407. *Liquid-phase Photolysis. Part III.* Isomerisation of Benzene and Some Benzene Derivatives to Fulvenes.*

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Ultraviolet irradiation of benzene at 55° under nitrogen produces a partial isomerisation to fulvene, apparently associated with $B_{2u} \longleftarrow A_{1g}$ excitation, and irreversible under a variety of conditions. The identity of fulvene has been established both spectroscopically and through the crystalline adducts with maleic anhydride. Analogous isomerisations have been observed with toluene, isopropylbenzene, and anisole.

ALTHOUGH several previous investigations have led to the conclusion that pure benzene is unaffected by ultraviolet radiation in the range of quartz transmission, a number of workers have observed a change when benzene in an organic glass is irradiated at the boiling point of nitrogen. For instance, Gibson, Blake, and Kalm [1] irradiated benzene in E.P.A. glass (a mixture of ether, isopentane, and ethanol) and observed absorption maxima in the spectrum of the melted glass which they attributed (unjustifiably, we suggest: see below) to the presence of hexa-1,3,5-triene. Rather surprisingly, no change was detected when this irradiation was conducted in the liquid phase at room temperature. Norman and Porter [2] recorded similar maxima in the spectra of irradiated glasses before melting. Ingram, Hodgson, Parker, and Rees,[3] using a paramagnetic resonance technique, found evidence for the formation of " trapped " free radicals in similar unmelted glasses. Leach and his co-workers [3a] have also investigated these effects.

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* Part II, *J.*, 1960, 1788.

[1] Gibson, Blake, and Kalm, *J. Chem. Phys.*, 1953, **21**, 1000.

[2] Norman and Porter, *Proc. Roy. Soc.*, 1955, *A*, **230**, 399.

[3] Ingram, Hodgson, Parker, and Rees, *Nature*, 1955, **176**, 1227.

[3a] Leach, *J. Chim. phys.*, 1954, **51**, 556; Leach and Migirdicyan, *ibid.*, 1957, **54**, 643; Leach, Migirdicyan, and Grajcar, *ibid.*, 1959, **56**, 749.

As mentioned in a preliminary report[4] we have observed that ultraviolet irradiation of benzene under nitrogen at 50—60° produces a partial isomerisation to fulvene. This appears to be the first example of the direct isomerisation of an aromatic to a non-aromatic hydrocarbon.

Irradiated benzene is yellow. Fractional distillation gives a yellow fraction, b. p. 80°, which has been found to contain up to 0·3 gram of fulvene per litre. Solutions of higher concentration have been obtained by fractional freezing; but complete separation from benzene has not been achieved, and has not proved necessary for identification of the product. The increased tendency for irradiated fulvene to polymerise as its concentration increases hinders the direct production of more concentrated solutions. Even for such small degrees of conversion it was necessary to keep the inner surface of the quartz cell optically clean by continuous rubbing during the irradiation. Previous failures to observe the isomerisation have probably arisen from the ready formation of relatively opaque material, presumably polymeric, on cell walls (cf., *e.g.*, Norman and Porter[2]).

The fulvene was identified both spectroscopically and through the adducts with maleic anhydride. The ultraviolet spectrum of fulvene in benzene solution was observed differentially against pure benzene. It quantitatively resembled that recorded by Thiec and Wiemann[5] for material prepared from cyclopentadiene and formaldehyde, although the zone of transparency between 265 and 310 mμ which these authors reported to exist for freshly distilled material, and to disappear after three days at —70° in an inert atmosphere, was not observed with either fresh or stale solutions.

The present solutions were decolorised when heated under reflux with maleic anhydride, and the acid formed by hydrolysis of the adduct was isolated. Elemental analyses and equivalent were consistent with the formula $C_6H_6,C_4H_4O_4$. Its identity with material prepared similarly from a solution of authentic fulvene (from cyclopentadiene and formaldehyde[6]) was confirmed by mixed m. p.s and infrared spectra.

The behaviour of the present isomerised material towards various reagents was very similar to that of a solution of authentic fulvene. Thus, both were strongly unsaturated towards bromine in carbon tetrachloride and aqueous potassium permanganate. They were instantly decolorised by piperidine and diethylamine, and more slowly by methylamine, benzylamine, or alcoholic sodium hydroxide, but were unaffected by triethylamine, pyridine, aniline, or mono- or di-methylaniline, except after long storage.

