The Mechanism of Friedel–Crafts Acylation.

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Halogen exchange between aluminium halide and 2 : 4 : 6-tribromo- and 2 : 4 : 6-trimethyl-benzoyl halides severally has been demonstrated and is explained by postulating a reversible process $\mathrm{Ar{\cdot}CX{:}\overset{+}{O}{\cdot}\overset{-}{Al}X_3 \rightleftharpoons Ar{\cdot}\overset{+}{C}O + \overset{-}{Al}X_4}$ in which the ions are present only as traces; similar results have been obtained on using tin and titanium chlorides.

The absence of steric hindrance when these acid halides are employed in the Friedel–Crafts reaction provides further evidence that the acyl cation is the acylating agent (Fairbrother, *J.*, 1937, 503). The apparent loss of a molecular proportion of aluminium halide during reaction and the effect of added reagents on the course of reaction (*J.*, 1949, S99) are explained.

When poured into water, a mixture of 2 : 4 : 6-tribromobenzoic anhydride and aluminium bromide affords the acid and its bromide in equimolecular amounts. The anhydride and bromide of 2 : 4 : 6-tribromobenzoic acid, unlike the methyl ester, dissociate in concentrated sulphuric acid.

INTERACTION of benzene derivative (ArH), acid halide (R·COX), and aluminium halide (formulated as $\mathrm{AlX_3}$) frequently provides a crystalline oxonium complex of aromatic ketone and aluminium halide:

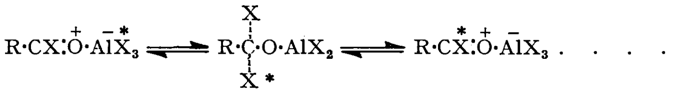
$$\mathrm{ArH + R{\cdot}COX + AlX_3 \longrightarrow Ar{\cdot}CR{:}\overset{+}{O}{\cdot}\overset{-}{Al}X_3 + HX}$$

and gradual addition of one component to a mixture of the other two, usually in a solvent, provides the three most popular methods.

Acid halides and aluminium halides often combine exothermally to provide crystalline addition compounds which are probably oxonium complexes $\mathrm{R{\cdot}CX{:}\overset{+}{O}{\cdot}\overset{-}{Al}X_3}$, since many ketones and ethers behave similarly whereas alkyl, aryl, and aralkyl halides do not. These complexes have been named as effective electrophilic reagents in the Friedel–Crafts reaction and this has been formulated as in (i). Meerwein (*Annalen*, 1927, **455**, 227) suggested the ionisation process (ii), and this has been substantiated by Fairbrother (*loc. cit.*) who, employing radioactive tracers, showed that halogen exchange occurs between acetyl and aluminium chlorides. Although a cation $\mathrm{R{\cdot}\overset{+}{C}O}$ is now accepted as acylating agent in the Friedel–Crafts reaction the evidence is not conclusive, since halogen exchange might be effected by a nucleophilic substitution process (iii) related to that effecting oxygen exchange between aldehyde and water: $\mathrm{R{\cdot}CH{:}O + H_2O \rightleftharpoons R{\cdot}CH(OH)_2}$. Mechanism (iii), in contrast to (ii), is susceptible to steric hindrance, and ready halogen exchange when the carbonyl group of the acid halide is enclosed by bulky vicinal substituents, as in 2 : 4 : 6-tribromo- and 2 : 4 : 6-trimethyl-benzoyl halide, would afford support for mechanism (ii). This is now provided; the data are assembled in Table 1.

$$\mathrm{R{\cdot}CX{:}\overset{+}{O}{\cdot}\overset{-}{Al}X_3 + ArH \longrightarrow R{\cdot}CAr{:}\overset{+}{O}{\cdot}\overset{-}{Al}X_3 + HX} \quad . \; . \; . \; . \; . \; . \; . \; . \quad \text{(i)}$$

$$\mathrm{R{\cdot}CO{\cdot}X + AlX_3 \rightleftharpoons [R{\cdot}CO]^+ + [AlX_4]^-} \quad . \; . \; . \; . \; . \; . \; . \; . \quad \text{(ii)}$$



$$\mathrm{R{\cdot}CX{:}\overset{+}{O}{\cdot}\overset{-}{Al}\overset{*}{X}_3 \rightleftharpoons R{\cdot}\underset{X^*}{\overset{X}{C}}{\cdot}O{\cdot}AlX_2 \rightleftharpoons R{\cdot}C\overset{*}{X}{:}\overset{+}{O}{\cdot}\overset{-}{Al}X_3} \quad . \; . \; . \; . \quad \text{(iii)}$$

$$\mathrm{R{\cdot}CX{:}\overset{+}{O}{\cdot}\overset{-}{Al}X_3 \rightleftharpoons [R{\cdot}CO]^+ + [AlX_4]^-} \quad . \; . \; . \; . \; . \; . \; . \; . \quad \text{(iv)}$$

