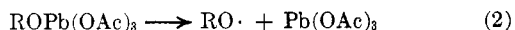
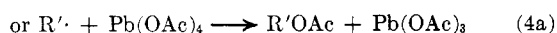
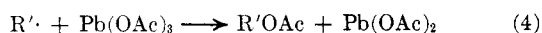
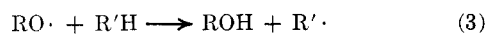


oxidative decarboxylation of carboxylic acids,⁴ and the conversion of long-chain alcohols into tetrahydrofurans.⁵ In particular, the last process has been formulated⁶ as involving an exchange to yield a Pb^{IV} alkoxide (eq 1), and homolytic scission (eq 2) followed



by intramolecular hydrogen abstraction, and oxidation of the resulting carbon radical to the tetrahydrofuran by Pb^{III} or Pb^{IV}.

Such a sequence suggests the possibility of carrying out an induced oxidation of a hydrocarbon using a short-chain alcohol and lead tetraacetate, involving bimolecular hydrogen abstraction *via* an intermediate alkoxy radical, *i.e.*, reactions 1 and 2 followed by reactions 3 and 4 or 4a.



To see whether this is in fact the case, we have examined the effect of *t*-butyl alcohol on the reaction of lead tetraacetate with representative hydrocarbons by shaking the acetate with hydrocarbon in sealed, degassed tubes at 85°, with and without the alcohol. *t*-Butyl alcohol was chosen because the reactions of *t*-butoxy radicals are well characterized⁷ and because it is not itself subject to easy oxidation. Unfortunately, it also appears to undergo exchange reactions with the acetate much more sluggishly than primary and secondary alcohols, although some acceleration of tetraacetate decomposition was observed.⁸ Thus with cyclohexane or toluene 0–30% unreacted tetraacetate remained after 6 days at 85° in the presence of *t*-butyl alcohol, compared with 60–65% in its absence.

Our rather qualitative results are summarized in Table I. With cyclohexane and toluene, *t*-butyl

TABLE I
EFFECT OF *t*-BUTYL ALCOHOL ON
LEAD TETRAACETATE OXIDATIONS

Substrate	Alcohol	Products (yield) ^a
Cyclohexane	No	Cyclohexyl acetate (8)
Cyclohexane	Yes	Cyclohexyl acetate (100), cyclohexene (5), benzene (1)
Toluene	No	Benzyl acetate (10)
Toluene	Yes	Benzyl acetate (100), xylenes (2), bibenzyl (1), benzaldehyde (0.5)
Benzene	No	Toluene (50)
Benzene	Yes	Toluene (100)

^a Yields relative to major product in presence of alcohol; see Experimental Section.

alcohol increases the yield of cyclohexyl acetate and benzyl acetate, respectively, at least 10-fold, and they become the major products of attack on the hydrocarbon. With benzene the yield of toluene is also increased, perhaps in part *via* methyl radicals arising

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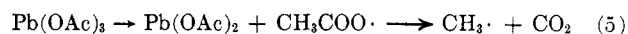
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(8) Attempts to use methyl alcohol simply led to its rapid oxidation with little or no attack on hydrocarbon.

from β scission of *t*-butoxy radicals to acetone and methyl. In addition, reactions in the presence of alcohol showed increased yields of CO₂, methane, and methyl acetate plus *t*-butyl acetate (approximately 60% of substrate acetate) and a small amount of acetone from the alcohol.

Alcohol-derived acetates are common by-products of other lead tetraacetate–alcohol reactions, and higher yields of other products may reflect rapid decomposition of intermediate Pb^{III} products, *e.g.*, eq 5.



Although our results are certainly consistent with our reaction scheme, we have also attempted to obtain further evidence for *t*-butoxy radical participation *via* competitive relative reactivity measurements, chiefly with cyclohexane–ethylbenzene mixtures. Here we were unsuccessful. Toward *t*-butoxy radicals from *t*-butyl hypochlorite, relative reactivities are 2.4.⁷ With lead tetraacetate, we obtained inconsistent values ranging from 0.9 to 2.2. In view of our previous discussion we believe that the inconsistency arises because attack on hydrocarbon involves both *t*-butoxy and methyl radicals, so that the results observed are actually a composite of the two reactions.

Experimental Section

Lead tetraacetate was commercial material; purity by titration⁹ was 90–95%.

Oxidations were carried out in sealed, degassed tubes, using equivalent quantities of alcohol and tetraacetate plus excess hydrocarbon and shaking in a thermostat at 85°, usually for 6 days. Products were analyzed by gas liquid partition chromatography and were usually identified by actual isolation. Because of the heterogeneous mixture of reaction products, only relative yields could be determined easily. In addition to products reported in the text, bicyclohexyl, cyclohexanol, cyclohexanone, and cyclohexyl *t*-butyl ether were shown to be absent in cyclohexane reactions; thus, cyclohexyl acetate was plainly the major product. Similarly with toluene benzyl alcohol, benzene and benzyl *t*-butyl ether were absent, although possible more complex products¹⁰ were not examined.

Competitive experiments were carried out similarly using less hydrocarbon diluted with *o*-dichlorobenzene, and relative reactivities were determined by hydrocarbon consumption.⁷

Registry No.—Lead tetraacetate, 546-67-8.

(9) O. Dimroth and R. Schweizer, *Ber.*, **56**, 1375 (1923).

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An Electrochemical Reduction of Unactivated Carbon–Carbon Double Bonds

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Unactivated double bonds are known to be difficult to reduce electrochemically,¹ although Sternberg, *et al.*,²

(1) F. D. Popp and H. P. Schultz, *Chem. Rev.*, **62**, 19 (1962).

(2) H. W. Sternberg, R. E. Markby, I. Wender, and D. M. Mohilner, *J. Amer. Chem. Soc.*, **89**, 186 (1967); H. W. Sternberg in the Synthetic and Mechanistic Aspects of Electroorganic Chemistry Symposium at the U. S. Army Research Office, Durham, N. C., Oct 14–16, 1968.

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 cm². It consisted of 25 mg of platinum black/cm² 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 $\frac{1}{16}$ 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% H₃PO₄ 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 H₃PO₄, 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 NaHCO₃ 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 ter-

minals 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% H₃PO₄ at 100° was the electrolyte.

Work is in progress on the mechanism of this reaction.

The Chemistry of

1-Lithio-2-chloroperfluorocycloalkenes¹

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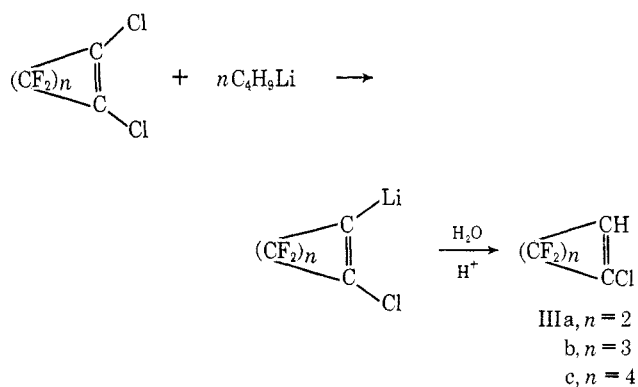
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Although vinyl lithium reagents derived from linear polyfluoro olefins have been the center of recent attention,²⁻⁵ the analogous lithium derivatives of alicyclic perfluoro olefins have little chemical precedent⁶ outside of our previously reported 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-



(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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