

Thallium(III) Chloride Tetrahydrate as a Lewis Acid Catalyst for Aromatic Alkylation and Acylation¹⁾

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From a study of aromatic alkylation and acylation using $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$ catalyst, it was revealed that this metal chloride was a milder Lewis acid catalyst than AlCl_3 and FeCl_3 and was similar in activity to ZnCl_2 . Although the yields of the products were generally low, the characteristics of this catalyst were observed in the formation of β, β' -dimethylstyrene and benzoylacetone upon the respective methallylation and acetylation of benzene and in the fact that the hydrated chloride was more effective than the anhydrous one. In a sharp contrast to aromatic bromination, $\text{Ti}(\text{OAc})_3$ showed little activity in these reactions.

Although many metal halides have been studied as Lewis acid catalysts for aromatic alkylation and acylation, $\text{Ti}(\text{III})$ salts seem to have received little attention so far²⁾; only one report on the benzylation, benzoylation, and acetylation of benzene using the anhydrous TiCl_3 catalyst has been found in the literature.³⁾ Recently, Taylor and McKillop showed that the acetylation of anisole could be catalyzed by $\text{Ti}(\text{OAc})_3$.⁴⁾ On the other hand, the use of $\text{Ti}(\text{III})$ salts, such as $\text{Ti}(\text{OAc})_3$ and $\text{TiBr}_3 \cdot 4\text{H}_2\text{O}$, has been reported to be very effective in aromatic bromination^{5,6)}, and their role has been considerably clarified.⁶⁾

Our study of the $\text{Ti}(\text{III})$ salt-catalyzed aromatic alkylation and acylation has been started in the hope of finding some specific use for the catalyst in these reactions, as in the case of the $\text{Ti}(\text{III})$ salt-catalyzed aromatic bromination. Unfortunately, no distinctive feature was found from a synthetic point of view. Considering the yields of the products of butylation, allylation, haloalkylation, and acylation, however, it is clear that the activity of $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$ is qualitatively comparable to that of ZnCl_2 and inferior to that of FeCl_3 or AlCl_3 . Here, it seems to be characteristic that the hydrated $\text{Ti}(\text{III})$ salt shows a moderate activity, in contrast to the fact that other active metal halide catalysts are used mostly in the anhydrous state. This report will deal with these observations.

Results and Discussion

The reactions were generally carried out by adding the alkylating or acylating agents to aromatic compounds (in excess as solvents) containing $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$ at various temperatures and by stirring the resulting mixtures for appropriate periods. Although an AlCl_3 - or FeCl_3 -catalyzed Friedel-Crafts alkylation and acylation generally proceeds at a low temperature, it was necessary to

heat the reaction mixture in most of these $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$ catalyzed reactions. Some typical results are summarized in Table 1.

Butylation and Benzylation. It has been reported⁷⁾ that, in the presence of AlCl_3 , *n*- and *t*-butyl chlorides reacted with benzene at 0°C to give *s*- and *t*-butylbenzenes in 50 and 60% yields respectively, and that the reaction of *t*-butyl chloride with benzene gave an 80% yield of *t*-butylbenzene at 25°C in the presence of the FeCl_3 catalyst. In the presence of the $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$ catalyst, the *s*- and *t*-butyl halides reacted with aromatic compounds to give *s*- and *t*-butylated compounds (I) respectively in 22–39% yields at 60–76°C. The lower the reaction temperature was, the lower the yields of I became. *n*-Butyl chloride or bromide afforded only a small amount of *s*-butylbenzene (*ca.* a 2% yield at 76°C for 10 hr) without any trace of *n*-butylbenzene which was expected to be formed by the attack of the strongly polarized but undissociated alkyl halide molecule. *t*-Butyl alcohol could not be used as an alkylating agent at 70°C because of its rapid oxidation by $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$; this is in sharp contrast to the reactions with other acidic catalysts (*e.g.*, H_2SO_4 , HF, AlCl_3 , FeCl_3 , and BF_3), in which *t*-butylbenzene was obtained in high yields from benzene.⁷⁾ In the benzylation of toluene with benzyl bromide or acetate, $\text{TiBr}_3 \cdot 4\text{H}_2\text{O}$ showed an activity similar to that of $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$ as a Lewis acid catalyst. Although $\text{Ti}(\text{OAc})_3$ was a very effective catalyst in aromatic bromination, the *s*-butylation of benzene using this catalyst was almost entirely unsuccessful because of the conversion of $\text{Ti}(\text{OAc})_3$ to inactive Ti_2O_3 .

