[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Studies in the Terpene Series. XXIV.[1] Sodium-catalyzed Double Bonds Migration and Dehydrogenation of *d*-Limonene, *l*-α-Phellandrene and of 2,4(8)- and 3,8(9)-*p*-Menthadiene[2,2a]

BY HERMAN PINES AND H. E. ESCHINAZI[3]

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d-Limonene on refluxing in the presence of sodium and "promoters" which can form organosodium compounds undergoes a rapid racemization. The latter reaction is accompanied by a slow evolution of hydrogen leading to an ultimate formation of *p*-cymene. The intermediate products of the reaction consisted of 2,4(8)- and 3,8(9)-*p*-menthadiene in the approximate ratio of 4:1. These two compounds are reversibly isomerized and ultimately dehydrogenated to *p*-cymene. α-Phellandrene under similar conditions undergoes racemization accompanied by a rapid dehydrogenation to *p*-cymene. A mechanism of the isomerization and dehydrogenation is discussed.

It was shown previously[4] that olefinic hydrocarbons such as 1-butene or 1-decene undergo a double bond migration when heated in the presence of sodium and compounds which can react with sodium to form organosodium compounds. In the case of *d*-limonene it was shown that double bonds migration, which leads to the formation of conjugated menthadienes, is also accompanied by a dehydrogenation which results in the formation of *p*-cymene.

The present investigation deals with a more detailed study of the latter reaction with the purpose of elucidating the mechanism of the isomerization and dehydrogenation of cyclohexadienes.

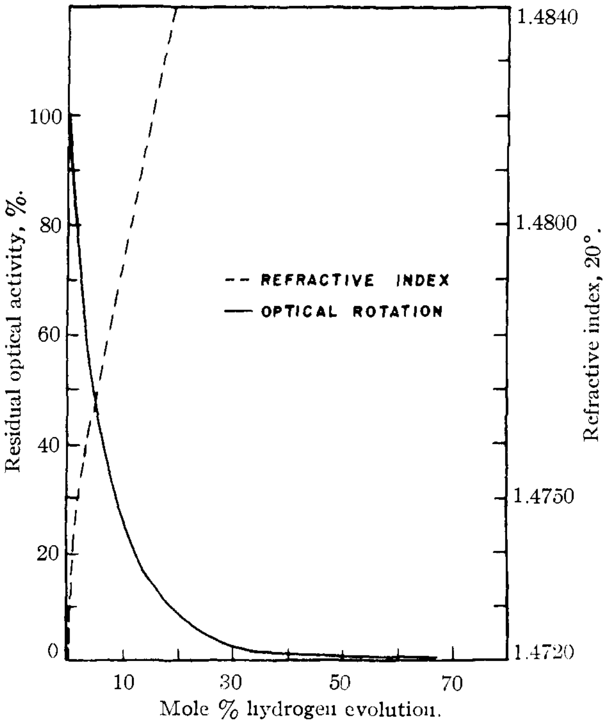

Fig. 1.—Reaction of *d*-limonene. The change in index of refraction and the drop in optical rotation in relation to hydrogen evolution.

d-Limonene was chosen for this study because of its availability in fairly pure form and, also, because the course of the reaction can be followed through easily determinable criteria, such as optical rotation, index of refraction, infrared absorption spectra, etc.

Discussion of Results

When *d*-limonene was refluxed in the presence of sodium sand and a small amount of a promoter, such as *o*-chlorotoluene or preferably freshly prepared benzylsodium, or sodium hydride, a reaction took place during which the optical rotation dropped rapidly at first, and then approached zero exponentially. The drop of optical activity was accompanied by a slow but steady evolution of hydrogen until amost 100 mole per cent. of hydrogen was evolved, based on *d*-limonene charged, with the ultimate formation of *p*-cymene of 98% purity. The relation between hydrogen evolution and the drop of optical activity is given in Fig. 1, which shows that this relation proved to be the same in seven experiments where different promoters or different methods of preparation of the same promoter were used.

The rate of hydrogen evolution, however, was related to the activity of the catalyst used. It was found that when sodium–benzylsodium was used as a catalyst the hydrogen evolution started as soon as *d*-limonene reached its reflux temperature. However in the case where sodium and *p*-chlorotoluene were used a certain time elapsed, amounting sometimes to several hours, before hydrogen started to liberate.

Figure 1 shows also a continuous increase of the refractive index in relation to the amount of hydrogen evolved.

It was observed that when the optical rotation dropped to about 20% of the original value of the *d*-limonene used, the hydrogen evolution was still at its beginning and did not exceed 13%. The bromine number of the reaction mixture during this period either did not change or was slightly higher than that of the starting material.[5] Reaction prod-

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[1] For previous paper of this series see H. Pines and J. Ryer, THIS JOURNAL, **77**, 4370 (1955).

[2] Paper III in the series, "Sodium-catalyzed Reactions." For paper II see H. Pines, J. A. Vesely and V. N. Ipatieff, *ibid.*, **77**, 554 (1955).

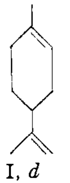
(2a) Presented before the Division of Petroleum Chemistry at the American Chemical Society Meeting, April 6, 1955, Cincinnati, Ohio.

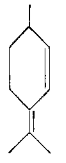
[3] Vladimir Ipatieff Postdoctoral Fellow, 1953–1954.

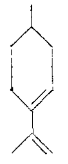
[4] H. Pines, J. A. Vesely and V. N. Ipatieff, THIS JOURNAL, **77**, 347 (1955).

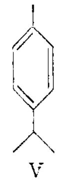
[5] It was later found that the bromine absorption of 2,4(8)-*p*-menthadiene (III) was 20–30% higher than calculated for this diolefin. It is probable that a partial dehydrobromination occurred during the addition of the bromine.

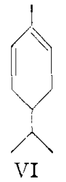
uct at this point was found to be composed of a mixture having the following approximate composition: 20% of unreacted *d*-limonene (I), 50% of racemized *d*-limonene, dipentene (II), 20% of a mixture consisting of 2,4(8)-(III) and 3,8(9)-*p*-menthadiene (IV) in the approximate ratio of 4 to 1, and 10% of *p*-cymene (V).


I, *d*
II, *dl*


III


IV


V


VI

As the reaction proceeded the concentration of *p*-cymene increased and it was in direct proportion to the amount of hydrogen liberated.

When *o*-chlorotoluene was used as a promoter, the reaction product contained toluene in amounts equivalent to the promoter used.

Without a promoter but in the presence of sodium at reflux temperature, *d*-limonene did not undergo dehydrogenation and its racemization was hardly noticeable.

