172. *The Chemical Effects of γ-Radiation on Organic Systems. Part VIII.*[1] *The Radiolysis of Allyl Phenyl Ether and Certain Other Ethers.*

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γ-Radiolysis of allyl phenyl ether yields phenol and a polymer as the main products, together with smaller amounts of acraldehyde, *o*-allylphenol, and very minor amounts of hexa-1,5-diene, propene, acetylene, and propadiene or propyne. This suggests that phenoxy- and allyl radicals are the main, primary products of radiolysis. Benzyl phenyl ether is also sensitive to radiation, but anisole, phenetole, and phenyl n-propyl ether are much more stable, yielding much less phenol.

EXTENSIVE investigations on the action of ionising radiation on aliphatic ethers have been carried out by Newton[2] and by Bakh and her collaborators,[3] who measured the yields of

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[1] Part VII, preceding paper.

[2] Newton, *J. Phys. Chem.*, 1957, **61**, 1485, 1490.

[3] Bakh, Medvedorsky, and Saraeva, Proc. 2nd United Nations Conference on the Peaceful Uses of Atomic Energy, 1958, Vol. XXIX, 128.

carbonyl compounds, alcohols, and peroxides formed. We are, however, unaware of work on the radiolysis of phenolic or unsaturated ethers, except for ethyl vinyl ketone studied by Murad.[4] We found that γ-radiolysis of anisole, ethyl phenyl ether, or phenyl n-propyl ether yielded phenol with *G* values of ∼0·7; but that allyl phenyl ether, benzyl phenyl ether, and cinnamyl phenyl ether gave phenol with *G* values of ∼3. We distilled irradiated allyl phenyl ether and by gas chromatography showed the first part of the distillate to contain acraldehyde, which we confirmed by preparation of the 2,4-dinitrophenylhydrazone. On the assumption that acraldehyde was the only carbonyl compound produced, we estimated it spectrophotometrically as the 2,4-dinitrophenylhydrazone. Two series of experiments were carried out: in one, the ether was irradiated in sealed, evacuated bulbs and in the other in glass-stoppered flasks, without rigorous exclusion of oxygen. In each the aldehyde was estimated after different doses, and the phenol formed was also determined spectrophotometrically, by using Folin's reagent.

Time of irradiation (hr.)	Dose (10^{20} ev/ml.)	*G* (acraldehyde)		*G* (phenol)	
		Non-evacuated	Evacuated	Non-evacuated	Evacuated
24	1·04	0·265	0·168	2·73	3·02
48	2·08	0·145	0·20	2·97	2·80
96	4·16	0·061	0·10	2·54	2·60
24 (unstoppered)	1·04			2·73	

As seen from the Table, acraldehyde is only a minor product, compared with phenol. According to Bakh *et al.*,[3] in the radiolysis of isopropyl ether carbonyl compounds are initially formed with *G* values of ∼25 and 10, in the presence and absence of oxygen, respectively, but the latter value rapidly decreases on prolonged irradiation to ∼2, which is in closer agreement with values obtained by Newton.[2] They found that the yields of carbonyl compounds were highly sensitive to the presence of impurities, especially carbonyl compounds, and concluded that the rapid decrease of *G* values of carbonyl compounds with increasing dose of radiation was caused by accumulation of these compounds, which interacted with intermediate radicals. Production of aldehydes in ethers irradiated in the presence of air almost certainly involves peroxide-radical intermediates and the yield arising from such processes falls off rapidly with consumption of the oxygen available. In the absence of oxygen, aldehydes might be formed by C–O bond-fission, so that allyl phenyl ether might undergo radiolysis to a minor extent to give phenyl and allyloxy-radicals. Campbell and Coppinger[5] showed that thermal decomposition of allyl t-butyl peroxide yields t-butyl alcohol and acraldehyde, the latter assumed to be formed by disproportionation of the intermediate allyloxy-radicals.

