Retene (1-methyl-7-isopropylphenanthrene) was pyrolized under the same conditions as used for the resin acids. The pyrolyzate was analyzed by gc, and the products were identified to be toluene, 5.29% (weight percent of gc volatile portion); styrene, 4.6; phenanthrene, 16.7; 2-methylphenanthrene, 4.8; 1-methylphenanthrene, 20.3; 2-vinylphenanthrene, 16.9; retene, 0.9; and 1-methyl-7-vinylphenanthrene, 19.4.

The retene experiment establishes that the phenanthrene ring system is quite stable under high-temperature pyrolytic conditions and that few naphthalene-related compounds are produced. Therefore, the high yield of naphthalene products during the pyrolysis of the resin acids must arise from cleavage in the A-ring of the parent molecule before complete aromatization occurs. Precedence for rupture of the A-ring is the fact that all compounds studied are converted to dehydroabietic acid under very mild conditions (*17*) and that phenyl nucleus is extremely stable to heat (*4*). Cleavage of the A-ring is most likely facilitated by the ease with which the resin acids undergo decarboxylation [differential thermal analysis and thermogravimetric analysis indicate that resin acids began to readily decarboxylate at 275°C (*13*)].

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Preparation of Dimethyl α,α'-Bis(diethylphosphono)adipate and α,α'-Bis(diethylphosphono)adipamide

JERRY P. MOREAU,[1] LEON H. CHANCE, GORDON J. BOUDREAUX, and GEORGE L. DRAKE, JR.
Southern Regional Research Laboratory, P. O. Box 19687, New Orleans, La. 70179

Dimethyl α,α'-bis(diethylphosphono)adipate and α,α'bis(diethylphosphono)adipamide have been prepared by conventional methods. Some nuclear magnetic resonance and infrared data have also been described.

Research is being conducted at the Southern Regional Research Laboratory to prepare new compounds containing phosphorus for use in the development of flame-retardant finishes for cotton products. One class of compounds of interest was dicarboxylic acid derivatives containing a phosphono group attached to the α,α' carbon atoms.

The only α,α'-bis(diethylphosphono) derivatives of a dicarboxylic acid reported are those for succinic acid, in which case acetylenedicarboxylic acid was used as the starting material (*5*, *7*). Because this method is not applicable with dicarboxylic acids containing more than four carbon atoms, the objective of the present investigation was to prepare α,α'-bis(dialkylphosphono)dicarboxylic acid esters and amides by an alternative route.

Esters of α-(diethylphosphono)alkylcarboxylic acids have been prepared by the Arbuzov reaction of triethyl phosphite and the ester of the appropriate C_4–C_{18} straight-chain α-

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[1] To whom correspondence should be addressed.

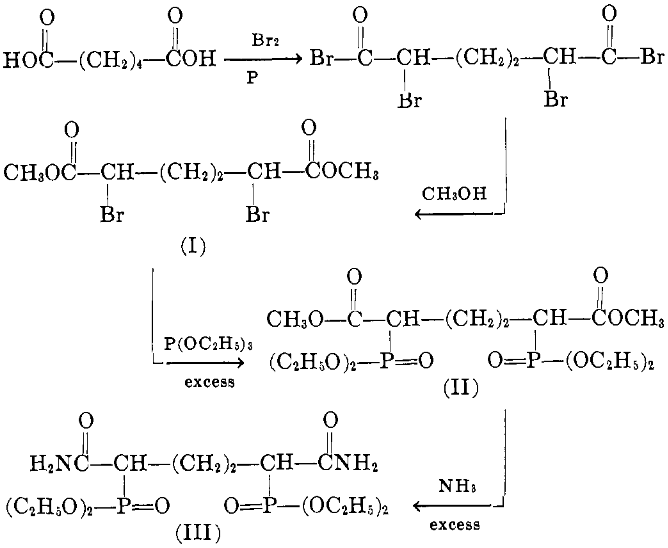

Figure 1

bromocarboxylic acid (1). Therefore, this method was used to prepare dimethyl α,α′-bis(diethylphosphono)adipate (II), which was then converted to α,α′-bis(diethylphosphono)adipamide (III) as shown in the reaction sequence in Figure 1.

