mechanism rather than accretion from the gas phase is operating, for no attack on the strip was noted unless direct physical contact was made with the lithium melt. When one of these lithium-doped samples is treated with water or dilute acid, microdispersion occurs. If left undisturbed, these colloidal suspensions do not settle out for several hours. The final black product, which can be powdered easily and brushed through a 325-mesh screen, still contains ~ 1-1.5 weight per cent. lithium. "Hydrolysis" of platinum–lithium admixtures prepared at the lower temperatures proceeds with a vigor comparable to that found for lithium itself. By contrast, the excess lithium leaches out of the reacted preparations rather slowly. The reaction product, $LiPt_2$, even when crushed to a very fine powder, appears to be unaffected by prolonged exposure to water.

Apart from an occasional lithium hydroxide line, X-ray diffractometer studies on the black, colloidal material yield only the spacings of the platinum lattice, broadened to such an extent that the crystallites appear to have dimensions in the 50–100 Å. range. It should be noted that the residual lithium content of these disperse preparations is slightly smaller than that of the compound $LiPt_2$.

Although $LiPt_2$ itself is comparatively inactive, we have found many of the "unreacted" platinum–lithium preparations to be highly effective catalysts for the hydrogenation of olefins. For example, the hydrogenation of cyclohexene in acetic acid under one atmosphere hydrogen pressure at room temperature will proceed up to twice as rapidly with our dispersed platinum–lithium catalyst as with an equal weight of the supported platinum oxide catalyst PS 14.[5]

We are currently investigating techniques for preparing catalysts with reproducible activity, the selectivity of these catalysts, and intermetallic compound formation in other systems involving alkali and noble metals.

(5) F. A. Vandenheuvel, *Anal. Chem.*, **28**, 363 (1956).

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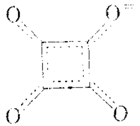
RECEIVED SEPTEMBER 24, 1960

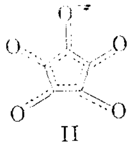
SYMMETRICAL RESONANCE STABILIZED ANIONS,[1] $C_nO_n^{-2}$

Sir:

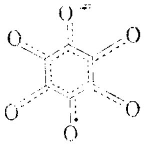
Recently Cohen, Lacher and Park have described the interesting compound diketocyclobutenediol, and have suggested that it ionizes to give the symmetrical resonance-stabilized anion I.[2] We now wish to point out that anion I represents only one member of a general series of symmetrical electron-delocalized anions, $C_nO_n^{-2}$, salts of which may be considered as a new class of aromatic substances. We also wish to report observations on the next two higher members of the series, $C_5O_5^{-2}$ (II) and $C_6O_6^{-2}$ (III).



I



II



III

A symmetrical structure for the dianion of croconic acid, $C_5O_5^{-2}$, already has been proposed by Japanese workers on the basis of the infrared spectra of croconate salts.[3] Definite evidence for the symmetrical structure is now available from Raman spectral measurements. Five lines were observed in the Raman spectrum of an aqueous solution of dilithium croconate: polarized lines at 1718 and 641 cm.$^{-1}$, and depolarized lines at 1584, 1241, and 556 cm.$^{-1}$. The totally symmetrical (D_{5h}) structure should have six Raman active fundamentals, two polarized and four depolarized. Our results are inconsistent with any structures in which all the oxygen atoms are not equivalent, since such anions should have a minimum of nineteen Raman-active fundamental modes. Thus the croconate ion must have the fivefold symmetrical structure, II. in aqueous solution.

An anion $C_6O_6^{-2}$ is produced by ionization of the analytical indicator rhodizonic acid, $H_2C_6O_6$. The Raman spectrum of the rhodizonate anion was not determined on account of its deep orange color. However, the symmetrical aromatic structure (III) for this anion seems probable because of the similarity of the infrared spectrum to that of croconate anion. Like the dipotassium salt of I, both rhodizonate and croconate salts have no infrared absorption in the usual carbonyl region, but instead show a very strong and broad band centered near 1500 cm.$^{-1}$.[4]

Qualitative observations suggest that stabilization of the dianion relative to its acid decreases from $C_4O_4^{-2}$ to $C_5O_5^{-2}$ to $C_6O_6^{-2}$. Thus for instance the dissociation constants for the acids decline in this order.[5] Preliminary LCAO molecular orbital calculations[7] of the delocalization energy in symmetrical anions $C_nO_n^{-2}$ have been carried out, considering only interactions between adjacent atoms. Results indicate that the total delocalization energy increases as ring size increases from $C_3O_3^{-2}$ to $C_8O_8^{-2}$. However, delocalization energy *per atom* decreases in the same sequence. The unknown anion $C_3O_3^{-2}$ is predicted to have an

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(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 49(638)-285. Reproduction in whole or part is permitted for any purpose of the United States Government.

(2) S. Cohen, J. R. Lacher and J. D. Park, THIS JOURNAL, **81**, 3480 (1959).

(3) K. Yamada, N. Mizuno and Y. Hirata, *Bull. Chem. Soc. Japan*, **31**, 543 (1958); A. Washino, K. Yamada and Y. Kurita, *ibid.*, **31**, 552 (1958).

(4) An X-ray crystallographic investigation of the structure of dipotassium rhodizonate now is being carried out by L. F. Dahl and M. Neuman of these laboratories.

(5) Values of pK_1 and pK_2: for $H_2C_4O_4$,[2] ~ 1 and 2.2; for $H_2C_5O_5$,[6] 2.17 and 4.0; and for $H_2C_6O_6$,[6] 3.15 and 4.9.

(6) E. Carpeni, *J. chim. phys.*, **35**, 208 (1938); G. Schwarzenbach and H. Sutler, *Helv. chim. acta.*, **24**, 617 (1941).

(7) J. D. Roberts, A. Streitweiser, Jr., and C. M. Regan, THIS JOURNAL, **74**, 4579 (1952), to which the reader is referred for additional references to the method. Coulomb integrals for C and O were taken as α and $\alpha + 2\beta$, and resonance integrals for C–C and C–O as β and $\sqrt{2}\beta$, respectively, following R. D. Brown, *Quart. Revs.*, **6**, 63 (1952). See also E. J. Smutny, M. C. Caserio and J. D. Roberts, THIS JOURNAL, **82**, 1793 (1960).

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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RECEIVED OCTOBER 26, 1960

A NEW SYNTHESIS OF PHOSPHORODITHIOATE ESTERS

Sir:

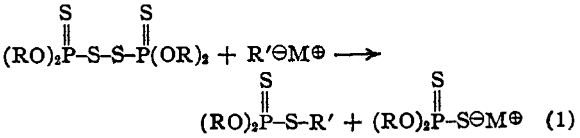
Esters of O,O-dialkyl phosphorodithioic acids are of marked interest because of their exceptional insecticidal properties and low mammalian toxicity.[1] S-Alkyl esters have been obtained by alkylation of salts of the acids[2] or addition of the acids to double bonds,[1a] while S-aryl phosphorodithioates 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.

TABLE I

PREPARATION OF O,O-DIALKYL PHOSPHORODITHIOIC ESTERS



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

R	R'	M	Yield (% $(RO)_2\overset{\overset{S}{\|}}{P}$-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	$C{\equiv}CPh$	Li	72	85–89[a]	0.01	1.592

[a] Evaporation temp. during molecular distillation.

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.

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RECEIVED OCTOBER 10, 1960

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[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.

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

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[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.