On the other hand, the radiolytic loss of a hydrogen atom from the methylene group α to the oxygen atom might be expected (cf. an analogous reaction in the alcohols[6] and amines[7]), and the resulting organic radical could then decompose to acraldehyde and a phenyl radical.

The yield of phenol obtained on radiolysis of allyl phenyl ether is almost independent of the presence of oxygen, rupture of the O–allyl bond to give phenoxy- and allyl radicals being apparently the major, primary step in the radiolysis. Alcohol-production from aliphatic ethers is said to increase three-fold in the presence of oxygen.[3]

In view of the very low yield of acraldehyde relative to phenol, we were led to search for products arising from the allyl radical. Allyl phenyl ether was irradiated in sealed, evacuated bulbs and the gaseous or very volatile products were then fractionated and examined mass-spectrometrically. The major very volatile products were hexa-1,5-diene, propene, and carbon dioxide, with smaller quantities of propadiene or propyne and acetylene. Quantitatively these compounds were quite insignificant, their combined *G*

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[4] Murad, *J. Amer. Chem. Soc.*, 1961, **83**, 1327.

[5] Campbell and Coppinger, *J. Amer. Chem. Soc.*, 1951, **73**, 1788.

[6] Swan and Wright, *J.*, 1958, 4673.

[7] Swan, Timmons, and Wright, *J.*, 1959, 9.

value being perhaps 0·0025, but the formation of hexa-1,5-diene confirms the primary formation of allyl radicals.

Szwarc, Ghosh, and Sehon [8] showed that allyl radicals, formed by pyrolysis of allyl bromide at 500°, can dimerise, react with other radicals, or abstract hydrogen from toluene. McNesby and Gordon [9] concluded that allyl radicals were less reactive than most radicals, as a result of resonance stabilisation. Although allyl radicals have been shown to abstract hydrogen atoms very poorly below 400°, they do so quite well at about 500°. It therefore seems likely that the allyl radicals produced during the radiolysis of allyl phenyl ether will tend to react in other ways, rather than take part in hydrogen abstraction; and this is supported by the extremely low yield of propene. Propadiene might arise from allyl radicals, although Ruzicka and Bryce [10] failed to detect its formation on pyrolysis of hexa-1,5-diene.

Having thus shown that only insignificant amounts of volatile products arise from the allyl radicals, we concluded that the latter must react mainly with the allyl phenyl ether itself, either in the benzene nucleus or in the allyl group. We therefore distilled the unchanged ether from an irradiated sample, but failed to detect the presence of allyl *o*-allylphenyl ether in the residue, which was a dark viscous liquid (*G* 2·5, based on mol. wt. 174), which yielded three fractions with boiling points within the range 130—280°/0·3 mm., the greater part, however, being undistillable. The infrared spectra of the various fractions were very similar to one another and showed very few important differences from the spectrum of allyl phenyl ether, except for the presence of hydroxyl peaks. There was no evidence of further substitution in the benzene nucleus. The molecular weights of the distilled fractions, calculated on the uptake of hydrogen in the presence of palladium–charcoal and on the assumption of one reducible double bond per molecule, are as follows: Fraction, b. p. 130—170°/0·3 mm., *M* 150; b. p. 170—220°/0·3 mm., *M* 170; b. p. 220—280°/0·3 mm., *M* 240. The fractions were progressively less soluble in ethanol, so that ethyl acetate had to be used as solvent for the hydrogenation of the third one. The infrared spectra of these fractions showed no evidence of the presence of groups of the type $R{\cdot}CH{:}CHR$, with characteristic strong absorption [11] at 965 cm.$^{-1}$, except for the one of lowest boiling point which gave a small peak at 955 cm.$^{-1}$. The ultraviolet spectrum of the last-mentioned fraction showed absence of conjugation in the side chain.

