941. *The Chemical Effects of γ-Radiation on Organic Systems. Part II.* The Action of Radiation on Benzyl Alcohol Alone or Mixed with Acetone or Bromobenzene.*

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Irradiation of benzyl alcohol with γ-rays gave rise to benzaldehyde, dibenzyl, 1 : 2-diphenylethanol, and *meso*- and racemic hydrobenzoin. In the presence of acetone, the last two compounds were produced in considerably greater energy yield. The products formed by the irradiation of a mixture of benzyl alcohol and bromobenzene were also investigated.

The most important contribution to the radiation chemistry of alcohols in the absence of water is McDonell and Newton's intensive study[1] of α-particle irradiation of aliphatic alcohols. By various analytical methods they established that the main organic products were aldehydes and α-glycols, relatively small amounts of hydrocarbons and ethers being formed. McDonell and Gordon[2] investigated the effect of γ-radiation on methanol; Skraba, Burr, and Hess[3] studied the decomposition of the same compound containing ^{14}C under the influence of its own β-rays; other workers have used α-particles[4] and X-rays or electrons.[5] Aldehydes are also known to be formed by the photolysis of alcohol vapours,[6] but in addition the production of ethylene glycol by photolysis of methanol vapour at low temperature has been reported.[7]

We studied the action of γ-radiation on benzyl alcohol, partly because the chemical reactivity of this compound differs somewhat from that of the purely aliphatic alcohols and partly because we thought that the products should be easier to isolate in this case. Also Chapiro[8] had measured the radical formation on irradiation of various types of compounds with γ-rays and had obtained the following values, taking the radical production from benzene as unity: *cyclo*hexane 4, ether 7, aniline 20, acetone 35, chloroform 50, alcohols 50—80, benzyl alcohol, butylamine, and benzylamine 80, and carbon tetrachloride 200. Thus benzyl alcohol appeared to be one of the more sensitive organic compounds towards radiolysis. Although we irradiated the benzyl alcohol for periods of nearly a week, only approximately 1% of it was converted into other products. Nevertheless, by the use of classical and chromatographic methods, we were able to isolate benzaldehyde, dibenzyl, 1 : 2-diphenylethanol, dibenzyl ether, and the two stereoisomeric hydrobenzoins, either in the free state or as crystalline derivatives. It was, however, clear that our separation was far from quantitative and we therefore decided to determine the yield of each product by the isotope-dilution method.

As we wished to determine the yield of each of the several products in one experiment, we labelled the benzyl alcohol isotopically and added a known weight of non-isotopic carrier after irradiation, rather than *vice versa*, despite the fact that we required a large amount of the benzyl alcohol. We chose ^{14}C as the isotope on account of the great dilution in which it can be determined (by the gas-counting method on $^{14}CO_2$). Our material was thus necessarily of very low specific activity and the effect of the soft β-rays emitted by the ^{14}C would be negligible compared with that due to the γ-radiation. Actually benzyl

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* Part I, preceding paper.

[1] McDonell and Newton, *J. Amer. Chem. Soc.*, 1954, **76**, 4651.

[2] McDonell and Gordon, *J. Chem. Phys.*, 1955, **23**, 208.

[3] Skraba, Burr, and Hess, *ibid.*, 1953, **21**, 1296.

[4] McLennan and Patrick, *Canad. J. Res.*, 1931, **5**, 470; Kailan, *Sitzungsber. Akad. Wiss. Wien*, 1931, IIa, **140**, 419; *Monatsh.*, 1913, **34**, 1269; Breger, *J. Phys. Colloid Chem.*, 1948, **52**, 551.

[5] Bakh and Sorokin, *Sbornik Rabot Radiatsionnoĭ Khim.*, *Akad. Nauk S.S.S.R.*, 1955, 163; *Chem. Abs.*, 1956, **50**, 4649; Bach, Proc. Internat. Conference, Peaceful Uses of Atomic Energy, Geneva, 1955, United Nations, New York, 1956, Vol. VII, p. 538.

[6] Patat and Hoch, *Z. Elektrochem.*, 1935, **41**, 494.

[7] Phibbs and Darwent, *J. Chem. Phys.*, 1950, **18**, 495.

