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REACTIONS OF ATOMS AND FREE RADICALS IN SOLUTION. XXX. DIMERIZATION OF FREE RADICALS PRODUCED FROM OLEFINS

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Experiments intended to ascertain the important structural features governing the dimerization of free radicals have for some years been underway in this laboratory. Resonance stabilization appears to be a sufficient but not a necessary condition for such dimerization. A few examples where resonance stabilization plays but a minor part are the formation of saturated dimeric hydrocarbons, $(C_{12}H_{25})_2$[1] and $(C_7H_{15})_2$, when dodecane and heptane are heated with *tert*-butyl peroxide and acetyl peroxide,[2] respectively. Furthermore, when 2-bromooctane is added to a Grignard solution of isopropylmagnesium bromide, containing five mole-% of cobaltous bromide, a 40–50% yield of a saturated hydrocarbon, presumably $[CH_3(CH_2)_5CHCH_3]_2$ is obtained.[3]

Of considerable theoretical interest are the dimers formed where a hydrogen atom is removed from an olefin, C_nH_{2n}. When diacyl peroxides[4] are used for this purpose, there is obtained a complex reaction mixture which contains some dimeric materials, some oxygenated olefin, and some oxygenated polymers of the olefin.[5] Even cyclohexene, when treated with benzoyl peroxide, gives a complicated mixture of products (1): benzene, benzoic acid, Δ^2-cyclohexenyl benzoate, phenyl-Δ^2-cyclohexene, Δ^2-cyclohexenyl-Δ^2-cyclohexene (di-Δ^2-cyclohex-

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[1] Kharasch, Fono, and Nudenberg, *J. Org. Chem.*, **16**, 105 (1951). Through an unfortunate oversight, the empirical formula for the hydrocarbon is given in this paper as $C_{40}H_{82}$ instead of $C_{24}H_{50}$. There is, however, no difficulty of ascertaining from the text that the latter hydrocarbon is the one in question.

[2] Kharasch and Jerome, unpublished work.

[3] Kharasch and Nudenberg, unpublished work. The mechanism of formation of this compound may be formulated as follows:

(a) $(CH_3)_2CHMgBr + CoBr_2 \rightarrow (CH_3)_2CHCoBr + MgBr_2$

(b) $(CH_3)_2CHCoBr \rightarrow (CH_3)_2CH\cdot + (CoBr)$

(c) $2\ (CH_3)_2CH\cdot \rightarrow CH_3CH{=}CH_2 + C_3H_8$

(d) $CH_3(CH_2)_5CHBrCH_3 + (CoBr)\cdot \rightarrow \underset{(A)}{CH_3(CH_2)_5CHCH_3}\cdot + CoBr_2$

(e) $2\ A\cdot \xrightarrow[\text{Disp.}]{\text{Dimer}} [CH_3(CH_2)_5CHCH_3]_2$

(f) $2\ A\cdot \longrightarrow C_8H_{16} + C_8H_{18}$

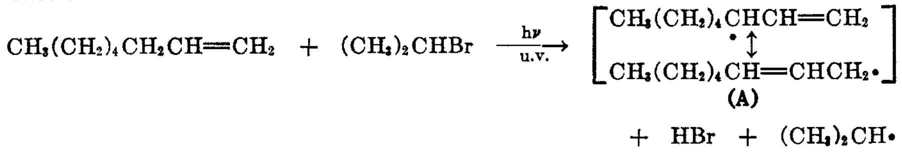
[4] It should be mentioned here that considerable isomerization of octene-1 to octene-2 takes place whenever the octene-1 is heated with sources of free radicals (acetyl peroxide, etc.) (unpublished work).

[5] Kharasch and Jerome, unpublished work. Note also that amylene when heated with benzoyl peroxide [Lippmann, *Monatsh.*, **5**, 562 (1884)] gives a variety of products. Farmer and Michael, *J. Chem. Soc.*, 514 (1942) have shown that the products formed in the reaction were incorrectly identified by the author. Farmer and Michael are also probably correct in their statement that the interpretation of Lippmann's findings by Gelissen and Hermans [*Ber.*, **58**, 2396 (1925)] is in error.

enyl) (21%), cyclohexyl benzoate, 2-Δ^2-cyclohexyl benzoate, and other substances, as yet unidentified.

