

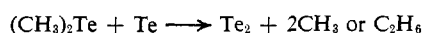
ference from the cracking pattern of the parent DMT. In 50 msec little decay had taken place.

The addition of ground-state tellurium atoms to olefins to form short-lived adducts resembles the behavior of selenium atoms which also form short-lived adducts with olefins.<sup>4-7</sup>

Some quantitative rate measurements were also carried out. Relative concentrations of  $\text{Te}(^3\text{P}_2)$  atoms were estimated by photometry of the 2143- and 2259-Å absorption lines. A Beer-Lambert factor of  $0.5 \pm 0.1$  has been established for the atomic transitions, relating changes in optical density to atomic concentrations.

Atomic decay has been investigated with various chaperons in the pressure range 30–300 Torr. Hydrogen,  $\text{CH}_4$ , and *i*- $\text{C}_4\text{H}_{10}$  were found to be efficient in bringing about spin-orbit relaxation of excited atoms,<sup>12</sup> while  $\text{O}_2$ ,  $\text{CO}_2$ , and Ar were much less efficient. The excitation energies of the  $^3\text{P}_0$  and  $^3\text{P}_1$  states of Te are 4707 and 4751  $\text{cm}^{-1}$ , respectively, and since  $\omega_e$  for  $\text{H}_2$  is 4395  $\text{cm}^{-1}$ , the high relaxation efficiency of  $\text{H}_2$  may be attributed to a resonance effect.

The decay of ground-state atoms has been found to be first order in all cases studied and the rate (in the absence of olefins) to be dependent on the concentration of DMT. Plate photometry showed the concentration of DMT to be constant throughout the atomic decay and was used to estimate the absolute concentration. A plot of the first-order rate constant in a variety of inert gases against DMT pressure during the decay was found to be a straight line passing through the origin. The second-order rate constant obtained was  $1.7 \times 10^{11}$  l. mole<sup>-1</sup> sec<sup>-1</sup>. This corresponds to a reaction between tellurium atoms and DMT at virtually every collision. The reaction implied would appear to be



or the formation of an intermediate adduct which may then decompose to these products.

The presence of an olefin accelerates the atomic decay. From the observed rate increase it was possible to derive rate constants for the addition reactions, olefin

(12)  $\text{Te}(^3\text{P})$  atoms would not be expected to attack paraffins or hydrogen, and no evidence has been found for such reactions.

+ Te  $\rightarrow$  epitelluride, for ethylene and propylene. These, along with the corresponding values for other members of the group, are shown in Table I. All rate

Table I

	O( <sup>3</sup> P)	S( <sup>3</sup> P)	Se( <sup>3</sup> P)	Te( <sup>3</sup> P)
$k_{\text{C}_2\text{H}_4}$	$3 \times 10^{10a}$ $6 \times 10^{10b}$	$7 \times 10^{10c}$	$1 \times 10^{10e}$	$2 \times 10^7$
$k_{\text{C}_2\text{H}_6}/k_{\text{C}_2\text{H}_4}$	5.8 <sup>a</sup>	6.8 <sup>d</sup>	3.5 <sup>e</sup>	10

<sup>a</sup> Reference 2. <sup>b</sup> Reference 13. <sup>c</sup> Reference 14. <sup>d</sup> Reference 3. <sup>e</sup> References 4–7.

constants are in units of l. mole<sup>-1</sup> sec<sup>-1</sup>. From the data, the Te atom addition is somewhat slower than the addition of O, S, or Se atoms and it is also more selective.

As an alternative source of tellurium atoms the flash photolysis of  $\text{H}_2\text{Te}$  has been briefly examined. Ground-state and spin-orbit excited Te atoms were observed along with  $\text{Te}_2$ . The 2750–2850-Å band progression was absent. A new transient species absorbing at about 2155 Å has been detected. The spectrum shows considerable rotational fine structure and may be due to the  $\text{TeH}$  radical.

Both first- and second-order plots of the atom decay showed curvature consistent with a transition from an initial second-order process for the removal of atoms to a first-order process.

A standard flash photolysis apparatus was employed. Spectra were recorded with a medium quartz spectrograph on Kodak 103a-O plates sensitized for the far-uv by sodium salicylate and developed for 4 min in Kodak D19 developer. Plates were photometered on a Joyce-Loebl Mark III recording microdensitometer.

