tracted with ether. Removal of the solvent gave 6.6 mg. of colorless crystalline material. Crystallization of the latter from aqueous acetone and aqueous methanol yielded 4.4 mg. of colorless crystals, m.p. 136–137.2°, $[\alpha]_D$ $-19.2°$ (chloroform), no depression of mixed melting point with starting material, infrared spectrum (chloroform) identical with that of starting ketone.

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Acenaphthene Arsenicals

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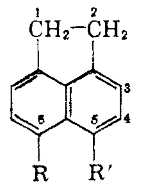
Several years ago, we gave some attention to the preparation of a number of acenaphthene arsenicals.[1] More recently,[2] we have repeated and extended this work. A search of *Chemical Abstracts* reveals no mention of acenaphthene arsenic compounds, a somewhat surprising situation, considering the number of acenaphthene compounds now in existence. Part of our interest in the series lies in the fact that the dimethylene bridge of acenaphthene can be oxidized into various forms some of which ought to prove of value as insecticidal or antifungal agents.

Since direct aromatic substitution of acenaphthenes produces, largely, 5-substituted compounds and disubstitution the 5,6- compounds, all of the compounds prepared by us belong to one of these structure types. The chemical literature describes satisfactorily the preparation of 5-nitroacenaphthene.[3] This compound was found to be reduced nicely in the laboratory to the corresponding amine either by low pressure hydrogenation using Raney nickel or palladium-charcoal, or by refluxing in hydrazine with the same catalysts. Other methods of reduction were found to be less satisfactory.

The 5-aminoacenaphthene was then converted into acenaphthene-5-arsonic acid, the first of the new compounds (I), *via* the Bart reaction on the diazotized amine. Application of the Scheller reaction (acetone solvent, arsenic trichloride, cuprous bromide catalyst) gave very poor yields even though conditions were varied extensively. The method of arsonation proceeding through the diazonium fluoborate (decomposition in aqueous as well as nonaqueous media) failed to give appreciable yields.

Acenaphthene-5-arsonic acid was then converted to the 5-dichloroarsine (II) and the 5-dibromoarsine (III) using the appropriate phosphorus trihalide in organic media. Attempts to convert the arsonic acid into the diiodoarsine (IV) with hydriodic acid in glacial acetic acid gave a tan product melting at 95–96°, but having an analysis some five or more per cent high in iodine. There is some question of the method to be employed in the analysis for iodine in the presence of arsenic, but the compound was probably contaminated with elemental iodine or arsenic iodide.



I. R = H, R' = AsO_3H_2
II. R = H, R' = $AsCl_2$
III. R = H, R' = $AsBr_2$
IV. R = H, R' = AsI_2
V. R = NO_2, R' = AsO_3H_2

The direct nitration of acenaphthene-5-arsonic acid was then attempted, leading to the supposed 6 - nitroacenaphthene - 5 - arsonic acid (V). After several exploratory runs, the correct conditions were established and a product giving the proper nitrogen content was obtained.

Several attempts to oxidize acenaphthene-5-arsonic acid into a naphthalic acid derivative with chromic anhydride failed to yield isolable material.

Structure proof for the supposed 6-nitro-5-arsonic acid based on the known 6-nitro-5-amine[4] is planned for the near future.

EXPERIMENTAL

Melting points were obtained on a Fisher-Johns melting point apparatus calibrated against pure compounds of known melting points.

Acenaphthene. Technical grade material was purchased from the Reilly Tar and Chemical Corporation of Indianapolis, and was recrystallized from glacial acetic acid with a charcoal treatment; m.p. 92–93°.

5-Nitroacenaphthene. This was prepared in 66% yield by direct nitration of acenaphthene using essentially the method of Sachs and Mosebach,[3] m.p. 101–102°.

