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ARTICLE

Indium(III) triflate — a catalyst for greener aromatic alkylation reactions

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Abstract: An environmentally friendly method for alkylating aromatic compounds with simple alcohols in the presence of a catalytic amount of indium(III) triflate is reported. Ionic liquids are used as solvents and energy-efficient heating is provided by microwave radiation. Good yields are obtained with benzyl, secondary, and tertiary alcohols. Simple primary alcohols are not effective alkylating agents under these conditions. With tertiary alcohols, activated aromatic compounds such as toluene and anisole must be used to obtain good yields. The catalyst, which is immobilized in a water-insoluble ionic liquid, can be easily recycled without significant loss of activity.

Key words: Friedel–Crafts alkylation, green chemistry, indium, ionic liquids, microwave radiation.

Résumé : On présente une méthode écologique d'alkylation de composés aromatiques au moyen d'alcools simples en présence d'une quantité catalytique de triflate d'indium(III). Des liquides ioniques sont utilisés comme solvants et un chauffage écoénergétique est assuré par rayonnement micro-ondes. On obtient de bons rendements avec les alcools benzyliques, tertiaires et secondaires. Les alcools primaires simples ne sont pas de bon agents d'alkylation dans ces conditions. Dans le cas des alcools tertiaires, il faut utiliser des composés aromatiques tels que le toluène ou l'anisole pour obtenir de bons rendements. Le catalyseur, qui est immobilisé dans un liquide ionique insoluble dans l'eau, peut être recyclé facilement sans perte importante d'activité. [Traduit par la Rédaction]

Mots-clés : alkylation de Friedel–Crafts, chimie verte, indium, liquides ioniques, rayonnement micro-ondes.

Introduction

The Friedel–Crafts reaction is widely used in industry for the manufacture of chemical intermediates. Almost 150 years after its discovery, it remains one of the more important methods for attaching groups of carbon atoms to benzene rings. The traditional method utilizes potentially polluting acidic catalysts (Lewis acids such as $AlCl_3$, BF_3, and $ZnCl_2$ or Bronsted acids such H_2SO_4, HF, etc.) and toxic or polluting volatile organic solvents. Additionally, hazardous by-products such as hydrohalic acids may be generated. This has led to a dramatic increase in research directed toward finding more environmentally friendly catalysts and solvents for Friedel–Crafts reactions.

Scandium(III) and several lanthanide(III) salts are water-stable Lewis acids that have shown catalytic activity in a wide variety of organic reactions.[1] In the past few years, indium(III) salts have become the focus of many Lewis acid catalyzed reactions. While weaker acids than their aluminum and boron counterparts, they are of great importance because of their relatively low toxicity as well as their stability in water and air.[2] A variety of indium(III) salts have been reported as catalysts in Friedel–Crafts electrophilic aromatic substitution reactions with carbonyl compounds,[3] alkyl halides,[4] sulfonyl chlorides,[5] alkenes,[6] alkynes,[7] aziridines,[8] cyclopropanes,[9] and epoxides.[10] This paper reports the results of indium(III) triflate (trifluoromethanesulfonate) catalyzed alkylation reactions where simple alcohols are used as alkylating agents.

Results and discussion

From a "green chemistry" perspective, alkylations utilizing alcohols are advantageous because the only reaction by-product is water. However, classical alkylations with alcohols often employ H_2SO_4 or BF_3 as catalysts.[11] In 1997, Fukuzawa and co-workers[12] reported that some alcohols, arenecarbaldehydes, and acetals reacted with aromatic compounds in the presence of catalytic amounts of scandium(III) triflate to form alkylated compounds. To compare the catalytic activity of indium(III) triflate with that of scandium(III) triflate and some lanthanide(III) triflates, the alkylation of benzene by benzyl alcohol in ionic liquid solvents was chosen as a model system. By using an inert solvent, the quantity of aromatic compound typically used as both reactant and solvent can be reduced. Since dialkylation is sometimes observed in Friedel–Crafts reactions, an approximate 6:1 molar ratio of aromatic hydrocarbon to alcohol was maintained. Under these conditions, negligible amounts of dialkylated products were observed. Ionic liquids were chosen as inert solvents because of their environmentally friendly properties. In particular, they are nonflammable, thermally stable below 200 °C, possess very low vapor pressures, can be readily recycled and dissolve a wide range of inorganic and organic compounds.[13] It has been shown previously that scandium(III) triflate immobilized in ionic liquids is an effective catalyst for Friedel–Crafts alkylation of aromatic compounds with alkenes.[14] Additionally, reaction media consisting of ionic liquids and aluminum chloride, indium chloride, or various metal bistriflimide or triflate salts have been shown to catalyze Friedel–Crafts acylation reactions.[15] The particular solvents selected for our study were trihexyl(tetradecyl)phosphonium bis(trifluoromethanesulfonyl) imide (referred to as [thtdp][NTf_2]) and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (referred to as [emim][NTf_2]). In addition to the properties mentioned above, ionic liquids containing the [NTf_2] ion have low viscosities even at room temperature,

