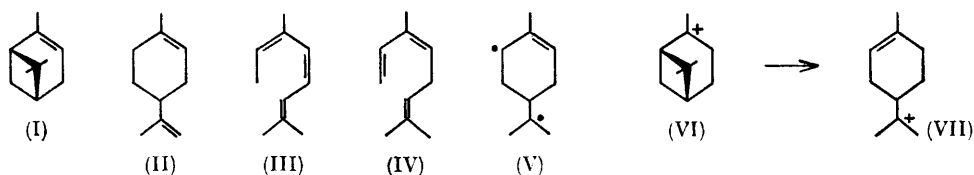


297. The Radiation Chemistry of α -Pinene.

By T. H. BATES, J. V. F. BEST, and T. FFRANCON WILLIAMS.

Gamma-irradiation of α -pinene at 30° results in formation of hydrogen, isomers of α -pinene, and polymeric material corresponding to a number-average molecular weight given by $(C_{10}H_{18})_{3.1 \pm 0.1}$. Initial G yields of hydrogen and monomer conversion into polymer are 0.5 and 5.2 molecules per 100 ev, respectively. Isolation of the individual isomerization products by gas-liquid chromatography and their identification by infrared and ultraviolet spectroscopy reveal dipentene and ocimene as the major constituents with initial G values of 0.9 and 2.6, respectively. Spectrophotometric determination of ocimene by the absorption peak at $237\text{ m}\mu$ gives a G value of 2.8. (+)- α -Pinene is partly racemized on irradiation, with a G yield of 1.6. Formation of ocimene is attributed to release of excess vibrational energy in an α -pinene molecule subjected to excitation. The racemization implies formation of an intermediate which can revert to either the (+)- or the (−)-form. It is suggested that an internal ion-pair intermediate could result from the primary processes of ionization and electron capture within a rearranged α -pinene molecule; the subsequent diverse reactions of the proposed internal ion pair are depicted as leading to dipentene, polymer, or optically inactive α -pinene.

PYROLYSIS of α -pinene (I) at $>200^\circ$ leads to a variety of products including dipentene (II) and allo-ocimene (III), but ocimene (IV) is a major precursor in the reaction sequence.¹ Burwell² has suggested that the mechanism involved an intermediate biradical (V) which could account for the above products and the racemization of (+)- α -pinene observed.



With acidic reagents,³ α -pinene gives mainly monocyclic terpenes, by proton transfer to the unsaturated group followed by a rearrangement of the carbonium ion (VI) with the opening of the bridge structure; the rearranged ion (VII) is stabilised to a diolefin by the loss of a proton.

This paper describes the chemical action of gamma-radiation on α -pinene and discusses the relation of the results to those obtained in pyrolysis and acid-catalysis from the standpoint of reaction mechanism. No previous work has been reported other than a preliminary communication of our findings.⁴

EXPERIMENTAL

Materials.— α -Pinene, supplied by B.D.H. Ltd., was purified in small quantities (0.5 ml.) by gas-liquid chromatography as described below. Larger quantities were distilled through a 200 cm. column packed with stainless-steel gauze spirals; the middle of a fraction with b. p. $61^\circ/30\text{ mm.}$ and $[\alpha]_D^{25} + 20.2^\circ$ was used. The total content of the other isomers in this α -pinene was estimated by gas-liquid chromatography to be less than 0.1%. After purification, the material was dried with (calcium hydride B.D.H. Ltd.) and stored in a refrigerator; calcium

¹ See Frost and Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, 1961, p. 373; Fuguitt and Hawkins, *J. Amer. Chem. Soc.*, 1945, **67**, 242; 1947, **69**, 319; Hunt and Hawkins, *ibid.*, 1950, **72**, 5618; Nitkin, *J. Gen. Chem. (U.S.S.R.)*, 1946, **16**, 1041.

² Burwell, *J. Amer. Chem. Soc.*, 1951, **73**, 4461.

³ Charlton and Day, *Ind. Eng. Chem.*, 1937, **29**, 92; Mosher, *J. Amer. Chem. Soc.*, 1947, **69**, 2139; Wystrach, Barnum, and Garber, *ibid.*, 1957, **79**, 5786.

⁴ Bates and Williams, *Nature*, 1960, **187**, 665.

sulphate and silica gel were unsatisfactory as drying agents in that they induced a relatively large and unpredictable degree of spontaneous isomerization. Apart from this uncertainty, there was no evidence that the use of different drying agents affected the magnitude of the radiation yields of either isomers or polymer. This result contrasts with the corresponding observations for β -pinene.⁵

A small sample of pure (+)- α -pinene supplied by the Hercules Powder Co. Inc. was distilled through a 20 cm. column packed as above. The first 25% of the distillate, b. p. 58°/25 mm., was collected; it contained <0.5% of isomers and had $[\alpha]_D^{25} +47.3^\circ$. This material was used for the study of radiation-induced changes in optical rotation. To obviate changes accruing from contact with drying agents, no further treatment was employed in this instance after distillation.

