596. *An Analysis of the Isomeric Composition of Bromodihydromyrcene.**

By L. Bateman, J. I. Cunneen, and H. P. Koch.

2 : 6-Dimethylocta-2 : 6-diene with *N*-bromosuccinimide yields a complex mixture of isomeric allylic bromides, $C_{10}H_{17}Br$, which has been analysed semi-quantitatively, largely with the aid of infra-red spectroscopy. The results accord with a theoretical analysis based on known differences in (*a*) the ease of removal of non-equivalent allylic hydrogen atoms, and (*b*) the equilibrium distribution of labile atoms in different allylic groupings.

The infra-red absorption spectra of the bromide and certain derivatives are described. They indicate that some of the usual frequencies characteristic of the substitutional environment of double bonds in hydrocarbons are displaced in these allylic systems.

The results of some dehydrobromination experiments (see following paper) prompted the investigation of the nature of the bromide obtained by the reaction of dihydromyrcene with *N*-bromosuccinimide (Bloomfield, *J.*, 1944, 114). Recent theoretical advances in olefinic chemistry, as well as experimental findings on the composition of similarly prepared allylic bromides (Bateman, Cunneen, Fabian, and Koch, *J.*, 1950, 936; cf. *Nature*, 1949, **164**, 242; Bateman and Cunneen, *J.*, 1950, 941), make it virtually certain that a highly heterogeneous product would result. We have attempted to interpret the isomer complexity in the light of certain theoretical principles and by systematic infra-red absorption studies.

$$CH_2R^1\cdot C(CH_2R^{2'}){:}CR^3\cdot CHR^4\cdot CHR^5\cdot C(CH_2R^{6'}){:}CH^7\cdot CH_2R^8$$
(I.)

$$CH_2R^1\cdot C(CH_2R^{2'}){:}CR^3\cdot CHR^4\cdot CH^5{:}C(CH_2R^{6'})\cdot CHR^7\cdot CH_2R^8$$
(II.)

Dihydromyrcene (I; $R^1 = R^{2'} = \ldots = R^8 = H$) possesses five non-equivalent allylic carbon atoms [1(= 2′), 4, 5, 6′, and 8] as sites for substitutional bromination; in addition, allylic rearrangement in compounds originally substituted at 1 or 2′, 4, 5 or 6′, and 8 can effect

---

* For descriptive convenience, dihydromyrcene refers throughout this and the following paper to pure 2 : 6-dimethylocta-2 : 6-diene.

substitution at 3, 2, 7, and 6, respectively. A product mixture of all the ten possible monobromo-isomers is therefore possible. Detailed analysis of such a system is impracticable, but location of the main substitutional centres would provide useful information and it is in this sense that the problem has been tackled.

