# **597.** *Dehydrobromination Experiments with Bromodihydromyrcene.*

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The olefinic mixture obtained by thermal decomposition of dihydromyrcene collidinium bromide has been analysed semiquantitatively; it contains about 20% of *allo*ocimene. Geranyl pyridinium bromide similarly yields ocimene and dipentene. Bromodihydromyrcene reacts with alkali to yield almost entirely substitution products. The mechanisms of these reactions are discussed.

*allo*Ocimene is not produced in appreciable yield from bromodihydromyrcene by Dulong, Dulou, and Defay's method (*Bull. Soc. chim.*, 1949, **16**, 310).

Following the classic work of Ziegler and his collaborators (*Annalen*, 1942, **551**, 80), the conversion of mono-olefins into conjugated diolefins by reaction with *N*-bromosuccinimide and subsequent dehydrobromination of the resulting allylic bromides has become a common procedure. The analogous preparation of acyclic conjugated trienes has received scant attention, but their formation from $\gamma$(or $\delta$)-bromo-$\alpha\varepsilon$-dienes would be expected to be facilitated by the complementary activation of the adjacent allylic hydrogen and bromine atoms by separate olefinic centres. The conversion of the long-chain polyisoprene, natural-rubber hydrocarbon, into the corresponding fully conjugated polyene would provide an extreme example of this process. The somewhat anomalous composition of the intermediate bromide (Bloomfield, *J.*, 1944, 114) and the physical nature of the components render this a difficult system for detailed study, and the dehydrobromination of the di-isoprenic derivative, bromodihydromyrcene, has therefore been examined first. The particular advantage, apart from the comparative molecular simplicity, is that the desired dehydro-product is the well-characterized hydrocarbon, *allo*ocimene (I), and any additional or alternative products will also be known monoterpenoid compounds or closely related isomers. On the other hand, a complicating factor arises from the isomeric heterogeneity of the bromide. In the preceding paper, this heterogeneity has been analysed semiquantitatively and it has been shown, consistently with certain theoretical considerations, that approximately 60% of the molecules have undergone substitution at one or other of the central methylene groups, 20% at a methyl group, and the remainder at one of the originally doubled-bonded carbon atoms. Dehydrobromination as envisaged above would thus afford *allo*ocimene to a maximum yield of 60%, but this could be increased by about 15% if isomerization of the 2-bromo-$\Delta^{3:6}$- and 7-bromo-$\Delta^{2:5}$-constituents accompanied their decomposition. Further, if the belief of Ziegler *et al.* (*loc. cit.*) to have synthesized dodeca-1 : 3 : 5-triene from 1 : 4-dibromododeca-2-ene is correct, then more deep-seated rearrangements leading to conjugated-triene formation are evidently possible. However, since all the transformation products which we have obtained from bromodihydromyrcene proved to be mixtures boiling over a wide range, the prevailing tendency seems to be for the isomeric complexity to be increased rather than diminished.

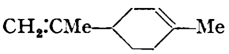
*Description of Experiments.*—Bromine elimination from bromodihydromyrcene occurred on reaction with cold dilute, and with hot concentrated, alcoholic alkali (*i.e.*, under extreme *E*1 and *E*2 conditions; Hughes, Ingold, Masterman, and MacNulty, *J.*, 1940, 899), with aliphatic and aromatic amines, with sodamide in liquid ammonia, and on passage through an alumina column. The latter treatment produced highly complex, partly polymeric mixtures containing a negligible proportion of acyclic conjugated triene (cf. Sutton and Datta, *J.*, 1949, 939). The common characteristic of the other reactions was a marked propensity for substitutive bromine replacement rather than elimination of the elements of hydrogen bromide.

