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 12N 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, 8N 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 6N 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 6N 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 6N 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
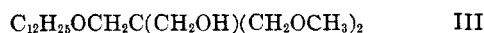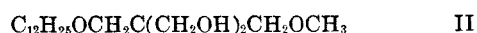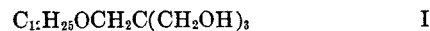
JIM S. BERRY

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

$$\mathrm{Log_{10}K_0} = A - B_n$$

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

$$\begin{array}{ll} C_{12}H_{25}OCH_2C(CH_2OH)_3 & \mathrm{I} \\ C_{12}H_{25}OCH_2C(CH_2OH)_2CH_2OCH_3 & \mathrm{II} \\ C_{12}H_{25}OCH_2C(CH_2OH)(CH_2OCH_3)_2 & \mathrm{III} \\ C_{12}H_{25}OCH_2C(CH_2OCH_3)_3 & \mathrm{IV} \end{array}$$

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

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

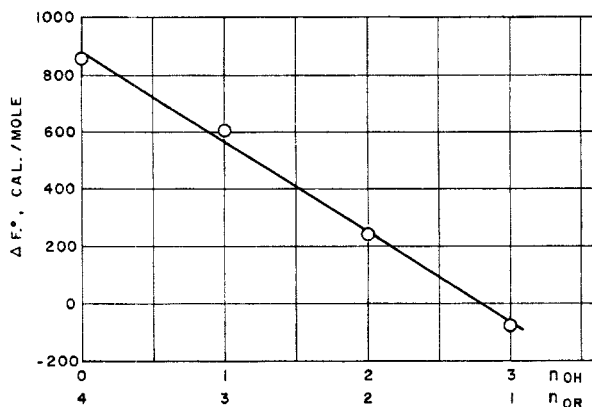(2) L. Alders, *Appl. Sci. Research*, **4A**, 171 (1954).

Fig. 1. Standard free energy vs. hydrophilic group content. Solvent: hexane—7 pts., chloroform—3 pts., ethanol—8 pts., water—2 pts.

directly related to the solvational energy changes accompanying the transfer of solute from one solvent phase to the other.[3] The data for the series of compounds are tabulated in Table I. Standard free energies are expressed as the energy change accompanying the transfer of solute from the upper, less-polar phase to the lower; i.e., $\Delta F^\circ = -nRT\ln 1/K$ where K is used in the conventional sense. Fig. 1 shows the plot of number of hydrophilic groups vs. the standard free energy. The least squares equation best expressing this relationship[4] is

$$\Delta F^\circ = 882\text{-}347\, N_{OH}$$
or, alternatively $\Delta F^\circ = -386\text{-}317\, N_{OR}$ (1)

The partition coefficient of n-hexadecane in the same solvent system (Table I) has been used as a reference point for comparing the relative contributions of the two functional groups in increasing polar character. While n-hexadecane is not an ideal choice for reference, the difference in molecular geometry should affect the partition coefficient of the hydrocarbon in this system only to a minor extent compared to the effects produced by introduction of ether or hydroxyl groups. The values of ΔF° for compounds I and IV computed from (1) can be used to calculate the contribution of each group to the free energy decrease accompanying the transfer of solute from upper to lower phase using (2) and (3).

$$\Delta F^\circ_{OR} = 1/4\,(\Delta F^\circ_{IV} - \Delta F^\circ \text{ hexadecane}) \quad (2)$$

$$\Delta F^\circ_{OH} = 1/3\,(\Delta F^\circ_I - \Delta F^\circ_{OR} - \Delta F^\circ \text{ hexadecane}) \quad (3)$$

The values of -242 and -559 cal./group respectively for ether and hydroxyl indicate the much greater effect of the hydroxyl group contribution in this system. Equation (2) assumes equivalence of methyl and dodecyl ether oxygens. The

(3) A. Frumkin, Z. physik. Chem., 116, 501 (1925).

(4) Ideally, distribution coefficients at infinite dilution should be employed in arriving at this equation; however, the maximum concentrations involved in the isolation (0.2%) are small enough to involve little error in using the values directly as determined.

validity of this assumption can be justified by using the values of ΔF°_{OH} and ΔF°_{OR} obtained to calculate ΔF°_{II} and ΔF°_{III}. The values 248 and 565 cal./mole calculated respectively for II and III correspond to the measured values, 240 and 605 cal./mole, within the limits of reproducibility of the partition coefficients.

