alcohol, chloroform, benzene, glacial acetic acid; slightly soluble in methyl alcohol.

Calc. for $C_{18}H_{14}O_8$: C, 60.3; H, 3.9. Found: C, 60.0; H, 3.9.

7. Di-guaiacyl Ester of Oxalic Acid,[1] $(CH_3O\text{-}C_6H_4)_2C_2O_4$.—Shiny, white plates from a mixture of alcohol and ether. M. p. 127°.

Calc. for $C_{16}H_{14}O_8$: C, 63.6; H, 4.6. Found: C, 63.8; H, 4.9.

II. Diatomic Phenols.

(*a*) **Di-*p*-hydroxyphenyl Ester of Oxalic Acid,** $(HO\text{-}C_6H_4)_2C_2O_4$.—As precipitated from the reaction mixture, this substance formed a white powder, only very slightly soluble in all the common solvents, or even heavier solvents, such as glacial acetic acid, anisol or benzyl alcohol. It started to shrink at 192° and melted at 212°. The compound was prepared for analysis by washing well with cold water, then several times with hot benzene. It was soluble with a yellow color in dilute sodium hydroxide.

Calc. for $C_{14}H_{10}O_6$: C, 61.3; H, 3.6. Found: C, 60.9; H, 3.8.

If the hydroquinone was added to the oxalyl chloride pyridine compound at room temperature, and the mixture allowed to warm up from the heat of reaction, then a mixture of compounds resulted from which one could be obtained by the action of glacial acetic acid. This crystallized in white needles from glacial acetic acid and melted at 226°. The analysis agreed well for the monoacetate of di-*p*-oxyphenyl ether. As the production of this compound was rather uncertain, and as we obtained but poor yields of it, we have not studied it further. Slightly soluble in ethyl and methyl alcohol, chloroform, ether, benzene.

Calc. for $C_{14}H_{12}O_4$: C, 68.8; H, 4.9. Found: C, 68.9; H, 4.7.

CAMBRIDGE, MASS.

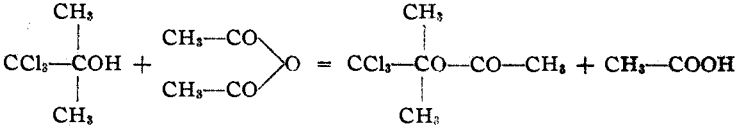
[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PARKE, DAVIS & CO.]

MONO-ACETYL-TRI-CHLOROTERTIARY-BUTYL-ALCOHOL. (ACETYL CHLORETONE.)

BY T. B. ALDRICH.

Received September 13, 1915.

When trichlorotertiary-butyl-alcohol (presumably tri-bromotertiary-butyl-alcohol acts in the same way) is acetylated in the usual manner with acetic anhydride and anhydrous sodium acetate, an acetyl compound is formed according to the following equation:



[1] *Ber.*, **35**, 3443 (1902).

Preparation.—One (1) part of chloretone was boiled with two (2) parts of acetic anhydride and one (1) part of anhydrous sodium acetate for two hours, using a reflux condenser. The solution, after cooling and diluting with water, was neutralized with sodium carbonate and subjected to steam distillation, the acetyl derivative passing over with the steam in the form of an oil that was practically colorless. The oil was collected with ether, the ethereal solution washed with water, then dried with calcium chloride, and finally filtered through a dry filter into a tared vessel. After evaporating the ether the residual oil gave, in one instance, a yield of about 80%. Slight decomposition took place when the oil was distilled at ordinary temperature; however, the greater part went over between 180–190° as a nearly colorless oil. When distilled in partial vacuum at 246 mm. the substance boiled fairly constant without any apparent decomposition at 145–146° and gave a yield of 85% of the amount started with. Chloretone under the same conditions (pressure, etc.) boils at 134–136°.

Combustion and chlorine determinations were made with a product, boiling at 151–153° under 250 mm. pressure. The bulb for holding the liquid for analysis was weighed empty, then warmed, and the neck of the bulb which had been drawn to a fine tube immersed in the acetyl chloretone. When, on cooling, sufficient oil had entered the bulb, it was reweighed.

The analytical results for carbon were somewhat lower and for chlorine somewhat higher than the calculated values, indicating the presence of some unchanged chloretone. This was verified by the results of the purification treatment.

In order to remove traces of chloretone, the acetyl compound already analyzed was heated on the steam bath for 20 min. with 100 cc. of a 10% NaOH solution in order to decompose the chloretone present. The acetyl derivative, which was unaffected by this treatment, was then collected with ether, washed, dried, and distilled in the usual manner under reduced pressure. The substance distilled at 151–152° under a pressure of 237 mm. The following chlorine determination (Carius) is sufficient to show that this compound is practically pure.

0.3831 g. gave 0.7535 g. AgCl or 0.1864 g. Cl.
Calc. for $C_6H_9O_2Cl_3$: 48.63%. Found: 48.65%.

Three cc. of the acetyl compound were placed in a pressure tube with 10 cc. of H_2O and heated for 3 hours at 160°. On opening the tube there was no apparent change. On heating the resealed tube for 3 hours at 250° complete decomposition of the substance took place, and on opening the tube there was considerable pressure. The substance was in part carbonized but there was no evidence of chloretone, the reaction of the liquid was acid and $AgNO_3$ gave a precipitate soluble in NH_4OH.

