The Alkylation of Aromatic Hydrocarbons with Saturated Hydrocarbons[1]

LOUIS SCHMERLING* AND J. A. VESELY

Universal Oil Products Company, Des Plaines, Illinois 60016

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Electron transfer resulting in alkylation of an aromatic hydrocarbon by a saturated hydrocarbon occurs when a mixture of the hydrocarbons is treated with cupric chloride and aluminum chloride at room temperature. The reaction of benzene and isopentane, for example, yields neopentylbenzene, *tert*-pentylbenzene, and *sec*-isopentylbenzene as well as some by-products. Aralkylation of benzene with ethylbenzene produces 1,1-diphenylethane. The cupric chloride may be replaced by ferric chloride or other higher valent halide of a metal which exists in more than one valence. The aluminum chloride may be replaced by another Friedel–Crafts catalyst, such as ferric chloride or zinc chloride. Isopentane serves as a promoter for the alkylation of benzene with other saturated hydrocarbons. During the reaction, cupric chloride is converted to cuprous chloride and hydrogen chloride: it may be regenerated, resulting in an increased yield of alkylbenzene, by carrying out the alkylation reaction in the presence of oxygen (air).

Aluminum chloride catalyzes the destructive alkylation of aromatic hydrocarbons with paraffins.[2] For example, *tert*-butylbenzene, *p*-di-*tert*-butylbenzene, and isobutane are the chief products of the reaction of benzene with 2,2,4-trimethylpentane at 20–50° [2a] while toluene, ethylbenzene, *n*-propylbenzene, propane, and isobutane are obtained by the reaction of benzene with isopentane at 175°.[2b]

Alkylation of an aromatic hydrocarbon by a paraffin or a cycloparaffin without accompanying cracking occurs when the saturated hydrocarbon undergoes hydrogen transfer to form an intermediate carbonium ion which then condenses with the aromatic hydrocarbon. For example, the reaction of a dihaloalkane with benzene in the presence of aluminum chloride and an isoparaffin or a methylcycloalkane yields a monoalkylbenzene corresponding to the dihaloalkane and an alkyl- or cycloalkylbenzene corresponding to the saturated hydrocarbon.[3] The reaction of 1,1-dibromoethane with benzene in the presence of 2,3-dimethylbutane produces ethylbenzene and hexylbenzenes, chiefly 3-phenyl-2,2-dimethylbutane;[3c] the reaction of 1,1-dichloro-3,3-dimethylbutane, benzene, and methylcyclopentane yields 1-phenyl-3,3-dimethylbutane and (methylcyclopentyl)benzene.[3a]

Another method for converting a saturated hydrocarbon to a carbonium ion is described in this paper. It is shown that aromatic hydrocarbons may be directly alkylated with paraffins and cycloparaffins in the absence of other organic compounds by treating the reactants with a higher valent chloride of a metal which exists in at least two valences (*e.g.*, cupric chloride) and and a Friedel–Crafts catalyst.[4]

Experimental Section

Cupric Chloride–Aluminum Chloride.—The metal chloride mixture was preformed for some of the experiments by mixing equimolar quantities of commercial anhydrous cupric chloride (B & A Allied Chemicals) and aluminum chloride powders (Baker Analyzed). An induction period of about 30 sec permitted efficient mixing of the powders, for example by manual shaking. There was then a sudden evolution of heat accompanied by evolution of hydrogen chloride (probably due to the presence of $CuCl_2 \cdot 2H_2O$ in the commercial "anhydrous" cupric chloride). The product, a mustard-colored powder, showed a small loss in weight. For example, when 38 g (0.28 mol) of cupric chloride was mixed with 36 g (0.27 mol) of aluminum chloride, the product weighed 73 g. On the other hand, when 30 g (0.22 mol) of freshly dried cupric chloride was shaken with 28 g (0.21 mol) of aluminum chloride, there was little evolution of hydrogen chloride and no loss in weight.

In other experiments, the cupric chloride and the aluminum chloride were added separately to the mixture of hydrocarbons.