[8] Chapiro, *J. Chim. phys.*, 1950, **47**, 764.

alcohol (275 ml.) containing ^{14}C in the alcohol group, of specific activity approximately 100 μc/mole, was irradiated at room temperature, then divided into a number of aliquot parts, to which accurately known weights of each pure, inactive product being assayed were added. A pure sample of this compound (or a crystalline derivative) was then isolated and burnt, and the specific activity of the resulting carbon dioxide was measured. It was thus possible to calculate the weight of this compound present in the irradiation mixture: the results are shown in Table 1.

TABLE 1. *Yields of products from γ-irradiation of* 275 *ml. of* [^{14}C]*benzyl alcohol* (*total dose* 1·37 × 10^{23} ev).

Compound estimated	Wt. of carrier (mg.)	Activity of CO_2 (counts/min.) *	Wt. of product (mg.)	*G* (product)
Benzyl alcohol	—	1860	—	—
Benzaldehyde	454	869	398	1·32
,, (control)	82·9	920	81·2	
Benzaldehyde dibenzyl acetal	883·1	16·7	<8	—
Dibenzyl	267·9	578	120·8	0·29
1 : 2-Diphenylethanol	280·1	968	304	0·68
Dibenzyl ether	1698	100·5	97	—
meso-Hydrobenzoin	234·8	535	95·0	0·20
Racemic hydrobenzoin	243·8	566	106·7	0·22

* For compounds isolated as derivatives these values have already been multiplied by an appropriate factor so that they represent the activities of CO_2 which would have been obtained if the pure compounds named in the left-hand column of the Table had been burnt.

From these it is seen that 1 : 2-diphenylethanol is produced in energy yield about half that of benzaldehyde, and that dibenzyl comes next in order of quantity. *meso*- and Racemic hydrobenzoin were formed in approximately equal amounts. The formation of these products can be explained on the assumption that under the influence of γ-radiation benzyl alcohol can break down in two different ways:

$$Ph{\cdot}CH_2{\cdot}OH \rightsquigarrow Ph{\cdot}CH(OH){\cdot} + H{\cdot} \quad . . . . (a)$$

and

$$Ph{\cdot}CH_2{\cdot}OH \rightsquigarrow Ph{\cdot}CH_2{\cdot} + HO{\cdot} \quad . . . . (b)$$

The resulting radicals could then give the observed products as follows:

$$2Ph{\cdot}CH(OH){\cdot} \longrightarrow [Ph{\cdot}CH(OH)]_2$$
$$2Ph{\cdot}CH_2{\cdot} \longrightarrow [CH_2Ph]_2$$
$$Ph{\cdot}CH(OH){\cdot} + Ph{\cdot}CH_2{\cdot} \longrightarrow Ph{\cdot}CH_2{\cdot}CHPh{\cdot}OH$$

The benzaldehyde might arise in various ways, such as the following:

$$2Ph{\cdot}CH(OH){\cdot} \longrightarrow Ph{\cdot}CHO + Ph{\cdot}CH_2{\cdot}OH$$

or by hydrogen abstraction by hydrogen atoms or hydroxyl radicals. From purely aliphatic alcohols, aldehydes and glycols are the main products presumably because the alkyl radicals are much less stable than the benzyl radical and fission (*a*) predominates over (*b*), the oxygen of the $R{\cdot}CH(OH){\cdot}$ radical helping to stabilise it. Thus McDonell and Newton [1] found that the products formed by radiolysis of aliphatic alcohols were consistent with the assumption that the principal bond rupture occurred at bonds joining groups (with ease $H > Et > Me$) to the $CH_2{\cdot}OH$ carbon atom, with little tendency for fission of the C–O bond (as seen by the very small production of ethers and of hydrocarbons containing the same number of carbon atoms as the alcohols). They worked in a totally enclosed system and attempted to determine all (including gaseous) products and to work out an oxidation–reduction balance, as well as a mass balance. However, there remained some water and hydrogen for which they could not account. On the other hand Coleby, Keller, and Weiss,[9] who investigated the effect of *X*-rays on various steroids in

