Compound D was identified as gallic acid chromatographically and spectrally. Paper chromatograms of D showed a weak ellagic acid spot and an intense spot whose R_f values were identical with those of gallic acid (R_f 0.50 in 10% aqueous acetic acid; R_f 0.74 in 1-butanol–acetic acid–water. Two-dimensional co-chromatograms of D and authentic gallic acid in these solvents showed only one major spot. The spectrum of the intense spot in a two-dimensional chromatogram of A was determined directly on the paper strip.[10] It had λ_{max} 279 mμ. After dipping it into alcoholic sodium acetate and drying it had λ_{max} 264 mμ. Gallic acid, similarly chromatographed, had λ_{max} 278 and 263 mμ, respectively.

Alkaline Hydrolysis of Juglanin.—Aqueous sodium hydroxide (50.0 ml., 10%) was added to a solution of juglanin (5.0 g.) in water (50.0 ml.) under an atmosphere of nitrogen. The stoppered reaction flask was allowed to stand at room temperature for 5 days during which time a yellow sodium salt crystallized. The sodium salt was collected, suspended in warm water and treated with excess of hydrochloric acid. Ellagic acid, m.p. >360°, was thereby obtained (1.7 g., 34%). After removal of the sodium ellagate, the sodium hydroxide filtrate was acidified with dilute sulfuric acid. A dark tar was precipitated. The aqueous acid solution was decanted from the tar and extracted with ether for 6 hours in a continuous liquid–liquid extractor. The ether extract was dried (Na_2SO_4) and evaporated. A slightly brown, crystalline solid, identified chromatographically and spectrally as gallic acid, was obtained (0.645 g., 12.9%). Recrystallized from water the product had m.p. 258–259°, undepressed on admixture with gallic acid.

Acknowledgments.—The author is indebted to L. M. White for the elementary analyses.

PASADENA, CALIF.

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[10] A. E. Bradfield and A. E. Flood, *J. Chem. Soc.*, 4740 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OHIO UNIVERSITY]

Reactions of Diolefins at High Temperatures. I. Kinetics of the Cyclization of 3,7-Dimethyl-1,6-octadiene[1]

BY WILLIAM D. HUNTSMAN AND THOMAS H. CURRY

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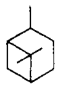
The cyclization of 3,7-dimethyl-1,6-octadiene at 382.5° and 409° is first-order, and the rate is not affected by the presence of nitric oxide or ethylene oxide. The Arrhenius energy of activation is 35.2 kcal./mole and the entropy of activation is −18 e.u. An intramolecular mechanism is proposed.

Pinane (I) isomerizes at 450–500° to give a mixture of 3,7-dimethyl-1,6-octadiene (II) and 1,2-dimethyl-3-isopropenylcyclopentane (III).[2,3] Furthermore, it has been shown that III arises by cyclization of II. Under similar conditions, 6,6-dimethylnorpinane (IV) isomerizes to 1-methyl-2-isopropenylcyclopentane (V), presumably *via* 7-methyl-1,6-octadiene (VI).[4]



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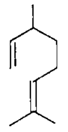

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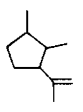

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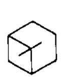

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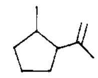
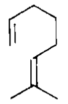


V



VI

It was suggested that the cyclization step in these reactions proceeds by a free radical chain mechanism. Several points, however, argue against such a mechanism. Among them may be mentioned the virtual absence of polymeric products. Also the reactions are surprisingly specific as compared with most hydrocarbon–pyrolysis reactions. One would expect a much more complex mixture if a radical chain mechanism were operative.[5]

It was felt that the cyclization of 1,6-diolefins warranted further study, with the particular goal of substantiating or ruling out a free radical chain mechanism. Accordingly, an investigation of the kinetics of cyclization of 3,7-dimethyl-1,6-octadiene was undertaken.