Apparatus and Procedure.—The radiations used consisted of a 1 Mev electron beam from a Van de Graaff generator, 3.8 Mev X-rays supplied by a linear accelerator, and cobalt-60 γ -rays from a 400-c annular source. The technique of electron beam irradiation and the cells employed in this work have been described;⁶ the dose rate was 1.5×10^{20} ev g.⁻¹ min.⁻¹, as calculated from measurements of beam voltage and cell current after appropriate corrections for cell-window absorption and back-scattering.^{6b} The X-ray irradiations were carried out at a dose rate of 3.12×10^{20} ev g.⁻¹ min.⁻¹. Samples irradiated in the uniform dose rate region of the cobalt-60 source received 2.53×10^{17} ev g.⁻¹ min.⁻¹ in α -pinene,* based on the use of the Fricke dosimeter with G (Fe²⁺ ions oxidized per 100 ev) taken as 15.6. The cells for the X- and γ -irradiation were cylindrical Pyrex tubes of diameter and height varying according to the amount of sample.

Samples were prepared *in vacuo* for irradiation. A quantity, usually ~10 ml., of α -pinene was placed in a flask attached to a high-vacuum line and de-gassed by the usual freeze-pump technique; the α -pinene was then allowed to distil simultaneously into a series of irradiation cells held at -196° and the samples were sealed off at this low temperature. From each filling operation, a single sample tube was preserved as a control. The ambient irradiation temperature was in the range 25–30° for γ -irradiation; for the electron and X-irradiation at a much higher rate of energy absorption, forced air-cooling was used to minimize the temperature rise due to direct heating.

Gas Analysis.—After irradiation, the cell was attached to a conventional vacuum-system through a fitted break-seal tube. The volatile gas was removed from the system connected to the cell and measured *en route* by means of a volume-calibrated Toepler pump. To estimate the hydrogen content, a measured volume of the entire fraction collected at -196° came into contact with a heated palladium tube through which the hydrogen readily diffused out of the apparatus; the residue was usually <5% of the initial volume and was assumed to consist of methane. By a similar procedure, the volume of C₂ hydrocarbons was estimated by repeating the Toepler pumping with the traps held at -120° in a bath of ethyl bromide cooled with liquid nitrogen.

Polymer Determination.—An aliquot part of the irradiated liquid was transferred to a flask on a vacuum-line; after the system had been evacuated, the α -pinene and other components of comparable volatility were distilled at room temperature into a receiver flask at -196° . In the final stages of the distillation, the polymer was stirred magnetically.

Gas-Liquid Chromatography.—A Perkin-Elmer fractometer (model 154 B) was used with helium as the carrier gas at a flow rate of 100 ml./min. and inlet pressure 0.86 kg./cm.² above the outlet pressure, at atmospheric pressure. The detector was a katharometer. A 250-cm. stainless-steel tube of 0.25 in. diameter was packed with 20 wt. % of polypropylene sebacate on a Chromosorb (Johns-Manville; 35/80; acid-washed) support and the column operated at 90°. Under these conditions, α -pinene had a shorter retention time than the main group of isomers formed by irradiation (Fig. 1) and hence it was possible to overload the column and still obtain a reasonable resolution of the separate components. By condensing the vapour at the exit pipe, small samples of pure α -pinene (<0.1% of isomers) could be obtained from 0.5 ml. portions. The same technique was applied to the isolation of each of the products

* This dose rate refers to August 1st, 1960, and the decay of the source was calculated by using the half-life of 5.3 years for cobalt-60.

⁵ (a) Bates, Best, and Williams, *Nature*, 1960, **188**, 469; (b) following paper.

⁶ (a) Amphlett and Williams, *J. Sci. Instr.*, 1956, **33**, 64; Wilkinson and Williams, *J.*, 1961, 4098; (b) *J. Chim. phys.*, 1955, **52**, 600.

A, B, and C formed by irradiation, but the quantity of liquid collected in these circumstances was considerably less. After several passages of 0.5-ml. samples of irradiated α -pinene through the apparatus, a few microlitres had accumulated in each of the three traps corresponding to the collection of A, B, and C. The products were separately re-injected and the process repeated. After two such operations, the isomer was usually separated from the other components, as indicated by absence of the latter from the recorder trace. The final purified sample of irradiation product was extracted from its trap by means of a fine capillary and half of it was dissolved in "AnalaR" carbon disulphide for infrared analysis; the remainder of the extract was dissolved in spectroscopic-grade cyclohexane (B.D.H. Ltd.) for the determination of its ultraviolet spectrum.

The components A, B, and C, in the irradiated α -pinene were determined quantitatively from the peak areas on the recorder trace, with the aid of a planimeter. Calibrations were made with known mixtures of β -pinene and dipentene in α -pinene and it was found that the area of the minor peaks, when normalized to the suitably attenuated area of the α -pinene, accurately represented the percentage composition. Injection volumes were within the range 20–500 microlitres, depending on the concentration of isomer present. A correction for the small amount of isomer in the control sample was applied.

