

Alkyltrifluoromethanesulphonates as Alkylating Reagents for Aromatic Compounds

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Methyl and ethyl trifluoromethanesulphonates ('triflates'), prepared by conventional routes involving either trifluoromethanesulphonic acid ('triflic acid') or its anhydride, contain traces of triflic acid as an impurity, which catalyse their alkylation reactions with aromatic compounds. Pure methyl triflate, obtained from reaction between CH_3I and $\text{CF}_3\text{SO}_3\text{Ag}$, does not alkylate *p*-cymene after several hours at 100 °C. Pure ethyl triflate, prepared by a similar method, is thermally less stable under these conditions, and alkylation takes place only after long induction periods during which some breakdown to triflic acid occurs. With aromatic substrates such as *p*-cymene or mesitylene the onset of alkylation is followed rapidly by the formation of isomerisation and disproportionation products. Benzyl triflate, prepared from PhCH_2Br and $\text{CF}_3\text{SO}_3\text{Ag}$, alkylates *p*-cymene even at room temperature. The strong Lewis acids SbF_5 and AlCl_3 similarly catalyse alkylation reactions of methyl and ethyl triflates, but BF_3 , FeCl_3 , and SnCl_4 are much less effective.

FRIEDEL-CRAFTS alkylation reactions are important synthetic reactions and a subject of continued interest.¹ Much of the work on this reaction has naturally centred around the alkyl halide-Lewis acid system, and there has been little investigation into the use of esters of organic and inorganic acids in this reaction. The efficiency of the trifluoromethanesulphonate (triflate) anion (CF_3SO_3^-) as a leaving group has attracted much interest of late, in particular in solvolysis processes,^{2,3} acylation,^{4,5} nitration,⁶ and sulphonation^{7,8} reactions. Triflate esters are known to be powerful alkylating reagents, which have been reported to alkylate deactivated alcohols at ambient temperatures in high yield,⁹ and alkylate hydroperoxides in the absence of a strong base.¹⁰ The use of triflate esters for the alkylation of aromatic compounds has received comparatively little attention. Haszeldine,¹¹ as early as 1957, reported the ethylation of benzene with ethyl triflate, and a more recent report by Olah¹² has described competitive Lewis-acid-catalysed alkylation of benzene and toluene with a series of esters including alkyl triflates and alkyl fluorosulphates. Limited alkylation has been reported for trifluoromethyl triflate,¹³ and the potential of vinyl triflates in aromatic substitution has also been described recently.^{14,15} Our interest in the use of triflic acid as a catalyst for the Koch carboxylation of alkenes,¹⁶ and for the formylation and acylation of alkylaromatic compounds,¹⁷ has led us to re-investigate the use of alkyl triflates in aromatic alkylation reactions.

RESULTS AND DISCUSSION

Reactions of Methyl Triflate.—In preliminary experiments carried out as part of this investigation methyl triflate was prepared either by reaction of methanol with triflic anhydride,¹⁸ or by reaction between dimethyl sulphate and triflic acid. Despite the care taken during the distillation of the ester, in our experience it is impossible to prevent traces of triflic acid contaminating the product. The alkylation reactions of methyl triflate were carried out under dry nitrogen, by addition of

the ester to the aromatic substrate and the mixture heated at 100 °C (or at reflux temperature in the case of benzene) on a water-bath. Each reaction was monitored at 10-min intervals by g.l.c. analysis, and the reaction products were identified either by comparison of their retention times with those of authentic samples, or by mass-spectrometric analysis. It was found that in each case there was an induction period before the onset of alkylation, and the length of this varied considerably depending upon the aromatic compound. The results, which are summarised in Table 1, show that the in-

TABLE 1
Reactions of methyl triflate^a

Substrate	Substrate : ester molar ratio	Induction period/h ^b	Products ^c (%)
Benzene	3.3	>6	(I) trace
Toluene	4.16	2	(II) 8, (III) 6
<i>p</i> -Cymene	2.27	0.75	(IV) 1, (I) 14, (II) 2, (III) 6, (V) 58, (VI) 14, (VII) 9

(I) Toluene, (II) *o*-xylene, (III) *p*-xylene, (IV) benzene, (V) a mixture of three methylisopropylbenzenes, (VI) a mixture of three dimethylisopropylbenzenes, and (VII) a mixture of five methyl-di-isopropylbenzenes.

^a At a bath temperature of 100 °C. ^b The time at 100 °C before detection of alkylation products. ^c The composition of the product mixture, excluding starting material, when no further change in composition could be detected by g.l.c. The percentages refer to percentage fractions, and the components are given in order of g.l.c. retention times.

duction period decreased in the order benzene > toluene > *p*-cymene, *i.e.* in the order of increasing nucleophilicity of these compounds. In the reaction with *p*-cymene the onset of alkylation, which occurred after only 15 min, was followed almost simultaneously by the appearance of isomerisation and disproportionation products leading to a complex mixture. No reaction occurred with chlorobenzene, but the more nucleophilic bromobenzene did react slowly to give traces of 2- and either 3- or 4-bromotoluene; these last compounds

could not be separated under the g.l.c. conditions employed.

