crystallize properly as well as its tendency to decompose during attempts to distil the ethyl-ψ-ionol from it. Oximation of the ketone and separation of the oxime by alumina chromatography was found the most convenient method for obtaining the ethyl-ψ-ionol in pure form.

The concentrate from the Grignard reaction was accordingly added to a solution of hydroxylamine, prepared from 35.0 g. of hydroxylamine hydrochloride and 20.0 g. of sodium hydroxide (95% pellets) in 100 ml. of water. Enough methanol was added to effect complete solution of the oil (about 300 ml.) and the precipitated sodium chloride filtered off. The filtrate was warmed to 50° and allowed to stand at room temperature for 24 hr. It was then worked up with water and petroleum ether. After drying with anhydrous potassium carbonate and concentrating to about 100 ml., the petroleum ether solution was poured onto a 4 × 60 cm. column of Alcoa F-20 alumina and the chromatogram developed with additional petroleum ether. The bands were not visible and elution (20% ether in petroleum ether) was followed spectroscopically. The ethyl-ψ-ionol, λ_{max} 240 mμ, came off first. Elution was continued with this solvent until the concentration of 240-mμ material substantially decreased. On changing then to 30% ether in petroleum ether, the 240-mμ band rather abruptly disappeared, giving way to only end-absorption. This proved to be the oxime, which was completely removed by this solvent. No other fractions were obtained.

The ethyl-ψ-ionol fraction was distilled, yielding 5.0 g. of product at 94.5–96° (0.75 mm.), $n^{20}D$ 1.5028; λ_{max} 240, ε 26,700.

Anal. Calcd. for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 80.92; H, 11.85.

The oxime fraction yielded 10.5 g. at 98° (0.001 mm.), $n^{20}D$ 1.4861.

Anal. Calcd. for $C_{15}H_{27}NO$: C, 75.89; H, 11.47. Found: C, 76.03; H, 11.51.

Ethynyl-ψ-ionol.—A specimen of this compound was prepared from lithium acetylide and ψ-ionone by the method of Oroshnik and Mebane.[5] The absorption spectral constants, which were not previously reported, are λ_{max} 242 mμ, ε 27,400.

Ozonolysis.—The apparatus and procedure was that described in Part I.[12]

Acknowledgment.—The authors are indebted to Mr. Joseph Grodsky for the microanalyses and to Mr. Walter Gall and Mr. Alexander D. Mebane for technical assistance.

RARITAN, NEW JERSEY

[CONTRIBUTION FROM THE U. S. NAVAL ORDNANCE LABORATORY]

Catalytic Esterification by Metal Halides[1]

BY MARION E. HILL

RECEIVED NOVEMBER 25, 1953

2,2,2-Trichloro-, tribromo- and trifluoroethanol and 2,4,6-trichlorophenol can be esterified under mild conditions in the presence of catalytic quantities of aluminum chloride or bromide. The halides of iron, titanium, antimony, tin and zinc and boron trifluoride are also effective in varying degree. The optimum concentration of catalyst is usually 10 to 30 mole per cent. of the reactants. The reaction proceeds by the formation of an acyl halide-metal halide complex and subsequent reaction with the alcohol.

Alcohols substituted in the beta position by halogens are difficult to esterify because of their acidic nature caused by the inductive effect of the halogens. Such alcohols as 2,2,2-trichloroethanol are not easily esterified directly by an acid. With an acid halide, esterification has previously been accomplished by heating the alcohol and halide at temperatures up to 130° for periods up to several hours without a solvent medium.[2] Only a few esters of 2,2,2-tribromoethanol and 2,2,2-trifluoroethanol have been reported in the literature. Recently, some experiments were reported in which trichloroethanol and tribromoethanol were easily esterified with acyl halides under mild conditions using catalytic amounts of aluminum chloride or aluminum bromide.[3] This paper reports some results of subsequent investigation on the nature of the reaction and its applicability in regard to the use of various metal halides and of acyl halides. Trifluoroethanol and 2,4,6-trichlorophenol have been esterified easily. Additional esters of trichloroethanol and tribromoethanol have been prepared from unreactive and sterically hindered acid chlorides.

