190. *The Reaction of Oct-*1*-ene with* N-*Bromosuccinimide.*

By L. Bateman and J. I. Cunneen.

The bromination of oct-1-ene with *N*-bromosuccinimide yields a monobromide mixture analogous to that given by hexa-1 : 5-diene (preceding paper) : 1-bromo-oct-2-ene and 3-bromo-oct-1-ene are the major and minor constituents, respectively. The relative proportions of these isomers agree closely with the equilibrium mixtures formed (at 100°) by certain homologous bromides (Young, Richards, and Azorlosa, *J. Amer. Chem. Soc.*, 1939, **61**, 3070).

Different proportions of the corresponding methyloctenes are formed (*a*) by treating the bromide with methylmagnesium iodide, and (*b*) by treating the derived Grignard derivative with methyl iodide. The product from the latter reaction is structurally similar to the octene dimer produced in a Grignard coupling reaction; the significance of this finding is discussed.

The known ready interconversion of allylic bromides under the conditions of Ziegler bromination necessarily implies the isolation of an equilibrium mixture of the isomeric bromides. Any interpretation of the mechanism of the reaction based on the composition of the product is therefore valueless. However, this limitation is not generally appreciated, and hence the principles governing the composition of reaction products in allylic systems are reviewed.

In the preceding paper, it was shown that the monobromination product obtained from hexa-1 : 5-diene (diallyl) by *N*-bromosuccinimide consisted of 1-bromohexa-2 : 5-diene containing *ca.* 10% of the isomeric 3-bromohexa-1 : 5-diene. Predominant substitution of the bromine atom at a terminal carbon atom and displacement of the relevant double bond were established unequivocally by infra-red spectrographic measurements, and by diagnostically significant substitution of the bromine by ethoxyl ions and identification of the resulting ether. However, the presence in diallyl of the second $CH_2{:}CH$ group which remains unaffected in the monobrominated product renders the demonstration of the double-bond displacement by infra-red spectral variations far less striking, and analysis of the isomeric bromide mixture far less straightforward, than would be the case with a singly unsaturated Δ^1-olefin. A parallel investigation of the bromination of oct-1-ene is therefore reported here.

For reasons not understood (preceding paper), oct-1-ene reacts far more readily with *N*-bromosuccinimide than does diallyl, and in boiling carbon tetrachloride containing a little benzoyl peroxide reaction is complete within 15 minutes. Analytically pure octene monobromide * boils over a range of about 8° and exhibits infra-red absorption which affords detailed information about its composition. In contrast to the parent hydrocarbon (I; X = H), strong absorption occurs at 965 cm.$^{-1}$, while absorption at 924 and 990 cm.$^{-1}$ is much weaker. The 965 cm.$^{-1}$ band specifies the presence of $CHR{:}CHR'$; the later bands denote a reduction in the concentration of $CH_2{:}CHR$ groups. Quantitative comparison of the molecular extinction coefficient

$$\text{(I.)}\quad CH_3\cdot[CH_2]_4\cdot CHX\cdot CH{:}CH_2 \qquad\qquad CH_3\cdot[CH_2]_4\cdot CH{:}CH\cdot CH_2X\quad\text{(II.)}$$

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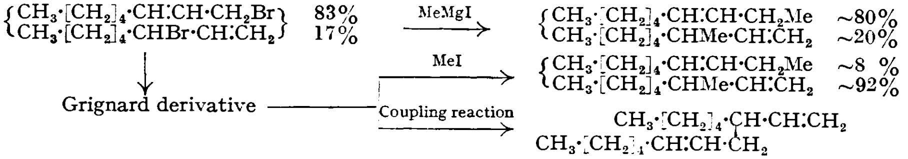
* Throughout this paper "octene monobromide" designates the isolated *substitution* product irrespective of its isomeric composition.

