[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

Boron Fluoride–Alcohol Alkylations. II. Some Studies on the Mechanism[1,2]

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In the alkylation of benzene with 3-pentanol and boron fluoride the stability of the product alkylate toward rearrangement is established. Unreacted starting alcohol was shown not to be rearranged. Olefins generally are not involved in alkylations with straight-chain secondary alcohols at 0°, although in some cases they apparently do participate to some extent as intermediates at 60°. 2-Pentanol and boron fluoride in pentane give no reaction under conditions that in benzene lead to rapid alkylation. The addition of a small amount of hexaethylbenzene to the pentane mixture leads to rapid decomposition of the alcohol with the formation of a polymeric olefin. These observations lead to a mechanism for the alkylation which involves a complex of some sort between the aromatic ring and a carbonium ion species, within which rapid rearrangements may take place.

Despite the substantial application of alcohols and boron fluoride to the alkylation of aromatic compounds[5] comparatively little research has been done on the mechanism of the reaction. Alcohols form relatively stable Lewis acid–base complexes with boron fluoride and there seems little doubt that such complexes are the actual reactants in the alkylation. The old mechanism of elimination to an olefin followed by addition of benzene across the double bond[6] was shown to be unlikely by Price and Ciskowski[7] who demonstrated that cyclohexanol with BF_3 gave no cyclohexene under conditions which in the presence of naphthalene resulted in rapid alkylation. This mechanism is conclusively disproved for some conditions by the deuterium experiment reported below. Price and Ciskowski suggested instead a heterolytic fission of the alcohol–boron fluoride complex to a carbonium ion which subsequently reacts with the aromatic nucleus. A carbonium ion mechanism of some type is consistent with the high reactivity of secondary alcohols relative to primary alcohols, with the extensive rearrangements often observed,[1] and is analogous to presumably closely related Friedel–Crafts alkylations with alkyl halides and Lewis acids. A carbonium ion mechanism is also consistent with the reaction of optically active 2-butanol and boron fluoride with benzene to yield 2-phenylbutane with about 1% net inversion of configuration,[8] although the significance of the large amount of racemization observed is obscured by the known facile rearrangements in these alkylations.[1,9] Even in a stereospecific reaction a concomitant isomerization of the type $\mathrm{C{-}C{-}\overset{+}{C}{-}C \rightarrow C{-}\overset{+}{C}{-}C{-}C}$ could result in racemization.[9]

The boron fluoride alkylation reaction with alcohols is presumably related closely to the corresponding alkylation with ethers. Important work on the mechanism of the latter reaction has been done by Burwell, Elkin and Shields.[9,10] There seem to be some significant differences between the reactions; their exact relationship has yet to be determined.

The Leaving Group.—The exact nature of the leaving group which is formed with the carbonium ion is not definitely known. Alkylations with boron fluoride and alcohols are promoted by water and especially by acid.[11] In alkylations with boron fluoride and ethers excess boron fluoride has been shown to be a potent catalyst.[10]

A series of experiments was run in which a solution of dried isopropyl alcohol in dried benzene was saturated with boron fluoride at 0°; the reaction was quenched after definite times at 0° by the addition of cold pyridine which precipitated a pyridine–boron fluoride complex. The intensity of the O–H stretching band in the infrared spectrum of the supernatant liquid was used as a measure of the amount of alcohol remaining using Beers' law. In several runs, the alcohol–benzene mixture was further dried by partial distillation to remove the azeotrope with water. The results are summarized in Table I. The three experiments with a reaction time of eight minutes gave extents of reaction within the range 68 ± 5%. The reproducibility is satisfactory and is within the estimated 10% experimental error. The additional drying process did not change the results. Although these experiments certainly were not carried out with the complete exclusion of water, the reproducibility obtained demands that if water is a *required* reagent the trace concentration of water in each experiment must be about the same, an unlikely but not a rigidly excluded possibility. The eight-minute run with added water demonstrates the catalytic effect of small amounts of water. In these experiments the mixture was simply saturated with boron fluoride. Since the amount of excess boron fluoride was not controlled and probably varied from run to run, the reproducibility obtained in Table I suggests that in this reaction excess boron fluoride is not an important catalyst. We hope to do further experiments of this type with rigidly controlled conditions. For the present, however, our working hypothesis is that the leaving group is $HOBF_3^-$ in the absence of promoters and of the type, $HOBF_3{\cdot}HX^-$, with water or other acidic promoters.