In order to determine whether the isomerization reaction is reversible and whether the conjugated menthadienes can convert into each other, pure 2,4(8)*p*-menthadiene (III) was isolated and treated with sodium under similar experimental conditions as used for *d*-limonene. It was found that III was converted to a small extent to IV, with the simultaneous evolution of hydrogen and the corresponding formation of *p*-cymene. The presence of each of the compounds and their respective yields was determined by a combination of ultraviolet and infrared spectroscopy and also through treatment with maleic anhydride.

Similarly when 3,8(9)-*p*-menthadiene (IV) was treated with sodium and benzylsodium under the same experimental conditions it underwent isomerization to compound III and dehydrogenation to *p*-cymene. The reaction mixture isolated after the evolution of 20 mole per cent. of hydrogen consisted of 20% *p*-cymene and a mixture of compound III and IV in a ratio of approximately 4:1. This is presumably the equilibrium ratio since it is the same as that obtained in the reaction product of limonene.

A careful study of the ultraviolet spectra of the intermediate reaction products obtained from I, III and IV failed to detect the presence of endocyclic conjugated *p*-menthadienes, whose absorption peaks, according to Woodward's rule,[6] should be in the region of 262–272 mμ.

In order to evaluate the reasons for the absence of endocyclic *p*-menthadienes in the intermediate reaction products, it was decided to investigate the effect of sodium and a promoter upon *l*-α-phellandrene (VI) under similar experimental conditions used for *d*-limonene. Since, however α-phellandrene underwent a slow but seemingly steady thermal change at its reflux temperature involving racemization and probably Diels–Alder type dimerization it was deemed important to carry out the study with very active catalysts in order to minimize as much as possible side reactions. This was achieved by using freshly prepared benzylsodium as a promoter or a catalyst recovered from an experiment made with *d*-limonene. In the presence of such catalysts the reaction with phellandrene started at once as evidenced by the evolution of hydrogen. After six hours of refluxing 50% of the theoretical amount of hydrogen was evolved with the formation of the corresponding amount of *p*-cymene. Simultaneously with the hydrogen evolution a drop in optical rotation was noticed. This drop was in excess to that expected for the combined effect of the dehydrogenation and of the thermal effect. Figure 2 represents the relation between the hydrogen evolution and the loss of optical rotation as a function of catalyst activity.

With a catalyst of high activity the rate of dehydrogenation was about twice as great as that of racemization (curve C Fig. 2).

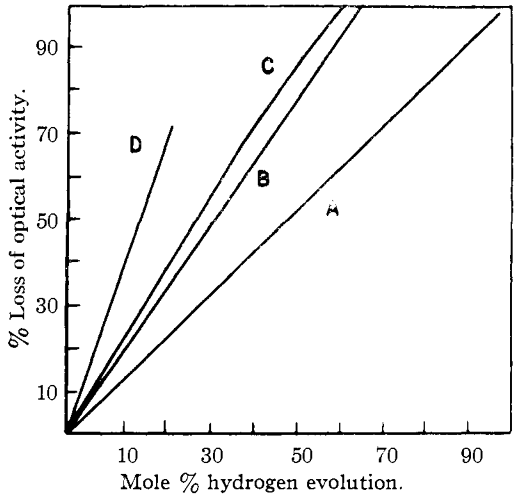
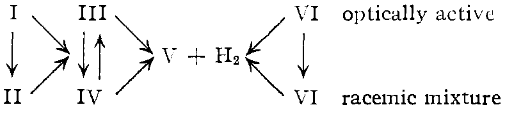


Fig. 2.—Sodium-catalyzed reaction of *l*-α-phellandrene: A, calculated for $C_{10}H_{16} \rightarrow C_{10}H_{14} + H_2$; B, calculated for $3C_{10}H_{16} \rightarrow C_{10}H_{16} + 2C_{10}H_{14} + 2H_2$; C, with benzylsodium; D, with used catalyst. $C_{10}H_{16}$ = *l*-α-phellandrene, $C_{10}H_{14}$ = *p*-cymene.

The reaction product from the partial dehydrogenation and racemization of α-phellandrene did not contain any semicyclic or exocyclic conjugated *p*-menthadienes, such as compounds III or IV.

The above described reactions can be summarized schematically as



Analytical Procedure and Characterization of the Products.—The methods used for the separation, characterization and determination of the various intermediate reaction products which were obtained from the sodium-catalyzed reactions of *p*-menthadienes are similar to those described below for *d*-limonene.

The intermediate reaction products of *d*-limonene were first removed almost quantitatively

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(6) R. B. Woodward, This Journal, **64**, 72 (1942).

TABLE I

COMPOSITION OF THE PRODUCTS OBTAINED FROM THE SODIUM-CATALYZED REACTION OF *d*-LIMONENE

The distillation was made in a 50-plate bubble-cap column with 850 ml. of a reaction mixture having $\alpha^{25}\text{D}$ 4.5°, $n^{20}\text{D}$ 1.4844: I, *d*-limonene; II, dipentene; III, 2,4(8)-*p*-menthadiene; IV, 3,8(9)-*p*-menthadiene; V, *p*-cymene.

Cut	B.p., °C. (20 mm.)	Total distillate, %	$\alpha^{25}\text{D}$	$n^{20}\text{D}$	Composition of cuts, wt. % I	II	III	IV	V
1	72–73	68.1	+6.0°	1.4788	6.0	63.1	0.2	0.7	30.0
2	73.5	4.8	5.7	1.4825	5.8	61.0	4.0	9.2	20.0
3	75.0	2.1	4.0	1.4868	4.0	49.0	12.9	21.6	12.5
4	75.8	6.0	3.0	1.4900	3.0	31.5	35.0	27.5	3.0
5	79.0	3.5	0	1.4988	..	..	55.0	45.0	..
6	80.3	4.7	0	1.5022	..	..	93.5	6.5	..
7	81.4	10.8	0	1.5048	..	..	98.8	1.2	..
Composition based on total distillate					4.5	48.7	20.0	5	21.8

from the catalyst under reduced pressure and then examined by a combination of physical and chemical methods. A preliminary examination of the ultraviolet spectra of the various reaction mixtures revealed that the conjugated dienes showing absorption maxima at 237 and 243 mμ were at optimum concentration when a loss of about 95% of the optical rotation occurred. At this point the concentration of *p*-cymene amounted to 22% and that of *d*-limonene to 5%.

The hydrocarbons recovered from such a reaction were fractionated and the various cuts were separately investigated (Table I).

p-Cymene (V) was identified and its composition in cuts 1 and 2 determined spectroscopically using its characteristic absorption peak of 273 mμ and its molar extinction ε 525.