Allylation and Haloalkylation. It has been reported^{8,9)} that the reaction of allyl halide and aromatic compounds gives 1-aryl-2-halopropane or 1,2-diarylpropane in the presence of mild Lewis acid catalysts, such as ZnCl_2 , or with strong catalysts, such as AlCl_3 , respectively, and that both of the products are derived from allylated compounds. Although $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$ has been shown by the aromatic butylation described above to be a milder Lewis acid catalyst than AlCl_3 or FeCl_3 , it is not known to what kind of metal salts the activity

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6) S. Uemura, K. Sohma, M. Okano, and K. Ichikawa, *This Bulletin*, **44**, 2490 (1971).

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TABLE 1

C ₆ H ₅ R R (1mol)	Alkylating or acylating agents (100 mmol)	TlCl ₃ · 4H ₂ O (mmol)	React. temp. (°C)	React. time (hr)	Products (yield, %) ^{a)}					
					I	II	III	IV	V	VI
H	<i>n</i> -BuCl ^{b)}	25	76	4	23					
H	<i>t</i> -BuBr	10	76	0.3	39 ^{c)}					
H	C ₆ H ₅ CH ₂ OAc	25	80	5	50 ^{d)}					
CH ₃	C ₆ H ₅ CH ₂ Br	25 ^{e)}	70	1	90 ^{f)}					
H	CH ₂ =CH-CH ₂ Cl	10	57	0.3		4	5	trace		
H	CH ₂ =CH-CH ₂ Cl	25	70	4		0	37	trace		
CH ₃	CH ₂ =CH-CH ₂ Cl	10	57	0.3		7 ^{g)}	22 ^{h)}	0		
CH ₃	CH ₂ =CH-CH ₂ Cl	10	65	4		0	52 ^{h)}	31 ⁱ⁾		
Cl	CH ₂ =CH-CH ₂ Cl	10	65	2		0	18 ^{j)}	trace		
H	CH ₃ COCl	25	56	5					3	6
CH ₃	CH ₃ COCl	25	56	5					19	3
CH ₃	CH ₃ COCl	25	25	0.3					23	0
CH ₃	CH ₃ COCl	25 ^{k)}	25	0.3					12	0

a) Based on alkylating of acylating agents.

b) 50 mmol.

c) The 12% yield of di-*p*-*t*-butylbenzene (mp 77—79° C; lit.¹⁷⁾ 76°C) was obtained.

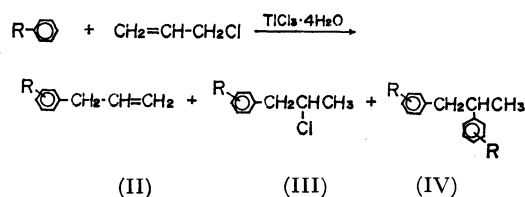
d) Diphenylethane.

e) TlBr₃·4H₂O.f) Phenyltolylmethane, *o/p* = 1.38.⁸⁾g) The *o/p* ratio was not determined.h) *o/p* = 0.15 (determined by NMR).

i) 1,1-Ditolylpropane/1,2-isomer = 3 (NMR).

j) *o/p* = 1.21 (glc).k) Anhydrous TlCl₃.

of TlCl₃·4H₂O is comparable. If TlCl₃·4H₂O is a milder catalyst than ZnCl₂, we could expect the allylated aromatic compounds to be isolated using this catalyst. In this connection, several aromatic compounds were treated at 55—70°C for 0.3—4 hr with allyl chloride or bromide in the presence of this catalyst. 1-Aryl-2-halopropanes (III) were generally isolated as the main products, along with small or trace amounts of monoallylated compounds (II) and diarylpropanes (IV) (Eq. 1).



