659. *Radiation Chemistry of Organic Halogen Compounds.*
Part II.[1] The Action of γ-Radiation on Allyl Halides.

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The yield of polymer formed by γ-irradiation of the allyl halides decreases in the sequence, chloride, bromide, iodide. A liquid polymer is the only product from the chloride but small amounts of at least ten other compounds accompany the dimer which is the main product from allyl bromide. Iodine and hexa-1,5-diene are produced during irradiation of the iodide.

The allyl halides have been polymerised by irradiation with ultraviolet light [2] (chloride and bromide), by heating them with diacyl peroxides (chloride [3] and bromide [4]), and by the action of boron trifluoride in presence of finely divided metals (chloride only [5]). All these methods produce polymers of low molecular weight and we have now shown that similar products are formed by the action of ^{60}Co γ-radiation.

An irradiated sample of allyl chloride contained no compounds detectable by gas–liquid chromatography other than the unchanged monomer. Evaporation yielded an involatile, viscous polymer ($G = 369$ molecules of monomer removed per 100 ev absorbed) of which the average degree of polymerisation was about 5, and which showed infrared absorptions attributable to terminal double bonds.

In contrast to this result with the chloride, but in agreement with the observations of Kharasch and Büchi [4] concerning the action of decomposing diacetyl peroxide on allyl bromide, the main product of γ-irradiation of the bromide was a dimer $CH_2:CH \cdot CH_2 \cdot CH(CH_2Br)_2$ ($G = 134$, in same units as for the chloride). Several other volatile compounds were produced in smaller amounts (G values not measured but probably less than 2) and, after partial separation by fractional distillation, were isolated by gas–liquid chromatography and identified by infrared spectroscopy. In order of decreasing volatility, the products detected were propene, hexa-1,5-diene, 5-bromo-4-methylpent-1-ene, *cis-* and *trans-*1,3-dibromopropenes, 1,3-dibromopropane, an unidentified unsaturated compound (Y), the above dimer, 1,2,3-tribromopropane, 1,4-dibromo-2-bromomethylpentane [$CH_3 \cdot CHBr \cdot CH_2 \cdot CH(CH_2Br)_2$], and a probable trimer. A black, involatile, solid residue containing 26·4% of bromine remained after distillation of these products.

Irradiation of allyl iodide produced small amounts of iodine and hexa-1,5-diene as the only identifiable products. A trace of dark, viscous oil remained after evaporation of the monomer.

It is probable that the primary excited and ionic species produced by irradiation of the allyl halides give rise, initially, to atoms and free radicals which then react to form the observed products. Since hydrogen production was not measured, the possibility of carbon–hydrogen bond fission cannot be excluded but predominant fission of the carbon–halogen bond seems more probable because the bond strength is less. Moreover, the formation of propene from allyl bromide is more easily accounted for if allyl radicals are produced in the primary homolytic reaction (1) since some of these may then abstract hydrogen from allyl bromide [reaction (7)]. No hydrogen halide was produced in any of the irradiations, indicating either that abstraction by halogen atoms does not occur or, less probably, that hydrogen halides are completely consumed in further reactions.

The decrease of carbon–halogen bond strength in the sequence chloride, bromide, iodide leads to the expectation of an increase in radical yields in that order. The same factor is,

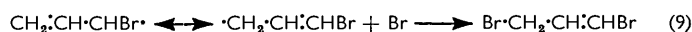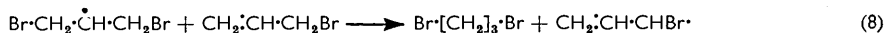[1] Part I, Miller, Stafford, Taylor, Leaver, and McQuillan, *J.*, 1961, 4485.
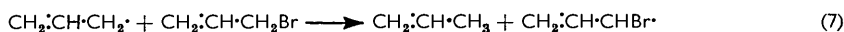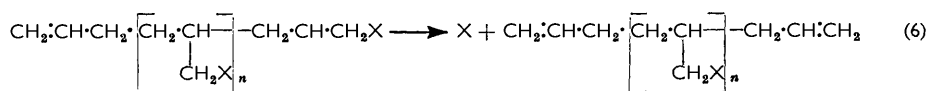[2] Staudinger and Fleitmann, *Annalen*, 1930, **480**, 92.
[3] Bartlett and Altschul, *J. Amer. Chem. Soc.*, 1945, **67**, 816.
[4] Kharasch and Büchi, *J. Org. Chem.*, 1949, **14**, 84.
[5] Adelson and Dannenberg, U.S.P. 2,331,869/1943.