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are insoluble in water, and readily dissolve the metal triflates. They also represent two major classes of ionic liquids, tetraalkylphosphonium and imidazolium salts. The reaction mixtures were heated by microwave radiation. Because of the polar nature of the ionic liquids,[16] reaction temperatures of 120 °C may be obtained within a few seconds and reactions can be completed in 1.5 h, thus making the entire process energy efficient. Results from the various reactions (Table 1) reveal that both tetraalkylphosphonium- and imidazolium-based ionic liquids are effective solvents for this alkylation reaction.

The imidazolium ionic liquid is the preferred solvent because of the ease of isolating the product. The product is isolated by simple extraction of the reaction mixture with pentane in which the product is soluble and the ionic liquid is insoluble. The catalyst remains in the ionic liquid and water formed as the by-product can be easily removed. By contrast, isolation of the product from the tetraalkylphosphonium ionic liquid is more difficult because the ionic liquid is also soluble in common solvents such as pentane, ethyl ether, and dichloromethane.

The catalytic activity of indium triflate was found to vary as the anion in the ionic liquid changes (Table 2). Similar variations have been reported for Friedel–Crafts acylation reactions carried out in ionic liquids.[15e,17] Reactions in hydrophobic ionic liquids such as [emim][NTf_2] proceed with high yields whereas those conducted in water-miscible ionic liquids such as [emim][BF_4] are largely ineffective. Since the reaction by-product is water, its exclusion from the reaction medium helps to drive the reaction toward completion. At elevated temperatures, the presence of water in ionic liquids leads to hydrolysis of the [BF_4] and [PF_6] counterions with liberation of HF.[18] This does not completely explain the lower activity, since HF is also known to catalyze the alkylation of aromatics by alcohols. By comparison, the [NTf_2] counterion is a stable, weakly coordinating anion with a high degree of charge delocalization. This may allow for an increase in the effective acidity of the In(III) ion, thus contributing to the overall efficiency of the reaction. From these results, it can be seen that indium triflate is an excellent catalyst for the Friedel–Crafts alkylation of benzene with benzyl alcohol utilizing [emim][NTf_2] as the solvent.

The effects of temperature and irradiation time on the rate of product formation are shown in Fig. 1. As can be seen, the reaction occurs faster at 120 °C than at 80 °C. Reaction rates at 100 °C are virtually identical to those at 120 °C. Below 80 °C, the formation of dibenzyl ether competes with the formation of diphenylmethane. Benzyl alcohols are known to undergo dehydration with the formation of dibenzyl ethers when heated in various phosphonium ionic liquids in the absence of additional catalysts.[19] In the current system, no dibenzyl ether was detected at reaction temperatures above 100 °C, even at shorter reaction times. When dibenzyl ether was added to the reaction mixture at temperatures above 100 °C, it was rapidly converted to diphenylmethane; therefore, it appears that any ether formed is also converted to alkylated product.

The study was expanded to determine the effect that various electron-withdrawing and -releasing groups attached to the benzene ring would have on the reaction. Results are shown in Table 3. As can be seen, benzyl alcohols possessing a variety of electron-withdrawing groups give high product yields (entries 2–7). Benzyl alcohols with an electron-releasing group at the meta-position also give excellent yields (entries 9 and 11) whereas electron-releasing groups attached at the para-position give significantly lower yields. These results are interesting because presumed reactive carbocation-like intermediates should be formed readily from benzyl alcohols possessing electron-releasing groups. To determine whether the high temperature employed in the reaction was responsible for the lower yields, reactions were conducted at lower temperatures (70 and 90 °C) with reduced microwave power; however, yields were not improved. The majority of the material formed in these reactions was insoluble in pentane and appeared to be polymeric in nature.

Table 1. Product yields in the reaction of benzyl alcohol with benzene utilizing various catalysts and ionic liquid solvents.

Catalyst	[thtdp][NTf_2], yield of diphenylmethane (%)	[emim][NTf_2], yield of diphenylmethane (%)
$Sc(OTF)_3$	79	85
$In(OTF)_3$	77	87
$Yb(OTF)_3$	63	76
$Sm(OTF)_3$	46	60
$Nd(OTF)_3$	3	0

The catalyst and ionic liquid can be recycled easily. Following the reaction of benzyl alcohol with benzene (Table 2, entry 1), droplets of water were observed in the reaction mixture. Extraction with pentane removed the product and any unreacted benzene, while the indium(III) triflate remained dissolved in the ionic liquid. Water was removed by warming the catalyst solution under reduced pressure. After the drying process was completed, additional benzyl alcohol and benzene were added to the catalyst solution and the reaction repeated. The system was cycled a total of three times with yields of 85%, 87%, and 86% obtained. A minimum of 95% of the mass of the catalyst solution was recovered after each reaction cycle. Spectral analyses of the catalyst solution before and after reaction indicated no decomposition of the ionic liquid. In related experiments, Seddon and co-workers[15e] found that insignificant amounts of indium(III) chloride were leached from the catalyst solution during acylation reactions conducted in [bmim][NTf_2].