The reactions in alcoholic alkaline media yielded mixtures of the corresponding alcohol and ether, containing only a very small amount of olefin. With sodamide in liquid ammonia bromodihydromyrcene reacted mildly (contrast the behaviour of certain allylic chlorides; Kharasch *et al.*, *J. Amer. Chem. Soc.*, 1939, **61**, 2318; 1940, **62**, 2034; 1943, **65**, 11) to form partly an amine substitution product (cf. geranyl chloride; Kharasch, Nudenberg, and Fields, *ibid.*, 1944, **66**, 1276) and partly an olefinic mixture. The latter contained only about 10% of (I) and about the same proportion of structures such as (II) and (III), possessing acyclic conjugated diene units.

$CMe_2{:}CH{\cdot}CH{:}CH{\cdot}CMe{:}CHMe$ (I.)

$CH_2{:}CMe{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CMe{:}CHMe$ (II.)

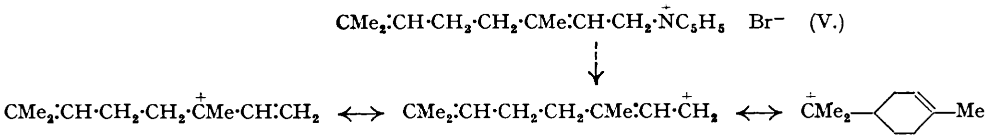
$CMe{:}CH{\cdot}CH_2{\cdot}CH{:}CMe{\cdot}CH{:}CH_2$ (III.)


(IV.)

When the quaternary ammonium salts derived from bromodihydromyrcene were heated to above 100° in the absence of oxygen—preferably in a hydrocarbon solvent—the usual decomposition ensued. The olefinic mixture thus obtained *via* the collidinium salt was examined in some detail. No separation of the constituents could be achieved, either by means of crystalline derivatives or by distillation through the available fractionating columns, but the refractive index and spectroscopic properties specify fairly definitely that the composition is approximately 20% of (I), 40% of (II) and ocimene (III) * in comparable proportions, and 40% of cyclic unconjugated dienes, probably mainly (IV). A similar experiment conducted with the structurally homogeneous geranyl bromide yielded no (I) or (II), but about 60% of (III) and 40% of (IV).

After completion of the above work, Dulong, Dulou, and Defay (*Bull. Soc. chim.*, 1949, **16**, 310) reported the preparation of bromodihydromyrcene by the addition of *N*-bromosuccinimide to the olefin dissolved in acetic acid at 15—20°, its hydrolysis in aqueous acetone containing calcium carbonate, and the dehydration of the resulting carbinol (not isolated or characterized) to *allo*ocimene. This triene was stated to be identified by its Raman spectrum; no reference was made to its refractive index ($n_D^{20}$ 1·5446) or ultra-violet absorption spectrum, or even its boiling point, nor were its Diels–Alder adducts prepared. We have confirmed the remarkable ease of allylic bromination under the conditions described, but the overall reaction is evidently more complex than indicated since bromodihydromyrcene is accompanied by an additive bromoacetoxy-derivative (cf. Backer, Stevens, and Dosi, *Rec. Trav. chim.*, 1948, **67**, 451). The claim to have synthesized *allo*ocimene, however, could not be substantiated. The paper of Dulong *et al.* is lacking in precise experimental details, but we have sought to repeat their work, using several possible modifications, and have failed to obtain analytically pure specimens of the intermediate carbinol or of its dehydration product. The refractive index of the latter was always less than 1·475 (at 20°), and the negligible *allo*ocimene content thus indicated was confirmed by spectroscopic examination. In view of the dehydrobromination results, this finding is not surprising because the carbinol will be of even greater isomeric complexity than the parent bromide because of the typical $S_N1$ hydrolysis procedure employed (Catchpole, Hughes, and Ingold, *J.*, 1948, 8).

*Discussion.*—The course of the quaternary-salt decomposition may be considered first for the simpler case of the pyridinium bromide derived from the structurally homogeneous geranyl bromide (V). It follows from the work of Hughes, Ingold, and Patel (*J.*, 1933, 526) on saturated 2-*p*-nitrophenylethyltrimethylammonium halides and hydroxides that in the case of weakly basic anions such as bromide, unimolecular ionic decomposition (*E*1) of the ammonium cation is the most likely process provided that the resulting carbonium cation is relatively stable: such stabilization certainly characterises the cation (VI) owing to resonance with the structures (VII) and (VIII). The actual products obtained, *viz.* (III) and (IV), are those to be expected to result from the subsequent loss of a proton from (VII) and (VIII), respectively, so that the


(V.)

