tained by subtracting the amount of HR_2PO_4 plus H_3PO_4 from the strong acid in the first titration.

The amount of pyrophosphate present was determined by Bell's technique using zinc salts.[7]

Glycidyl trimethylacetate. GTMA was prepared from trimethylacetic acid and epichlorohydrin according to the technique described in U. S. Patent **2,524,432.** Distilled GTMA was collected between 90.0 and 91.5° at 24 mm. in 81% yield, $n_D^{25} = 1.4219$.

2-Isobutyl-2-methyl-4-trimethylacetoxymethyl-1,3-dioxolane. An equimolar mixture of 85% phosphoric acid (79.1 g., 0.70 mole) and GTMA (110 g., 0.70 mole) was stirred for 1 hr. at 60° with a 20-fold mole excess of MIBK (2100 g.). Phosphoric acid and phosphate esters were removed from the reaction mixture by extraction with water in a separatory funnel. The organic layer was dried over anhydrous calcium sulfate and fractionated in a 30 cm. × 6 mm. spinning band column under reduced pressure. IMTD was obtained in 63% yield (112 g.). The product boiled at 120°/7 mm., and had a density of 0.9615 at 25° and an $n_D^{25} = 1.4305$.

Anal. Calcd. for $C_{14}H_{26}O_4$: C, 65.08; H, 10.15. Found: C, 65.35, 65.31; H, 10.14, 10.28.

The structure of IMTD was verified by mild acid hydrolysis to glycerol, trimethylacetic acid, and MIBK.

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Reactions of Zirconium Tetrachloride with Acetone

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The metal alkoxides have been studied extensively in recent years for the interesting data which they provide on stereochemical[1] and other fundamental chemical behavior,[2] as well as for their potential industrial applications, as in lacquers[3] and as catalysts.[4] Numerous zirconium alkoxides have been prepared, particularly by Wardlaw, Bradley, and their associates, and their work in this area has been summarized in a recent book.[5]

Acetone in its enol form is an alcohol, and the replacement of its hydroxyl hydrogen by metal should give an alkoxide of the unsaturated alcohol, isopropenol. Only scant attention has been given until the present time to the preparation of zirconium derivatives of acetone or other ketones, and little has been known about them beyond the findings of Jantsch[6] that an addition compound of zirconium tetrachloride and acetone forms at temperatures below about 0°, and that hydrogen chloride is liberated from this addition compound when it is allowed to warm up to somewhat above that temperature.

More recently, we have undertaken a study of the reactions of zirconium tetrachloride with acetone, as a result of the observation by one of us (W. B. B.) of the formation of colored, pungent, and resinous substances when zirconium tetrachloride solution in acetone is allowed to stand for considerable periods of time. The present paper deals with the preparation and isolation of some of the products of reaction of zirconium tetrachloride and acetone.

EXPERIMENTAL

Reagents. The zirconium tetrachloride used was resublimed from the commercial product; it contained the usual two parts hafnium per 100 parts total metal. Since there is no known reaction in which hafnium behaves qualitatively in a different manner from zirconium, the presence of the hafnium was ignored except for the use of the value 92.25 for the effective atomic weight of zirconium, rather than the standard value of 91.22. The sodium metal and the solvent used were the C.P. grades of commerce. The acetone was treated with a small amount of alkaline potassium permanganate solution to destroy alcohols, and subsequently distilled over anhydrous potassium carbonate and again over anhydrous calcium sulfate.

Zirconium tetrachloride–acetone addition compound. A dispersion of 11.7 g. (0.05 mole) of zirconium tetrachloride in 200 ml. of carbon tetrachloride was prepared at room temperature and then cooled in an ice and salt bath to −5° and held at this temperature. To the stirred suspension, 25 ml. (0.34 mole) of previously chilled acetone was added dropwise, over an hour's time. The zirconium tetrachloride appeared to dissolve, and a new white precipitate formed immediately. The stirring was continued for 2 hr. after the addition of the acetone, and the slurry was then filtered rapidly and the precipitate was washed with chilled acetone. The filter cake was finally dried under vacuum at −5°, and sealed into glass tubes for storage.