Results

The esterifications of trichloroethanol, trifluoroethanol and trichlorophenol were accomplished simply by adding 10 to 30 mole % of anhydrous aluminum chloride to a carbon tetrachloride solution of equimolar quantities of the reactants. In reactions with tribromoethanol the use of aluminum bromide improved the yield. Reaction was vigorous at temperatures from 25 to 50° in most cases, with only a short period at reflux temperature necessary to complete reaction. If no solvent was used, the reaction was extremely vigorous. The product was isolated by the usual Friedel–Crafts procedures. The results of the preparations of esters of representative acid chlorides, some of which are unreactive, are summarized in Table I which lists the melting point, % yield of recrystallized materials and the elemental analysis of new compounds.

The extent of the catalytic effect of aluminum chloride under preparative conditions was indicated by a series of experiments in which uncatalyzed reactions were run as controls at the same time as catalyzed reactions. Thus benzoyl chloride heated with trichloroethanol without solvent or catalyst at 100° for seven hours gave a 72% yield of ester. With 10 mole % of aluminum chloride, a 93% yield of ester was obtained in 25 minutes at 50°. With carbon tetrachloride as a solvent no esterification of benzoyl chloride occurred in five hours at 65°

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(1) Presented in part before the Organic Division at the 124th National Meeting, Chicago, September, 1953.

(2) (a) J. W. Cusic and A. L. Raymond, U. S. Patent 2,584,846 (1952); (b) H. M. Woodburn and C. E. Sroog, THIS JOURNAL, **71**, 1709 (1949); (c) J. R. Geigy, Swiss Patent 250,801 (1947); *C. A.*, **44**, 1530e (1950); (d) R. Nakai, *Biochem. Z.*, **152**, 272 (1924); (e) K. Garzarolli-Thurnlackh, *Ann.*, **210**, 63 (1881).

(3) M. E. Hill, THIS JOURNAL, **75**, 3020 (1953).

TABLE I

ESTERS OF POLAR ALCOHOLS

Ester	M.p., °C.	Yield, %	Carbon,[b] % Found	Carbon,[b] % Calcd.	Hydrogen, % Found	Hydrogen, % Calcd.	Halogen, % Found	Halogen, % Calcd.
2,2,2-Trichloroethyl								
benzoate	27	93						
fumarate[a]	107	85	25.66	25.36	1.57	1.60	55.90	56.15
phthalate[a]	83	89	33.59	33.60	1.88	1.88	50.04	49.60
anisate[a]	46	88	42.64	42.36	3.30	3.20	38.33	37.51
2,2,2-Tribromoethyl								
fumarate[a]	129	81	15.08	14.88	1.13	0.94	74.78	74.27
phthalate[a]	109	83	21.18	20.92	1.21	1.16	68.57	68.92
2,4,6-Tribromobenzoate[a]	89	83	17.48	17.33	0.86	0.65	77.60	76.89
2,2,2-Trifluoroethyl								
3,5-dinitrobenzoate	62	88						
2,4,6-Trichlorophenyl benzoate	73	87						
3,5-dinitrobenzoate[a]	164	83	39.69	39.87	1.24	1.29	27.58	27.17

[a] New compounds. [b] Analyses by Oakwold Laboratories, Alexandria, Va.

without catalyst as compared to 87% esterification in 20 minutes at 50 to 70° when 10 mole % aluminum chloride was added. Similarly, fumaryl chloride and trichloroethanol after 16 hours in carbon tetrachloride at reflux temperature gave only 3% of the bis ester while with 20 mole % of aluminum chloride 85% of the bis ester was obtained in 2 hours at 50 to 70°.