5-Aminoacenaphthene. I. *Palladium-hydrazine method.* Five grams (0.033 mole) of 5-nitroacenaphthene was dissolved in 60 ml. absolute ethanol and 5 ml. of 95% hydrazine was added. The solution was heated to near reflux temperature and 0.05 g. of 10% palladium on charcoal (Matheson Coleman & Bell) was added. The mixture was refluxed for 10 min., an additional 0.05-g. portion of catalyst was added and reflux was continued for 90 min. The material was then treated with charcoal, filtered hot, and poured slowly into 800 ml. of cold water. The white solid separating was filtered, washed with water, and dried to give a product (3.6 g., 84% yield) melting at 104–105°.

II. *Palladium or raney nickel with low-pressure hydrogen.* Five grams (0.033 mole) of acenaphthene was placed with 60 ml. of absolute alcohol in the pressure bottle (400 ml. capacity) of a low-pressure Parr hydrogenation apparatus and 0.1 g. of 10% palladium-on-charcoal or approximately 0.5 g. of Raney nickel[5] was added. Hydrogen gas at 35 p.s.i.g. was supplied and the suspension was shaked for 90 min. The

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[1] G. W. Batzis, Master's Thesis, Xavier University, Cincinnati, Ohio, 1952.

[2] J. O. Kroeger, Master's Thesis, Xavier University, Cincinnati, Ohio, 1959.

[3] F. Sachs and G. Mosebach, *Ber.*, **43**, 2473 (1910).

[4] H. J. Richter, *J. Org. Chem.*, **21**, 619 (1956).

[5] R. Mozingo, *Org. Syntheses*, **21**, 15, (1941).

suspension was then transferred to an Erlenmeyer flask, treated with charcoal, and filtered hot. The filtrate was poured into 800 ml. of cold water to give yields varying from 80 to 90% (3.5–4 g.), melting at 104–105°.

Acenaphthene-5-arsonic acid. Seven grams (0.04 mole) of 5-aminoacenaphthene was suspended in 225 ml. of water and 25 ml. of 12*N* hydrochloric acid. The mixture was heated to 75° to dissolve the amine and the solution was then cooled rapidly in an ice–hydrochloric acid bath to 0°. A solution of 2.5 g. (0.036 mole) of sodium nitrite dissolved in 20 ml. of water was added slowly below the surface over the period of 30 min. with stirring, keeping the temperature below 5°. A dark green color appeared as the diazotization progressed as well as some dark insoluble matter. After an additional hour of stirring at this temperature, the diazonium solution was quickly filtered into a chilled flask and the solid residue was discarded.

The diazonium solution, kept cold with the aid of an ice bath, was added in small portions over a period of 30 min. to a mixture, at room temperature, of 7 g. (0.036 mole) of arsenic trioxide, 7 g. of sodium bicarbonate, 24 g. of potassium hydroxide, and 1.5 g. of hydrated copper sulfate in 200 ml. of water. From time to time, 8*N* sodium hydroxide was added to maintain alkalinity. The dark brown solution was allowed to stand overnight, treated on a hot water bath for 90 min., and was filtered hot. The filtrate was treated with charcoal, filtered again, and reduced by boiling to 400 ml. After cooling to 40°, the solution was acidified with 6*N* hydrochloric acid and chilled in the ice box. The crystals of the product were filtered by suction and extracted with a hot solution of 6 g. of sodium bicarbonate in 200 ml. of water. After charcoal treatment and filtration, the solution was acidified with 6*N* hydrochloric acid, chilled, and the product was filtered and dried. The white crystalline material (2.6 g., 22% yield) melted at 168–169°.

Anal. Calcd. for $C_{12}H_{11}O_3As$: As, 27.06. Found: As, 26.88.

Acenaphthene-5-dichloroarsine. One gram (0.0036 mole) of acenaphthene-5-arsonic acid was suspended in 13 ml. of chloroform and the temperature was raised to reflux. Heating was interrupted and 1.2 ml. (0.017 mole) of phosphorus trichloride was added dropwise. The chloroform was boiled away on the water bath and the residue refluxed with 8 ml. of petroleum ether (b.p. 60–90°). The solution was filtered and chilled overnight in the ice box. The crystalline material was separated and recrystallized again from 8 ml. of petroleum ether. The product, weighing 1.1 g. (55%), melted at 88–90°.