however, partly responsible for the observed decrease in polymer formation [reactions (2—6)] because of its effect in (a) increasing the ease of loss of a halogen atom from the intermediate polymer-producing radicals [reactions (2), (4), and (6)], and (b), less directly, in the case of the iodide, causing an accumulation of free iodine which acts as an effective radical scavenger. Factor (a) is also responsible for the lower degree of polymerisation of the p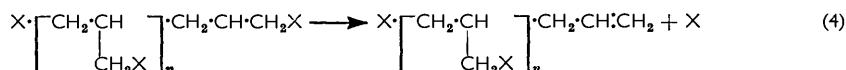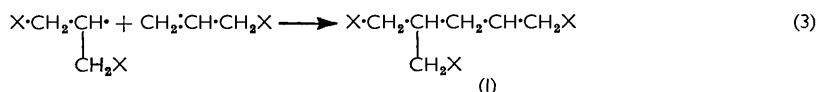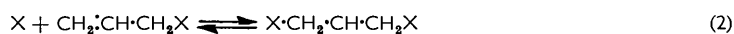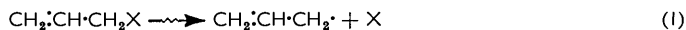olymer from the bromide than from the chloride. The absence of volatile products indicates that abstraction reactions are negligible for the chloride and that practically all free radicals in the system initiate polymer-producing chains. Some of the products from the bromide, however, must be produced by competing reactions of hydrogen abstraction from the monomer, suggesting that the lower polymer yield may be partly due to a lower reactivity of the monomer towards radical addition reactions.

$$CH_2\!:\!CH\!\cdot\!CH_2X \longrightarrow CH_2\!:\!CH\!\cdot\!CH_2\!\cdot\! + X \tag{I}$$

$$X + CH_2\!:\!CH\!\cdot\!CH_2X \rightleftharpoons X\!\cdot\!CH_2\!\cdot\!CH\!\cdot\!CH_2X \tag{2}$$

$$X\!\cdot\!CH_2\!\cdot\!\overset{\displaystyle |}{\underset{\displaystyle CH_2X}{CH}}\!\cdot\! + CH_2\!:\!CH\!\cdot\!CH_2X \longrightarrow X\!\cdot\!CH_2\!\cdot\!\overset{\displaystyle |}{\underset{\displaystyle CH_2X}{CH}}\!\cdot\!CH_2\!\cdot\!CH\!\cdot\!CH_2X \tag{3}$$

(I)

$$X\!\cdot\!\left[\overset{}{\underset{CH_2X}{CH_2\!\cdot\!CH}}\right]_n\!\!CH_2\!\cdot\!CH\!\cdot\!CH_2X \longrightarrow X\!\cdot\!\left[\overset{}{\underset{CH_2X}{CH_2\!\cdot\!CH}}\right]_n\!\!CH_2\!\cdot\!CH\!:\!CH_2 + X \tag{4}$$

$$CH_2\!:\!CH\!\cdot\!CH_2\!\cdot\! + CH_2\!:\!CH\!\cdot\!CH_2X \longrightarrow CH_2\!:\!CH\!\cdot\!CH_2\!\cdot\!CH_2\!\cdot\!\overset{\cdot}{C}H\!\cdot\!CH_2X \tag{5}$$

$$CH_2\!:\!CH\!\cdot\!CH_2\!\cdot\!\left[\overset{}{\underset{CH_2X}{CH_2\!\cdot\!CH}}\right]_n\!\!-CH_2\!\cdot\!CH\!\cdot\!CH_2X \longrightarrow X + CH_2\!:\!CH\!\cdot\!CH_2\!\cdot\!\left[\overset{}{\underset{CH_2X}{CH_2\!\cdot\!CH}}\right]_n\!\!-CH_2\!\cdot\!CH\!:\!CH_2 \tag{6}$$

$$CH_2\!:\!CH\!\cdot\!CH_2\!\cdot\! + CH_2\!:\!CH\!\cdot\!CH_2Br \longrightarrow CH_2\!:\!CH\!\cdot\!CH_3 + CH_2\!:\!CH\!\cdot\!CHBr\!\cdot\! \tag{7}$$

