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

Anal. Caled. for Cl₃Zr(CH₂COCH₃): 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 backtitrated 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. Caled. 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, $(CH_3)_2$: CHCOCH₃, b.p. 131°, characteristic odor; diacetone alcohol, HOC(CH₃)_2CH₂COCH₃, b.p. 118°; triacetone alcohol, HOC(CH₃)_2CH₂COCH₂C(CH₃)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, $(CH_3)_2$ C: CHCOCH: C(CH₄)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.

TITANIUM ALLOY MFG. DIVISION NATIONAL LEAD CO. BOX C, BRIDGE STATION NIAGARA FALLS, N. Y.

2-Amino-2-carboxyethanesulfonamide

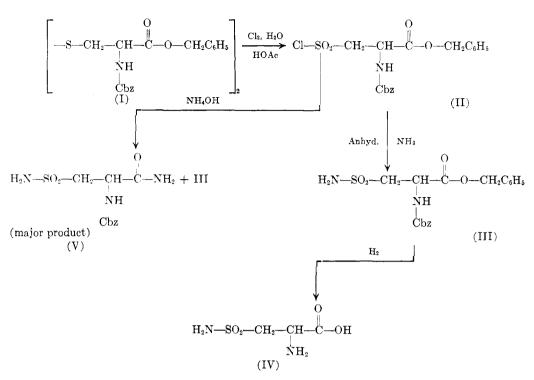
Donald L. Ross, Charles G. Skinner, and William Shive

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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

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



sulfonamide derivative III without effecting ammonolysis of the ester grouping. Hydrogenolysis of the intermediate III gave the desired amino acid analog, 2-amino-2-carboxyethanesulfonamide (IV).

2-Amino-2-carboxyethanesulfonamide (IV) is inhibitory toward *Escherchia coli* 9723 at a level of about 200 $\gamma/\text{ml.}$; however, it is not reversed by either asparagine or aspartic acid.

EXPERIMENTAL²

Di-N-carbobenzoxy-L-cystine dibenzyl ester. Di-N-carbobenzoxy-L-cystine was prepared by the method of du Vigneaud and Miller³, m.p. 115–117° (reported m.p. 113– 115°). A solution of 13 g. of di-N-carbobenzoxy-L-cystine, 1 g. of p-toluenesulfonic acid, and 26 g. of benzyl alcohol in 300 ml. of benzene was heated to reflux, and the water which was formed through the ester formation was azeotropically removed using a Stark and Dean head. The resulting organic phase was washed with sodium bicarbonate and with water, dried over calcium sulfate, and finally taken to dryness in vacuo. The residue was crystallized from toluene-*n*hexane to yield 17 g. of product, m.p. 59–60°.

Anal. Caled. for $C_{36}H_{36}N_2O_8S_2$: C, 62.77; H, 5.27. Found: C, 62.58; H, 5.51.

2-Carbobenzoxy-2-carbobenzoxyaminoethanesulfonyl chloride.⁴ Chlorine was bubbled, at room temperature and atmospheric pressure, througn a solution of 9.0 g. of di-Ncarbobenzoxycystine dibenzyl ester, 0.94 ml. of water, and 100 ml. of glacial acetic acid for about 10 min. The reaction was taken to dryness *in vacuo*, and the resulting residue was taken up in ethanol and again reduced to dryness to remove the excess chlorine. The resulting solid residue was crystallized from ethanol to yield 5.2 g. of material, m.p. 98-99°.

Anal. Calcd. for $C_{18}H_{18}NO_6ClS$: C, 52.49; H, 4.40; N, 3.40. Found: C, 52.38; H, 4.46; N, 3.46.

2-Carbamyl-2-carbobenzoxyaminoethanesulfonamide. A mixture of 2.6 g. of 2-carbobenzoxy-2-carbobenzoxyaminoethanesulfonyl chloride in 200 ml. of dioxane-ammonium hydroxide (1:1) was allowed to stand in the refrigerator overnight. The resulting mixture was reduced to dryness *in* vacuo, and the resulture was crystallized from alcohol-water, m.p. 197-198°.

Anal. Calcd. for $C_{11}H_{16}N_3O_5S$: C, 43.84; H, 5.02; N, 13.95. Found: C, 44.19; H, 4.89; N, 14.06.