The composition of the isolated product is governed by (i) the relative extent of substitution in the several allylic units, and (ii) the equilibrium distribution of the bromine atom within each unit. Concerning (i), it is well-known that methyl groups are brominated far less readily than methylene groups (Ziegler, Späth, Schaaf, Schumann, and Winkelmann, *Annalen*, 1942, **551**, 80), so that reaction with simple olefins is largely confined to the latter groups provided excess of *N*-bromosuccinimide is avoided. Assuming that the reaction proceeds by a mechanism in which the detachment of the hydrogen atom is a rate-determining step (see Bateman and Cunneen, *loc. cit.*), this effect may be discussed quantitatively. Bolland (*Trans. Faraday Soc.*, 1950, **46**, 358) has shown recently that the relative ease of extraction of hydrogen atoms by peroxide radicals from positions (*a*), (*b*), and (*c*) in the unit $\underset{(b)}{CH_2}R\cdot\underset{(d)}{C}(CH_3){:}\underset{(a)}{CH}\cdot\underset{(c)}{CH_2}R$ is $1 : 3{\cdot}3 : 3{\cdot}3^2$ (at 45°).* Comparable relative efficiency will undoubtedly be a characteristic of other similar reactions, and hence the various allylic groups in dihydromyrcene will be substituted proportionately thus: C_1–C_2–C_3, 1; $C_{2'}$–C_2–C_3, 1; C_2–C_3–C_4, 10; C_5–C_6–C_7, 3; $C_{6'}$–C_6–C_7, 1; C_6–C_7–C_8, 1. The knowledge required for assessing the effect of factor (ii) above is as follows. The equilibrium proportions of isomers in primary–secondary and primary–tertiary allylic systems are 85 : 15 (at 100°) (Young, Richards, and Azorlosa, *J. Amer. Chem. Soc.*, 1939, **61**, 3070) and *ca.* 99 : 1 (Catchpole, Hughes, and Ingold, *J.*, 1948, 8; note also the composition of geranyl bromide, p. 3050), respectively. Accurate studies of secondary–tertiary systems are lacking, but theory suggests close similarity with the primary–secondary relationship (Catchpole *et. al., loc. cit.*), and the isomeric composition of the bromo-olefin obtained from 2-methylpent-2-ene and *N*-bromosuccinimide supports this. Since the reaction now considered was carried out at *ca.* 80°, and distillation at a lower temperature, the secondary–tertiary and primary–secondary ratios can be taken with good approximation as 90 : 10. The bromine distribution calculated from the above data is given in Table I. Despite the evident complexity of the product, resolution in terms of the substitutional distinctions listed in column 5 should be possible if spectroscopic methods of structure analysis of the bromide, and of derivatives of known related structures, are sufficiently informative. This condition proved to be partly satisfied: the considerable molecular complexity and the disturbing influence of the allylic substituent (particularly bromine) made the interpretation of the infra-red spectra less decisive than in earlier work on simpler systems (Bateman, Cunneen, Fabian, and Koch; Bateman and Cunneen, *locc. cit.*) and severely limited the accuracy of estimating the constituent olefinic groupings. Since such estimates must be obtained, not by the precise procedure of comparing the relevant group absorption with that observed in the pure components of the mixture, but by comparison with related molecules containing similar groupings, the analyses can only be semi-quantitative and will almost invariably be too high because skeletal absorption tends to augment the characteristic group absorption by a fractional, but indeterminable, amount. For example, the number of $CR_2{:}CHR$ groups in the heterogeneous methoxydihydromyrcene actually appears greater (by about 25%) than in the isomeric, but homogeneous, geranyl methyl ether (I; $R^1 = R^{2'} = \ldots R^7 = H$; $R^8 = OMe$) as judged by the relative absorption intensity at 830 cm.$^{-1}$. In view of this trend, more significance should be attached to our relative estimates of the various groupings than to their absolute values.

Ziegler bromination of dihydromyrcene proceeds readily in boiling carbon tetrachloride containing a little benzoyl peroxide † and yields a monobromide, $C_{10}H_{17}Br$, which boils over a range of about 5° and exhibits a related refractivity variation. Close-boiling fractions of different refractive index possess almost identical infra-red spectra, which are similar to, but easily distinguishable from that of geranyl bromide. The characteristic infra-red frequencies of differently substituted $C{:}C$-units are partly displaced from their normal values in hydrocarbons (cf. arnard, Bateman, Harding, Koch, Sheppard, and Sutherland, *J.*, 1950, 915), but bands at 820 and 1655, at 905, and at 963 cm.$^{-1}$ probably reflect the presence of $CR_2{:}CHR$, $CHR(Br)\cdot CR{:}CH_2$, and $CHR{:}CHR$ groups, respectively (cf. Experimental). Further bromination produces considerable tar and a very unstable allylic dibromide which in contrast

---

* The difference between (*b*) and (*c*), as well as the fact that reactivity at (*c*) is influenced by alkyl substitution at (*d*) whereas (*b*) is not (Bolland, *loc. cit.*), may be attributed to hyperconjugation of the methyl group and the double bond being conjugated with (*c*) but cross-conjugated with (*b*).

† An even easier, but more complex, reaction in acetic acid is referred to in the following paper.

to its homologue prepared from the unsubstituted 1 : 5-diene, diallyl (Bateman, Cunneen, Fabian, and Koch, *loc. cit.*), contains no conjugated-diene units. Although this feature gives only restricted information about the substitution process since the more labile dibromide isomers probably disappear in reactions leading to the tar formation, it suggests only a small αδ-diene content for the monobromide.

TABLE I.

Theoretical distribution of the substituted bromine atom in bromodihydromyrcene.

