

171. *The Chemical Effects of γ -Radiation on Organic Systems. Part VII.*¹ *The Radiolysis of Mixtures of Benzoyl Chloride with Benzene, Anisole, or Nitrobenzene.*

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γ -Radiolysis of a mixture of benzene and benzoyl chloride yields benzophenone, biphenyl, and other products. A mixture of anisole and benzoyl chloride, when irradiated, yields the three isomeric methoxybenzophenones in a ratio which suggests a radical substitution; dianisoles are also formed. Irradiation of a mixture of nitrobenzene and benzoyl chloride gives 4-nitrobiphenyl and various dinitrobiphenyls.

ARYLATION of aromatic compounds by chemically generated aryl radicals is well known² and we have shown similar reactions to be due to radicals generated by γ -radiolysis of bromobenzene,^{3,4,5} but we are unaware of any discussion of arylation by free aryl radicals. However, the formation of benzophenone by the action of zinc on a mixture of benzoyl chloride and benzene⁶ and of 4-methoxybenzophenone by a similar reaction with anisole⁷ may proceed by a radical mechanism.

Kailan⁸ reported that benzoyl chloride became yellow when exposed to the radiation from radium and that benzoic acid was formed. We subjected a mixture of benzene and benzoyl chloride (37.5 : 1 by volume) to γ -radiation and obtained a viscous, yellow residue after removal of unchanged materials. From this, by chromatography, biphenyl (*G* 0.2) and benzophenone (as the 2,4-dinitrophenylhydrazone, *G* 0.057) were obtained, but the major constituent was a gum (*G* 0.43, based on mol. wt. 156). Irradiation of benzene alone has been reported⁹ to yield a liquid polymer. We found it to yield biphenyl, a solid polymer, and a liquid polymer. The latter polymer had similar chromatographic properties to the polymers formed on irradiation of benzene-benzoyl chloride but was obtained in much smaller amount (*G* 0.065, based on mol. wt. 156); the infrared spectra of these two polymers showed some similarity, both having methylene and phenyl peaks, but that from the benzene-benzoyl chloride product had a carbonyl peak at 1680 cm^{-1} . The polymer from benzene corresponds to that investigated by Gordon, van Dyken, and Doumani,¹⁰ consisting of a complex mixture of phenylcyclohexadiene and other hydrogenated biphenyls and terphenyls. These authors reported the polymer to absorb

¹ Part VI, preceding paper.

² Dermer and Edmison, *Chem. Rev.*, 1957, **57**, 77; Augood and Williams, *ibid.*, p. 123.

³ Swan and Timmons, *J.*, 1958, 4669.

⁴ Everard, Parrack, Swan, and Timmons, *J.*, Part V, 905.

⁵ Everard and Swan, *Proc. Chem. Soc.*, 1961, 212.

⁶ Zincke, *Ber.*, 1873, **6**, 137.

⁷ Kaufmann and Fuchs, *Arch. Pharm.*, 1924, **262**, 119.

⁸ Kailan, *Monatsh.*, 1929, **53**—**54**, 153.

⁹ Patrick and Burton, *J. Amer. Chem. Soc.*, 1954, **76**, 2626.

¹⁰ Gordon, van Dyken, and Doumani, *J. Phys. Chem.*, 1958, **62**, 20.

oxygen and it seems likely that our solid polymer had been formed during the working-up by absorption of oxygen from the air by the liquid polymer—its infrared spectrum indicated the presence of, not only methylene and phenyl groups, but also hydroxyl (3425 cm.^{-1}) and carbonyl (1720 cm.^{-1}) groups.

Benzophenone may be formed by an ion-molecule reaction; but, on the other hand, one could postulate that radiolysis of benzoyl chloride gives rise to benzoyl radicals and chlorine atoms:



The benzoyl radical may add to a benzene molecule, giving an intermediate from which hydrogen is abstracted by a chlorine atom. The higher yield of polymer produced from benzene-benzoyl chloride than from benzene alone may be due to the ability of benzoyl radicals to play a similar part to phenyl radicals.