Owing to the interference of the conjugated *p*-menthadienes III and IV with the absorption maxima of *p*-cymene, cuts 3 and 4 were selectively hydrogenated in the presence of copper chromite, prior to the determination of V. It was found, indeed that the determination of the amount of *p*-cymene by the base-line technique was unreliable when the ratio of the conjugated dienes III and IV exceeded that of *p*-cymene by a factor of two. The total amount of *p*-cymene determined spectroscopically corresponded to the amount of hydrogen evolved.

_d_-Limonene (I) and Dipentene (II).—The optically active *d*-limonene was determined from the optical rotation of the different cuts.

It was assumed that besides *d*-limonene in cut 1, the remaining non-conjugated *p*-menthadienes consisted of dipentene. This assumption was based on the facts: (a) infrared absorption spectra did not show the characteristic absorption bands for *cis*-ethylenic double bond characteristic of isolimonene (XIII) and (b) no characteristic blue coloraation was obtained when nitrosyl chloride was added. This indicates the absence of terpinolene (XIV).[7]

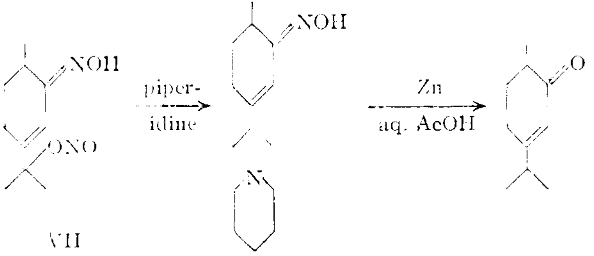
The treatment of cut 1 with nitrosyl chloride yielded dipentene nitrosochloride, m.p. 108–109°,[8] and *dl*-carvoxime. The total yield of the two compounds amounted to 60% based on the diolefins content, determined by the bromine absorption.[9] This yield compares favorably with the usual 70% yield when pure dipentene was used. The two solid derivatives were converted subsequently to *dl*-carvone,[10] thus establishing the presence of dipentene.

Having thus determined the concentration of *d*-limonene and dipentene in cut 1 and assuming their ratio to be constant in the remaining cuts, it was possible, from the optical rotation, to calculate their respective concentrations. The concentrations of compounds III, IV and V determined by spectroscopic means and those of compounds I and II calculated from the optical rotation, accounted for the total balance of the respective cuts.

2,4(8)-_p_-Menthadiene (III).—2,4(8)-*p*-Menthadiene (III) was isolated from cuts 6 and 7. This compound owing to its transoid dienic structure did not react with maleic anhydride. Advantage was taken of this property to separate it from compound IV. The maleic anhydride treated cuts 6 and 7 consisted of almost pure compound III. Compound III distilled at 188–189° at 760 mm., $n^{20}\text{D}$ 1.5050, d^{20}_4 0.8561, MR_D 47.15. Its molar extinction of ε 20,128 at ultraviolet absorption peak of 243 mμ was higher than the ε 15,843 published recently.[11]

Although the nitrosyl chloride reagent failed to yield a crystalline derivative of III it led, however, to the intense blue coloration which characterizes a tetramethylethylenic structure. Crystalline α-β-nitrosates and nitrosites VII were isolated from III in excellent yields, the latter (VII) being the only ones investigated.

III + 2HONO ⟶



VII α,β-isomers VIII IX

The unstable low melting, 110°, α-nitrosite was converted easily to its more stable and higher melting, 167°, β-isomer. Both the α- and the β-nitro-

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[7] A. v. Bayer, *Ber.*, **27**, 443 (1894).

[8] O. Wallach and E. Conrady, *Ann.*, **252**, 145 (1899), reported a melting point of 78° with a solidification and remelting of about 103–104° for an equimolar mixture of pure *d*- and pure *l*-limonene nitrosochloride.

[9] H. E. Eschinazi and E. D. Bergmann, THIS JOURNAL, **72**, 5651 (1950).

[10] H. Goldschmidt and R. Zürrer, *Ber.*, **18**, 2220 (1885).

[11] R. T. O'Connor and L. A. Goldblatt, *Anal. Chem.*, **26**, 1726 (1954).

sites yielded the same β-nitrolpiperide (VIII) upon treatment with piperidine.

The hydrolytic reduction of either VII or VIII by means of zinc and aqueous acetic acid resulted in the formation of *dl*-carvenone (IX), thus establishing the proof of the 1,4-addition of the nitrogen oxides to III. The *dl*-carvenone was identical with a sample prepared from *dl*-camphor according to Bredt.[12]

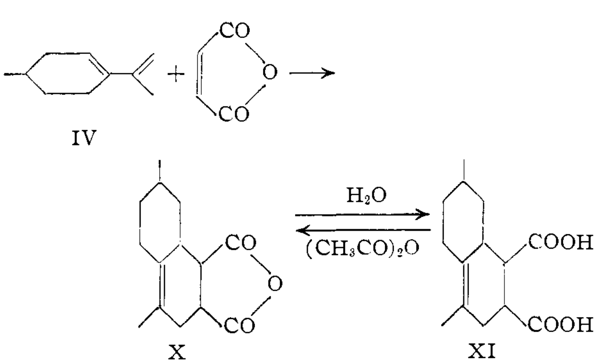
Compound III upon ozonization and oxidative decomposition of the ozonide yielded the expected 1-methylglutaric acid and acetone.

3,8(9)-*p*-Menthadiene (IV).—3,8(9)-*p*-Menthadiene (IV) in cut 4 was separated from compound III by a fractional distillation using a spinning band column of 70 plates efficiency. Compound IV thus separated was of high purity. Its infrared spectrum was identical with those obtained from an authentic sample kindly supplied by Hercules Powder Co. and with a synthetic sample, which was prepared according to the general method of Perkin and Wallach.[13] Compound IV distilled at 183–184° at 760 mm., $n^{20}\text{D}$ 1.4936, MR_D 46.43. Its molar extinction of ε 19,100 at the ultraviolet absorption peak of 233.5 mμ was higher than the reported ε 10,700 at 235 mμ[14] and of ε 6,995 at 235 mμ,[11] but was in close agreement (ε 18,950 at 233.5 mμ) with a sample obtained from Hercules Powder Co.

In a mixture consisting of one part IV to four parts of III there was a shift of the 233.5 mμ peak toward 237 mμ thus displaying a curve with twin neighboring peaks of 237 and 243 mμ similar to the one observed in the crude intermediate reaction mixture of *d*-limonene.

3,8(9)-*p*-Menthadiene (IV) unlike its conjugated isomer III showed a small affinity for silica gel. Thus when cut 2 was chromatographed, the first product to pass through the column was IV. The relative order of adsorptivity of the various *p*-menthadienes over silica gel is (Fig. 3): IV < I or II < III < V.

As expected from its cisoid structure, IV gave a characteristic maleic anhydride adduct, m.p. 68–69° (X). It formed upon hydrolysis the *cis* dicarboxylic acid, m.p. 204° (XI) which regenerated the anhydride X upon treatment with acetic anhydride.