The esterification of 2,4,6-tribromobenzoyl chloride with tribromoethanol exemplifies the extensive catalytic effect of aluminum bromide. Unlike ordinary acid chlorides, this one is quite unreactive because of the steric effect of the two ortho bromine atoms. Its rate of alcoholysis with methanol at 25° is 1/10000 as fast as the rate of alcoholysis of benzoyl chloride.[4] The steric effect of the ortho bromine atoms prevents the close approach to the aliphatic carbon atom by the tribromoethanol, a necessary condition for reaction.[5] The unreactivity of the acid chloride, coupled with the unreactivity of the alcohol, serves to indicate the many fold increase in rate accomplished by the catalyst.

The activity of aluminum chloride in catalyzing Friedel–Crafts reactions is generally ascribed to its powerful electrophilic or "Lewis acid" character. A comparison of the activity of a number of electrophilic metal halides in catalyzing the esterification of trichloroethanol was made by adding a mixture of benzoyl chloride and trichloroethanol to the metal halide in carbon tetrachloride. All conditions were the same for each experiment with the only variant being the metal halide used. Hydrogen chloride evolved by the reaction was swept out by nitrogen into a water absorption vessel and measured by titration. On the basis that only an equimolar amount of hydrogen chloride would be evolved, it was thought that measurement of the hydrogen chloride would be an accurate quantitative measure of the efficiency of the metal halides as catalysts. However in every case 3–8% more than an equimolar quantity of acid gas was produced in spite of careful manipulation to avoid moisture. The quantitative measurement of hydrogen chloride evolved nevertheless sufficed to indicate the relative activity of the catalysts and to indicate the effect of catalyst quantity. A possible source of the hydrogen chloride is from the reaction of the metal halide with the resultant ester. Aluminum chloride does react slowly and incompletely with trichloroethyl benzoate to give products as yet unidentified,[6] but does not prevent formation of high yields in the preparations of esters, however. The action of aluminum chloride on esters is under further investigation and will be reported later.

The results of the metal halide comparisons are summarized in Table II. The halides of iron(III), titanium, antimony(V), and aluminum are more effective as a group than the halides of tin(IV) and zinc or boron trifluoride etherate. Approximately 30 mole % of catalyst is all that is necessary for good reaction.

TABLE II

EFFECT OF METAL HALIDES ON TRICHLOROETHANOL ESTERIFICATION

Cat.	Mole % cat.	Time in min. for evolution of 70 mole % HCl Benzoate[a]	Time in min. for evolution of 70 mole % HCl 3,5-Dinitrobenzoate[b]
$FeCl_3$	30	Too fast to measure	22
$SbCl_5$	30	4	25
$AlCl_3$	30	6	118
$TiCl_4$	30	16	
$SnCl_4$	30	80	
$ZnCl_2$	30	115	
$BF_3 \cdot Et_2O$	30	145	
$HgCl_2$	30	(3% in 180)	
None	...	(1% in 300)	
$AlCl_3$	100		40
$AlCl_3$	20		(32% in 120)
$AlCl_3$	10	9	(13% in 120)
$AlCl_3$	3	(20% in 90)	

[a] From benzoyl chloride in CCl_4 at 65°. [b] From 3,5-dinitrobenzoyl chloride in nitrobenzene at 65°.

Carbon tetrachloride and chloroform were the most satisfactory solvents to use in the esterifications. Nitrobenzene is useful but retards the rate of reaction somewhat. The substitution of *sym*-tetrachloroethane or nitromethane for nitrobenzene

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(4) J. F. Norris and H. H. Young, THIS JOURNAL, **57**, 1424 (1935).

(5) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 446.

(6) *Cf.* J. F. Norris and B. M. Sturgis, THIS JOURNAL, **61**, 1413 (1939).

as a solvent for the formation of trichloroethyl dinitrobenzoate resulted in lower yields.

