

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

SILICON TETRACHLORIDE AS A REAGENT FOR THE PREPARATION OF ACID CHLORIDES^{1,2}

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RECEIVED JULY 13, 1927

PUBLISHED AUGUST 5, 1927

The action of silicon tetrachloride on organic acids has hitherto been but slightly investigated. Taurke³ obtained benzoyl chloride from benzoic acid by means of this reagent and Rauter⁴ prepared butyryl chloride by heating butyric acid with silicon tetrachloride in a sealed tube at 150–160°. These apparently constitute the only references in the literature.

In view of the author's previous success in the semi-industrial manufacture of acetyl chloride from acetic acid by this reagent (silicon tetrachloride), its action on other organic acids was investigated with a view to the preparation of a number of acid chlorides free from sulfur and phosphorus impurities.

The method followed was to dissolve the acid in an inert solvent (benzene, toluene, xylene, chloroform, etc.) and after raising the temperature to about 50° to run in the silicon tetrachloride. The acid chloride was distilled off through a fractionating column.

The mechanism of the reaction probably consists in the primary formation of a mixed anhydride of silicic and the organic acid,⁵ $4RCOOH + SiCl_4 = Si(OCOR)_4 + 4HCl$, and the secondary interaction of this with a further molecule of silicon tetrachloride, $Si(OCOR)_4 + SiCl_4 = 4RCOCl + 2SiO_2$. The following acids were investigated: acetic, propionic, butyric, isobutyric, benzoic, phenylacetic and sebacic, the yields obtained being 85, 50, 49, 51, 77, 61 and 37 per cent., respectively.

Other dibasic acids, *o*-nitrobenzoic and pyruvic acids were experimented with but negative results were obtained in all cases.

Experimental Part

Preparation of Acetyl Chloride.—Three hundred and sixty g. (six moles) of glacial acetic acid and 672 g. (six moles) of toluene are placed in a liter, round-bottomed, Pyrex flask fitted with a rubber stopper through which passed a dropping funnel and a reflux condenser. The upper portion of the latter is filled with glass beads and the condenser itself is, in turn, connected to an absorption system consisting of two wash-bottles containing acetic acid. The mixture is heated to 50° and at that temperature

¹ This paper is constructed from Part II of a dissertation presented by Ralph E. Montonna in June, 1924, to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy. The investigation was carried out in the laboratory of Dr. Harold Hibbert.

² Communicated to the Organic Division, American Chemical Society, Washington, D. C., April, 1924.

³ Taurke, *Ber.*, **38**, 1668 (1905).

⁴ Rauter, *Ann.*, **270**, 260 (1892).

⁵ Friedel and Ladenburg, *Ann.*, **145**, 174 (1868).

510 g. (three moles) of silicon tetrachloride is added from the dropping funnel during a period of 30 minutes. The same temperature is maintained until the vigorous evolution of hydrochloric acid almost ceases. The upright condenser is then replaced by a Glinsky or Hempel column carrying a thermometer and attached to a downward condenser, and the product fractionated over a free flame until the thermometer registers 80–85°. The product on redistillation gives 400 g. of acetyl chloride, b. p., 50–55°; yield, 85%.

The same method was applied to the other acids, the only difference being the use of other diluting media and a somewhat higher temperature, prior to fractionation, to ensure the completeness of the reaction.

The results obtained are tabulated below.