Allylic unit.	Relative extent of substitution, %.	Carbon atom.	Relative extent of substitution, %.	Substitutional type.	Relative extent of substitution, %.
C_1–C_2–C_3	6	C_1	5·4		
		C_3	0·6		
$C_{2'}$–C_2–C_3	6	C_3	0·6		
		$C_{2'}$	5·4	*A*. Peripherally at C_1, $C_{2'}$, $C_{6'}$ and C_8	22
C_2–C_3–C_4	59	C_2	5·9		
		C_4	53·1	*B*. Centrally at C_4 and C_5	62
C_5–C_6–C_7	17	C_5	8·5	*C*. At C_3 and C_7 with formation of $CH_2{:}CR_2$ units	2
		C_7	8·5		
$C_{6'}$–C_6–C_7	6	C_7	0·6	*D*. At C_2 and C_7 with formation of αδ-dienes (as, *e.g.*, II)	14
		$C_{6'}$	5·4		
C_6–C_7–C_8	6	C_6	0		
		C_8	6·0		

The infra-red spectrum of the structurally identical methoxy-analogue, obtained by the reaction of the monobromide with a hot concentrated solution of sodium methoxide in methyl alcohol (Roberts, Young, and Winstein, *J. Amer. Chem. Soc.*, 1942, **64**, 2157; Young and Andrews, *ibid.*, 1944, **66**, 421; Catchpole and Hughes, *J.*, 1948, 4), is more readily interpreted than that of the bromide, but is again not entirely unambiguous. The grouping $CR_2{:}CHR$, common to the substitutional types *A*, *B*, and in part *D* (substitution at C_7 in C_5–C_6–C_7, *vide* Table I), is definitely identified by strong absorption at 827 cm.$^{-1}$ accompanied by a weaker band at 1670 cm.$^{-1}$; comparison with geranyl methyl ether (I; $R^1 = R^{2'} = \ldots$; $R^7 = H$ $R^8 = OMe$) indicates a relative proportion of *ca.* 125% (see p. 3046). Bands at 963 and at 1645 and 900 cm.$^{-1}$ are indicative of much smaller amounts of *trans*-$CHR{:}CHR$ groups (*ca.* 5%) (resulting from substitution at C_2 in C_2–C_3–C_4) and $CHR(OMe){\cdot}CR{:}CH_2$ groups ($<5\%$) (*i.e.*, substitutional type *C*), respectively. Consistency with the theoretical picture is evident. Certain minor anomalies, however, appear in the ultra-violet spectrum, which reveals absorptions corresponding to conjugated acyclic diene (*ca.* 7%) and triene (*ca.* 3%) groups. The origin of the latter is uncertain. The former undoubtedly result from partial isomerisation of αδ-diene structures under the alkaline conditions of preparation; further treatment with hot alkali increases their concentration to *ca.* 10%. Significantly, the corresponding methyl derivative (see below) contains no conjugated diene units, but on treatment with alkali these are produced, also to the extent of *ca.* 10%. In model experiments, which will be reported later in a wider connection, we have found that an ααεε-tetra-alkyl-αδ-diene undergoes conjugative isomerisation under such conditions only to the extent of about 40%, whereas for an αε-dialkyl system the extent is about 80%. Accordingly, the degree of conjugation attained in the present experiments denotes an original αδ-diene content of 25 or 12·5%, depending on the prevailing alkyl substitution. The proportion of type-*D* products given in Table I is derived on the basis that the di- and tetra-substituted units are formed in the ratio of 5·9 : 8·5; on the same basis, the experimental figure is 18%.

The possibility that a purely hydrocarbon derivative might facilitate the spectroscopic analysis suggested the examination of methyldihydromyrcene,* which is prepared in high yield by condensing the parent bromide with methylmagnesium iodide. This type of reaction has been shown previously to cause no appreciable change in the composition of an isomeric allylic bromide mixture (Bateman and Cunneen, *loc. cit.*). Actually no marked advantage was realised as confusing skeletal absorption still persisted in the infra-red spectrum, but the structural deductions derived from the methoxy-derivative could be fully substantiated. Strong absorption at 820 cm.$^{-1}$ (as well as at 1670 cm.$^{-1}$) identified the main unsaturation pattern as $CR_2{:}CHR$; weaker absorption at 887 and 1645 cm.$^{-1}$ revealed a much smaller proportion of

---

* This and similar designations denote the isolated *substitution* products.

$CR_2{:}CH_2$ groups. Less than 5% of $CHR{:}CHR$ groups (as judged by adsorption at 965 cm.$^{-1}$) were present, a finding correlative with the absence of conjugated diene as shown by ultra-violet absorption (cf. methoxydihydromyrcene).