Bromine was substituted in the α,α′ positions of adipic acid by the Hell-Volhard-Zelinskii reaction (6). Bromine may also be substituted in the α,α′ positions by the use of thionyl chloride and bromine (3, 4). In either case, the resulting α,α′-dibromo acid halide was reacted with absolute methanol to give dimethyl α,α′-dibromoadipate (I) as reported by Buchman et al. (3). A mixture of the meso- and *d,l*-forms of I was obtained in a total yield of 82%.

Only the solid meso isomer of I, as obtained in the first crystallization, was used for further reaction. The liquid racemate of I, however, may be converted to the meso form in the presence of sodium methoxide as reported by Bernton et al. (2). It may be partly converted by distillation under reduced pressure. Bernton et al. also reported that both the liquid isomer of I and the solid isomer of I react with concentrated aqueous ammonia to give the same α,α′-dibromoadipamide.

Meso I was then reacted with excess triethyl phosphite by the Arbuzov reaction to give the phosphono ester (II) in approximately 80% yield. Finally, II was reacted with ammonia in aqueous solution to give a 55% yield of the phosphono adipamide (III). Attempts to prepare III by the reaction of α,α′-dibromoadipamide with triethyl phosphite were unsuccessful. Data obtained from nuclear magnetic resonance and infrared spectra were used in the analyses and evaluation of the structures of compounds II and III.

Of particular interest in the nmr data is the appearance of two signals for —NH_2 in compound III. The nmr spectra of a similar compound, $(BuO)_2P(O)CH_2C(O)NH_2$, also gave two very distinct signals. When both compounds were heated to 80°C these signals coalesced, indicating hindered rotation of the amide protons.

EXPERIMENTAL

Nuclear magnetic resonance (nmr) spectra were determined in chloroform-*d* or dimethylsulfoxide-d_6 solution with a Varian A-60-A spectrometer, using tetramethylsilane as an internal reference and a probe temperature of 37°C. Infared (ir) spectra were measured in potassium bromide discs with a Perkin-Elmer spectrophotometer, Model 21.

Dimethyl α,α′-Dibromoadipate (I). Adipic acid (146 grams, 1 mole) and red phosphorus (25 grams, 0.8 mole) were stirred while heating to 50°C. Bromine (720 grams, 4.5 moles) was added dropwise over a 7-hr period. The addition of bromine was regulated by the rate of evolution of HBr. The reaction mixture was heated an additional 16 hr as the temperature was slowly raised to 80°C. Excess bromine was then removed under slight vacuum while heating for 8 hr at 80°C. The crude acid bromide was decanted from the solid residue and slowly added to absolute methanol. The methanol solution was refluxed for 4 hr; then the methanol was removed. Crude I was dissolved in diethyl ether, and acidic materials were removed by washing with dilute sodium carbonate and with water. Residual water and color were removed from the ether solution with anhydrous sodium sulfate and decolorizing carbon. The ether solution was concentrated to 200 ml and an equal volume of petroleum ether added. After cooling, filtering, and washing with petroleum ether, 127 grams of meso I was obtained; mp 72–74°C (lit. mp 73.5–74.0°C) (3).

The nmr spectrum in $CDCl_3$ showed a complex multiplet centered at $\delta = 2.25$ ppm, —CH_2—; a singlet at $\delta = 3.83$ ppm, CH_3O—; and a complex multiplet at $\delta = 4.36$ ppm, —CHBr—, with ratios of 2:3:1. The ir spectrum in KBr disc showed an absorption band at 1740 cm^{-1}, (C=O) ester. Anal. Calcd. for $C_8H_{12}Br_2O_4$: C, 28.94; H, 3.64, Br, 48.14. Found: C, 28.80; H, 3.58; Br, 47.92.