For the reasons cited it was necessary to adopt a different approach in studying the behavior of the free radicals formed by abstraction of a hydrogen atom from an olefin. It appeared advisable to generate these free olefin radicals in an environment where they can not attack the reagent used to generate them. *A priori*, it appeared that the photochemical reaction which might take place when an olefin and isopropyl bromide are subjected to the action of ultraviolet light would meet this condition. Such, indeed, proved to be the case. The olefins studied were: octene-1, cyclohexene, and allylbenzene. The various products formed in these reactions will be discussed under separate headings. The details of the general reaction will be discussed in connection with octene-1.

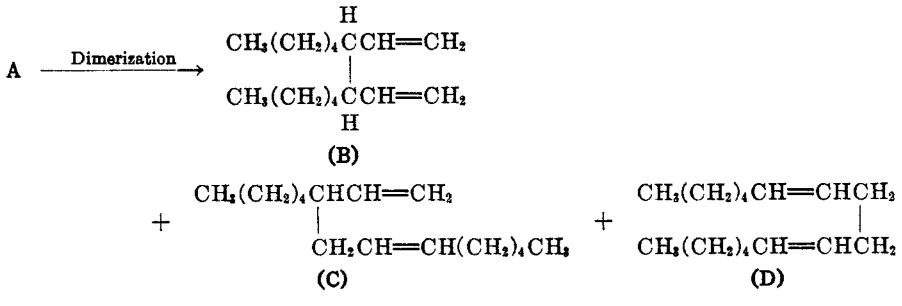
A. The photochemically-induced reaction of octene-1 with isopropyl bromide. The following products were obtained when a mixture of octene-1 and isopropyl bromide was illuminated with ultraviolet light: (a) *n*-octyl bromide; (b) a mixture of hexadecadienes; (c) octene-2; (d) hydrogen bromide (trace); (e) a gas which consisted of about equal quantities (50% and 42%, respectively) of propane and propylene; (f) a residue of a high molecular weight material. The formation of all these products may be accounted for by the following sequence of reactions.

1. 

$$CH_3(CH_2)_4CH_2CH{=}CH_2 + (CH_3)_2CHBr \xrightarrow[\text{u.v.}]{h\nu} \underset{\textbf{(A)}}{\left[\begin{array}{c} CH_3(CH_2)_4\dot{C}HCH{=}CH_2 \\ \updownarrow \\ CH_3(CH_2)_4CH{=}CHCH_2\cdot \end{array}\right]} + HBr + (CH_3)_2CH\cdot$$

2. $CH_3(CH_2)_4CH_2CH{=}CH_2 + HBr \xrightarrow[\text{u.v.}]{h\nu} CH_3(CH_2)_4CH_2CH_2CH_2Br$

3. $2\ (CH_3)_2CH\cdot \xrightarrow{\text{Disprop.}} C_3H_6 + C_3H_8$

4. 

$$A \xrightarrow{\text{Dimerization}} \underset{\textbf{(B)}}{\begin{array}{c} \overset{H}{CH_3(CH_2)_4CCH{=}CH_2} \\ | \\ \underset{H}{CH_3(CH_2)_4CCH{=}CH_2} \end{array}} + \underset{\textbf{(C)}}{\begin{array}{l} CH_3(CH_2)_4CHCH{=}CH_2 \\ \quad\quad | \\ \quad\quad CH_2CH{=}CH(CH_2)_4CH_3 \end{array}} + \underset{\textbf{(D)}}{\begin{array}{r} CH_3(CH_2)_4CH{=}CHCH_2 \\ | \\ CH_3(CH_2)_4CH{=}CHCH_2 \end{array}}$$

5. $A + CH_3(CH_2)_4CH_2CH{=}CH_2 \rightarrow CH_3(CH_2)_4CH{=}CHCH_3 + A$

6. A + octene-1 + isopropyl bromide $\xrightarrow{h\nu}$ unsaturated polymer containing some bromide

The detailed steps of reaction 1 are rather uncertain. The isopropyl bromide under the action of ultraviolet light may give an excited molecule which reacts with octene-1 to give the products noted in equation 1. On the other hand, the excited molecule may break down into a free isopropyl radical and a bromine atom which then reacts with octene-1. These early steps, however, have little bearing on the further course of the reactions here discussed.

