have recently described a procedure where solvated electrons were suggested to be the reducing agents. In addition Burke, *et al.*,[3] have shown that ethylene could be reduced by electrochemically generated hydrogen at a platinum wire electrode. With the development of fuel cell electrodes with their huge surface areas, electrochemical reductions of unactivated olefins on a preparative scale appeared possible.

Experimental Section

The cell and circuitry have been described previously.[4] The working electrode was a type LAA-25 (American Cyanamid Co., Commercial Products Division, Wayne, N. J.) having an active geometrical area of 20.3 cm^2. It consisted of 25 mg of platinum black/cm^2 and 25 wt % Teflon pressed together on a tantalum screen. A porous Teflon coating was applied to the gas side of the electrode to prevent electrolyte leakage into the gas space which was $^1/_{16}$ in. in depth over the active area of the working electrode. The reactant, whether propene, Matheson 99.7% research grade, or hexene-1, Phillips 99% pure grade, in a helium carrier was continuously introduced into the gas space through the top port. The reactant and product exited through the bottom port and were vented to the atmosphere after passing through a gas-sampling valve of a gas chromatograph or were trapped for injection into a gas chromatograph (Perkin-Elmer 154-D or Hewlett-Packard 5750). Potentials were measured against the dynamic hydrogen electrode, dhe,[5] in which hydrogen is generated *in situ* electrochemically. This reference electrode was typically 40 mV cathodic to the normal hydrogen electrode.

Results

Using propene as the reactant and 85% H_3PO_4 at 100° as the electrolyte, greater than 99% conversion of propene into propane was observed when the reactant flowed over the working electrode at a rate of 0.02 mol/hr or 9 sec/cc. The potential difference between the working electrode and the dhe was found not to be important as long as it was cathodic to 0.03 V. There was no rapid decrease in conversion with time as, after 7 continuous hr under the above conditions, greater than 99% conversion was still being obtained.

In addition to H_3PO_4, other electrolytes may be used. NaOH (1 *M*) at 60° gave a conversion of 97% at a flow rate of 19 sec/cc; 1 *M* $NaHCO_3$ also gave a 97% conversion of propene at 60° but at a flow rate of 40 sec/cc. Increases in flow rate at high conversions should be made possible for all electrolytes by baffles in the gas space to increase contact of reactants with catalyst and/or by using a larger working electrode.

Identical results could be obtained without potential control of the working electrode. In this experiment, four 1.5-V batteries were connected in series between the working and counter electrodes, and the potential difference between the reference and working electrodes was read off an electrometer. (No reference electrode or electrometer is necessary for reduction, but hydrogen must be present at the working electrode.) The working electrode could be cleansed of any adsorbed impurities by connecting the positive terminal of the battery to the working electrode and the negative terminal to the counter electrode. The working electrode surface was oxidized as the potential rose to 1.7 V *vs.* dhe. After a few minutes, the battery terminals were reversed, and the potential fell to −0.02 V *vs.* dhe. On passing propene over the working electrode at a flow of 9 sec/cc, essentially quantitative conversion of propene into propane was again observed.

Hexene-1 could also be easily hydrogenated. Hexene-1 was placed in a small reactor through which helium flowed so as to carry the olefin over the working electrode. The effluent from the gas space was condensed and analyzed by gas chromatography. At a flow rate of 0.02 mol/hr, 98% of the hexene-1 was converted into hexane. In this experiment, 85% H_3PO_4 at 100° was the electrolyte.

Work is in progress on the mechanism of this reaction.

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[4] H. J. Barger, Jr., and M. L. Savitz, *J. Electrochem. Soc.*, **115**, 686 (1968).

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The Chemistry of 1-Lithio-2-chloroperfluorocycloalkenes[1]

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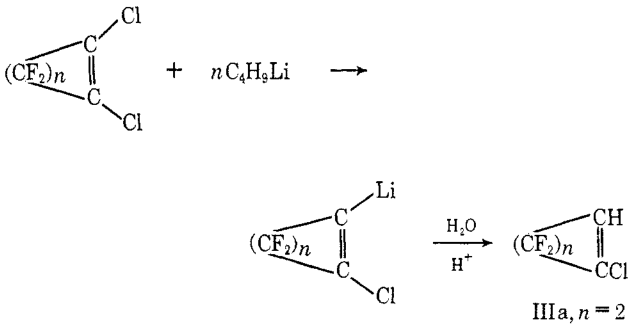
Although vinyllithium reagents derived from linear polyfluoro olefins have been the center of recent attention,[2-5] the analogous lithium derivatives of alicyclic perfluoro olefins have little chemical precedent[6] outside of our previously reported preliminary work.[7]

In this paper, we wish to report the facile preparation of the homologs of one particular series of these lithio derivatives [1-lithio-2-chlorotetrafluorocyclobutene (IIa), 1-lithio-2-chlorohexafluorocyclopentene (IIb), 1-lithio-2-chlorooctafluorocyclohexene (IIc)] and to demonstrate the utility of these reagents as intermediates in the synthesis of heretofore inaccessible or difficultly accessible substituted alicyclic polyfluoro olefins.

These lithio reagents (II) were prepared by the action of *n*-butyllithium on the readily available 1,2-



IIIa, *n* = 2
b, *n* = 3
c, *n* = 4

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[1] This paper represents part of the Ph.D. thesis of B. T. Nakatá submitted to the Graduate School, University of Colorado, Boulder, Colo., 1968.