Several preliminary experiments were conducted to gain an estimate of the effect of free radical chain initiators. The results of some of these experiments are summarized in Table I. *t*-Butyl peroxide and ethylene oxide have been widely used as initiators for reactions which occur by radical chain mechanisms. They are observed to accelerate reactions, and to induce reactions at temperatures where the reactants are normally stable. For example, *t*-butyl peroxide sensitizes the polymerization of olefins, and the decarbonylation of aldehydes[6]; ethylene oxide has been used as an initiator for the decomposition of alkanes, ethers and aldehydes.[7]

Inspection of Table I reveals that these initiators exerted little if any effect on the cyclization of II, the major effect being to increase the extent of polymerization. The small amount of cyclization observed in run 1 probably does not signify that the peroxide sensitized the cyclization reaction. Mixtures of II and III were used in these experiments

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[1] This research was supported by the United States Air Force, through the Office of Scientific Research of the Air Research and Development command.

[2] V. N. Ipatieff, W. D. Huntsman and H. Pines, THIS JOURNAL, **75**, 6222 (1953).

[3] H. Pines, N. E. Hoffman and V. N. Ipatieff, *ibid.*, **76**, 4412 (1954).

[4] H. Pines and N. E. Hoffman, *ibid.*, **76**, 4417 (1954).

[5] J. E. Leffler, "The Reactive Intermediates of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956, p. 242.

[6] F. F. Rust, F. H. Seubold and W. E. Vaughan, THIS JOURNAL, **70**, 95, 4253 (1948); E. H. Farmer and C. G. Moore, *J. Chem. Soc.*, 131 (1951); R. N. Haward and W. Simpson, *Trans. Faraday Soc.*, **47**, 212 (1951).

[7] C. J. M. Fletcher, THIS JOURNAL, **58**, 534 (1936); C. J. M. Fletcher and G. K. Rollefson, *ibid.*, **58**, 2135 (1936); L. S. Echols and R. N. Pease, *ibid.*, **58**, 1317 (1936).

TABLE I

PRELIMINARY EXPERIMENTS ON THE EFFECT OF CHAIN INITIATORS ON THE CYCLIZATION OF 3,7-DIMETHYL-1,6-OCTADIENE

Run	Temp., °C.	Initiator Kind	Initiator Wt., g.	Wt. of hydrocarbon,[a] g.	Time, hr.[b]	Polymerization, %	Cyclization, %
1[c]	147–158	*t*-Butyl peroxide	2.0	11.2	5.5	51	14
2	300	*t*-Butyl peroxide	3.0	11.2	2.0	20	5
3	300	None	..	6.1	1.0	3	5
4	496	Ethylene oxide	3.7	10.8	1.5	16	57
5	497	None	..	17.7	2.0	4	48

[a] The hydrocarbon used was a mixture of II and III. See Experimental part. [b] For gas phase experiments, this column represents the time of addition of the charge from a dropping funnel to the reaction tube—Pyrex, 1.8 cm. i.d., 50-cm. heated section, packed with 6-mm. Pyrex beads. [c] Liquid phase reaction. Volatile products formed by the decomposition of *t*-butyl peroxide were removed periodically by means of a distillate take-off head.

and it is likely that the radicals generated by the decomposition of the peroxide attacked II more rapidly than III. This is supported by the observation that mixtures of II and III undergo autoxidation readily at room temperature, and the hydrogen number of the hydrocarbon mixture isolated after partial autoxidation invariably was smaller than the hydrogen number prior to autoxidation.

The failure of these initiators to cause appreciable cyclization is an indication of the absence of a chain mechanism. This is established more conclusively by the results of the kinetics study.

Experimental

Materials.—α-Pinene, b.p. 52–53° (20 mm.), $n^{25}_{\rm D}$ 1.4630, was hydrogenated at 55–60° and 100 atmospheres initial pressure in the presence of nickel–kieselguhr. Fractionation in a 50-cm. column packed with glass helices gave pinene, b.p. 167–168°, $n^{25}_{\rm D}$ 1.4599.

