Corresponding R_f values reported for authentic quercetin are 0.07, 0.78 and 0.40.[9]

After recrystallization from ethanol–water, the m.p. of the quercetin was 315°, uncor.

The next band eluted from the magnesol column was yellow in the visible and brown under ultraviolet light. The portions containing this band were combined and concentrated *in vacuo* to 5 ml., and 50 ml. of pentane was added. The solid removed by centrifugation was dissolved in dry acetone. The chromatographic procedure was repeated until only one zone could be detected on paper chromatograms processed in the three solvent systems mentioned above. The product at this point was reddish brown in color and amounted to 75 mg. from the 20 lb. of currants. The crude product was dissolved in 95% ethyl alcohol, and a saturated solution of basic lead acetate in water added dropwise until no more precipitation was observed. The mixture was filtered, yielding an orange-yellow lead salt. The filtrate was discarded, and the precipitate was washed with alcohol, then water, to remove the unreacted material and excess lead acetate. The washings were discarded, and the lead salt was suspended in 10 ml. of ethyl alcohol. Concentrated sulfuric acid was then added dropwise until the formation of lead sulfate ceased. The lead sulfate was removed by centrifugation and discarded. To remove the excess acid the alcoholic filtrate was passed over an ion exchange column, 20 × 120 mm., packed from ethyl alcohol to a depth of 100 mm. with Amberlite IRA-45 (Rohm and Haas, Philadelphia, Pa.).[10] The eluate from the ion exchange column was taken to dryness *in vacuo*. The resulting solid was dissolved in 5 ml. of boiling water and allowed to cool in the refrigerator overnight. The precipitate was removed by centrifugation and recrystallized again. A brown, oily-like impurity persists in the product to this point. This impurity apparently increases the water solubility of the flavonoid, since in going from one recrystallization to the other, increasing amounts of boiling water are required to dissolve the product. Several recrystallizations are necessary to remove the impurity and produce a yellow solid. The yield at this point was 5 mg. The recrystallized solid was dried *in vacuo* at 80° in the presence of P_2O_5.

Identification of the Isoquercitrin.—The purified solid had a m.p. of 227° (uncor.) and showed R_f values of 0.46 in 15% acetic acid, 0.76 in butanol–acetic acid–water, and 0.75 in 60% acetic acid. These values correspond to the values recorded for both isoquercitrin and quercimeritrin (quercetin-7-glucoside) in these solvents. The unknown substance showed separation from rutin (quercetin-3-rhamnoglucoside) and quercitrin (quercetin-3-rhamnoside) by mixed paper chromatography in 15% acetic acid, but showed no separation from authentic isoquercitrin or quercimeritrin. The ultraviolet absorption spectrum was identical with that for isoquercitrin and quercimeritrin. To differentiate between the two possibilities, the tetramethoxy derivative was prepared by methylation and subsequent hydrolysis, according to the method of Shimokoriyama.[11] Three mg. of the isolated quercetin glucoside was dissolved in 10 ml. of anhydrous acetone, and 0.5 g. of anhydrous potassium carbonate and 0.3 ml. of dimethyl sulfate was then added. The mixture was refluxed for three hours and the acetone was removed *in vacuo*. The resulting cake was suspended in 5 ml. of water and neutralized by dropwise addition of concentrated sulfuric acid. Approximately three drops excess acid was added and the mixture refluxed for two hours to break the glycosidic linkage by hydrolysis. The contents of the reaction vessel were transferred to a centrifuge tube and allowed to cool overnight in the refrigerator. Centrifugation yielded a brown-yellow solid. The method was modified at this point to remove a brown impurity present. The solid was dried and then dissolved in anhydrous acetone. Then it was passed over a column packed with magnesol. Elution with ethyl acetate saturated with water removed a band that was light yellow under ultraviolet light, but not detectable in visible light. A visible brown remained at the top of the column. The eluate containing the yellow band was concentrated to 0.5 ml. and 5 ml. of pentane added. The solid was removed and washed twice with cold benzene. The product was a light yellow solid, m.p. 191–193° (uncor.) which agrees well with the literature value of 193–195°[12] for 3′,4′,5,7-tetramethoxy-3-hydroxyflavone. By this series of reactions, quercimeritrin would have yielded 3,3′,4′,5-tetramethoxy-7-hydroxyflavone which melts at 284–285°.[12] Thus, a quercetin glycoside in black currants has been identified as isoquercitrin.