In principle, the extent of peripheral bromine substitution (type *A* in Table I) may be estimated by making use of the structural feature of reactions between allylic magnesium halides and carbonyl compounds that substitution occurs exclusively at the more alkylated carbon atom of the allylic unit (Roberts and Young, *J. Amer. Chem. Soc.*, 1945, **67**, 148, 319; Young and Roberts, *ibid.*, 1946, **68**, 1472). For example, the Grignard derivative of geranyl bromide (I; $R^1 = R^{2'} = \ldots R^7 = H$; $R^8 = Br$) and carbon dioxide yield *iso*homogeranic acid (III; $X = CO_2H$). Bromine replacement thus generates an equivalent number of $CHR{:}CH_2$ and (or) $CR_2{:}CH_2$ groups, which are conveniently detected and estimated by infra-red absorption methods. The present proposed application met with an unexpected difficulty in that dihydromyrcenemagnesium bromide, in contrast to the isomeric geranyl compound, did not react with acetone, acetophenone, acetaldehyde, or carbon dioxide. During these attempted reactions, self-condensation of two $C_{10}H_{17}$ units occurred to yield a hydrocarbon mixture isomeric with the known digeranyl and *iso*digeranyl (Barnard and Bateman, *J.*, 1950, 932). Analysis of the unsaturated units of this product can actually provide the information sought, but the departure from equivalency between bromine replacement and vinyl-group formation, as well as the increased molecular complexity, impose a further limit to accuracy. Coupling reactions of the Grignard derivatives of primary allylic halides produce almost exclusively the olefins formed by primary–primary and primary–secondary (or -tertiary) union of the allylic carbon atoms. The relative proportion in which these are formed varies from compound to compound: for crotyl- (Young, Roberts, and Wax, *J. Amer. Chem. Soc.*, 1945, **67**, 841), cinnamyl- (Koch, *J.*, 1948, 1111), and geranyl-magnesium halides (Barnard and Bateman, *loc. cit.*), the ratios are 1 : 8, 1 : 4, and 1 : 2, respectively; or, in other words, the proportions of the whole dimerised products containing $CHR{:}CH_2$ or $CR_2{:}CH_2$ groups, as the case may be, are 89, 80, and 67%, respectively. The allylic units containing terminal carbon atoms in dihydromyrcene bromide are of two types: C_1–C_2–C_3, $C_{2'}$–C_2–C_3, and $C_{6'}$–C_6–C_7 are primary–secondary systems, and C_6–C_7–C_8 is primary–tertiary. From the above, it is reasonable to assume that 85% of the "dimer" molecules formed from the first type will contain $CR_2{:}CH_2$ units and 70% from the second type will contain $CHR{:}CH_2$ units. The infra-red spectrum of the total product isolated simulates the spectra of the related derivatives in showing strong absorption at 820 cm.$^{-1}$, indicating that $CR_2{:}CHR$ remains the main unsaturation pattern, and also bands at 890 and at 910 cm.$^{-1}$ (as well as 1645 cm.$^{-1}$), indicating considerable concentrations of $CR_2{:}CH_2$ and $CHR{:}CH_2$ groups, respectively. The existence of an appreciable fraction of peripherally substituted isomers in the parent bromide is thus established. Measurement of extinction coefficients at 890 and 910 cm.$^{-1}$ and comparison with appropriate standards (see Experimental) indicate that approximately 30 and 11% of the molecules contain the two vinyl groups, respectively. Accordingly, the proportions of the bromodihydromyrcene isomers substituted at C_1, $C_{2'}$, and $C_{6'}$, and at C_9 are about 31 * and 16% respectively.

$$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMeX{\cdot}CH{:}CH_2$$

(III.)

TABLE II.