The formation of an approximately equimolecular mixture of propane and propylene (equation 3) together with *n*-octyl bromide (from octene-1) and hydrogen bromide is in harmony with previous experience in this laboratory. Because of resonance the free radical formed by removal of the hydrogen atom from octene-1 would be expected to form the "dimers" **B**, **C**, and **D**. All three compounds have actually been isolated from the reaction mixture. There are various ways whereby octene-2 might be formed from octene-1. However, since the experiments here described do not allow a choice between the various reaction schemes, the indicated mechanism (equation 5) is the one which at present appears most plausible. As would be expected, the yield of *n*-octyl bromide (0.097 mole) is about twice the yield of hexadecadienes (0.048 mole).

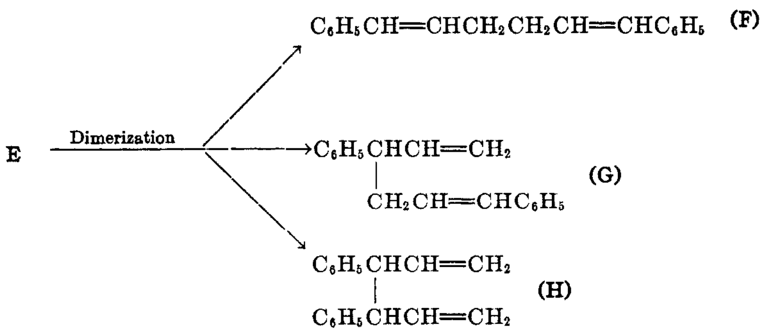
The propane, propylene, and *n*-octyl bromide were identified by the usual methods. The "dimers" (equation 4) were ozonized and the components of the mixture of acids (succinic, amylsuccinic, and diamylsuccinic acids) thus obtained were separated by partition chromotography on silicic acid (2). The various silver salts of these acids were then analyzed.

B. The photochemically-induced reaction of cyclohexene with isopropyl bromide. When a mixture of cyclohexene and isopropyl bromide is illuminated with ultraviolet light the products are: (a) bromocyclohexane (0.3 mole); (b) di-Δ^2-cyclohexenyl (0.15 mole); (c) a high-boiling residue (14.5 g.); (d) hydrogen bromide; (e) approximately equal amounts of propane and propylene. The mechanism proposed to explain the products formed in the reaction between octene-1 and isopropyl bromide suffices to account for all of these products. Note that here too the yield (in moles) of bromocyclohexane is twice that of the di-Δ^2-cyclohexenyl.

C. The photochemically-induced reaction of allylbenzene with isopropyl bromide. When a mixture of allylbenzene and isopropyl bromide is illuminated with ultraviolet light the products are: (a) propane and propylene; (b) γ-bromopropylbenzene; (c) diphenylhexa-1,5-dienes; (d) hydrogen bromide; (e) propenyl benzene; (f) residue.

$$C_6H_5CH_2CH{=}CH_2 + (CH_3)_2CHBr \xrightarrow[u.v.]{h\nu} (CH_3)_2CH\cdot + HBr + \left[\begin{array}{c} C_6H_5\underset{\cdot}{C}HCH{=}CH_2 \\ \updownarrow \\ C_6H_5CH{=}CHCH_2\cdot \end{array}\right]$$

(E)



