

positively rotating than the 1A_2 is negatively rotating. Woldbye⁷ has pointed out possible effects of conformation on the circular dichroism. With support from the point dipole model of Shinada and Sugano,⁸ which predicts the 1A_2 component to be nonrotating, he suggests that the 1E component may have opposite signs in the lel and ob conformations and that the small negative component may indicate the presence of at least two conformational isomers.

We have measured the circular dichroism of $\text{Co}(\text{en})_3^{3+}$ in solution at 17 and 65°. At 65° the bands are a bit broader; the integrated dichroism of the positive component is unchanged while that of the weaker negative component decreases by 9%. These data would seem to prove that the weak negative component is not due to less stable conformers although interpretation is difficult in view of the small changes in enthalpy and broadening of overlapping bands.

In order to discover the effect of conformation on the optical activity, we have studied some substituted diamines in which the rings are forced to adopt known conformations in cobalt complexes of known absolute configuration designated by Δ and Λ . We have characterized the isomers (+)- $\text{Co}(l\text{-chn})_3^{3+}$ and (-)- $\text{Co}(l\text{-chn})_3^{3+}$ (chn = *trans*-1,2-diaminocyclohexane)⁹ which are analogous to the corresponding isomers of propylenediamine¹⁰ but which have a higher symmetry D_3 . In Table II we list the data obtained on these compounds as well as some en and *d*-pn derivatives.

TABLE II
CIRCULAR DICHRISM DATA AT 25°

Compound	Configuration	$\Delta\epsilon_{\text{max}}$	λ_{max} , m μ
(+)- $\text{Co}(\text{en})_3\text{Cl}_3$	Λ	+1.76	491
		-0.15	430
		+0.23	350
(+)- $\text{Co}(d\text{-pn})_3\text{Cl}_3$	Λ , lel	+2.12	494
		-0.63	440
		+0.16	345
(-)- $\text{Co}(l\text{-chn})_3\text{Cl}_3$	Δ , lel	-2.28	500
		+0.69	443
		-0.18	350
(+)- $\text{Co}(l\text{-chn})_3\text{Cl}_3$	Λ , ob	+3.90	480
		-0.07	345

The most striking aspect of these data is the marked increase in the magnitude of the dichroism near 430 m μ for the lel isomers over that of $\text{Co}(\text{en})_3^{3+}$. We conclude that this weak band is characteristic of the lel isomers, and we reaffirm the earlier suggestion that both trigonal components are active. The relative magnitudes of the two visible bands suggest increased trigonal splitting in the order en, pn, chn. This is just the order of increasing pucker in the ring due to substitution.

The single ob isomer available shows no band

(7) F. Woldbye, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **24**, 197 (1963).

(8) M. Shinada and S. Sugano, unpublished work presented at International Symposium on Molecular Structure and Spectroscopy, Tokyo, Sept., 1962.

(9) T. S. Piper, to be published. One of these isomers had been prepared by F. P. Jaeger and L. Bijkerk, *Z. anorg. allgem. Chem.*, **233**, 97 (1937).

(10) F. P. Dwyer, T. E. MacDermott, and A. M. Sargeson, *J. Am. Chem. Soc.*, **85**, 2913 (1963); F. P. Dwyer, F. L. Garvan, and A. Shulman, *ibid.*, **81**, 290 (1959).

splitting, and therefore the trigonal field constant K must be very close to zero. From the sign of the band in the ultraviolet and our trigonal field theory, we conclude that K is, in fact, positive—the opposite sign from that deduced for the lel isomers.^{6,11} Note that the sign of the rotation does not change with the transformation lel \rightarrow ob since by inference from Table II the Δ ,ob form is net negatively rotating.

Now we may comment on the dichroism of $\text{d-Co}(\text{en})_3^{3+}$ ion in solution. The fact that the band at 430 m μ is relatively weaker is probably related in part to the presence of less stable conformers as well as to a smaller trigonal splitting. If the mixed conformers are all net positively rotating with decreasing trigonal splitting in the series lel to ob, then a ready explanation of the temperature dependence of the circular dichroism is provided.