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(1) Paper I, A. Streitwieser, Jr., D. P. Stevenson and W. D. Schaeffer, THIS JOURNAL, **81**, 1110 (1959).

(2) This research was supported in part by a grant from the Petroleum Research Fund, administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund. This paper was taken in part from the Ph.D. dissertations of W. D. S. (1956) and S. A. (1958), University of California.

(3) General Electric Fellow, 1955–1956.

(4) National Science Foundation Pre-doctoral Fellow, 1957–1958.

(5) For references, see in ref. 1.

(6) J. F. McKenna and F. J. Sowa, THIS JOURNAL, **59**, 470 (1937).

(7) C. C. Price and J. M. Ciskowski, *ibid.*, **60**, 2499 (1938).

(8) (a) C. C. Price and M. Land, *ibid.*, **62**, 3105 (1940); (b) R. L. Burwell, Jr., and S. Archer, *ibid.*, **64**, 1032 (1942).

(9) R. L. Burwell, Jr., L. M. Elkin and A. D. Shields, *ibid.*, **74**, 4570 (1952).

(10) R. L. Burwell, Jr., L. M. Elkin and A. D. Shields, *ibid.*, **74**, 4567 (1952).

(11) (a) N. F. Toussaint and G. F. Hennion, *ibid.*, **62**, 1145 (1940); (b) C. E. Welsh and G. F. Hennion, *ibid.*, **63**, 2603 (1941).

TABLE I

REPRODUCIBILITY OF RATE OF REACTION OF BENZENE WITH ISOPROPYL ALCOHOL AND BORON FLUORIDE AT 0°

Time, min.	log I_0/I[a]	Reaction, %
0	0.65	..
6.0[b]	.34	48
7.8[c]	.28	57
8.0[b]	.24	63
8.0[b,d]	.18	72
8.0[c]	.21	68
8.0[e]	.01	98
12.0	..	~99[f]

[a] Peak height at 2.9 μ. [b] Ordinary dried reagents used. [c] Ternary azeotrope removed from benzene-isopropyl alcohol mixture before reaction. [d] Pyridine mixture allowed to sit overnight before filtering. [e] Three drops of water added before reaction. [f] Distillation of reaction mixture showed about 1% alcohol remaining.

Product and Reactant Stability.—No adequate prior test has been made of the stability of the alkylation products to the reaction conditions. When boron fluoride was passed through a solution of 3-phenylpentane in benzene the 3-phenylpentane was recovered unchanged. The same result was found when the mixture contained added water. However, these experiments constitute inadequate controls since BF_3 and $BF_3\cdot H_2O$ may differ significantly in catalytic power from other species present during the alkylation.[12] An unambiguous demonstration was obtained as follows: benzene containing 3-phenylpentane was alkylated with isopropyl alcohol and boron fluoride at 0°. The phenylpentane fraction was isolated from the product and was found to be unchanged 3-phenylpentane containing no 2-phenylpentane; *i.e.*, the hydrocarbon persisted unchanged during an actual alkylation. A similar alkylation was carried out using *n*-propyl alcohol at 60° for 20 hours. Again, the recovered 3-phenylpentane contained no detectable 2-phenylpentane by infrared comparison. The alkylation of benzene with 3-pentanol gives a mixture of about two parts of 2-phenylpentane, one part of 3-phenylpentane and probably some *t*-amylbenzene.[1] The rearrangements involved must have occurred before the product-forming step.

In order to test the possibility that starting alcohols might be isomerized before reaction, an alkylation in benzene solution at 0° using 3-pentanol was interrupted at partial reaction. The recovered alcohol was found to be pure unrearranged 3-pentanol. Hence, the rearrangements observed in the alkylation experiments are not due to prior rearrangement of starting alcohol.

