

tritium distribution. For example, the decomposition of the RCHT· radical in eq. 1 will lead only to terminally tritiated olefins, and the presence of alkyl-tritiated olefins therefore provides evidence for a mechanism other than (1). This procedure has been made experimentally tractable through the development of gas chromatographic techniques capable of distinguishing position isomers of monotritiated olefins, separating the molecules with tritium in alkyl positions from those with it in olefinic positions.⁹

Two major radioactive peaks are found in the isobutene-*t* formed from neopentane, indicative of CH₂T-C(CH₃)=CH₂ and (CH₃)₂C=CHT, as shown in

TABLE I

INTRAMOLECULAR DISTRIBUTION OF TRITIUM IN LABELED OLEFINIC PRODUCTS FROM RECOIL TRITIUM REACTIONS

Product molecule	Parent molecule	Gas pressures, cm.		Yield of total tritium formed, %	Alkyl tritium in olefin, %
		Parent	Scavenger		
Isobutene- <i>t</i>	Neopentane	67	9.8(O ₂)	2.1	47 ± 5
Propylene- <i>t</i>	Neopentane	67	9.8(O ₂)	0.3	8 ± 3
Propylene- <i>t</i>	Isobutane	69	7.1(O ₂)	0.8	33 ± 3
Propylene- <i>t</i>	Propane	67	9.2(O ₂)	0.5	41 ± 5
Propylene- <i>t</i>	Isopropyl chloride	6.4	2.8(O ₂)	4 ^a	49 ± 2
Propylene- <i>t</i>	Isopropyl chloride	37.3	3.0(O ₂)	4 ^a	50 ± 3
Propylene- <i>t</i>	Isopropyl chloride	Liquid	DPPH	1	45 ± 6

^a Intersample comparison shows that the propylene-*t* yield is slightly larger (~10%) at the lower gas pressure.

Table I. The direct, simultaneous replacement of two H atoms, as in eq. 1, cannot account for the presence of the former, and the relative amounts of alkyl and olefinic tritium are consistent with the formation of the bulk of the isobutene-*t* by unimolecular elimination of CH₄ following the primary hot substitution of T for H. An important alkyl-tritiated fraction is also shown in Table I for propylene-*t* from isobutane and from propane, each again indicative of an initial hot reaction involving the displacement of but a single group. (The propylene-*t* from neopentane consists almost entirely of olefinic tritium, presumably CH₃CT=CH₂, as expected by either mechanism.)

The analogous experiment has also been carried out with isopropyl chloride as the target molecule, for which the simultaneous displacement of two H atoms from a group should lead only to CH₃CH=CHT. Two major peaks are found, corresponding to unimolecular elimination of HCl following the T for H primary reaction. Furthermore, the relative amounts of the two peaks are unchanged within the statistical error for all three samples in Table I. The observance of a phase and pressure dependence in the absolute yield of propylene-*t* confirms the existence of the hydrogen halide elimination mechanism. Since no change in per cent alkyl tritium was found for the propylene-*t* in the two phases, the inference can be drawn that the labeled propylene in the liquid phase experiments was also formed by the decomposition of excited molecules with equilibrated energy distributions.

Other examples have been recorded which correspond

(9) E. K. C. Lee and F. S. Rowland, *Anal. Chem.*, **36**, 2181 (1964).

formally to the stoichiometry of eq. 1, such as CH₂T· as a product from reactions with CH₃Cl.^{3,8} Our liquid phase experiments confirm the earlier postulate that decomposition processes (*e.g.*, CH₂TCl* → CH₂T + Cl) are still of significant importance in liquid phase experiments.^{8,10} Although the absolute yields of the labeled products measured in the present experiments are already down to the 1% range, no positive evidence has been found for any simultaneous energetic displacement of two groups by a recoil tritium atom in the formation of these "double-substitution" products. Within the statistical error of the presently available experiments, we therefore conclude that such a reaction is not an important hot process in hydrocarbons and halocarbons.

(10) E. K. C. Lee and F. S. Rowland, *J. Chem. Phys.*, **36**, 554 (1962).

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How Does Conformation of a Chelate Ring Influence the Optical Activity of Metal Complexes?

Sir:

Corey and Bailar¹ have analyzed the conformational isomers of metal ethylenediamine cycles; they have shown that of the conformers of D-Co(en)₃³⁺, one designated Dkkk or lel ought to be the most stable. Dwyer and his co-workers² have shown that an internal rotation in one of the chelate rings to the enantiomorphous conformation k' leads to a free energy increment of 0.6 kcal./mole per ring. The end product of this process is designated Dk'k'k' or ob. In Table I are recorded their

TABLE I

THERMODYNAMIC DATA AT 25°

Conformational change	K	ΔF, kcal./mole	ΔS	ΔH, kcal./mole
Dkkk → Dkkk'	1/2	0.6	R ln 3	1.3
Dkkk → Dkk'k'	1/7	1.2	R ln 3	1.9
Dkkk → Dk'k'k'	1/18	1.8	0	1.8

equilibrium constants and free energy changes² from which we estimate the enthalpies on the basis that the symmetry contribution to the entropy predominates. In aqueous solution a number of conformers ought to exist at comparable equilibrium concentrations.

The circular dichroism of the band of D-Co(en)₃³⁺ in the visible spectrum (¹A₁ → ¹T₁) consists in a dominant positive component and a small negative component in the high energy portion of the band.³ This has been interpreted⁴⁻⁶ in terms of partial resolution of the octahedral degeneracy by the trigonal field into ¹A₂ and ¹E components, the ¹E component being slightly more

(1) E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959).

(2) This research is reviewed by A. M. Sargeson in "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press Inc., New York, N. Y., 1964, p. 183.

(3) J.-P. Mathieu, *J. chim. phys.*, **33**, 78 (1936).

(4) T. S. Piper and A. Karipides, *Mol. Phys.*, **5**, 475 (1962).

(5) A. J. McCaffery and S. P. Mason, *ibid.*, **6**, 359 (1963).

(6) A. G. Karipides and T. S. Piper, *J. Chem. Phys.*, **40**, 674 (1964).

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.