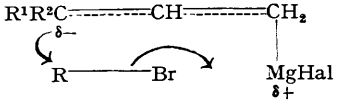
at 924 cm.$^{-1}$ of a typical reaction product of the boiling range given above with that found for the parent hydrocarbon showed the sample to consist of a mixture of *cis*- and *trans*-1-bromo-oct-2-ene (II; X = Br) and of 3-bromo-oct-1-ene (I; X = Br), containing 17 ± 3% of the latter. The proportions of the 1-bromo-Δ^2- and the 3-bromo-Δ^1-isomer in this mixture agree exactly (within experimental error) with the measured compositions of the homologous butenyl, pentenyl, and hexenyl bromides equilibrated at 100° (Young, Richards, and Azorlosa, *J. Amer. Chem. Soc.*, 1939, **61**, 3070) in which the 3-bromo-Δ^1-isomers are present to the extent of 14·5, 19·9, and 14·2%, respectively. The boiling-point variation is obviously indicative of partial isomeric separation on distillation; as with diallyl (preceding paper), differences in the infra-red spectra and refractive indices of small head and tail fractions demonstrated the accumulation of the 3-bromo- and 1-bromo-isomers in the lower- and higher-boiling material, respectively.

Carboxylation of the Grignard derivative of the octene bromide mixture yields homogeneous *oct-*1-*ene-*3-*carboxylic acid* (I; X = CO_2H) (p-*bromophenacyl* ester, m. p. 47—47·5°) which displays no infra-red absorption at 965 cm.$^{-1}$, but absorbs at 915 and 990 cm.$^{-1}$ with an intensity practically identical with that observed with oct-1-ene. This conversion of a bromide existing mainly in the primary allylic form (II) into an acid having entirely the secondary allylic structure (I) parallels exactly the behaviour of butenyl (Lane, Roberts, and Young, *J. Amer. Chem. Soc.*, 1944, **66**, 543) and geranyl (Barnard and Bateman, *J.*, 1950, 932) halides.

Reaction of the heterogeneous bromide with methylmagnesium iodide yielded a nonene mixture of (I; X = CH_3) and (II; X = CH_3) in proportion similar to those of the bromides. This finding is somewhat at variance with the product composition reported for the reaction between ethylallyl bromide (of unknown isomeric composition) and ethylmagnesium bromide (Prévost, *Compt. rend.*, 1928, **187**, 946; Prévost and Daujat, *Bull. Soc. chim.*, 1930, **47**, 588). Apart from any difference characteristic of the individual systems, the analytical procedure adopted by these authors (separate isolation and identification by oxidative degradation of the pure isomers) would appear to be quantitatively uncertain—a criticism which receives support from a similar discrepancy between the proportion of isomers produced in the Grignard coupling reaction of ethylallylmagnesium bromide as thus determined (Prévost and Richard, *Bull. Soc. chim.*, 1931, **49**, 1368) and the corresponding proportion obtained from crotylmagnesium bromide as carefully analysed by Young, Roberts, and Wax (*J. Amer. Chem. Soc.*, 1945, **67**, 841). In contrast, reaction of the Grignard derivative of the bromide with methyl iodide yielded a nonene mixture of quite different isomeric composition, the proportion of (II; X = Me) now being very small (*ca.* 8%). A similar result is derived from the structure of the hydrocarbon dimer isolated from the Grignard derivative, which proved to be essentially the unsymmetrical 6-vinyltetradec-8-ene. The reaction scheme summarises the results, which have a significant bearing on the mechanism of the coupling reaction and consequently on the nature of the Grignard derivative itself. In this example, the coupling reaction is clearly a special case of the decomposition of the Grignard compound by an alkyl halide, and illustrates the tendency of allylmagnesium halides to behave as if the MgHal unit were attached to the secondary (or tertiary) allylic, rather than to the primary allylic, carbon atom (Roberts and Young, *J. Amer. Chem. Soc.*, 1948, 1472, **68**; cf. *J.*, 1950, 932). This characteristic, which is not shared by the parent allylic halides (as the reaction now reported with methylmagnesium iodide demonstrates) could be taken as evidence that the MgHal group is actually attached to the secondary (or tertiary) carbon atom. However, Young and Roberts (*loc. cit.*) have carefully considered, and rejected, this deduction, and their arguments, although similarly inconclusive, appear very convincing. Accordingly, we interpret the mechanism of those reactions leading specifically to rearranged derivatives in terms of the intense polarity of the C–Mg bond. This polarity creates centres of high nucleophilic potential at both primary and secondary (or tertiary) carbon atoms, but since incipient ionisation of the MgHal group will be favoured by distribution of the unlike charges, reactivity at the latter position will be enhanced. Also, in reactions with alkyl halides or carbonyl compounds, the electrophilic power of the semi-cationic MgHal unit



