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]

(6) E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. I, 2nd ed., Reinhold Publishing Corp., New York, 1954, pp. 253–263.

(7) A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 889 (1949).

(8) D. M. Gardner and G. K. Fraenkel, THIS JOURNAL, **78**, 3279 (1956).

(9) A. H. Sehon and B. deB. Darwent, *ibid.*, **76**, 4806 (1954).

(10) D. A. McCaulay and A. P. Lien, *ibid.*, **75**, 2411 (1953), and references cited therein.

(11) C. D. Nenitzescu, I. Mecsoiu, A. Glatz and M. Zalman, *Ber.*, **92**, 10 (1959).

(12) R. M. Roberts, Y. W. Han, C. H. Schmid and D. A. Davis, THIS JOURNAL, **81**, 640 (1959).

(13) K. B. Wiberg and L. H. Slaugh, *ibid.*, **80**, 3033 (1958); G. B. Kistiakowsky and E. R. Van Artsdalen, *J. Chem. Phys.*, **12**, 469 (1944).

(14) C. Walling, THIS JOURNAL, **70**, 2561 (1948); R. A. Gregg, D. M. Alderman and F. R. Mayo, *ibid.*, **70**, 3740 (1948).

(15) J. H. Raley, F. F. Rust and W. E. Vaughan, *ibid.*, **70**, 2767 (1948).

(16) W. H. Urry and N. Nicolaides, *ibid.*, **74**, 5163 (1952).

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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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(1) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 23, 98; J. R. Van Wazer, "Phosphorus and Its Compounds," Interscience Publishers, New York, N. Y., 1958.

(2) P. S. Skell and A. Y. Garner, THIS JOURNAL, **78**, 5430 (1956); W. E. Doering and A. F. Hoffmann, *ibid.*, **80**, 5274 (1958).

(3) G. Wittig and G. Geissler, *Ann.*, **580**, 44 (1953).

(4) We are indebted to Dr. L. A. Miller of our Dayton Laboratories for the authentic sample. See also E. E. Harris and G. B. Frankfoster, THIS JOURNAL, **48**, 3144 (1926), and "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 270.

(5) N. R. Campbell, *Analyst*, **61**, 392 (1936).

(6) J. Hine and K. Tanabe, THIS JOURNAL, **79**, 2654 (1957); J. Hine and J. J. Porter, *ibid.*, **79**, 5493 (1957); J. Hine and P. B. Langford, *ibid.*, **79**, 5497 (1957); W. E. Parham and R. R. Twelves, *J. Org. Chem.*, **22**, 730 (1957).

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RECEIVED JANUARY 2, 1960

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.

TABLE I

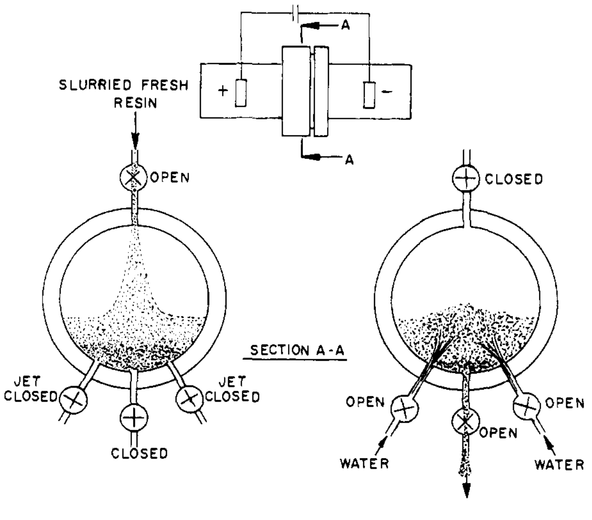
NITRATE ION TRANSFER ACROSS INORGANIC ANIONIC MEMBRANE AT 25°

Starting concn. HNO₃,[a] N	Average current, amp.	Current density (amp. ft.⁻²)	Time, hr.	Amp.-hr.	Equivalents Actual	Equivalents Theoretical	% Efficiency
0.3	0.351	28.7	0.99	0.344	0.00708	0.0128	55.4
.3	.335	27.3	1.02	.340	.00985	.0127	77.6
.3	.275	22.3	0.55	.151	.00345	.33564	62.8
.1	.119	9.70	1.00	.119	.00445	.00313	70.5
.1	.197	16.1	1.80	.355	.0065	.00527	81.0
.1	.096	7.85	1.00	.096	.00358	.00301	84.0

[a] Present in both anode and cathode compartments.

made by slurrying finely divided ion exchange resins between two fine frits which act as supporting walls, as shown in Fig. 1. Replacement of the spent membranes involved merely flushing the ion exchange resin out from between the frits by means of water jets and allowing a slurry of new resin to settle in its place. The entire replacement is made by a simple remote manipulation of valves.

