that its dark halo is accurately axisymmetric (*26*).

Bright ellipticals are observed to be slowly rotating, and if these galaxies are generically axisymmetric, their slow rotation implies nearly equal numbers of stars on tube orbits traveling in both directions. Such a configuration would arise naturally as the potential evolved from triaxiality into axial symmetry by way of the mechanism described here: Stars on boxlike orbits undergo periodic changes in the direction of their angular momenta, and eventually an ensemble of such stars would presumably populate a set of tube orbits with roughly equal numbers of rotating and counterrotating members. A galaxy with this orbital composition might reveal itself by a strongly flattened or double-peaked distribution of line-of-sight velocities (*27*).

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28. I thank M. Valluri for the calculations on which Fig. 3 was based and for helpful comments on the manuscript. S. Tremaine made a number of suggestions that improved the presentation. Supported by NSF grant AST 93-18617 and NASA grant NAG 5-2803.

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Mineralization of Chlorofluorocarbons and Aromatization of Saturated Fluorocarbons by a Convenient Thermal Process

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A chemical reaction has been discovered that mineralizes chlorofluorocarbons (CFCs) and enables the complete destruction of these environmentally hazardous species. The reaction products are easily handled solids, including recyclable alkali metal halides. Under milder conditions, the same reaction causes partial defluorination of cyclic perfluoroalkanes to yield perfluoroarenes, which are valuable chemical intermediates. The vaporized substrates are passed over a packed bed of heated sodium oxalate; heating at 270° to 290°C causes mineralization, whereas heating at 230°C causes aromatization.

Saturated fluorocarbons and CFCs are among the most inert substances known (*1*). This inertness has environmental consequences because, when released, these species are not destroyed in the lower atmosphere but survive to reach the stratosphere. For example, CF_4, released in electrolytic aluminum production, has a high global warming potential through the greenhouse effect (*2, 3*). CFCs, popular refrigerants, not only have global warming effects but also have a high potential for ozone depletion, because they can release Cl atoms under high-energy ultraviolet photolysis in the ozone layer (*3*). The same chemical inertness makes it very difficult to effectively dispose of existing stockpiles of CFCs and similar species, and this has been called "a problem of major dimensions" (*4*, p. 25). Very few reactions of fluorocarbons are known (*5*); most involve the more reactive fluoroarenes or require corrosive reagents (or reagents that are available only in research quantities). Few of these reactions are applicable to the most refractory saturated species, such as Freons, and none is convenient for routine use on a large scale.

We looked for a two-electron reducing agent, on the grounds that fluoroalkenes are stabler intermediates than are the radicals that would be formed in a one-electron reduction. We wanted to combine the reductant with a fluoride-abstracting component, such as a metal cation. Alkali metal oxalates therefore seemed a good choice. Here, we report an effective and inexpensive method of mineralizing CFCs by passing the vapor through a packed bed of powdered sodium oxalate ($Na_2C_2O_4$) at 270°C, with the use of a vapor-phase multipass apparatus for gases (*6*) or a reflux multipass apparatus for liquids (*7*). This reaction, as applied to CF_2Cl_2 (Freon-12), is shown in Eq. 1:

$$CF_2Cl_2(g) + 2Na_2C_2O_4(s) = 2NaF(s) + 2NaCl(s) + C(s) + 4CO_2(g) \quad (1)$$

Elemental carbon, which can be isolated and weighed, is formed in the stoichiometric amount expected from Eq. 1. The residue also contains NaCl and NaF in the expected amounts. Very high mineralization yields (*8*) were obtained from typical Freons (Table 1). No more than three passes were ever required, and for ClF_2CCF_2Cl (Freon-114), even a single pass through the bed caused complete mineralization. This reaction looks promising for the destruction of CFC stockpiles because it requires only very simple hot-tube chemistry, shows no tendency to give uncontrollable exotherms, and uses an inexpensive and noncorrosive reagent. The products (carbon and the al-

Table 1. Mineralization products of certain perhalocarbons. TM, trap-to-trap multipass apparatus (*6*); RM, reflux multipass apparatus (*7*); SP, single-pass apparatus; PS, passes (*12*). The number of passes required for complete mineralization is given.

Substrate	Method	PS (no.)	Product yield (%)		
			C	Cl^-	F^-
CCl_4	RM	–	99.5	100	–
$CFCl_3$	TM	2	100	98.1	98.0
CF_2Cl_2	TM	3	100	95.0	95.0
ClF_2CCF_2Cl	SP	1	96.0	100	99.0

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kali metal halides) are all easily handled solids; any oxalate salt remaining at the end of the reaction can be pyrolyzed to the carbonate at 350°C, if desired.

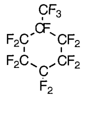
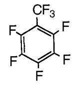
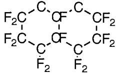
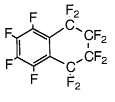
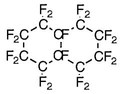
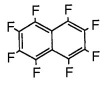
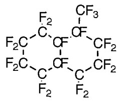
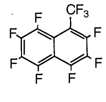
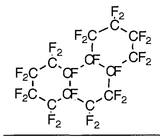
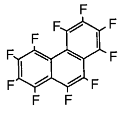
Perfluoroalkanes are much more readily available than their unsaturated derivatives, and a method that would enable their partial defluorination to perfluoroarenes would thus be very valuable. A number of attempts to do so have been reported (*5*), but they used reagents that are inconvenient and difficult to control. Metallic iron or nickel is often used at 450° to 500°C in commercial operations (*9*), but fluoride is lost as metallic fluoride (*10*) that requires disposal.