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[9] Coleby, Keller, and Weiss, *J.*, 1954, 66.

methanol, suggested that radiolysis of the C–O bond occurred in methanol. More recently Burr,[10] from a study of the radiolysis of five different deuterated ethanols with ^{60}Co γ-rays, concluded that the hydrogen production proceeded by a primary (rate-determining) radical process:

$$CH_3{\cdot}CH_2{\cdot}OH \longrightarrow CH_3{\cdot}CH(OH){\cdot} + H{\cdot}$$

From the deuterium content of the evolved hydrogen he concluded that the ensuing (rapid) abstraction affects principally the hydroxyl-hydrogen, with a small amount from the methyl group:

$$H{\cdot} + CH_3{\cdot}CH_2{\cdot}OH \longrightarrow CH_3{\cdot}CH_2{\cdot}O{\cdot} + H_2 \ (80\text{—}90\%)$$
$$H{\cdot} + CH_3{\cdot}CH_2{\cdot}OH \longrightarrow {\cdot}CH_2{\cdot}CH_2{\cdot}OH + H_2 \ (10\text{—}20\%)$$

The glycol could then be formed by combination of $CH_3{\cdot}CH(OH){\cdot}$ radicals, while the aldehyde could arise from either the latter or $CH_3{\cdot}CH_2{\cdot}O{\cdot}$ radicals and is therefore produced in greater amount (Burr found the amounts of aldehyde and glycol formed were in the ratio 2·2 : 1·05). For benzyl alcohol we found no conclusive evidence of a third type of radiolysis (*c*):

$$Ph{\cdot}CH_2{\cdot}OH \rightsquigarrow Ph{\cdot}CH_2{\cdot}O{\cdot} + H{\cdot} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (c)$$

However, we cannot rule out the possibility that part of the benzaldehyde might have arisen from the $Ph{\cdot}CH_2{\cdot}O{\cdot}$ radicals. For ethanol irradiated with *X*-rays or electrons, Bakh and Sorokin [5] showed that the energy yield of aldehyde increased in the presence of oxygen; but we have not studied this effect in the case of benzyl alcohol.

It was of interest to know whether acetal formation could be achieved in the absence of acid catalysts, under the influence of γ-radiation, and we therefore estimated the benzaldehyde dibenzyl acetal in the irradiation product of benzyl alcohol. A preliminary experiment showed that this acetal could be recovered unchanged after its ethereal solution had been treated with sodium hydrogen sulphite solution, so we removed the free benzaldehyde from the irradiation mixture under similar conditions before adding carrier acetal. The acetal which we isolated, however, was almost inactive, so we concluded that no appreciable amount of benzaldehyde had been converted into its dibenzyl acetal. We are, however, studying other carbonyl-addition reactions to see whether they are influenced by γ-radiation.

The status of the dibenzyl ether is uncertain and we regard it as very questionable whether it is a true irradiation product. The small amount which we isolated after isotope dilution was probably not quite pure, so the low activity recorded may have been due to radioactive contamination. It is known that when benzyl alcohol is heated for 5 days in a sealed glass tube at 210—215°, about 10% conversion into dibenzyl ether occurs.[11] As the working up of our mixture included distillation under water-pump vacuum it seems not impossible that traces of the ether might have thus been formed.

The relative proportions of *meso*- and racemic hydrobenzoin formed are of some interest, particularly as it had been reported [12] that mainly the *meso*-form results on ultraviolet irradiation of benzyl alcohol in acetone, the mechanism again presumably involving $Ph{\cdot}CH(OH){\cdot}$ radicals. The two isomers were therefore determined in separate portions of the irradiation mixture by addition of known weights of the respective inactive carriers. As there was the possibility, at any rate in the case of racemic hydrobenzoin, that part of the material might be present as a benzylidene derivative (cyclic acetal), the mixture was refluxed with hydrochloric acid to ensure that the carrier was effectively mixed. To avoid possible, subsequent loss of hydrobenzoin due to re-acetalisation, the benzaldehyde was removed by bisulphite treatment. The mixture of hydrobenzoins was isolated by chromatography and was separated into the *meso*- and the racemic form *via* the dibenzoates, as

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[10] Burr, *J. Phys. Chem.*, 1957, **61**, 1477.