Additional I, 146 grams, was obtained from the filtrate by distillation at 140–4°C (0.8 mm). The distillate, which soon solidified, was composed of meso I and racemic I. Elemental and nmr analyses of this distillate were very similar to those of meso I. Total yield of I was 82%.

Dimethyl α,α′-Bis(diethylphosphono)adipate (**II**). Meso I (100 grams, 0.3 mole) and triethyl phosphite (150 grams, 0.9 mole) were heated at 150–80°C. Nitrogen was swept through the system to facilitate the removal of ethyl bromide. The reaction mixture was heated for 3 hr, after which the evolution of ethyl bromide ceased. This occurred after collecting ca. 90% of the theoretical amount of ethyl bromide. The reaction mixture was fractionally distilled to give II (90 grams, 0.2 mole); bp 192°C (0.09 mm); n^{20}_D 1.4572. Additional II can be obtained from the adjacent fractions to give a total yield of 75–80%. II solidified to a waxy white solid.

The nmr spectrum in $CDCl_3$ showed a triplet centered at $\delta =$ 1.35, $CH_3CH_2O)_2$; a complex multiplet centered at $\delta =$ 2.00, —CH_2—; two complex multiplets centered at $\delta = 3.00$, —CHP—; a singlet at $\delta = 3.80$, CH_3O—; and a complex multiplet centered at δ 4.20, $CH_3CH_2O)_2$ with ratios of 6:2:1:3:4.

The ir spectrum as a smear on a KBr plate showed absorption bands at 1740 cm^{-1}, (C=O) ester; 1250 cm^{-1}, P=O; 1160 cm^{-1}, P—OEt; and 1020 cm^{-1}, P—O—C. Anal. Calcd. for $C_{16}H_{32}O_{10}P_2$: C, 43.05; H, 7.23; P, 13.88; mol wt, 446. Found: C, 43.01; H, 7.14; P, 14.00; mol wt, 436 (benzene).

α,α′-Bis(diethylphosphono)adipamide (**III**). II (45 grams, 0.1 mole) was dissolved in absolute methanol (30 grams) and concentrated ammonium hydroxide (170 grams, 29% NH_3) was added. The solution was cooled to 5°C while saturating with ammonia gas, then allowed to stand at room temperature for two weeks. The white crystalline solid, which began to precipitate after the second day, was filtered and washed with cold water and then with acetone to give a 55% yield of III (23 grams, 0.055 mole); mp 232–4°C. From a smaller run, a 44% yield of III was obtained with mp 235–35.5°C.

The nmr spectrum in DMSO-d_6 showed a triplet centered at $\delta = 1.23$, $CH_3CH_2O)_2$; a complex multiplet centered at $\delta =$ 1.67, —CH_2—; a complex multiplet centered at $\delta = 3.17$, —CHP—; a complex multiplet centered at $\delta = 4.06$, $CH_3CH_2O)_2$; and two signals at $\delta = 7.17$ and 7.50, coalescing at 80°C, attributed to hindered rotation of H_2N—, with ratios of 6:2:1:4:2.

The ir spectrum in KBr disc showed absorption bands at 3280 cm^{-1} and 3120 cm^{-1}, NH_2 stretching; 1680 cm^{-1}, (C=O) amide I; 1630 cm^{-1}, amide II; 1230 cm^{-1}, P=O; 1160 cm^{-1}, P—O—Et; and 1020 cm^{-1}, P—O—C. Anal. Calcd. for

$C_{14}H_{30}N_2O_6P_2$: C, 40.39; H, 7.26; N, 6.73; P, 14.88. Found: C, 40.37; H, 7.34; N, 6.70; P, 14.96.

