[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

The Reaction of Cyclohexene with Phosphorus Pentasulfide

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Cyclohexene and phosphorus pentasulfide in a mole ratio of 20:1 react slowly at reflux temperature, with the liberation of hydrogen sulfide, to yield a crystalline product $(C_6H_9PS_2)_2$. Hydrolysis of this product gave Δ^2-cyclohexene phosphonic acid. This suggests that the structure of the product is a dimeric thio-anhydride of Δ^2-cyclohexene trithiophosphonic acid, $C_6H_9PS(SH)_2$.

The reaction of olefins and cycloölefins with phosphorus pentasulfide has been reported frequently in the patent literature.[2,3,4] The reactions were usually carried out with mole ratios of olefin to P_2S_5 of two or three to one and at temperatures of from 90 to 160°. The reaction occurs with or without the loss of hydrogen sulfide, depending upon the nature of the olefin and the reaction conditions. The products are described as resinous in character, and their structure has not been established.

The present work is a study of the reaction between cyclohexene and phosphorus pentasulfide. Hull[5] obtained an amber resin by refluxing cyclohexene with P_2S_5 for 25–30 hours in a mole ratio of 2:1. Hydrolysis of the product gave, in a 40% yield, a volatile oil consisting largely of cyclohexyl mercaptan. In our preliminary work cyclohexene and phosphorus pentasulfide in a mole ratio of 4:1 were refluxed until all of the sulfide had dissolved. Several hours were required for the completion of the reaction and hydrogen sulfide was continuously evolved. Removal of the unreacted cyclohexene left a dark, brittle resinous product. The resin was acidic and was readily hydrolyzed. Attempts to isolate individual products from it were unsuccessful.

Further work revealed, however, that by using a large excess of cyclohexene, for example, mole ratios of cyclohexene to phosphorus pentasulfide of 20:1, the reaction under the same conditions gave a crystalline product in yields of from 45 to 55%. This product was very hygroscopic and for this reason was difficult to purify and to keep in a state of purity. Analysis and molecular weight agree closely with the formula $(C_6H_9PS_2)_2$. Hydrolysis prevented the determination of a neutralization equivalent, but four equivalents of standard sodium hydroxide per mole were consumed in saponifying it. These facts suggest that the product is a dimeric thioanhydride of cyclohexenetrithiophosphonic acid $C_6H_9PS(SH)_2$. The intramolecular elimination of hydrogen sulfide from the hypothetical intermediate $(C_6H_9PS(SH))_2S$ would account for its formation.

Attempts to prepare stable crystalline derivatives in the form of amides, anilides and p-bromoanilides gave products which could not be purified because of instability. The anhydride upon refluxing with an excess of methyl alcohol for several days gave a product boiling at 133° (3.5 mm.) which was shown by analysis to have the formula $C_6H_9PS(OCH_3)(SCH_3)$.

Hydrolysis of the anhydride by boiling with water gave a cyclohexene phosphonic acid, $C_6H_9PO(OH)_2$, melting at 104–106°. The latter gave a dibromocyclohexanephosphonic acid, m.p. 195–195.5°, upon treatment with bromine and cyclohexanephosphonic acid by low pressure hydrogenation with Raney nickel. The melting point of the cyclohexanephosphonic acid was in agreement with that reported by Clayton and Jensen.[6]

The position of the double bond in the cyclohexenephosphonic acid was investigated by synthesis, by ozonolysis, and by decomposition of the dibromide. For the synthesis of Δ^1-cyclohexenephosphonic acid, the method of Conant and Coyne[7] for the preparation of unsaturated phosphonic acids was used. 1-Hydroxycyclohexanephosphonic acid, prepared from cyclohexanone and phosphorus trichloride, was dehydrated at a temperature of 195°. For the synthesis of Δ^2-cyclohexenephosphonic acid the method of Kosolapoff[8] for the preparation of n-alkylphosphonic acids was used. Δ^2-Bromocyclohexene was refluxed with sodium dibutyl phosphite in heptane and the resulting dibutyl ester hydrolyzed to the acid. Both methods, however, gave the same cyclohexenephosphonic acid. This acid, m.p. 133°, gave a dibromocyclohexanephosphonic acid, m.p. 162–163°, and was converted by hydrogenation to cyclohexanephosphonic acid. It was obviously an isomer of the cylohexenephosphonic acid previously described.

Since synthesis failed to establish the position of the double bond, ozonolysis was employed. The higher melting cyclohexenephosphonic acid was ozonolyzed oxidatively and gave a 67% yield of adipic acid. This establishes the Δ^1-structure for this acid.