will powerfully assist the necessary polarisation of these reagents in a process sterically conducive to the mutual development of the complementary electronic displacements :



Factors enhancing the importance of alternative decompositions, and thus leading to greater complexity of reaction products in certain substituted allylic systems, are discussed elsewhere (*J.*, 1950, 932).

Correlation between Reaction Mechanisms and the Composition of Products in Allylic Systems.— The contribution of the data recorded in this and the preceding paper to the understanding of the mechanism of Ziegler bromination and related reactions merits consideration, particularly as Dewar (" The Electronic Theory of Organic Chemistry," Oxford, 1949, p. 273) has recently presented a misleading argument that confirmatory evidence for a free-radical reaction mechanism would be obtained if 1-bromo-Δ^2-compounds were found to be the major products in the systems now considered.* We agree that certain features of the reaction as now conducted, *viz.*, marked catalysis by benzoyl peroxide and by ultra-violet light, afford almost compelling evidence for this type of mechanism, and the chain reaction first suggested by Bloomfield (*J.*, 1944, 114) is highly plausible. Quite definitely, however, our identification of the monobromides isolated from diallyl (preceding paper) and oct-1-ene as equilibrium mixtures of the allylic isomerides offers no critical information about the course of the primary substitution process. As emphasised in a discussion of anionotropy and related reactions (Catchpole, Hughes, and Ingold, *J.*, 1948, 8; de la Mare, Hughes, and Ingold, *ibid.*, p. 17), reaction products from interconvertible isomeric systems have significance in a mechanistic sense only when they are representative of *kinetic* as distinct from *thermodynamic* control, *i.e.*, the products formed in the reaction concerned are stable towards isomerisation under the conditions of reaction and subsequent isolation. Dewar dismisses the possibility of interconversion of the bromides resulting from Ziegler bromination in the sentence " Since the reaction is carried out in a non-polar solvent, the product cannot be formed by anionotropic rearrangement. . . . ." If " anionotropic rearrangement " here denotes a process in which free bromide and carbonium ions participate, this statement is literally true, but it is quite unrelated to the facts concerning the ease of isomerisation of allylic bromides (Young *et al.*, *loc. cit.*) and accordingly is irrelevant. The isomeric mobility of the liquid bromides is such that to obtain the pure isomers separately very careful and efficient fractionation at temperatures below *ca.* 20° is required. Reversion of the pure compounds to mixtures occurs readily on warming, and contaminants such as hydrogen bromide or peroxides—both of which are present in the reactions now considered—are powerful catalysts which facilitate this change even at room temperature (Kharasch, Margolis, and Mayo, *J. Org. Chem.*, 1936, **1**, 393; Young *et al.*, *loc. cit.*; unpublished observations by Mr. D. B. England working in Professor Ingold's laboratory). The remoteness of kinetic control over the products isolated from the *N*-bromosuccinimide reactions also becomes obvious by reference to other systems involving bromine addition to allylic systems, *viz.*, the combination of butadiene with bromine (Farmer, Lawrence, and Thorpe, *J.*, 1928, 729) and hydrogen bromide (Kharasch *et al.*, *loc. cit.*). In these cases, the futility of attempting to ascertain the initial proportions of 1 : 2- and 1 : 4-addition from experiments performed in boiling carbon tetrachloride would be universally recognised.