(11) Our provisional theory predicts $\Delta\epsilon$ at 350 m μ to be proportional to K . This seems to hold for all compounds in Table II but $\text{Co}(\text{en})_3\text{Cl}_3$.

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The Alkylation of Elemental Phosphorus

Sir:

The chemical literature relating to the synthesis of organophosphorus compounds has been expanding rapidly in recent years. However, a surprisingly small effort has been devoted to the preparation of these substances from elemental phosphorus. White (or yellow) phosphorus is known to exist¹ as a P_4 molecule which is in a tetrahedral configuration containing an atom of phosphorus and an unshared pair of electrons at each apex. It, therefore, seems logical to expect that this allotrope of phosphorus would be subject to attack by electrophilic reagents such as carbonium ions, although no mention of this type of reaction could be located in the literature. This communication reports the results of studies which show that white phosphorus will react with alkyl carbonium ions to produce organophosphorus compounds.

A solution of white phosphorus in carbon disulfide and 1 molar equiv. (based on phosphorus) of aluminum chloride were cooled with stirring to -10° in a pressure bottle under an atmosphere of hydrogen chloride. Upon the dropwise addition of 1.5 molar equiv. of *t*-butyl chloride, a new red liquid layer formed. The upper solvent layer no longer contained any trace of elemental phosphorus, and the lower red liquid contained neither elemental phosphorus nor aluminum chloride *per se*. The reaction mixture was poured into ice-cold 4 *N* nitric acid (or cold 30% hydrogen peroxide), and the organic layer was separated, dried, and the solvent was removed at room temperature under a stream of nitrogen. From the resulting orange oil, a 30% yield of white crystalline di-*t*-butylphosphinic chloride (I) could be sublimed at 35° and 1 mm. After further purification by sublimation its m.p. was $80.1\text{--}80.9^\circ$. The compound was identical, as shown by n.m.r.,

(1) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1958, p. 96.

mass spectrum, infrared (Nujol and in carbon tetrachloride), and mixture melting point comparison with a sample prepared independently by oxidation with 30% hydrogen peroxide of the reaction mixture obtained from *t*-butylmagnesium chloride (2 moles) and phosphorus trichloride (1 mole).²

Anal. Calcd. for $C_8H_{18}ClOP$: C, 48.86; H, 9.23; Cl, 18.03; P, 15.75. Found: C, 48.84; H, 9.23; Cl, 18.02; P, 15.57.

The mass spectrum of compound I, determined at approximately 10 e.v. with an ionizing current of 20 μ a., showed significant peaks at $m/e = 198$ and 196 (molecular weight ions) in the correct relative intensities for the chlorine isotopic distribution, and two large fragmentation peaks at 139 and 141 which arise from the loss of one *t*-butyl group from the parent compound.

The proton magnetic resonance spectrum of I, obtained on a Varian A-60 instrument in carbon tetrachloride solution, showed only a doublet at 1.25 and 1.52 p.p.m. downfield from tetramethylsilane. The observed J_{P-H} of 17 c.p.s. is in excellent agreement with assigned values obtained^{3a,b} from more complex spectra.

A second product isolated from the alkylation of white phosphorus with *t*-butyl chloride was identified as di-*t*-butylphosphine oxide⁴ by its infrared spectrum (P—H, 2300 cm^{-1} , s; P=O, 1150 cm^{-1} , vs; in Nujol), its mass spectrum ($m/e = 162$ and 105), and by oxidation with air or bromine to di-*t*-butylphosphinic acid, m.p. 208–209.5° (lit.² 208–210°), $m/e = 178$. The factors determining the relative amounts of these two alkylation products have not yet been completely established.