The physical constants of X and XI failed, however, to agree with the data reported by Alder and Schinz.[15]

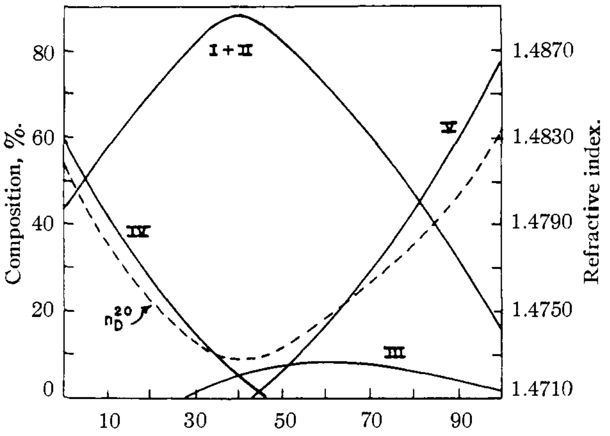


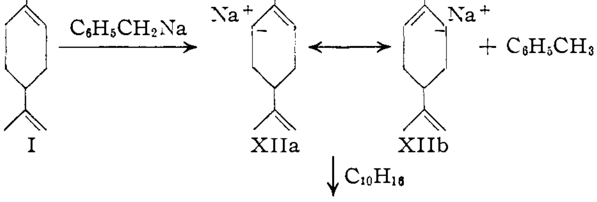
Fig. 3.—Relative order of adsorptivity of menthadienes over silica gel: composition of I + II, 67%; III, 4%; IV, 10%; V, 19%.

The quantitative determination of IV in a mixture with III was made by a combined procedure involving the treatment of the mixture with maleic anhydride, the weighing of the adduct and the determination by ultraviolet spectroscopy of compound(III) in the recovered hydrocarbons.

***l*-α-Phellandrene (VI).**—*l*-α-Phellandrene (VI) used for the reaction had an optical rotation of $\alpha^{25}\text{D}$ −138–145°. As an analytical standard, a sample of *l*-α-phellandrene of a high purity and specific optical rotation, $[\alpha]^{20}\text{D}$ −183°, was used. Its molecular extinction at 263 mμ was ε 3,345. This absorption peak was used for the calculation of the concentration of α-phellandrene in a reaction mixture. The molar extinction reported in the literature for α-phellandrene is ε 2,500 at 263 mμ.[14]

Mechanism of Reaction.—The experimental results indicate that sodium in conjunction with benzylsodium, added as such or formed *in situ*, catalyzed the isomerization and dehydrogenation of *p*-menthadienes. In the presence of this catalyst *d*-limonene underwent a rapid racemization, accompanied by a slow isomerization to the conjugated *p*-menthadienes III and IV and by a still slower dehydrogenation to *p*-cymene (V).

The racemization could be explained by a chain mechanism involving the intermediate formation of carbanions XIIa and XIIb; which are part of an allylic resonance hybrid.



Upon reaction with another molecule of *d*-limonene, XIIa and XIIb propagate the chain and generate optically inactive dipentene II. As indicated

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[12] J. Bredt, *Ann.*, **314**, 387 (1901).

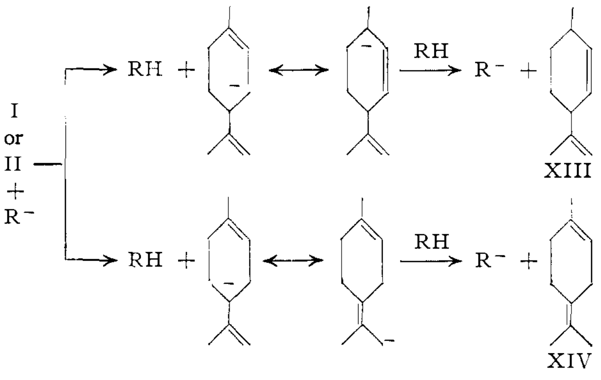
[13] W. H. Perkin, Jr., and O. Wallach, *ibid.*, **374**, 198, 215 (1909); *J. Chem. Soc.*, **97**, 1938 (1910).

[14] H. Booker, L. K. Evans and A. E. Gillam, *ibid.*, 1453 (1940).

[15] K. Alder and A. Schinz, *Ann.*, **565**, 118 (1949).

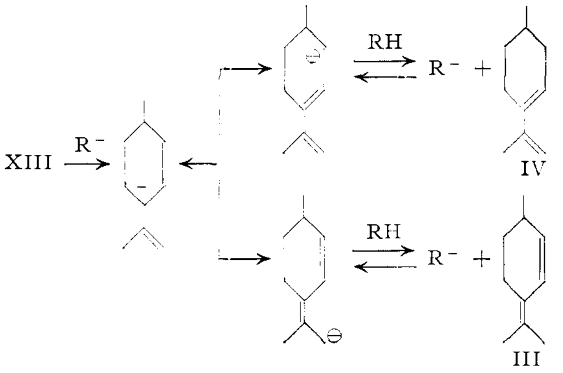
in the above equation, toluene was, indeed, found in the reaction product.

The isomerization of I or II to III and IV could be explained by a two-step reaction, as indicated by the scheme



For the sake of brevity Na^+ was omitted. R represents a *p*-menthadienyl ($C_{10}H_{15}$) radical.

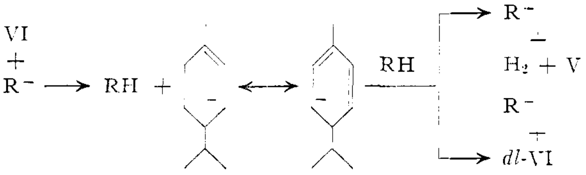
Compounds XIII and XIV were not found among the products of reaction. It is probable that these two compounds having a biallylic hydrogen could very readily undergo a further reaction leading ultimately to the formation of compounds III and IV.



The formation of III was favored over IV in a ratio of 4:1. Compounds III and IV, as indicated in the above scheme, are in equilibrium with each other. It was found that the same ratio of approximately 4:1 was obtained when either pure III or IV were treated under similar conditions.

Compound XIV by a similar series of steps would lead to the formation of IV and to an endocyclic *p*-menthadiene, α-terpinene, which was, however, not detected in the reaction product.

