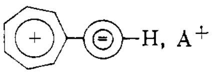
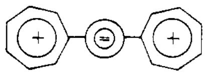
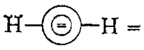
Reaction of hydronium decahydrodecaborate[3] with excess tropenium bromide in aqueous solution gives a heavy maroon precipitate and a red-orange solution; this solution contains a 7.2% yield of hydronium tropenylium nonahydrodecaborate (I).[2b] Concentration of this solution followed by treatment with cesium chloride yields 69% cesium tropenylium nonahydrodecaborate (II) as orange plates, no melting point or decomposition below 360°; ultraviolet and visible spectrum (water): λ_{max} 217 (ϵ 39,400), 262 (10,900), and 439 (13,600) mμ.


I, $A^+ = H_3O^+$
II, $A^+ = Cs^+$


III


= $B_{10}H_{10}^{2-}$

Anal. Calcd. for $C_7H_{15}B_{10}Cs$: C, 24.70; H, 4.44; B, 31.79. Found[4]: C, 24.39; H, 4.54; B, 31.95.

We have assigned the structure shown for this compound on the basis of the following observations: (1) the electronic spectrum is not that of a tropenium salt[5] but strongly resembles that of a substituted tropenium ion,[6] (2) the compound fails to give tropenium ion when extracted with 96% sulfuric acid but instead dissolves slowly to give a spectrum similar to that in water, (3) the long wave-length absorption—which we ascribe to electron transfer from the boron cage to the carbon ring in an internal charge transfer[8]—shows a strong hypsochromic shift with increasing solvent polarity (see Table I) which indicates a transition from a more polar to a less polar state on absorption of light which is hindered by solvation of a polar ground state, and (4) the infrared spectrum is in accord with the proposed structure; the B–H stretching band (2430 cm.$^{-1}$) has two shoulders (2520 and 2350 cm.$^{-1}$) and is not split as it is in the decahydrodecaborate anion, the boron cage bands (1010 and 975 cm.$^{-1}$) are diminished relative to the B–H compared to the free anion, and the C–H stretching (2920 (vw) and 2850 (sh) cm.$^{-1}$) and C–C single and double bond bands (1602 (w), 1493–1474 (s), 1429 (mw), 1358 (mw), 1277 (w), 1230 (m), and 1182 (m) cm.$^{-1}$) strongly resemble the pattern of tropone,[9] an electronically similar compound. Examination of the infrared spectra of tropenium ion, halotropenium ions, tropone, and II indicates that double bonding from ring to substituent is important in both II and tropone, but is less so in II.

TABLE I

Solvent	Absorption bands of II, mμ		
CH_3CN	222	265	513
50% CH_3CN–H_2O	221	263	485
H_2O	217	262	439
12 *N* HCl	217	262	427
96% H_2SO_4	217	262	373

The acid I is an orange oil which has electronic and infrared spectra similar to that of II except for the inclusion of O–H bands in the infrared. We believe that it is formed by electrophilic attack of tropenium ion on decahydrodecaborate anion followed by hydride transfer from the cycloheptatrienyl nonahydrodecaborate ion so formed to tropenium ion; at least 1 mole of cycloheptatriene per mole of original decahydrodecaborate anion can be isolated from the reaction solution. Reaction of II with additional tropenium bromide in aqueous solution gives cycloheptatriene and maroon crystals believed to be bistropenylium octahydrodecaborate (III). This material is remarkably thermally stable and is insoluble in most solvents (slightly soluble in dimethyl sulfoxide). The infrared spectrum of III is very similar to that of II; however, the cage absorption is missing, the B–H band is a symmetrical spike, and the ratio of C–C double bond intensity to B–H intensity is 1.75 compared to 0.77 in II. Further characterization of this compound is in progress.

The precipitated material which represents the major product in the reaction of tropenium ion with hydronium decahydrodecaborate appears to contain both carbonaceous material and polymeric acids of $-C_7H_6-B_{10}H_8-$ chain anions. When these are largely removed by continuous extraction with acetonitrile, a uniform maroon powder results with an infrared spectrum identical with that of III. Further purification and characterization is in progress.

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[3] Prepared from triethylammonium decahydrodecaborate generously furnished by M. Frederick Hawthorne.

[4] Analysis by Schwarzkopf Microanalytical Laboratory.

[5] W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **76**, 3202 (1954), report the spectrum of tropenium ion in water as λ_{max} 275 (4350) and 280 (sh) mμ; we find that the decahydrodecaborate anion only shows end absorption.

[6] H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, and D. L. Pearson (*ibid.*, **79**, 4557 (1957)) and H. J. Dauben, Jr., and K. M. Harmon (unpublished work in Ph.D. Thesis of K. M. H., University of Washington, 1958) report, for example, the spectrum in 96% sulfuric acid[7] of thiomethoxytropenium ion as λ_{max} 220 (ϵ 19,500), 259 (14,400), and 383 (16,500) mμ and of iodotropenium ion as λ_{max} 216 (ϵ 23,200), 263 (9300), 335 (sh), and 378.5 (5060) mμ.

[7] In cases where the ion is stable in water, the spectra of tropenium ions in water and sulfuric acid are similar.

[8] Similarly, examination of the shape and splitting of the long wave-length band of iodotropenium ion indicates that it arises from n–π* electron transfer from substituent to ring.

[9] Y. Ikegami, *Bull. Chem. Soc. Japan*, **35**, 967 (1962), gives the most detailed analysis of the infrared spectrum of tropone.

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The Cleavage of Ethers by Triphenyldibromophosphorane

Sir:

We report herein a new method of ether cleavage which has obvious advantages over the strongly acidic conditions commonly, or the strongly basic conditions[1] sometimes employed. The reagent of our method is triphenyldibromophosphorane, and the over-all reaction of this with aliphatic ethers may be summarized by the equation

$$ROR + Ph_3PBr_2 \rightarrow 2RBr + Ph_3PO$$

Illustrative results are given in Table I.

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[1] For example, dialkyl ethers are split by secondary and tertiary alkyl lithium reagents (*cf.* H. Gilman, F. W. Moore, and O. Baine, *J. Am. Chem. Soc.*, **63**, 2480 (1941)), and diallyl ether is cleaved by metallic sodium (*cf.* R. L. Letsinger and J. G. Traynham, *ibid.*, **70**, (1948)).

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
Tetrahydrofuran	...	75.1	1,4-Dibromobutane	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. Further investigations in these laboratories will cover other aspects of molecular rearrangements, and the scope, stereochemistry, and synthetic possibilities of this new reaction.

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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,

$$\mathrm{T} + \mathrm{RCHAB} \rightarrow \mathrm{RCHT}\cdot + \mathrm{A} + \mathrm{B}\ (\text{or AB}) \qquad (1)$$

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

(1) This research has been supported by A. E. C. Contract No. (AT-11-1)-407 and by the Directorate of Chemical Sciences, AFOSR Contract No. 534-64.

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