We applied our oxalate reaction to synthetic partial defluorination, in which the by-product, NaF, is a common fluorine source in synthesis and can be recycled (*11*). When the temperature of the oxalate bed was held at 230°C to prevent excessive mineralization, defluorination was no longer complete and a fluoroarene could be isolated. In the case of perfluorodecalin (**1**), this product was perfluorotetralin (**2**) or perfluoronaphthalene (**3**), depending on the exact conditions. The overall reaction for the case of **1** → **3** is shown in Eq. 2:

$$C_{10}F_{18}(g) + 5Na_2C_2O_4(s) = 10NaF + C_{10}F_8 + 10CO_2 \qquad (2)$$

Note that some of the substrate was still mineralized. Table 2 shows the results for this reaction with five different substrates.

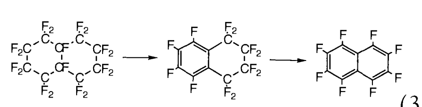
Table 2. Defluorination-aromatization products of some cyclic fluorocarbons. RM, reflux multipass apparatus (*7*); SP, single-pass apparatus (*12*). The yield is based on the amount of saturated fluorocarbon converted.

Substrate	Method	Product	Yield (%)
	RM		70
	RM		65
	SP		30*
	SP		53
	SP		40

*Perfluorotetralin (35%) also formed.

The products are well-known organofluorine compounds, and thus their identity was readily confirmed by physical measurements such as ^{19}F nuclear magnetic resonance (NMR), infrared spectroscopy, and gas chromatography–mass spectroscopy.

The reflux apparatus (*7*) used in the reflux multipass studies allows selective reactions to be achieved because the higher boiling point product concentrates in the liquid, whereas the vapor phase is enriched in the more volatile starting material. The intermediate reduction product (such as **2**) is therefore protected from further reaction by selective condensation out of the reactive vapor phase. This approach allowed us to obtain high selectivity for **2** over **3** in the reduction of **1** (Eq. 3):



1 **2** **3** (3)

Closer examination of this reaction showed that the reaction rate of the *cis* isomer of **1** (1:1 *cis*/*trans* mixture) was 2.5 times that of the *trans* isomer, which led to a substantial enrichment of the starting material in the *trans* isomer.

The reaction can also be run under single-pass conditions (*12*) by saturating an N_2 stream with the substrate vapor and passing the gas mixture through the oxalate bed. Under single-pass conditions, both rings of **1** were aromatized to give **3** in 30% yield. Side chain CF_3 groups were unaffected under either reflux multipass or single-pass conditions.

The mechanism remains speculative at this stage, but a plausible pathway involves $Na_2C_2O_4$ acting as a two-electron transfer agent to the fluorocarbon while the cation acts as an F^- acceptor. Accordingly, perhalocarbons react whereas partially halogenated species such as $ClCH_2CH_2Cl$ do not, because the latter are insufficiently powerful electron acceptors. The nature of the cation affects the outcome of the reaction and therefore must play a role. For example, the yields obtained in the reduction of perfluoromethylcyclohexane (C_7F_{14}) to perfluorotoluene (C_7F_8) varied as a function of temperature (at 200°C, the yield was 72% with $K_2C_2O_4$ as a reducing agent, whereas no reaction occurred with $Na_2C_2O_4$ or $Li_2C_2O_4$; at 230°C, the yields were 70% with $Na_2C_2O_4$ and 50% with $Li_2C_2O_4$). A time course for the $Na_2C_2O_4$ reaction at 230°C is shown in Fig. 1.

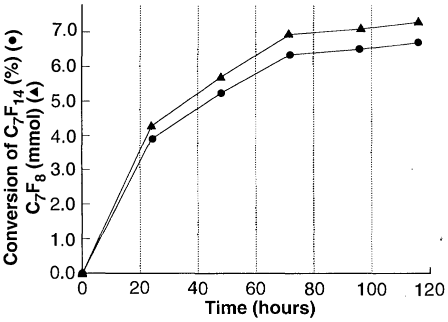


Fig. 1. Time course of the reduction of C_7F_{14} to C_7F_8 by $Na_2C_2O_4$ at 230°C in a reflux multipass apparatus.

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6. The trap-to-trap multipass apparatus consisted of two traps alternately cooled with acetone–CO_2 in such a way that the CFC evaporated from one trap, passed through a packed bed of $Na_2C_2O_4$ (20 mm by 20 cm; 34 g, 254 mmol) heated to 270°C (electrical heating tape; temperature monitored by thermocouple), and condensed in the second trap. In the first pass, the substrate was introduced at 4 ml/min (flowmeter, measured at 25°C, 1 atm) for 1.5 hours, passed through the oxalate bed, and condensed in the trap. The substrate supply and flowmeter were then removed and replaced with the second trap.
7. In the reflux multipass apparatus, the liquid substrate was refluxed in such a manner that the vapor passed through a packed bed of $Na_2C_2O_4$ (20 mm by 10 cm; 17 g, 127 mmol) heated to 270°C for mineralization and to 230°C for aromatization. The vapor was then condensed and returned to the reflux flask. Typical reaction time was 2 days.
8. The carbon was isolated and determined by weight, the chloride by titration (Mohr method), and the fluoride by ^{19}F NMR with $NaCF_3CO_2$ as internal standard.
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12. The single-pass apparatus had a flow rate (at 1 atm and 25°C) of 4.0 ml/min of substrate vapor (mineralization) or 200 ml/min of N_2 saturated with substrate vapor (aromatization). At T = 270°C and with a reaction bed of 20 mm by 20 cm, the typical reaction time was 2 hours (mineralization) or 10 hours (aromatization). For diagrams of all the apparatus, see J. Burdeniuc and R. H. Crabtree, *J. Am. Chem. Soc.*, in press.
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