The compound was unaffected by lithium aluminum hydride in tetrahydrofuran at room temperature. After one hour of refluxing in the same solvent with a large excess of lithium aluminum hydride, 50% of the starting material was recovered unchanged. No 1-(triphenylsilyl)-propan-2-ol was detected.

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AMES, IOWA

[JOINT COMMUNICATION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, AND THE SHELL DEVELOPMENT CO.]

Boron Fluoride–Alcohol Alkylations I. Benzene and the Amyl Alcohols[1]

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The alkylation of benzene with alcohols and boron fluoride has been carried out with all eight amyl alcohols. Primary alcohols require several hours at 60°; secondary alcohols react within minutes at 0°; *t*-amyl alcohol gave no alkylation products at 0°. Rearrangements are general. 2-Pentanol and 3-pentanol gave identical product mixtures containing 65% 2-phenylpentane, 25% 3-phenylpentane and apparently about 10% of *t*-amylbenzene. Neopentyl alcohol gave pure *t*-amylbenzene.

Although a number of investigations of the alkylation of aromatic compounds with boron fluoride and alcohols[3] and ethers[4] have been reported, many questions remain regarding the preparative usefulness of the reaction, the extent of the rearrangements which may occur, and the mechanism of the reaction. The reaction conditions used are often more severe than necessary; in many cases polyalkylbenzenes formed a substantial proportion of the products. Rearrangements are known to occur; *e.g.*, *n*-propyl alcohol gives isopropylbenzene and *n*-butyl alcohol gives *sec*-butylbenzene; however, there is some confusion about how prevalent or extensive these rearrangements may be. Toussaint and Hennion[3d] report that "alkylation apparently occurs without carbon skeleton rearrangement." The results of Hennion and Pieronik[3i] were presented with the implication that the boron fluoride alkylation of chlorobenzene with 2-pentanol yields 2-*p*-chlorophenylpentane and 3-pentanol yields 3-*p*-chlorophenylpentane, etc., although Burwell, *et al.*,[4i] found that 2-methoxypentane with boron fluoride and benzene yields a mixture of 75% of 2-phenylpentane and 25% of 3-phenylpentane. In preparation for experiments designed to examine the mechanism of the reaction between aromatic hydrocarbons and alcohols and boron fluoride, we studied the behavior of all of the eight isomeric amyl alcohols in this reaction.

In the present work alkylations were run with a large excess of benzene to minimize the production of dialkylated products. Generally, 10–20 g. of alcohol in 100 g. of benzene was saturated with boron fluoride and maintained at an appropriate temperature. With secondary alcohols reaction takes place rapidly at 0°; primary alcohols require several hours at 60°. Promoters such as phosphorus pentoxide and sulfuric acid which have been used frequently in such alkylations were not used in our experiments to avoid any complicating factors which they may introduce. Small amounts of water, however, were present in some cases; water is known to be a potent promoter.[5]

In agreement with previous workers[3b] we found that *n*-propyl alcohol and *n*-butyl alcohol give good yields of isopropyl- and *sec*-butylbenzene, respectively. Ethanol does not react under similar conditions.[3b,3d] The amyl alcohols generally give mixtures of monoalkylated products (Table I) which were analyzed by mass spectral and infrared spectral techniques. The mass spectra of primary alkylbenzenes have a prominent peak due to $C_7H_8^+$. The absence of this peak in all of the alkylation products demonstrated the complete absence of 1-phenylpentane, 1-phenyl-2-methylbutane, 1-phenyl-3-methylbutane and 1-phenyl-2,2-

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(2) General Electric Fellow, 1955–1956.