Since the denitration of radioactive waste resulting from fuel element dissolution is a potential use for permselective membranes (anionic), efficiencies were determined by the transfer of the nitrate ion. First frits 1.5″ in diameter with no ion exchange material between them were used to separate the two compartments of an electrolytic cell, and the resulting efficiency was found to be 16%. This value is in agreement with the theoretical value based on the relative velocities of the nitrate and hydrogen ions with the frit acting merely as a diffusion barrier. With ion exchange resin between the frits, the efficiencies were much higher (Table I), which showed that this type of membrane does have permselectivity to an extent that might be practically useful. To determine extent of upstream diffusion, 5.8 × 10^5 disintegrations per minute per milliliter of cesium-137 was placed in the cathode compartment of the cell. None of this isotope could be detected in the anode compartment after several hours of operation. If the radiation is moderate, finely divided organic resins may be expected to give extended service. In higher radiation fields a slurry of organic resin will require frequent changing and inorganic ion exchangers of sufficient chemical stability are preferable.



I

SLURRYING NEW RESIN INTO SPACE BETWEEN FRITS

II

REMOVAL OF SPENT RESIN BY FLUSHING WITH WATER JETS

To date membranes made from slurried resins have been studied on a bench scale only so that economic comparison with membranes containing a matrix is not justifiable; however, economy of easy replacement should be considered in the light of any increased installation cost and lower current efficiencies.

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RECEIVED JANUARY 11, 1960

A STEREOSPECIFIC REACTION OF CARBON MONOXIDE

Sir:

We wish to report on the stereochemistry of tertiary acid synthesis *via* high pressure reaction with carbon monoxide, and incidentally on an extremely facile synthesis of *trans*-2-methyl-2-carboxy-1-cyclohexanepropionic acid (I), a substance of considerable interest because of its conversion to *trans*-8-methylhydrindanone-1, the typical C/D ring system of the steroids.[1,2]

A mixture of ethyl 2-methylenecyclohexanepropionate (II)[3] with concentrated sulfuric acid was kept for several days under a carbon monoxide pressure of two hundred atmospheres.[4] The product from the reaction proved to be the *trans*-dicarboxylic acid I, formed in 80% yield. The melting point (178–179°) was not depressed upon admixture with an authentic sample.[2]

Similarly, and not unexpectedly, the mixture of olefinic esters (III) and lactone (IV) obtained together in the dehydration of V[5] also produced a high yield of I under the above conditions.

The ready decarboxylation of tertiary carboxylic acids in concentrated sulfuric acid made it appear very unlikely that the observed stereospecificity could be the result of kinetic control. We have been able to show that the product is indeed determined by thermodynamic considerations[7] by demonstrating that *cis* 2-methyl-2-carboxy-1-cyclohexanepropionic acid[2] is transformed into the *trans* isomer (I) under the conditions which led to its formation from II, III and IV. These results imply further that the steric requirements of the carboxyl group (quite possibly as its anhydride with sulfuric acid) are greater than that of a methyl group, perhaps because of the solvation requirements of the protonated function.

(1) W. E. Bachmann and S. Kushner, THIS JOURNAL, **65**, 1963 (1943).

(2) W. S. Johnson, *ibid.*, **66**, 215 (1944).

(3) This substance was prepared in this Laboratory by Dr. S. D. Darling from ketene and ethyl 2-oxocyclohexanepropionate[6] by a procedure which will be reported separately.

(4) Synthesis of tertiary acids, using the system olefin or alcohol, strong acid and carbon monoxide has been effected frequently, *e.g.*, T. A. Ford, H. W. Jacobson and T. C. McGrew, THIS JOURNAL, **70**, 3793 (1948), and H. Koch, *Brennstoff-Chem.*, **36**, 321 (1955).

(5) From the reaction of ethyl 2-oxocyclohexanepropionate[6] with methylmagnesium iodide.

(6) G. Stork and H. K. Landesman, THIS JOURNAL, **78**, 5128 (1956).

(7) Another case of equilibrium control in a related reaction has been reported very recently by R. E. Pincod, E. Grigat and P. D. Bartlett, *ibid.*, **81**, 6332 (1959).