added to destroy any residual peroxide, and the solution was evaporated under reduced pressure to a yellow solid. Recrystallization (methanol) gave 0.88 g. (83%) of the thiolsulfonate 2, m.p. 105–107°, which after further recrystallization had constant m.p. 108.5–110°. The infrared spectrum contained strong bands (–SO_2–) at 1150 and 1340 cm.$^{-1}$.

Anal. Calcd. for $C_{30}H_{46}O_2S_2$: C, 71.63; H, 9.22; S, 12.76. Found: C, 71.59; H, 9.02; S, 12.91.

Preparation and Structure of Dimethyl α-Conidendrin-8-methyl Sulfonate

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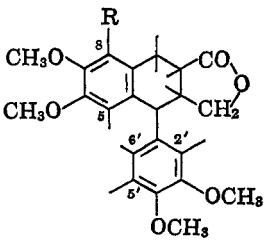
Contribution No. P-88 from the Department of Forestry of Canada, Forest Products Research Branch, Ottawa, Ontario, Canada

Received October 9, 1964

On the basis of Holmberg's preparation of α-conidendric acid in which concentrated sulfuric acid was used to open the lactone ring, a similar preparation of dimethyl α-conidendric acid from dimethyl α-conidendrin was attempted. Methylation of the product with diazomethane, however, failed to give the expected methyl dimethyl α-conidendrate and resulted instead in the 8-methyl sulfonate derivative of dimethyl α-conidendrin [2-naphthoic acid, 1,2,3,4-tetrahydro-3-hydroxymethyl-6,7-dimethoxy-4-(3,4-dimethoxyphenyl)-8-methyl sulfonate, γ-lactone or 3,4,3′,4′-tetramethoxy-2′-sulfonyl methyl-cyclolignan-olid (9.9′) by the proposed lignan nomenclature of Freudenberg and Weinges[3]], as shown by I. In view of these results Holmberg's reported α-conidendric acid[2] was probably the 8-sulfonic acid derivative.

Based on elemental analyses and a molecular weight determination an empirical formula of $C_{23}H_{26}O_9S$ was obtained for this compound. A ferric ferricyanide[4] color test for phenolic groups was negative. Since the infrared spectrum indicated that the lactone ring was intact and methoxyl analyses showed an additional methoxyl besides the four aromatic ring methoxyls expected, this fifth methoxyl group was apparently the methyl ester of a sulfonic acid group introduced into the compound. Although soluble in chloroform the new derivative was only moderately soluble in methanol, ethanol, and acetone, and was insoluble in water.

Comparison of aromatic ring proton magnetic resonance spectra (p.m.r.) of dimethyl α-conidendrin (II)



I, R = SO_3CH_3.
II, R = H

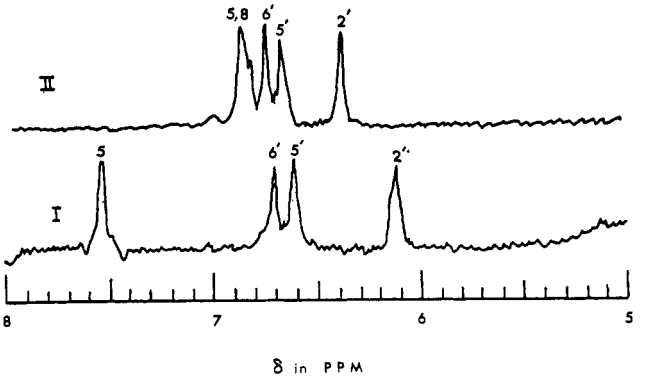


Figure 1.—Aromatic proton magnetic resonance spectra of dimethyl α-conidendrin-8-methyl sulfonate (I) and dimethyl α-conidendrin (II) in deuteriochloroform.

and this sulfur-containing derivative (Figure 1) together with stereochemical considerations strongly indicated that the sulfonic acid methyl ester group should be assigned to carbon 8.

Substitution of any one of the protons 2′, 5′, or 6′ by such a strong electron-withdrawing group as a sulfonic acid methyl ester would result in the displacement of the remaining two protons to higher δ-values. Since only one proton was so displaced, substitution must have involved protons 5 or 8. A choice between proton 8 and proton 5 was made on the basis of stereochemical models of the two possible structures (Courtauld atomic models). These models clearly indicated that substitution of a bulky sulfonic acid methyl ester group on carbon 5 would be restricted by the large aryl group on carbon 4.