A complete separation of the various diphenylhexa-1,5-dienes formed has not been accomplished. However, with the aid of chromatography it was possible to separate the complex mixture into three fractions. Molecular distillation of Fraction 1 gave a solid (m.p. 87°) which was shown (by ultraviolet absorption analysis) to be identical with meso-α,β-divinyldibenzyl (3,4-diphenylhexa-1,5-diene) (compound **H**) first isolated by Koch.[6] Ultraviolet absorption analysis also indicated that Fraction 2 was practically pure isodicinnamyl (1,4-diphenylhexa-1,5-diene), and that Fraction 3 was a mixture of isodicinnamyl (**G**) and dicinnamyl (**F**) (1,6-diphenylhexa-1,5-diene). The presence of dicinnamyl in this mixture was further confirmed by the isolation of its addition compound with 1,3,5-trinitrobenzene (m.p. 145°).

No undue theoretical significance should be attached at this time to the relative proportions of compounds **F** (3%), **G** (90%), and **H** (7%) formed because the structure of the polymeric material is still unknown. These polymers may have been formed by dimerization of the free radicals formed when a hydrogen atom is abstracted from **F**, **G**, and **H**; or they may have been formed by addition polymerization of allyl benzene with the free radical formed by abstracting a hydrogen atom from allylbenzene. Note, however, in this connection that the molar yield of these "dimers" is about half of the yield of γ-bromopropylbenzene (equations 1, 2, and 4). This result strongly suggests that the yields of **F**, **G**, and **H** here isolated represent the approximate amounts of the individual dimers formed in the reaction. The high-boiling residue (polymer) is probably formed by addition polymerization.

Note, also, that the illumination of allylbenzene and isopropyl bromide with ultraviolet light isomerizes the olefin.

$$C_6H_5CH_2CH{=}CH_2 \xrightarrow[\text{u.v.}]{(CH_3)_2CHBr} C_6H_5CH{=}CHCH_3$$

The probable mechanism of this reaction is indicated in equations 1 and 5.

EXPERIMENTAL

Photochemically-induced reaction of octene-1 with isopropyl bromide. A mixture of isopropyl bromide (b.p. 59°; n_D^{20} 1.4049; 0.62 mole) and octene-1 (3.75 moles; b.p. 120.8°/749 mm.; n_D^{20} 1.4090) was illuminated at 25–30° for 24 hours in an apparatus described by one of us and Friedlander (3), except that the Pyrex coil was replaced with a quartz coil. The air in the apparatus was replaced by nitrogen. The gases evolved in the reaction were collected in the usual way and analyzed by the procedure used by Kharasch, Lewis, and Reynolds (4). It consisted of a mixture of propane (58%) and propylene (42%). The reaction mixture was then distilled at reduced pressure (35–40°/20 mm.), and the unreacted isopropyl bromide and octene-1 were recovered. The recovered materials were again illuminated, and the residues of the two experiments were combined (43 g.).

Identification of octene-2 formed in the reaction. The recovered octenes and isopropyl

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[6] Koch, *J. Chem. Soc.*, 1111 (1948). Koch was also the first investigator to point out that the proportions of the three isomers **F**, **G**, and **H** in a mixture could be estimated by ultraviolet absorption analysis.

bromide were separated with the aid of a Fenske column, and the octenes (n_D^{20} 1.4103) (365 g.) which were free of halogen, were distilled in a Podbielniak column. Octene-1 (265 g.) distilled first (120.8°/740 mm.; n_D^{20} 1.4088). The boiling point and index of refraction of the next nine cuts of 10 ml. each approached the constants of a mixture of octene-1 and octene-2. Since the index of refraction of these olefins is a linear function of composition, we estimate that 45 g. of a mixture of *cis*- and *trans*-octene-2 was present in this mixture. (For purposes of calculation the index of refraction of octene-2 was taken as 1.4150.) The residue remaining from this distillation (10 g.) was distilled through a small Vigreux column. A material (5 g.) which boiled at 55–56°/70 mm.; n_D^{20} 1.4150 was obtained. This material is presumably *cis*-octene-2. Further identification of this material was made by ozonolysis (isolation of the methone derivative of acetaldehyde, which melted at 141°), and the preparation of the dinitrosulfenyl chloride derivative (m.p. 71.5–72°). No depression of the melting point was noted with the dinitrosulfenyl chloride derivative of an authentic sample of octene-2.