Analysis of the product indicated it to be zirconium tetrachloride monoacetonate.

Anal. Calcd. for $ZrCl_4 \cdot CH_3COCH_3$: Zr, 31.6; Cl, 48.5; C, 12.3; H, 2.1%. Found: Zr, 31.8; Cl, 47.8; C, 12.1; H, 1.9%.

Trichlorozirconium isopropenoxide. A dispersion of 11.7 g. of zirconium tetrachloride in 200 ml. of carbon tetrachloride was prepared at room temperature, and 100 ml. of acetone was added dropwise. Hydrogen chloride was evolved during the addition and for some time following. The pale yellow solution was filtered, avoiding contact with the atmosphere, to remove traces of insolubles derived from the zirconium tetrachloride. The filtrate was mixed with 100 ml. of benzene and refluxed. Hydrogen chloride continued to be evolved slowly for several hours, and a pale brown solid formed. This was filtered off and washed with acetone, then dried under vacuum.

The observations made during the experiment suggest that initially a carbon tetrachloride- and benzene-soluble trichlorozirconium isopropenoxide, containing acetone of solvation, was formed, but on refluxing acetone was split

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(1) D. C. Bradley, R. C. Mehrotra, and W. Wardlaw, *J. Chem. Soc.*, 5020 (1952).

(2) D. C. Bradley, F. M. Abd-el-Halim, R. C. Mehrotra, and W. Wardlaw, *J. Chem. Soc.*, 4960 (1952).

(3) I. C. Kraitzer, F. K. McTaggart, and W. Winter, *The Preparation and Utilization of Esters of Ortho Titanic Acid*, Council for Scientific and Industrial Research, Commonwealth of Australia, Serial No. 64. December, 1947.

(4) J. R. Caldwell and J. W. Wellman, U.S. Patent **2,727,881,** Dec. 20, 1955.

(5) Blumenthal, W. B., *The Chemical Behavior of Zirconium*, Van Nostrand, 1958, pp. 352–62.

(6) G. Jantsch, *J. prakt. Chem.*, **115,** 7–8 (1927).

off from the complex and benzene-insoluble trichlorozirconium isopropenoxide, was formed.

Anal. Calcd. for $Cl_3Zr(CH_2COCH_3)$: Zr, 36.1; Cl, 41.6; C, 14.1; H, 2.0%. Found: Zr, 35.9; Cl, 41.4; C, 13.7; H, 2.2%.

Infrared spectra of the zirconium tetrachloride monoacetonate and the trichlorozirconium isopropenoxide substantiated the chemical evidence for change from an addition product to an unsaturated alkoxide, by indicating disappearance of a carbonyl group, and the appearance of a terminal double bond.

During two preparations of trichlorozirconium isopropenoxide, the hydrogen chloride which was evolved was passed into an excess of $0.5N$ sodium hydroxide solution, and at the end of the procedure the excess of alkali back-titrated with standard hydrochloric acid. The titers for the evolved hydrogen chloride were equivalent to 1.1 and 1.2 moles of HCl per mole of zirconium compound, respectively. This is regarded as in reasonable agreement with the amount of hydrogen chloride that would be expected to be liberated, particularly in view of the fact that any water formed in the system would tend to increase the amount.

In a preparation similar to the above, using methyl isopropyl ketone in place of acetone, an analogous product was formed of composition $Cl_3Zr(CH_2COC_3H_7)$, mol. wt. 283.7.

Anal. Calcd. for $Cl_3Zr(CH_2COC_3H_7)$: Zr 32.5: Cl 37.5. Found: Zr 32.8: Cl 37.0.

Chlorozirconium polyisopropenoxides. A suspension of 12 g. of zirconium tetrachloride in 200 ml. of benzene was prepared at room temperature, and 100 ml. (a large excess) of acetone was added, dropwise. The zirconium tetrachloride was dissolved, presumably as solvated trichlorozirconium isopropenoxide. The solution was filtered to remove traces of insoluble matter. Anhydrous ammonia gas was passed into the filtrate. (In the preparation of zirconium alkoxide from alkanols, ammonia increases the number of chlorine atoms displaced from the zirconium atom by alkoxide groups.) When the exothermic reaction had ceased, the solution had become reddish brown and a precipitate consisting of ammonium chloride and some unidentified zirconium hydrolyzate had precipitated.