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(13) L. Elias, *J. Chem. Phys.*, **38**, 989 (1963).

(14) R. J. Donovan, unpublished results.

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## Additions and Corrections

**Structure of Chlorophyll *c*** [*J. Am. Chem. Soc.*, **88**, 5037 (1966)]. **Structure of Phycocyanobilin** [*J. Am. Chem. Soc.*, **89**, 3642 (1967)]. **A Perturbation Molecular Orbital Approach to the Interpretation of Organic Mass Spectra. The Relationship between Mass Spectrometric, Thermolytic, and Photolytic Fragmentation Reactions** [*J. Am. Chem. Soc.*, **90**, 5780 (1968)]. **Application of the Perturbation Molecular Orbital Method to the Interpretation of Organic Mass Spectra. The Hexahelicene Rearrangement and Other Electrocyclic Mass Spectrometric Reactions** [*J. Am. Chem. Soc.*, **90**, 5788 (1968)]. **Negative Ion Mass Spectra of Benzene, Naphthalene, and Anthracene. A New Technique for**

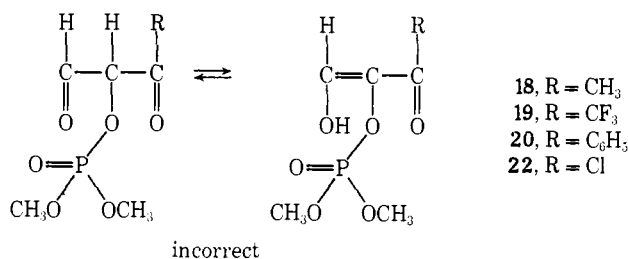
**Obtaining Relatively Intense and Reproducible Negative Ion Mass Spectra** [*J. Am. Chem. Soc.*, **90**, 6570 (1968)]. By R. C. DOUGHERTY, *et al.*, Evans Laboratory of Chemistry, The Ohio State University, Columbus, Ohio 43210.

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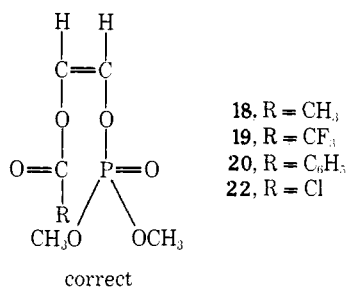
**Synthesis of Sugar-like Phosphates by the Oxyphosphorane Condensation. Reaction of Glyoxal with Trialkyl Phosphites and Preparation of Phosphate Esters**

of Glycoaldehyde,  $\alpha$ -Hydroxy  $\beta$ -Keto Aldehydes, and Hydroxymalonaldehyde Chloride [*J. Am. Chem. Soc.*, **91**, 496 (1969)]. By FAUSTO RAMIREZ, S. L. GLASER, A. J. BIGLER, and J. F. PILOT, Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11790.

The products of the reaction of 2,2,2-trimethoxy-2,2-dihydro-1,3,2-dioxaphospholene, **7** (made from glyoxal and trimethyl phosphite), with acetyl chloride, trifluoroacetyl chloride, benzoyl chloride, and phosgene,  $\text{COCl}_2$ , were formulated as oxo-enol tautomers of phosphate esters of  $\alpha$ -hydroxy  $\beta$ -keto aldehydes and hydroxymalonaldehyde chloride, respectively, **18**, **19**, **20**, and **22**.



These structural assignments are incorrect. The substances should be formulated as *phosphate-carboxylate esters of the enediol tautomer of glycolaldehyde*



The experimental data in Tables I and II remain valid, but the speculations contained in the section entitled Spectral Characteristics of the Hydroxy Aldehyde Phosphates are invalid when they apply to formulas **18**, **19**, **20**, and **22**. The new formulations are consistent with the published data and with other information to be published. The remaining experimental data and discussion in the paper, pertaining to the phospholene **7** and to the phosphoglycolaldehyde **11** ("diose phosphate"), are not affected by this correction.