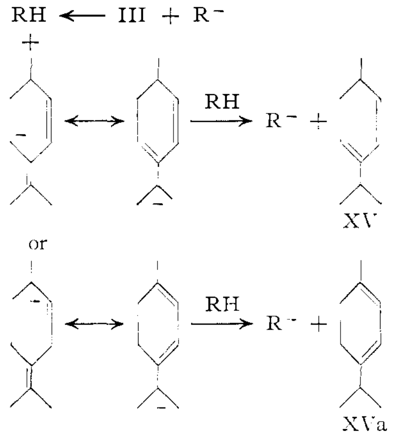
In the presence of the same catalyst the endocyclic *p*-menthadiene, *l*-α-phellandrene (VI), did not undergo isomerization to conjugated cyclic *p*-menthadienes. It was found that unlike *d*-limonene the rate of dehydrogenation of VI to *p*-cymene exceeded that of racemization by an approximate factor of two. The following may represent the mechanism of reaction.



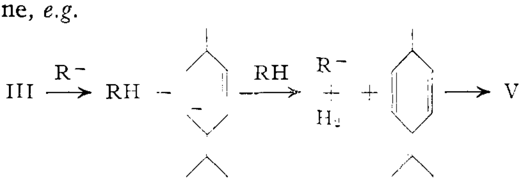
Inasmuch as α-terpinene was not detected in the intermediate reaction product, it seems less likely that the tertiary carbon atom in the ring was attacked.

The faster rate of dehydrogenation of *l*-α-phellandrene over the rate of racemization indicates the great tendency of the intermediate carbanions to lose a hydride and thus form a more stable aromatic ring.

Similarly, the dehydrogenation of *d*-limonene to *p*-cymene might have occurred from short lived endocyclic *p*-menthadienes, such as α-terpinene (XVa) or 2,4-*p*-menthadiene (XV), which might have resulted from III.



In view of the fact that no endocyclic conjugated *p*-menthadienes were present in the intermediate products from the reaction of *d*-limonene, it is not excluded that dehydrogenation also might take place directly from either compounds III or IV and followed by an immediate isomerization to *p*-cymene, *e.g.*



Experimental Part

Materials.—*d*-Limonene (I) was obtained from a steam-distilled orange oil.[16] The latter was again steam distilled and fractionated in a glass 50-plate bubble-cap column. The *d*-limonene was collected at 73–74° at 22 mm., $\alpha^{25}\text{D}$ +103°, $[\alpha]^{25}\text{D}$ +121.5°, $n^{20}\text{D}$ 1.4722; it amounted to about 96% of the total material submitted to distillation.

l-α-Phellandrene (VI) was separated from a sample consisting of the terpene fraction of the oil of Eucalyptus, *E. dives*, from which the piperitone had been removed.[17] The sample was steam distilled and the organic layer was fractionated in the presence of 0.5% of hydroquinone in a 50-plate bubble-cap column. The *l*-α-phellandrene was collected at 72–72.5° at 22 mm., $n^{20}\text{D}$ 1.4705–1.4715, $\alpha^{25}\text{D}$ −137° to −153°. The fraction with the highest optical rotation had the following constants: b.p. 72° at 22 mm., 172° at 744 mm.; $n^{20}\text{D}$ 1.4708; $\alpha^{25}\text{D}$ −153°; $[\alpha]^{20}\text{D}$ −183°. The maximum in the ultraviolet absorption spectra was at 263 mμ, ϵ_{mol} 3,345 in octane.

2,4(8)-*p*-Menthadiene (III).—A solution consisting of 125 g. of impure compound III, obtained from various reaction mixtures of *d*-limonene and corresponding to cuts 6 and 7 (Table I), 15 g. of maleic anhydride, 0.5 g. of hydroquinone and 125 ml. of ether was refluxed for 2 hours.

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[16] Kindly supplied by Minute Maid Corp., Plymouth, Fla.

[17] Kindly furnished by L. Givaudan, Inc., Delawanna, N. Y.

About 1 g. of an insoluble white polymer formed on the walls of the flask. The filtered solution was washed with water to remove the excess maleic anhydride and the ether distilled. The residue was steam distilled. Pure compound III was recovered having the following constants: b.p. 189° at 760 mm., $n^{20}D$ 1.5050, d_{20} 0.8561. The maximum in the ultraviolet absorption spectra was at 243 mμ, ϵ_{mol} 20,128 in isoöctane.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.24; H, 11.76. Found: C, 87.8; H, 11.8.

The infrared spectrum (Fig. 4) showed the absence of the bands at 6.25, 11.38 and 12.2 μ, while the ultraviolet spectrum showed no 235 mμ peak, indicating the removal of compound IV. When the maleic anhydride treatment was repeated, the terpene III was recovered totally unchanged. The infrared spectrum of III (Fig. 4) shows the characteristic absorption bands of a *cis* disubstituted ethylenic band at 13.7 μ.

The residue from the steam distillation consisted of approximately 15 g. of a heavy oil which crystallized upon standing. This solid was the adduct XI derived from IV as described under the characterization of products.

3,8(9)-*p*-Menthadiene (IV) was synthesized according to the method of Perkin and Wallach.[13] Its physical constants were identical with those of IV which was separated from the reaction products of the isomerization of *d*-limonene. The synthetic terpene upon treatment with maleic anhydride gave adducts X and XI, identical with those derived from IV.

Apparatus and Procedure. Apparatus.—The experiments were carried out in an apparatus consisting of a round-bottom flask provided with a thermometer well, a dropping funnel and connected by means of a distillation trap of 5-ml. capacity to a reflux condenser. The distillation trap, into which continuous stream of vapor flows, was provided with a sampling stopcock. The top of the condenser was connected through a safety trap and a three-way stopcock to a gas measuring bottle where the evolved gases were collected by displacement of a saturated sodium chloride solution.

Procedure.—The reagents consisting of the corresponding terpenes, sodium in the form of cleanly cut lumps and the "promoters" were placed in the reaction flask, the apparatus was then flushed with nitrogen and heated to vigorous reflux. At this point the apparatus was connected to the gas measuring bottle. Samples of 2 to 5 ml. of the continuously renewed condensate were withdrawn from the distilling trap during the course of the reaction. After analysis the remainder of each sample was subsequently returned to the reaction vessel through the dropping funnel. The temperature of the reaction mixture usually increased 2 to 3 degrees during the course of the reaction. The reaction usually was brought to a stop by removing the hydrocarbons directly from the reaction vessel by a flash distillation under reduced pressure. The residue obtained from the reaction of limonene consisted of a finely divided brown powder admixed with sodium. It possessed high catalytic activity and was used as a catalyst in some of the subsequent reactions. On the other hand, the residue recovered from α-phellandrene reaction, owing to a substantial thermal dimerization of the terpene, consisted of a dark viscous material containing sodium imbedded in it. This residue possessed only a slight catalytic activity.

The soluble limonene residue could be recovered by cooling the reaction mixture and filtering under a nitrogen blanket. After vacuum distillation, the clear residue showed no detectable catalytic activity. The volume of recovered distillate amounted usually to about 90% of that of starting material, but was slightly smaller, 75 to 80% in the case of α-phellandrene. The experimental results are summarized in Table II.