Toluene, isopropylbenzene, and anisole also formed small proportions of yellow compounds when irradiated. Although these cases have been examined in less detail than that of benzene, there seems little doubt that methyl-, isopropyl-, and methoxy-fulvene were produced, presumably as mixtures of isomers. The yellow products were unsaturated to bromine in carbon tetrachloride, and co-distilled with the parent compounds. Their ultraviolet spectra were of the fulvene type, although for the methoxy-compound the characteristic fulvene absorption at *ca.* 360 mμ was displaced to 325 mμ.

On the other hand, the following compounds failed to give detectable amounts of isomers on irradiation: biphenyl, naphthalene, pyridine, thiophen, phenol, nitrobenzene, chlorobenzene, benzyl chloride, benzoic acid, ethyl benzoate, salicylaldehyde. In particular, naphthalene gave no benzofulvene or azulene, benzyl chloride gave no tropylium chloride, and benzoic acid and salicylaldehyde gave no tropolone. Chlorobenzene and benzyl chloride suffered considerable decomposition to complex products which have not yet been investigated, and all of the above compounds suffered some degree of change. The behaviour of iodobenzene has already been detailed.[7]

With some of the above compounds, the apparent failure to isomerise may probably be attributed to poor overlap between their absorption regions and the spectrum of emission

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[4] Blair and Bryce-Smith, *Proc. Chem. Soc.*, 1957, 287.

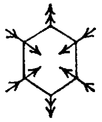
[5] Thiec and Wiemann, *Bull. Soc. chim. France*, 1956, 177.

[6] Angus and Bryce-Smith, *J.*, 1960, 1409.

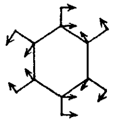
[7] Blair and Bryce-Smith, *J.*, 1960, 1788.

from the mercury lamp. In the case of benzene there is marked overlap between the so-called *B*-bands in the 250—260 mμ region and the strong mercury emission at 254 mμ. The only other possible region of useful overlap would involve the far ultraviolet bands of benzene near 183 mμ and the intense mercury emission around 185 mμ which is on or beyond the transmission limit of most specimens of fused quartz. Removal of radiation below 200 mμ by means of a filter still led to the production of fulvene in the expected amount. It is therefore probable that the present isomerisation is specifically associated with absorption in the *B*-band region of the benzene spectrum.*

Garforth, Ingold, and Poole [8] have shown that absorption in this region arises from forbidden transitions of the $B_{2u} \longleftarrow A_{1g}$ type following in-plane structural deformations of the skeleton of type (a). In the B_{2u} state, the electron wave-function symmetry will be



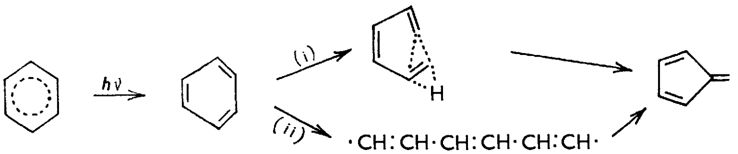
(a)



(b)

lower than in the A_{1g} ground state. Vertical $B_{2u} \longleftarrow A_{1g}$ transitions may be expected to produce excited molecules having relatively high vibrational energies whose equilibrium configuration will be subject to deformations of type (b). Kekulé-type structures will be approached at vibrational extremes. The evidence suggests that a benzene molecule may be excited to a B_{2u} state, or a state derived by transition therefrom, having vibrational energy sufficiently high to result in bond rupture. The quantum of radiation energy in the 260 mμ region is *ca.* 112 kcal. per mole. This, in principle, is more than sufficient to rupture a C–C bond. The apparatus was not specifically designed for measurement of the quantum yield, but calculations indicated an approximate value of 0·01.†

The question next arises whether the transformation to fulvene occurs directly, with the synchronous intramolecular shift of a hydrogen atom [scheme (i)], or whether a free hexatrienyl diradical is formed, which subsequently ring-closes to fulvene [scheme (ii)]. Both schemes imply considerable bond localisation in the fulvene precursors, but the experimental evidence does not yet allow a clear distinction to be drawn. Thus, the reports [1,2] that hexa-1,3,5-triene is formed when benzene in E.P.A. glass is irradiated are consistent with scheme (ii), the free hexatrienyl diradicals abstracting hydrogen atoms from the medium. Unfortunately the physical properties of the substance regarded by Gibson, Blake, and Kalm [1] as hexa-1,3,5-triene differ from those previously reported for this compound by Woods and Schwartzman.[9] The ultraviolet spectra were similar in structure, although that of the photolysis product was shifted *ca.* 7·5 mμ towards longer wavelengths. A more serious difficulty arises from Gibson, Blake, and Kalm's report that their photolysis product could be completely separated from benzene by distillation



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* We found no fulvene formation, or other detectable change, when benzene under nitrogen in a Pyrex tube was exposed to a 2 × 10^6 Röntgen dose of *X*-rays from a copper target: the tube itself was considerably blackened.

