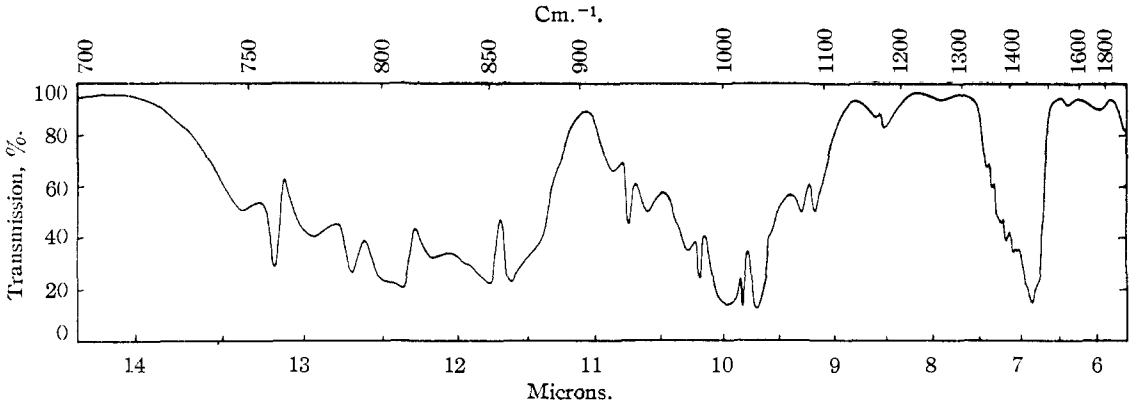

Fig. 1.—Infrared absorption spectrum of methylcyclopropane: pressure, 45.1 mm.; cell, 43 cm.

0.5 g. of propylene, 15.6 g. of propane, 1.1 g. of *i*-butane, and 14 g. of *i*-butylene.

The methylcyclopropane boiled constantly at 0° at 750 mm. rather than at 4–5°.[2] Its vapor pressure was 752 mm. at 0° (melting ice) and 128 mm. at −38.9° (melting mercury). Its infrared absorption spectrum, Fig. 1, was obtained with the instrument at the University of Oklahoma Research Institute.[3] Comparison with the already well-known spectra of *n*-butane, *i*-butane, 1-butene, *cis*- and *trans*-2-butenes, *i*-butylene, 1,2- and 1,3-butadienes, and ethylacetylene eliminated the possibility that the material on hand was any one of these or that it was seriously contaminated with any one of these. The boiling point, vapor pressure and infrared absorption spectrum of a different sample of methylcyclopropane, which was prepared from 1,3-dibromobutane by reduction with zinc in 80% ethanol (*cf.* ref. 2), agreed with those of the methylcyclopropane obtained from *i*-butyl chloride and propylsodium.

Acknowledgments.—The infrared absorption spectra were obtained by Miss Annette Herald and were interpreted by Mr. Vernon Thornton. Phillips Petroleum Company granted permission to publish the data.

(2) (a) Demjanow, *Ber.*, **28**, 21 (1895); (b) Lott and Christiansen, *J. Am. Pharm. Assoc.*, **27**, 126 (1938).

(3) Nielsen and Don C. Smith, *Ind. Eng. Chem., Anal. Ed.*, **15**, 609 (1943).

PHILLIPS PETROLEUM COMPANY
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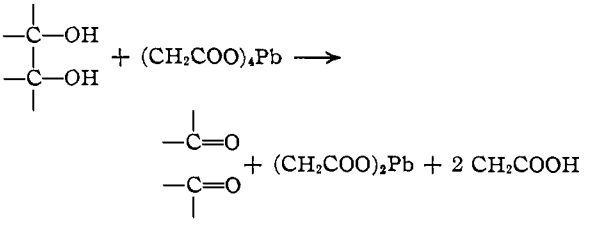
The Structure of Adenosine Triphosphate

BY GEORGE FAWAZ[1] AND KRIKOR SERAIDARIAN

The presence of a free α-glycol grouping in adenosine di- and triphosphate, a long debated question, has received support from the work of Lythgoe and Todd.[1a] These authors used Malparade's method of titration with periodate and found that each of the nucleotides consumed almost exactly one mole of the reagent.

We have utilized Criegee's method of titration with lead tetraacetate and came to the same conclusion. Thus, each of the following three compounds consumed one mole of lead tetraacetate: adenosine triphosphate[2] (sodium salt), muscle adenylic acid[3] and adenosine.[4] These results are to be expected if the compounds named contained one free α-glycol grouping according to the equation



Yeast adenylic acid,[5] on the other hand, was not oxidized by the reagent nor was adenosine itself altered.