Spectroscopic Analyses.—Infrared spectra of fractions A, B, and C in a 0.1 mm. thick micro-cell with potassium bromide windows were recorded on a Hilger H 800 double-beam instrument. The ultraviolet spectra were obtained with a Hilger "Uvispek" instrument. Quantitative measurements on the increase of the ultraviolet absorption at 237 m μ in irradiated α -pinene were carried out after dissolving 50-microlitre samples in 25 ml. of cyclohexane (B.D.H. spectroscopic grade; passed down a column of silica gel); the optical densities were measured in 1 cm. thick cells of fused silica against a similarly diluted sample of unirradiated α -pinene in the reference cell.

Optical Activity.—Measurements of optical rotation were made with a Hilger "Standard" polarimeter and a micro-cell of path-length 5 cm. and volume *ca.* 0.35 ml. The cell was thermostatically maintained at 25° and a sodium-vapour lamp provided illumination.

RESULTS AND DISCUSSION

The irradiation products of α -pinene were conveniently classified into three groups, in order of their decreasing volatility: gaseous compounds, mainly of hydrogen; the isomers of α -pinene and any other compounds of comparable molecular weight; polymeric residue. For the gaseous and polymeric products Table 1 summarises the results.

TABLE 1.
G values for gas and polymer formation.

Liquid	Radiations	Dose rate (10^{18} ev g. ⁻¹ min. ⁻¹)	Dose (10^{21} ev g. ⁻¹)	G(H ₂)	G(C ₂)	G * (monomer)
α -Pinene	Van de Graaff electrons	149	17.9	0.35	0.013	3.7
α -Pinene (+8 wt. % of dipentene)	" "	151	18.1	0.37	0.014	4.5
α -Pinene	Co-60 γ	0.253	3.65	0.52	0.015	5.6
"	"	0.253	5.02	—	—	4.7

* Conversion of monomer into polymer.

Since the irradiations with the Van de Graaff machine were carried to a higher dose range and conversion (exceeding 15% change) than the γ -irradiations, they cannot be directly compared so as to elucidate the effect of dose-rate on the yield. It is clear, however, that the G yield of polymer formation is reduced with increase in total γ -ray dose and this trend could well account for the lower G yields obtained by the high-dose electron-irradiations. G yields for hydrogen are also lower at the higher doses; this behaviour is typical for many hydrocarbons⁷ when a substantial conversion, \leq ~5%, of the original compound is achieved by the irradiation dose. The yield of methane (not recorded in

⁷ Burns, Wild, and Williams, Proc. Second U.N. Conference on Peaceful Uses of Atomic Energy, Geneva, 1958, 29, 266; Guenther, Hardwick, and Nejak, J. Chem. Phys., 1959, 30, 601.

Table 1) was always less than $G\ 0.05$; higher gaseous hydrocarbons were formed only in traces. A molecular-weight determination (following paper) for the polymer gave a mean value, $\bar{M}_n = 428 \pm 9$, which corresponds to the average formation of a trimer of α -pinene. The infrared spectrum of the polymer showed absorption bands at about $12.5\ \mu$ which could be due to the $\text{RR}'\text{C}:\text{CHR}''$ structure, as in α -pinene. A comparison of the above results with comparable work for saturated hydrocarbons illustrates some important differences. The molecular ratio for the yields of hydrogen gas to dimer exceeds 2.0 for n-hexane⁸ and cyclohexane.⁹ For a branched alkane such as neopentane,¹⁰ the dimer ($G\ 1.2$) and hydrogen ($G\ 1.6$) yields are comparable but that of methane is considerably higher ($G\ 3.7$). Since the ratio of hydrogen to polymer molecules formed from α -pinene is only about 0.3 and the yield of methane is insignificant, this evidence is consistent with

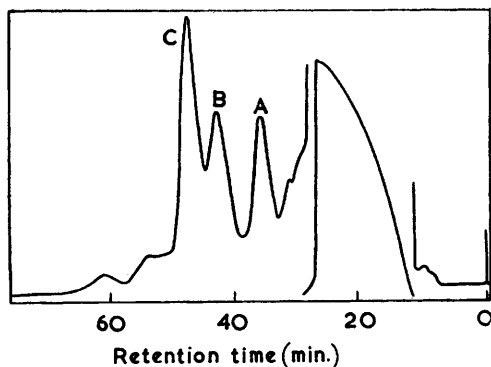
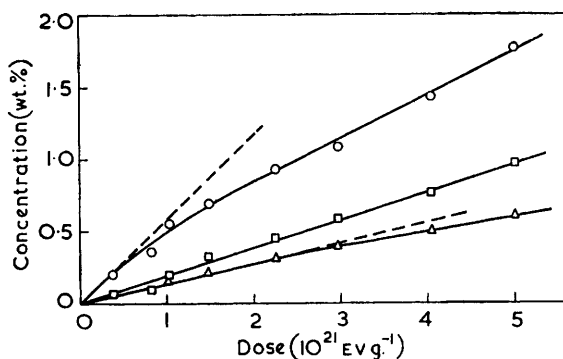


FIG. 1. Gas-liquid chromatogram of irradiated α -pinene.