The earlier suggestion¹¹ that the reaction between ethyl triflate and benzene may be catalysed by traces of triflic acid either present in the ester used or produced by breakdown on warming was examined further since the samples of esters used in our work were inevitably contaminated with traces of acid, and it seemed prudent to check this possibility. Pure methyl triflate free from any acid impurity, was prepared by the reaction of iodomethane with silver triflate and purified by distillation. A sample of ester prepared in this manner caused no alkylation of *p*-cymene even after 5 h at 100 °C. This is a clear indication that the alkylation reactions of methyl triflate are catalysed by traces of triflic acid. A similar catalytic effect has been noted previously¹⁹ in the alkylation of benzene with $\text{Pr}^i\text{SO}_3\text{F}$; a reaction which is severely retarded in the presence of a hindered Hunig base.

Reactions of Ethyl Triflate.—The preliminary experiments were carried out using ethyl triflate prepared by reaction between diethyl ether and triflic acid,¹¹ which would undoubtedly contain a trace of triflic acid impurity. The reactions, which were monitored throughout by g.l.c. analysis, are summarised in Table 2. From the results it can be seen that the length of the initiation period before onset of alkylation decreased in the order chlorobenzene > toluene > *p*-xylene > mesitylene > *p*-cymene. It is a measure of the increased reactivity of the ethyl ester that, unlike the methyl ester, it does react with chlorobenzene. In the reaction with *p*-cymene the onset of alkylation was followed rapidly by loss of the isopropyl cation leading to isomerisation and disproportionation products. Not surprisingly, with mesitylene there was a somewhat longer time gap between the start of alkylation and the onset of the secondary reactions. G.l.c. analysis showed that after only 15 min at 100 °C ethylmesitylene (18% of the total reaction mixture) was the only product. Disproportionation and isomerisation products did not appear until 10 min later, and an equilibrium mixture, which contained nine products, was reached only after 45 min.

These reactions were repeated under similar conditions but using samples of ethyl triflate prepared by reaction between iodoethane and silver triflate. The results, given in Table 2, indicate that unlike the pure methyl ester, which was unreactive under these conditions, the ethyl ester did react but only after much longer induction periods. The rather odd result obtained with *p*-xylene, which gave only ethyl-1,4-dimethylbenzene, may be caused by reaction of the silver iodide present during the reaction. Interaction of this with triflic acid formed on alkylation would give $\text{AgOSO}_2\text{CF}_3$ and the much weaker acid HI, which is a less efficient disproportionation agent. In all other reactions the silver iodide was removed before reaction. The increased reactivity of the ethyl ester could reflect a genuine difference in the rate of reaction on changing from the methyl to the ethyl ester (see the reaction of benzyl triflate below). However, it could

simply reflect a difference in thermal stability of the two esters. A sample of methyl triflate heated at 110–120 °C for 3.5 h showed no change in its ¹H and ¹⁹F n.m.r. spectrum over this period. In contrast, a sample of ethyl triflate heated at the same temperature for only 1.5 h gave a dark brown, viscous liquid. During this period the quartet (+2.85 p.p.m.) and triplet (+6.1 p.p.m. rel. to external *p*-C₆H₄Cl₂) signals of the ester

TABLE 2

Reactions of ethyl triflate^a

Substrate	Substrate: ester molar ratio	Induction period/h ^b	Products ^c (%)
Benzene	2.94 ^d	2.0	(I) 30, (II) 10
	3.16 ^e	4.5	(I) 30, (II) 5
Toluene	8.93 ^d	1.0	(III) 3, (IV) 4, (V) 2
	2.94 ^d	0.66	(VI) 2, (VII) 20, ^g (VIII) 2, (V) 7, (III) 1, (IV) 6, (IX) 31, (VII) 46 ^h
<i>p</i> -Xylene	5.56 ^f	0.92	(VI) 1, (X) 2, (XI) 18, ^g (XII) 2, (IX) 6, (XIII) 8, (XIV) 4
	2.94 ^d	0.25	(VI) 2, (X) 2, (XI) 12, (XII) 4, (IX) 5, (XII) 3, (XIV) 6
Mesitylene	3.45 ^e	0.58	(VI) 7, (X) 1, (V) 8, (XV) 2, (XVI) 12, (XVII) 26, (XVIII) 1,
	2.08 ^d	0.08	(VI) 4, (X) 3, (V) 7, (XV) 2, (XVI) 10, (XVII) + (XVIII) 14
<i>p</i> -Cymene	5.00 ^f	0.50	(XIX) 20
Chlorobenzene	4.94 ^d	3.5	

(I) Ethylbenzene, (II) *o* and/or *p*-diethylbenzene, (III) 4-ethyltoluene, (IV) 2-ethyltoluene, (V) 3-ethyltoluene, (VI) toluene, (VII) 2-ethyl-1,4-dimethylbenzene, (VIII) *o*-xylene, (IX) three ethyldimethylbenzene isomers, (X) *p*-xylene, (XI) 2-ethyl-1,3,5-trimethylbenzene, (XII) triethylbenzene or dimethyldiethylbenzene isomer, (XV) an ethylisopropylbenzene, (XVI) an ethylisopropylmethylbenzene, (XVII) two di-isopropylmethylbenzene isomers, (XVIII) a diethylisopropylbenzene, (XIX) two ethylchlorobenzene isomers.