The dried currants used in this investigation were purchased from a local grocery store. Labels on the unopened boxes indicated that they were of the Black Zante variety (California).

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[9] T. B. Gage, C. D. Douglass and S. H. Wender, *Anal. Chem.*, **23**, 1582 (1951).

[10] C. H. Ice and S. H. Wender, *Proc. of Okla. Acad. Sci.*, in press.

[11] M. Shimokoriyama, *Acta Phytochim. (Japan)*, **15**, 63 (1949).

[12] G. F. Attree and A. G. Perkin, *J. Chem. Soc.*, 234 (1927).

NORMAN, OKLAHOMA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Effect of Promoters on the Alkylation of Benzene by Secondary Butyl Methyl Ether in the Presence of Boron Trifluoride

BY ROBERT L. BURWELL, JR., LLOYD M. ELKIN AND ALFRED D. SHIELDS

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In mixtures of *s*-butyl methyl ether, benzene and boron trifluoride prepared under anhydrous conditions, alkylation occurs at negligible rate when the boron trifluoride–ether mole ratio is less than 0.9, slowly when it is 1.0 and rather rapidly when it is about 1.08. Addition of water or sulfuric or chlorosulfonic acids in small amounts greatly increases the rate of reaction. The relatively rapid reaction of secondary ethers ordinarily observed appears due to the presence of water and an excess of boron trifluoride beyond the stoichiometric. The reaction appears to involve the *s*-butylcarbonium ion but the ion seems not, in general, to result from mere dissociation of the boron trifluoride–ether complex. In a mixture of ethyl ether and benzene, five moles to one, which is saturated with boron trifluoride, no ethylbenzene can be detected in 10 days at 25°.

In accordance with the proposal of Price and Ciskowski[1] it has been generally assumed that alkylation reactions of alcohols and ethers caused by boron trifluoride proceed *via* the formation of an addition product which is unstable under the reaction conditions and decomposes into a carbonium ion and a hydroxy- or alkoxytrifluoroborate anion. The carbonium ion effects alkylation in the customary fashion.

$$ROR' + BF_3 \rightleftharpoons RR'O{:}BF_3 \longrightarrow R'OBF_3^- + R^+ \quad (1)$$

This paper reports results of the alkylation of benzene and toluene by *s*-butyl methyl ether which necessitate some modification of this mechanism, at least for secondary ethers. With mole ratios of boron trifluoride to *s*-butyl methyl ether of about 0.9 and aromatic hydrocarbon–ether ratios of about six, no alkylation can be observed in periods of months at room temperature. If one rejects the assumption that one mole of ether can in some

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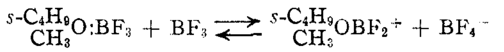
[1] C. C. Price and J. M. Ciskowski, THIS JOURNAL, **60**, 2499 (1938).

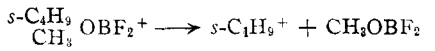
way inactivate nine moles of the ether–boron trifluoride complex, one must assume that the complex as such decomposes but very slowly at room temperatures. One may note also that the complex of boron trifluoride with isopropyl ether is a crystalline solid which begins to decompose detectably only at temperatures in excess of 50°.[2] Thus, mere dissociation of the complex is not responsible for the rapid alkylation reaction ordinarily observed at room temperatures when aromatic hydrocarbons, secondary ethers and boron trifluoride are brought together.[3]

Reasonably rapid alkylation with *s*-butyl methyl ether at room temperatures requires the presence of small additional quantities of boron trifluoride, of strong proton acids[4] or of substances which become strong proton acids[4] when complexed with boron trifluoride.

When benzene is alkylated, no toluene can be detected in the products. This[5] and the other data are consistent with a carbonium ion reaction. With a mole ratio of boron trifluoride to ether in the vicinity of one or greater, carbonium ions may be formed thus



$$\substack{s\text{-}C_4H_9\\ CH_3}O{:}BF_3 + BF_3 \rightleftarrows \substack{s\text{-}C_4H_9\\ CH_3}OBF_2^+ + BF_4^- \qquad (2)$$



$$\substack{s\text{-}C_4H_9\\ CH_3}OBF_2^+ \longrightarrow s\text{-}C_4H_9^+ + CH_3OBF_2 \qquad (3)$$

In the presence of strong acids, the reaction may proceed through the oxonium ion

$$(s\text{-}C_4H_9)(CH_3)OH^+ \longrightarrow s\text{-}C_4H_9^+ + CH_3OH \qquad (4)$$

or by a reaction sequence akin to (2) and (3) in which formation of the ion, $RR'OBF_2^+$, is favored by complexing the fluoride ion removed from $RR'OBF_3$ perhaps as solvated hydrogen fluoride.