$$Br\!\cdot\!CH_2\!\cdot\!\overset{\cdot}{C}H\!\cdot\!CH_2Br + CH_2\!:\!CH\!\cdot\!CH_2Br \longrightarrow Br\!\cdot\![CH_2]_3\!\cdot\!Br + CH_2\!:\!CH\!\cdot\!CHBr\!\cdot\! \tag{8}$$

$$CH_2\!:\!CH\!\cdot\!CHBr\!\cdot\! \longleftrightarrow \cdot CH_2\!\cdot\!CH\!:\!CHBr + Br \longrightarrow Br\!\cdot\!CH_2\!\cdot\!CH\!:\!CHBr \tag{9}$$

$$Br\!\cdot\!CH_2\!\cdot\!\overset{\cdot}{C}H\!\cdot\!CH_2Br + Br \longrightarrow Br\!\cdot\!CH_2\!\cdot\!CHBr\!\cdot\!CH_2Br \tag{10}$$

Most of the minor products from allyl bromide can be accounted for by reactions (5—10). The formation of propene, 1,3-dibromopropane, and 1,3-dibromopropene suggests that allyl and 1,3-dibromopropyl radicals abstract hydrogen from allyl bromide [reactions (7) and (8)] and that the resulting, mesomeric bromoallyl radicals combine with bromine atoms [reaction (9)]. Unless the steric preference for the 1,3-compound is too great, reaction (9) could also give 3,3-dibromopropene which is inseparable from 5-bromo-4-methylpent-1-ene (see above) by gas–liquid chromatography on either of the two stationary phases employed. A separated sample of the latter compound was shown, however, to be free from 3,3-dibromopropene by infrared spectroscopy.

The unidentified, unsaturated compound (Y) has the volatility expected of a dibromo-hexa-1,5-diene which could be formed by dimerisation of bromoallyl radicals but the product of combination of these radicals with allyl radicals could not be detected. [Such a product would be a bromohexa-1,5-diene, one possible isomer (3-bromo) of which was separated from the products of reaction of hexa-1,5-diene with N-bromosuccinimide and was found to run close to 5-bromo-4-methylpent-1-ene during gas–liquid chromatography.] It seems probable that few allyl radicals take part in radical–radical combination and that most of the observed hexa-1,5-diene is formed by reaction (5; X = Br) followed by loss of a bromine atom [reaction (6; X = Br, $n = 0$)] from the resultant bromo-hexenyl radical.

The mechanism of formation of 1,4-dibromo-2-bromomethylpentane is obscure; the compound can be formed by polar addition of hydrogen bromide to the dimer of allyl bromide but it seems unlikely to arise in this way during irradiation. Even if hydrogen bromide were available, at least a part of it would be expected to add by a free-radical mechanism to give the undetected, isomeric 1,5-dibromo-2-bromomethylpentane. Moreover, 1,2-dibromopropane, the product of polar addition of hydrogen bromide to allyl bromide, was not present among the irradiation products. The possibility of bromine atom migration from C-5 to C-4 in a proportion of the radicals (I; X = Br), followed by hydrogen abstraction from allyl bromide, is also unlikely since Skell, Allen, and Gilmour [6] have shown that a bromine atom in related radicals migrates exclusively in the opposite direction (*i.e.*, from secondary or tertiary to primary carbon atoms).

5-Bromo-4-methylpent-1-ene seemed likely to be a secondary product formed by radiolysis of a carbon–bromine bond in the dimer, followed by hydrogen abstraction by the resultant bromoalkenyl radical, and this view was supported by formation of the compound also by irradiation of the dimer.

The reaction between hexa-1,5-diene and *N*-bromosuccinimide deserves further comment. The monobromo-compound produced in this reaction was originally identified [7] as 3-bromohexa-1,5-diene, CH_2:CH·CHBr·CH_2·CH:CH_2, but Bateman *et al.*[8] pointed out that the previous evidence was inconclusive and presented infrared spectroscopic data to show that the product was mainly 6-bromohexa-1,4-diene, CH_2:CH·CH_2·CH:CH·CH_2Br, being accompanied by a smaller amount of 3-bromohexa-1,5-diene. We have verified this conclusion by re-examination of the spectra after gas-chromatographic separation of the two compounds. The spectrum of the 1,4-diene showed no evidence for the presence of the *cis*-isomer, but a medium band at 681 cm.$^{-1}$ in the spectrum of the 1,5-diene could be due to contamination of the latter with the *cis*-1,4-diene (cf. ref. 8).