Since the infrared spectrum of the monosulfonic acid intermediate showed it to be a mixture of the monosulfonic acids of both dimethyl and α-conidendric acids as well as their lactones, no rigorous purification of the intermediate was attempted. In any case, reaction of the intermediate with diazomethane produced only one crystalline end product I which was easily isolated. Undoubtedly, the 15-fold excess of diazomethane used in the reaction was involved in remethylation of free phenolic groups as well as combination with residual traces of sulfuric acids.

Experimental

Carbon, hydrogen, sulfur, and methoxyl analyses were performed by the Clark Microanalytical Laboratories, Urbana, Ill. Molecular weights were determined on the Mechrolab vapor pressure osmometer, Model 301A, using acetone as a solvent. P.m.r. spectra were recorded on a Varian, Model A-60, spectrometer in deuteriochloroform with tetramethylsilane as an internal standard. Infrared spectra were run in KBr disks on a Baird-Atomic infrared recording spectrophotometer, Model KM-1.

Preparation of the Monosulfonic Acid Intermediate.—Dimethyl α-conidendrin (4 g.) prepared by the method of Holmberg[5] was thoroughly mixed with concentrated sulfuric acid (12.6 ml.) and left at room temperature for 6 hr. Water (45 ml.) was then slowly added with stirring. The resultant precipitation was allowed to continue overnight at 4°. The excess acid solution was decanted and the product was recrystallized from water (35 ml.) by gentle warming. The slightly colored crystals (4.7 g.) melted with decomposition at 220–230°.

Dimethyl α-Conidendrin-8-methyl Sulfonate.—Dimethyl α-conidendrin-8-sulfonic acid (2 g.) in methanol (40 ml.) was added

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(2) B. Holmberg, *Svensk. Kem. Tidskr.*, **32**, 56 (1920).
(3) K. Freudenberg and K. Weinges, *Tetrahedron*, **15**, 115 (1961).
(4) G. M. Barton, R. S. Evans, and J. A. F. Gardner, *Nature*, **170**, 249 (1952).
(5) B. Holmberg, *Chem. Ber.*, **54**, 2389 (1921).

to a 15-fold excess of diazomethane in ether (110 ml.).[6] The slightly yellow solution was allowed to crystallize at 4° for several hours, filtered, and washed with cold methanol; yield 1.2 g., m.p. 245–247°. Recrystallization from boiling methanol afforded an analytical sample melting sharply at 250°: ν_{max}^{KBr} 2980 (m), 1780 (vs), 1520 (s), 1475 (s), 1365 (m), 1270 (s), 1220 (m), 1050 (m), 990 (s), 870 (m), 770 (s), and 660 cm.$^{-1}$ (m).

Anal. Calcd. for $C_{28}H_{26}O_5S$: C, 57.9; H, 5.49; S, 6.70; OCH_3, 32.4; mol. wt., 478. Found: C, 57.62, 57.45; H, 5.48, 5.52; S, 6.72; OCH_3, 31.41; mol. wt., 476.

Acknowledgment.—The authors wish to thank Crown Zellerbach, Chemical Products Division, Camas, Washington, for their generous sample of α-conidendrin.

(6) A. I. Vogel, "A Text Book of Practical Organic Chemistry," Longmans, Green and Co., London, 1948, p. 844.

Cyclodehydrohalogenation of Diarylphosphinous Chlorides[1]

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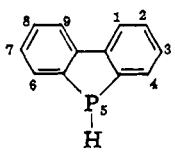
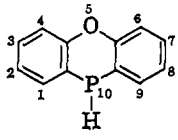
Cyclodehydrohalogenation of arylphosphonous dichlorides has previously been shown to be a useful method for the preparation of certain heterocyclic organophosphorus compounds.[2] By means of this method we have prepared derivatives of dibenzophosphole (I), phenoxaphosphine (II), and 5,10-dihydrodibenz[*b*,*e*]phosphorin (III).