Anal. Calcd. for $C_{12}H_9Cl_2AS$: Cl, 23.7. Found: Cl, 24.2.

Acenaphthene-5-dibromoarsine. The method described above for the preparation of the dichloroarsine was employed, using phosphorus tribromide. The yield of purified dibromoarsine was 56% and the compound melted at 72–73°.

Anal. Calcd. for $C_{12}H_9Br_2As$: As, 19.4. Found: As, 19.7.

Acenaphthene-5-diiodoarsine. One gram (0.0036 mole) of acenaphthene-5-arsonic acid was suspended in 20 ml. of glacial acetic acid and 8 ml. of 43% hydriodic acid was added with shaking. The suspended arsonic acid dissolved and a heavier precipitate appeared. The mixture was refluxed gently for a few minutes to dissolve the product, and the clear solution was placed in the ice box. After standing overnight, the crystals were separated by filtration and recrystallized from glacial acetic acid. The yield of yellow-tan product was 0.4 g. (30%) melting at 95–96°. Analysis for iodine gave values 5–6% too high (theoretical value: 52.7%).

6(?)-Nitroacenaphthene-5-arsonic acid. Into a 200-ml. 3-neck flask, equipped with stirrer, thermometer, and dropping funnel, was placed 2 g. (0.0072 mole) of acenaphthene-5-arsonic acid suspended in 23 ml. of glacial acetic acid. The contents were heated to dissolve the arsonic acid, then cooled to 15° with an ice bath. To the stirred solution was added 20 ml. of fuming nitric acid (*d* 1.5) dropwise over a period of 30 min. The temperature dropped to 5° and stirring was maintained at this temperature for an additional 3 hr. The mixture was then brought to room temperature and slowly added to 100 ml. of ice water with vigorous stirring. A yellow precipitate appeared, changing to light brown on standing. The solid material was filtered, washed with water until the filtrate showed no color, and dissolved in a solution of 6 g. of sodium bicarbonate in 200 ml. of water. The solution was treated with charcoal, filtered, and neutralized with 6*N* hydrochloric acid. The yield of nitroarsonic acid was 1.0 g. (43.5%); the compound did not melt below 300°.

Anal. Calcd. for $C_{12}H_{10}AsO_5N$: N, 4.33. Found: N, 4.36.

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Structure and Partition Coefficient. Synthesis and Properties of the Dodecyl Methyl Pentaerythrityl Ethers

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Relatively few attempts have been made to relate structure to distribution coefficients in a systematic manner. Collander[1] has developed several useful semiquantitative generalizations for a number of systems. Alders[2] has shown that K_0, the distribution coefficient at infinite dilution, can be related to the hydrophobic chain length n by the expression

$$\text{Log}_{10}K_0 = A - B_n$$

for several series of homologous compounds in a variety of solvent pairs. The constants A and B are dependent on the solvent pair and the nature of the solute.

This paper reports on some results encountered in the preparation and isolation of dodecyl pentaerythrityl ether, I, and its methylation products, II, III, and IV. Partition coefficient data from the

$C_{12}H_{25}OCH_2C(CH_2OH)_3$ I

$C_{12}H_{25}OCH_2C(CH_2OH)_2CH_2OCH_3$ II

$C_{12}H_{25}OCH_2C(CH_2OH)(CH_2OCH_3)_2$ III

$C_{12}H_{25}OCH_2C(CH_2OCH_3)_3$ IV

Craig separation of these compounds indicated that in the solvent system used the number of unmethylated hydroxyl groups was linearly related to the logarithm of the partition coefficient, similarly to Alders' equation relating chain length to distribution. These results have been expressed as standard free energy terms since they are more

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(1) R. Collander, *Acta Chem. Scand.*, **3**, 717 (1949); **4**, 1085 (1950); **5**, 774 (1951).

(2) L. Alders, *Appl. Sci. Research*, **4A**, 171 (1954).