Pyrolysis of 485 g. of pinane at 450°, followed by fractionation through a 90-cm. column packed with glass helices yielded 270 g. of a mixture of II and III, b.p. 155–159.5°, $n^{25}_{\rm D}$ 1.4388–1.4400.[3] 3,7-Dimethyl-1,6-octadiene, 41 g. of at least 97% purity, b.p. 92–93° (97 mm.), $n^{25}_{\rm D}$ 1.4359, was isolated by percolation of the mixture, in 25-ml. portions, over silica gel at 0°. This material was used in the kinetics experiments, and intermediate fractions containing greater proportions of III were used in preliminary experiments.

Apparatus.—A flow system was used for the kinetics experiments. Liquid hydrocarbon was admitted at a constant rate through a capillary feed to a vaporizer, where the vapors were mixed with a stream of nitrogen and swept into the reactor.

The vaporizing chamber was constructed of Pyrex tubing, 2.4 cm. i.d. × 22 cm. long, equipped with nitrogen inlet tube, thermometer well, hydrocarbon delivery capillary and outlet tube leading to the reactor. The vaporizing chamber, the nitrogen inlet tube and the outlet tube were wrapped with resistance wire which was connected to a variable voltage transformer. The temperature at the center of the vaporizing chamber was maintained at approximately 250°.

The rate of hydrocarbon delivery to the vaporizer was controlled by the constant rate feed device described by Lundsted and co-workers.[8] The drops of hydrocarbon evaporated almost instantaneously upon contact with the vaporizer wall.

The reactor was constructed of Pyrex tubing 2.5 cm. i.d. × 33.5 cm. long equipped with inlet tube, 1.0 cm. i.d. × 25 cm. long, and outlet tube 1.0 cm. i.d. × 26 cm. long. A thermocouple well ran axially along the entire length.

The volume of the reactor proper was 167 ml., and the combined volume of the delivery and exit tubes within the heated zone was 18 ml. The reactor was thermostated in a bronze block furnace of the type described by Thomas and Egloff,[9] modified by the addition of end heaters. The temperature of the furnace was regulated by an Elextromax Controller (Leeds and Northrup Co., Philadelphia, Pa.). The end heaters were controlled by variable voltage transformers which were adjusted to give the minimum temperature gradient in the reactor. The section of the inlet tube which was above the upper end heater was wrapped with resistance wire which was connected to a variable voltage transformer. The temperature in this section was maintained approximately 30° below that in the reactor.

Temperatures were measured with an iron–constantan thermocouple and a Leeds and Northrup Type 8662 potentiometer. The temperatures listed in Table II are mean temperatures in the reactor. The maximum deviation from these temperatures along the reactor was one degree. The temperature fluctuation during a run was less than 0.4°.

After leaving the exit tube, the product was passed through a water-cooled condenser and thence into a receiver immersed in Dry Ice–acetone. The gas exit tube from the receiver was attached to a gas collecting bottle, and the volume of nitrogen used in a run was determined by measuring the volume of water displaced. A correction was made for the vapor pressure of water.

When desired, nitric oxide or ethylene oxide was added to the nitrogen stream from a gas buret *via* a capillary. The pressure of the gas in the buret was maintained approximately constant during addition by means of a leveling bulb.

Procedure for the Kinetics Experiments.—After temperature equilibrium was established in the reactor, the nitrogen flow was adjusted to the desired rate. Hydrocarbon delivery to the vaporizer was then started and adjusted. During these operations the product receiver was *not* in place. After approximately 2 ml. of liquid product had issued from the condenser, the receiver was attached and the stopwatch started. The temperature distribution in the reactor was checked at least once during each run. At the end of a run, the receiver was removed and the elapsed time noted. The weight of product and volume of nitrogen were determined.