This aspect apart, the isolation of two isomeric diallyl or octene bromides in proportions approximating to their thermodynamic equilibrium proportions indicates that primary reaction products are not being considered. Thanks largely to work by Hughes and Ingold and by Young and their collaborators, some important principles correlating the composition of the products with reaction mechanism in allylic systems have recently become apparent. If we ignore certain special exceptions and modifications,† these, briefly, require : (i) that replacement

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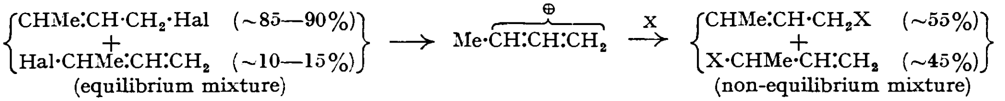
* Even more recently, Sutton and Datta (*J.*, 1949, 939) have attempted to draw mechanistic conclusions from the composition of the bromine-containing products of unknown heterogeneity derived from oleic, linoleic, and linolenic esters.

† *N.B.* (*a*) The possible accompaniment of an S_N2' with an S_N2 mechanism (cf. Barnard and Bateman, *J.*, 1950, 926). This is, however, difficult to realise deliberately, and circumstances conducive to its occurrence are well appreciated (Catchpole, Hughes, and Ingold, *loc. cit.*).

(*b*) Since there will be no sharp division between the conditions designated (i) and (ii), examples where " kinetically " free entities are unable to assume completely their equilibrium configurations are conceivable (Bateman, Church, Hughes, Ingold, and Taher, *J.*, 1940, 979). This phenomenon is maniof an allylic substituent in a reaction where the allylic residue (ion or radical) is without free existence leads to an isomerically homogeneous product; and (ii) that in a similar replacement where the allylic residue has free existence a mixture of isomerides results such that the proportion of the less stable isomer much exceeds the equilibrium value. As the theoretical basis of this behaviour and a wide survey of its ramifications have already been presented (Catchpole, Hughes, and Ingold *loc. cit.*; de la Mare, Hughes, and Ingold, *loc. cit.*), it remains here only to cite certain examples pertinent to the investigations described in this and the preceding papers.

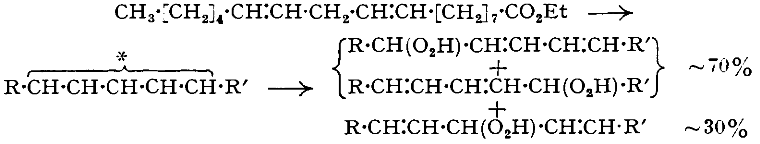
Product compositions governed by conditions (i) are clearly discernible in the interactions of allylmagnesium halides with carbonyl compounds (see, *e.g.*, *J.*, 1950, 932), where secondary (or tertiary) allylic derivatives are obtained irrespective of whether the Grignard complex is prepared from either form of pure halides or from mixtures (Young and Roberts, *J. Amer. Chem. Soc.*, 1945, **67**, 148). As Young and Roberts argue, the definite structural course of these reactions implies a specific bimolecular transition state. A similar factor undoubtedly operates in the reactions between diallyl or allylbenzene and maleic anhydride or azodicarboxylic ester, where the isolated 1 : 1 adducts consist solely of hexa-1 : 4-diene or propenylbenzene (cinnamyl) derivatives (Alder, Pascher, and Schmitz, *Ber.*, 1943, **76**, 27). Since the free-radical reaction mechanism postulated by Alder *et al.* cannot be seriously maintained on the evidence presented,* it is probably true, as the composition of the product indicates, that the reaction proceeds through an olefin–addendum complex, probably of the type envisaged for Diels–Alder reactions (see Koch, *J.*, 1948, 1111).