(3) (a) F. J. Sowa, G. F. Hennion and J. A. Nieuwland, THIS JOURNAL, **57**, 709 (1935); (b) J. F. McKenna and F. J. Sowa, *ibid.*, **59**, 470 (1937); (c) **60**, 124 (1938); (d) N. F. Toussaint and G. F. Hennion, *ibid.*, **62**, 1145 (1940); (e) C. C. Price and M. Lund, *ibid.*, **62**, 3105 (1940); (f) C. E. Welsh and G. F. Hennion, *ibid.*, **63**, 2603 (1941); (g) R. L. Burwell, Jr., and S. Archer, *ibid.*, **64**, 1032 (1942); (h) D. Nightingale, H. D. Radford and O. G. Shanholtzer, *ibid.*, **64**, 1662 (1942); (i) G. F. Hennion and V. R. Pieronik, *ibid.*, **64**, 2751 (1942); (j) G. F. Hennion and L. A. Auspos, *ibid.*, **65**, 1603 (1943); (k) D. Nightingale and J. R. Jones, *ibid.*, **66**, 154 (1944); (l) G. Vermillion and M. A. Hill, *ibid.*, **67**, 2209 (1945); (m) G. F. Hennion and N. F. Toussaint, U. S. Patent 2,390,835 (1946); (n) W. N. Axe, U. S. Patent 2,403,963 (1946); (o) G. B. Bachman and H. M. Hellman, THIS JOURNAL, **70**, 1772 (1948); (p) A. V. Topchiev, G. M. Egorova and R. S. Aizinson, *Doklady Akad. Nauk, S.S.S.R.*, **74**, 295 (1950); *C. A.*, **45**, 3825 (1951); (q) I. Romadane and T. I. Rendel, *J. Gen. Chem., U.S.S.R.*, **26**, 215 (1956) (Engl. transl.); (r) I. Romadane, J. Pelcere and O. Vitola, *Latvijas PSR Zinatnu Akad. Vestis*, No. 4, 143 (1957); *C. A.*, **52**, 10025 (1958).

(4) (a) F. J. Sowa, H. D. Hinton and J. A. Nieuwland, THIS JOURNAL, **54**, 2019 (1932); (b) G. F. Hennion, H. D. Hinton and J. A. Nieuwland, *ibid.*, **55**, 2857 (1933); (c) F. J. Sowa, H. D. Hinton and J. A. Nieuwland, *ibid.*, **55**, 3402 (1933); (d) M. J. O'Connor and F. J. Sowa, *ibid.*, **60**, 125 (1938); (e) A. J. Kolka and R. R. Vogt, *ibid.*, **61**, 1463 (1939); (f) W. J. Monacelli and G. F. Hennion, *ibid.*, **63**, 1722 (1941); (g) R. L. Burwell, Jr., and L. M. Elkin, *ibid.*, **73**, 502 (1951); (h) R. L. Burwell, Jr., L. M. Elkin and A. D. Shields, *ibid.*, **74**, 1567 (1952); (i) **74**, 1570 (1952).

(5) A. Streitwieser, Jr., W. D. Schaeffer and S. Andreades, *ibid.*, **81**, 1113 (1959).

TABLE I

REACTION OF BENZENE WITH ALCOHOLS AND BF_3

Alcohol	Moles^{a}	Temp., °C.	Hours	Product B.p., °C.	Product Yield, %
n-Propyl alcohol	0.33	60	24	148–153	55
n-Butyl alcohol	.33	60	24	165–174	80
Ethanol	.33	60	24	.....	0
Ethanol	.33	70	48	.....	0
1-Pentanol	.164	60	24	188–193	85
2-Pentanol	.113	0	1	187–192	67
2-Pentanol	.113	60^{d}	1	184–191	58
3-Pentanol	.113	60	1	187–192	62
3-Methyl-1-butanol	.113	60	12	186–191	68
2,2-Dimethyl-1-propanol	.113	60	12	186–191	61
2-Methyl-1-butanol^{b}	.113	60	9	185–191	68^{c}
3-Methyl-2-butanol	.113	0	1	182–191	42
2-Methyl-2-butanol	.136	0	1	^{d}	

[a] In 100 g. of benzene. [b] Optically active. [c] Optically inactive. [d] See Experimental section.