Oxidative ozonolysis of the lower melting cyclohexene phosphonic acid gave glutaric acid in 38% yield, which supports the Δ^2-structure. This was established by converting its dibromide to Δ^2-cyclohexenol by way of the Δ^2-bromide intermediate. This conversion to a bromide is reported by Conant and Coyne[7] as characteristic of 2-bromophosphonic acids upon treatment with cold, concentrated sodium carbonate solution.

(1) Standard Oil Co. (Ohio) Fellow in Chemistry, Western Reserve University, 1946–1948.

(2) R. L. May, U. S. Patent 2,356,073, August 15, 1944.

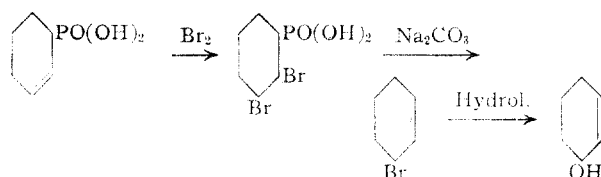(3) H. S. Angel, E. W. Fuller and H. G. Berger, U. S. Patent 2,381,377, August 7, 1945.

(4) C. M. Loane and J. W. Gaynor, U. S. Patent 2,316,078, April 6, 1943.

(5) C. M. Hull, U. S. Patent 2,351,763, June 20, 1944.

(6) J. O. Clayton and W. L. Jensen, THIS JOURNAL, 70, 3880 (1948).

(7) J. B. Conant and B. B. Coyne, ibid., 44, 2530 (1922).

(8) G. M. Kosolapoff, ibid., 67, 1180 (1945).

The Δ²-cyclohexenol was identified as a phenyl and also as an α-naphthylurethan.

The structure of this acid points to the crystalline product from cyclohexene and phosphorus pentasulfide as a dimeric thioanhydride of Δ²-cyclohexenetrithiophosphonic acid,
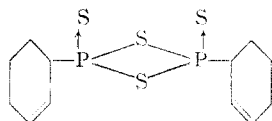
Experimental

Materials.—The phosphorus pentasulfide was a commercial grade purified by recrystallization from carbon disulfide in a continuous soxhlet extraction apparatus. It melted at 276–282°. The cyclohexene, Eastman Kodak Company, was fractionated and the fraction b.p. 81.8–82.0° (744 mm.), n^{25}D 1.4450, was used in this work.

Reaction of Cyclohexene with Phosphorus Pentasulfide; $(C_6H_9PS_2)_2$.—A mixture of 60 g. (0.27 mole) of phosphorus pentasulfide and 761 g. (9.27 moles) of cyclohexene was refluxed for 108 hours. Hydrogen sulfide was continuously evolved. Nineteen grams of unchanged phosphorus pentasulfide was filtered off, and the filtrate evaporated at room temperature until crystallization set in. After cooling in the ice-chest, the mixture was filtered. The yield of crystalline product was 38 g., 58% of theory, m.p. 113–115°. Crystallization from carbon disulfide raised the melting point to 118–120°. The product was almost colorless and hygroscopic; even brief exposure to the air lowered the fusion temperature appreciably.

Anal. Calcd. for $C_{12}H_{18}P_2S_4$: C, 40.89; H, 5.15; P, 17.58; S, 36.39; mol. wt., 352; sapn. equiv., 88. Found: C, 40.70; H, 5.17; P, 17.59; S, 36.33; mol. wt., 353; sapn. equiv., 87.

Reaction of $(C_6H_9PS_2)_2$ with Methanol; $C_6H_9PS(SCH_3)$ (OCH_3).—A mixture of the anhydride $(C_6H_9PS_2)_2$, 43.5 g. (0.123 mole), and absolute methanol, 236 g. (7.4 moles), was refluxed for 24 hours. Hydrogen sulfide and methyl mercaptan were evolved. Excess methanol was distilled off at atmospheric pressure and the residue fractionated *in vacuo* using a short Vigreux column. A fraction b.p. 133° (3.5 mm.), n^{25}D 1.5720, d^{25}_{25} 1.173, was collected in a yield of 15.8 g., 62%.

Anal. Calcd. for $C_8H_{15}PS_2O$: C, 43.22; H, 6.80; P, 13.94; S, 28.85. Found: C, 43.17; H, 7.10; P, 13.9; S, 28.7.

The product decolorized bromine in carbon tetrachloride and dissolved slowly in hot concentrated hydrochloric acid with evolution of methyl mercaptan.