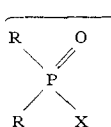
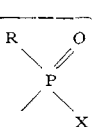
Other alkyl halides and Lewis acids also alkylate elemental phosphorus. With *t*-butyl bromide and aluminum tribromide, di-*t*-butylphosphinic bromide (II), m.p. 98–99°, was obtained. The structure of II was established by its mass spectrum, which had significant peaks at $m/e = 240$ and 242 (molecular weight ions), 183 and 185 (molecular weight ions minus one *t*-butyl group), with both sets of relative intensities having the correct bromine isotopic ratio, by identical infrared spectra in Nujol and an undepressed mixture melting point with a sample prepared unambiguously from phosphorus tribromide and *t*-butylmagnesium bromide by a procedure similar to that utilized for compound I. The n.m.r. spectrum of II was identical with that of I. Ferric chloride and titanium tetrachloride also effected alkylation of white phosphorus with *t*-butyl chloride although much lower yields of I (about 3%) were obtained. Zinc chloride, zirconium tetrachloride, and mercuric chloride gave no alkylation under these conditions.

The alkylation of white phosphorus with *t*-amyl chloride gave di-*t*-amylphosphinic chloride ($m/e = 224, 226; 153, 155$), di-*t*-butylphosphinic chloride ($m/e = 196, 198; 139, 141$), and *t*-amyl-*t*-butylphosphinic chloride ($m/e = 210, 212; 153, 155; 139, 141; 71$) as well as the corresponding secondary phosphine

oxides. Several recent papers^{5–7} and older literature³ report similar disproportionations with *t*-amyl chloride and other tertiary chlorides under the influence of aluminum trichloride.

White phosphorus may be alkylated with other alkyl chlorides. For example, in the presence of aluminum chloride the elemental phosphorus was entirely consumed upon the addition of 1.5 moles of either isopropyl, *n*-butyl, cyclohexyl, or *n*-octyl chlorides. The mass spectra of the crude acid hydrolysis products showed significant peaks at the m/e of the corresponding phosphinic acids since these phosphinic halides, if formed, would be destroyed by the acid hydrolytic work-up procedure employed. The major m/e values obtained from the crude organic product in each of these instances are shown in Table I. In all cases,

TABLE I

R	X	m/e	
			
<i>t</i> -C ₄ H ₉	Cl	196, 198	139, 141
<i>t</i> -C ₄ H ₉	Br	240, 242	180, 185
<i>t</i> -C ₄ H ₉	OH	178	121
<i>n</i> -C ₄ H ₉	Cl	196, 198	139, 141
<i>i</i> -C ₃ H ₇	OH	150	107
C ₆ H ₁₁	OH	230	147
<i>n</i> -C ₈ H ₁₇	OH	290	177
<i>t</i> -C ₈ H ₁₇	Cl	224, 226	153, 155

the principal fragmentation observed during the mass spectrographic analysis was the loss of one alkyl group from the parent molecule.

Control experiments run without alkyl halide failed to produce any evidence of the presence of phosphorus chlorides. White phosphorus appears to be unchanged by the action of aluminum chloride under the reaction conditions.

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(5) T. H. Siddall and C. A. Prohaska, *J. Org. Chem.*, **28**, 2908 (1963).

(6) S. H. Metzger, O. H. Basedow, and A. F. Isbell, *ibid.*, **29**, 627 (1964).

(7) G. J. Karabatsos, F. L. Vane, and S. Meyerson, *J. Am. Chem. Soc.*, **85**, 733 (1963).

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1,2-Bis(triphenylphosphoranyl)benzocyclobutene

Sir:

Efforts to obtain isolable derivatives of benzocyclobutadiene (I) as well as dianions of benzocyclobutadienes encouraged an investigation of the preparation and properties of a number of benzocyclobutenes of the type II (R = -NO₂, -P⁺(C₆H₅)₃Br⁻, -SO₂Ar). This communication reports the synthesis of *trans*-1,2-bis(triphenylphosphonium)benzocyclobutene dibromide

(2) P. C. Crofts and G. M. Kosolapoff, *J. Am. Chem. Soc.*, **75**, 3381 (1953).

(3) (a) J. B. Hendrickson, M. L. Maddox, J. J. Sims and H. D. Kaesz, *Tetrahedron*, **20**, 449, (1964); (b) S. L. Manatt, G. L. Juvinall, and D. D. Elleman, *J. Am. Chem. Soc.*, **85**, 2664 (1963).

(4) The yield of this product is not known exactly, but it is estimated from an uncalibrated v.p.c. tracing to be of the same magnitude as the phosphinic chloride.