Experimental

The reagent was a 0.152 *N* colorless solution of lead tetraacetate in glacial acetic acid, standardized according to Hockett and McClenahan.[6] In each case 0.05 millimole of the substance to be titrated was dissolved in 2 cc. of water, and 2 cc. of 0.152 *N* lead tetraacetate was added. After standing at room temperature for five minutes, 4 cc. of a solution containing 25 g. of sodium acetate and 2 g. of potassium iodide per 100 cc. was added and the liberated iodine was titrated with 0.1 *N* thiosulfate. In parallel control experiments it was found that the addition of 2 cc. of the reagent to 2 cc. of water followed after five minutes with 4 cc. of the acetate-iodide solution resulted in no measurable hydrolysis of the reagent.

The results are expressed in cc. of 0.1 *N* thiosulfate and represent the difference between the back titration of the above-mentioned control and that of the substance tested: adenosine triphosphate 0.98 cc.; muscle adenylic acid 1.00 cc.; adenosine 1.04 cc.; yeast adenylic acid 0.002 cc.; adenine 0.00 cc.

Baer, *et al.*,[7] were the first to utilize the lead tetraacetate method in aqueous medium. They recommended its use for preparative purposes in those cases where the rate of oxidation of the compound is greater than the rate of hydrolysis of the reagent. The results shown above, however, in particular the fact that there is no measurable hydrolysis of the reagent in 50% acetic acid

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(1a) Lythgoe and Todd, *Nature*, **155**, 695 (1945).

(2) Kerr, *J. Biol. Chem.*, **139**, 121 (1941).

(3) *Ibid.*, **139**, 131 (1941).

(4) Purchased from A. D. MacKay, New York City.

(5) Purchased from E. Machlett and Son, New York City, N. Y.

(6) Hockett and McClenahan, THIS JOURNAL, **61**, 1670 (1939).

(7) Baer, Grosheintz and Fischer, *ibid.*, **61**, 2607 (1939).

after five minutes, indicate that Criegee's method can be used for the quantitative determination of compounds that are soluble only in water. The advantages of this method are obvious: whereas the periodate oxidation requires many hours—forty-eight hours in the case of adenylic acid derivatives[1]—the oxidation with lead tetraacetate is complete within a few minutes.

Wormith and Rae[8] succeeded in titrating α-glycerophosphate in the presence of the β-isomer by means of lead tetraacetate in aqueous medium. These authors, however, allowed a period of six hours for the completion of the oxidation. In order to increase the solubility of the calcium and barium salts of these esters they had to add hydrochloric acid which they state decreases the oxidizing power of lead tetraacetate. The question arises as to whether the time of oxidation could not be appreciably shortened by the use of the soluble sodium salts.

(8) Wormith and Rae, THIS JOURNAL, **63**, 2523 (1941).

DEPARTMENT OF BIOLOGICAL CHEMISTRY
AMERICAN UNIVERSITY OF BEIRUT
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Ethyl β-Triethylsiloxycrotonate and Tetra-*n*-butylsilane

BY HENRY GILMAN AND RUSSELL N. CLARK

In connection with the preparation of some cyclic organosilicon compounds an examination was made of the reaction between sodioacetoacetic ester and triethylsilyl chloride to determine whether ethyl α-triethylsilylacetoacetate might be formed. However, the only product isolated was ethyl β-triethylsiloxycrotonate.

$$[CH_3COCHCO_2C_2H_5]^-[Na]^+ + (C_2H_5)_3SiCl \longrightarrow CH_3C(O\,Si(C_2H_5)_3)=CHCO_2C_2H_5 + NaCl$$

Hydrolysis of the siloxycrotonate by 10% hydrochloric acid gave acetone and hexaethyldisiloxane. Reaction of the siloxycrotonate with acetyl chloride yielded triethylsilyl chloride and ethyl β-acetoxycrotonate. It is possible that the procedure described by Hauser and co-workers[1] for C-alkylation with *t*-butyl alcohol by means of boron trifluoride might give some of the compound from triethylsilanol and acetoacetic ester.

In a study of group and bond refractions in organosilicon liquids, Sauer[2] has raised a question on a supposed tetra-*n*-butylsilane prepared[3] from ethyl silicate and *n*-butylmagnesium bromide. The molar refraction of that product is at variance with the value calculated for tetra-*n*-butylsilane and in agreement with that for tri-*n*-butylethoxysilane. We have prepared tetra-*n*-butyl-silane in excellent yields by reaction of *n*-butyllithium with ethyl silicate and with silicon tetrachloride. The compound prepared by these reactions[4] has a molar refraction in agreement with that for the R_4Si compound, and physical constants unlike those reported for the product from ethyl silicate and *n*-butylmagnesium bromide.