† From the result of an unduplicated experiment, very little isomerisation occurs at 30°. This, if confirmed, would imply that the isomerisation involves the intermediate production of an *activated* excited molecule in which there is necessarily some special distribution of thermal energy.

[8] Garforth, Ingold, and Poole, *J.*, 1948, 406, and later papers.

[9] Woods and Schwartzman, *J. Amer. Chem. Soc.*, 1948, **70**, 3394.

and remained as oily material from evaporation of a solution in methylcyclohexane (b. p. 100°) on a watch glass: hexa-1,3,5-triene, b. p. 79·5—80°, could not possibly have behaved in this manner, and it could scarcely have polymerised without modification of the ultraviolet spectrum. Beyond the indication that the photolysis product is an unsaturated material having an appreciably higher boiling point than benzene, we feel that its constitution remains to be determined. Comparison of its ultraviolet spectrum with that of products of low molecular weight from the radical polymerisation of hexa-1,3,5-triene would be a useful first step.

Further, with respect to the question of free-radical intermediates, no significant inhibition of fulvene formation was observed when benzene was photolysed in the presence of ferric chloride as a free-radical scavenger, and no ferrous chloride was produced. Similarly, the presence of liquid paraffin was without effect, although this would have been expected to provide a source of fairly readily available hydrogen atoms. The conversion of isopropylbenzene into a fulvene provides a further indication that hydrogen donors do not markedly suppress fulvene formation. Irradiation of benzene containing thiophenol gave no fulvene; but thiophenol was subsequently shown to react slowly with fulvene even in the absence of ultraviolet radiation, and it is therefore uncertain whether this inhibitor was acting in its capacity as hydrogen-donor. The conclusion at this stage is that the isomerisation involves either the direct intramolecular rearrangement of an excited molecule, or the formation and subsequent ring-closure of a hexatrienyl diradical having a particularly short half-life, or both of these. A clearer decision might be possible if it could be determined whether hexatrienyl diradicals trapped in a rigid *inert* glass, or even solid benzene, form fulvene when the glass is melted.

No indication that the present isomerisation is reversible has been found. Thus no conversion into benzene or other detectable change occurred when a dilute solution of fulvene in cyclohexane was kept under nitrogen in the dark for one month. Irradiation of such a solution led to rapid destruction of the fulvene, but no trace of benzene or unsaturated C_6 hydrocarbons was formed. Similarly, the passage of a gaseous mixture of fulvene, cyclohexane, and nitrogen through a tube at 360° destroyed *ca.* 75% of the fulvene, but gave no benzene.

EXPERIMENTAL

The irradiation apparatus was the water-cooled form of that previously described.[4,10]

Benzene (sulphur-free) was dried and fractionally distilled immediately before use, except where otherwise stated.

The following are details of a typical isomerisation experiment.

Benzene (125 ml.) was irradiated at 55° for 1 hr. under nitrogen. The yellow product was distilled under nitrogen through a column having *ca.* 10 theoretical plates. Fulvene codistilled with unchanged benzene and there was no indication of any separation. The ultraviolet spectrum of the yellow distillate was observed differentially against benzene, and resembled that given by Thiec and Wiemann [5] for fulvene: $\lambda_{\text{max.}}$ 242, 360—365 mμ; $\varepsilon_{242}/\varepsilon_{365} = 48{\cdot}3$: in similar experiments, values for $\varepsilon_{242}/\varepsilon_{365}$ of 48·4, 51·2, 54·4 were obtained. Thiec and Wiemann found $\varepsilon_{242}/\varepsilon_{373} = 51{\cdot}3$ for freshly distilled material, and $\varepsilon_{242}/\varepsilon_{362} = 45{\cdot}7$ for material stored at −70° for three days in an inert atmosphere. The present spectra always most closely resembled that given for the latter material, and were virtually unchanged after storage in air in near-darkness for a month and more. The optical density at 365 mμ was 0·50, indicating a fulvene concentration of 0·18 g./l. The spectrum of the irradiated benzene before distillation showed peaks at 335 (weak), 355, and 375 mμ which swamped those due to fulvene. These peaks, together with one at *ca.* 275 mμ, appeared in the spectrum of the orange-yellow residual oil (0·1 g.) from the above distillation. From the infrared spectrum, no more than the merest trace of biphenyl, if any, was present in this material (cf. Krassina [11] and Prilezhaeva [12]). We

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[10] Blair, Bryce-Smith, and Pengilly, *J.*, 1959, 3174.