To gain a better understanding of the mechanism of the indium(III) triflate catalyzed alkylation reaction, a variety of simple primary, secondary, and tertiary alcohols were used as substrates (Table 4). No alkylated product could be observed in the reaction mixture when primary alcohols were used (entries 1 and 2). Cyclic secondary alcohols gave high yields of the desired products (entries 4 and 5). Interestingly, 2-butanol (entry 6) formed only trace amounts of the alkylated product with the majority of the product appearing to be polymeric hydrocarbons. When 2-methyl-2-propanol (entry 9), a tertiary alcohol, was reacted with benzene, only a small amount of *tert*-butylbenzene was detected. Recently, it has been reported[20] that substantial amounts of isobutene dimers and trimers were formed during the attempted *tert*-butylation of aromatic hydrocarbons with *tert*-butyl chloride catalyzed by silica-supported indium salts. When more reactive aromatic hydrocarbons were substituted for benzene (entries 7, 8, 10, and 11), monoalkylated products were obtained in satisfactory yields. Elimination appears to be a competing reaction that is suppressed when more reactive arenes are used. Allyl alcohol (entry 3) reacted readily at lower temperatures (70 °C), but neither allylbenzene nor 1-phenylpropene was detected by NMR or IR analysis of the product mixture. Instead, a material with spectral properties similar to substituted polystyrene was obtained. To determine whether a radical mechanism might be involved, reactions were conducted in the presence of a radical inhibitor. When hydroquinone was added to a reaction mixture of benzene and benzyl alcohol, the reaction proceeded normally, suggesting that the alkylation reaction is not a radical process. Similarly, addition of hydroquinone to a reaction mixture of allyl alcohol and benzene did not prevent the formation of a polymeric product. Nonradical polymerization initiated by a carbocation intermediate has been proposed previously in indium alkylation reactions[20] and several transition metal bistriflimide salts are known to catalyze polymerization of styrene.[21] These observations suggest that highly reactive alcohols tend to form intermediates that polymerize unless captured rapidly by activated aromatic compounds. By contrast, even slightly deactivated aromatics such as chlorobenzene (entry 12) give acceptable yields with benzyl alcohol.

Table 2. Reaction of benzyl alcohol with benzene in various ionic liquids using indium(III) triflate as the catalyst.

Phosphonium-based ionic liquid	Yield of diphenylmethane (%)	Imidazolium-based ionic liquid	Yield of diphenylmethane (%)
[thtdp][NTf_2]	77	[emim][NTf_2]	87
[thtdp][PF_6]	27	[emim][PF_6]	52
[thtdp][BF_4]	11	[emim][BF_4]	10
		[bmim][PF_6][a]	4
		[bmim][BF_4][a]	0

[a] [bmim] is the 1-butyl-3-methylimidazolium ion.

Fig. 1. Conversion of benzyl alcohol to diphenylmethane at various reaction times and temperatures.

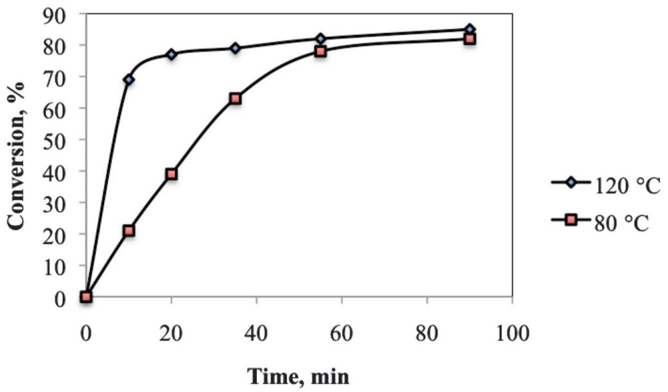
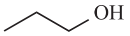
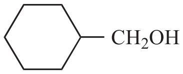
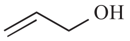
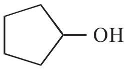
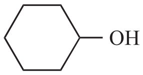
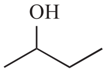
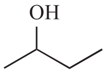
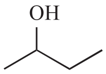
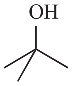
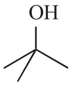
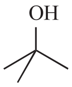
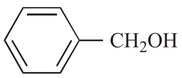


Table 3. Effect of benzyl alcohol substituents on product yields in alkylation of benzene catalyzed by indium(III) triflate.