(VII.) (VI.) (VIII.)

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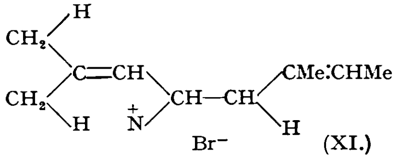
* Ocimene is sometimes formulated as the $\Delta^{1:5:7}$-isomer (Simonsen and Owen, "The Terpenes," Cambridge, 1947, p. 19), but the identity of its dihydro-derivative with that derived from myrcene, and recent physical evidence demonstrating the rarity of *iso*propenyl end-groups in natural acyclic monoterpenes seem to favour (III) almost decisively.

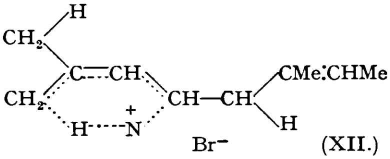
simple mechanism here outlined appears sufficient to account for the composition of the product. Bide, Henbest, Jones, Peevers, and Wilkinson (*ibid.*, 1948, 1783) similarly found that the *E*1 hypothesis afforded a satisfactory explanation of the isomeric products furnished by the allylic 7-bromo-compounds of certain esters of cholesterol. It should be pointed out that ionic (*trans*) *E*2 elimination (initiated by the weakly basic free bromide anion attacking a labile hydrogen) is in any case unlikely to occur in our own experiments on bromodihydromyrcene which were conducted in a non-ionizing medium in the presence of a hydrocarbon diluent.

Consideration of the decomposition product furnished by the quaternary salt derived from bromodihydromyrcene reveals that the unimolecular ionic-elimination mechanism no longer suffices to give a satisfactory account of the proportions of the various hydrocarbon isomers formed. In particular, it is difficult to explain the high yield of unconjugated cyclic diene, and to reconcile the low yield (*ca.* 20%) of *allo*ocimene (I) with the known high proportion (*ca.* 60%) of starting material substituted at one or other of the two central methylene groups of dihydromyrcene (cf. preceding paper). Thus, the carbonium cation (IX) derived from 4-bromodihydromyrcene would be expected to become most easily stabilized by loss of a proton to give the fully conjugated triene (I), rather than undergo the alternative stabilization provided for by the *E*1 process, *viz.* formation of the less highly conjugated (II) *via* the mesomeric form of the ion (X). The difficulty may be overcome if the possibility of a non-ionic intramolecular elimination process is envisaged (cf. Barton, *ibid.*, 1949, 2174). When the 4-substituted ammonium salt is written in the sterically plausible configuration (XI), it is seen that any incipient ionization to give the ion (X) may be powerfully assisted by the incipient proton being situated in close spatial proximity to the free base which is being liberated at the same time. In other words, a low-energy non-ionic cyclic transition state (XII) is possible, leading to the formation of conjugated diene (II) rather than the expected conjugated triene for whose formation no such favourable transition state exists. Direct intramolecular attack on a $C_5$ hydrogen by the bromide ion is not plausible since the negative charge will be strongly held by the neighbouring positive ammonium pole, and since in any case *E*2 eliminations are generally supposed to proceed in the *trans*-configuration only (cf. Hughes, Ingold, *et al.*, *ibid.*, 1948, 2093). Analogous intramolecular transformation through a cyclic transition state may be realised by the quaternary salt of dihydromyrcene substituted at $C_5$, leading to the conjugated diene (III). The unexpectedly low yield of the desired conjugated triene (I) may thus be understood.

$CMe_2{:}CH{\cdot}\overset{+}{C}H{\cdot}CH_2{\cdot}CMe{:}CHMe$ (IX.) $\overset{+}{C}Me_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CMe{:}CHMe$ (X.)