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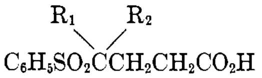
4-(Phenylsulfonyl)carboxylic Acids

Formation of Clathrate (Inclusion) Compounds by 4-Phenyl-4-(phenylsulfonyl)valeric Acid

THOMAS G. MILLER,[1] JOHN J. HILLER, JR., ANTHONY C. SAVITSKY, and DORIS A. WUNSCH
Department of Chemistry, Lafayette College, Easton, Pa. 18042

4-Phenyl-4-(phenylsulfonyl)valeric acid forms inclusion compounds with molecules such as ethyl ether, chloroform, carbon tetrachloride, cyclohexane, benzene, toluene, and benzene-heptane. The clathrates lose the volatile component when they are ground, heated under vacuum, or allowed to stand. Three other 4-(phenylsulfonyl)-carboxylic acids examined did not form clathrates.

Clathrate compounds are formed with a number of organic molecules by 4-phenyl-4-(phenylsulfonyl)valeric acid, 4, which we synthesized during the course of another investigation.



$$C_6H_5SO_2C(R_1)(R_2)CH_2CH_2CO_2H$$

Compound		Compound	
1	$R_1 = R_2 = H$	3	$R_1 = C_6H_5, R_2 = H$
2	$R_1 = CH_3, R_2 = H$	4	$R_1 = C_6H_5, R_2 = CH_3$

Accordingly, we report its preparation and properties, as well as those of the related 4-(phenylsulfonyl)carboxylic acids, 1, 2, and 3.

We use "clathrate" in the generic sense, as does *Chemical Abstracts*, to designate inclusion compounds of either the channel or caged type. The classification of inclusion compounds has not been standardized (*4*), but it has been the practice of some authors (*3, 4, 7, 9*) to reserve the word clathrate for the caged structures only.

DISCUSSION

A variety of compounds, both organic and inorganic, are known to act as "host" molecules having crystal structures with channels or cages of the proper geometry to trap and hold firmly certain "guest" molecules (*1, 4*). The geometry of the arrangement, rather than chemical bonding, is responsible for the stability of the resulting inclusion or clathrate compounds. Apparently, sulfones such as 4 have not previously been reported to act as host molecules. However, 4 is also a substituted valeric acid and in this structural feature does resemble desoxycholic and apocholic acids which have long been known to form inclusion compounds of the channel type, the choleic acids, with many types of smaller molecules (*1, 9*). In Table I are listed the clathrates formed when 4 is crystallized from various solvents. No attempt was made to establish any limits of size or geometry for the guest molecule, and whether the inclusion compounds are of the channel or caged type is not known.

Positive identification of the guest molecules in the inclusion compounds was complicated by the problem of getting pure 4 to use as a starting material. The compound will not crystallize without the inclusion of a guest, and separation of the volatile component from the clathrate is accomplished only with difficulty and with the risk of accompanying decomposition of 4 itself (vide infra). Water was excluded as a component by the lack of its characteristic absorption bands in the infrared and near infrared.

Positive identification was achieved in the case of the benzene-heptane solvent by careful vacuum heating of the clathrate and collecting the distillate in a cold trap. Infrared analysis of the distillate showed it to be an approximately 40-60 mix-

Table I. Clathrate Compounds from 4

Crystallizing solvent	Neutralization equiv of clathrate[a]	Moles guest/mole 4[b]
Ethyl ether	374	0.76
Carbon tetrachloride	400	0.53
Toluene	363	0.49
Benzene	355	0.47
Benzene-cyclohexane	363	0.54[c]
Benzene-*n*-heptane	360	[d]
Chloroform-*n*-heptane	440	1.0[e]

[a] Values given are averages of several trials. The expected range of values is ca. ±2% from the average (greatest range with CCl_4 and $CHCl_3$) and includes the imprecision of titrating small samples. [b] Calculated from the neutralization equivalent. [c] Guest is C_6H_{12}. [d] Guest is ca. 40-60 C_6H_6-C_7H_{16}. [e] Guest is $CHCl_3$.

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[1] To whom correspondence should be addressed.