[11] Krassina, *Acta Physicochim. U.R.S.S.*, 1939, **10**, 189.

[12] Prilezhaeva, *Acta Physicochim. U.R.S.S.*, 1939, **10**, 193.

suppose it to have been largely polyfulvenes; but the absorption spectrum, particularly at the longer wavelengths, is rather surprising, and the material formed when fulvene solutions stand in sunlight is a colourless solid almost insoluble in benzene. The above oily high-boiling material was strongly unsaturated to bromine in carbon tetrachloride.

In further experiments ordinary " crystallisable " benzene was used without purification: also benzene which was rigorously sulphur-free and had been further purified by repeated partial freezing. There was no significant variation from the above results.

Increase in the time of irradiation from 1 hr. to 4 hr. increased the yield of fulvene by 50%.

The presence of mercury, or ferric chloride, was found not significantly to influence the yield of fulvene under comparable conditions. In a modified apparatus a Hanovia 766/63 mercury-vapour lamp was employed in conjunction with a " Vycor " filter to eliminate radiation below 200 mμ. The yield of fulvene was found to be unaffected by the presence of the filter, allowance being made for its reduced transmission at 254 mμ.

Formation and Hydrolysis of the Fulvene–Maleic Anhydride Adduct.—The behaviour of " fulvene from benzene " towards a number of reagents, including maleic anhydride, has already been qualitatively described.[4] Twenty 100-ml. portions of benzene were irradiated as described above. After distillation, each was heated under reflux with maleic anhydride (0·04 g.) until colourless. Benzene was distilled from the combined products under reduced pressure and the colourless residue was dissolved in 5% sodium hydroxide solution (10 ml.), extracted with three 10-ml. portions of chloroform, and acidified with hydrochloric acid. The acidified solution was extracted with ether. Evaporation of the ethereal extract gave the crude adduct (0·47 g.). This was dissolved in dry chloroform, the solution filtered to remove maleic acid, and the filtrate concentrated until crystallisation commenced. Filtration gave crystals, m. p. 105—110° (0·12 g.). The m. p. was unchanged after recrystallisation from chloroform or water (Found: C, 62·2; H, 5·1%; equiv., 98·1. $C_{10}H_{10}O_4$ requires C, 61·9; H, 5·15%; equiv., 97·0).

A solution of fulvene in cyclohexane, prepared from cyclopentadiene and formaldehyde as previously described,[6] was caused to react with maleic anhydride as above. The acid formed by hydrolysis of the adduct was isolated and had m. p. 106—111° (Found: C, 62·0; H, 5·4%). The mixed m. p. with the material prepared from benzene, m. p. 105—110°, was 105—110°. The infrared spectra of the two materials were identical, the main peaks being at 5·8, 7·5, 8·1, 8·5, 9·3, 11·3, 12·3, and 13·8 μ.

The m. p. range suggests that the initial adducts were mixtures of endo- and exo-isomers. Thiec and Wiemann [5] reported the separation of these by hand-picking of crystals. The present products formed crystals too small for application of this technique.

Absorption spectra in the examples below were observed differentially, as with benzene.

Irradiation of Toluene.—Toluene (100 ml.; dry, sulphur-free) was irradiated for 1 hr. at 50—53° under nitrogen. The product was distilled at 170 mm. to give a pale yellow distillate, b. p. 60°, having $\lambda_{\text{max.}}$ 242, 355 mμ, and optical density 0·47 at 355 mμ. The yellow colour was discharged by bromine in carbon tetrachloride.

Irradiation of Isopropylbenzene.—Isopropylbenzene (60 ml.; freshly distilled from calcium hydride) was irradiated for 2 hr. at 64° under nitrogen. Distillation under reduced pressure gave a yellow distillate, b. p. 85° (55 ml.), $\lambda_{\text{max.}}$ 248, 360 mμ ($\varepsilon_{248}/\varepsilon_{360} = 33$). The optical density at 360 mμ was 1·06. The yellow colour was discharged by bromine in carbon tetrachloride. No 2,3-dimethyl-2,3-diphenylbutane was detected among the high-boiling products, although a resinous solid (12 mg.), probably a polyisopropylfulvene, was obtained.

Irradiation of Anisole.—Anisole (40 ml.) was irradiated at 120° for 1 hr. under nitrogen. Distillation under reduced pressure gave a very pale yellow product (35 ml.), $\lambda_{\text{max.}}$ 296, 325 (tailing into the visible) ($\varepsilon_{296}/\varepsilon_{325} = 4·7$).

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