TABLE II

REACTION PRODUCTS FROM BENZENE, BORON FLUORIDE AND THE AMYL ALCOHOLS

Alcohol	Temp., °C.	Product composition, %^{h} 2-Phenylpentane	3-Phenylpentane	*t*-Amylbenzene	Other components
1-Pentanol	60	53, *54*	20, *20*	25, *22*	3^{a}
2-Pentanol	60	55, *57*	21, *22*	13, *12*	*11*^{b}
2-Pentanol	0	66, *65*	23, *27*	9, *7*	2
3-Pentanol	0	64, *62*	23, *25*	10, *10*	3
3-Methyl-1-butanol	60	14,^{c} *9*	2, *6*	81, *83*	3
2-Methyl-1-butanol	60	20,^{c} *15*	4, *5*	75. *78*	2
Neopentyl alcohol	60	≤4,^{c} *~2*	<1, *~1*	≥96, *97*	0
3-Methyl-2-butanol	0	10,^{c,d} *0*	<1, *0*	88,^{e} *72*	28,^{f} *21*^{g}

[a] Mass spectrum indicates 3% of 2-methyl-3-phenylbutane. [b] 2% $C_{11}H_{22}$, 6% $C_{10}H_{20}$ and 2% $C_{10}H_{14}$ from mass spectra. [c] Includes 2-methyl-3-phenylbutane, if any. [d] Includes *sec*-butylbenzene, if any. [e] Includes *t*-butylbenzene. [f] 25% $C_{10}H_{14}$ (butylbenzenes). [g] *t*-Butylbenzene. [h] First figure from mass spec.; second figure (italics) from infrared.

dimethylpropane in these mixtures. The absence of characteristic peaks at 7.92 and 10.31 μ in the infrared showed the absence also of 2-phenyl-3-methylbutane. The analyses of the amylbenzenes produced reduced in most cases to determinations of a three component system: 2-phenylpentane, 3-phenylpentane and *t*-amylbenzene. Analyses were carried out by both methods. The mass spectral cracking patterns were compared with those of the standard compounds in the usual way. In all but two cases, the product mixtures obtained consisted of 97% amylbenzenes. 2-Pentanol at 60° gave 11% of other products including decenes and butylbenzenes. The mixture from 3-methyl-2-butanol contained 25% of *t*-butylbenzene. Friedman and Morritz[6] have reported the formation of some *t*-butylbenzene during the alkylation of benzene with isoamylene and boron fluoride. The infrared analyses were made by comparing the intensities at selected points with calibration curves prepared with the use of several mixtures of known composition. The results of the analyses are given in Table II. In general, the two sets of analyses agree rather well.

Results and Discussion.—Experimentally, the alkylation of benzene with alcohols and boron fluoride is a convenient reaction in which the reaction mixture remains almost colorless at all times and which can produce good yields of product. Nevertheless, the present results demonstrate that rearrangements are general and are sometimes apparently rather deep-seated. Consequently, the reaction is a preparative method only when such rearrangements are unimportant for reasons of symmetry or of thermodynamics. Several points deserve comment. Within experimental error 2-pentanol and 3-pentanol gave identical mixtures of products. The ratio of 2-phenylpentane to 3-phenylpentane in the products (2.6) may be compared to the ratios found in the alkylation of benzene with ethylcyclopropane and hydrofluoric acid, sulfuric acid or aluminum chloride (1.7),[7] with 2-pentanol and aluminum chloride (1.5),[8] with 3-pentanol and aluminum chloride (3.2)[8] and with 2-methoxypentane and boron fluoride (3.0) (*vide supra*). The equilibrium value found by treatment of either 2- or 3-phenylpentane with strong acids is 2.5.[9]

Although a detailed consideration of the reaction mechanism is deferred to subsequent papers[5] it is clear that intermediates of the carbonium ion type are involved. The rearrangement, represented schematically as $\mathrm{C{-}\overset{+}{C}{-}C{-}C{-}C \rightleftarrows C{-}C{-}\overset{+}{C}{-}C{-}C}$, is rapid compared to the alkylation step itself. In addition we found that about 10% of *t*-amylbenzene is formed, apparently the result of a more deep-seated rearrangement. Although such a small amount is difficult to determine, both sets of analyses gave consistent results and the presence of this compound seems probable.

t-Amyl alcohol gave only a polymeric olefin. The alkylbenzene products from all of the other amyl alcohols showed extensive rearrangements including skeletal rearrangements, some of which are only partially understood at present. With one exception the amyl alcohols are not suitable starting materials for the preparation of pure individual amylbenzenes. The exceptional case, neopentyl alcohol, gave a good yield of pure *t*-amylbenzene. Although Friedel–Crafts reactions of *t*-amyl chloride often give poor yields of this hydrocarbon frequently contaminated by other isomers,[6,10] convenient procedures are available which yield pure product.[6] The difference between the character of the product from neopentyl alcohol on the one hand and from isoamyl and active amyl alcohol on the other hand demonstrates that these alcohols do not yield exclusively the same *t*-amyl cation. Although the exact nature of the difference is not yet known, it is probably associated with complex formation with benzene.[5]

Experimental

Reaction of the Alcohols with Benzene and Boron Fluoride.—The amount of alcohol given in Table I was dissolved

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[6] B. S. Friedman and F. L. Morritz, THIS JOURNAL, **78**, 2000 (1956).