The *glyoxal-trimethyl phosphite adduct*, **7**, undergoes mainly O-acylation by acid chlorides and by phosgene. In contrast, the *biacetyl-trimethyl phosphite adduct*, **3**, undergoes C-acylation by acid chlorides and by phosgene, as stated in this paper and as demonstrated in a previous one [cf. F. Ramirez, S. B. Bhatia, A. J. Bigler, and C. P. Smith, *J. Org. Chem.*, **33**, 1192 (1968)]. The incorrect formulation resulted from the unwarranted assumption that the unsubstituted and the substituted phospholenes, **7** and **3**, reacted with the acid chlorides by the same mechanism under the same conditions.

**Chemical Synthesis and Structure Proof of a Stereoregular Linear Mannan, Poly- $\alpha$ -(1 $\rightarrow$ 6')-anhydro-D-mannopyranose** [*J. Am. Chem. Soc.*, **91**, 1161 (1969)]. By JEAN FRECHET and CONRAD SCHUERCH, Chemistry Department, State University College of Forestry, Syracuse, New York 13210.

In Table I, the column headed "monomer solvent ratio" should read "[monomer]  $\times$  100/[solvent] ratio."

**Thermal Reactions of Sulfonyl Azides** [*J. Am. Chem. Soc.*, **91**, 2273 (1969)]. By DAVID S. BRESLOW, MARTIN F. SLOAN, NORMAN R. NEWBURG, and WILLIAM B. RENFROW, Research Center, Hercules Inc., Wilmington, Delaware 19899.

In Table V, the gas evolved from *p*-toluenesulfonyl azide should read 102%.

**The Solid-State Structure of Monothiodibenzoylmethanato- $\pi$ -methallylpalladium(II)** [*J. Am. Chem. Soc.*, **91**, 2504 (1969)]. By STEPHEN J. LIPPARD and SHEILA M. MOREHOUSE, Department of Chemistry, Columbia University, New York, New York 10027.

In Table I, the *x* coordinate of C15 was published as 0.460; it should be  $-0.460$ . All calculations reported in the paper were done using the correct value. We thank Dr. W. Todd Wipke for drawing this to our attention.

**Variable-Temperature Proton Resonance Spectra of Trihaptocycloheptatrienylmetal Complexes** [*J. Am. Chem. Soc.*, **91**, 3089 (1969)]. By M. A. BENNETT, R. BRAMLEY, and R. WATT, Research School of Chemistry, Australian National University, Canberra, Australia.

In footnote *f* of Table I it was stated that the assignment of protons  $H_4$  and  $H_3$  in  $\text{C}_8\text{H}_8\text{Fe}(\text{CO})_3$  in ref 7 [R. Grubbs, R. Beslow, R. Herber, and S. J. Lippard, *J. Am. Chem. Soc.*, **89**, 6864 (1967)] differed from the assignment in ref 8 [W. K. Bratton, F. A. Cotton, A. Davison, A. Musco, and J. W. Faller, *Proc. Natl. Acad. Sci. U. S.*, **58**, 1324 (1967)], and that we followed the latter. This is incorrect; ref 7 and 8 are in complete agreement, and we follow the assignment of both. Footnote *f* therefore should be disregarded.

**Generation of Aryl Nitrenes in the Presence of Acetic Acid by Deoxygenation of Aromatic Nitro and Nitroso Compounds** [*J. Am. Chem. Soc.*, **91**, 3392 (1969)]. By RICHARD J. SUNDBERG, RICHARD H. SMITH, JR., and JOHN E. BLOOR, Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901.

The legend below should accompany the structural formulas on page 3392: a,  $R_1, R_2 = \text{H}$ ; b,  $R_1 = \text{CH}_3, R_2 = \text{H}$ ; c,  $R_1 = \text{H}, R_2 = \text{CH}_3$ ; d,  $R_1, R_2 = \text{CH}_3$ .

**Interactant Structure and Complex Stability for Complexes of Theophylline with Cinnamate Esters and Related Compounds in Aqueous Solution** [*J. Am. Chem. Soc.*, **91**, 3597 (1969)]. By KENNETH A. CONNORS, MARTIN H. INFELD, and BERRY J. KLINE, School of Pharmacy, University of Wisconsin, Madison, Wisconsin 53706.

The estimated planar areas in Table II, Figure 4, and Figure 5 are too large by a factor of 2.43. This was a consequence of a scaling factor error. We are indebted to Mr. Harald Christiansen for calling this to our attention.