The alternative method of reaction (ii) was considered by Hughes, Ingold, and their co-workers (*loc. cit.*) for examples involving ionic allylic intermediates. Allylic free radicals should necessarily exhibit the same general behaviour, for this merely reflects commonly accepted concepts concerning mesomeric entities. Few comparative data exist, but the following are illustrative. (*a*) In methylallyl halides, the equilibrium proportion of the minor constituent, the 1-methylallyl isomer, is about 10—15% between 0° and 100° However, in reactions of the mesomeric methylallyl cation with nucleophilic addenda, combination occurs to the extent of 55% at the primary, and 45% at the secondary, allylic carbon atom :



$$\underset{\text{(equilibrium mixture)}}{\left\{\begin{matrix}\text{CHMe:CH}\cdot\text{CH}_2\cdot\text{Hal} & (\sim 85\text{—}90\%) \\ + & \\ \text{Hal}\cdot\text{CHMe:CH:CH}_2 & (\sim 10\text{—}15\%)\end{matrix}\right\}} \longrightarrow \text{Me}\cdot\overbrace{\text{CH:CH:CH}_2}^{\oplus} \xrightarrow{\text{X}} \underset{\text{(non-equilibrium mixture)}}{\left\{\begin{matrix}\text{CHMe:CH}\cdot\text{CH}_2\text{X} & (\sim 55\%) \\ + & \\ \text{X}\cdot\text{CHMe}\cdot\text{CH:CH}_2 & (\sim 45\%)\end{matrix}\right\}}$$

(*b*) Autoxidation of ethyl linoleate (Bolland, *Proc. Roy. Soc.*, 1946, *A*, **186**, 218) is a chain reaction in which the free radical formed by loss of a hydrogen atom from the CH_2 group of the 1 : 4-diene unit adds one molecule of oxygen, and the resulting peroxide radical then reacts with the parent ester to produce a hydroperoxide and also the original substituted pentadienyl radical. Bolland and Koch (*J.*, 1945, 445; cf. Lindberg, Chipault, and Hendrickson, *J. Amer. Oil Chemists' Soc.*, 1949 **26**, 109) have determined the extent to which oxygen adds centrally or terminally to the pentadienyl radical by estimating spectrographically the proportion of conjugated diene in the hydroperoxide formed; approximately 70% † of the oxidised molecules possess the rearranged structure :



$$\text{CH}_3\cdot[\text{CH}_2]_4\cdot\text{CH:CH}\cdot\text{CH}_2\cdot\text{CH:CH}\cdot[\text{CH}_2]_7\cdot\text{CO}_2\text{Et} \longrightarrow$$

$$\text{R}\cdot\overbrace{\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}}^{*}\cdot\text{R}' \longrightarrow \begin{matrix}\left\{\begin{matrix}\text{R}\cdot\text{CH(O}_2\text{H)}\cdot\text{CH:CH}\cdot\text{CH:CH}\cdot\text{R}' \\ + \\ \text{R}\cdot\text{CH:CH}\cdot\text{CH:CH}\cdot\text{CH(O}_2\text{H)}\cdot\text{R}'\end{matrix}\right\} & \sim 70\% \\ + & \\ \text{R}\cdot\text{CH:CH}\cdot\text{CH(O}_2\text{H)}\cdot\text{CH:CH}\cdot\text{R}' & \sim 30\%\end{matrix}$$

The small preponderance of free-radical activity at the terminal carbon atoms thus demonstrated is to be contrasted, in the same way as in (*a*), with the fact that thermal- or alkali-induced isomerisation of *equivalently substituted* 1 : 4- to 1 : 3-diene molecules proceeds nearly to completion.

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fested in the partial retention of activity by the products of S_N1 reactions of certain optically active halides (Bateman *et al.*, *loc. cit.*); in radical chain reactions it will clearly tend to intrude if environmental factors render the life of a radical abnormally short.

* A free radical reaction, catalysed by benzoyl peroxide occurs between natural rubber and maleinimides at a much lower temperature than the olefin–maleic anhydride reactions now referred to (Delalande, *Proc. International Congress of Pure and Applied Chem.*, London, 1947, in the press).

† In their publication, Bolland and Koch gave this figure as 70—85% owing to uncertainty as to the characteristic extinction coefficient of the pure conjugated diene. More recent data (Bergström and Holman, *Nature*, 1948, **161**, 55) have largely resolved the uncertainty. We are indebted to Dr. Koch for informing us of the figure quoted.

