

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

Anal. Calcd. for $\text{Cl}_3\text{Zr}(\text{CH}_2\text{COCH}_3)$: 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 monoacetate 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 0.5*N* 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 $\text{Cl}_3\text{Zr}(\text{CH}_2\text{COC}_3\text{H}_7)$, mol. wt. 283.7.

Anal. Calcd. for $\text{Cl}_3\text{Zr}(\text{CH}_2\text{COC}_3\text{H}_7)$: 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, $(\text{CH}_3)_2\text{CHCOCH}_3$, b.p. 131°, characteristic odor; diacetone alcohol, $\text{HOC}(\text{CH}_3)_2\text{CH}_2\text{COCH}_3$, b.p. 118°; triacetone alcohol, $\text{HOC}(\text{CH}_3)_2\text{CH}_2\text{COCH}_2\text{C}(\text{CH}_3)_2\text{OH}$, 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, $(\text{CH}_3)_2\text{C}:\text{CHCOCH}:\text{C}(\text{CH}_3)_2$, 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 $\text{ZrCl}_4 \cdot \text{CH}_3\text{COCH}_3$. 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*-carbonylcystine 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

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

Anal. Calcd. for $C_8H_8N_2O_4S$: C, 21.42; H, 4.79; N, 16.67. Found: C, 21.20; H, 4.95; N, 16.38.

R_f value in lutidine:pyridine:water (3:3:4) was 0.51; ninhydrin gave a yellow spot which turned purple on standing.

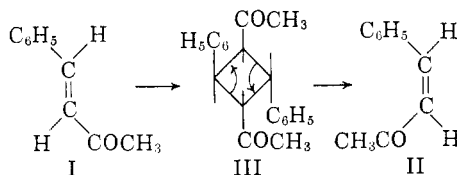
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Photochemical Isomerization of *trans*-Benzalacetone

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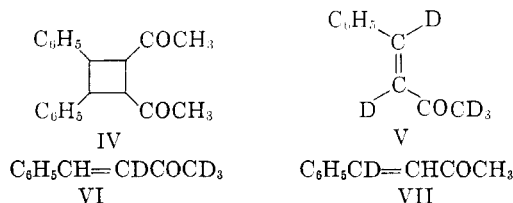
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Investigations of the photochemical isomerization of solutions of *cis*- and *trans*-ethylene derivatives¹⁻³ to have indicated that isomerization occurs *via* an excited singlet or triplet state which collapses to form both isomers. However, the observations that certain photodimers may be formed by irradiation of substituted ethylenes in the solid state but not in solution^{4,5} raised the question as to whether certain head-to-tail photodimers might be intermediates in the photochemical isomerization of substituted ethylenes. For example, a possible course for the isomerization of *trans*-benzalacetone (I) to the *cis* isomer (II) is represented in the accompanying equation.



The irradiation of an ether solution of *trans*-benzalacetone (I) with the light from a low-pressure mercury arc resulted in partial conversion of the *trans* isomer I to both the *cis* isomer (II)⁶⁻⁸ and to a high-boiling liquid which absorbs in the infrared at 1715 cm^{-1} as would be expected of the various stereoisomers of the photodimer III and as well as the corresponding cyclobutane derivatives in which the benzalacetone moieties have dimerized in a head-to-head fashion such as IV.⁹ The nature of this

high-boiling product, presumably a mixture of isomers, is still under investigation. In order to explore the possibility that the photochemical



isomerization of the *trans*-ketone I to the *cis*-ketone (II) involves an intermediate such as III, an equimolar mixture of the *trans*-ketone (I) and the pentadeutero-*trans*-ketone (V) was irradiated as previously described. The *cis*- and *trans*-ketones obtained from this irradiation mixture were examined in a mass spectrometer to determine if the partially deuterated ketones (VI and VII) were present as would be required if the photochemical isomerization involved an intermediate such as III. The results of this analysis indicated that less than 3% of the ketones VI and VII could have been formed and, consequently, that any head-to-tail photodimer such as III formed in the irradiation was not reconverted to monomer in the reaction mixture.

EXPERIMENTAL¹⁰

trans-Benzalacetone- d_5 (V). Benzaldehyde- d_1 , b.p. 85° (40 mm.), n_D^{20} 1.5377 (lit.¹¹ b.p. 178 – 179°), was prepared as previously described.¹¹ The mass spectrum of the product indicated that more than 98% of the material was benzaldehyde- d_1 . Acetone- d_6 was prepared by a series of eight equilibrations of a 0.5 mol. sample of acetone with 2 mol. samples of deuterium oxide containing 0.02 mol. of potassium carbonate. The mass spectrum of the product indicated the presence of 76.03 mol.-% acetone- d_6 , 21.03 mol.-% acetone- d_5 , 2.63 mol.-% acetone- d_4 and 0.25 mol.-% acetone- d_3 .

To a solution of 10.5 g. (0.098 mol.) of benzaldehyde- d_1 , and 10 ml. of deuterium oxide in 17 g. (0.27 mol.) of acetone- d_6 was added, dropwise and with stirring, a solution of sodium deuterioxide prepared from 0.2 g. (0.087 gram-atom) of sodium and 5 ml. of deuterium oxide. The resulting solution was stirred at room temperature for 100 min. and then diluted with a solution prepared from 1.6 g. (0.012 mol.) of phosphorus trichloride and 20 ml. of deuterium oxide. The product, extracted with three portions of benzene, was dried over magnesium sulfate and distilled under reduced pressure. The ketone, collected at 141 – 145° (17 mm.), amounted to 10.35 g. (70%). The gas chromatogram of the product exhibits a peak with essentially the same retention time as *trans*-benzalacetone and no peak corresponding in retention time to *cis*-benzalacetone. The infrared spectrum¹² has a

(9) A very small amount of a crystalline photodimer, m.p. 142 – 143° , has been obtained from benzalacetone by A. Butenandt, L. Karlson-Poschmann, G. Failer, U. Schiedt, and E. Biekert, *Ann.*, **575**, 123 (1951). This photodimer was assigned the structure IV.

(10) The infrared spectra were determined with a Baird, Model B, or a Perkin-Elmer, Model 21, double beam infrared recording spectrophotometer fitted with a sodium chloride prism. The gas chromatograms were obtained with an 8 mm. \times 215 cm. column packed with silicone oil on 50–80 mesh ground firebrick.

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- (3) For a discussion of the photochemical isomerization of azobenzene, see G. Zimmerman, L. Y. Chow, and U. J. Paik, *J. Am. Chem. Soc.*, **80**, 3528 (1958).
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