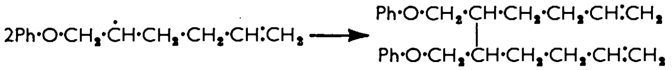
We therefore suggest that the major, primary step in the radiolysis:

$$Ph{\cdot}O{\cdot}CH_2{\cdot}CH{:}CH_2 \rightsquigarrow Ph{\cdot}O{\cdot} + {\cdot}CH_2{\cdot}CH{:}CH_2$$

is followed by attack of the double bond of the ether by the allyl radical:

$$Ph{\cdot}O{\cdot}CH_2{\cdot}CH{:}CH_2 + {\cdot}CH_2{\cdot}CH{:}CH_2 \longrightarrow Ph{\cdot}O{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2$$

The resulting radical might dimerise:



$$2Ph{\cdot}O{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2 \longrightarrow \begin{array}{l} Ph{\cdot}O{\cdot}CH_2{\cdot}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2 \\ \qquad\qquad\quad | \\ Ph{\cdot}O{\cdot}CH_2{\cdot}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2 \end{array}$$

The addition of allyl radicals to alkenes is already known.[12] The percentage of carbon and hydrogen in the product agrees with the values for the " polymer " before fractionation and the yields of phenol and " polymer " give a good material balance on this basis. Also, the hydrogen uptake by the two fractions of lower boiling point are in reasonable agreement with the expected values. However, the " polymer " appears to be more complex in nature than is indicated above, unless its apparent complexity is due to decomposition during attempted distillation. Various side-reactions seem possible during the

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[8] Szwarc, Ghosh, and Sehon, *J. Chem. Phys.*, 1950, **18**, 1142.

[9] McNesby and Gordon, *J. Amer. Chem. Soc.*, 1957, **79**, 4593.

[10] Ruzicka and Bryce, *Canad. J. Chem.*, 1960, **38**, 827.

[11] Bateman, Cunneen, Fabian, and Koch, *J.*, 1950, 936.

[12] Bryce and Ruzicka, *Canad. J. Chem.*, 1960, **38**, 835.

radiolysis, such as attack of the double bond of another ether molecule by the radical $Ph\cdot O\cdot CH_2\cdot\dot{C}H\cdot CH_2\cdot CH_2\cdot CH{:}CH_2$. This radical might also cyclise through attack of the radical on its own double bond, giving a substituted cyclopentyl radical which could then undergo further reaction such as dimerisation (cf. Whitmore and Gerecht [13]).

One reason why we originally decided to study the radiolysis of allyl phenyl ether was to find whether the Claisen shift might be induced radiolytically. We therefore examined the phenol formed for the presence of *o*- or *p*-allylphenol. In preliminary experiments, we separated a mixture of phenol and *o*-allylphenol by distribution between 30% sodium hydroxide solution and ether, almost all the former passing into the aqueous layer, while the ethereal layer yielded almost pure *o*-allylphenol, with some loss (cf. Schmid and Schmid,[14] Vavon and Zaharia [15]). *p*-Allylphenol behaved similarly to its *o*-isomer. It was also possible to separate a mixture of all three phenols by paper chromatography, by the general method of Chang, Hossfeld, and Sandstrom,[16] and this method was applied to the fractions obtained by the distribution method. We thus showed that irradiation of allyl phenyl ether yielded, not only phenol, but also *o*-allylphenol (*G* 0·044) and possibly a trace of *p*-allylphenol. The normal Claisen rearrangement is intramolecular and involves a cyclic intermediate; the migrating allyl group enters the *ortho*-position, if the latter is unoccupied. Kharasch, Stampa, and Nudenberg [17] have reported that photolysis of allyl phenyl ether gives a mixture of phenol and *p*-allylphenol, and a similar *para*-migration by a radical mechanism in the case of 2,6-dimethylphenol has been demonstrated by Schmid and Schmid.[14] In the radiolysis, the migration might be intramolecular. On the other hand, as allyl radicals and mesomeric oxyphenyl radicals are believed to be present, *o*-allylphenol might be formed by combination of these, which seems likely in view of the low yield. A tracer experiment would be required to distinguish between these two mechanisms. The presence of hydroxyl peaks in the infrared spectrum of the irradiation " polymer " may suggest the incorporation of some *o*-allylphenol into the " polymer." Although such *ortho*-substitution is not clear from the 700 $cm.^{-1}$ region of the spectrum, a band occurs at 1630 $cm.^{-1}$.