Unsaturated group.	Derivative examined.	Spectro-scopic method.	%, Found.	%, Calc.*	Relative propn. of total groups listed, %. Found.	Relative propn. of total groups listed, %. Calc.
$CR_2{:}CHR$	methoxy †	infra-red	125	92	62·5	68
$CR_2{:}CH_2$	methoxy ‡	infra-red	<5	2	<2·5	2
$CHR{:}CHR$	methyl ‡	infra-red	<5 (of *trans*)	6	<2·5 (of *trans*)	4
αδ-Diene	methoxy methyl	ultra-violet	18	14	9	10
$CR_2{:}CH_2$ indicative of $CHR{:}CR{\cdot}CH_2Br$ in bromide	dimer ‡	infra-red	31	16	15·5	12
$CHR{:}CH_2$ indicative of $CR_2{:}CH{\cdot}CH_2Br$ in bromide	dimer ‡	infra-red	16	6	8	4

* See Table 1. † Comparison standard: geranyl methyl ether.
‡ See p. 3051 for comparison standard.

A summary of the estimations of the various groupings is given in Table II. It will be seen that compared with the calculated values all are too high in an absolute sense (cf. p. 3046), but

---

* This figure has been corrected for the 10% contributed by the isomeric $CH_2{:}CR{\cdot}CH(Br)R$ groups.

that good agreement exists in their relative proportions. Although the inadequacy of our methods for detailed analysis is obvious, we believe that these results leave no doubt concerning the general correctness of the theoretical picture and the product heterogeneity that it specifies.

EXPERIMENTAL.

Bromodihydromyrcene.—2 : 6-Dimethylocta-2 : 6-diene (138 g., 1 g.-mol.) (Bateman and Koch, *J.*, 1944, 600), *N*-bromosuccinimide (62·4 g., 0·35 g.-mol.), carbon tetrachloride (200 ml.), and benzoyl peroxide (0·2 g.) were heated under reflux until the reaction was complete (20 minutes). The product consisted of three fractions : (1) b. p. 42—48°/0·04 mm., 7 g., n_D^{18} 1·4902 (Found : C, 56·8; H, 8·2. Calc. for $C_{10}H_{17}Br$: C, 55·3; H, 7·9; Br, 36·8%); (2) b. p. 48—56°/0·04 mm., 39 g., n_D^{18} 1·5050 (Found : C, 55·4; H, 7·9; Br, 36·7%); (3) b. p. 56—68°/0·04 mm., 9 g., n_D^{18} 1·5085 (Found : C, 54·4; H, 7·8%); and some tar. Redistillation of 12·5 g. of fraction (2) gave : (2*a*) b. p. 36—38°/0·01 mm., 3 g., n_D^{20} 1·5035; (2*b*) b. p. 38—39°/0·01 mm., 3 g., n_D^{20} 1·5038; (2*c*) b. p. 39°/0·01 mm., 3 g., n_D^{20} 1·5051; (2*d*) b. p. 39—40°/0·01 mm., 3 g., n_D^{20} 1·5070. Fractions (2*a*)—(2*d*) showed almost identical infra-red absorption between 720 and 1800 cm.$^{-1}$ (figure, curve *C*); a bulked sample displayed no selective ultra-violet absorption (at $>$2100 A.), but the absorption intensity at 2350 A. ($\log \varepsilon = 3{\cdot}6$) resembled that of other allylic halides (Bateman, Cunneen, Fabian, and Koch; Bateman and Cunneen; *locc. cit.*). The bromine (98%) was eliminated by treatment with boiling alcoholic silver nitrate for 20 minutes (cf. Bloomfield, *loc. cit.*).

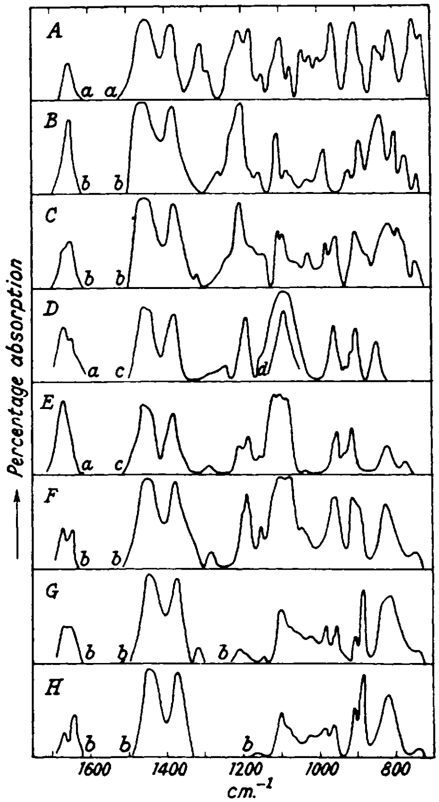
The bromide was also obtained, although in poorer yield (based on the *N*-bromosuccinimide), by heating under reflux equimolecular proportions of the reactants in carbon tetrachloride containing a little benzoyl peroxide for eight hours, and by ultra-violet irradiation (Hanovia S.500 mercury lamp) for one hour of a similar but peroxide-free mixture refluxing in glass vessels.