It should be noted that in the boron fluoride alkylation of benzene with 2-methoxybutane, Burwell, *et al.*,[10] carefully demonstrated the optical stability of reactant and product.

Aromatic Hydrocarbon Catalysis.—Price and Ciskowski[7] have observed that cyclohexanol by itself saturated with boron fluoride is stable under conditions which promote rapid alkylation in naphthalene. The full significance of this fact seems to have escaped notice. Similarly, when 2-pentanol in pentane is saturated with boron fluoride and is maintained at 0° for one hour, the 2-pentanol is recovered unchanged. In particular, there is no observable decomposition or rearrangement to 3-pentanol. Yet, in benzene under similar conditions, rapid alkylation occurs. Benzene apparently is necessary in the rate-determining step of the alkylation. The necessity of the aromatic hydrocarbon for reaction was emphasized by another experiment: Hexaethylbenzene should not be alkylatable by 2-pentanol for the equivalent of a secondary carbonium ion would be replaced by a much less stable ethyl cation. When 2-pentanol in pentane or heptane solution was saturated with boron fluoride and maintained at 0° for one hour with 0.2 equivalent of hexaethylbenzene, a rapid reaction occurred; the alcohol decomposed completely to a polymeric unsaturated oil. The hexaethylbenzene was recovered unchanged in good yield. The hexaethylbenzene catalyzed the decomposition of the alcohol–boron fluoride complex! A similar reaction using cyclohexene in place of the hexaethylbenzene gave no reaction. Since olefins are generally more reactive to addition than are aromatic rings this result suggests that some sort of complex, perhaps of the π-complex type, with the aromatic ring is involved in the reaction (*vide infra*).

At higher temperatures alcohol–boron fluoride complexes decompose to polymeric materials without additional catalysts. This uncatalyzed reaction may compete more or less effectively with the aromatic hydrocarbon catalyzed reaction even at low temperatures with favorably constituted alcohols. *t*-Amyl alcohol in heptane at 0° rapidly decomposes with boron fluoride. Similarly, 3-methyl-2-butanol with boron fluoride in an inert solvent at 0° gives an unsaturated polymer. It seems significant that the alkylation of benzene with this alcohol gives a complex mixture containing large amounts of *t*-butylbenzene,[1,13] which probably is formed from the cracking products of dimers, trimers or higher polymers. The facile reaction of 3-methyl-2-butanol probably is associated with the neighboring tertiary hydrogen.

Olefins as Intermediates.—Alkylations with at least some secondary alcohols at 0° do not involve significant reaction *via* olefin. The alkylation of benzene with 2-butanol-*d* at 0° gave 2-phenylbutane with no detectable C–D stretching band in the infrared. If a significant amount of alkylation proceeded by way of carbonium ions produced *via* butene, partially deuterated product would be expected because of the reactions

$$C_4H_9OD\cdot BF_3 \longrightarrow C_4H_8 + HOD\cdot BF_3$$

$$\begin{array}{cc} \downarrow & \downarrow \\ C_4H_9{}^+ + BF_3OD^- & C_4H_8D^+ + BF_3OH^- \end{array}$$

The reaction of 2-propanol-1-*d* with benzene at 0° gives 2-phenylpropane-1-*d*, the infrared spectrum of which shows no observable loss or rearrangement of deuterium by comparison with similar material prepared below.[14] No propene could be found in

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(12) We wish to thank Professor H. C. Brown for pointing out this inadequacy.

(13) B. S. Friedman and F. L. Morritz, THIS JOURNAL, **78**, 2000 (1958).

(14) A. Streitwieser, Jr., S. Andreades and W. D. Schaeffer, paper presented at the 132nd Meeting of the American Chemical Society, New York, N. Y., September 10, 1957; Absts., p. 33P. Details will be published separately.