Preparation of Sodium-"Benzylsodium" Catalyst.—The following is a typical example of a reaction carried out with sodium-"benzylsodium" catalyst and refers to experiment 3 in Table II. The preparation of the catalyst was the same in other experiments using the same catalyst, but the amount of catalyst used was in proportion to the quantity of terpene used.

A mixture consisting of 3 ml. of *o*-chlorotoluene, 30 ml. of toluene and 6 g. of cleanly cut sodium pieces was refluxed under a nitrogen blanket for 4 hours. The resulting black suspension then was freed from the excess of toluene under vacuum. The residue was cooled under nitrogen and after washing with a few ml. of *d*-limonene, it was transferred to the reaction vessel with 200 ml. of the terpene. The first few ml. of the trap distillate were discarded because they contained small amounts of toluene. The reaction usually started almost at once with catalyst prepared in this way.

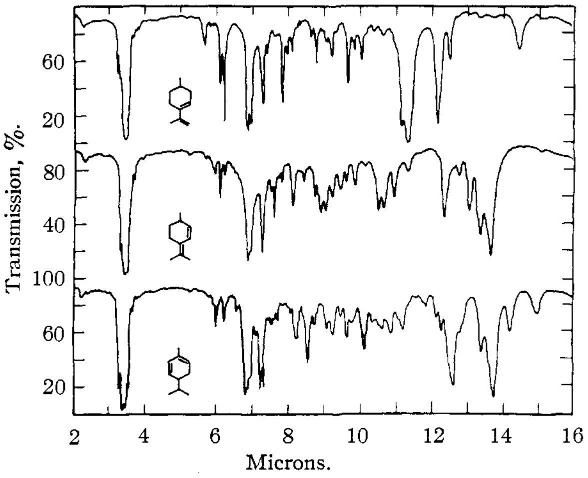

Fig. 4.—Infrared spectra of conjugated *p*-menthadienes (0.0268 mm. sodium chloride cell).

Characterization of Products. Dipentene (II). Dipentene Nitrosochloride.—Ethyl nitrite, from the dropwise addition of 25 ml. of 40% sodium nitrite and 5 ml. of ethanol into 50 ml. of 20% sulfuric acid and 5 ml. of ethanol, was bubbled over 1.5 hours into a stirred mixture of 16 ml. of cut 1 (Table I) and 20 ml. of concd. hydrochloric acid with cooling to keep the temperature below 5°. Stirring was continued 30 minutes, then 40 ml. of ice-cold ethanol was added. Decantation of the aqueous layer and trituration of the green semi-crystalline product with twice its volume of cold ethanol gave crystalline product. This was purified by dissolving in the minimum volume of chloroform and precipitating with cold ethanol; yield 3 g., m.p. 101–103°. A slow reprecipitation with ethanol furnished fine needles, m.p. 108–109°,[18] which were optically inactive.

Anal. Calcd. for $C_{10}H_{16}ONCl$: C, 59.55; H, 7.95; N, 6.97. Found: C, 59.50; H, 7.88, N, 7.11.

***dl*-Carvoxime.**—The mother liquors from the nitrosochloride reaction were treated with an excess of water and extracted with chloroform. Upon evaporation, the residue was mixed with 15 ml. of pyridine and refluxed for 5 minutes. After cooling, 50 ml. of water was added and the oil extracted with ether, washed with water, diluted acid and sodium bicarbonate solution and finally dried with anhydrous sodium carbonate. The ether was then evaporated and the residue was steam distilled. From the distillate was obtained 4.5 ml. of *p*-cymene (27%). The residue from the steam distillation contained 4.5 g. of *dl*-carvoxime, which was separated as a crystalline mass. Recrystallization from 40% ethanol yielded lustrous plates, m.p. 92–93°.

Anal. Calcd. for $C_{10}H_{15}ON$: C, 72.72; H, 9.09; N, 8.48. Found: C, 73.01; H, 9.06; N, 8.48.

When 1 g. of the dipentene nitrosochloride, m.p. 108–109°, was refluxed in 2 ml. of pyridine for 5 minutes, the same *dl*-carvoxime was precipitated by addition of water; m.p. 92–93°. It showed no depression in melting point when admixed with an authentic sample.

Dipentene Nitrolpiperide.—A solution consisting of 0.3 g. of dipentene nitrosochloride, 0.5 ml. of piperidine and 3 ml. of ethanol was refluxed for 10 minutes. After cooling and addition of 10 ml. of water a solid precipitated which on crystallization from ethanol formed long needles melting at 157–158°.[19]

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[18] O. Wallach and E. Conrady, *Ann.*, **252**, 145 (1889), reported that an equimolar mixture of *d*- and *l*-limonene nitrosochlorides melted initially at 78°; the solution, however, became turbid and then clarified at about 103–104°; J. L. Simonsen, "The Terpenes," Vol. I, University Press, Cambridge, England, 1931, p. 135, reports only the lower melting point.

[19] J. L. Simonsen, "The Terpenes," Vol. I, 2nd edition, University Press, Cambridge, England, 1931, p. 137, reports m.p. 154° for dipentene α-nitrolpiperide and 152° for the β-nitrolpiperide.

TABLE II

ISOMERIZATION AND DEHYDROGENATION OF *p*-MENTHADIENES

			Catalysts				Hydrogen evoln.		Flash distillate			
Expt.	Terpene	Quant., ml.	Na, g.	Promoter	G.	Time, hr.	Max. ml./hr.	Mole %[a]	$n^{20}D$	$\alpha^{25}D$	Yield, %	*V* in distillate, %
1	I	1000	30	[b]	15	29[c]	1300	22	1.4843	+ 4°	85[p]	24
2	I	500	None	[d]		28	3400	82	1.4894	....	80	98
3	I	200	[e]	[e]		7	2200	31	....	+ 2$^1/_2$	92[p]	33
4	I	250	15	None		48	..	..	1.4720	+99	96	None
5	I	200	2	[f]	10	24	..	..	1.4720	+99	95	None
6	I	200	15	NaH	6	10	None	31	1.4860	+ 1	90	33
7	III	115	[e]	[e]		4	1500	24	1.4940	0	85[g]	25
8	IV	4.5	[e]	[e]		2	50	17	1.4990	0	82[h]	20
9	VI	265	[e]	[e]		15	2500	70	1.4850	0	90[p]	73
10	VI	200	None	[i]		12	4400	71	1.4865	0	85	78
11	VI	200	10	[j]		28	1200	32	1.4790	−15	77[k]	None
12	VI	200	None	None		27	None	None	1.4742	−38	65[l]	None
13	VI	200	10	None		29	None	None	1.4745	−32	65[m]	None
14	VI	200	None	[n]	2	29	None	None	1.4745	−43	65[o]	None