FIG. 2. Yield of isomers plotted against dose. Dose rate, $2.7 \times 10^{17}\ \text{ev g}^{-1}\ \text{min}^{-1}$.

Δ , Unknown; \square , dipentene;
 \circ , ocimene.



other observations that the presence of a double bond considerably modifies the radiation chemistry, particularly between alkanes¹¹ and alkenes.¹²

It was of particular interest in this investigation to study the possibility of radiation-induced isomerization. A typical gas-chromatographic recording of irradiated α -pinene is illustrated in Fig. 1 and it indicates the formation of three major products corresponding to the peaks A, B, and C. The presence of at least two other components formed by irradiation was detected but as their individual yields were determined to be $G < 0.1$, they are not major products and will not now be considered further. Evidence for the assignment of peaks B and C to dipentene (II) and ocimene (IV), respectively, is based on a comparison of the infrared spectra of the isolated components (in Fig. 5) with the

⁸ Dewhurst, *J. Phys. Chem.*, 1958, **62**, 15; *J. Amer. Chem. Soc.*, 1958, **80**, 5607.

⁹ Dewhurst, *J. Phys. Chem.*, 1959, **63**, 813.

¹⁰ Taylor, Mori, and Burton, *J. Amer. Chem. Soc.*, 1960, **82**, 5817.

¹¹ Williams, *Trans. Faraday Soc.*, 1961, **57**, 755.

¹² Chang, Yang, and Wagner, *J. Amer. Chem. Soc.*, 1959, **81**, 2060.

spectra of these compounds given by Hawkins and Burris.¹³ Further confirmation of material C as ocimene was afforded by the identity of the ultraviolet absorption band (max. 237 $m\mu$; $10^{-4}\epsilon \approx 1.5$), as measured for dilute solutions of C in cyclohexane, with published data.¹⁴ The product A remains unidentified but, since its gas-chromatographic retention time lies between those of α -pinene and ocimene, it is assumed to have a molecular weight comparable with that of these isomers and this value has been used in the calculation of G values. The production of A, B, and C, deduced from the results of gas chromatography, is shown in Fig. 2 as a function of the irradiation dose. Whereas ocimene formation with an initial G yield of 2.6 ± 0.3 shows a pronounced curvature with increasing irradiation dose, the initial G yield of dipentene (0.9) is maintained with but slight decrease up to a dose of 5.0×10^{21} ev g.⁻¹. The growth kinetics of the component A represents an intermediate case, showing a slight fall-off in yield per unit dose from the initial G of 0.6. We may ascribe the reduced rate of ocimene production (per unit of dose) on protracted irradiation to either a reduced rate of primary formation or its incorporation in polymer being easier than that of α -pinene. Evidence on this point is furnished by Fig. 3 which shows the growth of the extinction at 237 $m\mu$ in irradiated α -pinene. Since this absorption is characteristic of the diene conjugation in ocimene and as the other components (A and

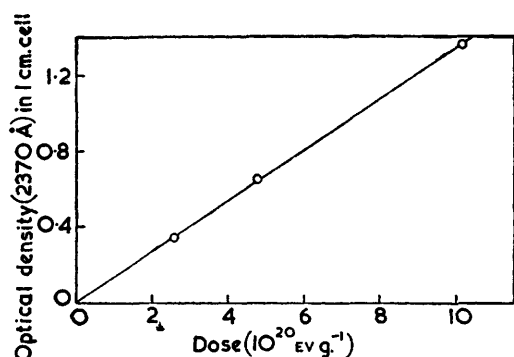


FIG. 3. Optical density (2370 Å) of irradiated α -pinene plotted against dose. Dose rate, 2.7×10^{17} ev g.⁻¹ min.⁻¹. Comparison cell: α -pinene. Dilution in cyclohexane, 1/500.

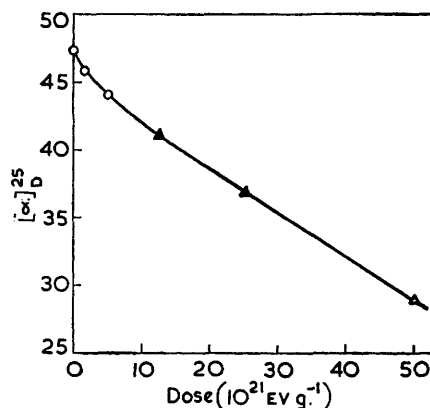


FIG. 4. Decrease of optical activity on irradiation of α -pinene.