The extent of halogen exchange between 2 : 4 : 6-tribromobenzoyl bromide and metal chloride and between the acid chloride and metal bromide was readily determined: these acid halides do not react with water at room temperature, and decomposition of mixtures of acid and metal halides with iced water provided mixtures of acid chloride and bromide which could be isolated and analysed. Since decomposition with water gave no measurable amount of carboxylic acid, the acyl cation shown in (ii) is present only in traces, and addition compounds of acid and aluminium halides are therefore to be represented by (iv). The above analytical method is not applicable to reaction of aluminium bromide with benzoyl chloride and its 2 : 4 : 6-trimethyl derivative since these are readily hydrolysed; instead, reaction mixtures were placed in an atmosphere of dry hydrogen bromide (1 mol.) and a rough estimate of halogen exchange between acid and aluminium halides (1 mol.) was afforded by analysis of the gas phase:

$$\mathrm{Ar{\cdot}COCl + AlBr_3 \rightleftharpoons Ar{\cdot}COBr + AlClBr_2}$$
$$\mathrm{AlClBr_2 + HBr \rightleftharpoons AlBr_3 + HCl}$$

The method is based on the comparatively slow exchange between acid and hydrogen halides (compare data in Table 2 with those in Table 1) and on rapid exchange between hydrogen halide and aluminium halide which is in solution as a complex (*e.g.*, exchange is rapid between hydrogen chloride and aluminium bromide in nitrobenzene). The method has limitations.

TABLE 1. $\mathrm{2:4:6\text{-}C_6H_2Br_3{\cdot}COCl + 2AlBr_3 \rightleftharpoons 2:4:6\text{-}C_6H_2Br_3{\cdot}COBr + AlClBr_2 + AlBr_3}$.

Solvent	Temp.	Time (hr.)	Exchange (%) Found	Calc.*	Solvent	Temp.	Time (hr.)	Exchange (%) Found	Calc.*
$C_6H_5\cdot NO_2$...	25·0°	1·00	83·6	85·7	CS_2	18·0°	1·00	78·2	85·7
	25·0	3·00	86·2	,,					

$$\mathrm{Ar{\cdot}COCl + AlBr_3 \rightleftharpoons Ar{\cdot}COBr + AlClBr_2 \ in\ CS_2}$$
$$\mathrm{AlClBr_2 + HBr \rightleftharpoons AlBr_3 + HCl}$$

Ar·COCl	Temp.	Time (hr.)	100 [HCl]/([HCl] + [HBr]) for the gas phase: Found	Calc.*
$C_6H_5\cdot COCl$	18·0°	1·00	25	20
2 : 4 : 6-$C_6H_2Me_3\cdot COCl$	18·0	1·00	21·5	,,

$$\mathrm{2:4:6\text{-}C_6H_2Br_3{\cdot}COBr + Metal\ chloride\ (2\ mols.) \longrightarrow 2:4:6\text{-}C_6H_2Br_3{\cdot}COCl + etc.}$$

Metal chloride	Time (hr.)	in ethylene chloride at 20·0° Exchange (%) Found	Calc.*	Metal chloride	Time (hr.)	in ethylene chloride at 20·0° Exchange (%) Found	Calc.*
$AlCl_3$	6	94·8	100 †	$SnCl_4$ ...	6	70·1	89
$TiCl_4$	6	85·0	89				

TABLE 2. *Extent of exchange* $\mathrm{Ar{\cdot}COCl + HBr \longrightarrow Ar{\cdot}COBr + HCl}$ *after* 3 *hr. in* CS_2 *at* 18·0°.

Ar·COCl	Exchange (%) Found	Calc.*	Ar·COCl	Exchange (%) Found	Calc.*
2 : 4 : 6-$C_6H_2Me_3\cdot COCl$	29·7	50·0	2 : 4 : 6-$C_6H_2Br_3\cdot COCl$	3·6	50·0
$C_6H_5\cdot COCl$	15·5	,,			

* For random distribution of halogen.

