practical purposes, the steryl esters were inactive in this test.

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The Effect of Solvent on the Ultraviolet Absorption Spectra of Phosphine Oxides and Sulfides

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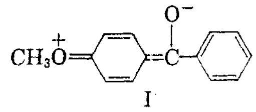
From a study of the effect of solvent on the ultraviolet absorption spectra of sulfones, it was suggested[1] that the sulfur-oxygen bond in sulfones is semipolar and not doubly covalent. It was interesting to study in a similar way the nature of the phosphorus-oxygen and phosphorus-sulfur bonds in phosphine oxides and phosphine sulfides, respectively.

From the data recorded in Table I it is seen that the solvent effect on the absorption spectra of phosphine oxides and phosphine sulfides is analogous to that observed for sulfones.[1] With change of solvent from cyclohexane to ethanol there is practically no change in λ_{max} for phosphine oxides and sulfides, while for ketones, there is a considerable bathochromic shift. This shift is even more pronounced for p-nitrosodimethylaniline. In the case of ketones and p-nitrosodimethylaniline, polar structures (I and II) make a more significant contribution to the excited state than to the ground state; the excited state is thus more stabilized in a polar solvent and a red shift of the λ_{max} is seen to occur with change of solvent from cyclohexane to ethanol. If the phosphorus-oxygen and phosphorus-sulfur bonds in phosphine oxides and sulfides are semipolar, both the ground and excited states are zwitterionic (as illustrated by III and IV) and they will be stabilized almost to the same extent in a polar solvent. Hence there will be no significant change in λ_{max} with change of solvent. Such a semipolar concept of the phosphorus-oxygen linkage in phosphine oxides is in conformity with the experimental evidence supplied by the parachors,[2] dipole moments,[3] and bond refractions.[4]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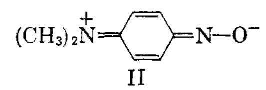
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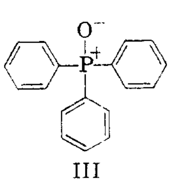
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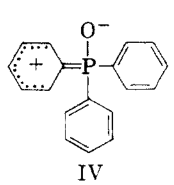
IV

TABLE I

SOLVENT EFFECT ON THE ABSORPTION SPECTRA OF TRIARYLPHOSPHINE OXIDES, TRIARYLPHOSPHINE SULFIDES, AND DIARYL KETONES[a]

	C_6H_{12}		C_2H_5OH	
	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}
$(C_6H_5)_3PO$	224	23,000	224	26,100
$(p\text{-}CH_3\cdot C_6H_4)_3PO$	231	32,800	232	35,500
$(p\text{-}CH_3O\cdot C_6H_4)_3PO$	244	43,700	246	46,000
$(p\text{-}CH_3\cdot C_6H_4)_3PS$	227	30,800	227	30,300
$(p\text{-}CH_3O\cdot C_6H_4)_3PS$	240	35,300	242	35,300
$(C_6H_5)_2CO$	249	18,900	253	17,500
$(p\text{-}CH_3\cdot C_6H_4)_2CO$	258	22,100	265	20,600
$(p\text{-}CH_3O\cdot C_6H_4)_2CO$	279	22,300	295	21,900
$p\text{-}(CH_3)_2N\cdot C_6H_4'NO$	393	23,800	428	28,600

[a] The high intensity bands only are given. Wave lengths are in mμ.

EXPERIMENTAL

Tri-p-anisylphosphine oxide. A saturated solution of potassium permanganate was added in excess to tri-p-anisylphosphine[5] (3.5 g.) dissolved in glacial acetic acid. After 2 to 3 hr., sodium bisulfite was added to decolorization and the acid was neutralized carefully with ammonium hydroxide. The oil (3 g.) that was obtained solidified on cooling and scratching with a few drops of ether. Recrystallization from petroleum ether (b.p. 60–70°) gave shining needles, melting at 142–143°.

Anal. Calcd. for $C_{21}H_{21}O_4P$: C, 68.45; H, 5.74. Found: C, 68.03; H, 5.64.

Tri-p-anisylphosphine sulfide. A mixture of tri-p-anisylphosphine[5] (3.5 g.) and sulfur (0.4 g.) in carbon disulfide (25 ml.) was refluxed for 2 hr. Distillation of the carbon disulfide left an oily product (3.2 g.) which solidified on cooling. It crystallized from ethanol as colorless needles and melted at 109–110°.

Anal. Calcd. for $C_{21}H_{21}O_3PS$: C, 65.63; H, 5.51. Found: C, 65.12; H, 5.36.

Tri-p-tolylphosphine oxide. To p-tolylmagnesium bromide prepared from magnesium (5.2 g.) and p-bromotoluene (36.7 g.) dissolved in sodium-dried ether (100 ml.) was added phosphoryl chloride (7.6 g.) in dry ether (50 ml.) during the course of 0.5 hr. with vigorous shaking and cooling in a freezing mixture. The resulting complex was decomposed with a saturated solution of ammonium chloride and the ether layer was separated. The aqueous layer was extracted twice with ether and the combined ether extracts were washed with sodium hydroxide solution to remove any di-p-tolylphosphinic acid formed. The ethereal extract was dried with anhydrous sodium sulfate and the ether was removed by distillation. The oily product (12 g.) that was left

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over solidified on cooling and scratching. Recrystallization from benzene gave crystals melting at 145°. Michaelis,[6] who prepared it by the oxidation of tri-*p*-tolylphosphine, reported the same melting point.