Entry	Substituent on benzyl alcohol	Yield of substituted diphenylmethane (%)
1	H	87
2	*p*-F	85
3	*p*-Cl	88
4	*m*-Cl	88
5	*o*-Cl	92
6	*p*-NO_2	93
7	*p*-CO_2CH_3	69
8	*p*-CH_3	52
9	*m*-CH_3	83
10	*p*-OCH_3	17
11	*m*-OCH_3	90

Table 4. Indium(III) triflate catalyzed alkylation of aromatic hydrocarbons with various simple alcohols.

Entry	Arene	Alcohol	Yield of alkylated product (%)
1	Benzene		—
2	Benzene		—
3	Benzene		—[a]
4	Benzene		76
5	Benzene		77
6	Benzene		<5
7	Toluene		52[b]
8	Anisole		58[c]
9	Benzene		8[a]
10	Toluene		55[d]
11	Anisole		73[e]
12	Chlorobenzene		61[f]

[a] Reaction temperature of 70 °C.
[b] 2% para, 41% ortho, 17% meta.
[c] 56% para, 42% ortho, 2% meta.
[d] 91% para, 8% ortho, 1% meta.
[e] 88% para, 11% ortho, 1% meta.
[f] 58% para, 40% ortho, 2% meta.

When the secondary alcohol 1,1-diphenylmethanol was used as the reactant, the product was found to consist of a mixture of triphenylmethane, diphenylmethane, and benzophenone. As the amount of benzene in the reaction mixture is increased, the proportion of alkylation product (i.e., triphenylmethane) increases. The amount of diphenylmethane and benzophenone can be suppressed, but not totally eliminated. The indate counterion may play a significant role, since a free diphenylmethylcarbocation intermediate should lead to the formation of some dibenzhydryl ether;[22] however, none is observed. Under the same reaction conditions, 1-phenylethanol produces only a trace of 1,1-diphenylethane. The remainder of the product appears to be a mixture of higher molecular weight hydrocarbons with an IR spectrum similar to that of polystyrene. This outcome may be rationalized in terms of an intermediate that preferentially eliminates a proton to produce styrene, which in turn reacts further to produce various oligomers.

In conclusion, it has been shown that indium(III) triflate immobolized in a water-insoluble imidazolium ionic liquid is a highly effective catalyst for the alkylation of aromatic hydrocarbons using benzyl, secondary, and tertiary alcohols as the alkylating agents. The process is environmentally friendly because of the stability of the catalyst in air and water and ease of recycling the system and because the only reaction by-product is water.

Experimental

General

The imidazolium ionic liquids were purchased from Aldrich Chemical Company and Ionic Liquid Technologies, Inc. The phosphonium ionic liquids were a generous gift from Cytec Canada, Inc. The metal triflates were purchased from Aldrich Chemical Company. All chemicals were used as received from the vendors.

Characterization of the reaction products

Each of the compounds synthesized in these reactions is a known compound whose physical and spectral properties have been previously described in the chemical literature. Purity of compounds isolated from these reactions was established by GC–MS. The identity of reaction products was established by obtaining IR, NMR, and mass spectra and comparing them with those of the authentic compound. When gas chromatography was used to establish isomer ratios, retention times of authentic compounds were used to verify chromatographic peak assignments. Gas chromatographic and mass spectra data for some representative reaction products are provided in the supplemental data (Table S1) (see Supplementary material section).

Typical procedure for the alkylation reaction (synthesis of diphenylmethane)

All reactions were performed in a Discover-SP microwave reactor (CEM Corp., Matthews, North Carolina) using a thick-walled 10 mL glass vessel equipped with a magnetic stir bar and a PTFE-lined pressure cap. Into the vessel was placed 0.035 g (0.10 mmol) of indium(III) triflate, 0.108 g (1.00 mmol) of benzyl alcohol, 0.5 mL of benzene, and 0.5 mL of [emim][NTf_2]. The capped vessel was placed in the microwave reactor, stirring begun, and the mixture heated at 120 °C for 1.5 h. At the end of this time, small droplets of water could be seen on the walls of the vessel. Five millilitres of pentane was added to the vessel and it was shaken vigorously to extract the product. When agitation was discontinued, two layers were observed in the vessel. The upper layer of pentane and product was removed with a pipet. This extraction process was repeated a total of three times. The combined pentane layers were filtered through a 1 in. column of activated alumina to remove any traces of ionic liquid. Solvent was removed from the filtrate to yield 0.143 g (87% yield) of diphenylmethane. Identity of the product was confirmed by NMR and IR spectral analysis.

Supplemental material

Supplementary material for this article is available on the journal Web site at http://nrcresearchpress.com/doi/suppl/10.1139/cjc-2013-0290. Gas chromatographic and mass spectral data for the products of several representative reactions are found in Table S1.

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