^a At a bath temperature of 100 °C. ^b The time at 100 °C before detection of alkylation products. ^c The composition of the product mixture, excluding starting material, when no further change in composition could be detected by g.l.c. The percentages refer to percentage fraction, and the components are given in order of g.l.c. retention times. ^d Ethyl triflate contained a trace of triflic acid. ^e Ethyl triflate prepared *in situ* from C₂H₅I and CF₃SO₃Ag but not isolated. ^f Ethyl triflate prepared by silver salt method and isolated by evaporation of solvent. ^g Formed during early stages but not present in the final mixture. ^h Yield of isolated product.

disappeared almost completely, and were replaced by a complex pattern over the range +4 to +6.5 p.p.m., together with a strong signal at –5.0 p.p.m. for triflic acid. The ¹⁹F n.m.r. spectrum after heating showed one major signal at +0.44 p.p.m. [relative to external trifluoroacetic acid (TFA)] for the acid, and seven smaller resonances at –2.18, –1.7, –0.2, –0.07, +1.14, +2.95, and +7.5 p.p.m. The catalytic effect of traces of triflic acid generated on thermal decomposition of ethyl triflate could account for the higher reactivity of this ester.

Reaction of Benzyl and Isopropyl Triflates.—Benzyl triflate, prepared in 53% yield by reaction of benzyl bromide with silver triflate, reacted immediately with

p-cymene at room temperature to give a 48% yield of a product thought to be 1-methyl-2-benzyl-4-isopropylbenzene, although the spectroscopic data available did not allow a distinction between this and the isomer, 1-methyl-3-benzyl-4-isopropylbenzene. There was no evidence for isomerisation or disproportionation products from this reaction.

Attempts to extend these alkylation studies to isopropyl triflate were not entirely successful. Although isopropyl triflate has been prepared previously by reaction of propan-2-ol with triflic anhydride in pyridine,¹² and by reaction of triflic acid with propene,⁹ it decomposes on attempted distillation even at 50 °C under vacuum. When a sample of isopropyl triflate, prepared by the last method, as a solution in CCl₄ was added to toluene at room temperature a 55% yield of *p*-cymene was obtained, together with some polymeric residue. This indicates that isopropyl triflate is a more active alkylating agent than either methyl or ethyl triflate, but naturally under the conditions used triflic acid would also have been present. Attempts to synthesise the ester by mixing di-isopropyl ether with an equimolar quantity of triflic acid gave an exothermic reaction but it is unlikely that the product of this reaction is isopropyl triflate. A comparison of the ¹H n.m.r. chemical shifts of neat di-isopropyl ether, with those observed for Prⁱ₂O·CF₃SO₃H at 0 °C and 35 °C, is given in Table 3. The

TABLE 3

¹H N.m.r. spectra ^a of ether-triflic acid mixtures

	δ	
	CH	Me
Pr ⁱ ₂ O	+3.9	+6.4
Pr ⁱ ₂ O·CF ₃ SO ₃ H (1:1)	+2.85	+6.0
Pr ⁱ OSO ₂ CF ₃ ^b	+2.1	+5.76
Et ₂ O	+4.2	+6.35
Et ₂ O·CF ₃ SO ₃ H (1:1)	+3.25	+5.85
EtOSO ₂ CF ₃	+2.85	+6.1

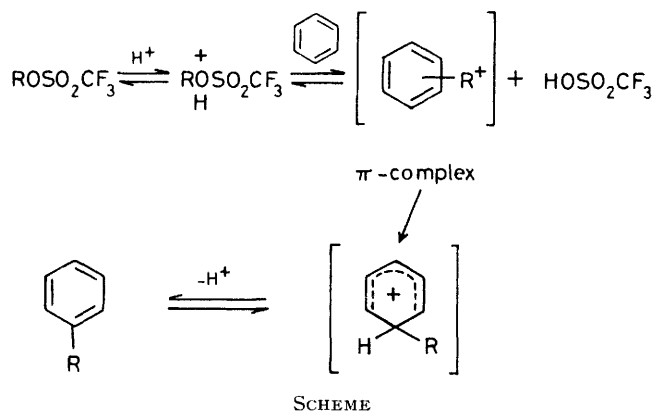
^a At 35 °C; chemical shifts quoted in p.p.m. relative to external *p*-C₆H₄Cl₂ reference. ^b Obtained by conversion of the reported chemical shifts¹² (quoted relative to SiMe₄) into values relative to external *p*-C₆H₄Cl₂, assuming the chemical shift of the latter to be -7.26 p.p.m. relative to SiMe₄.

chemical-shift differences observed compare very closely with the literature values reported¹² for isopropyl triflate prepared by the reaction of PrⁱOH and (CF₃SO₂)₂O in pyridine. It is significant, however, that there is no evidence for the formation of propan-2-ol, which should be present in an amount equivalent to that of the triflate ester according to the equilibrium ROR + TfOH ⇌ ROTf + ROH.