Dissociation according to equation (1) has also been postulated to account for the substantial electrical conductivity of the highly purified liquid complex of ethyl ether and boron trifluoride.[6] The proposed presence of ethylcarbonium ion seems inconsistent with the fact that benzene can be alkylated by primary ethers only at about 160°.[3] To avoid possible repression of (1) occasioned by reduction in dielectric constant resulting from dilution with benzene, a mixture of ethyl ether and benzene in a mole ratio of five was prepared and saturated with boron trifluoride. At the end of 10 days, no ethylbenzene could be detected. A reaction resembling (2) could accommodate all the data.

$$2(C_2H_5)_2OBF_3 \rightleftarrows (C_2H_5)_2OBF_2^+ + BF_4^- + (C_2H_5)_2O \qquad (5)$$

On this formulation, an ion of the type $RR'OBF_2^+$ is stable at room temperatures when the alkyl radicals are primary but decomposes by equation (3) when one or more is secondary.

Purity of Boron Trifluoride.—Commercial boron trifluoride is reported to contain small quantities of nitrogen, sulfur dioxide and silicon tetrafluoride. Removal of these was found to be without detectable effect.

Effect of Excess Boron Trifluoride.—With ratios of boron trifluoride to *s*-butyl methyl ether of about 1.00 reaction requires about two weeks. When the reaction mixture is saturated with boron trifluoride (ratio about 1.1) reaction occurs in about one day. This last rate also applies when the reaction mixture is prepared with intensive drying and by use of vacuum line techniques. While the possibility of catalysis by trace impurities cannot absolutely be excluded, it appears at present that stoichiometric excess of boron trifluoride promotes the reaction.

In the cases described above, the reaction mixture is initially homogeneous. If reaction occurs, the mixture becomes turbid and slowly separates into two layers. The upper contains benzene and alkylbenzene, and lower, the boron trifluoride complex with methanol. The unreacted ether continues to react and the lower layer grows to a terminal volume.

Effect of Promoters.—Addition of water, sulfuric acid or chlorosulfonic acid in quantities amounting to a few mole % of the ether results in greatly shortening the reaction time for mixtures in which the boron trifluoride–ether ratio is about 1.00. The reaction time is taken as the time to the appearance of turbidity.

The added promoter forms a small lower layer from which *schlieren* can be seen to rise in the cases of more rapid reaction. The reaction appears largely to occur within or at the surface of the promoter layer.

However the alkylation proceeds initially, reaction *via* oxonium ion, $RR'OH^+$, is likely to be involved in later stages as the strong acid, CH_3OHBF_3, accumulates. This acid is strong enough to cause conjunct polymerization of *s*-butyl methyl ether.[7]

Addition of small quantities of methanol to reaction mixtures whose mole ratio of boron trifluoride to ether is about 1.0 results in inhibition rather than promotion. Methanol, unlike water, does not form a separate phase. A carbonium ion reaction would be less likely to occur in the benzene layer with its much lower dielectric constant than in a water–boron trifluoride complex. In the quantities employed here, the basic qualities of methanol (as complexing boron trifluoride) must compensate the acid characteristics of the complex. With the much stronger acid, ethanesulfonic acid, reaction occurs, however, even though no separate phase is visible until midway in the reaction.

In reaction mixtures prepared without drying and without protection from atmospheric moisture, reaction occurs usually in less than a day at room temperatures when the ratio of boron trifluoride to *s*-butyl methyl ether is 1.00 and in a few hours when the mixture is saturated with boron trifluoride. One can often observe a droplet of a heavier phase from which *schlieren* rise. The relatively rapid reaction between secondary ethers and benzene observed in preparative experiments[3] would appear

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(2) H. C. Brown and R. M. Adams, THIS JOURNAL, **64**, 2557 (1942).

(3) M. J. O'Connor and F. J. Sowa, *ibid.*, **60**, 125 (1938).

(4) R. L. Burwell, Jr., and L. M. Elkin, *ibid.*, **73**, 502 (1951).

(5) On a carbonium ion mechanism, one would expect the formation of *s*-butylcarbonium ion enormously to outweigh that of methylcarbonium ion.