Triphenylphosphine oxide, m.p. 153–154°, was obtained from triphenylphosphine[7] by the method of Michaelis and Soden.[8] Tri-*p*-tolylphosphine sulfide, m.p. 185–186°, was prepared by the action of sulfur on tri-*p*-tolylphosphine[5] as described by Michaelis.[6] *p,p'*-Dimethoxybenzophenone, m.p. 143–144°, was prepared by the method of Bergmann and Harvey.[9] *p,p'*-Dimethylbenzophenone, m.p. 93–94°, was obtained by the Friedel-Crafts reaction of *p*-toluoyl chloride with toluene. The sample of *p*-nitrosodimethylaniline used was recrystallized from petroleum ether (b.p. 30–50°) and melted at 94–95°.

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Preparation of Difunctional Cyanoalkylsilanes by the Grignard Reaction

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Recent reports that the reaction of methylmagnesium bromide with β-cyanoethyltrichlorosilane in diethyl ether results in a low yield of a mixture of products[1] and that a tertiary amine is required as a cosolvent for improved results[2] has prompted us to report on a brief investigation along similar lines. By carrying out the Grignard reaction at −50° in tetrahydrofuran solution, greatly improved selectivity of the Grignard reagent is realized, workup of the products is simplified, and difunctional β-cyanoethylchlorosilanes are readily isolated in good yield. The results of the reaction of methyl- and ethylmagnesium chlorides with β-cyanoethyltrichlorosilane are summarized in Table I.

TABLE I

REACTION PRODUCTS OF β-CYANOETHYLTRICHLOROSILANE WITH GRIGNARD REAGENTS AT −50°[a]

	Mole-% Conversion to	
RMgCl	β-NC(CH$_2$)$_2$-SiRCl$_2$	β-NC(CH$_2$)$_2$-SiR$_2$Cl
Methyl	73	7
Ethyl	69	9

[a] Grignard reagents and β-cyanoethyltrichlorosilane were allowed to react in equimolar amounts. See Experimental section.

The effect of reaction temperature on product distribution was examined for the reaction of methylmagnesium chloride with β-cyanoethyltrichlorosilane. The results are summarized in Table II.

TABLE II

EFFECT OF TEMPERATURE ON SELECTIVITY IN THE REACTION OF β-CYANOETHYLTRICHLOROSILANE WITH METHYLMAGNESIUM CHLORIDE[a]

	Mole-% Conversion to	
Reaction Temperature	β-NC(CH$_2$)$_2$-Si(CH$_3$)Cl$_2$	β-NC(CH$_2$)$_2$-Si(CH$_3$)$_2$Cl
−50°	73	7
−30°	61.6	10.6
+ 5°	52.4	16.1

[a] Grignard reagent and β-cyanoethyltrichlorosilane were allowed to react in equimolar quantities.

It is noteworthy that as the reaction temperature is raised from −50° to +5° the conversion to β-cyanoethyldichloromethylsilane falls about 20% while an equivalent amount of Grignard reagent is consumed by the formation of by-product β-cyanoethylchlorodimethylsilane. It is likely that at 20–35° reaction of the Grignard reagents will be rather nonselective. In addition, at these temperatures attack of the cyano group by the Grignard reagent probably becomes important. From these results it is concluded that for optimum conversion to difunctional cyanoalkylsilanes the reaction with Grignard reagents should be carried out at −30° or lower.

EXPERIMENTAL

All experiments were carried out following essentially the same procedure. Workup of the reaction products was simplified by removal of the salts by filtration while the reaction mixture was still cold.

β-Cyanoethyldichloromethylsilane (I). To 3.3 moles of β-cyanoethyltrichlorosilane (II) in 1.4 l. of tetrahydrofuran previously cooled to −50° with a Dry Ice–acetone bath there was added over a 2-hr. period the Grignard reagent prepared from 80 g. (3.3 moles) of magnesium turnings treated with excess methyl chloride in 1 l. of tetrahydrofuran. The reaction mixture was stirred for an additional hour as it was allowed to warm to +10° and then rapidly filtered. The filtrate was stripped of solvent under vacuum and refiltered. Flash distillation gave 457 g. of crude product which was fractionally distilled at atmospheric pressure through a 20-inch column packed with Helipak Hastelloy B (0.1 inch × 0.05 inch × 0.1 inch) rated at 20 plates. The forerun b.p. 200–214°/750 mm. (60 g., hydrolyzable chlorine, 34.7%) was a mixture of 34 g. (7% conversion) of β-cyanoethylchlorodimethylsilane (calcd. hydrol. chlorine, 24.0%) and 26 g. of I. The presence of minor amounts of II and β-cyanoethyltrimethylsilane cannot be rigidly

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(1) G. D. Cooper and M. Prober, Presented before the Division of Organic Chemistry at the 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September 1959.

(2) M. Prober, U. S. Patent 2,913,472 (1959).