Also included in Table 3 are the chemical shifts obtained for neat Et₂O, Et₂O·CF₃SO₃H (1:1), and ethyl triflate. Again it can be seen that there is no evidence for ethanol formation. This implies that the species formed in quantitative yield on mixing equimolar quantities of an ether and triflic acid is the oxonium salt, R₂OH⁺ CF₃SO₃⁻. Only on heating does this break down to give, in the case of diethyl ether, ethyl triflate. With the di-isopropyl oxonium salt formation of isopropyl triflate is accompanied by extensive decomposition.

Nevertheless, addition of *p*-cymene to an equimolar mixture of di-isopropyl ether and triflic acid at 0 °C gave a 59% yield of an isopropylcymene derivative, thought to be 1,3-di-isopropyl-4-methylbenzene. With toluene under similar conditions the products were *p*-cymene (46%) and the same di-isopropylmethylbenzene isomer (26%).

From these alkylation reactions of triflate esters the reactivity appears to be in the order benzyl > (isopropyl) > ethyl > methyl. It is envisaged that in aromatic solvents the mechanism is probably of the S_N2 type, where dissociation of the leaving group does not occur before approach of the aromatic molecule. Protonation of an oxygen of the triflate anion leaving group by any triflic acid present would increase the leaving group efficiency, and explain the catalytic action of the acid according to the reaction sequence given in the Scheme.



Normally for an S_N2 mechanism the methyl ester might be expected to react at a faster rate than the ethyl ester. However in less polar solvents, for example, an excess of the aromatic substrate, as Nakane²⁰ has pointed out previously, the alkylating agent may be present as a 'freer' ion-pair or dipolar intermediate which reacts in a more S_N1-like fashion with the aromatic compound. This is likely to be particularly true of a protonated triflate ester. The observed trend of reactivities benzyl > isopropyl > ethyl > methyl probably reflects the degree of partial ionisation of the carbon-leaving group bond.

Olah and Nishimura¹² have reported that reactions of 1:1 molar mixtures of benzene and toluene with alkyl triflates are catalysed by AlCl₃ and SbF₅. We have also examined the influence of various Lewis-acid catalysts upon the alkylation reactions of methyl and ethyl triflates, and can confirm that SbF₅ is a particularly effective catalyst.

SbF₅ as Catalyst.—The antimony pentafluoride used in these experiments was freshly-prepared by fluorination of SbF₃ at 260–280 °C, and collected and stored under dry nitrogen. Addition of a known quantity of neat SbF₅ into a mixture of benzene and methyl triflate (molar ratio 2.5:1) with stirring at room temperature gave, after 1 h, a mixture of toluene (19%), *m*- and *p*-

xylene (5%) [these were not completely resolved under the g.l.c. conditions employed, but the *m*-isomer was present in a minor quantity only], and *o*-xylene (1%); where the percentages refer to percentage fractions, *i.e.* a conversion of 78% based on methyl triflate taken. After a further 30 min a small amount of 1,2,4-trimethylbenzene appeared in the product mixture, and 93% of the ester had been converted (see Table 4). In the absence of SbF_5 the methylation of benzene by methyl triflate is so slow that only a trace of toluene is formed after 10 h at reflux temperature (see Table 1). Similarly, methylation of toluene and *p*-xylene, which normally requires several hours at 100 °C, occurred at room temperature on addition of neat SbF_5 . After only 15 min, *ca.* 70% of the methyl triflate had reacted in these cases. After 45 min the reaction mixture for *p*-xylene showed evidence of disproportionation and isomerisation products, and after 1.5 h the disproportionation product, toluene, accounted for 4% of the product mixture (see Table 4). Samples of SbF_5 tended to lose some of their

the *meta*-isomer, suggesting that this arises by loss of a methyl group from 2-ethyl-1,4-dimethylbenzene rather than by ethylation of toluene which leads to the expected *ortho*- and *para*-ethyltoluenes only (see Table 5). These results again illustrate the effectiveness of SbF_5 as a catalyst for these alkylation reactions. In the absence of catalyst, reaction does not occur up to a temperature of 100 °C, and gives a higher proportion of isomerisation and disproportionation products (see Table 2). As previously observed with the reactions of methyl triflate,

TABLE 4
Antimony pentafluoride-catalysed reactions of methyl triflate^a

Substrate	Reaction time/h	Products (% of total mixture)
Benzene	1.0 ^b	(I) 19, (II) 5, (III) 1
	1.5 ^b	(I) 17, (II) 6, (III) 2, (IV) 2
	0.25 ^c	(I) 20, (II) + (III) 5
Toluene	0.25 ^b	(II) 7, (III) 7
	1.5 ^b	(II) 10, (III) 7
	0.25 ^c	(II) + (III) 28, (IV) + (V) 7
<i>p</i> -Xylene	1.5 ^b	(I) 4, (IV) 20, (VI) 4
	0.25 ^c	(I) 3, (IV) 16, (VI) 1