Since metal halides can be used in catalytic quantities to promote the esterification of polar alcohols, any representation of the mechanism of the reaction must account for the apparent lability of the aluminum chloride and its regeneration for further use. Two possible ways by which the reaction proceeds are (1) by formation of an intermediate alcoholate I, (2) or by formation of a highly reactive acyl halide complex II.

$$CX_3CH_2OH + AlCl_3 \xrightarrow{-HCl} \underset{I}{CX_3CH_2OAlCl_2} + RCOCl \longrightarrow RCOOCH_2CX_3 + AlCl_3(\text{complex}) \quad (1)$$

$$RCOCl + AlCl_3 \longrightarrow \underset{II}{\overset{(+)\quad(-)}{RCOClAlCl_3}} + CX_3CH_2OH \xrightarrow{-HCl} RCOOCH_2CX_3 + AlCl_3(\text{complex}) \quad (2)$$

Evidence has been obtained which indicates that the reaction can occur by both routes.

The isolation and characterization of the alcoholate I, was accomplished in order to determine if its formation was a detrimental side reaction or could lead to an ester as written in equation 1. The reaction of trichloroethanol and aluminum chloride went very smoothly at 50° to give trichloroethyl dichloroaluminate which was isolated and characterized. Furthermore substitution of the second and third chlorine atoms of aluminum chloride by excess trichloroethanol was unsuccessful though more hydrogen chloride was evolved than was equivalent to one chlorine atom. To determine whether the alcoholate could be esterified, the reaction was run in two steps under nitrogen atmosphere; first the alcoholate was formed in solution and then esterified with benzoyl chloride. With provision for hydrogen chloride measurement, two reaction vessels were set up in such a way that when the alcoholate preparation was completed in the first flask, it could be tipped and the clear solution forced by nitrogen through a filter into the second vessel containing a carbon tetrachloride solution of benzoyl chloride. In this manner the aluminate was esterified in 83% yield in two hours at reflux temperature. However additional hydrogen chloride was evolved, apparently because of thermal decomposition of the alcoholate.

The formation of very active complexes of aluminum chloride with acyl halides is well known in Friedel–Crafts reactions.[7] The reactivity of the acyl halide–aluminum chloride complex (II) might be greater than the reactivity of the molecular species, trichloroethyl dichloroaluminate (I). Assuming this is correct then the rate of hydrogen chloride evolution of reaction 1 would not be as high as the evolution according to equation 2. A comparison of rates from the two systems would be particularly useful if the rates were very different. Also if the rate of gas evolution from the complex II, and the alcohol was the same as the rate from the system in which a mixture of the reactants is added to a mixture of solvent and catalyst, then it should constitute evidence that route (2) is plausible but would not preclude the possibility of simultaneous occurrence of both mechanisms.

This evidence was obtained in the following manner. First, a mixture of trichloroethanol and benzoyl chloride was added all at once to 30 mole % of aluminum chloride. The hydrogen chloride evolved was measured and the data plotted. The linear portion of the resulting curve indicated a maximum gas evolution of 0.67 milliequivalent per minute. A benzoyl chloride–aluminum chloride complex was prepared by adding 30 mole % aluminum chloride to benzoyl chloride. The resultant benzoyl chloride solution of the complex dissolved completely in carbon tetrachloride upon warming to the reaction temperature, 50°. Trichloroethanol was added to this solution and the progress of the reaction was followed as before. The plot of data from this reaction almost exactly superimposed the curve from the catalyzed reaction of the acid chloride–alcohol mixture. Under identical conditions, the rate of gas evolution from the reaction of trichloroethanol with 30 mole % aluminum chloride was 0.19 milliequivalent per minute. To this solution of trichloroethanol and trichloroethyl aluminate, benzoyl chloride was added. The rate of gas evolution increased to 0.32 milliequivalent per minute.

Both of the reaction mechanisms proposed indicate that the final system consists of free ester and an aluminum chloride–ester complex. This is in accordance with the experimental observation that the more dilute reaction systems become homogeneous as the reaction proceeds then become murky with precipitate near the end of the reaction period. Isolation of this precipitate and subsequent characterization showed that it was an aluminum–chlorine–ester complex. Furthermore, when trichloroethyl benzoate and aluminum chloride were warmed at 65° in carbon tetrachloride, a small amount of hydrogen chloride was evolved and a homogeneous solution resulted. To this solution was added a mixture of trichloroethanol and benzoyl chloride which reacted. This experiment indicated a possible source of the excess hydrogen chloride previously mentioned and showed that the ester–aluminum chloride complex was capable of catalyzing the reaction.