[7] H. Pines, W. D. Huntsman and V. N. Ipatieff, *ibid.*, **73**, 4343 (1951).

[8] H. Pines, W. D. Huntsman and V. N. Ipatieff, *ibid.*, **73**, 4483 (1951).

[9] R. L. Burwell, Jr., and A. D. Shields, *ibid.*, **77**, 2766 (1955).

[10] M. Inatome, K. W. Greenlee, J. M. Derfer and C. E. Boord, *ibid.*, **74**, 292 (1952).

in 100 g. of dry benzene in a 250-ml. flask equipped with a gas dispersion tube and a calcium chloride tube. With the primary alcohols a few drops of water was added. Boron fluoride taken directly from a cylinder (Ohio Chemical and Manufacturing Co., Cleveland, O.) was passed through the mixture until saturation was achieved as evidenced by fuming at the end of the calcium chloride tube attached to the gas exit. In both cases in which the reaction flask was weighed before and after the introduction of boron fluoride, the weight difference corresponded to an equimolar amount of boron fluoride relative to the alcohol present. With the primary and seconary alcohols the flask was immersed in an ice-bath during the introduction of the boron fluoride. The flask was stirred either in the ice-bath or in a 60 ± 0.5° thermostat for the time indicated in Table I. During this period the mixture became turbid due to the separation of an aqueous phase. With the secondary alcohols at 0°, the turbidity developed shortly after saturation with boron fluoride was complete. With the *n*-alkanols at 60° turbidity developed after 10 hours, although the branched chain primary alcohols developed such turbidity after only 1.5 hours. At the end of the reaction the mixture was cooled to room temperature when necessary and was washed with cold 10% potassium hydroxide. The organic phase was dried with sodium sulfate and distilled through a five plate all-glass column containing a tight spiral wound about a central rod ("glass spiral column"). The yields of products and their boiling ranges are given in Table I.

To ensure the purity of the starting alcohols several were synthesized. 2-Pentanol was prepared from methylmagnesium iodide and freshly distilled butyraldehyde; 3-pentanol was prepared similarly from ethylmagnesium bromide and propionaldehyde. Neopentyl alcohol was prepared from pivalic acid, and 3-methyl-2-butanol from methyl isopropyl ketone by reduction with lithium aluminum hydride in the usual way. Optically active 2-methyl-1-butanol ($[\alpha]^{23}\text{D} - 4.75°$) was the kind gift of Professor H. Mosher. The reaction product in this case was totally racemic. The other alcohols were commercial materials which were distilled before use. The exceptional reactions are given.

Ethanol.—No ethylbenzene could be obtained in the two experiments listed in Table I. A similar attempt to alkylate anisole with ethanol and boron fluoride also failed; 92% of ethanol was recovered by distillation.

2-Pentanol at 60°.—A solution of 10.0 g. (0.113 mole) of 2-pentanol in 60 ml. of *n*-heptane was saturated with boron fluoride at 0° as above. A small phase separation occurred. This mixture was added during 15 minutes to magnetically stirred benzene (100 g.) in a 60° thermostat. The system was protected by calcium chloride drying tubes. After two-thirds of the heptane mixture was added, turbidity developed and thereafter phase separation occurred. After the addition was complete the mixture was stirred in the thermostat for an additional hour and worked up as above.