(I) Toluene, (II) *m*- and *p*-xylenes, (III) *o*-xylene, (IV) 1,2,4-trimethylbenzene, (V) mesitylene, (VI) 1,2,4,5- and/or 1,2,3,5-tetramethylbenzene (these had identical retention times on three different stationary phases). ^a Molar ratio of substrate : ester : SbF_5 10 : 4 : 1 at room temperature. ^b Neat SbF_5 . ^c Freshly-distilled SbF_5 in Freon-113.

catalytic activity on storage even for only a few hours under a nitrogen atmosphere, and the 'age' of the sample had a pronounced effect upon the rate of alkylation. In a separate series of experiments the antimony pentafluoride was distilled under a nitrogen-fluorine atmosphere into a graduated receiver containing a known volume of Freon-113. Injection of the required volume of this Freon solution into the alkylation mixture caused immediate reaction at room temperature, and no ester remained after 15 min even with the less reactive hydrocarbons benzene and toluene. The isomer distribution in each case was very similar to that obtained with neat SbF_5 (see Table 4).

Addition of neat SbF_5 to a mixture of ethyl triflate and these aromatic compounds (molar ratio 1 : 2 : 5) caused a rapid, exothermic reaction to give the alkylation products shown in Table 5. With *p*-xylene after 15 min at room temperature 2-ethyl-1,4-dimethylbenzene was the only product, and even after 1 h the extent of disproportionation as evidenced by the appearance of toluene, ethyl-, diethyl-, and triethyl-toluenes was quite small. It is of interest that the ethyltoluene in the mixture was

TABLE 5
Antimony pentafluoride-catalysed reactions of ethyl triflate^a

Substrate	Reaction time/h	Products (% of total mixtures)
Benzene	0.33 ^b	(I) 39, (II) 5
	0.25 ^c	(I) 37, (II) 7
Toluene	0.75 ^b	(III) 32, (IV) 4, (V) 10 ^d
	0.25 ^c	(III) 37, (IV) 2, (V) 15 ^d
	0.25 ^b	(VI) 28
<i>p</i> -Xylene	1.0 ^b	(VI) 22, (VII) 3, (VIII) 5, (IX) 6 (V) 3, ^d (X) 8 ^d
	0.25 ^c	(VI) + (IX) ^d 31, (VII) 3, (III) + (IV) + (VIII) 13%, (IX) 4, ^d (X) 3 ^d
	0.5 ^b	(XI) 26

(I) Ethylbenzene, (II) diethylbenzenes, (III) 4-ethyltoluene, (IV) 2-ethyltoluene, (V) a diethyltoluene isomer,^d (VI) 2-ethyl-1,4-dimethylbenzene, (VII) toluene, (VIII) 3-ethyltoluene, (IX) two ethyldimethylbenzene isomers,^d (X) two triethylmethylbenzene isomers,^d (XI) 2-ethyl-1,3,5-benzene.

^a Molar ratio of substrate : ester : SbF_5 10 : 4 : 1 at room temperature. ^b Neat SbF_5 . ^c Freshly-distilled SbF_5 in Freon-113. ^d Identified by mass spectrometry only.

the use of freshly-distilled SbF_5 as a solution in Freon-113 resulted in an increased rate of reaction, although the composition of the product mixture was not changed significantly (see Table 5). In all these alkylation reactions addition of SbF_5 resulted in immediate formation of fumes and a dark brown tar, which is possibly composed of arylstibines and polyphenylenic polymers as suggested previously by Olah.²¹ This may reduce the effect of the catalyst especially where less reactive hydrocarbons which require longer reaction times are employed.

AlCl_3 as Catalyst.—Addition of ethyl triflate to a suspension of powdered, anhydrous AlCl_3 in *p*-xylene with efficient stirring under nitrogen did not cause alkylation to take place at room temperature. Only on heating at 60 °C over 30 min did alkylation occur to give 2-ethyl-1,4-dimethylbenzene in *ca.* 50% yield based on the ethyl triflate taken. Unlike the reactions of SbF_5 the formation of free triflic acid was not observed during this reaction, but HCl was evolved and when the mixture was poured into water the aqueous solution was hardly acidic. When this reaction was repeated using a *p*-xylene : ethyl triflate molar ratio of 2.5 : 1 and adding a catalytic amount of AlCl_3 as a solution in nitromethane at room temperature, slow ethylation occurred to give 2-ethyl-1,4-dimethylbenzene in *ca.* 30% yield after 60 min. On warming to 40 °C for 30 min the yield of this product increased to 60%. At no time during the reaction was there any evidence for the formation of free trifluoromethanesulphonic acid, and on work-up of the