Hydrolysis of $(C_6H_9PS_2)_2$; Δ²-Cyclohexenephosphonic Acid.—Forty-five grams (0.127 mole) of the anhydride $(C_6H_9PS_2)_2$ was dissolved in 400 cc. of hot water, and the solution was refluxed for three days, when evolution of hydrogen sulfide was no longer perceptible. A trace of resinous material was filtered off, the solution was evaporated to a volume of 150 cc. and continuously extracted with ether for 4 days. The ether extract was dried over anhydrous calcium sulfate, evaporated to a thick sirup, and allowed to crystallize in an open dish. The solid cake which formed in time was broken up and dried *in vacuo;* yield 32 g. (82.5%), m.p. 87–101°. Recrystallization from benzene raised the melting point to 104–106°.

Anal. Calcd. for $C_6H_{11}PO_3$: C, 44.45; H, 6.84; P, 19.11; neut. equiv., 162. Found: C, 44.44; H, 6.86; P, 19.2; neut. equiv. (chlorphenol red), 163.

The phosphonic acid is very soluble in water and in ether, moderately soluble in benzene, almost insoluble in petroleum ether.

Proof of Structure of Δ²-Cyclohexene Phosphonic Acid.

a. Hydrogenation.—A solution of 5.2 g. (0.038 mole) of the cyclohexenephosphonic acid, m.p. 102–106°, in 100 cc. of water was neutralized with sodium hydroxide and shaken for 24 hours at room temperature with 1 g. of Raney nickel under hydrogen at a pressure of 70 pounds per square inch. Consumption of hydrogen was approximately 0.03 mole. The catalyst was filtered off, the solution acidified with dilute sulfuric acid and extracted with ether. A yield of 3.7 g. (70%), m.p. 159–164°, was obtained. Upon recrystallization from ether, it melted at 164.5–166°. Clayton and Jensen,[6] since this work was done, have reported a melting point of 166–167° for cyclohexanephosphonic acid.

b. Ozonolysis.—A solution of 6.5 g. (0.04 mole) of the cyclohexenephosphonic acid in ethyl acetate was ozonized for 60 hours at room temperature. The solution was refluxed overnight with an excess of 30% hydrogen peroxide and evaporated to a dark sirup which failed to crystallize and was water-insoluble, apparently an ethyl ester. It was hydrolyzed by refluxing for 3 hours with dilute hydrochloric acid and evaporated to a sirup which crystallized readily. After recrystallization from benzene 2 g. of a colorless crystalline acid, m.p. 89–95°, was obtained. It did not depress the melting point of a sample of glutaric acid, m.p. 93–97°. The yield was 38%.

c. Decomposition of the Dibromide.—The dibromide was prepared as follows. Five grams (0.3 mole) of bromine in 50 cc. of carbon tetrachloride was added slowly to 5 g. (0.3 mole) of cyclohexene phosphonic acid, m.p. 102–106°, in 100 cc. of ether at 0°. After standing for a day at 0° the bromine color was nearly gone. Evaporation of the solvent gave 7.7 g. (77%) of crystalline dibromide, m.p. 181–190° with decomposition. It was recrystallized from ether and then melted at 195–195.5° with decomposition.

Anal. Calcd. for $C_6H_{11}Br_2PO_3$: C, 22.38; H, 3.44; neut. equiv., 322. Found: C, 22.39; H, 3.54; neut. equiv. (chlorphenol red), 318.

The dibromide was decomposed by the method of Conant and Coyne.[7] A solution of 1.91 g. (0.006 mole) of dibromocyclohexanephosphonic acid, m.p. 192–193°, in 50 cc. of a 25% solution of sodium carbonate rapidly became cloudy. After standing overnight, a layer of yellow oil collected on the surface in a yield of 0.37 g. after drying over anhydrous calcium sulfate. The product decolorized bromine. It was shown to be Δ²-cyclohexenol by formation of phenyland α-naphthylurethan from the isocyanates, m.p. 107–108° and 157–158°, respectively; Willstätter and Sonnenfeld[9] report 107° and 156°.