The residue (43 g.) was distilled at reduced pressure using a Vigreux column, provided with a still-head, and the fractions were collected. A slow stream of nitrogen was bubbled through the mixture during the distillation.

The following fractions were collected: Fraction I (19.1 g.; b.p. 85–86°/19 mm.; n_D^{20} 1.4530); Fraction II (11 g.; b.p. 65–70°/0.2 mm.; n_D^{20} 1.4530); Residue (8.8 g.).

Fraction I was shown to be *n*-octyl bromide.

Anal. Calc'd for $C_8H_{17}Br$: C, 49.75; H, 8.87; Br, 41.38; Mol. wt., 193.

Found: C, 49.6; H, 8.9; Br, 41.4; Mol. wt., 197.

The *n*-octylmercuric bromide, prepared from this material, melted at 111–112°, and did not depress the melting point of an authentic sample of *n*-octylmercuric bromide, prepared from an authentic sample of *n*-octyl bromide.

Fraction II was shown by analyses and molecular weight to be a mixture of hexadecadienes, since two moles of hydrogen were taken up per mole of the compound.

Anal. Calc'd for $C_{16}H_{30}$: C, 86.40; H, 13.60; Mol. wt., 222.

Found: C, 85.7; H, 13.6; Mol. wt., 230.

The structure of the hexadecadienes comprising the mixture was established by ozonolysis.

Ozonolysis of Fraction II. (*a*) *Ozonolysis in carbon tetrachloride as solvent.* Fraction II (2.5 g.) was dissolved in 200 cc. of carbon tetrachloride, cooled to 0°, and a stream of ozone passed through the solution. The volatile material was collected in water saturated with methone. The crystalline material which separated from the water solution melted at 189°, and did not depress the melting point of an authentic sample of the methone derivative of formaldehyde.

(*b*) *Ozonolysis in ethyl acetate.* Fraction II (6 g., 0.027 mole) was dissolved in 300 ml. of dry ethyl acetate (free of acids) and the mixture was cooled to −80°, and ozone was passed through the reaction mixture for complete saturation (0.054 mole). The amount of ozone consumed indicated the presence of two double bonds for compounds of mol. wt. 222. The solvent was removed and the colorless residue was treated with 125 ml. of NaOH (1 *N*) and 7.5 ml. of perhydrol (30% hydrogen peroxide). The mixture was then slowly heated to 110°, and maintained at that temperature until complete solution resulted (12 hours). An additional amount of perhydrol was then added, followed by sodium carbonate (3 g.) and the mixture was heated until all of the hydrogen peroxide had decomposed. The mixture was then cooled, saturated with sodium chloride, and the whole extracted with ether and the layers separated. The water solution was acidified with dilute hydrochloric acid (*p*H 2) and extracted with ten portions of ether and the extracts were combined. This ether extract was washed with small amounts of water until the washings were free of chloride ions; the layers were separated and the ether removed. The residue was steam-distilled. The volatile acids were extracted with ether and the ether removed leaving a liquid (b.p. 191–193°) which had a strong odor of the C_6 and C_5 aliphatic acids. The benzylthiouronium salt of this material was not homogeneous. Since many attempts to separate these acids had failed, the silver salt of this acidic material was prepared and analyzed. It appears to be a mixture of caproic and valeric acids.

ANALYSES

ELEMENT	SILVER CAPROATE (calc'd)	SILVER VALERATE (calc'd)	FOUND
C	32.31	28.73	29.6
H	4.97	4.34	4.3
Ag	48.37	51.62	50.6

At first glance, the formation of some valeric acid in the ozonolysis of a compound of the type **C** or **D** appears most unusual. However, others have noted the loss of a carbon atom in working up ozonides of similar compounds (5).