EXPERIMENTAL

The ^{60}Co source and techniques of irradiation were similar to those described previously.[1] Dose-rates reported were determined by using the aqueous ferrous sulphate–sulphuric acid system [9] and are corrected for the greater absorption coefficients of the absorbing liquids. Infrared spectra were measured with Hilger H 800 or Perkin–Elmer Infracord double-beam spectrophotometers. Absorptions reported are strong unless otherwise indicated.

Gas–Liquid Chromatography.—Analytical separations were carried out, with nitrogen as the carrier gas, on columns of kieselguhr (60—90 mesh) or crushed firebrick (various grades) impregnated, respectively, with silicone elastomer E301 (Griffin and George Ltd.) and tritolyl phosphate. The columns used for isolation of reaction products were packed with firebrick–tritolyl phosphate and varied in diameter from 1·5 to 2·5 cm. and, correspondingly, in length from 1·5 to 8 ft. Liquids were applied to the column from a pressure-equilibrated dropping funnel which discharged into a vaporisation chamber packed with glass helices. Part of the effluent gas (N_2; flow rate 200—400 ml. per min.) was passed through a thermal conductivity detector, but the major portion was passed through two, easily replaceable U-tubes cooled in liquid nitrogen. The greater part of the eluted material was collected in the first U-tube and the remainder (80—90% total recovery) in the second tube, which was filled with glass helices to intercept droplets suspended in the gas stream.

Allyl Halides.—Allyl chloride and bromide were dried over sodium sulphate and purified by fractional distillation through a helix-packed column (3 ft.). Allyl bromide required for measurement of dimer production was further purified by distillation through an electrically heated column (4 ft.) packed with Stedman, stainless-steel gauze cones. Allyl iodide was dried and fractionally distilled under reduced pressure in darkness.

Dibromopropenes.—A mixture of *cis*- and *trans*-1,3-dibromopropene, obtained by the action [10]

[6] Skell, Allen, and Gilmour, *J. Amer. Chem. Soc.*, 1961, **83**, 504.
[7] Karrer and Schneider, *Helv. Chim. Acta*, 1948, **31**, 395.
[8] Bateman, Cunneen, Fabian, and Koch, *J.*, 1950, 936.
[9] Hochanadel and Ghormley, *J. Chem. Phys.*, 1953, **21**, 880.
[10] von Braun and Kühn, *Ber.*, 1925, **58**, 2168.

of phosphoryl chloride on 1,3-dibromopropan-2-ol, was separated by gas–liquid chromatography (column, 2 × 90 cm.; 98°). The strongest infrared absorptions of the two isomers (*cis*, 1616, 1434, 1308, 1215, 1202, and 725 cm.$^{-1}$; *trans*, 1621, 1239, 1200, and 934 cm.$^{-1}$) did not correspond to the spectra reported by Hatch and Harwell,[11] but the bands at 725 cm.$^{-1}$ (:CH· out-of-plane deformation for *cis*-double bond [12]) and 934 cm.$^{-1}$ (*trans*-CH:CHBr[1]) indicate that our stereo-chemical assignments are correct.

3,3-Dibromopropene (infrared absorptions at 1620w, 1410, 1207m, 1145, 977, 937, and 730 cm.$^{-1}$) was prepared by the method of Kirrmann and Renn.[13]

5-Bromo-4-methylpent-1-ene.—2-Methylpent-4-enoic acid [14] (11 g.) in ether (100 ml.) was added, dropwise with stirring, to lithium aluminium hydride (5 g.) in ether (180 ml.) and the whole was boiled for 0·5 hr. After destruction of the excess of hydride with water, 2N-sulphuric acid was added and the layers were separated. The aqueous layer was saturated with sodium chloride and extracted with ether, and the combined ethereal solutions were dried (Na_2SO_4) and evaporated, to yield 2-methylpent-4-en-1-ol (9 g.) which afforded a *3,5-dinitrobenzoate*, m. p. 33—35° (from methanol) (Found: C, 53·4; H, 4·5; N, 9·7. $C_{13}H_{14}N_2O_6$ requires C, 53·1; H, 4·8; N, 9·5%). Phosphorus tribromide (3·4 g.) in benzene (5 ml.) was added to the alcohol
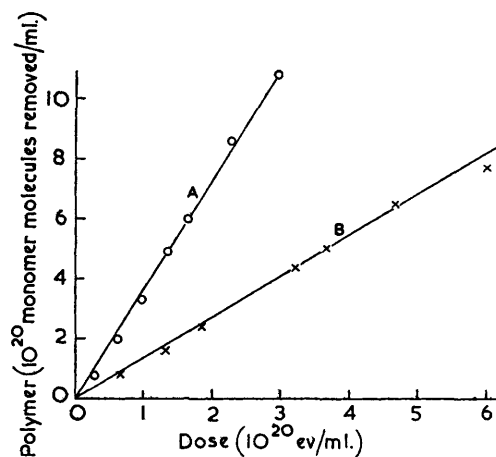
Formation of polymer during irradiation of allyl halides; A, polymer from allyl chloride; B, dimer from allyl bromide.