Although data sufficiently accurate for significant comparison cannot be quoted, similar rearrangement occurs in reactions involving simple allylic radicals: a physical implication of the comparably high resonance energies of the two types of radical (allyl, 19 kcals./g.-mol.; pentadienyl, 30 kcals./g.-mol., Bolland and Orr, *Trans. Inst. Rubber Ind.*, 1945, **21**, 133) is that the similarity should be roughly quantitative, and the behaviour of allylic cations described under (*a*) affords convincing, if indirect, corroboration. Therefore, if bromination of Δ^1-olefins with *N*-bromosuccinimide proceeds by a radical chain mechanism we should expect a mixture of the 1-bromo-Δ^2- and 3-bromo-Δ^1-compounds to be formed in which the proportion of the latter is substantial, *i.e.*, probably *ca.* 40%, and certainly far more than the proportion present in the equilibrium mixture. Clearly then, the isolation of isomeric bromides from the diallyl and oct-1-ene reactions in relative amounts numerically the same as their equilibrium proportions, far from offering confirmatory evidence, is not directly related to such a mechanism.

EXPERIMENTAL.

Purchased oct-1-ene of American origin was found to contain <1% of non-terminal unsaturation. Fractionation through a Fenske-type column yielded a substantial fore-fraction, b. p. 120·1°/745 mm., free from this impurity.

*Reaction of Oct-*1*-ene with* N*-Bromosuccinimide.*—Oct-1-ene (112 g., 1 g.-mol.), *N*-bromosuccinimide (preceding paper) (63 g., 0·35 g.-mol.), carbon tetrachloride (200 ml.), and benzoyl peroxide (0·2 g.) were refluxed for 20 minutes, during which the imide reacted completely. When the product was worked up as usual, a liquid (63 g.) was obtained which on fractionation gave the following mixtures of 1-bromo-oct-2-ene (II; X = Br) and 3-bromo-oct-1-ene (I; X = Br): (1) 15·3 g., b. p. 71—73°/10 mm., n_D^{15} 1·4462 (Found: C, 50·3; H, 7·9; Br, 42·1. $C_{18}H_{15}Br$ requires C, 50·3; H, 7·9; Br, 41·9%); (2) 24·8 g., b. p. 73—79°/10 mm., n_D^{15} 1·4766 (Found: C, 50·1; H, 7·9; Br, 42·2%).

Infra-red Spectrographic Examination of Octene Monobromide.—Fractions (1) and (2) exhibited strong absorption at 965 cm.$^{-1}$ (in contrast to the parent olefin which is non-absorbing at this frequency) and weaker absorption at 924 cm.$^{-1}$ and 990 cm.$^{-1}$.

Quantitative estimation of the isomeric composition of the bulked product was carried out as described for diallyl monobromide (preceding paper). The presence of *cis-* and *trans-*1-bromo-Δ^2-isomer was again evident, but in the present example the fact that the compounds possess only one olefinic centre renders measurement of the concentration of the component $CH_2{:}CHR$ groups, *i.e.*, of 3-bromo-oct-1-ene, much more sensitive than with the mixture of substituted hexa-1 : 4- and hexa-1 : 5-dienes. The relevant data are:

Frequency, cm.$^{-1}$.	Molecular extinction coefficient: observed.	standard.	3-Bromo-oct-1-ene, %.	*trans*-1-Bromo-oct-2-ene, %.
924 *	20	117	17±3	—
965	66	150	—	44

* The strong absorption occurring maximally at 965 cm.$^{-1}$ partly overlaps the 990 cm.$^{-1}$ absorption band, and thus prevents an equivalent estimate of the $CH_2{:}CHR$ group concentration being derived.

The presence of *cis*-1-bromo-oct-2-ene (the above analysis indicates about 40%) was confirmed qualitatively by the existence of a broad absorption band at 680 cm.$^{-1}$.