○, 2.4×10^{17} ev g.⁻¹ min.⁻¹. △, 3.12×10^{20} ev g.⁻¹ min.⁻¹.

dipentene) have extinction values comparable with that of α -pinene at this wavelength, Fig. 3 represents a linear growth of ocimene in the irradiated system up to a dose of 10^{21} ev g.⁻¹. If the molar extinction coefficient at 237 $m\mu$ for ocimene in cyclohexane is assumed to be the same as in iso-octane,¹⁴ i.e., 16,700, the G yield of ocimene calculated from Fig. 3 is 2.8, in good agreement with the initial yield of 2.6 ± 0.3 derived from Fig. 2. We conclude that the difference between the linear growth of ultraviolet absorption at 237 $m\mu$ in Fig. 3 and the curvature of "free" ocimene in Fig. 2 reflects the secondary reaction of ocimene in the formation of polymer as the irradiation proceeds to high doses.

The decrease in optical activity of (+)- α -pinene on irradiation is shown in Fig. 4. Additional results obtained from three irradiations carried out to high conversion are recorded in Table 2 and give the specific optical activities of the distillate, recovered α -pinene and separated polymer, the latter being measured as a solution in chloroform.

The results (Table 2) fail to show an equivalence between the activity of the total sample and the sum of the activities of polymer and distillate according to their respective

¹³ Hawkins and Burris, *J. Org. Chem.*, 1959, **24**, 1507.

¹⁴ O'Connor and Goldblatt, *Analyt. Chem.*, 1954, **26**, 1726.

TABLE 2.
Changes in optical rotation.

Expt.	Dose (10^{22} ev g. $^{-1}$)	Polymer (wt. %)	$[\alpha]_D^{25}$ of total	$[\alpha]_D^{25}$ of distillate	$[\alpha]_D^{25}$ of recovered α -pinene	$[\alpha]_D^{25}$ of polymer
	0	0	47.3°	47.3°	47.3°	—
m	1.25	11.6	41.5	42.6	45.2	20.6°
n	2.5	21.0	36.9	39.3	43.3	19.8
o	5.0	34.1	28.9	33.1	39.7	—

weight fractions; thus the latter sum is calculated to be 40.0° and 35.2° for experiments m and n compared with the respective values of 41.5° and 36.9° observed for total sample. This discrepancy is attributed to loss of activity by partial racemization of optically active centres in the polymer during drying at 100° or on subsequent dissolution in chloroform. The distillate samples from m, n, and o were analysed by gas-liquid chromatography to determine the concentration of A, dipentene, and ocimene. Also, the α -pinene fraction

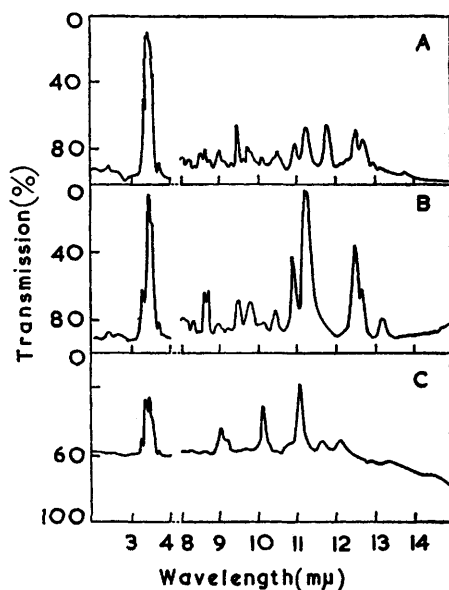


FIG. 5. Infrared spectra of isomers in CS_2 :
A, Unknown; B, dipentene; C, ocimene.

of the distillate was isolated by the chromatographic technique described earlier and its optical activity measured (Table 2); it had been established that no change in optical rotation occurred after a sample of pure (+)- α -pinene had been passed through the column under identical conditions. Therefore, the observed decrease in the specific rotation of α -pinene recovered from the distillate signifies either racemization or formation of an inactive product with a retention time less than that of α -pinene, such that no separation was achieved by using 500 microlitre samples under the operating conditions. The latter possibility is discounted since high-resolution chromatographic separations on smaller volumes of irradiated material revealed only one component, in traces, with a retention time less than that of α -pinene; it is estimated that the last substance is formed with a *G* yield less than 0.1 and therefore cannot account for the racemization yield deduced below.

A satisfactory feature of the results in Table 3 is the agreement between the total loss of optical activity in the distillate and the combined sum of isomer and racemized α -pinene concentrations. It suggests that no appreciable amount of other isomers is formed by irradiation. It is noteworthy that the *G* values for isomer formation at high doses listed in Table 4 are considerably lower than the initial values previously deduced from Fig. 2.

TABLE 3.
Analysis of distillate.

Expt.	Loss (%) of distillate activity referred to initial α -pinene	Formation (%) of products in distillate				Total products (%)
		A	Dipentene	Ocimene	Racemic α -pinene *	
m	9.9	0.7	1.9	2.2	4.2	9.0
n	16.9	1.1	3.7	4.3	7.7	16.8
o	29.9	4.0	8.2	5.6	12.6	30.4

* Calc. from loss in activity of recovered α -pinene and the known fraction of α -pinene in distillate.