The mixture was distilled, and the following compounds were identified by the indicated physical properties: mesityl oxide, $(CH_3)_2{:}CHCOCH_3$, b.p. 131°, characteristic odor; diacetone alcohol, $HOC(CH_3)_2CH_2COCH_3$, b.p. 118°; triacetone alcohol, $HOC(CH_3)_2CH_2COCH_2C(CH_3)_2OH$, m.p. 56–57°, m.p. of its phenylhydrazone 171–172°; 2,2,6,6-tetramethyltetrahydro-1,4-pyrone, b.p. 70°, characteristic camphorlike odor; and phorone, $(CH_3)_2C{:}CHCOCH{:}C(CH_3)_2$, m.p. 28°, b.p. 199°.

The formation of these derivatives of acetone was accompanied by the splitting out of water. This converted the zirconium tetrachloride to zirconyl chloride and possibly other hydrolysis products. It was not feasible to isolate organic compounds containing zirconium under these conditions.

Properties of products. A solution of zirconium tetrachloride in acetone was observed to change from colorless to reddish brown when allowed to stand for a period of days at room temperature. The changes were accelerated by the addition of hydrogen chloride to the solution. Fractional distillation revealed the presence of mesityl oxide and phorone. Water must therefore have been split off, with consequent hydrolysis of zirconium tetrachloride and of any chlorozirconium isopropenoxide which formed. It is apparent from this that chlorozirconium isopropenoxide must be prepared by fairly rapid procedures to minimize the superposition of hydrolysis upon other reactions.

When trichlorozirconium isopropenoxide was added to water, it reacted vigorously with formation of zirconyl chloride, hydrogen chloride, and acetone. The latter was positively identified by the preparation of its phenylhydrazone. A dispersion of trichlorozirconium isopropenoxide in carbon tetrachloride was observed visually (by disappearance of color) to absorb bromine. Its action on chlorine appeared to be similar, but the visual observation of this was not as reliable. Presumably, the isopropenoxide radical was converted to chloropropoxide or dichloropropoxide.

CONCLUSIONS

Zirconium tetrachloride reacts with acetone at −5° to form an addition product of composition $ZrCl_4 \cdot CH_3COCH_3$. At room temperature, the same reagents form trichlorozirconium isopropenoxide. Conditions for isolating both compounds have been established. The latter compound appears to form first as a benzene-soluble compound containing acetone of solvation, and to precipitate during refluxing as the unsolvated compound. Trichlorozirconium isopropenoxide is stable in the absence of moisture, but is readily hydrolyzed to zirconyl chloride and acetone.

Zirconium tetrachloride and its reaction products with acetone tend to promote the condensation of acetone with the splitting out of water. This militates against the formation of di- or polyisopropenoxides, since when these form the ligands tend to combine with one another, and to decompose the zirconium isopropenoxide structures by hydrolysis.

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2-Amino-2-carboxyethanesulfonamide

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L-Cysteic acid (2-amino-2-carboxyethanesulfonic acid) has been studied in several biological systems as an antagonist of aspartic acid.[1] The relationship between the antagonist and the natural metabolite is one in which the ω-carboxyl group of aspartic is replaced by the sulfonic acid grouping in the analog. Since a sulfonamide group is also similar structurally to a carboxamide group, the sulfonamide derivative of cysteic acid is of interest as a possible antagonist of asparagine. Accordingly, the sulfonamide derivative of cysteic acid, 2-amino-2-carboxyethanesulfonamide, was prepared for biological studies.

As indicated in the accompanying equations, di-*N*-carbobenzoxycystine benzyl ester (I) was converted directly to the sulfonyl chloride derivative II in one step. When the latter derivative was treated with aqueous ammonium hydroxide the major product isolated was the diamide V; however, treatment of II with ammonia dissolved in benzene under anhydrous conditions produced the

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[1] For general references see: W. Shive and C. G. Skinner, *Ann. Rev. Biochem.*, **27**, 643 (1958).