Most of the experiments were carried out in a fluted glass flask equipped with a mechanical stirrer, an efficient (usually Dry Ice cooled) condenser, and a thermometer well. A mixture of the hydrocarbon reactants (*e.g.*, 0.3 mol of benzene and 0.3–0.6 mol of isopentane) and 0.08–0.17 mol of the metal chloride complex was vigorously stirred at the desired temperature, usually for 2–4 hr. The product consisted of two layers: an upper layer, which was chiefly unreacted hydrocarbons and contained only a very small amount of reaction product; and a viscous lower layer, which was hydrolyzed with ice–water, yielding hydrocarbon [unreacted aromatic hydrocarbon, alkylated hydrocarbon, *p*-polyphenyl[5]—more properly named poly(*p*-phenylene)] and cuprous chloride. The *p*-polyphenyl and cuprous chloride were separated from the other products by filtration and the latter were then water and alkali washed, dried over potassium carbonate, and analyzed by gas–liquid chromatography (glc, F & M Model 720 instrument), the peaks being identified by comparison of their retention times with those of authentic samples and by preparative glc (Varian Aerograph Autoprep) combined with ir (Beckman IR-9), nmr (Varian A 60), and/or mass spectrum (CEC, Model 103C). In many cases pure samples for characterization were isolated by fractional distillation.

Some of the experiments were carried out in a 1-l. stainless steel turbomixer autoclave. The procedure and work-up were similar to those used with the glass alkylating flask except that usually no attempt was made to separate the reaction product layers. The entire product was treated with ice–water, suction filtered, washed, dried, and then distilled to remove unreacted hydrocarbons. The composition of the high-boiling residue was usually determined with the aid of chromatography and vacuum distillation.

Cupric Chloride–Zinc Chloride.—A mixture of the hydrocarbons (1.0 mol of isopentane and 0.8 mol of benzene), anhydrous cupric chloride powder (0.4 mol), and crushed zinc chloride (0.15 mol) in a glass liner was sealed into an Ipatieff-type rotating autoclave, nitrogen pressure (usually 30 atm) was added (chiefly for the purpose of keeping the reactants in the liner), and the rotating autoclave was heated (usually at 200°) for 4 hr. The hydrocarbon product was decanted or filtered from the metal chlorides, washed, dried, and characterized in the usual manner.

Results and Discussion

Cupric Chloride and Aluminum Chloride. A. Benzene and Isopentane.

—Alkylation of aromatic hydro-

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[1] Presented before the Division of Petroleum Chemistry, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 28 to April 2, 1971.

[2] (a) A. V. Grosse and V. N. Ipatieff, *J. Amer. Chem. Soc.*, **57**, 2415 (1935); (b) A. V. Grosse, J. M. Mavity, and V. N. Ipatieff, *J. Org. Chem.*, **3**, 137 (1938).

[3] (a) L. Schmerling, J. P. Luvisi, and R. W. Welch, *J. Amer. Chem. Soc.*, **77**, 1774 (1955); (b) L. Schmerling, R. W. Welch, and J. P. West, *ibid.*, **78**, 5406 (1956); (c) L. Schmerling, R. W. Welch, and J. P. Luvisi, *ibid.*, **79**, 2636 (1957).

[4] L. Schmerling, U. S. Patent, 3,420,908 (Jan 7, 1969).

[5] P. Kovacic and A. Kyriakis, *Tetrahedron Lett.*, 467 (1962); *J. Amer. Chem. Soc.*, **85**, 454 (1963).

carbons by saturated hydrocarbons occurs when the reactants are stirred at near room temperature with a mixture of aluminum chloride and cupric chloride. For example, treating a mixture of benzene and isopentane with cupric chloride and aluminum chloride at 17–21° resulted in the production of pentylbenzenes (about 40 mol % based on the formation of 0.5 mol per mol of cupric chloride) together with smaller amounts of ethylbenzene, isopropylbenzene, and 1,1-diphenylethane; polymerization of benzene to *p*-polyphenyl[5] occurred in about 12 mol % yield based on the cupric chloride. About one-third of the pentylbenzene was neopentylbenzene, the remainder being *tert*-pentylbenzene and *sec*-isopentylbenzene (3-phenyl-2-methylbutane).