TABLE 4.
Integral G values for products at high doses.

Expt.	Dose (10^{22} ev g. ⁻¹)	G (— monomer) for polymer formation			
		G (A)	G (dipentene)	G (ocimene)	
m	1.25	4.1	0.22	0.59	0.69
n	2.5	3.7	0.15	0.52	0.59
o	5.0	3.0	0.24	0.48	0.33

On the other hand the G value for polymer formation is less sensitive to increase in total dose (Tables 1 and 4). The high reactivity of ocimene in the irradiated α -pinene suggests that a limiting concentration of ocimene may be reached at sufficiently large doses when its rate of formation would be balanced by an equal rate of reaction to produce polymer.

Calculation of the G yield for the racemization of α -pinene requires a measurable decrease in the optical activity of the recovered α -pinene to be detected. Such a change could, therefore, be measured with accuracy only at high doses. Although the G value for isomerization decreases drastically at high doses, there is no reason to suppose that the racemization would be similarly affected. Since the formation of both polymeric and isomeric products would be expected to occur with equal probability from either active or the racemized α -pinene, the change in optical activity of the separated α -pinene after irradiation should be a measure of the racemization yield, independently of the amount of the other products formed. The only circumstance we can visualise whereby the yield for racemic α -pinene could be affected by prolonged irradiation dose is the possibility of energy transfer from α -pinene to some other component formed by irradiation, thus decreasing the yield of primary changes in α -pinene. Since we are unable to assess the latter effect on a quantitative basis, we proceed on the initial assumption that with increasing dose the fraction of energy absorbed in the active α -pinene will depend only on the concentration of the latter relative to the total amount of α -pinene present. Thus first-order decay kinetics will apply and a simple relation can be derived for G_0 , the initial racemization yield:

$$G_0 = (100c_0/D) \ln [1/(1 - f)], \quad (1)$$

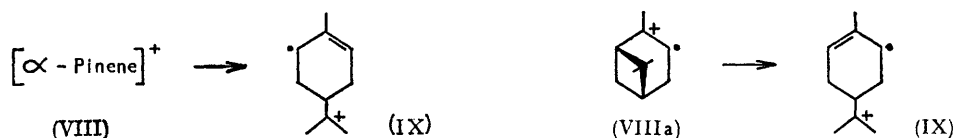
where c_0 is the initial concentration of (+)- α -pinene in molecules per g., and f is the fraction which has undergone racemization after a dose of D ev g.⁻¹.

The results in Table 5 are in good agreement, indicating $G_0 = 1.6$. The constancy of G_0 over a large range of absorbed dose indicated that energy-transfer effects are unimportant in this system.

TABLE 5.
Racemization yield of α -pinene.
($c_0 = 4.43 \times 10^{21}$ molecules/g.)

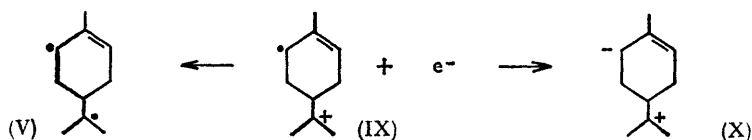
Expt.	Dose (10^{22} ev g. ⁻¹)	f (from Table 2)	$\ln [1/(1 - f)]$	G_0
m	1.25	0.044	0.0449	1.59
n	2.5	0.085	0.0889	1.57
o	5.0	0.16	0.1739	1.54

Mechanism.—We previously⁴ indicated some possible mechanisms to account for ocimene, dipentene, and polymer formation in the radiolysis of α -pinene. The present discussion starts with the postulate that the parent ion (VIII) rearranges to the structure



(IX), a change that can be considered either as an exothermic ion-dissociation^{4,11} at the quaternary carbon atom in the cyclobutane ring, or as the rearrangement (VIIIa) \rightarrow (IX) analogous to the conversion (VI) \rightarrow (VII) considered above. A structure analogous to (VIIIa) in which a π -electron is removed from the parent compound has been suggested¹² for the parent ion of hex-1-ene. Electron capture by the ion (IX) can be envisaged as leading to the biradical (V) or the internal ion pair (X) as possible intermediates.