[11] Lachman, *J. Amer. Chem. Soc.*, 1923, **45**, 2356.

[12] Ciamician and Silber, *Ber.*, 1910, **43**, 945.

described by Meerwein and Schmidt.[13] To test whether the racemic was converted into the (presumably) more stable *meso*-form during working up, in the case of that portion of the reaction mixture to which the racemic form had been added, we isolated not only this, but also the *meso*-form (as its dibenzoate) and measured its activity. If part of the racemic form had been converted into the *meso*-form, then the specific activity of the carbon dioxide produced by combustion of the *meso*-hydrobenzoin dibenzoate should be less than one-half of that of the original benzyl alcohol. As seen from Table 2, the activity of this *meso*-material was one half that of the benzyl alcohol (within the limits of experimental error), showing absence of interconversion.

TABLE 2.

	Activity of CO_2 formed by combustion (counts/min.)
Benzyl alcohol	1860
meso-Hydrobenzoin dibenzoate (Calc.)	930
,, ,, (Found)	912

Ciamician and Silber [12] reported that the action of light on a solution of benzyl alcohol in acetone yields *meso*-hydrobenzoin, with very little of the racemic isomer. We therefore studied the γ-irradiation of an equimolecular mixture of acetone and radioactive benzyl alcohol, the results being shown in Table 3. The only irradiation products estimated were the two hydrobenzoins; but in each of the two isotope dilution experiments (that is one to which *meso*- and one to which racemic carrier was added) *both* isomers were isolated. The results show that, in each case, the specific activity of the " undiluted " hydrobenzoin is, in fact, equal to that of the benzyl alcohol, thus confirming that interconversion of isomers has not occurred during the working up. It is also seen that the *meso*- and the racemic form are produced in approximately equal amounts, in contrast to the results reported for the light-induced reaction. It would be interesting to apply our method of analysis to the latter case as a check on Ciamician and Silber's results. It is unlikely although not impossible that the racemic might be converted into the *meso*-form under the influence of ultraviolet radiation.

TABLE 3. *γ-Irradiation of an equimolecular mixture of* [^{14}C]*benzyl alcohol and acetone of total volume* 275 *ml.* (*total dose* $1{\cdot}25 \times 10^{23}$ ev).

Compound	Wt. of carrier (mg.)	Activity of CO_2 (counts/min.) *	Wt. of product (mg.)	*G* (product)
Benzyl alcohol	—	1949	—	—
meso-Hydrobenzoin	194·5	1236	337	0·76
Racemic hydrobenzoin	266·3	1077	330	0·75
" Undiluted " *meso*-hydrobenzoin	—	1956	—	—
" Undiluted " racemic hydrobenzoin	—	1904	—	—

* In the case of *meso*-hydrobenzoin, the dibenzoate was burnt; but the values in this column have already been multiplied by two so that they represent the activities of CO_2 which would have been obtained if the hydrobenzoin itself had been burnt.

In the case of pure benzyl alcohol, the hydrobenzoins were produced with a *G* value of 0·42, while in acetone solution the value was 1·51. The reason for this may be that acetone is a good hydrogen-acceptor.

We also investigated the irradiation of a mixture of benzyl alcohol and bromobenzene; hydrogen bromide and benzaldehyde were produced with *G* values of 2·9 and 0·76 respectively. Benzaldehyde dibenzyl acetal, racemic benzylidenehydrobenzoin (*G* value 0·24), and dibenzyl ether were also isolated; but we do not regard the ether as a true irradiation product. It seems that benzyl bromide is formed during the irradiation and that this probably reacts with benzyl alcohol, either then or during the subsequent working-up. Thus, when a solution of hydrogen bromide in benzyl alcohol had been irradiated, dibenzyl ether was isolated; but a similar solution which was kept without irradiation for the same

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[13] Meerwein and Schmidt, *Annalen*, 1925, **444**, 221.

length of time yielded the ether in not greatly reduced yield. Also, the amount of dibenzyl ether isolated from the irradiated benzyl alcohol–bromobenzene mixture was much reduced when the mixture was treated with sodium hydrogen sulphite solution before distillation, and the residue left after removal of the bromobenzene and benzyl alcohol was then not completely soluble in light petroleum containing 2% of benzene. This was thought to be due to reaction of benzyl bromide with the sodium hydrogen sulphite solution. Dibenzyl was apparently not formed by irradiation of benzyl alcohol in the presence of bromobenzene.