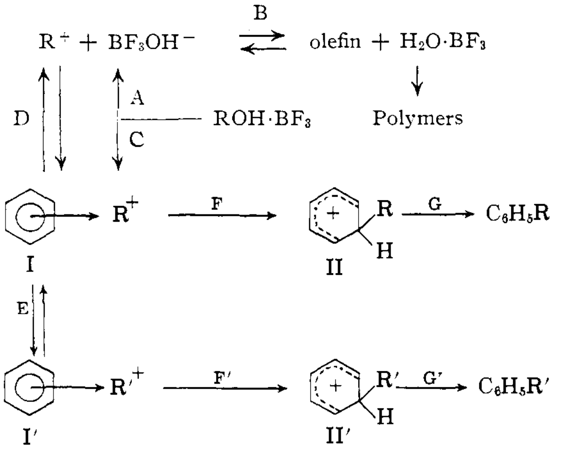
the exit gases from an alkylation of benzene with isopropyl alcohol at 0°.

At higher temperatures, however, olefins are apparently involved to some extent as intermediates. The alkylation of benzene with 2-pentanol-*d* at 61° gives a product alkylate having significant absorption in the C–D stretching region of the infrared. Olefins are known to alkylate aromatic hydrocarbons under comparable conditions.[7,13,15]

Mechanism of the Reaction.—In an excellent review which summarizes many available data, Brown and Nelson[16] recently have presented a comprehensive mechanism of alkylation reactions developed as a particular of electrophilic aromatic substitution. It is appropriate to discuss our results in terms of an extension of this mechanism, as in Chart I.

CHART I

MECHANISM OF BORON FLUORIDE–ALCOHOL ALKYLATION



Tertiary carbonium ions are probably formed so readily that reaction occurs entirely by path A with tertiary alcohols. Path A is apparently also important with secondary alcohols and some primary alcohols at elevated temperatures as indicated by the experiments with deuterated alcohols and with the alcohol-boron fluoride compounds in inert media (*vide supra*). With some secondary alcohols at lower temperatures and with some primary alcohols formation of the complex I can predominate. The reaction of straight-chain secondary alcohols in benzene at 0° proceeds entirely by path C. The necessity of an aromatic nucleus for any reaction to occur in this case brings to mind the kinetic results of Brown, *et al.*,[17] in which the presence of the aromatic ring at the rate-determining step was established in some Friedel–Crafts alkylation. The data do not suffice for the further structural characterization of the complex produced in the rate-determining step of our system [*i.e.*, whether it be of the π-type (I) or σ-type (II)[16]] although the hexaethylbenzene results (*vide supra*) strongly suggest a π-complex and that step C is rate-determining.[18] In the formulation of this complex as I, the role of the leaving group has been omitted. This specie may still be present in a "tight" or "loose ion-pair" and may perhaps still be involved to some extent in covalent bonding to the carbonium ion; indeed, there may be more than one such complex depending on the nature of the bonding, if any, to the leaving group.

A step such as D involving the dissociation of I or II to a carbonium ion which can subsequently form olefin and polymerize is required to account for the formation of polymer in the hexaethylbenzene experiment (*vide supra*) in which path G of the normal alkylation is blocked. The corresponding reverse step of D will account for the incorporation of deuterium into the side chain of alkylation products of reactions at elevated temperatures with ROD.

The identity of the product mixture from 2-pentanol and 3-pentanol[1] necessitates that the isomerization reaction E, be much faster than the product-determining alkylation reaction F. This facile isomerization further suggests that the complexes I and I′ are, indeed, π-complexes in which the groups R and R′ retain much carbonium ion character. Although the rearrangement E is apparently more rapid than F or F′ whenever the rearranged cation I′ is of approximately equal or greater stability than I, reactions F and F′ are clearly more rapid than D. This conclusion is affirmed by the results that neopentyl alcohol yields pure *t*-amylbenzene in good yield, undoubtedly by way of a *t*-amyl cation complexed to benzene, although *t*-amyl alcohol yields polymer undoubtedly by way of *t*-amyl cations not complexed to benzene in the same manner.

The reaction of primary alcohols is slower than that of secondary alcohols undoubtedly because positive charge is being developed at a primary center. Nevertheless, the fact that *n*-propyl alcohol reacts under conditions to which ethyl alcohol is inert suggests that the rearrangement to an isopropyl cation of some type is important and is reflected in the rate-determining step. The ethyl system, of course, cannot rearrange to a secondary carbonium ion. The role of such a rearrangement in the reaction sequence in Chart I cannot be detailed on the basis of the evidence presented here but will be the subject of a subsequent paper.