Since the initial isomerization products of radiolysis and pyrolysis are qualitatively similar, it seems consistent to assign a major role to radical (V) in radiolysis, as for pyrolysis.² Nevertheless, the biradical intermediate does not represent a unique path to the above products. Formation of ocimene by pyrolysis of α -pinene exemplifies the usual thermal fission of cyclobutane and its derivatives.¹⁵ Such reactions are unimolecular in the gas phase with abnormally high frequency factors¹⁶ and are unaffected by the presence of radical scavengers such as nitric oxide and propene. An alternative^{15b} to the biradical theory in the pyrolysis of cyclobutane is that the two ethylene molecules are incipiently formed in the transition state by a concerted electronic rearrangement. Similarly, the mechanism of ocimene formation in the pyrolysis of α -pinene can be accommodated in an intramolecular change following gain of sufficient vibrational energy by the molecule. In the radiolysis of α -pinene, the release of excess vibrational energy for the conversion into ocimene would follow the electronic processes of ionization, excitation, and neutraliz-



ation. It is now pertinent to consider why ocimene does not undergo a further isomerization to allo-ocimene under the conditions of radiolysis. In thermal studies¹⁷ it has been shown that the half-life for the conversion of ocimene into allo-ocimene is only 3 minutes at 204.5°; the isolation of intermediate ocimene from the pyrolysis of α -pinene at comparable temperatures in the liquid phase has never been reported¹⁷ and methods for the preparation of ocimene from α -pinene^{13,17} depend upon heating the vapour to a high temperature for short periods. It follows that the Arrhenius parameters as measured for the liquid-phase thermal isomerization of α -pinene to allo-ocimene¹ reflect the values for the initial conversion of α -pinene into ocimene since this is the rate-determining stage in the overall reaction at the temperature employed; the corresponding parameters for the first-order transformation of ocimene into allo-ocimene are also recorded in Table 6. Although the change of ocimene into allo-ocimene requires less activation energy than

¹⁵ (a) Genaux and Walters, *J. Amer. Chem. Soc.*, 1951, **73**, 4497; Genaux, Kern, and Walters, *ibid.*, 1953, **75**, 6196; Kern and Walters, *Proc. Nat. Acad. Sci., U.S.A.*, 1952, **38**, 937; Wellman and Walters, *J. Amer. Chem. Soc.*, 1957, **79**, 1542; (b) Pritchard, Sowden, and Trotman-Dickenson, *Proc. Roy. Soc.*, 1953, *A*, **218**, 416; (c) Srinivasan and Kellner, *J. Amer. Chem. Soc.*, 1959, **81**, 5891.

¹⁶ Gowenlock, *Quart. Rev.*, 1960, **14**, 133.

¹⁷ Hawkins and Hunt, *J. Amer. Chem. Soc.*, 1951, **73**, 5379.

TABLE 6.
Arrhenius parameters for thermal isomerization.^{2,17}
[Rate constant = $A \exp (-E_0/RT)$]

Reaction	$10^{-13} A$ (sec. ⁻¹)	E_0 (kcal./mole)
α -Pinene \longrightarrow Ocimene	6.6	42.7
Ocimene \longrightarrow Allo-ocimene	0.00037 *	26.0

* Calc. from ref. 17.

the change of α -pinene to ocimene, the low frequency factor for the former reaction indicates a large decrease of entropy in the formation of the transition state. In the radiolysis of α -pinene, electronically excited molecules are formed by direct excitation or by neutralization of the parent ion. The average energy imparted by fast charged particles to a medium of hydrogen-like atoms in a direct excitation process has been calculated¹⁸ to be about 5 ev, whereas the energy of neutralization is given by the ionization potential, which is estimated for α -pinene to lie between 8 and 10 ev. Thus the total energy E of an excited α -pinene molecule, referred to the vibrational ground state, immediately after excitation will be less than 10 ev. The electronic process will communicate the excitation energy to the molecule in a time less than 10^{-16} sec. If we assume, in accordance with the statistical theory of unimolecular dissociation developed by Rosenstock, Wallenstein, Wahrhaftig, and Eyring,¹⁹ that a large number of crossing points exist between excited states, then the excitation energy is converted into vibrational energy in a time comparable with that of a vibration period (10^{-13} to 10^{-14} sec.). Thereafter, the unimolecular decomposition of the molecule (or ion) may be expressed in the simplified form,

$$k_i(E) = \nu_i(1 - E_0/E)^{N-1}, \quad (2)$$

where $k_i(E)$ is the specific rate constant for molecules of energy E undergoing reaction path i and measures the probability of dissociation per unit time, ν_i is a frequency factor, E_0 the activation energy, E the total energy as defined above, and $N = (3x - 6)$ where x is the number of atoms in the molecule. In the liquid state the excited molecule will lose energy by collisional interaction with a frequency of 10^{12} sec.⁻¹ and it has been estimated²⁰ that a highly excited species is completely quenched to ambient thermal energy in 10^{-10} sec. Thus, to a first approximation, for unimolecular decomposition to proceed under these conditions.

$$10^{-10}k_i(E) \geq 1; \quad (3)$$

so

$$\nu_i(1 - E_0/E)^{N-1} \geq 10^{10}. \quad (4)$$

The substitution of ν_i and E_0 from Table 6 for the conversion of α -pinene into ocimene, where E is taken as 10 ev (230 kcal./mole), leads to a calculated value of $N = 44$. Although this value is less than the theoretical value $N = 72$ for α -pinene, some recent work²¹ on the use of the above theory to predict the experimental mass spectra of propane suggests that only about half the total number of oscillators is effective in that instance. Also, in a comparison of calculated and experimental mass spectra of n -propylamine,²² a value of N only one-fifth of the theoretical was used to obtain correspondence with theory. We therefore regard the above result as satisfactory within the uncertainty limits of the statistical theory. In relation to the possible radiation-induced change of ocimene molecules to allo-ocimene, the low frequency factor of Table 6 almost rules out any probability of reaction as given by expression (4) above. Thus, even if ocimene is formed from

¹⁸ Pollard, *Adv. Biol. Med. Phys.*, 1953, **39**, 53.