The material remaining in the steam-distillation apparatus deposited some crystals and an oil. The crystals were collected and upon crystallization from a mixture of ether and ligroin a solid was obtained which melted at 134–136°. Additional confirmation that this acid was amylsuccinic acid was obtained from the analyses of the silver salt of the acid. The oil was dissolved in chloroform and subjected to chromatography following the procedure suggested by Marvel and Rands (2). The effluent from the first peak (chloroform) was evaporated and the silver salt of the acid prepared. The analysis showed it to be the silver salt of diamylsuccinic acid. The second peak (eluted with 25% butanol in chloroform) was shown to be monoamylsuccinic acid. No other peaks were noted.

The water solution remaining after removal of the mono- and di-amylsuccinic acids was strongly acidic and contained some formic acid (Tollen's reagent, etc.) which was removed by distillation. The water solution was then extracted with ether, the ether rejected, and the water solution neutralized with ammonia, and treated with silver nitrate. Analyses of the silver salt showed it to be silver succinate.

ANALYSES OF SILVER SALTS

SILVER SUCCINATE (calc'd)	FOUND	SILVER MONOAMYLSUCCINATE (calc'd)	FOUND	SILVER DIAMYLSUCCINATE (calc'd)	FOUND
C, 14.48	14.9	C, 26.89	27.2	C, 35.62	35.4
H, 1.21	1.34	H, 3.51	3.62	H, 5.12	5.3
Ag, 65.02	65.0	Ag, 53.68	53.0	Ag, 45.70	45.9

Photochemically-induced reaction of isopropyl bromide with cyclohexene. The mixture of isopropyl bromide (136 g., b.p. 59.5°; n_D^{20} 1.4049) and cyclohexene (543 g., b.p. 83.5°; n_D^{20} 1.4464) was illuminated in the apparatus previously described for 24 hours at 25–30°. The evolved gas was collected and shown to be a mixture of propane and propylene. The unreacted isopropyl bromide and cyclohexene were recovered and illuminated again. The combined residues from three such experiments were combined (88 g.).

The residue (a light yellow oil) was distilled at reduced pressure through a 10-inch Vigreaux column and the following fractions were collected: Fraction I, bromocyclohexane, 49.3 g. (0.3 mole), b.p. 62–63°/21 mm.; n_D^{20} 1.4960. Fraction II, di-Δ^2-cyclohexenyl, 24.3 (0.15 mole), b.p. 41–42°/0.05 mm.; n_D^{20} 1.5110. Residue, 14.5 g.

Fraction I, bromocyclohexane, was identified by analyses.

Anal. Calc'd for $C_6H_{11}Br$: C, 44.2; H, 6.8; Br, 49.0; Mol. wt., 163.1.

Found: C, 44.6; H, 6.9; Br, 48.9; Mol. wt., 164.

Upon conversion to cyclohexylmercury bromide the melting point of the material (148.5°) was not depressed by admixture with a known sample of cyclohexylmercury bromide.

Fraction II, di-Δ^2-cyclohexenyl, was identified by analyses.

Anal. Calc'd for $C_{12}H_{18}$: C, 88.8; H, 11.2; Mol. wt., 162.

Found: C, 88.7; H, 11.4; Mol. wt., 169.

Upon conversion to the tetrabromo derivative crystals of m.p. 158–159° were formed. The recorded melting point of the tetrabromo derivative of di-Δ^2-cyclohexenyl is 158–159° (1, 6).

Photochemically-induced reaction of allylbenzene with isopropyl bromide. Isopropyl bromide (12 g.) and allylbenzene (62 g.) (b.p. 65°/30 mm.; n_D^{20} 1.5120) were illuminated in the previously described apparatus for 24 hours. The evolved gases were collected in the usual way and shown to be a mixture of propane (45%) and propylene (55%). The unreacted materials were recovered at reduced pressure and illuminated again. The residues from three such experiments (11 g.) were combined and distilled at reduced pressures: Fraction, I (4 g.) allylbenzene; Fraction II γ-bromopropylbenzene (2 g.); Residue (4.8 g.).