product mixture a white, hygroscopic solid, thought to be $\text{Al}(\text{O}_3\text{SCF}_3)_3$, was isolated. The ^1H n.m.r. spectrum of the solid showed no evidence for hydrogen, and the ^{19}F n.m.r. spectrum (in acetone, TFA external reference) showed a singlet at +3 p.p.m. The i.r. spectrum showed strong bands at 1 260, 1 180, and 1 140 cm^{-1} , typical of a trifluoromethanesulphonate group.¹¹ As the compound was extremely hygroscopic a satisfactory microanalysis could not be obtained. In a separate experiment it has been shown that this compound does not catalyse the alkylation of *p*-xylene by ethyl triflate at room temperature over several hours, and even at 60 °C only a trace of alkylation product could be detected after 1 h. It would appear that in these reactions the aluminium trichloride reacts with the trifluoromethanesulphonic acid generated on alkylation, and is slowly converted into inert $\text{Al}(\text{O}_3\text{SCF}_3)_3$; when the conversion to the aluminium salt is complete no further alkylation will occur at moderate temperature. So, for example, when the reaction of *p*-xylene, ethyl triflate, and AlCl_3 (molar ratio 50 : 20 : 3) in nitromethane was maintained at room temperature over 15 min the ratio of unreacted *p*-xylene : 2-ethyl-1,4-dimethylbenzene gradually decreased to 19 : 1. On heating the mixture at 40 °C for a further 15 min the ratio decreased to 14 : 1, but there was no further significant change in the ratio even on heating at 60 °C for a further 45 min. Addition of more AlCl_3 (3 mmol) caused immediate reaction at this temperature, since the ratio decreased to 9 : 1 only 5 min after the addition of further catalyst. For similar reasons the rate of alkylation depends critically upon the amount of AlCl_3 employed. When the same reaction between *p*-xylene, ethyl triflate, and AlCl_3 in nitromethane was carried out using 5 mmol of catalyst (molar ratio 50 : 20 : 5) the ratio of unreacted *p*-xylene : 2-ethyl-1,4-dimethylbenzene after 1 h at room temperature was 7.5 : 1. When, in a separate experiment, the amount of AlCl_3 was increased to 10 mmol the ratio, after only 30 min at room temperature, dropped to 3.5 : 1. There seems little doubt that not only is AlCl_3 a poorer catalyst than SbF_5 in these alkylation reactions, but it is necessary to use high catalyst concentrations to overcome the problem of conversion into $\text{Al}(\text{O}_3\text{SCF}_3)_3$. The only advantage appears to be that in nitromethane solvent, which is known to reduce side reactions, there is no evidence for isomerisation or disproportionation products under the reaction conditions employed in this work.

Other Lewis-acid Catalysts.—Injection of a solution of BF_3 in nitromethane into a mixture of *p*-xylene and ethyl triflate at room temperature gave ca. 1% of 2-ethyl-1,4-dimethylbenzene after 30 min at room temperature. On heating the mixture at 70 °C over a further 15 min the yield increased to 27%. With both iron(III) chloride and tin(IV) chloride in nitromethane no ethylation was detectable after 30 min at room temperature, and even after heating at 70 °C for a further 35 min the yield of 2-ethyl-1,4-dimethylbenzene was only 1%. The order of catalyst effectiveness appears to be $\text{SbF}_6^- > \text{AlCl}_3 > \text{BF}_3 > \text{FeCl}_3 \approx \text{SnCl}_4$, which differs in some respects from the

order $\text{SbF}_5 \approx \text{AlCl}_3 > \text{FeCl}_3 > \text{SnCl}_4 > \text{BF}_3$ found by Olah²² for the reactions of benzene and toluene with substituted benzyl chlorides. Comparison of these orders is probably not meaningful as in the latter reactions activation by the Lewis acid occurs by halogen co-ordination whereas activation of the triflate esters takes place by co-ordination of the Lewis acid to oxygen.

EXPERIMENTAL

All chemical reagents were commercial samples which were purified (> 97% purity by g.l.c.) and dried prior to use. Triflic acid was purified by distillation immediately before each reaction. In all reactions carried out using alkyl triflates all apparatus was flame dried under dry, oxygen-free nitrogen immediately before injection of the reactants. In the reactions of methyl and ethyl triflate the esters were either distilled immediately prior to use, or stored in a dry box until required. Antimony pentafluoride was prepared by fluorination of SbF_3 at 260–280 °C in a nickel tube and collected under nitrogen in a graduated tube fitted with a Rotaflo tap. In alkylation reactions where Freon-113 was used as solvent the SbF_5 was collected from the fluorination apparatus in the pot of a 10-ml distillation unit, and distilled immediately before use into a pre-weighed graduated receiver containing Freon-113 (5 ml). This completely miscible solution was then used immediately for an alkylation reaction.

