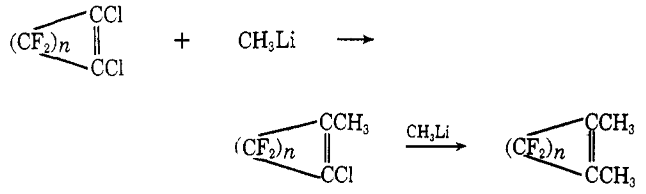
dichloro compounds, 1,2-dichlorotetrafluorocyclobutene (Ia), 1,2-dichlorohexafluorocyclopentene (Ib), and 1,2-dichlorooctafluorocyclohexene (Ic).

This is a radical departure from our previously reported method of preparing the same lithio derivatives[7] which necessitated the reaction of $CH_3Li$ on the iodohalocycloalkenes. Under similar conditions $CH_3Li$ reacts with Ia, b, and c to yield methyl-substituted products.



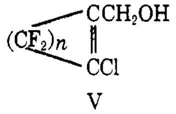
The preparation of II can be conveniently carried out by the dropwise addition of *n*-butyllithium in hexane solution (1 equiv) to a stirred solution of the 1,2-dichloro olefin in ether under a nitrogen blanket and held at −70° by means of a Dry Ice–acetone bath. Under these conditions, an extremely rapid and facile metal–halogen exchange occurs, giving rise to solutions of IIa, b, and c. The extent of the exchange may be determined by hydrolyses of these solutions II with aqueous acid measuring the amount of 1-hydro-2-chloropolyfluoro olefin III produced. In each instance, the yields of the hydro derivatives were in excess of 60%.

To demonstrate the synthetic utility of these polyfluorolithio derivatives, we prepared a number of previously inaccessible compounds through treatment of solutions of II at −70° with a variety of reagents.

Accordingly, carbonation of II with either Dry Ice or gaseous carbon dioxide offered the corresponding 2-chloropolyfluorocycloalkene-1-carboxylic acid IV in good yield (see Table I, p 1491).

The p*K*'s of these acids were determined in aqueous solution and are shown in Table I. Because of the admitted somewhat crude nature of these determinations, we hesitate to attach much significance to the apparent variation of p*K* values with ring size and would only comment at the moment that these compounds are extremely strong organic acids.

The treatment of solutions of IIa, b, and c, at −70°, with formaldehyde gave the corresponding carbinols, V.

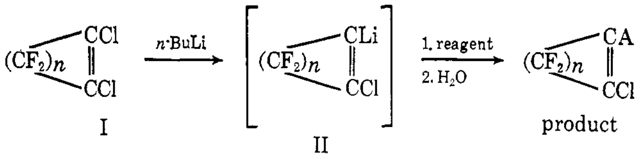


V

The halogens, bromine and iodine, combined with anions IIa, b, and c at −70° to yield the corresponding mixed dihalofluoro olefins VIa, b, and c and VIIa, b, and c listed in Table I. These syntheses of the various 1-halo-2-chloro derivatives are much easier than those previously reported in the literature.

### Experimental Section

**General Procedure.**—To a precooled (−70°) stirred solution of 0.05 mol of 1,2-dichloroperfluorocycloalkene in 100 ml of anhydrous ether was added 0.05 mol of *n*-butyllithium in hexane. The mixture was maintained at −70° for 1 hr with stirring. The resulting dark, reddish violet solution of 1-lithio-2-chloroperfluorocycloalkene was subsequently treated with 0.06 mol of reagent. The reaction mixture was allowed to come to room temperature and hydrolyzed with water. The aqueous phase was extracted twice with two 25-ml portions of ether and the combined organic phase and ether extracts were dried over anhydrous magnesium sulfate. Distillation of this material then yielded the product.



When the above reaction was carried out with $CH_3Li$ under similar conditions no lithiochloroperfluorocycloalkenes were obtained. Thus with 1,2-dichloro-hexafluorocyclopentene, 1-methyl-2-chlorohexafluorocyclopentene, bp 98° (626 mm) [lit.[8] bp 97.5° (621 mm)], was obtained.

Table I is a compilation of the various reactions carried out along with the properties and analyses of the various products isolated. The literature references are given when the products were previously prepared by other routes.

**Acknowledgments.**—The authors wish to express their appreciation to the 3M, St. Paul, Minn., and to the U. S. Army Natick Laboratories, Natick, Mass., for their partial support of this work.

**Registry No.**—IIIa, 695-44-3; IIIb, 3761-95-3; IIIc, 777-96-8; IVa, 19614-54-1; IVb, 19640-45-0; IVc, 19614-55-2; Va, 2898-26-2; Vb, 2890-35-9; Vc, 19640-46-1; VIa, 697-07-4; VIb, 13169-17-0; VIc, 19614-59-6; VIIa, 697-10-9; VIIb, 14627-45-3; VIIc, 19614-62-1.

