TABLE I

Ether	Yield of RBr, %[a]	Total RBr, %[b]	Alkyl bromide product[c]	B.p., °C.[d]
n-Pentyl	77.8	98.9	n-Pentyl	128–129.5
n-Butyl	71.9	...	n-Butyl	100–101
Allyl	63.4	68.6	Allyl	69–70
Isopropyl	59.2	66.7	Isopropyl	59–60
Tetrahydro-furan	...	75.1	1,4-Dibromo-butane	94–95(14 mm.)

[a] The yield of pure isolated product. The purity was determined by gas chromatographic analysis. [b] Total recovered yield of halide: the yield of pure product plus the percentage of product in other distillation fractions as determined by gas chromatography. [c] Shown by gas chromatography to be identical with an authentic sample. [d] Boiling range of pure product fraction.

A typical reaction was carried out by adding 8.3 g. (0.052 mole) of bromine slowly to a cooled solution of 13.6 g. (0.052 mole) of triphenylphosphine in 50 ml. of benzonitrile. The reaction mixture was heated to 125°, and 7.9 g. (0.05 mole) of n-pentyl ether was then added. The progress of the reaction was followed by gas chromatographic analysis of small samples, and the ether was no longer present after ca. 4 hr. The volatile components of the cooled mixture were separated from the solid triphenylphosphine oxide by vacuum distillation and then redistilled through a 2-ft. column packed with glass helices. The gas chromatogram of the fraction collected at 128–129.5° (11.7 g., 77.8%) showed a single peak with a retention time identical with that of an authentic sample of n-pentyl bromide.

Benzonitrile, acetonitrile, chlorobenzene, dimethylformamide, and 1-methyl-2-pyrrolidone have thus far been used as solvents. A longer reaction time was required with the lower boiling acetonitrile. Rapid darkening of the reaction mixture, the evolution of gas, and the formation of small amounts of unknown side products occurred with dimethylformamide and 1-methyl-2-pyrrolidone, but the yields of halide were essentially the same.

When phenetole was allowed to react with triphenyldibromophosphorane, the reaction seemed to proceed in the normal manner, and ethyl bromide was isolated in 40% yield. The crystalline solid which remained after vacuum distillation was not triphenylphosphine oxide, and, as no volatile product containing the phenyl group was obtained, it is likely that the solid was a compound composed of the unrecovered moieties of the phosphorane and phenetole. This is being investigated.

The ether cleavage reaction is analogous to the single example of the cleavage of tetrahydrofuran by triphenoxydibromophosphorane,[2] and similar to conversion of alcohols to alkyl halides with alkylhalotriphenoxyphosphoranes,[3] and more recently with tertiary phosphine dihalides.[4] In agreement with the findings in these studies, we have noted no rearrangements thus far. It is noteworthy that the unsaturation in allyl ether was not affected by the phosphorane reagent.

(2) A. Zamojski, Chem. Ind. (London), 117 (1963).

(3) S. R. Landauer and H. N. Rydon, J. Chem. Soc., 2224 (1953); D. G. Coe, S. R. Landauer, and H. N. Rydon, ibid., 2281 (1954); 1. T. Harrison and B. Lythgoe, ibid., 843 (1958); J. W. Cornforth, R. H. Cornforth, and K. K. Mathews, ibid., 112 (1959); S. R. Landauer and H. N. Rydon, ibid., 2224 (1963).

(4) G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, J. Am. Chem. Soc., 86, 964 (1964); G. A. Wiley. B. M. Rein, and R. L. Hershkowitz, Tetrahedron Letters. No. 36, 2509 (1964).

Further investigations in these laboratories will cover other aspects of molecular rearrangements, and the scope, stereochemistry, and synthetic possibilities of this new reaction.

Acknowledgment.—The support of this research in part by a grant from the Petroleum Research Fund of the American Chemical Society is gratefully acknowledged.