We also wished to investigate the radiolysis of diallyl ether, but we found this compound to undergo autoxidation so readily that it was difficult to detect true radiolysis products.

Irradiation of benzyl phenyl ether gave phenol (*G* 3) and a high-boiling residue, thought to consist of a mixture of benzylphenols and benzyl benzylphenyl ethers. A residue, which could not be distilled, possibly consisted of a dimer formed by radical formation at the methylene group (cf. refs. 6 and 18). Homolysis of benzyl phenyl ether to benzyl and phenoxy-radicals by thermal decomposition is already known.[19]

EXPERIMENTAL

Arrangements for the irradiations and dosimetry were as described in Part I.[20] Allyl phenyl ether [21] was washed several times with 10% sodium hydroxide solution, dried, and fractionated.

Detection and Estimation of Acraldehyde in Irradiated Allyl Phenyl Ether.—The ether (50 ml.) was irradiated for 168 hr. (total dose $4{\cdot}24 \times 10^{22}$ ev), then distilled, the first 2 ml. of distillate being collected in an ice-cooled receiver. By gas chromatography over Silicone fluid (30% by

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[13] Whitmore and Gerecht, *J. Amer. Chem. Soc.*, 1950, **72**, 790.

[14] Schmid and Schmid, *Helv. Chim. Acta*, 1953, **36**, 687.

[15] Vavon and Zaharia, *Compt. rend.*, 1928, **187**, 346.

[16] Chang, Hossfeld, and Sandstrom, *J. Amer. Chem. Soc.*, 1952, **74**, 5766; Hossfeld, *J. Amer. Chem. Soc.*, 1951, **73**, 852.

[17] Kharasch, Stampa, and Nudenberg, *Science*, 1952, **116**, 309.

[18] Huang and Yeo, *J.*, 1959, 3190.

[19] Elkobaisi and Hickinbottom, *J.*, 1960, 1286.

[20] Swan and Timmons, *J.*, 1958, 4669.

[21] " Organic Reactions," Wiley, New York, 1944, Vol. II, p. 26.

wt.) on Celite 525, this was shown to contain ~10% of acraldehyde. It was redistilled, the first few drops of distillate being collected in aqueous 2,4-dinitrophenylhydrazine hydrochloride solution. The resulting precipitate (8 mg.; m. p. 155°) was chromatographed on alumina, elution with benzene yielding orange-red crystals, m. p. 165° (3·6 mg.), shown by mixed m. p. and ultraviolet spectrum in ethanol ($\lambda_{max.}$ 235, 242, 252, 282, and 365 mμ; log ε 4·21, 4·20, 4·18, 3·98, and 4·47) to be acraldehyde 2,4-dinitrophenylhydrazone.

The aldehyde was estimated by Johnson and Scholes's method.[22] Water (10 ml.) and 2 ml. of the reagent (1 g. of 2,4-dinitrophenylhydrazine in 200 ml. of water and 200 ml. of 60% perchloric acid) were pipetted into a separatory funnel. The allyl phenyl ether being examined (1 ml.) was then added and the mixture was shaken and set aside for 30 min. Carbon tetrachloride (20 ml.) was then added and the mixture shaken for 1 min. The lower layer was run off into a 50-ml. graduated flask. Further carbon tetrachloride (5 ml.) was added to the separatory funnel, the mixture shaken for 30 sec., and the lower layer was run off into the graduated flask. The volume was made up to 50 ml. with ethanol and the absorption of the solution was measured at 360 mμ. The absorption of acraldehyde 2,4-dinitrophenylhydrazone having been measured, it was possible to calculate the yield of acraldehyde. For determination of the yields of aldehyde and phenol given, 14 ml. samples of the ether were irradiated.