Experimental

Materials.—2,2,2-Tribromo- and 2,2,2-trichloroethanol were purchased from Delta Chemical Corporation. The trichloroethanol was redistilled under vacuum before use. A research sample of 2,2,2-trifluoroethanol was kindly furnished by Minnesota Mining and Manufacturing Corporation. The metal halides were commercial C.P. grade reagents and used without further purification. 2,4,6-Tribromobenzoyl chloride was prepared by action of phosphorus pentachloride on 2,4,6-tribromobenzoic acid, made according to Bunnett, *et al.*[8]

Ester Syntheses.—The preparation of bis-(2,2,2-trichloroethyl)-fumarate is typical of the method of esterification generally used.

A solution of 10 ml. of carbon tetrachloride and 1.53 g. (0.010 mole) of fumaryl chloride was mixed with 3.2 g. (0.021 mole) of trichloroethanol at room temperature. No reaction was observed. To this solution was added 0.52 g. (0.004 mole) of crushed anhydrous aluminum chloride. After the initial surge of hydrogen chloride gas had subsided,

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[7] C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publ. Corp., New York, N. Y., p. 57.

[8] J. F. Bunnett, M. M. Robison and F. C. Pennington, THIS JOURNAL, **72**, 2378 (1950).

the reaction was warmed to reflux and held 30 minutes to complete the reaction. At the end of this period evolution of gas was virtually nil. Upon cooling, the reaction mixture set to a mass of crystals which were filtered off. The solid was then slurried with dilute hydrochloric acid, filtered, slurried with bicarbonate, filtered and dried. Recrystallization from hexane gave 3.24 g. of bis-(2,2,2-trichloroethyl)-fumarate (85%), m.p. 105.6–106°. Without a catalyst 16 hours of refluxing gave only 3% ester using the same concentration of reactants.

For tribromoethanol esterification, anhydrous aluminum bromide was used, since aluminum chloride gave somewhat lower yields, *e.g.*, 43% tribromoethyl dinitrobenzoate compared to 91%.

Results of other preparations are given in Table I.

Typical of a preparation where no solvent was used was the synthesis of trichloroethyl benzoate.

A solution of 2.81 g. (0.020 mole) of benzoyl chloride and 3.00 g. (0.020 mole) of trichloroethanol was prepared at room temperature. No reaction was observed over a period of 20 minutes. To this solution was added 0.26 g. (0.002 mole) of crushed anhydrous aluminum chloride. A violent exothermic reaction ensued and the temperature rose to 50°. After five minutes the reaction subsided and the reaction vessel was then held for 20 minutes longer at 50°. Treatment of the resulting oil with iced dilute hydrochloric acid by emulsification gave a mass of fine white crystals. These were filtered from the iced solution and dried. Short path distillation of the crude product to a cold finger at 70° (1 mm.) gave 4.70 g. of trichloroethyl benzoate (93%), m.p. 27–28°.

Without catalyst the reactants were heated 7 hours at 100°. Upon working up the product, a 72% yield of ester was obtained.

Experiments Comparing Metal Halide Efficiency and Effect of Catalyst Concentration.—A 50-ml. round bottom flask was sealed onto an 8″ straight condenser whose exit was sealed to a tube leading to a gas bubbler. Dry nitrogen gas presaturated with solvent was led into the reaction flask through one leg of a Y shaped input tube sealed into the apparatus below the condenser and extending down into the flask to just above a magnetic stirring bar. The other leg consisted of a standard tapered joint in which was inserted a small dropping funnel. Nitrogen was led to the opening of the funnel to maintain constant pressure and inert atmosphere over the reactants. The reaction flask was surrounded by a constant temperature water-bath. The output gas bubbler was immersed in water which was vigorously stirred by a magnetic stirrer.