As we were unable to isolate the products formed from the phenyl radicals which had presumably been liberated we irradiated an equimolecular mixture of benzyl alcohol and [^{14}C]bromobenzene; by subsequent addition (as inactive carrier) of compounds which we thought might be formed we showed the formation of diphenyl (*G* value 0·18), but diphenylmethane appeared to be absent. The greater part of the material of higher boiling point than bromobenzene remained in gummy fractions which failed to crystallise.

EXPERIMENTAL

Arrangements for the irradiations and spectroscopic measurements were as described in Part I. The radioactivity measurements were all made by the gas-counting method on $^{14}CO_2$ as described by Swan.[14] The alumina used for chromatography was supplied by Savory and Moore.

Isolation of Products Formed by Irradiation of Benzyl Alcohol.—Commercial benzyl alcohol was washed several times with 40% sodium hydrogen sulphite solution followed by sodium carbonate solution, then dried and fractionated. The purified alcohol (275 ml.) was irradiated for 140 hr. (total dose $1·69 \times 10^{23}$ ev). The benzaldehyde formed was extracted by shaking it with 40% sodium hydrogen sulphite solution (3×40 ml.). The extract was boiled with 5N-sulphuric acid, and the benzaldehyde was distilled in steam. With Brady's reagent the distillate gave benzaldehyde 2 : 4-dinitrophenylhydrazone (0·424 g.).

The benzyl alcohol layer was washed with sodium carbonate solution, dried, and distilled at 12 mm. through a fractionating column until a residue of ~4 ml. remained. A solution of this residue in light petroleum (b. p. 40—60°; 200 ml.) containing benzene (2%) was chromatographed on alumina (80 g.), fractions of 50 ml. being collected. Elution was continued with light petroleum containing benzene (5%). The first few fractions yielded crystalline dibenzyl, identified by its m. p. and ultraviolet spectrum and by conversion into the tetranitro-derivative, m. p. 163—164°. A mixture of the latter with authentic 2 : 2′ : 4 : 4′-tetranitrodibenzyl[15] (m. p. 164—165°) melted at 163°.

Further elution of the chromatogram with light petroleum containing benzene (5%) yielded dibenzyl ether, b. p. 150° (bath-temp.)/1 mm., n_D^{20} 1·5648 (for pure dibenzyl ether, 1·5625). Elution was continued with benzene, then with chloroform. The first chloroform fraction contained mainly racemic deoxybenzoin and this was followed by benzyl alcohol. The former, when recrystallised from light petroleum (b. p. 60—80°), had m. p. 67° (Found: C, 84·8; H, 7·2. Calc. for $C_{14}H_{14}O$: C, 84·8; H, 7·05%), identified by comparison with an authentic sample prepared by Gerrard and Kenyon's method.[16] The phenylurethane had m. p. 91° and the 3 : 5-*dinitrobenzoate* m. p. 184—185° (Found: C, 64·3; H, 4·45. $C_{21}H_{16}O_6N_2$ requires C, 64·3; H, 4·1%). The alcohol could be isolated (as this derivative) from fractions also containing benzyl alcohol by removing the latter by distillation in bulbs and treating the residue with 3 : 5-dinitrobenzoyl chloride in pyridine.

Finally, by elution of the chromatogram with chloroform containing methanol (25%), a mixture of *meso*- and racemic hydrobenzoin was obtained. These were separated as the dibenzoates as described in the experiment using radioactive benzyl alcohol.

In a similar experiment in which the bisulphite treatment was omitted, in addition to the products mentioned above, benzaldehyde dibenzyl acetal, b. p. 220° (bath-temp.)/1 mm. (0·8 g.), was isolated. This was eluted along with dibenzyl ether and separated by distillation. It is almost certain that this acetal had been formed during the distillation rather than during the irradiation.