Estimation of Phenol in Irradiated Allyl Phenyl Ether.—The ether being examined (1 ml.) was pipetted into a separatory funnel containing diethyl ether (10 ml.). The resulting solution was extracted with 0·1N-sodium hydroxide (3 × 3 ml.), and the alkaline extracts were made up to 10 ml. with distilled water. An aqueous solution of phenol (0·026 mg./ml.) was used as a standard and a series of solutions of different concentrations were obtained by dilution of this solution with one of sodium carbonate (2%) in 0·1N-sodium hydroxide. A series of these standards was run alongside each estimation from irradiated or control material; Folin's reagent [23] was added to each solution, after which they were kept at 40° for 20 min., then the optical densities at 750 mμ were measured. A graph of optical density against phenol concentration enabled the concentration of phenol in the irradiated ether to be determined. Measurements were made in duplicate. Similar measurements were made on anisole (14 ml.) which had been irradiated (*a*) in an evacuated, sealed bulb and (*b*) in an open flask (dose $1{\cdot}04 \times 10^{20}$ ev/ml.), the *G* values for phenol obtained being (*a*) 0·64 and (*b*) 0·69.

Investigation of Volatile Products of the Radiolysis of Allyl Phenyl Ether.—The ether (11 ml.) was irradiated for 96 hr. (total dose $4{\cdot}55 \times 10^{21}$ ev) in an evacuated, sealed bulb provided with a break-seal. The seal was then broken under a high vacuum and the volatile products were condensed in a trap cooled in liquid nitrogen. This bath was then replaced by one of carbon dioxide–ethanol, and the material then volatilising was condensed in another trap cooled by liquid nitrogen, yielding fraction A. Distillation of the residue in the trap (−78°) from −30° to −78° gave fraction B, and again from 0° to −30° gave fraction C. Each of these fractions was examined mass-spectrometrically. Fraction A consisted of 0·26 ml. of gas at N.T.P. (*i.e.*, ~0·5 mg., or total *G* ~0·0017) containing propene (37%), propadiene or propyne (15%), acetylene (10%), and carbon dioxide (38%). Fraction B was much smaller still and contained nothing organic. Fraction C was approximately equal in amount to A and its cracking pattern corresponded fairly closely with that of hexa-1,5-diene, with one or two discrepancies, suggesting the presence of at least one other component.

Isolation of the Major Products of the Radiolysis of Allyl Phenyl Ether.—The ether (275 ml.) was irradiated for 216 hr. (total dose $2{\cdot}67 \times 10^{23}$ ev), then extracted with 10% sodium hydroxide solution, washed with water, and dried. The unchanged ether was removed under reduced pressure and the residue was washed with 10% sodium hydroxide solution, followed by water, then dried and distilled. Some unchanged ether was followed by a brownish liquid, b. p. 100—110°/1 mm. (0·05 g.), the infrared spectrum of which resembled that of allyl *o*-allylphenyl ether, but contained, in addition, two strong hydroxyl bands. The residue was an extremely viscous, brown liquid (1·95 g.) (Found: C, 82·0; H, 8·8. Calc. for $C_{12}H_{15}O$: C, 82·3; H, 8·6%) which was distilled from bulbs at 0·3 mm., fractions of the following bath-temperature being collected: 130—170° (100 mg.), 170—220° (50 mg.), and 220—280° (250 mg.); a dark, extremely viscous residue remained.

The original, alkaline extract was acidified and extracted with ether. Distillation of the

[22] Johnson and Scholes, *Analyst*, 1954, **79**, 217.