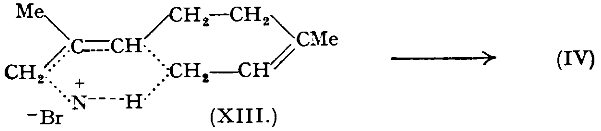


(XI.)



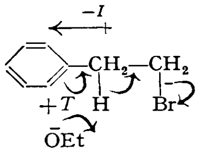
(XII.)

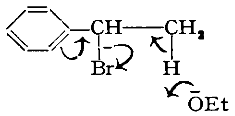
The apparent formation of about 40% of unconjugated cyclic diene, presumably in the main dipentene (IV), is more difficult to explain. The *E*1 mechanism is clearly insufficient since only that proportion of bromodihydromyrcene substituted at $C_{(8)}$, *i.e.* the geranyl form (V), could furnish dipentene by this process. Possibly, the compounds substituted at $C_{(1)}$ and $C_{(2)}$ can decompose through an intramolecular cyclic transition complex such as (XIII).



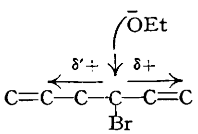
(XIII.)

In the case of the other decomposition reactions which we have studied, the almost exclusively substitutional behaviour of the bromide towards hydroxylic solvents and ethoxide ions seems remarkable. This is especially so in view of the conclusion, evident from an exceedingly comprehensive study of hydrogen halide elimination from saturated alkyl and aralphyl halides under comparable conditions, that the formation of the double bond is strongly facilitated by unsaturated substituents at its ends (Hughes, Ingold, *et al.*, *loc. cit.*). Thus 2-phenylethyl bromide reacts some ten times faster than *n*-propyl bromide with alcoholic sodium ethoxide at 55° and the proportion of the decomposition yielding styrene is about ten times that yielding propene. A bromodihydromyrcene isomer produced by bromine substitution at one of the central methylene groups may be considered as a composite 1- and 2-ethenyl substituted ethyl bromide. Now, in the analogous phenyl compounds (no ethenyl compounds were examined), the ease of the elimination reaction when the substituent is in the 2- rather than the 1-position is attributed to the inductive electron-attraction and the mesomeric electron-release powers of the substituent both being exerted favourably from the 2-position (the $-I$ effect aiding the removal of the relevant hydrogen atom by the nucleophilic reagent, the $+T$ effect aiding the formation of the double bond as a consequence of the development of conjugation), but only the second of these is exerted effectively from the 1-position :





However, it is well known that a substantial fraction of an inductive electronic displacement is transmitted through one carbon atom, and hence in an α-bromo-αβ-diethenyl structure the dual activation of the α-carbon in this way will enhance its electropositive character and thus increase its susceptibility to nucleophilic attack (inset). The present findings suggest that such activation actually predominates over the alternative modes. This behaviour is expected to be more markedly developed in ethenyl than in phenyl derivatives, since the former groups exhibit less extensive electromeric polarizability than the latter, but are similar in their $-I$ character.



## EXPERIMENTAL.

Except where stated otherwise, bromodihydromyrcene was prepared as described in the preceding paper and had b. p. 35—40°/0·01 mm.