G.l.c. analyses were carried out using a Pye 104 (FID) instrument fitted with standard 2-m 10% SE 30 or 10% APL analytical columns. Calibration factors obtained for an equimolar mixture of toluene, *p*-xylene, mesitylene, ethylbenzene, and *p*-cymene, and averaged over several injections, showed that the detector response for each of these compounds was the same within $\pm 5\%$, and the percentage fractions given for the components of a mixture represents their integrated peak areas. Where specific isomers are named these have been identified by 'spiking' the mixtures with authentic samples, and examination of the mixtures on two different g.l.c. columns. Where this was not possible the products were identified by g.l.c.-m.s. using an AEI MS 902 double-focusing spectrometer connected to a Pye series 104 chromatograph. ^1H N.m.r. spectra were recorded on a 60-MHz Perkin-Elmer R20 instrument, and i.r. spectra were determined using a Perkin-Elmer model 157 instrument.

Reactions of Methyl Triflate.—In some reactions the ester was prepared by the previously reported method^{9,11} by reaction between methanol and triflic anhydride (1 : 2 molar ratio), and the product was dried by distillation from P_2O_5 to give yields of 70–80%. In other reactions, the ester was prepared in 73% yield by addition of dimethyl sulphate (100 mmol) to triflic acid (78 mmol) followed by efficient stirring at 0 °C for 30 min and then at room temperature for 2 h, before distillation under nitrogen to give a fraction of b.p. 98–102 °C. The alkylation reactions were carried out using dry aromatic compound (50 mmol), and the methyl triflate was added dropwise under an atmosphere of dry nitrogen with efficient stirring. In each case no reaction could be detected by g.l.c. analysis after 2 h at room temperature, and the mixture was heated at 100 °C on a water bath. Samples were withdrawn at 10-min intervals for g.l.c. analysis.

In reactions where it was necessary to avoid contamination by triflic acid the ester was prepared in the required

aromatic substrate (50 mmol) by addition of silver triflate (11 mmol) under nitrogen, followed by dropwise addition of iodomethane (11 mmol). The heterogeneous mixture was stirred for 1 h at room temperature, or until g.l.c. analysis of the mixture indicated complete reaction. The mixture was then heated on a water bath at 100 °C and the progress of any alkylation reaction was followed by g.l.c. analysis.

Reactions of Ethyl Triflate.—In the majority of reactions the ethyl triflate was prepared in 58% yield according to the method of Gramstad and Haszeldine,¹¹ by condensing dry diethyl ether (100 mmol) onto triflic acid (50 mmol) held at -196 °C *in vacuo*. On warming to room temperature an exothermic reaction occurred, and reaction was completed by warming at 85 °C for 2 h. The ester (b.p. 112–115 °C) was purified by distillation under nitrogen. In a few cases the ester was prepared in *ca.* 30% yield by bubbling ethylene (5–6 ml min⁻¹) through triflic acid (76 mmol) with efficient stirring at room temperature until there was no further weight increase; again the ester was purified by distillation.

Where it was necessary to avoid the presence of triflic acid the ester was prepared in 72–96% yield by addition of iodoethane (28 mmol) to silver triflate (28 mmol) in Et₂O, CCl₄, or CH₂Cl₂, followed by stirring at room temperature under nitrogen for 2 h. The silver iodide was removed by filtration, and the solvent was either removed by careful distillation (CCl₄ or CH₂Cl₂), or by evaporation using a fast flow of nitrogen (Et₂O). The purity of the ethyl triflate prepared in this way was estimated by g.l.c. In one case, with *p*-cymene, the ester was prepared *in situ* by addition of iodoethane (17 mmol) to a paste formed between silver triflate (17.5 mmol) and *p*-cymene (75 mmol). The silver iodide was removed by filtration, and the solution of the ester (82% yield by g.l.c.) and the *p*-cymene was then heated at 100 °C to give alkylation products. With this exception, the procedure adopted for the alkylation reactions using ethyl triflate was similar to that employed for the reactions of the methyl ester described above.

Reactions of Isopropyl Triflate.—Dry di-isopropyl ether (100 mmol) was condensed onto triflic acid (100 mmol) *in vacuo* at -196 °C, and the mixture was allowed to reach room temperature, whereupon an exothermic reaction occurred. The aromatic compound (toluene or *p*-cymene, 100 mmol) was then added, and the mixture was shaken at room temperature for 30 min. The mixture was extracted with ether and the extract was washed with water (2 × 20 ml), dried (MgSO₄), and analysed by g.l.c. In each case the extract was also distilled to give the pure components, *p*-cymene and an isopropyl-*p*-cymene, which were characterised by ¹H n.m.r. spectroscopy and mass spectrometry.

In a separate experiment dry propene (6–7 ml min⁻¹) was bubbled through triflic acid (40 mmol) under nitrogen until a weight increase of 2.0 g was obtained. Then CCl₄ (100 ml) was added, and this solution was added dropwise to dry toluene (200 mmol) under nitrogen with efficient stirring at room temperature. After 30 min the mixture was extracted with ether, and the extract was distilled to give *p*-cymene (11 mmol, 55% based on toluene taken), and a dark polymeric residue (1.1 g).