A small amount of solid polymer was formed on irradiation of benzene, and as none of this was encountered in the benzoyl chloride-benzene work and as hydrogen chloride was produced in the latter, we wondered whether addition of this to an irradiation product (*e.g.*, phenylcyclohexadiene) was occurring under the influence of γ -radiation (*cf.* ethylene plus hydrogen bromide¹¹), thereby preventing subsequent reactions which would otherwise lead to solid polymer. We therefore irradiated benzene saturated with dry hydrogen chloride but were unable to establish the structures of the products formed, except for biphenyl. The presence of products containing methylene groups was indicated by infrared spectroscopy.

Previous work in this laboratory¹² having shown anisole to be rather stable to irradiation, we irradiated a mixture of anisole and benzoyl chloride (37.5 : 1 by volume). The residue left after removal of unchanged materials was chromatographed and ketonic material was isolated by the Girard T reagent, giving a mixture of 2-, 3-, and 4-methoxybenzophenones (total *G* 0.22). The proportions of the three isomers, as estimated by infrared spectroscopy,¹³ were 54, 19, and 27%. These figures point to a radical substitution (presumably by benzoyl radicals). Part of the non-ketonic residue (*G* 0.19, based on mol. wt. 214) gave an infrared spectrum which was very similar to that of a mixture of 2,2', 3,3', and 4,4'-dimethoxybiphenyl, although analytical results suggested also the presence of monomethoxybiphenyl. By chromatography, small amounts of 2,2'- and 4,4'-dimethoxybiphenyl were isolated from this. Another fraction was distillable and when treated with diazomethane yielded a product the infrared spectrum of which suggested that it was the methyl ester of a carboxylic acid. Phenol was also isolated (*G* 0.35).

We also irradiated a mixture of nitrobenzene and benzoyl chloride (37.5 : 1 by volume), but were unable to detect the formation of nitrobenzophenone, although small quantities of the following were isolated: 4-nitrobiphenyl (*G* 0.023), 3,3', 3,4', and 4,4'-dinitrobiphenyl, and benzanilide. From irradiated nitrobenzene we isolated small amounts of 4-nitro- (*G* 0.01) and 3,4'- and 4,4'-dinitro-biphenyl. The formation of benzanilide points to reduction of nitrobenzene to aniline during the radiolysis. Moreover, when irradiated nitrobenzene was distilled, the first part of the distillate was green, presumably owing to the formation of nitrosobenzene. The products isolated indicate the formation of both nitrophenyl and phenyl radicals by radiolysis of nitrobenzene. In the case of the mixture with benzoyl chloride, phenyl radicals might arise from benzoyl radicals, although it has been reported that carbon monoxide is not formed by the action of radical catalysts on benzaldehyde, presumably because of the high resonance energy of benzoyl radicals.¹⁴ However, in the case of nitrobenzene alone, the phenyl radicals must be radiolysis products

¹¹ Armstrong and Spinks, *Canad. J. Chem.*, 1959, **37**, 1002.

¹² Everard, Swan, and Timmons, following paper.

¹³ Augood, Hey, and Williams, *J.*, 1953, **44**.

¹⁴ Kharasch, Urry, and Kuderna, *J. Org. Chem.*, 1949, **14**, 248; Harris and Waters, *J.* 1952, 3108; Walling and Savas, *J. Amer. Chem. Soc.*, 1960, **82**, 1738.

of the nitrobenzene. Biphenyl was not detected but may have been lost during distillation of unchanged nitrobenzene. The apparent preponderance of 4-nitrobiphenyl over the dinitrobiphenyls may be accounted for, in part, by the fact that phenyl radicals attack nitrobenzene four times as fast as do *p*-nitrophenyl radicals.²

2,2'-Dinitrobiphenyl was not detected in our experiments, although reddish-brown gums formed may have been derived from this. Thus, reduction of 2,2'-dinitrobiphenyl by hydrazine and Raney nickel yields reddish-brown products.¹⁵ We reduced our gums and benzooylated the resulting base, but benzanilide was the only compound we were able to isolate.