*Dehydrobromination of Geranyl Bromide.*—A mixture of geranyl bromide (10 ml.) and redistilled pyridine (20 ml.) was degassed, sealed under vacuum in a glass bulb, and heated at 140° for 0·5 hour. After cooling, the mixture was poured into water and extracted with ether. The product consisted of two fractions : (*a*) (1 g.) b. p. 58—62°/14 mm., $n_D^{18}$ 1·4785 (Found : C, 88·0 ; H, 11·8. Calc. for $C_{10}H_{16}$ : C, 88·2 ; H, 11·8%) ; (*b*) (1·5 g.) b. p. 110—114°/14 mm., $n_D^{18}$ 1·4748 (Found : C, 78·4 ; H, 11·9. Calc. for $C_{10}H_{18}O$ : C, 78·0 ; H, 11·8%). The latter is apparently a primary alcohol, not geraniol but possibly a *cyclo*geraniol, whose origin has not been investigated. Fraction (*a*) possesses a single, strong ultra-violet absorption band at 2280 A. (ε = 14,700), indicating the presence of about 60% of an acyclic conjugated 1 : 2- and/or 1 : 3-diakylbutadiene chromophore (Booker, Evans, and Gillam, *J.*, 1940, 1453 ; " American Petroleum Institute, Research Project 44, Ultra-violet Absorption Spectrogram," No. 67). The infra-red spectrum (fig., *A*) exhibits characteristic olefinic absorption at 890—910 and at 990 cm.$^{-1}$, but no bands near 965 or 700 cm.$^{-1}$, so that the butadiene chromophore cannot be 1 : 3-substituted but must be the 1 : 2-substituted compound (III). The remaining ultra-violet-transparent 40% of this fraction is assumed to be mainly dipentene, in agreement with the strong absorptions at 890 and 800 cm.$^{-1}$ (cf. A.P.I., *loc. cit.*, Infra-red Absorption Spectrogram, No. 563).

*Reaction of Bromodihydromyrcene with Collidine.*—The addition of *s*-collidine (54 ml.) to bromodihydromyrcene (18 g.) in *cyclo*hexane (54 ml.) resulted in the precipitation of the water-insoluble collidinium salt. When the mixture was heated in an evacuated sealed tube at 140° for 1 hour, water-soluble collidine hydrobromide was precipitated. This was filtered off and washed several times with *cyclo*hexane (200 ml. in all). The filtrate and washings were extracted twice with 3N-sulphuric acid, washed with water, and dried, and the solvent evaporated. The residue was distilled from sodium ; the distillate (6·5 g. ; 58%) had b. p. 59—77°/13 mm., $n_D^{20}$ 1·490 [Found : C, 88·0 ; H, 11·8% ; ╒ (by micro-hydrogenation), 2·58. Calc. for $C_{10}H_{16}$ : C, 88·2 ; H, 11·8%].

This mixture could not be resolved either chemically or by the available physical techniques, but analysis of the main constituents is possible as follows : The origin and elementary analysis of the mixture specify its constituents as acyclic trienes having at least two of the double bonds conjugated, or cyclic structures containing two double bonds. Quantitative hydrogenation shows both these types to be present in the proportion 58 : 42, respectively.* The ultra-violet absorption spectrum has two bands, $\lambda_{max.}$, 2280 A. (ε = 10,000) and 2730 A. (ε = 7,500), which signify respectively the presence of 40% of an acyclic conjugated 1 : 3- (II) and/or 1 : 2-dialkylbutadiene (III) chromophore (see above), and 20% of acyclic conjugated triene, *i.e. allo*ocimene (I) (*not* a substituted *cyclo*hexa-1 : 3-diene such as a pyronene which would absorb at 2630 A. ; comparative ultra-violet data privately communicated by Dr. L. A.

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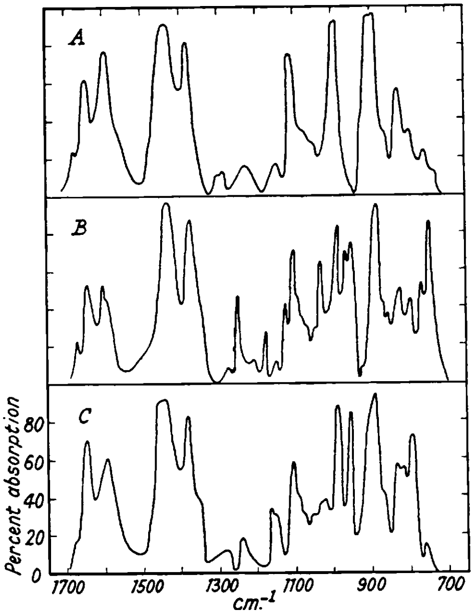
* Bromine absorptions were : hydrocarbon from geranyl bromide, 2·04 ; hydrocarbon from bromodihydromyrcene, 2·00 ; synthetic mixture (p. 3055), 2·08 ; dipentene, 2·00 ; *allo*ocimene, 2·26 g.-mol./g.-mol. α-Pyronene differed from the above in evolving hydrogen bromide, and consistent results were not obtained.