The reaction of benzene with boron fluoride and 1-butanol-*d* or 1-pentanol-*d* gave deuterated product including side-chain deuteration as indicated by a medium band at 4.6μ in the infrared. A weak band at 4.4μ in these products is due to ring deuteration[19] which undoubtedly arises by electrophilic reaction with $D_2O \cdot BF_3$. The product from 2-pentanol-*d* at 61° does not contain this band—the reaction time was much shorter. Apparently, olefin intermediates are involved to some extent in the reactions of these alcohols, *i.e.*, the

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(15) (a) V. N. Ipatieff and A. V. Grosse, THIS JOURNAL, **58**, 2339 (1936); (b) F. E. Condon, *ibid.*, **70**, 2265 (1948); (c) **71**, 3544 (1949).

(16) H. C. Brown and K. L. R. Nelson, Chapter 56 in B. T. Brooks, S. S. Kurtz, Jr., C. E. Boord and L. Schmerling, "The Chemistry of Petroleum Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1955, Vol. 3, p. 465.

(17) (a) H. C. Brown and M. Grayson, THIS JOURNAL, **75**, 6285 (1953); (b) H. C. Brown and H. Jungk, *ibid.*, **77**, 5584 (1955); (c) H. Jungk, C. R. Smoot and H. C. Brown, *ibid.*, **78**, 2185 (1956).

(18) This proposition is supported by additional results still of a preliminary nature, which will be reported later.

(19) The principal C–D stretching absorption for ring substituted deuteriotoluene occurs at 4.44–4.50 μ; see J. Turkevich, H. A. McKenzie, L. Friedman and R. Spurr, THIS JOURNAL, **71**, 4045 (1949).

reaction sequence A, B and D in Chart I is important. When a heterogeneous mixture of 1-pentanol, boron fluoride and hexane, either "dry" or in the presence of water, was maintained at 65° for three days, almost complete decomposition of the alcohol occurred. In alkylations with these alcohols a number of competing reactions probably take place; these systems are apparently quite complex and are little suited for further studies of mechanism. On the other hand, the reactions of *n*-propyl alcohol seem rather straightforward.

1-Propanol-1-*d* (prepared from propionaldehyde and lithium aluminum deuteride) yields 2-phenylpropane-1-*d* (C–D band, 2188 cm.$^{-1}$) without significant loss or rearrangement of deuterium. The infrared spectrum is identical with that of the product obtained from the alkylation of benzene with 2-propanol-1-*d* (*vide supra*). 1-Propanol-2-*d* yields a mixture of 2-phenylpropane-1-*d* and 2-phenylpropane-2-*d* (C–D doublet, 2155, 2222 cm.$^{-1}$) with no significant loss of deuterium.[14] 1-Propanol-*d* with benzene and boron fluoride at 61° yields cumene having only the weak band at 2260 cm.$^{-1}$ due to ring deuterium. These results subsequently will be discussed in detail; we wish to point out at this time only that they demonstrate the absence of any significant involvement of propylene in this alkylation. The greater simplicity of the reactions in the *n*-propyl system lend themselves satisfactorily to further studies of the alkylation mechanism, although the reason for this difference from the other primary alcohols is not completely clear.

Experimental

Boron fluoride was obtained from Ohio Chemical and Manufacturing Co. and from the Matheson Co., Inc., and was used directly. Benzene was commercial thiophene-free benzene which was distilled and stored over sodium ribbon. Pentane, hexane and heptane were commercial grade solvents which were shaken repeatedly with fuming sulfuric acid, washed, dried, distilled, and stored over sodium ribbon. The infrared spectra were taken on a Baird infrared double beam recording spectrophotometer with sodium chloride optics.