[a] Based on terpene charged. [b] *o*-Chlorotoluene. [c] Induction period: 3.5 hours. [d] One-half of the residue from the flash distillation of expt. 1. [e] See Experimental Part under "Preparation of Sodium–Benzylsodium Catalyst." [f] Soluble residue from expt. 3 obtained after filtration and flash distillation. [g] Contains 57% of III and 18% of IV. [h] Contains 63% of III and 20% of IV. [i] One-quarter of the residue from the flash distillation of expt. 1. [j] Residue obtained from the flash distillation of expt. 1. [k] 12% of *l*-α-phellandrene dimer was isolated, b.p. 145° at 6 mm., $n^{20}D$ 1.5025, $\alpha^{25}D$ −21°. Ultraviolet spectrum does not show presence of conjugation. *Anal.* Calcd. for $C_{20}H_{32}$: C, 88.25; H, 11.75. Found: C, 88.56; H, 11.72. Semmler and Jonas, *Ber.*, **47**, 2078 (1914), reported the following constants for the dimer: b.p. 175–185° at 10 mm., $n^{20}D$ 1.5080, α_D +9.5°. [l] 18% of *l*-α-phellandrene dimer was obtained having the same physical constants as in ref. *k*. [m] 13% of *l*-α-phellandrene dimer was obtained. [n] Hydroquinone. [o] 25% of *l*-α-phellandrene dimer was obtained. [p] Toluene was found in the reaction product, amounting to about 60–70% based on the amount of *o*-chlorotoluene or benzylsodium used.

Anal. Calcd. for $C_{15}H_{26}ON_2$: C, 72.00; H, 10.40; N, 11.20. Found: C, 72.40; H, 10.10; N, 11.3.

***dl*-Carvone 2,4-dinitrophenylhydrazone** was prepared from *dl*-carvone which was obtained from the hydrolysis of 4 g. of *dl*-carvoxime with 125 ml. of 5% oxalic acid solution. The dinitrophenylhydrazone was recrystallized from ethanol as orange red needles melting at 189–190° , no depression with an authentic sample.

2,4(8)-*p*-Menthadiene (III). α- **and** β-**Nitrosites: 2-Isonitroso-8-nitrito-3-*p*-menthene** (VII).—To a stirred mixture consisting of 8 ml. of cut 7 (Table I) dissolved in 20 ml. of ether and 25 ml. of 40% aq. sodium nitrite was added at 5° 50 ml. of 20% sulfuric acid. The stirring was continued for an additional 15 minutes. The semi-crystalline mass thus formed was mixed with 25 ml. of water to dissolve the inorganic salts, and 30 ml. of ether was added to loosen the crystalline cake. The insoluble α-isomer was separated from the two layers by filtration; yield 2 g., m.p. 100–102°. By quick recrystallization from ethanol, diamond-shaped crystals were obtained melting at 110°, which after resolidification melted at 148–150°.

Anal. Calcd. for $C_{10}H_{16}O_3N_2$: C, 56.60; H, 7.55; N, 13.20. Found: C, 56.9; H, 7.6; N, 13.5.

The ether solution containing the more soluble β-isomer was washed with water and with a sodium bicarbonate solution and the ether was distilled. The crystalline residue was triturated with a few ml. of 30% benzene in pentane and filtered. The β-nitrosite thus isolated weighed 2 g. and melted at 153–155°. Recrystallization from hexane gave silky needles, m.p. 166–167°.

Anal. Calcd. for $C_{10}H_{16}O_3N_2$: C, 56.60; H, 7.55; N, 13.20. Found: C, 57.0; H, 7.56; N, 13.2.

From the mother liquors 0.8 g. of the β-nitrosite was recovered as the β-nitrolpiperide described below.

β-Nitropiperide (VII): N-(2-Isonitroso-3-*p*-menthen-8-yl)-piperidine.—When either α-, m.p. 110°, or β-, m.p. 166–167°, nitrosite (VII) was refluxed for five minutes with twice its weight of piperidine, a heavy oil separated upon addition of water and crystallized upon trituration with ethanol. Recrystallization from ethanol gave long rods, m.p. 166–167°. The crystals readily dissolved in dilute organic and mineral acids and were recovered unchanged upon adding excess of alkali.

Anal. Calcd. for $C_{15}H_{26}ON_2$: C, 72.00; H, 10.40; N, 11.20. Found: C, 72.1; H, 10.3; N, 11.5.

***dl*-Carvenone (IX). A. From β-Nitrosite (VII).**—Zinc dust, 12.5 g., was added at 25° to a solution containing 5 g. of β-nitrosite (VII) in 65 ml. of acetic acid and 5 ml. of water. The reaction mixture was then heated for a half-hour on a steam-bath and the product, after dilution with 250 ml. of water, was steam distilled. The organic layer distilled at 74–76° at 7 mm., $n^{20}D$ 1.4835, yield 2.4 g.

The 2,4-dinitrophenylhydrazone was recrystallized from 80% ethanol as orange red needles, m.p. 167°.

Anal. Calcd. for $C_{16}H_{20}O_4N_4$: N, 16.94. Found: N, 16.8.

The semicarbazone, when recrystallized from 50% ethanol formed plates, m.p. 201–202°. *Anal.* Calcd. for $C_{11}H_{19}ON_3$: N, 20.04. Found: N, 20.4. Neither derivatives gave depression of melting point with samples derived from *dl*-carvenone as described by Bredt.[12]

B. From β-Nitropiperide (VIII).—Two grams of VIII was converted to carvenone according to the procedure described for A; yield 1.3 g., $n^{20}D$ 1.4832. The same 2,4-dinitrophenylhydrazone, m.p. 167°, and semicarbazone, m.p. 201–202°, were obtained.

Ozonolysis.—A solution of 3.8 g. of cut 7 (Table I) in 25 ml. of ethyl chloride was ozonized at −78° and hydrolyzed oxidatively as described,[20] except that no sulfuric acid was added. During the hydrolysis carbon dioxide was evolved continuously and collected in a saturated barium hydroxide solution. White crystals of diacetone peroxide deposited on the neck of the condenser. The reaction mixture was evaporated under vacuum, and the volatile vapors collected in a Dry Ice-acetone cooled trap. About 2.9 g. of viscous, colorless residue remained. This was neutralized with about 20 ml. of 1 *N* sodium hydroxide and evaporated to dryness. The amorphous solid obtained after grinding with ethyl acetate, filtering and washing with ethyl acetate weighed 3.6 g. corresponding to 70% yield of sodium α-methylglutarate. The salt was dissolved in about 13 ml. of 20% sulfuric acid and extracted with ether and ethyl acetate and dried. After removal of the solvent about 1.9 g. of a sirupy product was obtained which solidified upon standing. When spread over porous clay it yielded white crystals melting at 70–72°. Upon recrystallization from a solution of benzene and pentane it melted at 74–76°, no depression with an authentic sample of α-methylglutaric acid.