This means that the catalytic activity of TlCl₃·4H₂O is qualitatively similar to that of ZnCl₂ and milder than that of AlCl₃ in aromatic allylation. The formation of II was observed only under milder conditions (a short reaction time or a low reaction temperature), though the yields were very poor. The yields of III, which was probably formed by the hydrochlorination of II, decreased in the following order of aromatics, as would be expected; toluene > benzene > halobenzenes. The allylation of halobenzenes with this catalyst at 65—70°C for 1.5—2 hr gave only 9—18% yields of III, while with the FeCl₃ catalyst somewhat higher yields (24—53%) were recorded, even at lower reaction temperatures (−21—−16°C).¹⁰⁾ Compound IV was probably

produced by aromatic alkylation with III. An isomer of IV, 1,1-diarylpropane, was also formed, and the amount of which was larger than that of IV. The presence of such an isomer indicates that the hydrogen transfer has occurred in the intermediary cation (ArCH₂⁺CHCH₃) derived from III on prolonged heating, as in the case of the *n*-butylation of benzene described above. The use of a solvent led to a significant decrease in the reaction rate; e.g., with benzene and allyl chloride, no reaction occurred at 50°C after 4 hr in carbon disulfide, and only 6% of the III was obtained at 65°C after 4 hr in chloroform. Allyl bromide reacted more easily with benzene than allyl chloride, but a mixture of 2-bromo- and 2-chloro-1-phenylpropanes (in 4:1 ratio) was obtained in a 43% yield, together with diphenylpropanes (14% yield), when the reaction was at 55°C for 0.3 hr. The allylation with allyl alcohol, which was easily achieved by other Lewis acid catalysts, was unsuccessful when we used TlCl₃·4H₂O, which has a strong oxidizing property. The reaction with *trans*-crotyl chloride showed a behavior similar to that of the reaction with allyl chloride. With methallyl chloride, however, β,β'-dimethylstyrene was obtained in a 9% yield without any trace of such compounds as III and IV when the reaction was at 75°C for 5 hr. This compound, which is probably formed by the isomerization of the methallylated compound, has not been reported to be formed by a Friedel-Crafts reaction using any Lewis acid catalyst; rather its formation seems to be one of the characteristics of the TlCl₃·4H₂O catalyst.

The attacking species in this reaction seem to be rather reactive, because the *k_T/k_B* ratio in the formation of II and III by the competitive reaction of toluene and

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pane), 8.78 (d, $J=8$ Hz, 3H, 1,2-isomer).

β,β' -Dimethylstyrene: Bp 85—86°C/25 mmHg. NMR τ 8.18—8.05 (m, 6H) 3.8—3.65 (m, 1H), 2.8—2.65 (m, 5H).

p-Anisylacetophenone (V , $R=CH_3O$): Bp 113—122°C/6 mmHg. NMR τ 7.48 (s, 3H), 6.17 (s, 3H), 3.1 (d, $J=9.5$ Hz, 2H), 2.05 (d, $J=9.5$ Hz, 2H).

α -Methylchalcone, $C_6H_5C(CH_3)=CHCOC_6H_5$: Bp 160—163°C/2 mmHg (lit.¹⁶) bp 225°C/22 mmHg, IR (liq. film) 1670 (s, $\nu_{C=O}$), 1610 (s, $\nu_{C=C}$) cm^{-1} .

Benzoylacetone: Bp. 115°C/5 mmHg (lit.¹²) bp 103—105°C/1.8 mmHg, mp 59°C (lit.¹⁸) 60—61°C). Found: C, 74.03; H, 6.42%. Calcd for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22%.

Spectral Measurements. The IR spectra were measured on Hitachi EPI-2 and EPS-3T spectrometers. The NMR spectra were determined on a Varian A-60 spectrometer, using TMS as the internal standard in $CDCl_3$. Glc analysis was carried out on Shimadzu 5APTF apparatus, using PEG 6000 (25%)-Chromosorb-W 3-m and Apz-L (30%)-Celite 3-m columns, and on a Hitachi F-6 apparatus, using Apz-L 1-m columns.

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17) A. Baur, *Ber.*, **27**, 1608 (1894).

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