Two cc. of the acetyl compound were placed in a sealed tube with 25 cc. H_2O and heated to 160° for 8 hours. On opening the tube, there was considerable pressure, and a reddish brown oil was noticed ($^1/_2$ cc.) at the bottom of the tube, the supernatant liquid being slightly yellow. Its reaction was strongly acid and $AgNO_3$ gave a voluminous precipitate soluble in NH_4OH.

When boiled with water for a long time (108 hours), using a reflux condenser, some crystals resembling chloretone were observed in the condenser and neck of the flask (that is, on standing overnight). These were collected on a filter, dissolved in dilute alcohol and recrystallized. White needles; taste and smell like chloretone. M. p. 78°.

When acetyl chloretone is boiled with water to which H_2SO_4 has been added, the saponification takes place much more rapidly. Boiling 7 hours is sufficient to obtain considerable chloretone in the condenser tube.

Although saponification takes place slowly by boiling with water, or water and dilute acids, it is extremely interesting to note that saponification takes place very rapidly when the ester is boiled with an excess (three or four times its volume) of *concentrated* nitric acid. Indeed, after boiling only a few minutes a large amount of chloretone may be thrown out of the acid solution in a crystalline form by the addition of water.

The solubilities of the acetyl ester are practically the same as those of chloretone. It dissolves very readily in alcohol, acetone, ether, chloroform, benzene, etc., and is *practically insoluble* in water, even less soluble than chloretone. (Upon placing 0.5 g. in 100 cc. measuring flasks and adding water to mark, very little, if any, passed into solution after shaking occasionally for several days.)

It is volatile, though less so, than chloretone.

(1) 1 cc. was placed on watch glass and allowed to stand at room temperature; at the end of 14 hours $^1/_2$ had evaporated.

(2) 1 cc. was placed in an incubator at 37°; at the end of 14 hours it had evaporated completely.

Acetyl chloretone has anesthetic properties similar to chloretone and brometone; but, since it is so slightly soluble in water, its effect does not appear for several hours, and therefore it cannot be used to advantage as a substitute for chloretone for inducing general anesthesia in animal experiments. On account of its more agreeable odor, it might be used in some instances to advantage in place of chloretone. The toxicity of the acetyl ester, when introduced subcutaneously into guinea pigs, is slightly less than that of chloretone; its bactericidal efficiency was not tested.

It is generally accepted that the esters of the tertiary alcohols, on

heating alone above their boiling point in a sealed tube, are decomposed into acids and unsaturated hydrocarbons,[1] and we might expect a similar behavior in the case of acetyl-trichloro-tertiary-butyl-alcohol when heated similarly. The decomposition products of acetyl chloretone when heated *alone* were not determined, but with water or acids it gave rise, in part as far as could be observed, to chloretone without the above decomposition.

DETROIT, MICH.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, NO. 255.]

THE SYNTHESIS OF CERTAIN SUBSTITUTED SYRINGIC ACIDS.

BY MARSTON TAYLOR BOGERT AND EDWARD PLAUT.[2]

Received October 14, 1915,

Introductory.

Over a century ago, Braconnot[3] undertook an examination of various plants with particular reference to the acids they contained. Among the plants studied was the common lilac (*Syringa vulgaris*), and he called attention to the presence therein of a bitter substance, precipitable by basic lead acetate, the nature of which was not determined.

Since this early research, various chemists have made the lilac the subject of their investigations. In 1823, Robinet and Petroz[4] examined the seeds and capsules, and found therein a saccharin principle, later shown to be mannite,[5] and a bitter principle; but failed to isolate the latter in sufficient amount or purity to determine its nature.

Fifteen years later, Favrot[6] recovered an oil from the flowers.

In 1841, Bernays[7] obtained from the bark, and also from the leaves and green twigs, a crystalline substance which he believed to be analogous to salicin and phloridzin and therefore termed "syringin." At about the same time, Meillet[8] reported the discovery, in the leaves and green seed capsules, of a crystalline substance which he designated "lilacine." Bernays' article appeared in abstract in Liebig's Annalen[9] under the

[1] Lassar-Cohn, "Arbeits methoden," 3d. ed., p. 1152.

[2] The experimental work upon which this paper is based was submitted by Mr. Edward Plaut in partial fulfilment of the requirements for the degree of Doctor of Philosophy under the Faculty of Pure Science of Columbia University.

[3] *Ann. chim. phys.*, 70, 281–5 (1809).

[4] *J. Pharm.*, 9, 474 (1823); 10, 139–57 (1824).

[5] Ludwig, *Archiv. Pharm.*, [2] 91, 289–96 (1857); Kromayer, *Ibid.*, 109, 18, 216 (1862).

[6] *J. chim. med.*, 14, 212 (1838).

[7] Buchner's *Repert. d. Pharm.*, [2] 24, 349 (1841); *J. pharm. chim.*, [3] 1, 27 (1842).

[8] *J. pharm. chim.*, [3] 1, 25 (1842).

[9] *Ann.*, 40, 320 (1841).