[23] Snell and Snell, "Colorimetric Methods of Analysis," van Nostrand, New York, 1937, Vol. II, p. 348.

extract yielded: (*a*) a colourless liquid, b. p. 80°/15 mm. (0·8 g.), which crystallised and proved to be phenol and (*b*) a colourless liquid, b. p. 110°/15 mm. (0·23 g.), the infrared spectrum of which suggested that it was a mixture of phenol and *o*-allylphenol.

Further Investigation of the Phenolic Products of the Radiolysis of Allyl Phenyl Ether.—(*a*) The ether (64 ml.), which had been irradiated for 168 hr. (total dose 5·5 × 10^{22} ev), was extracted with 10% sodium hydroxide solution. The extract was acidified and extracted with ether. The ethereal extract was extracted with 30% sodium hydroxide solution (1 × 10 and 3 × 5 ml.), leaving an ethereal layer (A). These alkaline extracts were acidified and extracted with ether, the ethereal extract being B. Solutions A and B were dried and the solvent was removed. From A was obtained a yellow liquid which was kept overnight with 3,5-dinitrobenzoyl chloride in benzene–pyridine and thus afforded a gum which eventually solidified and gave, from benzene–light petroleum (b. p. 40—60°), pale yellow crystals (10 mg.), m. p. and mixed m. p. with *o*-allylphenyl 3,5-dinitrobenzoate 65°. Solution B yielded a brown liquid (280 mg.) which similarly afforded pale yellow crystals of phenyl 3,5-dinitrobenzoate, m. p. 144°.

(*b*) The ether (275 ml.) was irradiated for 336 hr. (total dose 3·65 × 10^{23} ev) and extracted as in (*a*), the extraction with 10% sodium hydroxide solution being carried out ten times, each with 20 ml. of solution, and that with 30% sodium hydroxide four times, each with 15 ml. Extract A yielded a residue of 36 mg. and B gave 1·88 g.

These phenolic fractions were coupled with diazotised sulphanilic acid, and the resulting azo-dyes were subjected to paper chromatography in the way described by Chang, Hossfeld, and Sandstrom and by Hossfeld.[16] Preliminary experiments showed that phenol, *o*-allylphenol, and *p*-allylphenol could be thus easily separated, affording yellow, orange, and pink spots of R_F 0·22, 0·63, and 0·89, respectively. In this way, residue A was shown to be almost pure *o*-allylphenol, containing possibly a trace of the *para*-isomer, and residue B was phenol, containing some *o*-allylphenol.

In an experiment in which allyl phenyl ether (275 ml.) was kept for 336 hr. in the dark, without irradiation, extraction with 10% sodium hydroxide solution afforded a material (33 mg.), shown by paper chromatography to be phenol.

Irradiation of Benzyl Phenyl Ether.—Benzyl phenyl ether was washed exhaustively with 4% sodium hydroxide solution, then with water, dried, and fractionated, the fraction of b. p. 124—126°/1 mm. being re-fractionated; in the second distillation material of b. p. 120°/0·8 mm. was collected. This ether (275 ml.) was irradiated for 504 hr. (total dose 6·17 × 10^{23} ev) at 45°, then dissolved in diethyl ether and extracted first with 10% sodium hydroxide solution (5 × 20 ml.), then with 4% sodium hydroxide solution (5 × 20 ml.), washed with water, and dried. The unchanged ether was removed under reduced pressure and the residue was distilled, affording fractions (all b. p./0·3 mm.): (1) 120—150° (1·21 g.), (2) 150—180° (0·62 g.), (3) 180° (0·58 g.), (4) 180—190° (1·37 g.), (5) 190—220° (0·47 g.), (6) >220° (0·45 g.). The infrared spectra of these fractions were very similar; all contained hydroxyl peaks (3535 and 3400 cm.$^{-1}$), weakest in fractions (4) and (particularly) (5).

The sodium hydroxide extracts were acidified and extracted with ether, yielding phenol, b. p. 78°/16 mm. (2·91 g.), a pale yellow liquid, b. p. 120—220°/0·1 mm. (0·11 g.), and a black residue (0·26 g.).