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[5] F. G. Drakesmith, O. J. Stewart, and P. Tarrant, *ibid.*, **33**, 472 (1968).

[6] S. F. Campbell, R. Stephens, and J. C. Tatlow, *Chem. Commun.*, 151 (1967).

[7] (a) J. D. Park and B. T. Nakatá, Abstracts, 154th Meeting of the American Chemical Society, Chicago, Ill., 1967, p K-12; (b) J. D. Park, C. Bertino, and B. T. Nakatá, Abstracts, 156th Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, p Fluo-22.

TABLE I

SUBSTITUTED 2-CHLOROPERFLUOROCYCLOALKENES PREPARED FOR THIS STUDY

0.05 mol — 0.06 mol ≡ 19.5 ml of 2.57 M in hexane — 0.06 mol

Ia = 9.75 g
b = 12.7 g
c = 14.8 g

Product	n	Reagent	A	Yield, g	Theory, %	Mp or bp (mm), °C	$n_D{}^t$, °C	Calcd,[h] % C	Calcd,[h] % H	Calcd,[h] % Cl	Calcd,[h] % F	Found, % C	Found, % H	Found, % Cl	Found, % F	Neut equiv Calcd	Neut equiv Found	Proton nmr, τ	Ir, cm^{-1}
IIIa[a]	2	H_3O+	-H	9.3	74	54 (628)	1.3496^{25}											3.33 (multiplet)	C=C, 1596
IIIb[b]	3	H_3O+	-H	7.46	71	73 (630)	1.3232^{20}											3.50 (multiplet)	C=C, 1640
IIIc[c]	4	H_3O+	-H	10.5	81	90 (627)													C=C 1660
IVa	2	CO_2	-COOH	7.96	78	93–94	1.8									204.5	203.7		C=C, 1640 C=O, 1735
IVb	3	CO_2	-COOH	10.6	83	64.5–65.5	1.9 pK	28.31	0.39	13.93	44.79	28.09	0.3	13.71	44.70	254.6	256.0		C=O, 1730 C=C, 1640
IVc	4	CO_2	-COOH	10.3	67	55.5	2.0	27.61	0.33	11.64	49.91	27.67	0.43	11.85	49.66	304.5	303.6		C=C, 1640 C=O, 1740
Va	2	CH_2O	$-CH_2OH$	6.46	68	153 (625)	1.402^{20}	31.52	1.58	18.61	39.89	31.65	1.60	18.46	39.74			5.52 (multiplet) 5.46 (singlet)	—OH, 3400 C=C, 1660
Vb	3	CH_2O	$-CH_2OH$	7.48	65	158 (628)	1.3928^{20}	29.96	1.26	14.74	47.39	30.11	1.36	15.02	47.03			5.43 (singlet)	C=C, 1660 —OH, 3400
Vc	4	CH_2O	$-CH_2OH$	12.0	82	42.5–43.5		28.94	1.04	12.20	52.31	28.66	1.01	12.29	52.37				—OH, 3300 C=C, 1655
VIa[d]	2	Br_2	-Br	7.78	65	81 (630)	1.3966^{25}												C=C, 1600
VIb[e]	3	Br_2	-Br	10.3	71	101 (629)	1.3890^{25}												C=C, 1610
VIc	4	Br_2	-Br	10.5	62	122 (630)	1.3901^{27}	21.2		10.4	44.7	21.01		10.59	44.9				C=C, 1620
VIIa[d]	2	I_2	-I	9.58	67	110 (630)	1.4420^{25}												C=C, 1580
VIIb[f]	3	I_2	-I	9.74	58	128 (628)	1.4268^{28}												C=C, 1600
VIIc[g]	4	I_2	-I	14.7	76	144 (632)	1.4218^{26}												C=C, 1605

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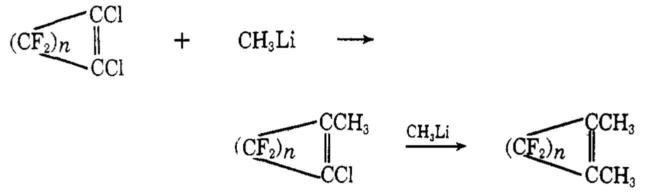
dichloro compounds, 1,2-dichlorotetrafluorocyclobutene (Ia), 1,2-dichlorohexafluorocyclopentene (Ib), and 1,2-dichlorooctafluorocyclohexene (Ic).

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.



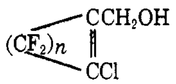
The preparation of II can be conveniently carried out by the dropwise addition of *n*-butyllithium in hexane solution (1 equiv) to a stirred solution of the 1,2-dichloro olefin in ether under a nitrogen blanket and held at −70° by means of a Dry Ice–acetone bath. Under these conditions, an extremely 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.

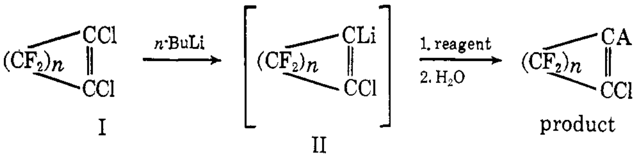


V

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).

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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[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).