(6) N. N. Greenwood, R. L. Martin and H. J. Emeleus, *J. Chem. Soc.*, 3030 (1950).

(7) R. L. Burwell, Jr., L. M. Elkin and L. G. Maury, THIS JOURNAL, **73**, 2430 (1951). In this experiment an equimolar mixture of alcohol and ether was saturated with boron trifluoride.

due to the presence of a stoichiometric excess of boron trifluoride and small amounts of water.

The use of relatively large quantities of strong acids as "assistants" in the alkylation of benzene with boron trifluoride has been reported.[8] These are essential for the alkylation by primary alcohols at moderate temperatures.

Materials and Techniques

Materials.—*s*-Butyl methyl ether was distilled from and stored over potassium. Reagent grade benzene was dried over Drierite. Tank boron trifluoride of two different suppliers was employed (Ohio Chemical Company, Matheson). Where specified, it was purified by formation of the benzonitrile–boron trifluoride addition complex.[9] This was exposed to reduced pressures to remove volatile impurities. Upon warming the complex to nearly 100°, boron trifluoride was evolved. A Dry Ice trap was used to remove volatilized benzonitrile.

Techniques.—Alkylation experiments were run in three ways: (1) Boron trifluoride was bubbled through the ice-cold reaction mixture in conventional apparatus with no attempt to avoid atmospheric moisture. (2) Reagents and apparatus were dried. Guard tubes of Drierite were provided. However, some transfer in air was necessary and thoroughly anhydrous conditions were not achieved. (3) An all glass apparatus and high vacuum techniques were employed. Stopcocks were lubricated by perfluorolube grease (E. I. du Pont de Nemours and Co.). No sign of attack by boron trifluoride was observed on this grease. The apparatus consisted of a reaction tube to which was connected a mercury manometer, a lead to pumps and McLeod gage and a tubing leading through a stopcock and two traps to a standard taper joint. The apparatus was first pumped out and flamed. A mixture of previously dried ether and benzene was placed in a flask provided with a standard taper joint. A mirror of potassium was volatilized onto the inner wall of this flask before inserting the ether–benzene mixture. The flask was attached to the apparatus, frozen, pumped out, filled with dry, oxygen-free nitrogen and the contents of the flask were refluxed. The mixture was then transferred to the reaction flask by distillation in high vacuum. The flask was replaced by another containing boron trifluoride–benzonitrile addition complex. After pumping out, the addition complex was warmed. The traps were cooled with Dry Ice. The boron trifluoride distilled into the reaction mixture until its pressure reached 20 cm. The boron trifluoride generator was then isolated, the reaction tube frozen with liquid air and then sealed off. Solutions of the composition employed absorbed 1.08 to 1.10 moles of boron trifluoride per mole of ether at a pressure of boron trifluoride of 75 cm. Very little residual pressure appears until the mole ratio of boron trifluoride to ether becomes nearly one. A mixture so prepared (*s*-butyl methyl ether, 0.0265 mole; benzene 0.193 mole), saturated at a boron trifluoride pressure of 20 cm., became turbid in 28 hours at 25°.

Experimental Results

With reaction mixtures in which the mole ratio of boron trifluoride to ether is between 0.98 and 1.00 and the aromatic hydrocarbon–ether ratio is between 5 and 7, turbidity appeared in from 11 to 21 days in those cases in which routine precautions against water admixture were observed. On humid days when no effort was made to ensure anhydrous conditions, reaction occurred in about 1 day.

A study was made of the effect of water and various other substances upon the time required for the appearance of turbidity. In mixtures of otherwise identical composition, this time permits an ordering of degree of reactivity The results of a typical experiment are shown in Table I. A mixture of the indicated composition was prepared by procedure (2) and divided among seventeen tubes. Indicated quantities of other materials were added. In this experiment, purified boron trifluoride was used, but tank boron trifluoride gave similar results.