The alkylation of benzene by isopentane proceeds by an oxidative (electron transfer) reaction involving the cupric chloride.

$$(CH_3)_2CHC_2H_5 + CuCl_2\cdot AlCl_3 \longrightarrow (CH_3)_2\overset{+}{C}C_2H_5 + HCl + CuCl + AlCl_3$$

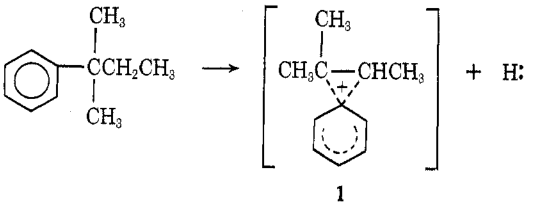
$$C_6H_6 + (CH_3)_2\overset{+}{C}C_2H_5 \longrightarrow C_6H_5C(CH_3)_2C_2H_5 + H^+$$

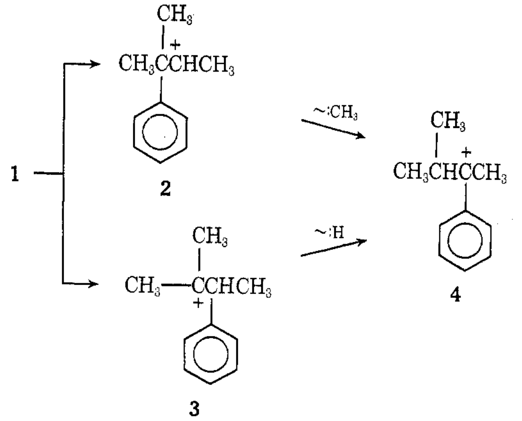
$$H^+ + CuCl_2 \longrightarrow HCl + CuCl$$

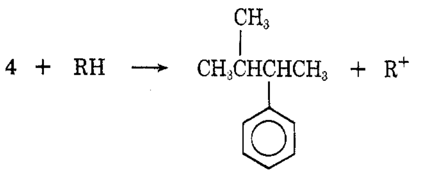
The overall reaction is

$$(CH_3)_2CHC_2H_5 + C_6H_6 + 2CuCl_2 \xrightarrow{AlCl_3} C_6H_5C(CH_3)_2C_2H_5 + 2CuCl + 2HCl$$

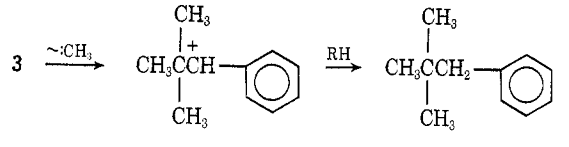
Most of the *tert*-pentylbenzene underwent isomerization to *sec*-isopentylbenzene[6] and neopentylbenzene.[7] The isomerization is believed to involve abstraction of hydrogen attached to a secondary carbon with neighboring phenyl group participation resulting in formation of a phenonium ion.[3c] (Conversion of **1** to **4** may occur directly by migration of H: or CH$_3$: without formation of **2** and **3**; **4** is stabilized by resonance of the benzylic ion.)





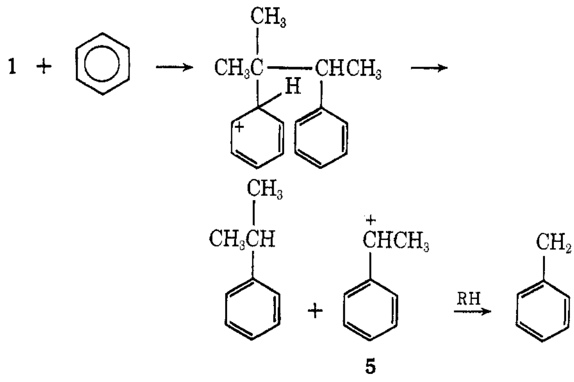


Migration of a methyl group in **3** yields neopentylbenzene.[7] (RH may be isopentane or *tert*-pentylbenzene.)



The fact that about one-third of the pentylbenzene formed by the alkylation of benzene with isopentane at 17–21° was neopentylbenzene suggests that isomerization of the primarily formed *tert*-pentylbenzene to neopentylbenzene occurs in the presence of the mixture of cupric chloride and aluminum chloride under milder conditions than those reported in the literature with aluminum chloride as catalyst. The ease of isomerization may be related to the fact that, at the end of the reaction, most of the alkylbenzene was in the viscous catalyst layer (presumably as a complex from which it was recovered by hydrolysis) rather than in the organic upper layer (excess benzene and isopentane).