Irradiation of [^{14}C]*Benzyl Alcohol.*—The radioactive alcohol was prepared in almost

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[14] Swan, *J.*, 1955, 1039.

[15] von Braun and Rawicz, *Ber.*, 1916, **49**, 799.

[16] Gerrard and Kenyon, *J.*, 1928, 2564.

theoretical yield by reduction of benz[^{14}C]oic acid (4 g., 300 μc) with lithium aluminium hydride (2·4 g., 2 mol.) in ether; it was diluted to 300 ml. with inactive benzyl alcohol, giving a product of specific activity of approximately 100 μc/mole. This (275 ml.) was irradiated for 121 hr. (total dose $1{\cdot}37 \times 10^{23}$ ev). The extra energy absorbed due to the radiation from the ^{14}C is negligible (approximately 10^{20} ev). A separate sample of the same benzyl alcohol was kept in the dark, without irradiation, for the same period, after which the benzaldehyde in it was determined (control value).

The irradiated material was divided into a number of separate (not all equal) portions, for assay of different products by isotope dilution. A carefully purified and weighed sample of the inactive compound the yield of which was to be determined was added to an appropriate portion of the benzyl alcohol. In the following description, however, the amount of inactive carrier mentioned is that which would have corresponded to the use of the full 275 ml. of the irradiated material in each case. In other words, the work was carried out on a smaller scale than is described from now on; but the yields shown in Table 1 correspond to 275 ml. of benzyl alcohol.

(i) Benzaldehyde. The irradiated benzyl alcohol was mixed with pure benzaldehyde (454 mg.). The aldehyde was then isolated by extraction with sodium hydrogen sulphite solution and was converted into the 2 : 4-dinitrophenylhydrazone (as described above) which when recrystallised from ethyl acetate had m. p. 234° and was used for the radioactivity measurements. The control value in the sample not irradiated was likewise determined.

(ii) Benzaldehyde dibenzyl acetal. The irradiated benzyl alcohol was washed with sodium hydrogen sulphite, then with sodium carbonate solution. Benzaldehyde dibenzyl acetal (883·1 mg.) was added and the bulk of the benzyl alcohol was removed by distillation. The residue was chromatographed (as above), the various fractions of the eluate being treated with Brady's reagent. Had any of the hydrobenzoin formed an acetal with benzaldehyde during the irradiation, it is likely that the product would have had similar adsorption on alumina to benzaldehyde dibenzyl acetal and hence been mixed with the latter. The very weak radioactivity of the benzaldehyde 2 : 4-dinitrophenylhydrazone, however, counts also against this acetalisation.

(iii) Dibenzyl. The irradiated benzyl alcohol was treated with dibenzyl (267·9 mg.). The dibenzyl was recovered as above, by making use of its very weak adsorption on alumina, and when recrystallised from methanol had m. p. 52° and was used as such for the radioactivity measurements.

(iv) 1 : 2-Diphenylethanol. The irradiated benzyl alcohol was treated with the alcohol (280·1 mg.), which was then recovered as described above and was recrystallised twice from light petroleum (b. p. 60—80°) containing benzene (5%); it had m. p. 67° and was assayed as such.

(v) Dibenzyl ether. The irradiated benzyl alcohol was treated with dibenzyl ether (1698 mg.) which was then recovered as described above. The isolated material had b. p. 150° (bath-temp.)/1 mm., n_D^{20} 1·559, and, although probably not quite pure, was used for the radioactivity measurements.

(vi) Racemic hydrobenzoin. *meso*- and Racemic hydrobenzoin were prepared by Meerwein and Schmidt's method.[13] The *meso*-form, when recrystallised from ethanol, had m. p. 135—136°. The three previously described forms of racemic hydrobenzoin (m. p. 95°, 104°, and 119—120°) were all encountered; but that of m. p. 119—120° was used as carrier in the isotope dilution experiment.