Approximate Rate of Reaction of Benzene with Isopropyl Alcohol and Boron Fluoride.—In each run a mixture of 90 g. of benzene and 10 g. of dry isopropyl alcohol was prepared. In some cases this mixture was used directly; in others the solution was further dried by distillation of 1.5-2 cc. of azeotrope. The solution was contained in a flask arranged for gas inlet and magnetic stirring and closed with a drying tube. While stirring in an ice-bath boron fluoride was rapidly bubbled through the mixture; saturation was achieved within 2-3 minutes, but boron fluoride was passed in during the entire course of the reaction. At the end of the indicated time 14 g. of ice-cold pyridine was poured into the mixture to quench the reaction. After stirring for an additional 20 minutes, a sample of the supernatant liquid was removed, dried with anhydrous potassium carbonate and filtered. The infrared spectrum was taken in a 0.117-mm. cell against a salt plate as the reference. The absorbance at 2.9 μ was compared with that in a spectrum of a mixture prepared by the addition of 10 g. of isopropyl alcohol saturated with boron fluoride at 0° to a solution of 90 g. of benzene and 14 g. of dry pyridine at 0°. The 2.9 μ band of the supernatant solution from the latter mixture was comparable in intensity to a 10% solution of isopropyl alcohol in benzene but differed significantly in shape. In those cases in which some azeotrope was removed from the isopropyl alcohol–benzene mixture before reaction, the initial concentration of isopropyl alcohol was not considered to be changed significantly. The results are summarized in Table I.

Stability of 3-Phenylpentane to Boron Fluoride.—For two hours boron fluoride was passed slowly through a solution of 9.0 g. of 3-phenylpentane in 100 g. of dry benzene. Thirty-three grams of this mixture was decanted into 100 ml. of ice-cold 10% potassium hydroxide. After separating and drying the organic phase over anhydrous sodium sulfate, distillation yielded 2.1 g. of material boiling between 186-193° and having an infrared spectrum identical with that of the starting 3-phenylpentane.

To the remaining benzene solution was added 2 ml. of water, and boron fluoride was again introduced with stirring for two hours. The mixture was then worked up as above; distillation gave 5.1 g. of material, b. 186–192°, which was again identical with the starting 3-phenylpentane.

Stability of 3-Phenylpentane during Alkylation.—A mixture of 8.0 g. of isopropyl alcohol, 100 g. of dry benzene and 8.0 g. of 3-phenylpentane was saturated with boron fluoride with stirring at 0°. After one hour the mixture was worked up as usual; distillation gave 2.0 g., b. 120–186°, and 4.0 g., b. 186–187°. An infrared spectrum of the latter fraction was essentially identical with a spectrum of the starting 3-phenylpentane. In particular, there was no absorption at 10.1 μ; 2-phenylpentane has an intense absorption at this point.

A mixture of 100 ml. of dry benzene, 10 g. of *n*-propyl alcohol and 6 g. of 3-phenylpentane was saturated with boron fluoride at 0° and maintained at 60 ± 0.5° for 24 hours. The mixture was worked up as usual. Distillation gave 1 cc. of a fraction, b. 191–192°. The infrared spectrum of this fraction indicated that it was impure 3-phenylpentane (diisopropylbenzenes were probably present), but the absence of absorption at 10.1 μ demonstrated the absence of any 2-phenylpentane.

Non-rearrangement of Recovered Alcohol.—A mixture of 150 ml. of dry benzene and 20 g. of 3-pentanol was treated with boron fluoride at 0° for 5 minutes. After the usual work-up, distillation through a small column gave 0.5 cc. of a fraction, b. 115–116°, with an infrared spectrum identical with that of the starting 3-pentanol; the strong peaks at 9.4, 10.0 and 11.2 μ present in 2-pentanol were completely absent in the recovered alcohol.

The Decomposition of 2-Pentanol–Boron Fluoride With Hexaethylbenzene.—A solution of 5.0 g. (0.0203 mole) of hexaethylbenzene, 100 g. of *n*-pentane and 10 g. (0.113 mole) of 2-pentanol was saturated with boron fluoride at 0°. After several minutes an orange liquid phase separated. After stirring for an additional hour at 0° the mixture was poured into 150 ml. of cold 10% potassium hydroxide. An infrared spectrum of the dried organic phase showed the absence of any alcohol band. The solution gave a positive unsaturation test with bromine. After removal of the pentane no further material could be distilled up to a pot temperature of 225°. The hot residue solidified on cooling but still gave a positive test for unsaturation.