The Dry Ice trap contained acetone, which was charac-

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(20) A. L. Henne and P. Hill, THIS JOURNAL, **65**, 752 (1943).

terized by its 2,4-dinitrophenylhydrazone, together with about 0.35 g. of acetone peroxide isolated by filtration. The total amount of acetone and its derivatives isolated accounted for about 40% of the theoretical.

3,8(9)-*p*-Menthadiene (IV). Maleic Anhydride Adducts. A. 4,7-Dimethyl-1,2,3,5,6,7,8,9-octahydronaphthalene-1,2-dicarboxylic Acid (XI).—The residue obtained from the steam distillation during the purification of compound III by treatment with maleic anhydride (see above) consisted of about 15 g. of heavy oil which crystallized on standing. The solid thus obtained was dissolved in ether and nearly quantitatively extracted from it with a 10% aqueous potassium hydroxide. Extraction of the acidified aqueous layer with ether and trituration with 40% aqueous acetic acid gave 12 g. of a white crystalline powder, m.p. 170–190°. Recrystallization from 40% aqueous acetic acid gave colorless cubes, m.p. 203–204°.

Anal. Calcd. for $C_{14}H_{20}O_4$: C, 66.66; H, 7.94. Found: C, 66.4; H, 7.82.

The adduct m.p. 203–204° was formed also when both pure 3,8(9)-*p*-menthadiene[21] and a synthetic sample of IV prepared according to Perkin and Wallach[13] were treated with an ether solution of maleic anhydride at reflux.

B. 4,7-Dimethyl-1,2,3,4,6,7,8,9-octahydronaphthalene-1,2-dicarboxylic Acid Anhydride.—Six grams of the dicarboxylic adduct XI was refluxed for 4 hours with 28 ml. of acetic anhydride. The mixture then was distilled until the liquid temperature reached 155–160° and then distilled under vacuum; b.p. 178° at 7 mm., yield 5 g. The resulting oil solidified when treated with pentane and was recrystallized from this solvent by stirring the solution while cooling. The amorphous precipitate melted at 68–69°.

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 71.79; H, 7.60. Found: C, 71.8; H, 7.69.

The anhydride dissolved slowly when treated with a hot solution of 10% potassium hydroxide. The dicarboxylic acid XI was recovered, m.p. 203–204°; no depression with the starting material.

Chromatography of Cut 2 (Table I).—Five ml. of cut 2 dissolved in 10 ml. of *n*-pentane was passed over 25 ml. of 60 to 200 mesh silica gel[22] in a water-jacketed column, 8 mm. i.d., according to the described procedure.[23] Figure 3 shows the eluate reaches a minimum refractive index which corresponded to a maximum optical rotation. The ultraviolet spectra of the successive eluate fractions showed first a continuous decrease with a final disappearance of the 235 mμ peak of IV; second, the appearance at 25% elution proceeding through a maximum, of the 243 mμ peak of III; and third, the appearance at 40% elution of the 273 mμ peak of V. This peak increased in absorbancy consistently to the end of the process. The elution of I and II was followed by observing the optical rotation of the eluate. It proceeded through a maximum at about 38% elution (Fig. 3).

The infrared spectrum of the first few drops of the eluate showed that they consisted of IV, practically free from III.

The estimation of components in each portion of the eluate was determined by means of ultraviolet and infrared spectroscopy and optical rotation as described under "Analytical Procedure."

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[21] Obtained through the courtesy of Hercules Powder Co., Wilmington, Del.

[22] The Davison Chemical Corporation, Baltimore, Maryland.

[23] B. J. Mair and A. F. Forziatti, *J. Research Natl. Bur. Standards*, **32**, 151, 165 (1944).

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Azulene. V. Alkylation Experiments. Chloromercuration[1,2,3]

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The Friedel–Crafts alkylation of azulene has been attempted with a number of reagents and catalysts and under a wide range of conditions. Some evidence for the formation of 1-alkylazulenes was obtained from a number of runs but only two products, a 1-hexylazulene and 1-benzylazulene, were obtained in sufficient yield and purity for analysis. Chloromercuration gives a dichloromercuriazulene in high yield.

Since the theoretical considerations previously discussed[5] had led us to expect that electrophilic substitution would occur predominantly at the 1-position, it was felt that the alkylation of azulene would lead to mono- and (or) dialkyl derivatives which could be readily identified, even if formed in quite low yield, by their characteristic absorption spectra.[6] Consequently some of our earliest experiments on the electrophilic substitution of azulene involved alkylation reactions.

As naphthalene[7] and thiophene,[8] in contrast to benzene, give low yields (5–10%) of alkyl derivatives in the Friedel–Crafts reaction, it was suspected that the yields of alkylazulenes realized might be small but it was hoped that isolation of the products, which would differ in color from azulene, by chromatography would be possible. As the yields, for the most part, proved to be very low (<1%), a large number of trial reactions were run (using *ca.* 5 mg. of azulene) in which the conditions of time and temperature were varied over a wide range and different solvents and catalysts were tried. The following discussion includes only illustrative examples chosen from runs performed on a somewhat larger scale (20–320 mg. of azu-

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[2] From the Ph.D. theses of J. A. Nelson, J. J. Tazuma and E. J. Cowles; supported in part by a grant from the Research Corporation.

[3] Paper IV, A. G. Anderson, Jr., and E. J. Cowles, THIS JOURNAL, **77**, 4617 (1955).

[4] Shell Oil Fellow, 1949–1950.

[5] A. G. Anderson, J. A. Nelson and J. J. Tazuma, THIS JOURNAL, **75**, 4980 (1953).

[6] Pl. A. Plattner and E. Heilbronner, *Helv. Chim. Acta*, **30**, 910, 1320 (1947); **31**, 804 (1948). See also T. Wagner-Jauregg, H. Arnold, F. Hüter and J. Schmidt, *Ber.*, **74B**, 1522 (1941).

[7] F.-K. Tchéow and F. Yung, *Contrib. Inst. Chem., Nat. Acad. Peiping*, **2**, 127, 149 (1936); O. Brunel, *Ber.*, **17**, 1179 (1884); L. Roux, *Ann. chim. phys.*, **12**, 307 (1887); C. Marchetti, *Gazz. chim. ital.*, **11**, 265, 439 (1881).

[8] E. Schleicher, *Ber.*, **19**, 672 (1886); A. Tohl and A. Nalke, *ibid.*, **29**, 2205 (1896).