DEPARTMENT OF CHEMISTRY   ARTHUR G. ANDERSON, JR.
UNIVERSITY OF WASHINGTON   FRANCIS J. FREENOR
SEATTLE, WASHINGTON   98105

The Mechanism of Recoil Tritium Reactions. Formation of Labeled Alkenes from Saturated Hydrocarbons and Halocarbons[1]

Sir:

The substitution of recoil tritium atoms onto the carbon skeleton of many saturated hydrocarbons or halocarbons leads to significant yields of various labeled olefins.[2–4] A possible mechanistic explanation for these products is the simultaneous replacement of two groups in the primary energetic process, as in eq. 1,

$$T + RCHAB \rightarrow RCHT\cdot + A + B \text{ (or AB)} \quad (1)$$
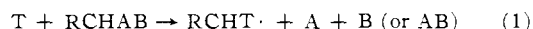
followed by decomposition of the excited radical through loss of an H atom or a small radical.[2,5] Alternatively, the mechanism could involve the replacement of a single group in the primary process, followed by the unimolecular elimination of a small molecule from the excited labeled product. The key difference between these mechanisms is involved in the question of simultaneity of loss of A and B; for the loss of both to be part of the same hot process, the two groups should be eliminated within the period of a single vibration or less. However, if a time delay of several vibrations or longer occurred between the loss of A and that of B (or of the small molecule containing it), then the primary reaction would be best described as a single-group replacement.

Time delays characteristic of competition between unimolecular reaction and collisional stabilization have been detected in other recoil tritium systems by carrying out measurements at various gas pressures.[6–8] This procedure has the disadvantage that it does not provide any information about that fraction of a product observed in liquid phase experiments, and further can involve the measurement of rather small differences for gas phase products of lesser yields, such as most olefins from hydrocarbons. In certain cases, however, the separate loss of the groups A and B can be established through determination of the intramolecular

(2) D. Urch and R. Wolfgang, J. Am. Chem. Soc., 83, 2982 (1961).

(3) R. Odum and R. Wolfgang, ibid., 85, 1050 (1963).

(4) Y. N. Tang, F. Schmidt-Bleek, and F. S. Rowland, unpublished results.

(5) R. Wolfgang, "The Hot-Atom Chemistry of Gas Phase Systems," NYO-1957-50, to appear as a chapter in "Progress in Reaction Kinetics," Vol. III.

(6) J. K. Lee, B. Musgrave, and F. S. Rowland, Can. J. Chem., 38, 1756 (1960).

(7) E. K. C. Lee and F. S. Rowland, J. Am. Chem. Soc., 85, 897 (1963).

(8) Y. N. Tang, E. K. C. Lee, and F. S. Rowland, ibid., 86, 1280 (1964).

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 $CH_2T\text{-}C(CH_3)\!=\!CH_2$ and $(CH_3)_2C\!=\!CHT$, as shown in

TABLE I

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

Product molecule	Parent molecule	Gas pressures, cm. Parent	Scavenger	Yield of total tritium formed, %	Alkyl tritium in olefin, %
Isobutene-t	Neopentane	67	9.8(O_2)	2.1	47 ± 5
Propylene-t	Neopentane	67	9.8(O_2)	0.3	8 ± 3
Propylene-t	Isobutane	69	7.1(O_2)	0.8	33 ± 3
Propylene-t	Propane	67	9.2(O_2)	0.5	41 ± 5
Propylene-t	Isopropyl chloride	6.4	2.8(O_2)	4[a]	49 ± 2
Propylene-t	Isopropyl chloride	37.3	3.0(O_2)	4[a]	50 ± 3
Propylene-t	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 CH_4 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 $CH_3CT\!=\!CH_2$, 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 $CH_3CH\!=\!CHT$. 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 CH_2T· as a product from reactions with CH_3Cl.[3,8] Our liquid phase experiments confirm the earlier postulate that decomposition processes (e.g., $CH_2TCl^* \rightarrow CH_2T + Cl$) 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).
(11) Department of Chemistry, University of California, Irvine, Calif.

UNIVERSITY OF KANSAS　　　　　　EDWARD K. C. LEE
LAWRENCE, KANSAS　　　　　　　　　　　Y. N. TANG
　　　　　　　　　　　　　　　　　F. S. ROWLAND[11]

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

Sir:

Corey and Bailar[1] have analyzed the conformational isomers of metal ethylenediamine cycles; they have shown that of the conformers of $D\text{-}Co(en)_3{}^{3+}$, one designated Dkkk or lel ought to be the most stable. Dwyer and his co-workers[2] 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 changes[2] 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 $D\text{-}Co(en)_3{}^{3+}$ in the visible spectrum ($^1A_1 \rightarrow {}^1T_1$) consists in a dominant positive component and a small negative component in the high energy portion of the band.[3] This has been interpreted[4–6] in terms of partial resolution of the octahedral degeneracy by the trigonal field into $^1A_2$ 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. F. Mason, ibid., 6, 359 (1963).
(6) A. G. Karipides and T. S. Piper, J. Chem. Phys., 40, 674 (1964).