† Halogen exchange occurs between aluminium bromide and the solvent.

2 : 4 : 6-Tribromobenzoyl halide, by reacting readily with mesitylene, *m*-xylene, *p*-xylene, benzene, and naphthalene (rates decrease in this order) in the presence of aluminium halide, provides evidence that acyl cation and not sterically hindered oxonium complex is the acylating agent in these reactions. 2 : 4 : 6-Trimethylbenzoyl halide, however, reacts with none of these hydrocarbons, but this inertness is caused by the comparatively low reactivity of the 2 : 4 : 6-trimethylbenzoyl cation and not by steric hindrance, since addition of anisole provides a ready Friedel–Crafts reaction.

Interaction of benzoyl chloride and benzene affords benzophenone in yields which are proportional to the amount of aluminium chloride added, and is complete when little more than a molecular proportion of reagent (as $AlCl_3$) is used (Riddell and Noller, *J. Amer. Chem. Soc.*, 1930, **52**, 4365). This relationship applies to the preparation of many aromatic ketones, and Ulich and Heyne (*Z. Elektrochem.*, 1935, **41**, 509) concluded that the reagent is firmly attached to the resulting ketone and no longer able to activate more acid halide; this conclusion is not wholly true, since we now show (Table 3) that halogen exchange between tribromobenzoyl chloride and aluminium bromide occurs, though slowly, in the presence of *excess* of benzophenone. Friedel–Crafts reaction does not occur under these conditions, even when anisole is added; apparently, presence of the ketone does not prevent formation of acyl cation, but lowers its efficacy as an acylating agent; this deactivation is probably effected by association:

TABLE 3. $2:4:6\text{-}C_6H_2Br_3{\cdot}COCl \xrightarrow{2AlBr_3} 2:4:6\text{-}C_6H_2Br_3{\cdot}COBr$ *in nitrobenzene at 25·0° and in the presence of* (a) *benzophenone* (3 *mols.*) *and* (b) *benzophenone* (3 *mols.*) *and anisole* (2 *mols.*).

In $C_6H_5{\cdot}NO_2$		(a)			(b)		
			Exchange (%)			Exchange (%)	
Time (hr.)	Exchange (%)	Time (hr.)	Exp. 1	Exp. 2	Time (hr.)	Exp. 1	Exp. 2
1	83·6	1	5·7	6·5	1	6·8	6·3
3	86·2	2·5	18·4	15·2	3	17·3	18·2
		4	26·8	28·0	6	30·1	29·0
		6	31·8	31·6			

$$\overset{+}{C}R{:}O + Ar{\cdot}CR{:}O \longrightarrow [Ar{\cdot}CR{:}O \;.\;.\;.\;.\; CR{:}O]^+$$

Similarly, ability of added substances, *e.g.*, *m*-dinitrobenzene<nitrobenzene<benzophenone<*p*-methoxybenzophenone, to retard or even to suppress Friedel–Crafts reactions is related to their ability to solvate acyl cation as well as to engage aluminium halide. Further, as these added substances may provide bulky solvated acyl cations which are susceptible to steric hindrance, they may alter the course of reaction; *e.g.*, they increase the extent of β-substitution in naphthalene (*loc. cit.*).

Acid anhydride combines with 2 mols. of aluminium halide to afford one of acylating agent; it is probable that half the metal halide provides acid halide (reaction v) (Adrianowsky, *J. Russ. Phys. Chem. Soc.*, 1879, **11**, 116) which combines with the other half of the metal halide (reaction vi). These formulations are now further substantiated: 2 : 4 : 6-tribromobenzoic anhydride (obtained by addition of water to the product of interaction of the acid halide and pyridine in ether) and aluminium bromide were brought together in carbon disulphide and afforded equimolecular amounts of the acid and its bromide when poured into water:

$$(R{\cdot}CO)_2O + AlX_3 \longrightarrow R{\cdot}COX + R{\cdot}CO{\cdot}OAlX_2 \quad . \; . \; . \; . \; . \; . \quad (v)$$