The experiment was repeated using *n*-heptane as the solvent. After the work-up as above, distillation of the dried organic phase yielded no material boiling below *n*-heptane (absence of pentenes). The solid pot residue was washed with pentane leaving 4.2 g. of a solid having m.p. 129–130°, undepressed when mixed with hexaethylbenzene.

Treatment of 2-Pentanol with Boron Fluoride in Heptane–Cyclohexene.—The experimental conditions were the same as in the previous experiment except that 4.0 g. (0.049 mole) of cyclohexene was used instead of the hexaethylbenzene. Following the work-up, distillation gave 3.2 g. of material, b. 79–85°, which was identified as cyclohexene. The remainder of the material distilled between 95 and 98° to pot dryness (indicating an azeotrope between *n*-heptane and 2-pentanol). An infrared spectrum of the distillate was identical with that of a synthetic mixture of 2-pentanol in *n*-heptane.

Test for Evolution of Propene during Alkylation with Isopropyl Alcohol.—A solution of 100 ml. of dry benzene and 12 g. of isopropyl alcohol was distilled to remove 2 ml. of azeotrope boiling up to 70°. Boron fluoride was bubbled through the resulting solution for 10 minutes at 0° in a flask carrying an exit tube which led successively to a Dry Ice cooled trap, a calcium chloride tube, a gas trap containing water, a calcium chloride tube, and a trap containing a solution of bromine in carbon tetrachloride. The reaction vessel was replaced with a fresh charge of dried isopropyl alcohol–benzene solution and the boron fluoride treatment was repeated. No propylene was found in the Dry Ice trap and no propylene dibromide could be recovered from the bromine–carbon tetrachloride solution.

TABLE II

BORON FLUORIDE ALKYLATION OF BENZENE WITH DEUTERATED ALCOHOLS

Alcohol	Wt. in 100 g. of benzene, g.	Reaction conditions	Infrared spectrum of product alkylate,[a] μ
2-Butanol-*d*	10	0°, 1 hr.	No deuterium
2-Pentanol-*d*	8.5	61°, 2.5 hr.	4.6(m)[b]
1-Propanol-*d*	7	61°, 24 hr.	4.43(w)[c]
1-Butanol-*d*	7	61°, 68 hr.	4.4(w),[c] 4.6(m)[b]
1-Pentanol-*d*	8	61°, 68 hr.	4.4(w),[c] 4.6(m)[b]
1-Pentanol-*d*	10	61°, 20 hr.[d]	4.6(s),[c] 4.6(s)[c]

[a] w, weak; m, medium; s, strong intensity. [b] Side chain C–D. [c] Ring C–D. [d] Mixture was wet with several drops of D_2O. Some unreacted alcohol was recovered from this run which had an infrared spectrum identical with 1-pentanol.

Alkylations with Deuterated Alcohols.—The hydroxy hydrogen of several alcohols was largely replaced either by two exchanges with deuterium oxide or by treatment of the sodium alkoxide with deuterium oxide. The infrared spectra showed that the alcohols used were 75–90% deuterated. In all but one case the solution of the alcohol in benzene was saturated with boron fluoride at 0°, maintained at the appropriate temperature for a given length of time and worked up in the usual way. The alkylate products were examined for deuterium in the infrared. For the case of 2-pentanol-*d* at 61°, the solution of alcohol in heptane was saturated with boron fluoride and added dropwise and with stirring to benzene maintained at 61°. The results are summarized in Table II.

Alcohol–Boron Fluoride Complexes in Inert Media.—A solution of approximately 10% of the alcohol in the hydrocarbon was saturated with boron fluoride; with the secondary and tertiary alcohols the mixture was stirred in an ice-bath for an hour and worked up with aqueous sodium hydroxide in the usual way. In the primary cases, the dense complex was allowed to settle as a lower layer and the mixture was maintained in a constant temperature flask using hexane as the heating bath. The results are summarized in Table III.