Formation of the small amounts of ethylbenzene and isopropylbenzene which were by-products of the isopentane reaction may be explained by a number of pathways. One involves destructive alkylation.[2] Another involves the phenonium ion (**1**) or another intermediate ion (**2** or **3**).



Alternatively, the phenylpentyl ion (**4**) may have added to benzene. The isopropyl cation may be converted to cumene, to propane or to polymeric product.[8]

Some other routes may be postulated to explain the formation of 1,1-diphenylethane. A phenylethyl ion (**5**) formed as indicated or by the action of cupric chloride and aluminum chloride on ethylbenzene may have added to benzene.

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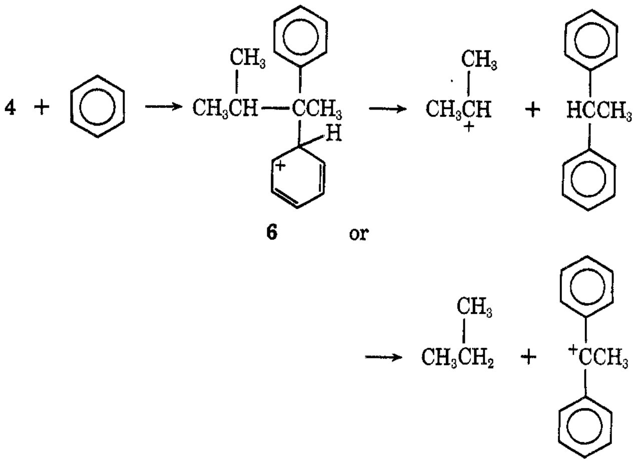
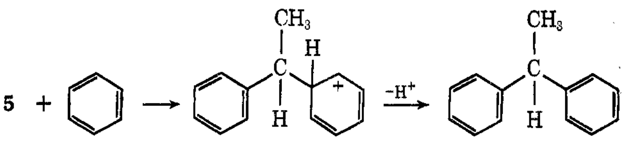
[6] L. Schmerling and J. P. West, *J. Amer. Chem. Soc.*, **76**, 1917 (1954).

[7] (a) C. D. Nenitzescu, I. Necsoiu, A. Glatz, and M. Zalman, *Chem. Ber.*, **92**, 10 (1959); (b) R. M. Roberts and Y. W. Han, *J. Amer. Chem. Soc.*, **85**, 1168 (1963).

[8] A referee has pointed out that an objection to this pathway is that it favors the formation of 2,2-diphenyl-3-methylbutane (none of which was observed) by the simple (and energetically favorable) elimination of the ring proton of **6** (aromatization).





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B. Benzene and Alkylbenzene.—The aralkylation of benzene by ethylbenzene in the presence of cupric chloride plus aluminum chloride is, of course, analogous to its alkylation by isopentane; a benzylic hydrogen is readily abstracted from ethylbenzene by electron transfer involving cupric chloride. When a solution of ethylbenzene in excess benzene was contacted with cupric chloride and aluminum chloride at 23-30°, 1,1-diphenylethane was produced in 40-45 mol % yield based on the cupric chloride present. Some other diarylalkanes also were formed, the major one being 1-phenyl-1-(ethylphenyl)ethane obtained in about 10% yield; its formation indicates addition of the intermediate benzylic cation to ethylbenzene, rather than to the more predominant benzene. It seems worth noting that again the ethylbenzene-benzene layer of the product contained only a small amount of the reaction products. Practically all of the diarylethane was recovered by hydrolyzing the catalyst layer (the so-called "lower layer").

Aralkylation also occurred when benzene was treated with cumene and a mixture of cupric chloride and aluminum chloride at 23-27°. An 8 mol % yield of 2,2-diphenylpropane based on the copper salt was obtained, together with a 15 mol % yield (based on the cumene) of diisopropylbenzene.