TABLE I

EFFECT OF PROMOTERS ON ALKYLATION OF BENZENE BY SECONDARY BUTYL METHYL ETHER AND BORON TRIFLUORIDE[a]

Filling Sequence	Promoter	Mole %[b] promoter	Reaction time,[c] hr.
1	None	..	>140[d]
16	None	..	>140
17	None	..	~400[e]
2	H_2SO_4	5.5	2.2
15	H_2SO_4	5.5	2.4
3	H_2O	18	11–17
14	H_2O	18	11–17
5	H_2O	36	22
13	H_2O	36	25
4	H_2O	55	30–34
12	H_2O	55	30–34
6	CH_3OH	14	>360[f]
11	CH_3OH	14	>360[f]
7	CH_3OH	14	30–34
	$+H_2O$	18	
10	CH_3OH	14	30–34
	$+H_2O$	18	
8	CF_3COOH	5.5	~240[f]
9	$C_2H_5SO_3H$	6.6	30–34[f]

[a] Moles ether:BF_3:benzene = 1.00:1.00:6.44. [b] Mole % of moles of ether. [c] Where time ranges are shown, reaction occurred during an unobserved period. [d] 10 mole % HSO_3Cl added. Reaction in 3.5 hours. [e] Reaction mixture was stored in wax-sealed, glass-stoppered flask. Other samples were in rubber-stoppered tubes. [f] System one phase. All others were two phase, the promoter layer lying at the bottom of the tube.

In similar experiments with smaller quantities of water, variation in quantity of added water from 2.2 to 17% of that of the boron trifluoride made little difference in the reaction time which lay in the range of 8–14 hours. Larger amounts of water led to somewhat slower reaction. In the absence of added water, reaction occured in 11 days. This set of experiments was run in glass-capped tubes.

In comparison experiments it was found that chlorosulfonic acid was distinctly more active as a promoter than sulfuric acid.

Experiments were run with the benzene replaced by toluene. Similar results were obtained. Stannic chloride and acetic acid do not seem to act as promoters.

In all cases in which promotion occurred, the promoter formed a separate phase save for the case of ethanesulfonic acid. The time required for turbidity was roughly inversely proportional to the quantity of ethanesulfonic acid

No investigation was made of the effect of conditions upon yields. In a mixture of composition similar to that in Table I and with a 0.03 mole proportion of sulfuric acid as promoter, a 67% yield of *s*-butylbenzene was obtained on distilling the re-

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(8) S. J. Slanina, F. J. Sowa and J. A. Nieuwland, THIS JOURNAL, **57**, 1547 (1935); H. L. Wunderly, F. J. Sowa and J. A. Nieuwland, *ibid.*, **58**, 1007 (1936); N. F. Toussaint and G. F. Hennion, *ibid.*, **62**, 1145 (1940); C. E. Welsh and G. F. Hennion, *ibid.*, **63**, 2603 (1941); G. F. Hennion and L. A. Auspos, *ibid.*, **65**, 1603 (1943).

(9) H. C. Brown and R. B. Johannesen, *ibid.*, **72**, 2937 (1950).

action mixture in a 25-plate semimicro column. If the residue be taken as di-*s*-butylbenzene, the yield was 24% of di-*s*-butylbenzene. No toluene could be detected.

A mixture of 0.975 mole of ethyl ether and 0.196 mole of benzene was saturated with boron trifluoride. After 10 days at 25° the hydrocarbon portion was isolated by washing with water and then phosphoric acid. Its infrared absorption spectrum as measured on the Beckman IR2T spectrograph differed negligibly from benzene. Less than 1.5% of ethylbenzene could have been present.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

The Alkylation of Aromatic Hydrocarbons by Optically Active Secondary Butyl Methyl Ether in the Presence of Boron Trifluoride

BY ROBERT L. BURWELL, JR., LLOYD M. ELKIN AND ALFRED D. SHIELDS

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Alkylation of benzene by optically active *s*-butyl methyl ether with boron trifluoride yields *s*-butylbenzene of inverted configuration and optical purity of a little greater than 1%. The drastic racemization occurs during the alkylation step and is not, in significant degree, due to racemization of ether before reaction or of product after formation. The racemization may be connected with isomerization of the carbonium ion since 2-methoxypentane gives a mixture of 2- and 3-phenylpentane of near the equilibrium composition.

When benzene is alkylated by optically active *s*-butyl alcohol, *s*-butylbenzene of low rotation, opposite in sign to that of the starting alcohol, is reported to result.[1,2] Of the various alkylating agents, the rotation was largest, 0.007 of the optically pure product, for boron trifluoride and hydrogen fluoride.

