb P, was used.

(33) R. Pummerer and F. Graser, *Ann.*, **583**, 291 (1953).

The n.m.r. spectrum showed a doublet (*ca.* 1 c.p.s.)³⁴ at 8.31 τ (allylic methyl, 6 protons), a multiplet centered at 7.70 τ (allylic methylenes, 8 protons), and a multiplet centered at 4.64 τ (2 olefinic protons). Ozonolysis of III and subsequent oxidative work-up afforded 2,5-hexanedione [bis-(2,4-dinitrophenyl-hydrazone), m.p. and mixture m.p. 256°³⁵] and succinic acid (m.p. and mixture m.p. 184°³⁶).

The unidentified minor products had retention times on a number of v.p.c. columns which did not correspond to those of any of the known thermal dimers^{14,15} or photodimers¹¹ of isoprene.

Kinetic Determinations.—For each kinetic run the following compounds were pipetted into a 10-ml. flask equipped with a micro reflux condenser, a thermometer inlet, and a septum-covered outlet arm: I (1.00 cc.), *n*-nonane (1.00 cc., internal standard), and *o*-dichlorobenzene (5.00 cc., solvent). The reaction flask was then partially submerged in an oil bath (550 in.³) which had been preheated to constant temperature. Temperature control was maintained by a Jumo thermometer connected to resistance heating coils and a mercury relay which served as a thermostat (H-B Instrument Co.). Control of $\pm 0.2^\circ$ was thus maintained.

(34) For similar examples of $-\text{CH}=\text{C}(\text{CH}_3)-$ coupling, see E. I. Snyder, and J. D. Roberts, *J. Am. Chem. Soc.*, **84**, 1582 (1962); G. S. Reddy, R. T. Hobgood, Jr., and J. H. Goldstein, *ibid.*, **84**, 338 (1962); "NMR Spectra Catalog," Varian Associates, National Press, Palo Alto, Calif., 1962, pp. 272-273.

(35) F. Nerdel, E. Henkel, R. Kayser, and G. Kannelbley, *J. prakt. Chem.*, **43**, 153 (1956).

Microliter samples, withdrawn periodically and quenched, were analyzed by v.p.c.³¹ Disappearance of I was determined by comparison to the internal standard. Previous v.p.c. analyses of I and *n*-nonane in varying ratios established the relationship between peak areas and molar amounts. The constancy of the internal standard throughout a run was demonstrated by independent experiments.³⁷

The disappearance of I over the temperature range 101-128° proved to be cleanly first order up to high conversions. The kinetic data obtained are compiled in Table II.

Effect of Additives.—Three thick-walled glass tubes were charged with identical solutions of compound I (2.0 g.) in chlorobenzene (10.0 ml.). The solutions were outgassed three times by conventional techniques and saturated with oxygen, nitric oxide, and nitrogen (control), respectively, by repeated additions of the gases to the evacuated systems. The tubes were then sealed and heated simultaneously in an oil bath for 1 hr. After cooling, the tubes were opened and analyzed by v.p.c.³¹ In each case reaction had proceeded to $87 \pm 2\%$ conversion.

Acknowledgments.—The authors are grateful to Prof. P. R. Schleyer (Princeton) and Prof. H. H. Wasserman (Yale) for helpful suggestions.

(36) M. T. Leffler and R. Adams, *J. Am. Chem. Soc.*, **58**, 1553 (1936).

(37) The importance of precise temperature control and internal standard constancy was illustrated by earlier runs in which erroneously low values were obtained for a number of the specific rate constants.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OREGON, EUGENE, ORE.]

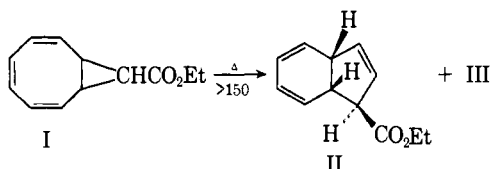
The Thermal Rearrangement of 9-Ethoxycarbonylbicyclo[6.1.0]nona-2,4,6-triene

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9-Ethoxycarbonylbicyclo[6.1.0]nona-2,4,6-triene (I) undergoes rearrangement at 150° giving the 9,10-dihydroindene derivative II as the main product. The structure and stereochemistry of II have been established through degradation and aromatization studies.

In the course of an investigation directed toward the preparation of the cyclononatetraene anion, we have examined 9-ethoxycarbonylbicyclo[6.1.0]nona-2,4,6-triene (I) as a possible precursor. Its preparation has been previously described by Akiyoshi and Matsuda¹ and by Phillips,² who utilized the reaction of cyclooctatetraene and ethyl diazoacetate for its preparation. Although the structure of I seemed secure from the earlier work, we were interested in having material of high purity and so subjected I to vapor phase chromatography. Two products were observed, neither of which corresponded to the starting ester I. Further, when compound I was subjected to careful distillation using an efficient spinning-band column, the main product was not I but was instead an isomer. Subsequently, it was shown that I undergoes a rearrangement at temperatures above 150° giving II as the main product and another product III in minor amounts.



The main features of II were readily deduced from spectral data. In the ultraviolet, II showed absorption maxima at 282 (log ϵ 3.35), 261 (log ϵ 3.66), and 252 $m\mu$ (log ϵ 3.56) in good accord with the spectrum of 8,9-dihydroindene recorded by Vogel and Kiefer,^{3,4}

(1) S. Akiyoshi and T. Matsuda, *J. Am. Chem. Soc.*, **77**, 2476 (1955).

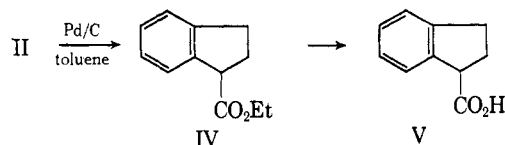
(2) D. D. Phillips, *ibid.*, **77**, 5179 (1955).

(3) E. Vogel and H. Kiefer, *Angew. Chem.*, **73**, 548 (1961).

(4) We are grateful to Professor Vogel for making the details of this spectrum available to us. Through this correspondence we learned that he has also observed this same rearrangement and we are indebted to him for re-

but in sharp contrast to the starting ester I [λ_{max} 244 $m\mu$ (log ϵ 3.56)]. In the infrared the ester carbonyl of II showed a normal absorption ($\nu_{\text{C}=\text{O}}$ 1736 cm^{-1}) and the absence of conjugation was confirmed when hydrogenation of II did not affect the frequency of the carbonyl absorption. For the n.m.r. studies, the corresponding hydrazide of II proved to be most suitable and its spectrum showed clearly that the ratio of olefinic to aliphatic protons was 6:3.

Since the spectral data were nicely compatible with a structure such as II, chemical studies were undertaken to test this hypothesis. In accord with the proposed *cis*-conjugated diene grouping, II readily underwent a Diels-Alder addition with *N*-phenylmaleimide. Further, as expected for an 8,9-dihydroindene, II was easily aromatized on heating with a 10% palladium-on-charcoal catalyst in toluene to give 1-ethoxycarbonylindane (IV), whose identity was established by hydrolysis to the known crystalline acid, 1-carboxyindane (V).



Although this evidence provided strong support for the over-all structure represented by II, it was of interest to establish the stereochemistry of the molecule as well. This was done by degradation of the corresponding saturated derivatives. As would be expected, both II and its hydrazide when subjected to hydrogenation over a palladium catalyst in ethanol absorbed 3 moles of hydrogen rapidly and cleanly,

porting his work to us prior to publication (*cf.* E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, *Tetrahedron Letters*, **11**, 673 (1963)).