C. Benzene and 2,3-Dimethylbutane.—Alkylation of benzene with 2,3-dimethylbutane in the presence of an equimolar mixture of cupric chloride and aluminum chloride at 25-30° resulted in 9 mol % (based on the copper chloride) of hexylbenzenes and a small amount of ethylbenzene. The hexylbenzenes were the isomers obtained by the aluminum chloride catalyzed reaction of benzene with 1-chloro-3,3-dimethylbutane or with 2-chloro-2,3-dimethylbutane:[6] 2,2-dimethyl-3-phenylbutane (about 80% of the mixture) and 2,3-dimethyl-2-phenylbutane.

D. Benzene and Cycloparaffins.—The reaction of cyclohexane with benzene at 26-30° yielded only a trace of cyclohexylbenzene. The chief product was *p*-polyphenyl, which was obtained in 60 mol % yield based on the reaction of 1 mol of benzene per 2 mol of cupric chloride.

Under the same conditions, the reaction of benzene with methylcyclohexane resulted in a 52 mol % yield of (*x*-methylcyclohexyl)benzene.

Reaction of decahydronaphthalene with benzene gave a 48 mol % yield of decahydronaphthylbenzene (evidently a mixture chiefly of the cis and trans isomers of 2-phenyldecahydronaphthalene, apparently the same isomers as those obtained by the aluminum chloride catalyzed reaction of benzene with 1,1-dichloroethane and decahydronaphthalene[3c]). Only a very small amount of *p*-polyphenyl was produced.

E. Isopentane As a Promoter.—Isopentane serves as a promoter for the alkylation of aromatic hydrocarbons with other alkanes and cycloalkanes. For example, reaction at room temperature of 2.5 mol of benzene with 1 mol of 2,3-dimethylbutane mixed with 0.13 mol of isopentane produced 17 mol % of hexylbenzenes (about 80% 3-phenyl-2,2-dimethylbutane and 20% 2-phenyl-2,3-dimethylbutane) and 2 mol % pentylbenzenes, compared to 9 mol % of hexylbenzenes obtained in the absence of added isopentane. The yields of ethylbenzene (10 mol %) and isopropylbenzene (3%) by-products also were approximately double the yields (5 and 1%, respectively) obtained in the absence of isopentane.

Addition of a minor amount of isopentane (0.06-0.11 mol) to cyclohexane (1.0 mol) and benzene (2.5 mol) also increased the amount of cyclohexylbenzene formed, from merely a trace amount to 20 mol % (based on the cupric chloride in the 0.5 mol of complex used). Pentylbenzenes were obtained in 6-7 mol % yield based on the isopentane (about 3% based on the cupric chloride) while ethylbenzene and isopropylbenzene were formed in 16-23 and 13-21 mol % yields, respectively, based on 1 mol of either per mol of isopentane. *p*-Polyphenyl was formed in about 60% yield based on the cupric chloride.

The mechanism of the promoting effect of isopentane was not proved. However, it seems possible that isopentane is more readily converted to cation than the other hydrocarbons investigated (for example, 2,3-dimethylbutane and cyclohexane) and that the *tert*-pentyl cation abstracts hydride ion from the alkane or cycloalkane to regenerate the isopentane and form a new cation (2,3-dimethylbutyl or cyclohexyl) which yields alkylbenzene by condensing with benzene. The low yield of pentylbenzene which is produced is due to reaction of some of the *tert*-pentyl cation with benzene instead of alkane or cycloalkane.

F. Alkylation of Toluene.—At 25-28°, reaction of toluene with isopentane during 0.5 hr yielded 12 mol % of pentyltoluenes based on the cupric chloride. Alkylation with 2,3-dimethylbutane under the same conditions gave a 1 mol % yield of hexylbenzenes, chiefly a mixture of 2-tolyl-2,3-dimethylbutane and 2-tolyl-3,3-dimethylbutane, identified by comparison of the glc chromatogram with that of the product of the alkylation of toluene with neohexyl chloride. The only by-product seemed to be polytolylene, a granular, dark brown powder, obtained in about 30 mol % based on the formation of 0.5 mol of tolylene per mol of cupric chloride.

Cupric Chloride-Zinc Chloride.—It was of obvious interest to obtain information about the scope of the cupric chloride promoted alkylation. Zinc chloride was tested as an example of a Friedel-Crafts catalyst which is markedly inferior to aluminum chloride in its activity and in its ability to catalyze reactions, such as isomerization and isoparaffin alkylation, which proceed *via* hydride ion abstration.