Reaction of Benzyl Triflate with *p*-Cymene.—Benzyl bromide (2.56 g, 15 mmol) was added dropwise to silver triflate (4.0 g, 15.5 mmol) in *p*-cymene (6.7 g, 50 mmol) with efficient stirring under nitrogen. After 30 min. the mixture was extracted with CCl₄, and the extract was filtered, washed several times with water, and dried (Na₂SO₄). The

solvent was removed and the residue distilled to give unreacted *p*-cymene (4.6 g, 34 mmol), unreacted benzyl bromide (1.3 g, 8 mmol), and a benzylcymene isomer (1.7 g, 7.6 mmol, 48% based on *p*-cymene consumed) thought to be 1-methyl-2-benzyl-4-isopropylbenzene on the basis of its mass spectrum and ¹H n.m.r. spectrum [CCl₄, SiMe₄ reference]; δ 1.2 (d, 6 H, (Me₂CH, J = 7 Hz), 2.2 (s, 3 H, Me), 2.85 (septet, 1 H, Me₂CH), 3.9 (s, 2 H, PhCH₂), 7.2, m, 8 H, ABX pattern overlapping with Ph of benzyl group).

General Procedure for Antimony Pentafluoride-catalysed Reactions.—The SbF₅ (1.08 g, 0.36 ml, 5.0 mmol) either neat, or as a solution in Freon-113 (5 ml), was added with efficient stirring to a mixture of the ester [3.56 g (ethyl ester), 3.28 g (methyl ester); 20 mmol] and dry aromatic compound (50 mmol) under an atmosphere of dry nitrogen. The colourless solution darkened rapidly, and an exothermic reaction occurred with evolution of acid fumes and formation of a tar. After 10–15 min when the temperature had dropped to room temperature, samples were withdrawn at regular intervals and analysed by g.l.c. before being quenched by pouring into ice-water. In the case of the reactions using SbF₅ in Freon-113 the reaction mixture was quenched after 15 min. In the majority of cases the data reported in Tables 4 and 5 are those of at least two reproducible determinations.

General Procedure for Aluminium Chloride-catalysed Reactions.—Ethyl triflate (2.5 g, 14.0 mmol) was added with efficient stirring to a suspension of anhydrous, powdered, aluminium chloride (1.0 g, 7.5 mmol) in *p*-xylene (3.71 g, 35 mmol) at room temperature under an atmosphere of dry nitrogen. During this period a heavy yellow liquid was formed and this gradually changed to a yellow paste. After 30 min a sample was withdrawn for analysis by g.l.c. The apparatus was then arranged for reflux, and the mixture was heated at 60 °C for a further period. Samples were withdrawn at intervals for analysis. The analytical results with this heterogeneous system were not very reproducible and an average of three analyses was taken in each case.

This reaction was repeated by addition of a mixture of *p*-xylene (2.3 g, 21.7 mmol) and ethyl triflate (3.56 g, 20 mmol) to a homogeneous mixture of *p*-xylene (3.0 g, 28.3 mmol) and anhydrous aluminium chloride (0.66 g, 5 mmol) in nitromethane (2.0 g) with efficient stirring at room temperature, and the mixture was analysed at intervals. After 30 min at room temperature the mixture was heated at 60 °C for approximately 1 h, when all the ester disappeared, and the reaction contained a yellow semi-solid. In the majority of reactions the mixture was then poured into ice-water, and extracted with diethyl ether. The ether extract was then dried and the ether removed before analysis of the residue by g.l.c.

In one reaction the mixture was extracted with ether without prior treatment with ice-water, to give a yellow solid. This was dissolved in acetone, filtered, and the filtrate was evaporated to dryness to give a hygroscopic, white solid, thought from its i.r. and ¹⁹F n.m.r. spectra to be aluminium triflate.

When ethyl triflate (1.43 g, 8.0 mmol) was added dropwise to *p*-xylene (2.12 g, 20.0 mmol) containing aluminium trifluoromethanesulphonate (0.4 g, previously dried to constant weight for 6 h at 100 °C) in nitromethane (2 g) with efficient stirring at room temperature there was no evidence of alkylation after 30 min. The mixture was then heated at 60 °C for 1 h when a trace (< 1%) of 2-ethyl-1,4-dimethylbenzene was detected.

General Procedure for Other Lewis-acid-catalysed Reactions.—Boron trifluoride was bubbled through nitromethane (5 g) with efficient stirring at room temperature until *ca.* 4 mmol of gas was absorbed. This solution was then injected immediately into a mixture of ethyl triflate (3.56 g, 20 mmol) and *p*-xylene (5.3 g, 50 mmol) under nitrogen, which was then stirred at room temperature for 30 min, and for a further 30 min at 70 °C. The mixture was analysed by g.l.c. at regular intervals.

The reaction with anhydrous iron(III) chloride (0.81 g, 5 mmol) and anhydrous tin(IV) chloride (1.3 g, 5 mmol) were carried out using ethyl triflate (3.56 g, 20 mmol) and *p*-xylene (5.3 g, 50 mmol) in nitromethane (2 g) according to the procedure used for the reactions with aluminium chloride.

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