The irradiated benzyl alcohol was treated with racemic hydrobenzoin (243·8 mg.), then refluxed for 1 hr. with N-hydrochloric acid (200 ml.). The organic layer was washed with sodium hydrogen sulphite, followed by sodium carbonate solution, then dried and the benzyl alcohol was removed by vacuum-distillation. A solution of the residue in benzene was chromatographed on alumina (70 g.). The column was eluted with benzene and chloroform and the hydrobenzoin mixture was finally eluted with chloroform containing methanol (25%). A mixture of the hydrobenzoins, benzoyl chloride (1 g.), and pyridine (4 ml.) was kept at room temperature for 12 hr., then treated with water. The precipitated dibenzoate mixture was collected, dried, boiled with ethanol (8 ml.), and filtered hot. The solid left on the filter was *meso*-hydrobenzoin dibenzoate (100 mg.) and the filtrate on cooling deposited impure racemic hydrobenzoin dibenzoate, m. p. 125° (166 mg.). The latter was refluxed for 3 hr. with potassium hydroxide (100 mg.) in ethanol (4 ml.), and the product was isolated by distillation of the ethanol and addition of water. The m. p. of this racemic hydrobenzoin was raised to 95° by recrystallisation from dilute acetic acid and finally to 119—120° from benzene–light petroleum (b. p. 60—80°). The last form was used for the radioactivity measurements. The *meso*-hydrobenzoin dibenzoate was recrystallised from acetic acid, affording needles, m. p. 244—245°, used for radioactivity measurements.

(vii) *meso*-Hydrobenzoin. The irradiated benzyl alcohol was treated with *meso*-hydrobenzoin (234·8 mg.) and this was then isolated as the dibenzoate, which was used for the radioactivity measurements.

Irradiation of an Equimolecular Mixture of [^{14}C]*Benzyl Alcohol and Acetone.*—The alcohol was prepared as described above; it was a fresh batch to obviate any possible spurious results due to impurities in the recovered material. The acetone was shaken for 20 hr. with potassium permanganate, from which it was then distilled and dried ($MgSO_4$). The mixture (275 ml.) was irradiated for 138 hr. (total dose 1·25 × 10^{23} ev) and divided into two portions, *meso*- or racemic hydrobenzoin being added to each severally. The mixture was then fractionated and the residue treated as described above for the isolation of the hydrobenzoin, both isomers being isolated in each case.

In a blank experiment, in which a mixture of acetone and benzyl alcohol was kept for a week in the dark, no trace of hydrobenzoin could be detected.

Irradiation of a Mixture of Benzyl Alcohol and Bromobenzene.—(1) An equimolecular mixture of benzyl alcohol and bromobenzene (275 ml.) was irradiated for 120 hr. (total dose 1·77 × 10^{23} ev). The hydrogen bromide formed (0·70 g.) was extracted with water and titrated with standard alkali. The benzaldehyde was separated from the organic layer by treatment with sodium hydrogen sulphite solution in the way described under the irradiation of benzyl alcohol alone and yielded the 2 : 4-dinitrophenylhydrazone (0·770 g.). However, a similar experiment in which the mixture had been kept in the dark without irradiation for the same period yielded benzaldehyde 2 : 4-dinitrophenylhydrazone (0·134 g.), indicating that the weight of benzaldehyde formed by the radiation was 0·636 g.

The organic layer, after treatment with sodium hydrogen sulphite, was washed with alkali, dried, and distilled at 12 mm. through a fractionating column until a residue of ~6 ml. remained. The part of this which was soluble in light petroleum (b. p. 40—60°) containing benzene (2%) was chromatographed from this solvent on alumina (80 g.). For development the percentage of benzene was increased to 5. The earlier fractions yielded dibenzyl ether (0·4 g.), b. p. 150° (bath-temp.)/1 mm. (identified by infrared spectrum). The subsequent fractions yielded a solid which, when recrystallised from methanol, formed colourless crystals, m. p. 85° (0·2 g.), of racemic benzylidenehydrobenzoin (Found: C, 83·4; H, 6·5. Calc. for $C_{21}H_{18}O_2$: C, 83·4; H, 6·0%). This, on treatment with an acidified ethanolic solution of 2 : 4-dinitrophenylhydrazine, yielded benzaldehyde 2 : 4-dinitrophenylhydrazone. Its ultraviolet spectrum ($\lambda_{max.}$ 2575 Å, log ε 2·82; $\lambda_{min.}$ 2350 Å, log ε 2·14) was identical with that of a synthetic sample,[17] m. p. 85°, and no depression occurred on admixture.