$$(R{\cdot}CO)_2O + 2AlX_3 \longrightarrow R{\cdot}CX{:}\overset{+}{O}{\cdot}\overset{-}{Al}X_3 + R{\cdot}CO{\cdot}OAlX_2 \; . \; . \; . \; . \; . \quad (vi)$$

$$\downarrow {\scriptstyle H_2O}$$

$$R{\cdot}COX + R{\cdot}CO_2H$$

The bromide and anhydride of 2 : 4 : 6-tribromobenzoic acid are stable in water but, unlike the methyl ester (Hammett and Treffers, *J. Amer. Chem. Soc.*, 1937, **59**, 1708), dissociate in concentrated sulphuric acid; the former evolves hydrogen bromide and, when poured into water, both solutions afford the organic acid. These observations support the view that dissociation:

$$Ar{\cdot}COY + H_2SO_4 \longrightarrow Ar{\cdot}\overset{+}{C}O + YH + SO_4H^-$$

increases with increase in electronegativity of Y (Br and O·COAr>OAlk).

It is noteworthy that methyl 2 : 4 : 6-trimethylbenzoate dissociates in sulphuric acid (*idem, ibid.*), but not in combination with aluminium halide at room temperature.

EXPERIMENTAL

$$2:4:6\text{-}C_6H_2Br_3{\cdot}COCl + AlBr_3 \longrightarrow 2:4:6\text{-}C_6H_2Br_3{\cdot}COBr + AlClBr_2.$$

(i) *In carbon disulphide.* Aluminium bromide (1·40 g., 2 mols.) was distilled into a reaction flask (50 c.c.) and dissolved in dry carbon disulphide (15 c.c.); the acid chloride (1·0 g.) in carbon disulphide (10 c.c.) was added and the flask was sealed and placed in a thermostat at 18·0°. After 1 hr., the mixture was poured on crushed ice, the lower layer was separated, and the aqueous layer was further extracted with carbon disulphide (3 × 10 c.c.); the extracts were washed with water till free from chloride ion and dried (K_2CO_3). Removal of solvent afforded a residue, m. p. 32·5°, which did not depress the m. p. (33°) of the acid bromide on admixture. [This observation did not identify the residue since small additions of the acid chloride did not depress the m. p. of the bromide which was obtained by the action of phosphorus pentabromide on the acid; the *bromide*, b. p. 195—200°/15 mm., crystallised from light petroleum in colourless cubes, m. p. 32·5—33° (Found: Br, 75·2. $C_7H_2OBr_4$ requires Br, 75·8%).] The residue was heated with aqueous ammonia (*d* 0·88; 25 c.c.) until most of the ammonia had volatilised, and the acid amide (0·90 g.) was separated, washed with water, and dried; the filtrate was acidified with nitric acid, and halide ion precipitated by addition of silver nitrate solution; silver halide was separated, dried, and weighed (Found: 0·4659 g.) and afforded silver chloride (0·3750 g.) when heated in a stream of dry chlorine to constant weight. Recovered acid halide was therefore a mixture of acid bromide (78·2) and chloride (21·8 mols. %). The experiment was repeated in a reaction flask fitted with inlet and outlet tubes (the former reaching to the bottom of the flask), and a stream of dry nitrogen saturated with carbon disulphide at room temperature was passed through the reaction mixture to remove the little hydrogen bromide which was present; after an hour, recovered acid halide contained bromide (73·5%).

(ii) *In nitrobenzene.* (*a*) Acid chloride (5·0 g.) in nitrobenzene (20 c.c.) was added to aluminium bromide (7·0 g., 2 mols.) in nitrobenzene (20 c.c.) and the mixture was made up to 50 c.c. in a graduated flask and kept at 25·0°; acid halide recovered after 1 and 3 hr. contained bromide 83·6 and 86·2%, respectively.

(*b*) A homogeneous solution (65 c.c.) of acid chloride (5·0 g.), benzophenone (7·5 g., 3 mols.), and aluminium bromide (7·0 g., 2 mols.) in nitrobenzene was placed in a thermostat at 25·0°, and samples (10 c.c.) were analysed after 1, 2·5, 4, and 6 hr.; recovered acid halide contained bromide 5·7 (6·5), 18·4 (15·2), 26·8 (28·0), and 31·8 (31·6%), respectively. The values in parentheses were provided by a duplicate experiment.