Δ¹-Cyclohexenephosphonic Acid. a. From Δ²-Bromocyclohexene.—Δ²-Bromocyclohexene was prepared by the action of N-bromosuccinimide on cyclohexane as reported by Ziegler.[10] A 74% yield of bromide, b.p. 90–92° (62 mm.), was obtained. It was identified by hydrolysis with 25% sodium carbonate to Δ²-cyclohexenol, which gave a phenylurethan, m.p. 107–108°, and an α-naphthylurethan, m.p. 157–158°, upon treatment with the respective isocyanates. The addition of the corresponding urethans described in the previous paragraph to each did not lower the melting point. The reaction of Δ²-bromocyclohexene with sodium dibutyl phosphite was carried out as follows. Sodium dibutyl phosphite was prepared *in situ* by the dropwise addition of 39.8 g. (0.2 mole) of dibutyl phosphite (courtesy of Monsanto Chemical Company) to 4.47 g. (0.2 mole) of sodium in 350 cc. of boiling heptane with stirring. All of the sodium dissolved within 12 hours. Δ²-Bromocyclohexene, 32.8 g. (0.2 mole) was then added dropwise over a period of eight hours and reflux continued for 13 hours. The precipitated sodium bromide was washed out with water and recovered by evaporation; 21.5 g. (0.2 mole) were obtained indicating complete reaction. After removing the solvent, the residue was distilled under reduced pressure. A fraction boiling at 143–147° (2 mm.) was collected; yield was 16.7 g. (30%). Hydrolysis of 15.5 g. (0.057 mole) by refluxing with concentrated hydrochloric acid gave on evaporation 7.6 g. (82%) of a crystalline acid, m.p. 110–126°. Recrystallization from ether raised the melting point to 132–133°.

Anal. Calcd. for $C_6H_{11}PO_3$: C, 44.45; H, 6.83; neut. equiv., 162. Found: C, 44.29; H, 7.12; neut. equiv., 162 (chlorphenol red).

(9) R. Willstätter and E. Sonnenfeld, *Ber.*, **46**, 2957 (1914).
(10) K. Ziegler, *et al.*, *Ann.*, **551**, 80 (1942).

The acid decolorized bromine water and dilute permanganate solution. Hydrogenation of the cyclohexenephosphonic acid by the method previously described for its isomer gave cyclohexanephosphonic acid, m.p. 164–165°, in practically quantitative yield. Bromination of the cyclohexenephosphonic acid with bromine in carbon tetrachloride gave an 80% yield of 1,2-dibromocyclohexanephosphonic acid, m.p. 160–161° with decomposition. Recrystallization from ether raised the melting point to 162–163°.

Anal. Calcd. for $C_6H_{11}Br_2PO_3$: C, 22.38; H, 3.44; neut. equiv., 322. Found: C, 22.3; H, 3.47; neut. equiv., 320 (chlorphenol red).

Ozonolysis.—A solution of 0.6 g. of cyclohexenephosphonic acid, m.p. 132–133°, in 90 cc. of reagent grade ethyl acetate was ozonized for 30 minutes at a rate of 8–12 millimoles of ozone per hour. Five grams of 30% hydrogen peroxide were added and the ethyl acetate distilled off under reduced pressure. The residue was refluxed overnight with 40 cc. of water and crystallized readily upon evaporation in an open dish; yield 0.36 g., m.p. 110–136°. Upon recrystallization from nitric acid, it melted at 148–150°. The addition of a sample of adipic acid, m.p. 149–151°, did not lower the melting point. Yield of adipic acid was 67%.

b. From 1-Hydroxycyclohexanephosphonic Acid.—1-Hydroxycyclohexanephosphonic acid was prepared from cyclohexanone by the method of Conant and Coyne.[7] Ninety-eight grams (1 mole) of cyclohexanone was added slowly with cooling and stirring to 154 g. (1.11 moles) of phosphorus trichloride in 243 g. of glacial acetic acid. After a short period the reaction became violent and required cooling in an ice-bath. The temperature of the mixture was held below 30° for 24 hours. It was then filtered and the filtrate poured into a liter of water and evaporated to hydrolyze the complex and remove acetic acid. The residue was treated with 500 cc. of water and again evaporated. The residue was light brown in color and on cooling set to a hard cake. Yield was 174 g. (86%), m.p. 170–181°. Recrystallization from alcohol gave a colorless crystalline product, m.p. 191–192°.

Anal. Calcd. for $C_6H_{13}PO_4$: C, 40.00; H, 7.27; neut. equiv., 180. Found: C, 40.1; H, 7.35; neut. equiv., 183 (chlorphenol red).

The 1-hydroxycyclohexanephosphonic acid was converted to Δ^1-cyclohexenephosphonic acid by thermal decomposition. The hydroxy acid, 15.9 g. (0.88 mole), was heated to 195° on an oil-bath for 25 minutes. A distillate, 3.03 g., consisting of water, cyclohexene and cyclohexanone, was collected. The residue was dissolved in hot water, and the solution clarified with charcoal. Continuous extraction of the solution with ether yielded 7.2 g. (50%) of a crystalline acid, m.p. 122–128°. Recrystallization from ether raised the melting point to 130.5–132°. The addition of the cyclohexene phosphonic acid prepared from Δ^2-bromocyclohexene to this acid did not lower its melting point.