Some of the gummy products produced by irradiation of the nitrobenzene-benzoyl chloride mixture may have arisen as the result of addition of free radicals to the nitro-group. Morris¹⁶ reported that whereas energetic radicals, such as methyl, tend to form nuclear-substitution products with polynitrobenzenes, less energetic radicals, such as 2-cyanopropyl, preferentially attack the oxygen atom of the nitro-group, yielding substituted hydroxylamines, through a nitrosobenzene intermediate. Other workers have noted similar attack by benzoyl radicals.¹⁷ Hastings and Matsen¹⁸ showed that the vapour-phase photolysis of nitrobenzene produced nitrosobenzene and *p*-nitrophenol, which suggests rupture of an N-O bond under these conditions. Contrary to Shelegova's findings¹⁹ these authors found no evidence for the production of nitrogen dioxide or polynitrobenzenes.

Although we postulate benzoyl radicals as intermediates in the radiolysis of benzoyl chloride, we have been unable to isolate benzil from the products. The ultraviolet spectra of various fractions obtained on irradiation of benzene-benzoyl chloride were examined, but no evidence of the presence of benzil was found. It is possible that any benzil formed was retained in the unidentified gums.

EXPERIMENTAL

Arrangements for the irradiations and dosimetry were as described in Part I.³ Light petroleum refers to a fraction of b. p. 40–60°.

Irradiation of a Mixture of Benzene and Benzoyl Chloride.—A mixture of benzene (268 ml.) and benzoyl chloride (7.15 ml.) was irradiated for 456 hr. (total dose 3.33×10^{23} ev). The unchanged benzoyl chloride was removed by shaking the mixture with water for several days, then with dilute sodium hydrogen carbonate solution. Unchanged benzene was removed by distillation under reduced pressure and the residue was chromatographed on alumina. Development with light petroleum yielded biphenyl (0.16 g.), which gave the 4-nitro-derivative, m. p. and mixed m. p. 114°. Further development with light petroleum-benzene (9:1) and then with benzene yielded fractions which, when treated with 2,4-dinitrophenylhydrazine, yielded an orange-coloured solid (0.113 g.); recrystallised from chloroform-ethanol this afforded benzophenone 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 240°, identical in infrared spectrum with authentic material. The carbon values found on this sample (as on authentic material) were always low (Found, on material from irradiation: C, 61.7, 61.8; H, 3.6, 3.2. Found, on authentic material: C, 61.85, 62.15; H, 3.85, 3.85. Calc. for $C_{19}H_{14}N_4O_4$: C, 63.0; H, 3.9%). Development with chloroform yielded a dark brown gum (0.37 g.) which had infrared bands corresponding to carbonyl (1680 cm^{-1}), methylene (2933, 2859, and 1449 cm^{-1}), and phenyl groups (3055, 3026, and 700 cm^{-1}), but failed to yield a dinitrophenylhydrazone. This gum absorbed hydrogen (1 mole per 200 g.) in the presence of Adams catalyst, contained halogen, and appeared to resist alkaline hydrolysis. Development of the chromatogram with chloroform-methanol (3:1) yielded a brown gum which on distillation gave a colourless liquid, b. p. 60–100° (bath)/0.2 mm., which afforded crystals, m. p. 90–98° (4 mg.).

¹⁵ Moore and Furst, *J. Org. Chem.*, 1958, **23**, 1504.

¹⁶ Morris, *J. Amer. Chem. Soc.*, 1959, **81**, 4239.

¹⁷ Jackson, Waters, and Watson, *Chem. and Ind.*, 1959, 47; Goble, Lidstone, and Pauwels, *ibid.*, p. 1489.

¹⁸ Hastings and Matsen, *J. Amer. Chem. Soc.*, 1948, **70**, 3514.

¹⁹ Shelegova, *J. Exp. Theor. Phys. (U.S.S.R.)*, 1939, **9**, 1527; *Chem. Abs.*, 1941, **35**, 1700.

A similar mixture of benzene and benzoyl chloride which had been stored in the dark for 456 hr. without irradiation yielded no residue on removal of the unchanged benzene and benzoyl chloride.