In quick succession 1.49 g. (0.010 mole) of trichloroethanol and 1.40 g. (0.010 mole) of benzoyl chloride were weighed into the dropping funnel. Then 30 mole % of the catalyst being used was weighed into 2 ml. of carbon tetrachloride and washed into the reaction flask by 45 ml. of carbon tetrachloride. The apparatus was assembled, nitrogen flush started, and the solvent and catalyst were brought to temperature (65°) by the water-bath. The contents of the absorption vessel was made slightly basic by 0.2424 *N* NaOH and then the reactants were added all at once from the dropping funnel. The time necessary to reach the end-point of brom thymol blue indicator was noted, additional base added, and so on until the gas evolution became very slow. Then the nitrogen was shut off, the apparatus disassembled, and the reaction solution was quickly cooled to room temperature. The metal halide was decomposed by pouring the solution over ice. After separating and washing the solution with sodium bicarbonate solution, the solvent was evaporated. The residual oil was purified by short path distillation at 70° (1 mm.). The yields obtained from the various catalysts were: $AlCl_3$, 95%; $SbCl_5$, 80%; $SnCl_4$, 80%; $ZnCl_2$, 67%; $TiCl_4$, 63%; $BF_3 \cdot Et_2O$, 49%.

Solutions of 10 ml. of nitrobenzene and 2.30 g. (0.010 mole) of 3,5-dinitrobenzoyl chloride and of 15 ml. of nitrobenzene and 30 mole % of catalyst were placed in the reaction vessel. An additional 22 ml. of solvent was added. Esterification with trichloroethanol was accomplished as outlined above. After decomposition of the catalyst, nitrobenzene was removed by steam distillation, and the crude products purified. The yields obtained were: $AlCl_3$, 95%; $SbCl_5$, 72%; $FeCl_3$, 73%.

Substitution of the same quantity of nitromethane or *sym*-tetrachloroethane for nitrobenzene gave no ester in the former solvent, and only 36% in the latter solvent with $AlCl_3$.

Preparation of Trichloroethyl Dichloroaluminate—$Cl_3CCH_2OAlCl_2$.—A solution of 1.50 g. (0.010 mole) of trichloroethanol was added dropwise to 1.33 g. (0.010 mole) of crushed anhydrous aluminum chloride in 25 ml. of carbon tetrachloride at 50°. The reaction continued for about 1.5 hours. The homogeneous solution resulting was filtered to remove small discolored particles and evaporated under vacuum. The yield was 2.15 g. (88%) of crystalline material which gave off hydrogen chloride when exposed to air. Decomposition of the compound with water and extraction with ether gave an oil which froze at the freezing point of trichloroethanol (16°), and could be esterified catalytically with benzoyl chloride. The aqueous solution at methyl red end-point deposited a flocculent precipitate characteristic of aluminum hydroxide.

This experiment was repeated except the hydrogen chloride evolved was measured by the method above and the trichloroethanol was in excess by 3 moles to 1 of aluminum chloride. The rate of gas evolution dropped off sharply after one molecular equivalent was evolved. A quantitative yield of product was isolated and identified as before.

Esterification of Trichloroethyl Dichloroaluminate.—Two 100-ml. 3-neck flasks were set up side by side. Flask I was equipped with a nitrogen Y inlet tube, reflux condenser, magnetic stirrer, constant temperature bath and a tube leading from the third neck to a male spherical joint. The reflux condenser top was connected to a gas bubbler immersed in water. Flask II was equipped similarly except the neck next to flask I was fitted with a sintered glass funnel which in turn was connected to a female spherical joint. Dry nitrogen was led into the inlet tube of flask II, into one leg of the Y inlet tube of flask I, and into the dropping funnel to maintain constant pressure and inert atmosphere over the reactants.