TABLE I

PARTITION COEFFICIENTS AND FREE ENERGY DATA OF ETHERS

Compound	Solvent: hexane-chloroform/ ethanol-water (7-3/8-2)	
	K	ΔF° cal./mole
Dodecyl pentaerythrityl ether, I	0.88	-77
Dodecyl methyl pentaerythrityl ether, II	1.50	240
Dodecyl dimethyl pentaerythrityl ether, III	2.77	605
Dodecyl trimethyl pentaerythrityl ether, IV	4.26	858
n-Hexadecane	22.7	1851

The regularity of the pentaerythrityl ether series in this case is probably due to the stereochemical equivalence of oxygens attached to the neopentyl moiety. Results obtained with the isomeric 1- and 2-monoglycerides[5] indicate that this may well be the case, as the two position isomers, identical in functional group content, show different partition coefficients. It is possible that systematic study of selected series of compounds using methods similar to those used here could afford much valuable quantitative information about some of the effects which operate in the solvation of organic compounds.

EXPERIMENTAL

Dodecyl pentaerythrityl ether (I). To a well-stirred mixture of n-dodecyl alcohol (435 g., 2.33 moles) and 40 drops of concd. sulfuric acid was added 14.0 g. (0.118 mole) of 3,3-bis(hydroxymethyl)oxacyclobutane[6] dissolved in 1400 ml. chloroform. The chloroform solution was added over a 2-hr. period to the reaction mixture heated on the steam bath. After 1 hr. additional reflux the chloroform was removed *in vacuo* until the chloroform odor was very faint. Hexane (2 l.) was added to the residue and the solution chilled to 0° and filtered. The solid filter cake was redissolved in hot chloroform and filtered. Chloroform was removed from the filtrate and the residue recrystallized from hexane to give 12.9 g. (36% yield) crude dodecyl pentaerythrityl ether, I, m.p. 53.5–55.0° (uncorr.).

The crude product was contaminated at this stage by small amounts of dipentaerythritol and dodecyl alcohol. Purification was effected by solvent partition in a 200 stage Craig apparatus using a hexane-chloroform/ethanol-water mixture (7-3/8-2 parts by volume). The principal peak, $K = 0.88$, was the desired product I, m.p. 60–61°.

(5) E. S. Perry and G. Y. Brokaw, J. Am. Oil Chemists Soc., 32, 191 (1955).

(6) C. H. Issorides and A. I. Matar, J. Am. Chem. Soc., 77, 6382 (1955).

Anal. Calcd. for $C_{17}H_{36}O_4$: C, 67.18; H, 11.91; H.V., 553. Found: C, 66.77; H, 11.74; H.V., 547.

Dodecyl methyl pentaerythrityl ethers (II, III, and IV). To a mixture of 10 g. (0.033 mole) of crude I was added 3.95 g. (0.099 mole) of sodium hydroxide and 2.8 ml. water. The mixture was heated to 75° and 14.0 g. (0.099 mole) of methyl iodide was added over a 2-hr. period. After a 6-hr. period of heating at 70–75°, with stirring, the mixture was cooled and extracted with ether four times. The combined ether extracts were washed with water, dried over sodium sulfate, and the ether removed by evaporation. After repetition of the same methylation procedure, the mixture of ethers was separated on the Craig apparatus. The chloroform-hexane/ethanol-water system gave incomplete separation of III and IV. Dodecyl methyl pentaerythrityl ether, II, K = 1.50, could be cleanly separated from III and IV. For separation of the latter, the better solvent system isooctane-methanol (1:1) was used. Partition coefficients in this solvent system were 0.75 and 2.36 for III and IV, respectively. The dodecyl methyl pentaerythrityl ethers were all liquids.

Anal. Calcd. for $C_{18}H_{38}O_4$, II: C, 67.72; H, 12.03; H.V., 352. Found: C, 67.58; H, 11.90; H.V., 344. Calcd. for C_{19}-$H_{40}O_4$, III: C, 68.63; H, 12.13; H.V., 169. Found: C, 69.15; H, 12.01; H.V., 161. Calcd. for $C_{20}H_{40}O_4$, IV: C, 69.31; H; 12.22; H.V., O. Found: C, 70.28; H, 12.36; H.V., O.

n-Hexadecane. The partition coefficient for *n*-hexadecane (Matheson) was obtained by partitioning the hydrocarbon between the equilibrated solvent phases at 0.5% total concentration. It was essential to remove solvents by efficient fractionation to avoid evaporation losses. Recoveries averaged 97%.