43% yield from *m*-trifluoromethylphenol and ω-bromoundecylic acid. The compound boiled at 195–199° at 1 mm. and when recrystallized from Skellysolve B it melted at 42–43°.

Anal. Calcd. for neutral equivalent: 346. Found: 351.

Benzilidene-9,10-dihydroxystearic Acid.—Dry hydrogen chloride was passed into a solution of 24 g. (0.076 mole) of 9,10-dihydroxystearic acid and 9 g. (0.084 mole) of benzaldehyde in 300 cc. of dry benzene. The solution was refluxed and the water removed as formed. On distillation there was obtained 21 g. (68%) of product boiling at 240° at 0.1 mm.

Anal. Calcd. for $C_{25}H_{40}O_4$: C, 74.2; H, 9.9; neut. equiv., 405. Found: C, 74.0; H, 10.0; neut. equiv., 401.

o-Chlorobenzilidene-9,10-dihydroxystearic Acid.—This compound was prepared by the same procedure as above. From 75 g. (0.24 mole) of 9,10-dihydroxystearic acid and 35 g. (0.25 mole) of *o*-chlorobenzaldehyde there was obtained 63.7 g. (62%) of product boiling at 245–250 at 0.1 mm.

Anal. Calcd. for $C_{25}H_{39}ClO_4$: C, 68.4; H, 8.9; Cl, 8.1. Found: C, 68.8; H, 9.1; Cl, 7.7.

Dilauryl Mercaptal of 4-Aldehydophenoxyacetic Acid.—Dry hydrogen chloride was passed into a solution of 22 g. (0.12 mole) of 4-aldehydophenoxacetic acid and 50 g. (0.25 mole) of lauryl mercaptan in 250 cc. of dioxane. The solution was refluxed for one hour and then poured into ice water. The crystals were collected and after recrystallization from alcohol melted at 70–74°; yield, 41 g. (54%). An analytical sample recrystallized from Skellysolve B melted at 74–75°.

Anal. Calcd. for $C_{33}H_{58}O_3S_2$: C, 69.8; H, 10.3; neut. equiv., 566. Found: C, 69.7; H, 10.6; neut. equiv., 568.

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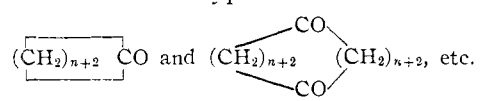
RECEIVED OCTOBER 7, 1946

COMMUNICATIONS TO THE EDITOR

A NEW SYNTHETIC METHOD FOR MANY-MEMBERED CARBON RINGS

Sir:

The recently described method for obtaining ketene dimers[1] made it seem likely that under conditions of high dilution an appropriate bifunctional ketene should undergo self-condensation to form macrocyclic diketenes readily convertible to many-membered carbocyclic ketones. Thus, a b.functional ketene such as O=C=CH—$(CH_2)_n$—CH=C=O should afford, after dimerization followed by hydration and decarboxylation, cyclic ketones of the type



The usefulness of this method has been tested employing sebacyl chloride as the starting material for the preparation of a bifunctional ketene of the type described above. From a consideration of the relative ease of forming many-membered carbon rings,[2] this ketene (n = 6) should cyclize to yield ultimately cycloöctadecane-1,10-dione as the principal product.

To a stirred, refluxing mixture of 7.2 g. (0.071 mole) of triethylamine, 0.4 g. of triethylamine hydrochloride and 500 cc. of absolute ether was added during thirty-eight hours 4.403 g. (0.0184 mole) of sebacyl chloride in 200 cc. of absolute ether. Stirring and refluxing were continued for four and one-half hours more. Then, after standing at room temperature overnight, all but 250 cc. of the ether was distilled. The remaining ether was separated from the precipitated amine salt by washing with water. A small amount of solid material (probably polymeric compounds) proved to be insoluble in both ether and water. The ether solution was washed once with 3 *N* hydrochloric acid and twice with water. After drying over magnesium sulfate, the ether was distilled, leaving a light yellow, mobile oil. To a solution of the oil in 10 cc. of absolute ethanol was added 3 g. (0.053 mole) of potassium hydroxide dissolved in 50 cc. of 95% ethanol. After refluxing on the steam-bath for three hours, the clear solution was acidified to litmus with dilute hydrochloric acid. To this was added 150 cc. of water and 100 cc. was then distilled in order to remove alcohol and any cyclononanone present. The distillate had a very pleasant odor, but attempts to isolate cyclononanone as the semicarbazone were unsuccessful. The residue from the steam distillation was made basic to phenolphthalein with 10% sodium carbonate and extracted with ether. Distillation of the dried ether layer left a small amount of pale yellow liquid, which crystallized into beautiful, large crystals on standing. Vacuum distillation gave 430 mg. (16%) of crude crystalline cycloöctadecane-1,10-dione, collected from 135–214° (0.4 mm.). The light yellow crystalline product was used directly in the preparation of the disemicarbazone (m.p. 225–227° dec. (cor.)) and the dioxime (m.p. 163–165° (cor.)). A sample of diketone after sublimation melted at 95–96° (cor.).[3]

(1) Hanford and Sauer, "Organic Reactions," Vol. III, pp. 108–140 (1946). This excellent chapter presents a complete literature survey of the preparation of ketenes and ketene dimers.

(2) K. Ziegler and R. Aurnhammer, *Ann.*, **513**, 43–64 (1934).

(3) L. Ruzicka, *et al.*, *Helv. Chim. Acta*, **11**, 506 (1928). These workers report cycloöctadecane-1,10-dione (m. p. 96–97°); disemicarbazone (m. p. above 230° dec.); and dioxime (m. p. 166–168°).