(*c*) When anisole (0·90 g., 2 mols.) was also present, acid halide recovered after 1, 3, and 6 hr. contained bromide 6·8 (6·3), 17·3 (18·2), and 30·1 (29·0%), respectively. Acid halide was recovered in 98·5% yield.

$$2:4:6\text{-}C_6H_2Br_3{\cdot}COBr \xrightarrow{\text{Metal chloride}} 2:4:6\text{-}C_6H_2Br_3{\cdot}COCl.$$

(i) *Aluminium chloride.* Acid bromide (1·00 g.) in ethylene chloride (10 c.c.) was added to the metal chloride (0·65 g., 2 mols.) under ethylene chloride (10 c.c.). The mixture was shaken for 6 hr. in a closed vessel at 18°, and recovered acid halide then contained chloride (94·8%).

(ii) *Stannic chloride.* Procedure was similar to that in (i). The reaction mixture was decomposed with ice and the lower layer was washed with dilute sodium hydroxide solution till free from tin, and dried (K_2CO_3). Removal of solvent provided acid halide containing chloride (70·1%). The same result was obtained when the reaction mixture also contained benzene (2 mols.). Friedel–Crafts reaction was not detected at room temperature or at 70°. Reaction occurred when mesitylene was added in place of benzene, and afforded mesityl 2 : 4 : 6-tribromophenyl ketone, m. p. and mixed m. p. 174°.

(iii) *Titanium tetrachloride.* In this experiment the reaction mixture was decomposed with ice and hydrochloric acid (5N). The lower layer was thoroughly washed to remove titanium and halide ion, and afforded acid halide containing chloride (85·0%). Addition of benzene and of mesitylene to the reaction mixture provided results similar to those in the previous experiment.

$$Ar{\cdot}COCl + HBr \rightleftharpoons Ar{\cdot}COBr + HCl \textit{ in carbon disulphide.}$$

Acid chloride (0·100 mole) was dissolved in solvent (25 c.c.) in an all-glass flask (250 c.c.) filled with dry hydrogen bromide (225 c.c., 0·100 mole). The mixture was shaken at 18·0° for a selected time before hydrogen halide was swept from the flask by a stream of dry nitrogen and absorbed in water; the ratio 100[HCl]/([HCl] + [HBr]) was determined in the usual way and was in good agreement with the ratio 100[Ar·COBr]/([Ar·COBr] + [Ar·COCl]) for recovered acid halide. The data are assembled in Table 2.

$$ArCOCl + AlBr_3 \rightleftharpoons ArCOBr + AlClBr_2$$

$$AlClBr_2 + HBr \rightleftharpoons AlBr_3 + HCl$$

A tube containing benzoyl chloride (1·4 g.) in carbon disulphide (5 c.c.) was placed in a reaction vessel (250 c.c.) containing aluminium bromide (2·7 g., 1 mol.) in carbon disulphide

(20 c.c.) and the vessel was filled with dry (P_2O_5) hydrogen bromide. After the mixture had been shaken at 18° for an hour, hydrogen halide was swept from the system and analysed; it contained hydrogen chloride (25%). A similar experiment in which 2 : 4 : 6-trimethylbenzoyl chloride was used afforded hydrogen halide containing the chloride (21·5%).

Relative rates of reaction $2:4:6\text{-}C_6H_2Br_3{\cdot}COCl + ArH \xrightarrow{AlBr_3} 2:4:6\text{-}C_6H_2Br_3{\cdot}COAr + HBr$ (or HCl).