In flask I, 1.50 g. (0.010 mole) of trichloroethanol reacted with 1.33 g. (0.010 mole) of $AlCl_3$ in 50 ml. of carbon tetrachloride at 47°. When titration of the hydrogen chloride evolved indicated complete reaction of the alcohol the bath was removed and the nitrogen flow stepped up. In quick succession the spherical joints were connected and the reflux condenser was replaced by a stopper. The flask was tipped and rotated so that the aluminate solution was forced from flask I through the sintered funnel into flask II. Flask II contained a 10-ml. carbon tetrachloride solution of 1.40 g. (0.010 mole) of benzoyl chloride. The nitrogen flow was shifted to the inlet tube of flask II and the transfer tube was stoppered. After two hours at reflux the reaction solution was worked up. A yield of 85% of pure trichloroethyl benzoate was obtained. Additional hydrogen chloride (0.0036 mole) was evolved during the last step. Its source was not determined but is considered to be the result of some decomposition of the alcoholate.

Esterifications Relating to the Mechanism. A.—Aluminum chloride (0.40 g., 0.003 mole) was added to 1.40 g. (0.010 mole) of benzoyl chloride. By application of heat complete solution was obtained. This was dissolved in carbon tetrachloride at 50° and esterified with an equivalent of trichloroethanol by the method described above. The amount of hydrogen chloride evolved was plotted as a function of time. The rate was 0.67 meq. per minute. Upon working up the product, a yield of 85% pure ester was obtained.

B.—Under the same conditions a mixture of 1.40 g. (0.010 mole) of benzoyl chloride and 1.50 g. (0.010 mole) of trichloroethanol was added to the catalyst in carbon tetrachloride. The plot of the amount of hydrogen chloride evolved as a function of time fell almost exactly on the plot for the esterification of the benzoyl chloride–catalyst complex. A yield of 93% pure ester was obtained.

C.—Under the same conditions and by the same method, trichloroethanol was added to the catalyst in carbon tetrachloride. The rate of gas evolution was less than in either of the experiments above (0.19 meq. as against 0.67 meq. per minute). When the gas evolution had become very slow, benzoyl chloride was added. The rate of gas evolution increased and became higher than that of the trichloroethanol–aluminum chloride reaction (0.32 meq. per minute), but not as high as that for the trichloroethanol–benzoyl chloride–aluminum chloride system. A yield of 87% was obtained from this reaction.

Isolation of an Aluminum Chloride–Ester Complex.—In the benzoyl chloride esterification it was noted that a homogeneous solution occurred at the time of highest rate of gas evolution. Near the end of the experiment a very fine precipitate appeared. Isolation of the precipitate gave 0.23 g. of a powdery material which was affected by moisture in the air but failed to dissolve completely in dilute hydrochloric acid. Upon ether extraction of an oil suspended in the acid solution and washing with sodium carbonate, 0.1 g. of trichloroethyl benzoate was obtained.

Reaction of Aluminum Chloride and Trichloroethyl Benzoate.—In the apparatus previously described 0.40 g. (0.003 mole) of aluminum chloride and 47 ml. of carbon tetrachloride were mixed and brought to 50°. Trichloroethyl benzoate (2.54 g., 0.010 mole) was added all at once to the reaction vessel. Over a period of 90 minutes, 0.0015 mole of gas was evolved. The reaction solution became homogeneous during this period and slightly discolored. After cooling, the solution was filtered under nitrogen to remove a few dark particles remaining and returned to the reaction vessel. Upon reaching reaction temperature, a mixture of 1.49 g. (0.010 mole) of trichloroethanol and 1.40 g. (0.010 mole) of benzoyl chloride was added all at once. Hydrogen chloride evolution was rapid at first and then tapered off. In a period of 2 hours, 0.010 mole of gas was titrated. After working up the product in the manner previously described, a yield of 90% of trichloroethyl benzoate was recovered.