Experimental

Ethyl β-Triethylsiloxycrotonate.—Sodioacetoacetic ester was prepared[5] by adding 6.5 g. (0.05 mole) of ethyl acetoacetate in 30 cc. of dry toluene to 1.12 g. (0.05 g. atom) of sodium sand and 100 cc. of toluene. To the clear, stirred resulting solution was added 7.5 g. (0.05 mole) of triethylsilyl chloride[6] in 30 cc. of dry toluene, and the resulting mixture was heated between 80–100° for twelve hours. The mixture was filtered, the filtrate distilled free of solvent, and the residue fractionated to give 7.4 g. (61%) of compound distilling at 108–110° (6 mm.), $n^{20}D$ 1.4560, d^{20}_4 0.9590, MR_D 69.42 (calcd. MR_D, 69.12).

Anal. Calcd. for $C_{12}H_{24}O_3Si$: Si, 11.48. Found: Si, 11.54.

Reaction with 2,4-dinitrophenylhydrazine gave only the 2,4-dinitrophenylhydrazone of ethyl acetoacetate[7] (mixed m. p.).

A mixture of 2.44 g. (0.01 mole) of the siloxycrotonate in 50 cc. of 10% hydrochloric acid was refluxed for one-half hour. The cooled organic layer was separated, taken up in ether, dried, and fractionated to give hexaethyldisiloxane; MR_D 75.88 (calcd. MR_D 76.07). The aqueous layer was treated with benzaldehyde, and the product isolated was dibenzalacetone[8] (mixed m. p.).

A solution of 4.9 g. (0.02 mole) of the siloxycrotonate and 1.58 g. (0.02 mole) of freshly distilled acetyl chloride was heated for six hours at 135–150°. Fractional distillation of the product gave two compounds, one of which was triethylsilyl chloride.

Anal. Calcd. for $C_6H_{15}ClSi$: Si, 18.62. Found: Si, 18.85.

The other compound distilled at 206–209° (736 mm.); $n^{15}D$ 1.4466; d^{15}_4 1.0664. One-half of this product was refluxed for one hour with 10% hydrochloric acid, and the hydrolysate gave no test for acetylacetone. The other half was made basic with a sodium hydroxide solution and then treated with benzaldehyde to give dibenzalacetone. Acetone is an expected hydrolysis product of ethyl β-acetoxycrotonate.

Tetra-*n*-butylsilane.—To 17 g. (0.1 mole) of silicon tetrachloride in 100 cc. of ether was slowly added, in a nitrogen atmosphere, 0.41 mole of *n*-butyllithium[9] in 350 cc. of ether. The reaction flask was immersed in an ice-bath, and the rate of addition was such as to maintain a gentle reflux. Finally, the mixture was refluxed for one-half hour. Subsequent to hydrolysis of the cooled mixture, the ether layer was separated, and washed with concd. sulfuric acid to remove any silanol.[10] The ether layer was separated, washed with water, dried over

(1) Adams, Abramovitch and Hauser, THIS JOURNAL, **65**, 552 (1943).

(2) Sauer, *ibid.*, **68**, 954 (1946).

(3) Post and Hofrichter, *J. Org. Chem.*, **5**, 572 (1940); see, also, Tseng and Chao, *Science Repts. Natl. Univ. Peking*, **1** (No. 4), 21 (1936) [C. A., **31**, 655 (1937)].

(4) Gilman and Clark, THIS JOURNAL, **68**, 1675 (1946). We inadvertently omitted mention in this article of a patent which was reported in *C. A.* of this year by Fleming, U. S. Patent 2,386,452 [*C. A.*, **40**, 603 (1946)] on the preparation of some unsymmetrical silicon compounds by means of RLi compounds.

(5) Breslow, Yost, Walker and Hauser, *ibid.*, **66**, 1921 (1944).

(6) DiGiorgio, Strong, Sommer and Whitmore, *ibid.*, **68**, 1380 (1946).

(7) Huntress and Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 255.

(8) Huntress and Mulliken, *ibid.*, p. 374.

(9) Gilman, Zoellner and Selby, THIS JOURNAL, **55**, 1252 (1933); Gilman and Stuckwisch, *ibid.*, **65**, 1461 (1943); Gilman and Haubein, *ibid.*, **66**, 1515 (1944). This last reference describes the analytical procedure used.

(10) Friedel and Crafts, *Ann. chim. phys.*, **4**, 19 (1895).