Dibromodihydromyrcene.—The olefin (8 g.), *N*-bromosuccinimide (20 g.), carbon tetrachloride (40 ml.), and benzoyl peroxide (0·1 g.) were heated under reflux for 12 hours. The product consisted of a small quantity of the monobromide, a brown oil, b. p. 70—100°/0·01 mm. (4·5 g.), and much tar. Fractionation of the oil yielded *dibromodihydromyrcene*, b. p. 80—90°/0·01 mm. [Found : Br (by reaction with boiling alcoholic silver nitrate), 53·7. $C_{10}H_{16}Br_2$ requires Br, 54·1%], as an unstable straw-coloured oil (2·5 g.). Redistillation at 10^{-5} mm. from a bulb at 60° to an adjacent one cooled in liquid oxygen afforded a very pale yellow product, whose ultra-violet absorption spectrum simulated that of the monobromide (no selective absorption at $\lambda > 2100$ A., $\log \varepsilon_{2350} = 3{\cdot}8$).

Methoxydihydromyrcene.—Bromodihydromyrcene (b.p. 46—54°/0·05 mm.; n_D^{20} 1·5045) (7 g.), sodium methoxide (6 g.), and methyl alcohol (50 ml.) were heated under reflux in nitrogen for two hours. Distillation of the product, b. p. 80—95°/14 mm., from sodium gave the analytically pure *ether* (3·7 g.), b. p. 78—87°/12 mm., n_D^{20} 1·4597 [Found : C, 78·6; H, 12·0%; ⊨ (by hydrogenation), 1·90. $C_{11}H_{20}O$ requires C, 78·6; H, 11·9%; ⊨, 2·00]. Its ultra-violet spectrum had $\lambda_{max.}$ 2350 A. ($\varepsilon = 1650$), 2710 A. ($\varepsilon = 1200$) (in ethyl alcohol); $\lambda_{max.}$ 2350 A. ($\varepsilon = 2650$), after it had been heated with methyl alcoholic potassium hydroxide (20%) at 165° for 48 hours.

Infra-red absorption spectra.

(*Path lengths : a* ~0·1 mm., *b* ~0·05 mm., *c* ~0·035 mm., *d* ~0·001 mm.)



A. Bromo-2-methylpent-2-ene. B. Geranyl bromide. C. Bromodihydromyrcene. D. Methoxy-2-methylpent-2-ene. E. Geranyl methyl ether. F. Methoxydihydromyrcene. G. Methyldihydromyrcene. H. Dihydromyrcenyldihydromyrcene.

Methyldihydromyrcene.—Bromodihydromyrcene (as used in the above preparation) (10 g.) in dry ether (15 ml.) was added during ten minutes to a small excess of methylmagnesium iodide in ether at room temperature, and the mixture then heated under reflux for 15 minutes. *Methyldihydromyrcene* was collected in two fractions : (1) (2·4 g.) b. p. 62—63°/10 mm., n_D^{18} 1·4543 (Found : C, 86·6; H, 13·3. $C_{11}H_{20}$ requires C, 86·8; H, 13·2%); and (2) (2·5 g.) b. p. 63—65°/10 mm., n_D^{18} 1·4558 (Found : C, 86·7; H, 13·3%), which had indistinguishable infra-red absorption spectra (figure, curve *G*). The ultra-violet spectrum of a combined sample showed $\lambda_{max.}$ 2740 A. ($\varepsilon = 1500$). On treatment with alcoholic potassium hydroxide as described for the methyl ether, another absorption band appeared, $\lambda_{max.}$ 2355 A. ($\varepsilon = 3150$).

Preparation and Attempted Reactions of Dihydromyrcenemagnesium Bromide.—Bromodihydromyrcene showed reluctance to form a Grignard derivative and the addition of a little methyl iodide was essential to initiate the reaction. The solution obtained failed to react with acetone, acetophenone, acetaldehyde, or carbon dioxide, and attempts to condense the liquids directly with the bromide in the presence of magnesium were equally unsuccessful. It was noted that the reaction between the bromide and magnesium was actually suppressed by the addition of the carbonyl compounds.