(8) R. J. McMurtry, unpublished work (University of Colorado, 1966).

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## Dechlorinative Coupling of *gem*-Dichlorides by Sodium Selenide

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There are a few publications on the reaction of alkyl halides with sodium selenide. Alkyl halides react with sodium selenide to give symmetrical selenides.[1] Cyclic selenides are made from polymethylene dibromides and sodium selenide.[2] However, the reaction of vicinal alkyl dihalide with sodium selenide results in the formation of the dechlorinated product, *i.e.*, the alkene instead of alkyl selenide.[3,4]

We wish now to report another interesting reaction of dechlorinative coupling of alkyl *gem*-dichlorides by sodium selenide. Thus sodium selenide effects dechlorination of dichlorodiphenylmethane to give tetra-

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(1) L. Brandsma and H. Wijes, *Rec. Trav. Chim. Pays-Bas*, **82**, 68 (1963).

(2) G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1096, 1497, 2197 (1929); 1497 (1930).

(3) M. Prince, B. W. Bremer, and W. Brenner, *J. Org. Chem.*, **31**, 4292 (1966).

(4) M. Prince and B. W. Bremer, *ibid.*, **32**, 1655 (1967).

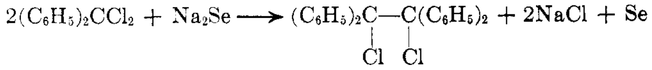
phenylethylene in good yield in accord with the equation[5]

$$2(C_6H_5)_2CCl_2 + 2Na_2Se \longrightarrow (C_6H_5)_2C{=}C(C_6H_5)_2 + 4NaCl + 2Se$$

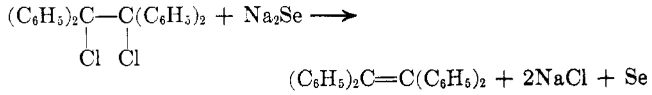
The reaction was conducted with excess sodium selenide in dioxane at the refluxing temperature, 101°, for 24 hr under nitrogen atmosphere.

The formation of the condensed olefin may have involved a carbene intermediate. However, treatment of dichlorodiphenylmethane with sodium selenide in the presence of cyclohexene did not produce the expected carbene-cyclohexene addition product, 7,7-diphenylnorcarane.

The latter reaction was carried out at 80° in the presence of a large excess of cyclohexene. Under these conditions (lower reaction temperature and lower dielectric constant of the medium), dichlorotetraphenylethane was the main product. When the dichlorotetraphenylethane was further treated with sodium selenide in dioxane, tetraphenylethylene was isolated quantitatively. Furthermore, when chlorodiphenylmethane was treated with sodium selenide in dioxane, tetraphenylethane was obtained. Therefore, the dechlorinative coupling reaction may involve two consecutive steps, namely, the intermolecular dechlorination and the intramolecular dechlorination.



$$2(C_6H_5)_2CCl_2 + Na_2Se \longrightarrow (C_6H_5)_2\underset{Cl}{C}{-}\underset{Cl}{C}(C_6H_5)_2 + 2NaCl + Se$$



$$(C_6H_5)_2\underset{Cl}{C}{-}\underset{Cl}{C}(C_6H_5)_2 + Na_2Se \longrightarrow (C_6H_5)_2C{=}C(C_6H_5)_2 + 2NaCl + Se$$

The reaction also was carried out with methyl methacrylate as a solvent at 100° for 1 hr. Dichlorotetraphenylethane was isolated but poly(methyl methacrylate), which would indicate a free-radical intermediate, was not obtained.

A similar reaction was observed with other *gem*-dichlorides. Benzotrichloride with sodium selenide produced *trans*-α,α'-dichlorostilbene. Benzal chloride gave *trans*-stilbene, but in rather poor yield (10%). However, from the reaction of 1,1-dichlorobutane with sodium selenide, the dechlorinative coupling product, octene was not obtained. Methylene chloride gave, instead of ethylene, various cyclic poly(selenomethylenes.[6] Therefore, in order to effect dechlorinative coupling of *gem*-dichlorides, the carbon bonded with the two chlorines must be substituted by at least one, and preferably two, groups such as phenyl.

### Experimental Section

The chloride compounds were obtained from commercial sources and purified by distillation or recrystallization. Sodium selenide, a purified grade (>95% pure), was obtained from City Chemical Co., New York, N. Y., and was used as the powder (<100 mesh) without further purification. The products obtained were identified by infrared and mixture melting point measurements with authentic compounds. Melting points were uncorrected. All the reactions were carried out under an atmosphere of nitrogen. Dioxane was distilled over calcium hydride and stored with sodium wire.