¹⁹ Rosenstock, Wallenstein, Wahrhaftig, and H. Eyring, *Proc. Nat. Acad. Sci., U.S.A.*, 1952, **38**, 667.

²⁰ Wallenstein, Wahrhaftig, Rosenstock, and H. Eyring, Symposium on Radiobiology, John Wiley and Sons, Inc., New York, 1952, p. 70.

²¹ E. M. Eyring and Wahrhaftig, *J. Chem. Phys.*, 1961, **34**, 23.

²² Chupka, *J. Chem. Phys.*, 1959, **30**, 191.

α -pinene with excess vibrational energy it will not undergo further isomerization because the rapid quenching of the molecule in the liquid state does not allow sufficient time for the energised molecule to pass into the transition state. We conclude that thermal processes involving low frequency factors ($<10^{10}$ sec.⁻¹) are unlikely to occur by radiolysis in the liquid state.

The radiation-induced racemization of (+)- α -pinene implies the formation of a transient species which can revert to (+)- or (-)- α -pinene with equal probability. Both the internal ion-pair (X) and the biradical (V) could fulfil the necessary role and also account for dipentene formation.⁴ A choice on theoretical grounds alone would involve a calculation of the respective probabilities for electron capture for the processes (V) \leftarrow (IX) \rightarrow (X). The strongest argument in favour of the internal ion-pair configuration (X) is derived by analogy; since the radiation-induced polymerization of the isomeric β -pinene is deduced⁵ to be an ionic chain mechanism, it is likely that a resonance-stabilized internal ion-pair formed from β -pinene and analogous to (X) is the initiating species.^{5b} The alternative explanation involving a biradical initiation of β -pinene polymerization is highly improbable in view of the general tendency for biradicals to undergo termination by cyclization without appreciable chain growth,²³ and it is completely at variance with the evidence of our following paper.^{5b} Although the polymerization of α -pinene gives only a low yield in comparison with β -pinene, it is reasonable to conclude that similar primary species (*i.e.*, internal ion-pairs) are formed in both cases but that the subsequent polymerization is governed by the relative reactivities of the olefinic bond. In this respect it is well known that protons and carbonium ions display much greater affinity for exocyclic than for endocyclic double bonds.²⁴ The generation of (X) from the neutral α -pinene molecule in a solvent of low solvating power requires a higher energy than bond homolysis to produce a biradical. Nevertheless, such energetic differences are not decisive in radiation chemistry since the primary act of ionization is itself a high-energy process. It is the capacity of the charged centres to remain separated for sufficient time that determines the importance of the ion pair as a chemical intermediate.^{5b} Hence, if the activation barrier is overcome in the primary act as represented by the conversion (VIII) \rightarrow (X), the subsequent stability of (X) before collapse could be due to resonance at the locations of charge. Both intimate ion-pairs and solvent-separated ion-pairs have been proposed²⁵ as intermediates for reactions occurring in solvents of low dielectric constant. The racemization of α -pinene in this instance can therefore be visualised as a process of internal return from the transition state (X) with loss of configurational identity.

We conclude by noting that the combined *G* yield for dipentene (0.9), racemization (1.6), and polymer initiation ($5.2/3.1 \approx 1.7$) is 4.2 which is of the same order as the measured ion-pair yield in gaseous hydrocarbons.²⁶ If the ion-pair mechanism suggested above is valid, it seems probable the ocimene formation occurs exclusively as a result of primary excitation events.

The authors acknowledge the helpful discussions with Dr. W. Wild during this investigation. They are grateful to the Hercules Powder Company for the gift of (+)- α -pinene, and to Dr. G. B. Pickering of the Tropical Products Institute, Gray's Inn Road, London, W.C.1, for providing terpene samples in the early stages of this work.

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[Received, July 12th, 1961.]

²³ Tobolsky, *Ann. Rev. Phys. Chem.*, 1956, **7**, 167.

²⁴ Cf. Cope, Ambros, Ciganek, Howell, and Jacura, *J. Amer. Chem. Soc.*, 1959, **81**, 3153.

²⁵ Winstein and Robinson, *J. Amer. Chem. Soc.*, 1958, **80**, 169; Smith, Fainberg, and Winstein, *ibid.*, 1961, **83**, 618.

²⁶ For summary, see Swallow, "Radiation Chemistry of Organic Compounds," Pergamon Press, London, 1960, p. 14.