The existence of finite, if low, rotations is of interest in the theory of carbonium ion reactions. Interpretation of the reported rotations[1,2] is made difficult by three considerations: (1) absence of rotation due to optically active impurities was not rigorously demonstrated, (2) absence of racemization of *s*-butylbenzene subsequent to its formation was not demonstrated, (3) absence of racemization of the alcohol previous to reaction was not demonstrated and, indeed, some racemization previous to reaction is known to occur with some of the alkylating agents studied.[3]

Study of the alkylation of benzene by optically active *s*-butyl methyl ether with boron trifluoride was undertaken to clarify these details. The ether was chosen because it is much less likely to undergo racemization before reaction[4] owing to the absence of ways in which a racemic or racemizable intermediate can be reconverted to the ether; boron trifluoride because it gave as high rotations as any of the alkylating agents.[1,2]

The alkylation gives *s*-butylbenzene of inverted configuration[5] and of an optical purity of 1.1 to 1.4% (Table I). The stereochemistry thus resembles that reported for *s*-butyl alcohol but the optical purity is roughly twice as great.

That the rotation was due to optically active *s*-butylbenzene was shown by careful purification of the product and by the identity of the rotatory dispersion of the product and that of optically pure *s*-butylbenzene.

The absence of racemization of the ether before reaction was shown by interrupting an alkylation and isolating unreacted ether. Its rotation was

TABLE I

ALKYLATION WITH OPTICALLY ACTIVE *s*-BUTYL METHYL ETHER

Technique	Aromatic hydrocarbon, moles	Ether, mole	BF_3, mole	Additive (mole)	Corrected rotation[a] monoalkylate, deg.
	Benzene				
(2)	0.272[b]	0.0360	0.0371	HSO_3Cl (0.0003)	0.30 (1.3%)
(2)	.272[b]	.0360	0.0371	H_2SO_4 (0.0015)	.26 (1.1%)
(2)	.340	.0423	Sat.[c]	H_2SO_4 (0.0008)	.33 (1.4%)
	Mesitylene				
(1)	0.18	.0415	Sat.	None	.36
	p-Xylene				
(1)	0.22	.0415	Sat.	None	.71
	Toluene				
(1)	0.24	.0415	Sat.	None	.57
(1)	.076[b]	.0166	0.0166	H_2SO_4[d]	.85[g]
(1)	.076[b]	.0166	.0166	H_2SO_4[d]	.82
(1)	076[b]	.0166	.0166	H_2O[d]	.55
(1)	.076[b]	.0166	.0166	CH_3OH[d]	.88
(1)	.076[b]	.0166	.0166	None	.85
(2)	.24[e]	.0415	.044	H_2SO_4[d]	.69
(2)	.12[i]	.021	.022	H_2O[f]	.46
(2)	.26[i]	.021	.022	H_2O[f]	.46
(1)	.12[b]	.021	Sat.	None	.80
(1)	.12[b]	.021	Sat.	CH_3OH	No reacn.[h]
(2)	.24	.0415	Sat.	H_2SO_4 (0.001)	0.48

[a] In the first three runs, optical purity is also listed. The rotations are corrected to optically pure ether. [b] A batch of hydrocarbon, ether and BF_3 was prepared, and split into two or more parts for treatment with different additives. [c] Purified BF_3. [d] One small drop. [e] Reaction period was two days at −10°. [f] Two small drops. [g] Centrifuged during reaction period. [h] No turbidity appeared, no *s*-butyltoluene could be isolated by distillation. [i] A batch was split between two tubes and inoculated with water. Extra toluene was added to one tube.

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[1] C. C. Price and M. Lund, THIS JOURNAL, **62**, 3105 (1940).

[2] R. L. Burwell, Jr., and S. Archer, *ibid.*, **64**, 1032 (1942).

[3] R. L. Burwell, Jr., *ibid.*, **64**, 1025 (1942).

[4] R. L. Burwell, Jr., L. M. Elkin and L. G. Maury, *ibid.*, **73**, 2428 (1951).

[5] J. Kenyon, H. Phillips and V. P. Pittman, *J. Chem. Soc.*, 1072 (1935), reported that (+)*s*-butyl *p*-toluenesulfonate reacts with phenylmagnesium bromide to give (−)*s*-butylbenzene. (+)*s*-Butyl *p*-toluenesulfonate is configurationally related to (+)*s*-butyl alcohol. By analogy with the work of R. L. Letsinger (THIS JOURNAL, **70**, 406 (1948)) on the condensation of organosodium compounds with optically active 2-bromoalkanes, the reaction of Kenyon, *et al.*, probably involves inversion. Thus, *s*-butyl alcohol and *s*-butylbenzene of like sign are probably configurationally related. That assumption will be made in this paper.