The reaction of benzene with isopentane at 200° in the presence of a mixture of cupric chloride and zinc chloride was very similar to that which occurred at 17–21° in the presence of cupric chloride and aluminum chloride. The liquid product (not the catalyst) contained ethylbenzene, isopropylbenzene, pentylbenzene, and 1,1-diphenylethane in about one-fourth the total yield obtained when aluminum chloride was used. Chlorobenzene was also formed.

The pentylbenzene consisted of a mixture of *tert*-pentylbenzene and *sec*-isopentylbenzene, no neopentylbenzene being observed. This is to be expected in view of the low reactivity of zinc chloride in isomerizations. The formation of *sec*-isopentylbenzene (and, indeed of any alkylation product) is apparently due to hydride ion abstraction (*via* electron transfer) involving the cupric chloride.

As suggested by the formation of 1,1-diphenylethane, the mixture of cupric chloride and zinc chloride caused the aralkylation of benzene by ethylbenzene. When a mixture of the hydrocarbons and the metal chlorides was heated at 200°, 1,1-diphenylethane was obtained in 12 mol % yield together with a 7 mol % yield of chlorobenzene and a 10 mol % yield of *o*- and *p*-chloroethylbenzene. Formation of the latter compounds suggests that ethylbenzene undergoes chlorination more readily than does benzene, which was present in the reaction mixture in four times the quantity of ethylbenzene.

tert-Butylbenzene (about 20 mol % yield) and small amounts of chlorobenzene, diphenylmethane, and triphenylmethane were obtained by the reaction of benzene and isobutane at 200° in the presence of cupric chloride and zinc chloride.

Ferric Chloride. Catalyst and Electron-Transfer Agent.—Ferric chloride is usually a more active condensation catalyst than zinc chloride but less active than aluminum chloride. At 50° a mixture of cupric chloride and ferric chloride catalyzed little reaction between benzene and isopentane; at 150°, it produced pentylbenzenes, consisting of a mixture of *tert*-pentylbenzene and *sec*-isopentylbenzene with little or no neopentylbenzene, in 40 ml % yield based on the cupric chloride.

Ferric chloride also serves as an electron-transfer agent, but is less effective than cupric chloride. The reaction of benzene and isopentane at 21–24° in the presence of an equimolar mixture of ferric chloride and aluminum chloride resulted in an 8 mol % yield of pentylbenzenes based on the ferric chloride. Ethylbenzene and cumene were also produced.

Effect of Oxygen.—As shown above, formation of pentylbenzene from benzene and isopentane involves conversion of cupric chloride to cuprous chloride, the theoretical yield being 0.5 mol of product per mol of cupric chloride. Experiments were performed to determine whether carrying out the reaction in the presence of oxygen pressure would increase the yield of alkylation products by regenerating the cupric chloride.

$$4CuCl + 4HCl + O_2 \longrightarrow 4CuCl_2 + 2H_2O$$

Stirring a solution of isopentane (1.0 mol) and benzene (2.5 mol) with a mixture of 0.5 mol each of cupric chloride and aluminum chloride at 21–26° in a stainless steel turbomixer resulted in 25 mol % yield of the three pentylbenzenes together with small amounts of the usual by-products; the metal reactor apparently had an adverse effect on the reaction compared to glass. Carrying out the reaction under 1200 psi air pressure almost doubled the yield of pentylbenzenes (46 mol %). Use of hydrogen chloride (0.6 mol) and air had little additional effect (the yield of pentylbenzenes was 48 mol %) other than to increase the yield of *p*-polyphenyl by about 50%. (The average yield of benzene polymer was 3–4 g, whereas the yield in the presence of added hydrogen chloride was about 6 g.)

Similarly, in the presence of cupric chloride and zinc chloride at 200°, the yield of pentylbenzenes (3%) and of 1,1-diphenylethane (4%) by the reaction of benzene with isopentane and ethylbenzene, respectively, were very markedly increased (to 14 and 22%, respectively) by carrying out the reaction under air pressure. Since zinc chloride, unlike aluminum chloride, is not inactivated by water, it is not affected by the water formed during the oxidation of the cuprous chloride/hydrogen chloride and the catalyst mixture may be used in continuous flow alkylation.