Product Analysis.—The infrared spectra of products from preliminary experiments showed the presence of only II and III. The proportions of these substances in the products from the rate runs were determined by quantitative hydrogenation of 0.2–0.3-g. samples in acetic acid solution in the presence of pre-reduced platinum oxide. The accuracy of this method was ±0.5% as determined with samples of known composition.

Treatment of the Data.—The integrated rate expression for a first-order reaction in a flow system in which diffusion is small compared with the linear velocity through the reactor is

$$\ln(1/f) = k_1(V/u) \qquad (1)$$

where f is the fraction of unchanged reactant, k_1 is the first-order rate constant, V is the volume of the reactor and u is the volume of gas entering the reactor per unit time at the reactor temperature and pressure.[10] The fraction (V/u) defines the time of reaction, *i.e.*, the contact time.

The rate of gas flow into the reactor was taken as the sum of the volume of nitrogen and hydrocarbon vapor (assuming ideal behavior) divided by the total reaction time. The fraction of unreacted diolefin, f, was calculated from the quantitative hydrogenation data.

The results of experiments at 382.5° and 409.0° are summarized in Table II and plotted in Fig. 1. The linear relationship for the plot of log $(1/f)$ *versus* contact time supports the assumption of first-order kinetics. The straight

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[8] L. G. Lundsted, A. B. Ash and N. L. Koslin, *Anal. Chem.*, **22**, 626 (1950).

[9] C. L. Thomas and G. Egloff, in "Temperature, Its Measurement and Control in Science and Industry," Reinhold Publ. Corp., New York, N. Y., 1941, p. 167.

[10] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 183–184.

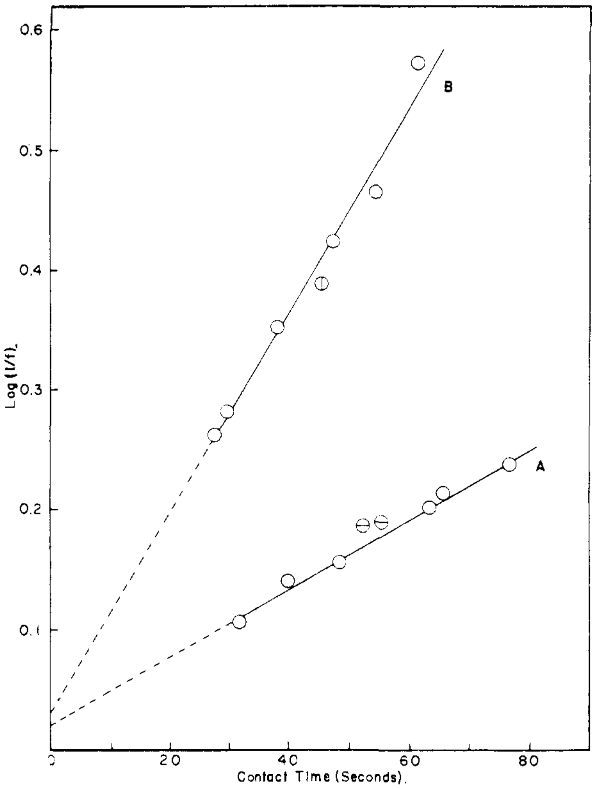


Fig. 1.—First-order plot for cyclization of 3,7-dimethyl-1,6-octadiene: curve A, 382.5°, ⊖, nitric oxide added; curve B, 409°, ⦶, ethylene oxide added.

lines are the "best fits" obtained by a least squares treatment of the data. Runs 12, 13 and 20, in which nitric oxide or ethylene oxide was added, were not included in the least squares computation. The rate constants, as calculated from the slopes of the respective lines, are $6.65 \times 10^{-3} \pm 0.0002$ sec.$^{-1}$ at 382.5° and $1.96 \times 10^{-2} \pm 0.0008$ sec.$^{-1}$ at 409°. The failure of these lines to pass through the origin may be due to the occurrence of a small amount of reaction in the delivery and exit tubes. At high flow rates, it was not possible to attain temperature equilibrium in the gas stream, hence accurate data for very short contact times could not be obtained.