Goldblatt). These compounds account for the triene constituents; appreciable cyclic conjugated diene is judged to be absent from the absence of further selective absorption regions in the ultra-violet and also from the absence of infra-red absorption near 720 cm.$^{-1}$ (fig., *B*) which would be expected to occur in the presence of an unsubstituted double bond in a *cyclo*hexene ring (*e.g.* a pyronene) (cf. also footnote p. 3054). The remaining 40% of the hydrocarbon mixture must therefore consist essentially of a non-conjugated cyclic diene, presumably dipentene (IV). These conclusions are supported by the satisfactory overall similarity of the ultra-violet [$\lambda_{max.}$ 2290 A. $\varepsilon$ = 9500) and 2750 A. ($\varepsilon$ = 8000)] and infra-red (fig., *C*) spectra of a " synthetic " hydrocarbon mixture ($n_{D}^{17}$ 1·492) (made by adding one part by volume each of authentic *allo*ocimene and dipentene to three parts of the above described hydrocarbon from geranyl bromide) to the corresponding spectra of the product under discussion. The most significant differences are the two extra bands at 968 and 745 cm.$^{-1}$ found in the hydrocarbon from bromodihydromyrcene (fig., *B*). The former is undoubtedly associated with the *trans*-CHR:CHR group of the 1 : 3-dialkylbutadiene (II), the same group absorbing at 950 cm.$^{-1}$ in *allo*ocimene (I) (fig., *C*). The similar intensites of the 968 and 950 cm.$^{-1}$ absorptions in curve *C* suggest that the proportion of (II) in the mixture may be comparable to that of (I) (*i.e.* 20%), so that the total conjugated diene (40% from the ultra-violet spectra) appears to contain comparable amounts of (II) and (III). The origin of the strong band at 745 cm.$^{-1}$ is obscure.



*A*, *Hydrocarbon from geranyl bromide.*
*B*, *Hydrocarbon from bromodihydromyrcene.*
*C*, *Synthetic hydrocarbon mixture* (*cf. Experimental*).

*Reaction of Bromodihydromyrcene with Other Amines.*—The bromide reacted rapidly with pyridine, quinoline, or triethylamine in dry ether at room temperature, the quaternary salts (oils from the aromatic amines, a solid from the aliphatic) separating within a few minutes.

*Reaction of Bromodihydromyrcene with Sodamide in Liquid Ammonia.*—To a solution of the bromide (30 g.) in liquid ammonia cooled to −40°, sodamide (6 g.) was added with vigorous stirring. No noticeable reaction occurred. The cooling bath was removed, the stirring continued for two hours, and the solution then kept for a further five hours. Ethanol (100 ml.) and water (750 ml.) were added successively and the product extracted with light petroleum (b. p. 60—80°). The extract was washed three times with dilute hydrochloric acid, then worked up in the usual way, and the product distilled from sodium : (*a*) (3 g.), b. p. 58—63°/12 mm., $n_{D}^{20}$ 1·465, $\lambda_{max.}$ 2280 A. ($\varepsilon$ = 1770), 2730 A. ($\varepsilon$ = 4850) (Found : C, 87·1; H, 12·9%); (*b*) (0·5 g.), b. p. 63—76°/12 mm., (*c*) b. p. 76—81°/12 mm., $n_{D}^{20}$ 1·529 (Found : C, 84·5; H, 11·6%). The acid washings yielded *aminodihydromyrcene* (3·5 g.), b. p. 93—96°/12 mm., $n_{D}^{20}$ 1·4769 (Found : C, 78·0; H, 12·4; N, 9·5. $C_{10}H_{19}N$ requires C, 78·4; H, 12·5; N, 9·1%), which reacted rapidly with atmospheric carbon dioxide.