Dihydromyrcenyldihydromyrcene—The solution from bromodihydromyrcene (15 g.), magnesium (5 g.), ether (110 ml.), and a little methyl iodide was poured on excess of solid carbon dioxide. No acidic product could be isolated. The neutral product was *dihydromyrcenyldihydromyrcene* (8 g.), b. p. 89—100°/0·02 mm., n_D^{18} 1·4840 (Found : C, 87·6; H, 12·6. $C_{20}H_{34}$ requires C, 87·6; H, 12·4%). Its infra-red spectrum (figure, curve *H*) differs notably from the related derivatives in showing quite strong absorption due to $CHR{:}CH_2$ and $CR_2{:}CH_2$ groups; the respective molecular extinction coefficients at 910 and 890 cm.$^{-1}$ measured in carbon tetrachloride were 17 and 47.

*Geranyl Bromide.**—Purified geraniol (64 g.), anhydrous pyridine (39 ml.), and ether (175 ml.) were cooled to 0° and thionyl bromide (" Inorganic Syntheses," Vol. 1, p. 113, McGraw Hill Book Co., New York, 1939) (b. p. 63—65°/52 mm.; 87 g.) added dropwise during 1·5 hours. The mixture was left at room temperature overnight, the precipitate filtered off, the filtrate washed with aqueous sodium hydroxide (0·5N.) and then with water, and dried, and the solvent evaporated. Geranyl bromide (38 g.) distilled from the residue at 47—48°/0·005 mm. It had n_D^{20} 1·5027 [Found : Br (by combustion), 36·8; (by reaction with boiling alcoholic silver nitrate), 35·9. Calc. for $C_{10}H_{17}Br$: Br, 36·8%). This bromide has been prepared previously by different methods (*Sci. Ind. Rep. Roure-Bertrand Fils*, 1909, **10**, 19; 1911, **3**, 1; Wagner-Jauregg and Arnold, *Annalen*, 1937, **529**, 274) but inadequately characterised. Its infra-red absorption spectrum shows it to be essentially the primary allylic isomer [cf. geranyl chloride (Barnard *et al.*, *loc. cit.*)]. Whilst exhibiting the usual instability associated with allylic bromides, it is much more stable than bromodihydromyrcene.

Geranyl Methyl Ether.—This *ether*, prepared as described for its dihydromyrcene isomer, had b. p. 90—91°/12 mm., n_D^{16} 1·4600 (Found : C, 78·9; H, 12·1. $C_{11}H_{20}$ requires C, 78·6; H, 11·9%). Spectroscopic examination proves it to be virtually pure (I; $R^1 = R^{2'} = \ldots R^7 = H$; $R^8 = OMe$), which establishes that the bromide is similarly constituted (cf. above).

iso*Homogeranic Acid.*—The solution from geranyl bromide (10 g.), magnesium (4 g.), and ether (90 ml.) was poured on excess of solid carbon dioxide (100 g.). The acidic product (0·5 g.), b. p. 102°/0·06 mm. (Found : C, 72·4; H, 10·1. Calc. for $C_{11}H_{18}O_2$: C, 72·5; H, 9·9%), was pure *iso*homogeranic acid (III; $X = CO_2H$) (Barnard and Bateman, *loc. cit.*).

Geranyl Dimer.—Fractional distillation of the non-acidic product from the above reaction gave (after rejection of a little lower-boiling material) a hydrocarbon, b. p. 100—110°/0·06 mm., n_D^{23} 1·4829 (Found : C, 87·6; H, 12·4. Calc. for $C_{20}H_{34}$: C, 87·6; H, 12·4%). Direct comparison identified this product with the digeranyl–*iso*digeranyl mixture isolated previously by Barnard and Bateman (*loc. cit.*). The infra-red spectrum (cf. Barnard *et al.*, *loc. cit.*) differs from that of the dihydromyrcene dimer in showing no absorption attributable to $CR_2{:}CH_2$ groups, but stronger absorption due to $CHR{:}CH_2$ groups. The molecular extinction coefficient at 910 cm.$^{-1}$, measured in carbon tetrachloride, was 95, indicating that 61% of the molecules contain these groups. This figure is in good agreement with Barnard and Bateman's separation of the mixture into 1 part of digeranyl (containing no $CHR{:}CH_2$ groups) and 2 parts of *iso*digeranyl (containing one such group).