A complete study of the applicability of the synthetic method outlined above is in progress.

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RECEIVED JANUARY 20, 1947

THE CRYSTALLINE OCTAACETATE OF 6-α-D-GLUCOPYRANOSIDO-β-D-GLUCOSE

Sir:

The polysaccharide dextran ($[\alpha]^{20}D$ + 180°; *c* 1, water) produced by *Leuconostoc dextranicum* was hydrolyzed at room temperature in 2% solution in 30% hydrochloric acid to approximately two-thirds completion ($[\alpha]^{20}D$ of solution + 105°). After removal of inorganic ions by successive treatment with lead carbonate, hydrogen sulfide, sodium bicarbonate and Amberlite resins (IR-100 and IR-4), the D-glucose was removed by yeast fermentation and the sirup obtained on solvent removal was acetylated with hot acetic anhydride and sodium acetate. The resultant mixture of sugar acetates was chromatographed[1] on Magnesol–Celite employing benzene–ethanol development under such conditions that any monosaccharide present would be removed from the column. The material from the lowest zone was rechromatographed in similar fashion and the lowest zone material again obtained was crystallized (elongated prisms) from ethanol; m. p. 143–144°, $[\alpha]^{25}D$ + 97° (*c* 2.7, chloroform).

Anal. Calcd. for $C_{12}H_{14}O_{11}(CH_3CO)_8$: C, 49.56; H, 5.63; CH_3CO, 11.79 cc. of 0.1 *N* sodium hydroxide per 100 mg.; mol. wt., 678.6. Found: C, 49.74; H, 5.67; CH_3CO, 11.86 cc.; mol. wt. (Rast), 680.

Since methylation studies[2,3] have demonstrated that the polysaccharide employed in this work is built up of α-D-glucopyranose units linked in the 1,6-position, it follows that the disaccharide isolated must be 6-α-D-glucopyranosido-β-D-glucose octaacetate. Its determined rotation is in agreement with the value predictable by application of the isorotation rules of Hudson. The same acetylation and chromatographic procedure was applied to the sirup soluble in 80% ethanol that was obtained essentially according to the procedure of Örtenblad and Myrbäck[4] from the enzymic hydrolyzate of amylopectin (waxy maize) after removal of most of the maltose and D-glucose by yeast fermentation. In this case the lowest zone on the chromatogram was composed of β-maltose octaacetate (m.p. 159–160°, mixed melting point 159–160° unchanged; $[\alpha]^{25}D$ + 62°, *c* 1.1, chloroform) and from the zone immediately above this there was obtained by acetone elution and crystallization from ethanol, a substance crystallizing in tufts of fine needles; m. p. 134–136°, mixed melting point with 6-α-D-glucopyranosido-β-D-glucose octaacetate 120–125°, $[\alpha]^{24}D$ + 86° (*c* 1.6, chloroform). This material is the hendecaacetate of a trisaccharide and its structure is under further investigation.

Anal. Calcd. for $C_{18}H_{21}O_{16}(CH_3CO)_{11}$: C, 49.69; H, 5.63; mol. wt., 966.8. Found: C, 49.46; H, 557; mol. wt. (Rast), 971.

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RECEIVED JANUARY 17, 1947

THE ANTIBACTERIAL ACTIVITY OF *p*-AMINOBENZENEPHOSPHONOUS ACID

Sir:

It has been shown by Kuhn, Möller and Wendt[1] that phosphanilic acid (*p*-$H_2NC_6H_4PO(OH)_2$) has a slight antibacterial action, similar in nature to that of the sulfonamides in being antagonized by *p*-aminobenzoic acid. Proceeding on the assumption that the strength of the sulfonamide–enzyme complex is increased with decreasing acidity,[2] we have prepared *p*-aminobenzenephosphonous acid, *p*-$H_2NC_6H_4P(OH)_2$, by the procedure

$$C_6H_5Br + PCl_3 \xrightarrow{AlCl_3} p\text{-}BrC_6H_4PCl_2 \xrightarrow{H_2O} p\text{-}BrC_6H_4P(OH)_2 \quad (1)$$

$$p\text{-}BrC_6H_4P(OH)_2 + NH_4OH \xrightarrow{Cu_2O} p\text{-}H_2NC_6H_4P(OH)_2 \quad (2)$$

The first step, the preparation of *p*-bromobenzenephosphonous acid, has been carried out previously.[3] The second step, the synthesis of the amino compound, is similar to that used by Bauer[4] to prepare phosphanilic acid.

The product obtained has these properties: m.p. 169°; equivalent weight, calculated 157.1, found 158.0; analysis, calculated P 19.74%, found P 19.66%; solubility in water at 0° about 5%; *pK*, 3.68.

The activity of *p*-aminobenzenephosphonous acid was tested against *E. coli* and found to be slightly less than that of sulfanilamide. This antibacterial action was antagonized by *p*-aminobenzoic acid at concentrations approximately equal to those necessary to counteract sulfanilamide. Further tests on this substance and related compounds are in progress.

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RECEIVED JANUARY 16, 1947

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(2) E. C. Fairhead, M. J. Hunter and H. Hibbert, *Can. J. Research*, **B16**, 151 (1938).

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(4) B. Örtenblad and K. Myrbäck, *Biochem. Z.*, **303**, 335 (1940).

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(3) A. Michaelis, *Ann.*, **293**, 193 (1897).

(4) H. Bauer, THIS JOURNAL, **63**, 2137 (1941).