Fraction II (b.p. 108°/17 mm.; n_D^{20} 1.5462) was identified as γ-bromopropylbenzene. The iso-thiouronium picrate (m.p. 142–143°) of this material did not depress the melting point of a sample prepared from an authentic sample of γ-bromopropylbenzene.

The residue (4.8 g.) was separated by chromatography on neutral Alcoa Alumina, F. 20. The ratio of substance to alumina was 1:150.

The solvent used was ligroin 30–60° (free of olefins). The sample in 20 ml. of ligroin was forced down the column with the same solvent. The elution from the column was done with ligroin containing 2.5%, 5%, 10%, and 15% of benzene.

The eluate **A** (1.067 g.) eluted with ligroin containing 10% of benzene is followed rapidly by eluate **B** (0.73 g.) (with the same solvent). Eluate **C** (0.17 g.) is eluted with ligroin containing 15% of benzene.

Ultraviolet absorption analyses showed that eluates **A** and **C** were impure, whereas eluate **B** had a sharp and symmetrical maximum at 255 mμ. Eluate **A** was distilled in a molecular still at 50°/0.01 mm. An oil (485 mg.) and a crystalline material (62 mg.) were obtained. The residue (520 mg.) was a high polymeric material. The oil contained bromine and also some isodicinnamyl, as indicated by ultraviolet absorption analysis. The crystalline material upon crystallization from alcohol melted at 85°. Ultraviolet absorption analysis of this material (max. 260 mμ; E, 500) was in agreement with that recorded for meso-α,β-divinyldibenzyl (compound **H**). The eluate **B** was practically pure isodicinnamyl (compound) **G**. The total amount of isodicinnamyl present in Eluates **A**, **B**, and **C** was estimated by ultraviolet analyses. Ultraviolet absorption analysis indicated that Eluate **C** was a mixture of isodicinnamyl and dicinnamyl (compound **F**). Dicinnamyl combines with 1,3,5-trinitrobenzene to give a compound melting at 145°, while isodicinnamyl does not. This method and ultraviolet analysis was therefore used to estimate the composition of the mixture.

The ratio of the three isomers formed when allylbenzene and isopropyl bromide are irradiated with ultraviolet light and here isolated is approximately as follows:

1. Meso-α,β-divinyldibenzyl (compound **H**)	62 mg.	7%
2. Isodicinnamyl (compound **G**)	867 mg.	90%
3. Dicinnamyl (compound **F**)	30 mg.	3%

SUMMARY

1. The following products were isolated when a mixture of octene-1 and isopropyl bromide was illuminated with ultraviolet light: *n*-octyl bromide, a mixture of hexadecadienes, octene-2, propane, and propylene, and a high-boiling material.

2. The following products were isolated when a mixture of cyclohexene and isopropyl bromide was illuminated with ultraviolet light: bromocyclohexane, di-Δ^2-cyclohexenyl, propane, propylene, and a high-boiling material.

3. The following products were isolated when a mixture of allylbenzene and isopropyl bromide was illuminated with ultraviolet light: γ-bromopropylbenzene, a mixture of diphenylhexa-1,5-dienes, propenylbenzene, propane, propylene, and a high-boiling material.

4. A mechanism is suggested which accounts satisfactorily for the products isolated in 1, 2, and 3.

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REFERENCES

(1) Farmer and Michael, *J. Chem. Soc.*, 513 (1942).
(2) Marvel and Rands, Jr., *J. Am. Chem. Soc.*, **72,** 2642 (1950).
(3) Kharasch and Friedlander, *J. Org. Chem.*, **14,** 245 (1949).
(4) Kharasch, Lewis, and Reynolds, *J. Am. Chem. Soc.*, **65,** 493 (1943).
(5) Stoll and Rouve, *Helv. Chim. Acta*, **27,** 950 (1944).
(6) Frederick, Cogan, and Marvel, *J. Am. Chem. Soc.*, **56,** 1815 (1934).