The all-glass reaction flask was fitted with a dropping-funnel and a gas-distributor conveying dry nitrogen saturated with carbon disulphide at 18°. The flask contained aluminium bromide (0·60 g., 1·5 mols.) in carbon disulphide (15 c.c.), and acid chloride (0·60 g., 1·0 mol.) in solvent (10 c.c.) and then aromatic hydrocarbon (2 mols.) in solvent (10 c.c.) were added. Rate of reaction was determined by titrating the hydrogen halide which was swept from the system; the gases issuing from the reaction vessel were freed from aluminium halide by passage through a plug of glass wool. Times of half-reaction (in min.) for the following hydrocarbons are given in parentheses: Mesitylene (8), *m*-xylene (18), *p*-xylene (24), benzene (46), and naphthalene (70). In each instance the resulting ketone was isolated and crystallised from ligroin: 2 : 4 : 6-*Tribromo*-2′ : 4′ : 6′-*trimethylbenzophenone* as rods, m. p. 174° (Found: Br, 51·8. $C_{16}H_{13}OBr_3$ requires Br, 52·1%), 2 : 4 : 6-*tribromo*-2′ : 4′-*dimethylbenzophenone* as rods, m. p. 117° (Found: Br, 53·2. $C_{15}H_{11}OBr_3$ requires Br, 53·7%), 2 : 4 : 6-*tribromo*-2′ : 5′-*dimethylbenzophenone* as rods, m. p. 135° (Found: Br, 53·2%), and 2 : 4 : 6-tribromobenzophenone as needles, m. p. 147° (Montagne, *Rec. Trav. chim.*, 1915, **34**, 115). Naphthalene afforded the α-*naphthyl ketone* as plates, m. p. and mixed m. p. 175—176° (Found: Br, 50·9. $C_{17}H_9OBr_3$ requires Br, 51·2%). An authentic sample was prepared as follows: Naphthalene (7 g.) in ethylene chloride (15 c.c.) was gradually added to a mixture of *m*-nitrobenzoyl chloride (10 g.) and aluminium chloride (30 g.) in ethylene chloride (25 c.c.); a ready reaction afforded α-*naphthyl* m-*nitrophenyl ketone* (13·4 g.), which crystallised from glacial acetic acid in light brown prisms, m. p. 122—123° (Found: C, 74·1; H, 3·9; N, 5·1. $C_{17}H_{11}O_3N$ requires C, 73·6; H, 4·0; N, 5·1%). Reduction by stannous chloride afforded the corresponding amino-ketone which was identified as an α-naphthyl ketone by deamination (Friedlander, *Ber.*, 1889, **22**, 587) to α-naphthyl phenyl ketone, m. p. and mixed m. p. 74°. Addition of bromine to a solution of the amino-ketone in hydrochloric acid precipitated 3-*amino*-2 : 4 : 6-*tribromophenyl* α-*naphthyl ketone*, which crystallised from glacial acetic acid in light brown prisms, m. p. 177—178° (Found: C, 41·8; H, 2·1; N, 3·3; Br, 49·3. $C_{17}H_{10}ONBr_3$ requires C, 42·15; H, 2·1; N, 2·9; Br, 49·6%). Deamination afforded the required ketone, m. p. 175—176°.

Friedel–Crafts Reaction with 2 : 4 : 6-*Trimethylbenzoyl Chloride.*—The acid chloride (0·55 g.) in carbon disulphide (10 c.c.) was added to aluminium bromide (1·1 g., 1·5 mols.) in solvent (15 c.c.); addition of benzene and naphthalene did not effect reaction, whereas ready evolution of hydrogen halide occurred on addition of anisole (0·65 g.). 4-Methoxy-2′ : 4′ : 6′-trimethylbenzophenone (0·63 g.) was isolated as needles, m. p. 78—79°, from light petroleum (Burton and Praill, *J.*, 1951, 533). It was identified by comparison (m. p. and mixed m. p.) with an authentic sample obtained by interaction of mesitylene (2·4 g.), aluminium bromide (2·7 g., 2 mols.), and anisoyl chloride (1·7 g., 1 mol.) in carbon disulphide (Found: C, 80·1; H, 6·9. Calc. for $C_{17}H_{18}O_2$: C, 80·3; H, 7·1%).

2 : 4 : 6-*Tribromobenzoic Anhydride.*—Pyridine (0·45 g.) was added to the acid chloride (1·0 g.) in ether (10 c.c.); deliquescent crystals separated overnight and, after removal of ether under reduced pressure, addition of water afforded the *anhydride* (0·85 g.); it crystallised from glacial acetic acid in needles, m. p. 149° (Found: Br, 68·3. $C_{14}H_4O_3Br_6$ requires Br, 68·6%).

Reaction with aluminium halide. The anhydride (0·960 g.) in carbon disulphide (10 c.c.) was added to aluminium bromide (5 g.) in solvent (15 c.c.). After 24 hr. at room temperature, the solution was poured on ice and provided 2 : 4 : 6-tribromobenzoyl bromide (0·58 g., 98% of theoretical) and 2 : 4 : 6-tribromobenzoic acid (0·40 g., 82%). Similarly, aluminium chloride in ethylene chloride converted the anhydride into equimolecular proportions of acid and acid chloride.

A solution of the anhydride in concentrated sulphuric acid afforded the organic acid when poured into water.

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