After this work had been carried out we read Elkobaisi and Hickinbottom's paper, in which the purification of benzyl phenyl ether is discussed.[24]

Dimer of 1*H-Benzopyran.*—We investigated the radiolysis of 1*H*-benzopyran [25] (a cyclic analogue of allyl phenyl ether), but purification of the small amount of phenolic product was difficult. A very small amount of a yellow, fluorescent compound, m. p. 122—123°, with strong absorption at 285 and 342·5 mμ, was isolated. The benzopyran which had been irradiated and then washed with 10% sodium hydroxide solution was recovered largely unchanged on distillation, but the residue, when chromatographed on alumina, yielded a colourless *dimer*, m. p. 184—185°, from ether (Found: C, 81·6; H, 6·6%; *M*, 244. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·05%; *M*, 264). The spectrum of this in ethanol [$\lambda_{max.}$ 228·5 and 277·5 mμ (log ε 3·86 and 3·72); $\lambda_{min.}$ 246 mμ (log ε 2·74)] resembled that of chroman [25] [$\lambda_{max.}$ 228·5, 277·5, and 284 mμ (log ε 3·37, 3·22, and 3·17), $\lambda_{min.}$ 244 mμ (log ε 1·96)] much more closely than that of benzopyran [$\lambda_{max.}$ 232, 267, and 310 mμ (log ε 3·55, 3·57, and 3·46), $\lambda_{min.}$ 242·5 and 285·5 mμ (log ε 3·17 and 3·12)]. The dimer was insoluble in aqueous alkali, gave no colour with ferric chloride, and was not

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[24] Elkobaisi and Hickinbottom, *J.*, 1959, 1873.

[25] Normant and Maitte, *Compt. rend.*, 1952, **234**, 1787; Maitte, *Ann. Chim.* (*France*), 1954, **9**, 431.

unsaturated towards bromine in carbon tetrachloride. Chroman and dibenzo[*b*,*d*]pyran,[26] when irradiated, yielded very little phenolic material.

1,6-*Di*-p-*methoxyphenylhexa*-1,3-*diene*.—We were led to synthesise this compound by the possibility that 1,6-di-*o*-hydroxyphenylhexa-1,3-diene might arise by the radiolysis of 1*H*-benzopyran. 3-*p*-Methoxyphenylpropyl bromide [27] (2·5 g.) in ether (20 ml.) was added gradually to a stirred suspension of magnesium (0·27 g.) in ether (10 ml.). When reaction was complete, 4-methoxycinnamaldehyde (1·85 g.) in ether (20 ml.) was added gradually and the mixture was refluxed for 30 min., cooled, treated with 30% sulphuric acid (15 ml.), and refluxed for 20 min. The ethereal layer was separated and the aqueous layer was extracted with ether (2 × 10 ml.). The combined ethereal extracts were washed with water, 5% sodium hydroxide solution, saturated ammonium chloride solution, and finally water. The residue left on evaporation of the dried extract crystallised from methanol (charcoal) as pale, yellow plates, m. p. 122—125°, of the *diene*, which separated from light petroleum (b. p. 60—80°) as colourless plates, m. p. 126—127° (2·5 g.) (Found: C, 81·3; H, 7·35. $C_{20}H_{22}O_2$ requires C, 81·6; H, 7·5%), $\lambda_{max.}$ 220 and 292 mμ (log ε 4·47 and 4·74), $\lambda_{min.}$ 243 mμ (log ε 3·71). 1-*p*-Methoxyphenylbuta-1,3-diene has $\lambda_{max.}$ 220, 284, and 291 mλ (log ε 4·20, 4·54, and 4·54).[28]

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[26] Cavill, Dean, Keenan, McGookin, Robertson, and Smith, *J.*, 1958, 1545.
[27] Zanden, *Proc. Acad. Sci. Amsterdam*, 1937, **40**, 706.
[28] Braude, Jones, and Stern, *J.*, 1947, 1087.