2-Carbobenzoxy-2-carbobenzoxyaminoethanesulfonamide. Anhydrous ammonia was bubbled through a cool solution of 3.5 g. of 2-carbobenzoxy-2-carbobenzoxyaminoethanesulfonyl chloride in 60 ml. of benzene for about 30 min. During the ammonia addition, a precipitate formed. The reaction mixture was taken to dryness *in vacuo*, and the excess ammonia was removed by the addition and evaporation of additional benzene. The residue was then taken up in a large volume of hot benzene and carefully filtered to remove the insoluble salts, after which, the cooled filtrate yielded 2.3 g. of precipitated organic material. The product was recrystallized from ethyl alcohol-water, and dried *in vacuo*, m.p. 125-126°.

Anal. Calcd. for $C_{18}H_{20}N_2O_6S$: C, 55.09; H, 5.14; N, 7.14. Found: C, 55.35; H, 5.35; N, 6.99.

2-Amino-2-carboxyethanesulfonamide. A solution of 3.0 g. of 2-carbobenzoxy-2-carbobenzoxyaminoethanesulfonamide in 60 ml. of 95% ethyl alcohol was treated with hydrogen at atmospheric pressure and room temperature in the presence of 500 mg. of palladium black catalyst for about 4 hr. The resulting nihydrin-positive solution was then filtered to remove the catalyst, and the filtrate was taken to drypess *in vacuo*. The residual material, which was highly soluble in water, was crystallized from alcohol-water to yield 500 mg. of crude product, m.p. 183–185°; recrystallized from water-methyl alcohol, m.p. 197–198° (dec.).

⁽²⁾ All melting points are uncorrected. The R_I values were determined by the ascending technique using the solvent systems indicated, and the resulting chromatograms were developed with ninhydrin reagent. The authors are indebted to Dr. J. M. Ravel for the microbiological studies, and to Miss Judith Morehead and Mr. A. G. Lane for the chemical analyses.

⁽³⁾ Biochemical Preparations, Vol. 2, E. G. Ball, ed., John Wiley and Sons, Inc., New York, 1952, p. 74.

⁽⁴⁾ Patterned after the procedure of S. W. Lee and G. Dougherty, J. Org. Chem., 5, 81 (1940).

Anal. Calcd. for C₃H₈N₂O₄S: 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 stand-

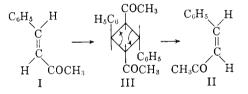
CLAYTON FOUNDATION BIOCHEMICAL INSTITUTE AND THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS AUSTIN, TEX.

Photochemical Isomerization of trans-Benzalacetone

HERBERT O. HOUSE

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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 transbenzalacetone (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 headto-head fashion such as IV.9 The nature of this

(1) G. M. Wyman, Chem. Revs., 55, 625 (1955).

(2) C. Reid, Quart. Revs. (London), 12, 205 (1958).

(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).

(4) A. Mustafa, Chem. Revs., 51, 1 (1952).

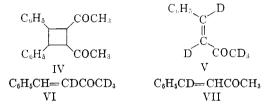
(5) D. B. Miller and H. Shechter, 133rd Meeting of the American Chemical Society, San Francisco, Calif., April 13-18, 1958, Abstracts of Papers, p. 79 N.
(6) E. Baroni and H. Seifert, Naturwissenschaften, 29,

560 (1941); Chem. Abstr., 37, 2358 (1943).

(7) G. van Bree, Bull. soc. chim. belges, 57, 71 (1948).

(8) R. E. Lutz, C. R. Bauer, and R. H. Jordan, J. Am. Chem. Soc., 72, 4300 (1950).

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 cisketone (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.), $n_{\rm D}^{29}$ 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-d₁. Acetone-d₅ 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-d₆, 21.03 mol.-% acetone-d₅, 2.63 mol.-% acetone-d₄ and 0.25 mol.-% acetone-d₃.

To a solution of 10.5 g. (0.098 mol.) of benzaldehyde-di, and 10 ml. of deuterium oxide in 17 g. (0.27 mol.) of acetone d_{δ} was added, dropwise and with stirring, a solution of sodium deuteroxide 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

(11) K. Wiberg, J. Am. Chem. Soc., 76, 5371 (1954).

⁽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. imes 215 cm. column packed with silicone oil on 50-80 mesh ground firebrick.