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β,γ-Benzotropolone[1] and Related Compounds

By Gordon A. Nicholls[3] and D. Stanley Tarbell

Nitration of β,γ-benzotropolone methyl ether in acetic anhydride at low temperatures leads to four products: (a) the 2(or 3)-nitro compound, as shown by oxidation of its demethylated derivative to 4-nitrophthalic acid, (b) the α-nitro compound, (c) a hemihydrate of this compound, and (d) a nitro derivative, isomeric with the above, but of uncertain structure. Thus nitration of β,γ-benzotropolone methyl ether leads to substitution in the benzene ring, whereas with β,γ-benzotropolone itself substitution occurs in the tropolone ring. α-Nitro- and 2(or 3)-nitro-β,γ-benzotropolone were reduced catalytically to the corresponding amines. Unlike the monocyclic aminotropolones, α-amino-β,γ-benzotropolone failed to lead to a hydroxynaphthoic acid on treatment with nitrous acid; with acetic anhydride it formed an oxazole derivative. The infrared spectra of some β,γ-benzotropolones are discussed.

It has recently been established[4,5] that aminotropolones can be prepared from the corresponding nitro-, nitroso- and azotropolones. We are now able to record some of our results in connection with the preparation of two amino-β,γ-benzotropolones from the corresponding nitro-compounds.

(1) In the interests of uniformity and convenience, we have adopted the nomenclature used by English workers for tropolones, according to which the structure previously[2] referred to as 4,5-benzotropolone, is now called β,γ-benzotropolone, and is numbered as shown. The
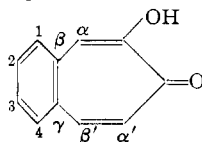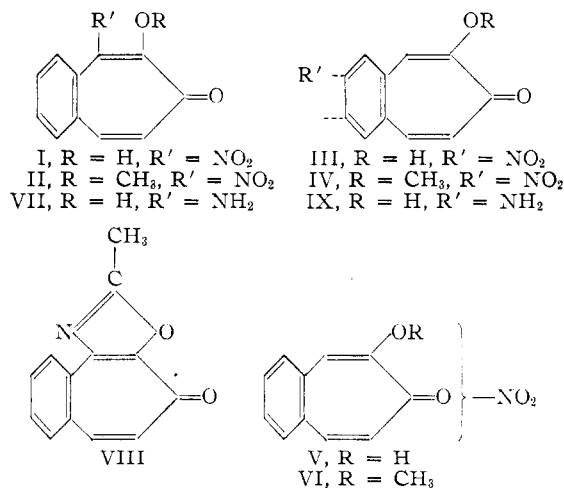

Ring Index name for β,γ-benzotropolone is 6-hydroxy-7H-cycloheptabenzene-7-one. We are greatly indebted to Drs. J. W. Cook, R. S. Cahn, A. M. Patterson and L. T. Capell for correspondence on this point.

(2) D. S. Tarbell and J. C. Bill, This Journal, **74**, 1234 (1952).

(3) Postdoctoral Fellow of the National Cancer Institute of the National Institutes of Health, Public Health Service, Federal Security Agency, 1950–1952.

(4) (a) T. Nozoe, *et al., Proc. Japan Acad.*, **26** [8], 24 (1950); **26** (9), 38, 45 (1950); **27** (1), 10, 18 (1951); **27** (4), 188, 193 (1951); **27** (8), 426 (1951); (b) T. Nozoe, S. Seto, S. Ebine and S. Ito, This Journal, **73**, 1895 (1951).

(5) (a) R. D. Haworth and J. D. Hobson, *J. Chem. Soc.*, 561 (1951); (b) R. D. Haworth and J. D. Jefferies, *ibid.*, 2067 (1951).

I, R = H, R' = NO₂
II, R = CH₃, R' = NO₂
VII, R = H, R' = NH₂

III, R = H, R' = NO₂
IV, R = CH₃, R' = NO₂
IX, R = H, R' = NH₂

VIII

V, R = H
VI, R = CH₃

In a previous paper[2] the nitration of β,γ-benzotropolone to give α-nitro-β,γ-benzotropolone (I) was described. This compound has now been converted to the methyl ether II which formed a 2,4-dinitrophenylhydrazone. In addition, the nitration of β,γ-benzotropolone methyl ether in acetic anhydride at low temperature has been investigated. The reaction appears to be complex and