unusually great resonance stabilization. Refinements of these calculations are under way, as are studies of the reactions of these anions and attempts to prepare additional members of the series.

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A NEW SYNTHESIS OF PHOSPHORODITHIOATE ESTERS

Sir:

Esters of O,O-dialkyl phosphorodithioic acids are of marked interest because of their exceptional insecticidal properties and low mammalian toxicity.[1] S-Alkyl esters have been obtained by alkylation of salts of the acids[2] or addition of the acids to double bonds,[1a] while S-aryl phosphorodithioates have been prepared with greater difficulty by reaction of thiol salts with O,O-dialkyl phosphorochloridothioates[3] or decomposition of aryl diazonium salts in the presence of the acids.[4] No simple S-alkenyl or S-alkynyl phosphorodithioates have been prepared by these methods.[5]

I now wish to report a new procedure which allows the preparation of S-alkyl, aryl, alkenyl and alkynyl phosphorothioates in high yields, with complete absence of side reactions.

Disulfides of O,O-dialkyl phosphorodithioic acids[6] react very rapidly and exothermally with Grignard reagents or alkyl or aryl lithium reagents to give excellent yields of the S-substitution products (equation 1). The reactions are run conveniently in ether or hydrocarbon solvents at room temperature[7] and usually are complete within 2–3 minutes, but may require a somewhat longer reaction time if the metallo-organic reagent is insoluble in the solvent employed. The order of addition of the reagents is unimportant. S-Alkenyl and S-alkynyl phosphorodithioates are prepared similarly in somewhat lower yields. No attempt was made to obtain maximum yields for any reaction.

All of the products were identified by elementary analysis or by comparison with compounds synthesized by independent routes. The infrared spectra of alkenyl and alkynyl phosphorodithioates exhibit the expected peaks at 6.3 and 4.6μ, respectively, and undergo typical addition reactions of alkenes and alkynes.

Careful examination of the crude and distilled products revealed no evidence of attack by the organo-metallic reagent at a phosphorus atom rather than at sulfur, or of any rearrangements occurring during the reaction.

TABLE I

PREPARATION OF O,O-DIALKYL PHOSPHORODITHIOIC ESTERS

$$(RO)_2\overset{S}{\overset{\|}{P}}-S-S-\overset{S}{\overset{\|}{P}}(OR)_2 + R'\ominus M\oplus \longrightarrow (RO)_2\overset{S}{\overset{\|}{P}}-S-R' + (RO)_2\overset{S}{\overset{\|}{P}}-S\ominus M\oplus \quad (1)$$

R	R'	M	Yield (% $(RO)_2\overset{S}{\overset{\|}{P}}$-SR')	B.p. °C.	B.p. Mm.	n_D^{25}
Et	Ph	MgBr	78	88–95[a]	0.01	1.558
Et	*sec*-Bu	MgBr	88	65–75[a]	0.01	1.499
Et	*i*-Bu	MgBr	100	65–75[a]	0.01	1.497
Et	*n*-Bu	Li	86	60–70[a]	0.01	1.497
Et	CH_2Ph	MgCl	93	87–94[a]	0.01	1.555
Et	$CH{=}CH_2$	MgBr	62	108–112	0.7	1.512
Me	$CH{=}CH_2$	MgBr	58	74–77	2.0	1.533
Et	CH=CHPh	MgBr	59	110–122[a]	0.01	1.582
Et	$C{\equiv}CCH_3$	Li	79	95–99	0.8	1.524
Me	$C{\equiv}CCH_3$	Li	57	115–117	2.3	1.539
Et	C≡CPh	Li	72	85–89[a]	0.01	1.592

[a] Evaporation temp. during molecular distillation.

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DISULFIDE BONDING OF ANTIGEN SUBUNITS IN THE PHOTOCHEMICAL APPARATUS OF BACTERIA

Sir:

Disulfide bonds are known to be important cross-linking groups for maintenance of protein structure.[1] Their role in preserving the structural integrity of certain cellular components, such as the mitotic apparatus, is well documented.[2] In this communication I wish to report chemical and immunochemical evidence for disulfide bonding of repeating subunits in another cellular structure, the chromatophores of photosynthetic bacteria, which contain the photochemical apparatus of the cell.

An antiserum was prepared to chromatophores which were first purified by differential centrifugation from extracts of light-grown *Rhodospirillum rubrum*. An extract of *R. rubrum* grown aerobically in the dark was added to the serum at the equivalence point so that antibodies reactive to the extract would be absorbed quantitatively. The supernatant serum obtained reacted only with components formed by the cells during photosynthetic growth, *i.e.*, the antigenic components of the chromatophores elaborated specifically as a consequence of photosynthesis. Although the chemical nature of these unique chromatophore antigens is unknown, that they are held together by disulfide

(1) (a) G. A. Johnson, J. H. Fletcher, K. G. Nolan and J. T. Cassaday, *J. Econ. Entomol.*, **45**, 279 (1952); (b) D. E. H. Frear, "Chemistry of the Pesticides," Third Ed., D. Van Nostrand Co., New York, N. Y., 1955, pp. 86–90.

(2) E. I. Hoegberg and J. T. Cassaday, THIS JOURNAL, **73**, 557 (1951).

(3) G. Schrader, German Patent 855,176 (1953).

(4) (a) N. N. Mel'nikov, A. F. Grapov and K. D. Shvestsova-Shilovskaya, *Zhur. Obshchei Khim.*, **27**, 1905 (1957); (b) G. Bianchetti, *Rend. ist. lombardo sci.*, Pt. I, **91**, 68 (1957) [*Chem. Abs.*, **52**, 11769b (1958)].

(5) A phosphorodithioate of *p*-dioxene, which is formally an S-alkenyl phosphorodithioate, has been prepared: W. R. Diveley, *et al.*, THIS JOURNAL, **81**, 139 (1959).

(6) The disulfides were prepared by oxidation of phosphorodithioic acids with bromine or nitrous acid. *Chemical Abstracts* names these disulfides thioperoxydiphosphates, which is vague, confusing and incorrect. A referee has suggested the name O,O-dialkyl phosphorothionyl disulfides, which is closely related to accepted organic chemical practice (*e.g.*, acetyl disulfide), but unfortunately does not seem generally applicable to more complex phosphorothioates. The name used above, while somewhat inelegant, seems clear and of general utility.

(7) External cooling is recommended for large scale reactions.

(1) R. Benesch, *et al.*, editors, "Symposium on Sulfur in Proteins," Academic Press, Inc., New York, N. Y., 1959.

(2) D. Mazia, *ibid.*, p. 367.