Irradiation of Benzene.—Benzene (275 ml.) was irradiated for 168 hr. (total dose 1.23×10^{23} ev) and the product was concentrated to a small volume under reduced pressure. An amorphous yellow solid (16 mg.) was filtered off and the residue was chromatographed on alumina. Light petroleum eluted biphenyl (75 mg.), and development with chloroform yielded a yellow gum (20 mg.), having infrared bands at 2928, 2853, 1453, 3065, 3029, and 702 cm^{-1} .

Irradiation of Benzene Saturated with Hydrogen Chloride.—Benzene, saturated with dry hydrogen chloride (275 ml.), was irradiated for 168 hr. (total dose 1.23×10^{23} ev). The hydrogen chloride was then removed by shaking the mixture with 10% sodium hydroxide solution, and the unchanged benzene was removed by distillation after drying. The residue was chromatographed, light petroleum eluting a mixture of crystalline biphenyl and a colourless liquid (180 mg.), b. p. 45—105° (bath)/0.2 mm. (Found: C, 63.25; H, 6.85. Calc. for $\text{C}_{12}\text{H}_{10}\text{Cl}_2$: C, 62.3; H, 6.9%). Development with benzene yielded a viscous, yellow liquid (225 mg.), which on distillation gave a colourless liquid, b. p. 140—180° (bath)/0.4 mm. (Found: C, 55.0; H, 6.5. Calc. for $\text{C}_{12}\text{H}_{15}\text{Cl}_3$: C, 54.3; H, 5.7%) (absorbing hydrogen in the presence of palladium-charcoal), and an opaque liquid, b. p. 180—230° (bath)/0.4 mm. Development with chloroform yielded a viscous, yellow gum (125 mg.).

Irradiation of a Mixture of Anisole and Benzoyl Chloride.—A mixture of anisole (268 ml.) and benzoyl chloride (7.15 ml.) was irradiated for 288 hr. (total dose 2.37×10^{23} ev). Unchanged benzoyl chloride was removed as before. Phenolic material was then extracted with 10% sodium hydroxide solution (A), and unchanged anisole was removed by distillation under reduced pressure. The residual, dark viscous liquid was chromatographed on alumina, light petroleum eluting the last traces of anisole, while light petroleum-benzene (9:1) eluted a colourless liquid (95 mg.). Further development with benzene gave a yellow liquid (0.37 g.). These two liquids were combined and refluxed for 5 hr. with 20% sodium hydroxide solution (to hydrolyse methyl benzoate, found, by preliminary experiments, to be present), then extracted with ether. The residue from the ethereal extract was extracted three times with the Girard T reagent.²⁰ For each extraction the material was refluxed for 5 hr. with acetic acid (10%) in ethanol (6 ml.). Non-ketonic compounds were extracted with benzene. The aqueous solution was then refluxed with a few drops of concentrated hydrochloric acid for 2 hr. and the liberated ketonic material was extracted with ether. Evaporation of the combined and dried ethereal extracts yielded a liquid (0.18 g.), all of the peaks of the infrared spectrum of which could be accounted for by peaks of the spectra of 2-, 3-, or 4-methoxybenzophenone (Found: C, 80.0; H, 5.95. Calc. for $\text{C}_{14}\text{H}_{12}\text{O}_2$: C, 79.2; H, 5.65%).

The proportions of the three isomers in this mixture were estimated as infrared bands at 762, 727, and 744 cm^{-1} , respectively, following the general directions of Augood, Hey, and Williams.¹³ The spectra of the pure isomers were measured in concentrations of approximately 20 mg. per 450 mg. of nitromethane, the densities of the solutions being determined by a micro-pycnometer. The spectrum of the mixture was measured at a concentration of ~30 mg. per 480 mg. of nitromethane and, after the result had been calculated, the spectrum was compared with the spectra of the following mixtures, at the same total concentration: (a) 55.5, 16.0, 28.5, (b) 50.0, 20.0, 30.0, and (c) 53.6, 19.1, and 27.3% of 2-, 3-, and 4-isomer, respectively. Mixture (c) gave the closest match.

The non-ketonic fraction, remaining after extraction with the Girard reagent, was a yellow liquid (0.16 g.), from which, by chromatography on alumina, 2,2', m. p. 128—133° (2 mg.), and 4,4'-dimethoxybiphenyl, m. p. 170—172° (10 mg.), were isolated.