The energy of activation, as calculated from the ingrated Arrhenius equation, is 35.2 kcal./mole, and the entropy of activation as calculated in the customary way is −18 e.u.[11]

Discussion of Results

The results of these experiments are strong evidence that the cyclization of II does not occur by a free radical chain mechanism. Ethylene oxide failed to accelerate the reaction to a measurable extent (run 20). Of greater significance, however, is the failure of nitric oxide to inhibit the reaction (runs 12, 13). Many investigators have observed marked inhibition of reactions which apparently proceed by free radical chain mechanisms upon the addition of small amounts (0.01-1%) of nitric oxide.[12]

Reactions involving the formation of a cyclic transition state from an acyclic reactant are characterized by negative entropies of activation due to the conversion of rotational to vibrational degrees of freedom in the activated complex. The Cope rearrangement[13] and the Claisen rearrangement of allyl ethers[14] are examples of reactions in this category. The entropy of activation for these reactions ranges from about −7 e.u. to −14 e.u.

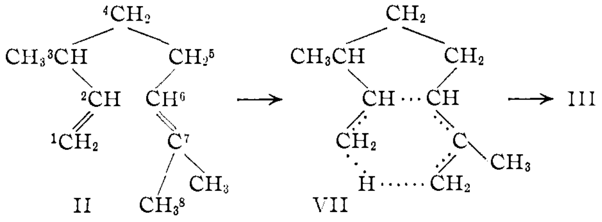
Table II

Data from Kinetics Experiments

Run	Wt. RH, g.	Vol. N_2, ml.[a]	Press., mm.	Contact time, sec.	log (1/f)
		Temperature 382.5°			
6	1.39	410	748	31.5	0.107
7	2.48	606	749	40.0	.142
8	5.82	866	747	48.4	.157
9	4.38	929	747	63.6	.202
10	4.00	1446	741	65.4	.216
11	3.96	1053	743	76.8	.238
12[b]	0.74	426	750	55.5	.191
13[c]	1.36	610	750	53.4	.187
		Temperature 409°			
14	1.22	525	752	27.4	0.262
15	1.53	507	752	29.9	.283
16	1.26	1055	753	38.3	.355
17	1.41	702	753	47.4	.423
18	1.58	503	748	54.4	.465
19	1.71	697	750	61.4	.570
20[d]	1.45	724	750	45.4	.388

[a] Volume of N_2 calculated at the reactor temperature and pressure. [b] Nitric oxide added, $p_{NO}/p_{RH} = 0.0073$. [c] Nitric oxide added, $p_{NO}/p_{RH} = 0.032$. [d] Ethylene oxide added, $p_{oxide}/p_{RH} = 0.30$.

The entropy of activation for the cyclization of II is approximately −18 e.u., thus indicating considerable constraint in the transition state. A formulation which agrees with the experimental facts is illustrated by VII.



Models reveal that II readily can achieve the proper orientation for the formation of VII. Carbons 1 and 8 can move sufficiently close together for the hydrogen transfer to occur, while simultaneously atoms 2 and 6 are properly positioned for bond formation.

This scheme offers a rationalization of the fact that the double bond occurs exclusively in an isopropenyl group in the products of cyclization of both II and VI. Further support for this mechanism is the fact that 1,6-octadiene *but not* 1,6-heptadiene cyclizes at 450°.[15]

Athens, Ohio

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(11) Reference 10, pp. 95-97.

(12) E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. I, Reinhold Publishing Corp., New York, N. Y., 2nd edition, 1954, pp. 107-125.

(13) E. G. Foster, A. C. Cope and F. Daniels, This Journal, **69**, 1893 (1947).

(14) F. W. Schuler and G. W. Murphy, *ibid.*, **72**, 3155 (1950).

(15) W. D. Huntsman, Victor C. Solomon and Donald Eros, unpublished results.