Bromo-2-methylpent-2-ene.—Fraction (iii) of the preparation of 2-methylpent-2-ene, described by Barnard *et al.* (*loc. cit.*) (37 g.), *N*-bromosuccinimide (78·5 g.), carbon tetrachloride (250 ml.), and benzoyl peroxide (0·2 g.) were heated under reflux for 30 minutes. The required product (10 g.) had b. p. 51—60°/20 mm. (Found : C, 44·0; H, 6·6. $C_6H_{11}Br$ requires C, 44·2; H, 6·8%). The corresponding methoxy-derivative had b. p. 114—121°/776 mm. (Found : C, 73·6; H, 12·7. $C_7H_{14}O$ requires C, 73·7; H, 12·3%).

Interpretation of the Infra-red Spectra.—The correlation of " characteristic " infra-red absorption bands with the mode of ethylenic substitution followed well-established rules (see Barnard *et al.*, *loc. cit.*); certain anomalies were also noted, however, which are discussed below.

Bromo-2-methylpent-2-ene, geranyl bromide, and bromodihydromyrcene all displayed an unusual $CH_2{:}CHR$ double-bond stretching frequency value of 1653 cm.$^{-1}$, whereas the derived methyl ethers and hydrocarbons, as well as geranyl chloride (Barnard *et al.*, *loc. cit.*) absorbed normally at 1670 cm.$^{-1}$. The cause of this apparent anomaly is obscure, particularly in view of the usual, expected value of 1640 cm.$^{-1}$ occurring in the analogous allyl bromide. The band observed at 905 cm.$^{-1}$ in both bromo-2-methylpent-2-ene and bromodihydromyrcene is confidently attributed to the group $CHRBr{\cdot}CR{:}CH_2$ since the displacement from the normal hydrocarbon characteristic frequency value of 890 cm.$^{-1}$ is quite analogous to that of the $CHR{:}CH_2$ 910 cm.$^{-1}$ band to 925—930 cm.$^{-1}$ which occurs in allyl chloride or bromide (cf. Barnard *et al.*, *loc. cit.*). Similarly, the $CR_2{:}CH_2$ groups absorb at 900 cm.$^{-1}$ in the allyl-substituted methyl-2-methylpent-2-ene, but normally at 890 cm.$^{-1}$ in the two hydrocarbons shown.

The uncertainties introduced by " skeletal " frequencies are well illustrated by the series of methyl ethers. The structurally pure geranyl methyl ether (I; $R^1 = R^{2'} = \ldots R^7 = H$; $R^8 = OMe$) exhibits non-characteristic bands at 914 and 952 cm.$^{-1}$, whereas methoxy-2-methylpent-2-ene evidently possesses structurally characteristic absorptions at 900 and 962 cm.$^{-1}$. As might be expected, all four frequencies appear in methoxydihydromyrcene, making structural diagnosis uncertain and quantitative analysis impossible.

---

* An imprecisely worded addition to an earlier paper (*J.*, 1950, 938) classified geranyl bromide as a bromo-1 : 4 diene. This inadvertence in no way weakens the argument advanced therein.

The following molar decadic extinction coefficients were employed in analytical estimations: $CR_2{:}CH_2$, ε (at 890 cm.$^{-1}$) = 155 (Barnard *et al.*, *loc. cit.*); *trans*-$CHR{:}CHR$, ε (at 965 cm.$^{-1}$) = 140 (Hampton, *Analyt. Chem.*, 1949, **21**, 923); and $CHR{:}CH_2$, ε (at 910 cm.$^{-1}$) = 155 (Hampton, *loc. cit.*, and our own unpublished data on oct-1-ene).

Most of the spectra were recorded by Miss J. M. Fabian with a Grubb–Parsons single-beam instrument (cf. Barnard, Fabian, and Koch, *J.*, 1949, 2442), but the hospitality of Mr. H. A. Willis of the Infra-red Laboratory of Imperial Chemical Industries Limited (Plastics Division), where a Hilger D.209 spectrometer was available, is also gratefully acknowledged.

British Rubber Producers' Research Association,
48, Tewin Road, Welwyn Garden City, Herts.

[*Received, June 29th,* 1950.]