WHITE OAK, MD.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Formation of Tetraarylsilanes from the Reactions of Triarylsilylmetallic Compounds.[1] II. Reactions with Triarylsilanes

BY A. G. BROOK AND HENRY GILMAN

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Triarylsilylmetallic compounds react at room temperature with triarylsilanes to give high yields of tetraarylsilanes. The only by-products of the reaction, other than hydrolysis products of the unconsumed reagents, are hydrogen and an inorganic silica-like material. The course of the reaction has been investigated but it has been found impossible under the present conditions to establish whether the aryl group migrates from the silane or from the silylmetallic compound, due to the fact that hydrogen–metal interconversion between the silylmetallic and the silane occurs. The sodium or potassium reagents are equally effective in this reaction, but with triphenylsilyllithium, the reaction is slower and takes predominantly an alternative route.

A number of examples have been reported from this Laboratory[1] and by other workers[2,3] of the isolation of tetraphenylsilane from reactions involving phenylsilanes, particularly triphenylsilylmetallic compounds. When this same product was isolated from several investigations in which we were engaged, either as a major product, or as a minor contaminant, the present study was undertaken to attempt to account for its formation.

An extensive investigation has revealed the following facts. The formation of tetraphenylsilane, as a specific example of what appears to be a general reaction, in reactions of triphenylsilylmetallic compounds either with triphenylsilane, or with a variety of compounds containing active hydrogen, is due to the reaction of the triphenylsilylmetallic reagent with triphenylsilane. If this latter species is not a reagent in the reaction, then it is formed by metalation of the hydrocarbon species by part of the triphenylsilylmetallic compound, with the concomitant formation of triphenylsilane, which then reacts with the remaining triphenylsilylmetallic reagent. This latter phase of the investigation, namely, the reactions of triarylsilylmetallic compounds with hydrocarbons, and the reactions of triarylmethylmetallic compounds with triarylsilanes, is discussed more fully in the accompanying paper.

A superficial examination of the reaction of triphenylsilylmetallic compounds with triphenylsilane might suggest that the reaction could be described by the equation

$$(C_6H_5)_3SiK + (C_6H_5)_3SiH \longrightarrow (C_6H_5)_4Si + \text{"other products"} \quad (1)$$

However, an examination of the products of the reactions of a number of triarylsilylmetallic reagents with several triarylsilanes, as listed in Table I, indicated that the course of the reaction cannot be that described by equation 1. In the first place, yields of tetraphenylsilane in excess of 100%, as based on this equation, have been obtained. Secondly, were the simple migration of an aryl group the only reaction occurring, then diphenylsilyl derivatives should constitute the bulk of the "other products," whereas none are actually obtained. Instead, other than the isolation of some triphenylsilyl derivatives, which can be accounted for as recovered reagents, or derivatives of these, the other product isolated appears to be a largely crystalline, inorganic solid, containing a relatively high percentage of silicon. A similar product has been reported by Benkeser and Foster,[3] and by Hauser and Hance.[3a]

The isolation of this inorganic silicon-containing compound suggests that the end product of the reaction of triphenylsilylmetallic compounds with triphenylsilane is silane (SiH_4) or some simple derivative, and this in turn suggests a sort of chain mechanism for the course of the reaction. The first step of this chain is the transfer of an aryl group from one reagent to the other to yield a tetraarylsilane and a diarylsilyl derivative. This diarylsilyl derivative is evidently more susceptible to further aryl migration than is the original triaryl derivative, so that it successively transfers the two remaining aryl groups, yielding in the end silane (SiH_4), or a metalated derivative of silane, and 3 moles of tetraarylsilane, as depicted in the following equations. Since it is uncertain at present as to whether the silane or the silylmetallic compound is

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(1) For paper I of this series, see H. Gilman and T. C. Wu, THIS JOURNAL, **75**, 2509 (1953).

(2) R. A. Benkeser and D. J. Foster, *ibid.*, **74**, 4200 (1952); R. A. Benkeser, H. Landesman and D. J. Foster, *ibid.*, **74**, 648 (1952).

(3) R. A. Benkeser and D. J. Foster, *ibid.*, **74**, 5314 (1952).

(3a) C. R. Hauser and C. R. Hance, *ibid.*, **74**, 1856 (1952).