***t*-Amyl Alcohol.**—The reaction was carried out according to the standard procedure. Before saturation by boron fluoride at 0° was complete the mixture became turbid and a second phase appeared. After stirring for an additional hour in the cold, the mixture was washed with cold 10% potassium hydroxide and dried with sodium sulfate. The infrared spectrum of this mixture in a 0.1-mm. cell using benzene in the reference cell showed the absence of alcohol and of alkylated benzenes. The mixture was unsaturated to bromine. On distillation, after the removal of benzene, 2 g. of material was collected, b.r. 155–160°. No more distillate could be obtained up to a pot temperature of 225°. The infrared spectrum of the distillate showed it to be non-aromatic; this material probably consists of isomeric decenes. The clear, colorless pot residue, 8.5 g., was a non-aromatic (infrared spectrum) liquid.

Analysis by Mass Spectra.—The nature of the mass spectra of the amylbenzenes is such that the general isomer analysis problem is mass spectrometrically insoluble. However, the existence of certain relations between the structure of the alkyl substituent on the benzene and the intensities of ions characteristic of the alkylbenzene mass spectra permit the solution of a simplified isomer analysis problem, and in the case of the alkylates under consideration permit a satisfactory solution of the isomer distribution. Furthermore, it is possible to determine the presence of homologs as well as other hydrocarbon types. From the magnitude of the intensity of the ion of $m/q = 92$ ($C_7H_8^+$) in the mass spectra of the alkylates it was possible to conclude that in all cases the concentration of alkylbenzenes of the type $C_6H_5CH_2–C_mH_{2m+1}$ ($m \geq 3$) was less than 1%. This finding reduced the isomer problem from an eight component one to a four component one.

Of the four amylbenzenes that do not have the structure $C_6H_5CH_2C_mH_{2m+1}$, the sums of the concentrations of 2-phenyl-3-methylbutane and 2-phenylpentane are essentially determined by the intensity of the ion of $m/q = 105$ in the mass spectra of an alkylate and the relative concentration of the two isomers is inaccurately determined from the intensity of the ion, $m/q = 104$. The concentrations of the other two isomers, 3-phenylpentane and *t*-amylbenzene, are effectively determined from the intensities of the ions of $m/q = 91$ and 119. The mass spectra were interpreted analytically by the solution of the system of four simultaneous equations relating concentrations of the four isomers to the intensities of the four ions specified.

The concentrations of butylbenzenes and the higher homologs of amylbenzene were estimated from the specific intensities of the appropriate parent ions ($m/q = 134$, 162, 176, etc.) under the assumption that the higher homologs are monoalkylbenzenes. Only in the case of the reaction of 2-pentanol at 60° were there found in the mass spectra ions of other than aromatic substance origin. These ions in the series with $m/q = 154$, 140, 126, 112, 111, etc., quite clearly derive from olefins, primarily $C_{11}H_{22}$ and $C_{10}H_{20}$.

It is difficult to make an estimate of the absolute reliability of the distribution of isomeric amylbenzenes in the alkylates as calculated from the mass spectra. The relative accuracy as measured by repeatability is of the order of ±1 to ±2 based on the total sample. The absolute reliability involves evaluation of the authenticity of the "pure isomers" used in the instrument calibration. The presence of homologs of the amylbenzenes in the alkylates introduces uncertainties of the order of magnitude of the homolog concentrations.

Analyses by Infrared Spectra.—The infrared spectra of the samples were taken with a Baird AB2, recording infrared spectrophotometer with the samples in a 0.1-mm. cell against a salt plate as reference. The spectra of many of the amylbenzenes have been published previously.[7] The spectra of standard hydrocarbons were run as were several mixtures of known composition. Standard 2- and 3-phenylpentane were prepared by the appropriate Grignard reactions followed by hydrogenolysis of the corresponding phenylpentanols.[11] The spectra of these hydrocarbons compared well with samples generously supplied by Professor Herman Pines and by the Universal Oil Products Co.

In the analyses, the primary amylbenzenes were assumed to be absent. These various peaks were used in the analyses: 3-phenyl-2-methylbutane, 7.92 and 10.31 μ (absent in all of the samples); 2-phenylpentane, 10.11 and 13.66 μ; 3-phenylpentane, 8.78, 11.98, 12.8 and 13.66 μ; *t*-amylbenzene, 8.09, 9.93 and 12.8 μ; *t*-butylbenzene, 7.87 μ. Correlation curves prepared from known mixtures were used for the analyses. The results are given in Table II.

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[11] We wish to thank Mr. M. Hight and Mr. S. Suzuki for these preparations.