Development of the original chromatogram with chloroform yielded a viscous, brown liquid (0.18 g.), part of which (50 mg.) was distillable [b. p. 80—120° (bath)/0.4 mm.]. This part, when treated with diazomethane in ether, yielded a liquid of approximately the same b. p.

Development with chloroform-methanol (9:1) yielded a reddish-brown oil (140 mg.), which was dissolved in chloroform and extracted with 10% sodium hydroxide solution. The latter was acidified and extracted with ether, and the extract was distilled, affording a fraction, b. p. 50—80° (bath)/15 mm. (20 mg.), shown by infrared spectrum and by preparation of its 3,5-dinitrobenzoate to be phenol, and a second fraction, b. p. 80—110° (bath)/15 mm. (36 mg.). The chloroform extract afforded a yellow liquid, b. p. 100—110° (bath)/0.7 mm. (45 mg.).

²⁰ Girard and Sandulesco, *Helv. Chim. Acta*, 1936, 19, 1095.

The original, alkaline extract (A) was acidified and extracted with ether, yielding a brown oil (0.33 g.) which, after distillation (b. p. 180°), crystallised, yielding phenol (0.13 g.). A yellow liquid, b. p. 150—200° (bath)/0.5 mm., was also obtained.

A control experiment, in which a mixture of anisole and benzoyl chloride was kept for 288 hr. in the dark without irradiation, yielded none of the above products.

Irradiation of a Mixture of Nitrobenzene and Benzoyl Chloride.—A mixture of nitrobenzene (268 ml.) and benzoyl chloride (7.15 ml.) was irradiated for 336 hr. (total dose 3.34×10^{23} ev). The unchanged benzoyl chloride was removed from the dark brown liquid as before. Unchanged nitrobenzene was removed by distillation under reduced pressure and the residue was chromatographed on alumina. Elution with light petroleum–benzene (9 : 1) removed the last traces of nitrobenzene, and further development with benzene yielded various nitrobiphenyls. An early benzene eluate gave 4-nitrobiphenyl (37 mg.; m. p. 107—110°), which, when recrystallised from ethanol, had m. p. 114° (25 mg.) (Found: C, 72.3; H, 4.8. Calc. for $C_{12}H_9NO_2$: C, 72.3; H, 4.5%). A later fraction yielded 3,3'-dinitrobiphenyl (1 mg.), m. p. and mixed m. p. 199°, identical in infrared spectrum with the authentic compound. The next fraction yielded 3,4'-dinitrobiphenyl (2 mg.), m. p. and mixed m. p. 187—188°, identical in infrared spectrum with the authentic compound. The final benzene eluates yielded 4,4'-dinitrobiphenyl (1 mg.), pale cream-coloured needles, m. p. and mixed m. p. 238—242° (from benzene), identical in infrared spectrum with the authentic compound. Further development with benzene–chloroform (3 : 1) yielded an orange-coloured solid (30 mg.) which, when recrystallised from benzene, afforded cream-coloured crystals (6 mg.), m. p. 158—162°, identical in infrared and ultraviolet spectra [λ_{\max} 266.5 m μ (ϵ 12,900), λ_{\min} 241 m μ (ϵ_{\min} 8000)] with benz-anilide. Development with chloroform–methanol (3 : 1) yielded a reddish-brown gum (80 mg.) which, when reduced with stannous chloride in hydrochloric acid, afforded aniline [identified as benzanilide (1 mg.)].

Irradiation of Nitrobenzene.—Nitrobenzene (275 ml.) was irradiated for 384 hr. (total dose 3.82×10^{23} ev), unchanged material was removed by distillation under reduced pressure, and the residue was chromatographed on alumina. Successive benzene eluates afforded 4-nitrobiphenyl (12 mg.), 3,4'-dinitrobiphenyl (1 mg.), and 4,4'-dinitrobiphenyl (3 mg.). Chloroform–methanol eluted a reddish-brown gum (130 mg.), which on reduction and benzylation afforded benzanilide, m. p. 158—159° (8 mg.).

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