TABLE I
SUMMARY OF RESULTS

Exp. no.	Acid used,		Solvent	SiCl ₄		Temp., °C.	Acid chloride recovered		
	name	amt., g.		g.	g.		g.	%	b. p., °C.
1	Propionic	148	Xylene	212	170	50	93	50	75–80
2	Butyric	176	Xylene	212	170	50	104	49	102–105
3	Isobutyric	176	Xylene	212	170	50	109	51	93–98
4	Isobutyric	88	Xylene	106	85	50	56	52.5	93–98
5	Benzoic	122	None	...	85	50	32	23	192–195
6	Benzoic	122	Benzene	135	90	50	108	77	194–196
7	Phenylacetic	272	Benzene	186	170	60	Decomp. on distillation		
8	Phenylacetic	136	Benzene	120	85	60	94	61	115–125/30 mm.
9	Sebacic	50.5	Benzene and ether	175	42.5	50	22	37	185–195/30 mm.
10	Maleic	58	Benzene and ether	175	42.5	50	None		
11	Malonic	52	Benzene and ether	195	85	50	None		
12	Malonic	52	Xylene	106	85	100	None		
13	Oxalic	90	Ether	100	170	50	None		
14	Oxalic	90	Ether and benzene	240	170	75	None		
15	Oxalic	90	Ether	100	170	0	None		
16	<i>o</i> -Nitrobenzoic	42	Benzene	80	22	50	None		
17	<i>o</i> -Nitrobenzoic	42	Ether	75	22	50	Blew up on distill.		
18	<i>o</i> -Nitrobenzoic	42	Ether and benzene	160	22	50	Crude product only		
19	Pyruvic	88	Chloroform	120	90	50	None		
20	Pyruvic	50	Ether	100	50	–10	None		

Synthesis of Acetic Anhydride

The same reagent (silicon tetrachloride) can also be used for the preparation of acid anhydrides from the sodium salts of the corresponding acid using a diluent, preferably the anhydride itself.

In the following experiment acetic anhydride itself was used as diluent. 130 g. of anhydrous sodium acetate and 300 g. of 99% acetic anhydride were warmed to 50° and, while stirring, 67 g. of silicon tetrachloride was added during a period of one hour. The temperature rose to 80° and the heating was continued for three hours at 90°. The yield was 75% of 96% anhydride.

A second experiment carried out in glassware, using benzene as diluent and heating for five hours at 50–60°, gave a yield of 50%.

Summary

A laboratory method is described for the preparation of "phosphorus-

and sulfur-free" acid chlorides by the action of silicon tetrachloride on the corresponding organic acid.

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NOTES

Action of Ethylene on Pure Starch.—It has been found that fruits and vegetables treated with ethylene have a higher sugar content than the same kind of fruits and vegetables not treated with the gas.¹

Because ripening is known to be accompanied by change of starch into sugar the attempt to change pure starch into sugar by the use of ethylene was made.

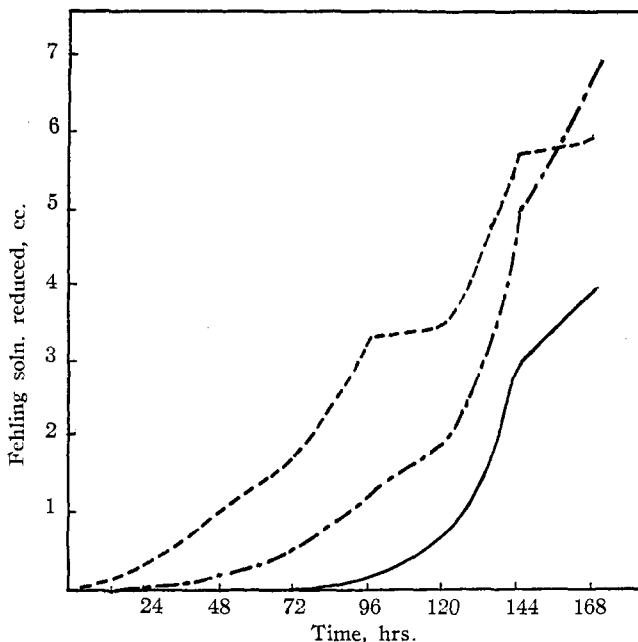


Fig. 1. ----, 10-min. boil; - · - · - ·, 5-min. boil; — 1-min. boil.

Dry starch (both corn and wheat starch were used) was placed in an atmosphere of ethylene at 21° and atmospheric pressure and, as shown by the Fehling test, was partially changed into a reducing sugar. The action was slow and was accompanied by a change in color from pure white to a pale, yellowish tint. No quantitative determination of the rate of conversion of dry starch was made, merely a qualitative test. Untreated starch showed no change in the same length of time. The same kind of

¹ Harvey and Regeimbal, "Physiology of Blanching Celery," *Proc. Am. Assoc. Advancement Sci.*, Washington Meeting, vol. 79, 1924.