(2) An irradiation similar to the above was performed, but the irradiated mixture was not treated with sodium hydrogen sulphite. It was washed with sodium carbonate solution, dried, and worked up otherwise as before. The residue from the distillation was completely soluble in light petroleum (b. p. 40—60°) containing benzene (2%). The earlier fractions from the chromatogram yielded: (*a*) dibenzyl ether (3 g.), b. p. 158°/11 mm., n_D^{20} 1·5648 (Found: C, 84·4; H, 7·4. Calc. for $C_{14}H_{14}O$: C, 84·6; H, 7·1%), the infrared spectrum being identical with that of dibenzyl ether; and (*b*) benzaldehyde dibenzyl acetal, b. p. 220° (bath-temp.)/11 mm. (Found: C, 83·05; H, 6·65. Calc. for $C_{21}H_{20}O_2$: C, 82·9; H, 6·6%), which with acidified, ethanolic 2 : 4-dinitrophenylhydrazine yielded benzaldehyde 2 : 4-dinitrophenylhydrazone.

(3) An experiment similar to the above in which the mixture was kept without irradiation, then worked up as before, yielded no residue after removal of the bromobenzene and benzyl alcohol by distillation.

(4) A 1 : 10 molar mixture (275 ml.) of benzyl alcohol and bromobenzene was irradiated for 168 hr. (total dose 2·64 × 10^{23} ev). Hydrogen bromide (1·0 g., *G* value 2·8) and benzaldehyde (0·46 g., *G* value 1) were formed and were estimated in an aliquot portion. The main bulk of the irradiated mixture was worked up as in (2) and yielded dibenzyl ether (1 g.) and benzaldehyde dibenzyl acetal (1·3 g.). No racemic benzylidenehydrobenzoin was isolated.

Irradiation of a Mixture of Benzyl Alcohol and Hydrobromic Acid (with A. F. EVERARD).—A mixture of benzyl alcohol (270 ml.) and 47% hydrobromic acid (2·7 ml.) was irradiated for

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[17] Read, Campbell, and Barker, *J.*, 1929, 2305.

168 hr. (total dose 1·70 × 10^{23} ev), then washed with sodium carbonate solution, dried, and fractionated. Dibenzyl ether (1·18 g.) and benzaldehyde dibenzyl acetal (0·73 g.) were obtained and identified by infrared spectra. A similar mixture which had been kept in the dark, without irradiation, for the same period yielded dibenzyl ether (0·82 g.) and none of the acetal.

Irradiation of an Equimolecular Mixture of Benzyl Alcohol and [^{14}C]*Bromobenzene.*—[^{14}C]-Benzene was brominated as described for the preparation of bromobenzene by Gattermann.[18]

(1) The mixture (275 ml.) was irradiated for 134 hr. (total dose 1·86 × 10^{23} ev) and worked up as above. The mixture was distilled through a fractionating column and the benzyl alcohol was collected in several fractions, the specific activity of each being measured. However all were of very low activity. The residue (4 g.), b. p. >130°/2 mm., had an activity which suggested that it contained phenyl residues (0·4 g.). The chromatogram fractions containing dibenzyl ether and benzaldehyde dibenzyl acetal were distilled to remove these compounds; the residue was gummy and did not distil at 250°/1 mm. The specific activity of the residue corresponded with the presence of one phenyl residue to every 3—4 benzyl residues.

(2) Carrier diphenyl and diphenylmethane were added to aliquot parts of a similar mixture which had been irradiated for 120 hr. (total dose 1·47 × 10^{23} ev). The former was re-isolated by chromatography of the high-boiling residue and converted into 4-nitrodiphenyl,[19] m. p. 110—112°, the specific activity of which indicated that 67 mg. of diphenyl had been formed in the whole irradiation. Diphenylmethane was re-isolated by making use of its very weak adsorption on alumina and was converted into 2 : 2′ : 4 : 4′-tetranitrodiphenylmethane,[20] m. p. 168—169°, which was almost inactive.

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