(3 g.) and dry pyridine (0·5 ml.) in benzene (5 ml.) at such a rate that the temperature did not exceed 10°. The mixture was then set aside for 16 hr., boiled for 7 hr., diluted with ether, and filtered. The filtrate was washed with water and aqueous sodium hydrogen carbonate, dried, and distilled, a fraction of b. p. 30—40°/14 mm. being collected. Fractional distillation of this then yielded *5-bromo-4-methylpent-1-ene* (0·5 g.), b. p. 36°/14 mm., n_D^{18} 1·4658, $\nu_{max.}$ 1644, 1456, 1438, 992, and 912 cm.$^{-1}$ (Found: C, 43·9; H, 6·6; Br, 49·6. $C_6H_{11}Br$ requires C, 44·1; H, 6·75; Br, 49·1%).

1,4-Dibromo-2-bromomethylpentane.—5-Bromo-4-bromomethylpent-1-ene containing a little aluminium bromide was treated with hydrogen bromide and distilled, to give 1,4-dibromo-2-bromomethylpentane, b. p. 90—95°/0·05 mm., n_D^{20} 1·5458 (lit.,[4] n_D^{20} 1·5454).

Reaction of Hexa-1,5-diene with N-Bromosuccinimide.—Carbon tetrachloride (200 ml.) containing hexa-1,5-diene (24 g.), N-bromosuccinimide (62·3 g.), and benzoyl peroxide (0·2 g.) was boiled for 8 hr., filtered, and distilled. The fraction (8 g.) containing monobromo-compounds, b. p. 43—44°/14 mm., was shown by gas–liquid chromatography to consist mainly of two components in the approximate ratio 1 : 3. Chromatography on a larger scale (column, 2 × 90 cm.; 98°) afforded 3-bromohexa-1,5-diene (minor component), $\nu_{max.}$ 1643m, 1420, 985, 920, 738m, and 681m cm.$^{-1}$, and 6-bromohexa-1,4-diene (major component), $\nu_{max.}$ 1660w, 1448m, 1205, 990m, 965, and 915 cm.$^{-1}$.

Irradiation of Allyl Chloride.—Allyl chloride (435 ml.) which had been irradiated for 150 hr.

[11] Hatch and Harwell, *J. Amer. Chem. Soc.*, 1950, **75**, 6002.
[12] Sheppard and Simpson, *Quart. Rev.*, 1952, **6**, 1.
[13] Kirrmann and Renn, *Compt. rend.*, 1936, **202**, 1934.
[14] Bhide and Sudborough, *J. Indian Inst. Sci.*, 1925, **8**, [A], 89; *Chem. Zentr.*, 1926, I, 81.

(total dose ~5·9 × 10²⁰ ev ml.⁻¹) in a stoppered vessel contained no compounds detectable by gas–liquid chromatography (other than starting material) and no chlorine or hydrogen chloride. Removal of monomer by distillation yielded a colourless, viscous *polymer* (120 g.) which did not distil below 200°/0·01 mm. (Found: C, 47·2; H, 5·9; Cl, 46·3%; M, 390. $C_{15}H_{25}Cl_5$ requires C, 47·1; H, 6·5; Cl, 46·4%; M, 383). Samples (approx. 80 ml.) of allyl chloride, which had been distilled under nitrogen, were irradiated for different times at a dose-rate of 2·36 × 10¹⁶ ev ml.⁻¹ min.⁻¹ in sealed ampoules. The amounts of polymer produced were determined by distillation until the residues attained constant weight (Figure).

Irradiation of Allyl Bromide.—Allyl bromide (435 ml.) which had been irradiated for 336 hr. (total dose ~18 × 10²⁰ ev ml.⁻¹) in a stoppered vessel contained no bromine or hydrogen bromide. Gas–liquid chromatograms of the irradiated liquid, obtained at 80° and at 160° with a column of firebrick–tritolyl phosphate, showed nine definite peaks (products 1—9) and a number of base-line irregularities caused by less volatile products; the third peak was caused by allyl bromide. The separation of the compounds responsible for these peaks is next described.