A representative experimental procedure is as follows. Dichlorodiphenylmethane (2.4 g, 0.010 mol) in 40 ml of dried dioxane was gradually added to a rapidly stirred suspension (in 40 ml of dioxane) of sodium selenide (4.3 g, 0.035 mol). The reaction was carried out at the refluxing temperature for 24 hr. The solid materials were removed by filtration and the dioxane was distilled off. The yellow solid obtained was recrystallized from a mixture of benzene and ethyl alcohol and gave 1.0 g (60% yield) of pure tetraphenylethylene, mp 215° (lit. mp 220–222,[7] 220°[8]). When an equivalent quantity of sodium selenide was used, the yield was poor (20–30%) and a large amount of unreacted chloride was recovered. The reason for the low yield is not clear at this time, but it may have been due to the heterogeneity of the reaction system. A search for a suitable solvent is currently being made.

The reaction of dichlorodiphenylmethane (9.5 g, 0.040 mol) with sodium selenide (11.0 g, 0.090 mol) in 80 ml of dioxane was carried out in the presence of cyclohexene (8.4 g, 0.090 mol) at 80° for 20 hr. Recrystallization of the product, from carbontetrachloride, gave 6.0 g (yield 75%) of pure dichlorotetraphenylethane, mp 183° dec (lit.[9] mp 182–184° dec). The reaction in methyl methacrylate at 100° for 1 hr also gave dichlorotetraphenylethane (60%) yield). The reaction of chlorodiphenylmethane (7.1 g, 0.020 mol) with sodium selenide (4.3 g, 0.035 mol) in dioxane gave 4.4 g (yield 70%) of tetraphenylethane, mp 209–211° (lit.[10] mp 207–208°).

Treatment of dichlorotetraphenylethane (1.0 g, 0.0025 mol) with sodium selenide (1.0 g, 0.0080 mol) yielded tetraphenylethylene (0.60 g, yield 80%, after recrystallization).

*trans*-α,α'-Dichlorostilbene, mp 145° (lit.[11] mp 143–145°), 3.5 g, 52% yield, was obtained from the reaction of benzotrichloride (4.5 g, 0.022 mol) with sodium selenide (10 g, 0.065 mol). The reaction of benzal chloride (3.2 g, 0.020 mol) with sodium selenide (5.9 g, 0.05 mol) gave, upon vacuum distillation of the product, 1.8 g (10% yield) of *trans*-stilbene, mp 120° (lit.[12] mp 124°). The distillation residue contained selenium compounds. Structures have not as yet been established. 1,1-Dichlorobutane (2.3 g, 0.025 mol) was also treated with sodium selenide (7.0 g, 0.056 mol) in dioxane. Gas chromatographic analysis did not show any octene in the reaction product. A dark selenium-containing liquid material was also obtained.

**Acknowledgment.**—The authors gratefully acknowledge the financial support of the Selenium–Tellurium Development Association, Inc.

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(5) A similar dechlorinative coupling reaction was reported with gem-dihalides by iron pentacarbonyl: C. Eugene Coffey, *J. Amer. Chem. Soc.*, **83**, 1623 (1961).

(6) M. Russo, L. Mortillaro, L. Credali, and C. DeChecchi, *J. Polym. Sci.*, **4**, 248 (1966).

(7) C.-H. Wang and S. G. Cohen, *J. Org. Chem.*, **26**, 3301 (1961).

(8) H. Güsten and L. Horner, *Angew. Chem.*, **74**, 586 (1962).

(9) T. L. Jacobs and D. M. Fenster, *J. Org. Chem.*, **30**, 1808 (1965).

(10) L. L. Alexander and R. C. Fuson, *J. Amer. Chem. Soc.*, **58**, 1745 (1936).

(11) Y. Ogata and H. Nakamura, *J. Org. Chem.*, **21**, 1170 (1956).

(12) O. H. Wheeler and H. N. Battle DuPabon, *ibid.*, **30**, 1473 (1965).

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## The Oxidation of Ethylbenzene with Aqueous Sodium Dichromate

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*Received October 25, 1968*

Aqueous sodium dichromate has been used by Friedman, Fishel, and Shechter[1] to oxidize alkylated aromatic compounds to the corresponding carboxylic acids in high yields. The procedure is particularly useful with polynuclear aromatic compounds since the side chain can be oxidized without the occurrence of extensive nuclear degradation. For example, 2-methyl-

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(1) L. Friedman, D. L. Fishel, and H. Shechter, *J. Org. Chem.*, **30**, 1453 (1965).