The proposed mechanism is substantiated by several lines of evidence: (1) substances[5] known to produce free radicals, either directly or as a result of chain transfer reactions, upon pyrolysis, and only such substances, catalyze this type of isomerization. By way of comparison, Lewis acids produce no such isomerizations (1,2-phenyl migrations),[10-12] but instead give rise to disproportionation reactions,[10] which yield benzene and polyalkylbenzenes, or to methyl migration processes.[11,12] No disproportionation or methyl migration occurs in the present isomerization reaction.

(2) Hydrogen bromide[13] and mercaptans[14] are noted chain transfer agents and even the relatively strong H–Cl bond in hydrogen chloride is susceptible to free radical attack.[15]

(3) The isomerization of *p*-cymene (1-methyl-4-isopropylbenzene) exclusively to 1-methyl-4-*n*-propylbenzene is consistent with known free radical rearrangements[16] in that the relative positions of the two ring substituents are unchanged during the isomerization.

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[5] Iodine, alkyl iodides,[6] alkyl bromides,[6] disulfides,[7] sulfur,[8] mercaptans,[9] and, with less certainty, alkyl chlorides.[6]

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A NOVEL SYNTHESIS OF 1,1-DIHALOOLEFINS

Sir:

The nucleophilic character of tertiary phosphines[1] and the recent observation that carbenes are electrophilic[2] suggested to us that the interaction of these two reagents should produce phosphinemethylenes. We wish now to report the formation of the ylid triphenylphosphine dichloromethylene I and its use in the synthesis of 1,1-dichloroolefins.

$$(C_6H_5)_3P + :CCl_2 \longrightarrow \underset{\text{I}}{(C_6H_5)_3P{=\!=}CCl_2}$$

$$\text{I} + (C_6H_5)_2C{=\!=}O \longrightarrow \underset{\text{II}}{(C_6H_5)_2C{=\!=}CCl_2} + (C_6H_5)_3PO$$

Treatment of a suspension of potassium *t*-butoxide and triphenylphosphine in pentane with chloroform at 0–5° produced I as a golden yellow solid. Preliminary attempts to isolate I in the pure state led to isolation of large amounts of triphenylphosphine oxide and as yet other unidentifiable products. The parent compound, triphenyl-phosphinemethylene, also has been shown by Wittig and Geissler[3] to be unstable.

Reaction of the yellow solid with benzophenone in pentane–ether mixture gave rise to 1,1-diphenyl-2,2-dichloroethylene (II), triphenylphosphine oxide, and unreacted benzophenone. A quantitative yield of potassium chloride also was isolated. II was isolated in 46% yield based on benzophenone consumed: m.p. 79–80°. A mixture melting point with an authentic[4] sample was not depressed and the infrared spectra of the two were superimposable. Triphenylphosphine oxide (m.p. 152–153°) was isolated in 92% yield and shown to be identical with an authentic[1] sample. The unreacted benzophenone was recovered as its 2,4-dinitrophenylhydrazone (48% recovery; m.p.[5] 238–239°).

The high yield of triphenylphosphine oxide as compared to the dichloroethylene may indicate competitive reaction of the phosphine dichloromethylene with *t*-butyl alcohol which was formed during carbene preparation. The reaction of carbenes[6] with tertiary phosphines to yield compounds of type I is being investigated. The reaction of phosphinedihalomethylenes with carbonyl compounds would lead to unusual 1,1-dihaloolefins which normally would be difficult to prepare.

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ION EXCHANGE MEMBRANES FOR USE IN HIGH RADIATION FIELDS[1]

Sir:

The radiation instability of organic membranes has limited their use for processing high radioactive solutions. The necessary frequent replacement of these membranes by remote handling techniques would be difficult and expensive not only because of the cost of the membrane itself but also because of the damage to the electrodes, particularly where platinum is used. At Brookhaven National Laboratory one approach to the solution of this problem has been the development of an inexpensive membrane that can be replaced easily.

Work done at this Laboratory has indicated that a matrix between the particles to minimize diffusion is not necessary for an efficient ion exchange membrane. Membranes were therefore

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[1] Work performed under the auspices of the U. S. Atomic Energy Comm.