TABLE III

STABILITY OF ALCOHOL–BORON FLUORIDE COMPLEXES

Alcohol	Medium	Reaction conditions	Result
2-Pentanol	Pentane	0°, 1 hr.	No reaction[a]
t-Amyl alcohol	Heptane	0°, 1 hr.	Complete reaction[b]
3-Methyl-2-butanol	Heptane	0°, 1 hr.	Complete reaction[b,c]
1-Pentanol	Hexane	65°, 3 days	Almost complete reacn.[d]
1-Pentanol[e]	Hexane	65°, 3 days	Almost complete reacn.[d]

[a] No rearrangement to 3-pentanol evident in the infrared spectrum. [b] No recovered alcohol apparent in the infrared. [c] Solution after normal work-up gave positive tests for olefin. [d] Infrared showed traces of unreacted alcohol. Product was mostly a non-volatile oil. [e] One milliliter of water was added.

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γ-Ray Initiated Reactions. III. Aldehyde Reactions Affected by Carbon Tetrachloride

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Under the influence of γ-rays, *n*-aliphatic aldehydes undergo hydrogen–chlorine exchange with excess of carbon tetrachloride yielding the corresponding acyl chlorides. When carbon tetrachloride concentration was decreased, self condensation of the aldehydes took place and the best yield of the corresponding dehydrated aldol was obtained when carbon tetrachloride concentration was kept at one-fifth mole per mole of aldehyde. The aldol type of condensation with reactive methylenic compounds was found to be general when aliphatic or aromatic aldehydes were used. The yield of the reaction was found to be affected by the dose rate and by the substituents in the aromatic aldehydes. A proposed mechanism is discussed.

Winstein and Seubold[2] have reported that carbon tetrachloride inhibited the decarbonylation of isovaleraldehyde and β-phenylisovaleraldehyde when methyl radicals derived from the thermal decomposition of di(*t*-butyl) peroxide were used as initiators. The formation of the corresponding acid chloride was suggested to be due to a chain reaction propagated by steps 2 and 3.

$$\dot{C}H_3 + R\overset{H}{C}{=}O \longrightarrow R\dot{C}O + CH_4 \qquad (1)$$

$$R\dot{C}O + ClCCl_3 \longrightarrow RCOCl + \cdot CCl_3 \qquad (2)$$

$$RCHO + \dot{C}Cl_3 \longrightarrow R\dot{C}O + HCCl_3 \qquad (3)$$

In the present investigation it has been found that these reactions are general when γ-rays are used as the chain initiator. When *n*-aliphatic aldehydes (1 mole) in solution in carbon tetrachloride (6 moles) under a dry nitrogen atmosphere were irradiated, a significant amount of ionizable chlorine resulted and the acid chloride in the form of its acid was separated in a yield of 10 to 20%. The isolation of hexachlorethane from the reaction product indicates the formation of trichloromethyl radicals during the radiation; hexachloroethane was not found in the absence of aldehydes.

At low concentration of carbon tetrachloride the formation of acid chlorides diminished and self condensation of the aliphatic aldehydes took place. The maximum yield of the corresponding aldol type of condensation was obtained when carbon tetrachloride was present at 0.2 or 0.1 molar ratio of the aldehyde used. Under these latter conditions the crotonization of aliphatic aldehydes and the alkylations of reactive methylenic compounds ($R'CH_2 \cdot COR''$) with aromatic aldehydes took place readily. None of these condensations was effected by γ-radiation in the absence of carbon tetrachloride.

Irradiation of aliphatic aldehydes alone or even in the presence of water[3] did not produce any condensation products. The aldol type of condensation under the influence of γ-rays and in the presence of carbon tetrachloride was not due to the presence of hydrochloric acid that might be

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[1] Post-Doctoral Fellow under Michigan Memorial Phoenix Project No. 98 given by the Chrysler Corporation.

[2] S. Winstein and F. H. Seubold, THIS JOURNAL, **69**, 2916 (1947).

[3] Compare Y. Hirshberg and L. Farkas, *ibid.*, **59**, 2453 (1937).