*Reaction of Bromodihydromyrcene with Hot Concentrated Alcoholic Sodium Hydroxide.*—The bromide (8 ml.) was added dropwise during 2·5 hours to a boiling solution of sodium hydroxide (10 g.) in ethanol (90 ml.) and water (10 ml.). After removal of most of the alcohol by distillation, the residue was diluted with water and extracted with ether. The product thus isolated consisted of : (*a*) (0·5 g.), b. p. 70—80°/14 mm. (Found : C, 85·0; H, 12·3. Calc. for 65% of $C_{10}H_{16}$ + 35% of $C_{12}H_{22}O$ : C, 85·0; H, 11·9%); (*b*) (0·5 g.), b. p. 80—90°/14 mm. (Found : C, 81·3; H, 12·5. Calc. for 24% of $C_{10}H_{16}$ + 76% of $C_{12}H_{22}O$ : C, 81·4; H, 12·0%); (*c*) *ethoxydihydromyrcene* (2·5 g.), b. p. 90—95°/14 mm. (Found : C, 79·2; H, 12·3. $C_{12}H_{22}O$ requires C, 79·2; H, 12·1%); (*d*) *hydroxydihydromyrcene* (3 ml.), b. p. 95—102°/14 mm. (Found : C, 77·3; H, 11·9. $C_{10}H_{18}O$ requires C, 77·9; H, 11·7%). The analytical data indicate that the proportion of olefin in the total product is *ca.* 7%.

*Reaction of Bromodihydromyrcene with Cold Dilute Aqueous Alcoholic Potassium Hydroxide.*—The bromide (3·1 g.), ethanol (40 ml.), water (10 ml.), and potassium hydroxide (0·8 g.) were left at room temperature for 9 days. After dilution with water, the mixture was extracted with ether, and the recovered product fractionated : (*a*) (0·5 g.), b. p. 83—90°/12 mm., $n_{D}^{18}$ 7·467 (Found : C, 76·9; H, 11·4; Br, 4·6%); (*b*) (0·8 g.), b. p. 90—95°/12 mm., $n_{D}^{18}$ 1·468 (Found : Br, 7·4%); (*c*) (0·8 g.), b. p. 95—97°/12 mm., $n_{D}^{18}$ 1·470 (Found : Br, 9·1%). The analytical figures show that (3·1 − 0·43) g. of bromide had decomposed and that not more than 0·1 g. of olefin was present in the product.

*Reaction of Dihydromyrcene with* N-*Bromosuccinimide in Acetic Acid.*—*N*-Bromosuccinimide (17·8 g., 0·1 g.-mol.) (see *J.*, 1950, 939) was added during 15 minutes to the olefin (13·8 g., 0·1 g.-mol.) in acetic acid (100 g.) at 15—20° (Dulong, Dulou, and Defay, *loc. cit.*). The product was isolated by dilution of the solution with water and extraction with ether. Fractionation gave : (*a*) (6 g.), b. p. 45—56°/0·04 mm., $n_{D}^{20}$ 1·495 (Found : C, 55·9; H, 8·1; Br, 35·9. Calc. for $C_{10}H_{17}Br$ : C, 55·3; H, 7·9; Br, 36·8%); (*b*) (6 g.), b. p. 56—74°/0·04 mm., $n_{D}^{20}$ 1·488; (*c*) (5 g.), b. p. 74—77°/ 0·04 mm., $n_{D}^{20}$ 1·481. The infra-red spectrum of fraction (*a*) was similar to those of specimens of bromodihydromyrcene prepared otherwise (p. 3049). Redistillation of (*c*) gave : ($c_1$) (2 g.), b. p. 48—60°/0·03 mm., $n_{D}^{19}$ 1·484; ($c_2$) (3 g.), b. p. 60—62°/0·03 mm., $n_{D}^{19}$ 1·478 (Found : C, 51·5; H, 7·8; Br, 29·6. $C_{12}H_{21}O_2Br$ requires C, 52·0; H, 7·6; Br, 28·9%). Strong infra-red absorption at 1245 cm.$^{-1}$ confirms the presence of an acetate group (absorption at 1720 cm.$^{-1}$ and absorption at 1370 cm.$^{-1}$ additional to that observed in bromodihydromyrcene reveals the component carbonyl and methyl groups, respectively); non-selective ultra-violet absorption at 2350 A. is about 15 times less than that of bromodihydromyrcene, but about twice as strong as that of one $CR_2{=}CHR$ group, thus indicating the absence of allylic bromide and the presence of an additional weakly absorbing group (*e.g.*, $CO_2Me$).