*Oct-*1*-ene-*3*-carboxylic Acid* (I; X = CO_2H).—Octene bromide (20 g.) in dry ether (100 ml.) was added very slowly (during 2·5 hours) to magnesium turnings (8·5 g.) and ether (45 ml.). On completion of reaction (which proceeded steadily after initiation with a crystal of iodine) the solution was poured rapidly on a well-stirred excess of powdered carbon dioxide. The acidic product isolated by the usual procedure through its sodium salt proved to be the pure *oct-*1*-ene-*3*-carboxylic acid* (8 g.), b. p. 128°/11 mm. (Found: C, 69·0; H, 10·2%; equiv., 154. $C_9H_{16}O_2$ requires C, 69·2; H, 10·3%; equiv., 156). Its infra-red spectrum displayed no absorption at 965 cm.$^{-1}$ (indicating the complete absence of $CH{:}CH$ groups), but strong absorption at 915 and 990 cm.$^{-1}$. p*-Bromophenacyl oct-*1*-ene-*3*-carboxylate* had m. p. 47—47·5° after crystallisation from aqueous ethanol (Found: C, 57·9; H, 6·1; Br, 22·8. $C_{17}H_{21}O_3Br$ requires C, 57·8; H, 6·0; Br, 22·7%).

Methyloctenes.—(*a*) *From octene monobromide and methylmagnesium iodide.* Octene monobromide (10 g.) in dry ether (15 ml.) was added during 20 minutes to a slight excess of methylmagnesium iodide in ether (30 ml.). A vigorous reaction occurred after each addition of the bromide solution. When addition was complete the reaction mixture was refluxed for 15 minutes, then cooled, and treated with aqueous ammonium chloride, and the product isolated in the usual way. The following mixtures of non-3-ene (II; X = Me) and 3-methyloct-1-ene(I; X = Me) resulted: (1) 2·2 g., b. p. 130—134°/754 mm., n_D^{15} 1·4210 (Found: C, 85·5; H, 14·3. Calc. for C_9H_{18}: C, 85·7; H, 14·3%), and (2) 2·9 g., b. p. 134—136°/754 mm., n_D^{15} 1·4216 (Found: C, 85·6; H, 14·3%). The isomeric composition of these fractions was found by infra-red spectroscopic examination to correspond closely to that of the original bromide: (1) contained 15—20%, and (2) 10—15%, of the Δ^1-isomer. Since the nonene isomerides are certainly not interconvertible under the reaction conditions, this finding provides sound evidence that methyl group substitution by this process occurs at the carbon atom bearing the displaced bromine atom.

(*b*) *From octenylmagnesium bromide and methyl iodide.* To an ethereal solution of octenylmagnesium bromide (prepared as described above from 7 g. of the halide) was added methyl iodide (6 g.) in ether (10 ml.) dropwise. Vigorous interaction occurred. When all the methyl iodide solution had been added, the mixture was refluxed for 10 minutes, and the product isolated in the usual way. A non-3-ene–3-methyloct-1-ene mixture different from that produced in (*a*) was obtained, *viz.*, 2 g., b. p. 118—120°/747 mm., n_D^{17} 1·4130 (Found: C, 85·6; H, 14·5. Calc. for C_9H_{18}: C, 85·7; H, 14·3%). From the infra-red absorption intensities at 910 and 990 cm.$^{-1}$ (strong) and at 965 cm.$^{-1}$ (weak), the concentration of 3-methyloct-1-ene was estimated to be *ca.* 92%.

Dimerised Octene.—The Grignard derivative prepared from 6 g. of octene monobromide was refluxed in ether for 10 minutes, cooled, and decomposed with ice and dilute hydrochloric acid, and the product collected in the usual way and fractionated. After a fore-run of some octene, a fraction, b. p. 135—136°/13 mm., n_D^{19} 1·4503 (Found : C, 86·5; H, 13·7. $C_{16}H_{30}$ requires C, 86·4; H, 13·6%) (3 g.), was collected. The near constancy of the boiling point offers strong evidence of structural homogeneity, and, since the relative intensities of infra-red absorption at 965, 910, and 990 cm.$^{-1}$ indicate that $CH_2{:}CHR$ and $CHR{:}CHR$ groups are present in similar concentration, this hydrocarbon is considered to be 9-*vinyltetradec*-6-*ene*, possibly contaminated with a small amount of isomer.

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