I



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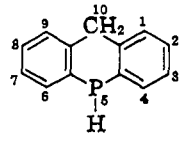
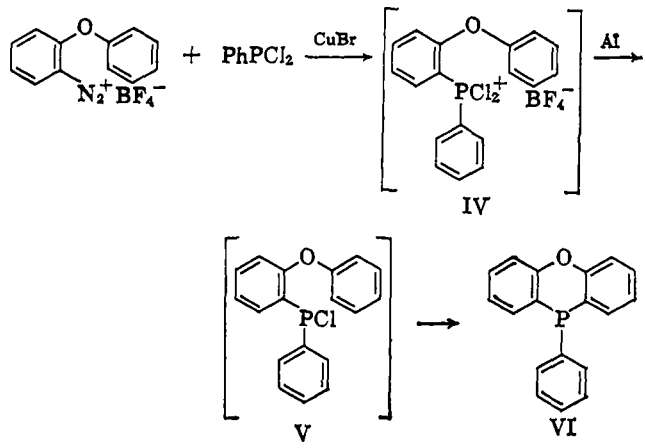


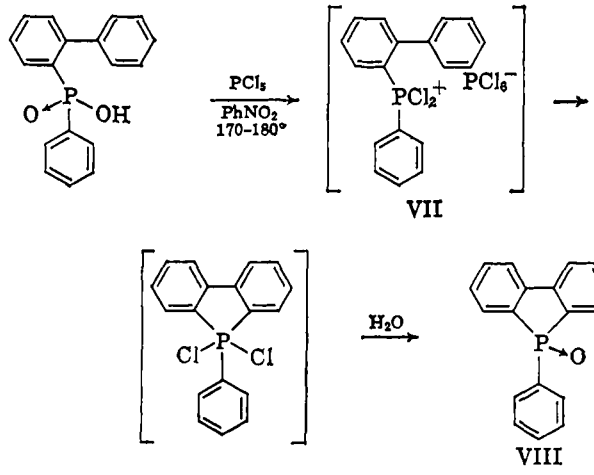
III

We have now found that suitably substituted diarylphosphinous chlorides[3] also undergo cyclodehydrohalogenation. Thus 10-phenylphenoxaphosphine[4] (VI) was prepared in 26% yield by the following series of reactions. Neither IV nor V was isolated from these reactions. (*o*-Phenoxyphenyl)phenylphosphinous chloride (V) presumedly underwent cyclodehydrohalogenation during the preparation and yielded the desired cyclic compound. The intermediate formed from the reaction of a diazonium tetrafluoroborate with an arylphosphonous dichloride has not been isolated, but structures similar to IV have been proposed.[3,5,6]

Campbell and Way have suggested that intermediate VII was formed in their preparation of 5-phenyldibenzophosphole 5-oxide (VIII) from *o*-biphenylylphenylphosphinic acid.[7] Since the structure suggested for IV is similar to that given for VII, we have investigated the possibility that cyclodehydrohalogenation occurs before the aluminum reduction in the preparation of 10-phenylphenoxaphosphine. Accordingly, *o*-phenoxybenzenediazonium tetrafluoroborate was allowed to react with phenylphosphonous dichloride, and the resulting mixture was hydrolyzed. The uncyclized compound, (*o*-phenoxyphenyl)phenylphosphinic acid, was isolated in 52% yield. This result strongly suggests that cyclodehydrohalogenation occurred after the aluminum reduction in our preparation of 10-phenylphenoxaphosphine.



IV V VI



VII VIII

Some cyclization did occur, however, when the reaction mixture was distilled rather than hydrolyzed. Thus, when the highest boiling fraction of the distillate (b.p. 175–177° at about 5 μ) was treated with an alkaline hydrogen peroxide solution (to hydrolyze the mixture and to oxidize any trivalent phosphorus compound which may have been formed from thermal decomposition of a pentavalent phosphorus compound), the resulting mixture gave a 3% yield of 10-phenylphenoxaphosphine 10-oxide and a 32% yield of (*o*-phenoxyphenyl)phenylphosphinic acid. It is of interest to note that we have been unable to cyclize this acid by the method used by Campbell and Way for the cyclization of *o*-biphenylylphenylphosphinic acid.

(1) Supported by Research Grant GM-09479 from the National Institutes of Health, U. S. Public Health Service.

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(6) P. C. Crofts, *Quart. Rev.* (London), **12**, 341 (1958).

(7) I. G. M. Campbell and J. K. Way, *J. Chem. Soc.*, 2133 (1961).