*Hydrolysis of Bromodihydromyrcene in Aqueous Acetone, and Dehydration of the Resulting Product.*—(i) The bromide [as fraction (*a*) above; 6 g.], acetone (40 ml.), water (80 ml.), and powdered calcium carbonate (10 g.) were heated at 100° for 7 hours. The product was separated into: (*a*) (7·3 ml.), b. p. 60—130°/12 mm., $n_D^{20}$ 1·474 (Found: C, 68·6; H, 10·5. Calc. for $C_{10}H_{18}O$: C, 77·9; H, 11·7%); (*b*) (2 ml.), b. p. 130—134°/12 mm., $n_D^{20}$ 1·461. On being boiled with 10% aqueous oxalic acid (20 ml.) for 4 hours, (*a*) yielded a product, b. p. 63—67°/14 mm., $n_D^{18}$ 1·459; and a combined sample of (*a*) and (*b*) gave a more complex mixture, b. p. 61—88°/13 mm., $n_D^{15}$ 1·474. In other experiments, one half of the crude alcoholic product obtained from the hydrolysis of the bromide was heated under reflux with 10% aqueous oxalic acid solution (25 ml.) for 5 hours, the other half was heated with anhydrous oxalic acid at 130° for 2·5 hours. The respective products had b. p. 54—60°/13 mm., $n_D^{20}$ 1·458 (Found: C, 84·6; H, 12·6%); and b. p. 60—71°/13 mm., $n_D^{20}$ 1·457 (Found: C, 84·4; H, 12·8%). Infra-red spectra showed the absence of *trans*-CHR:CHR grouping in both these liquids, and only the former displayed ultra-violet absorption at 2750 A. ($\varepsilon$ = 800, if substance is $C_{10}H_{16}$).

*Hydroxydihydromyrcene.*—This carbinol, previously isolated from the reaction of the bromide with hot concentrated aqueous-alcoholic alkali, and also considered by Dulong *et al.* (*loc. cit.*) to result from the hydrolysis procedure described immediately above, is readily prepared *via* the corresponding acetoxy-derivative. Silver acetate (28 g.) was added with vigorous stirring to bromodihydromyrcene (26 g.) in benzene (150 ml.). When the exothermic reaction had subsided, the mixture was heated under reflux for 12 hours, more silver acetate (14 g.) being added after 6 hours. The benzene solution yielded *acetoxydihydromyrcene* (9 g.), b. p. 100—112°/11 mm. [Found: C, 73·4; H, 10·1%; ╒ (microhydrogenation), 2·03. $C_{12}H_{20}O_2$ requires C, 73·5; H, 10·2%; ╒, 2·00]. Saponification of this ester with potassium hydroxide (6 g.) in ethanol (30 ml.) at room temperature for 24 hours gave *hydroxydihydromyrcene* (4 g.), b. p. 94—106°/11 mm. [Found: C, 77·4; H, 11·8; active hydrogen (Zerewitinoff), 0·649%; ╒ (microhydrogenation), 2·06. $C_{10}H_{18}O$ requires C, 77·9; H, 11·7; active hydrogen, 0·650%; ╒, 2·00]. Light absorption in ethanol: $\lambda_{max.}$ 2350 A., $\varepsilon$ = 950.

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