During removal of monomer by distillation, product (1) collected in a trap cooled by liquid nitrogen. It was identified as propene by gas–liquid chromatography on alumina–dioctyl phthalate. Careful redistillation of the recovered monomer afforded a fraction enriched in product (2). This was isolated by gas–liquid chromatography (column, 2·5 × 240 cm.; 20°) and shown to be hexa-1,5-diene by comparison of its infrared spectrum with that of an authentic specimen.

During distillation (at 15 mm.) of the irradiation products (85 g.) less volatile than allyl bromide, a mixture (1·5 ml.) was collected in a cold trap attached to the receiver. Separation by gas–liquid chromatography (column, 2 × 90 cm.; 98°) afforded (*a*) product (4) shown, by comparison of its infrared spectrum with that of an authentic specimen, to be 5-bromo-4-methylpent-1-ene and to be free from 1,2-dibromopropane, 3,3-dibromopropene, and 3-bromo-hexa-1,5-diene (all of which possess similar retention times), (*b*) product (5) shown by its infrared spectrum to be *cis*-1,3-dibromopropene, and (*c*) product (6), the infrared spectrum of which indicated that it was a mixture of *trans*-1,3-dibromopropene and 1,3-dibromopropane. Treatment of product (6) with bromine, and further chromatography afforded pure 1,3-dibromopropane.

The largest fraction obtained by distillation of the irradiation products was a slightly impure (96%) dimer of allyl bromide, 5-bromo-4-bromomethylpent-1-ene [product (8)], b. p. 93—95°/15 mm., n_D^{20} 1·5260 (lit.,[4] b. p. 93—95°/15 mm., n_D^{20} 1·5256). On treatment with bromine it yielded 1,2,5-tribromo-4-bromomethylpentane, n_D^{20} 1·5907 (lit.,[4] n_D^{20} 1·5909) and it reacted with N-sodiophenylhydrazine to give 4-allyl-1-phenylpyrazolidine which afforded a picrolonate, m. p. 185° (lit.,[4] m. p. 186—187°). The dimer fraction contained small quantities of products (7) and (9) which could not be removed by distillation, but treatment of the mixture with an excess of bromine, followed by gas–liquid chromatography, showed that product (7), like the dimer, was unsaturated. Product (9) was unaffected by bromine and corresponded in retention time to 1,2,3-tribromopropane; it was isolated by distillation (b. p. 60°/0·5 mm.) followed by gas–liquid chromatography (column, 1·5 × 45 cm.; 130°) and shown by its infrared spectrum to be 1,2,3-tribromopropane.

The residual irradiation products, after removal of the dimer fraction, were subjected to short-path distillation which afforded two liquid fractions and a black, solid residue (Found: Br, 26·4%). The first liquid fraction, after redistillation, was almost pure 1,4-dibromo-2-bromomethylpentane, b. p. 90°/0·5 mm., n_D^{20} 1·5461, whose infrared spectrum was identical with that of an authentic specimen. The second liquid fraction was probably a *trimer*, b. p. 140° (bath-temp.)/0·1 mm., n_D^{20} 1·5540 (Found: C, 29·5; H, 3·9; Br, 66·7. $C_9H_{15}Br_3$ requires C, 29·8; H, 4·1; Br, 66·8%).

Allyl bromide was also irradiated (dose-rate, 3·31 × 10¹⁶ ev ml.⁻¹ min.⁻¹) in sealed ampoules under the conditions described for the chloride. Samples (5 ml.) of the irradiated solutions were added to standard solutions (1 ml.) of *o*-dichlorobenzene in chloroform, and the resulting mixtures were examined by gas–liquid chromatography on kieselguhr–silicone elastomer. The concentrations of dimer were estimated by comparing the ratio, dimer peak height : *o*-dichlorobenzene peak height, with the same ratio found for chloroform solutions containing known concentrations of both compounds. The results are presented in the Figure.

Irradiation of Allyl Iodide.—Allyl iodide (55 ml.) was irradiated for 160 hr. (total dose

$\sim$18·3 $\times$ 10^{20} ev ml.$^{-1}$) in a stoppered vessel and had then become red owing to dissolved iodine. Gas–liquid chromatography failed to detect any volatile compounds other than starting material and a trace of hexa-1,5-diene. Evaporation yielded a small amount of dark viscous residue.

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