

DISSOLVING METAL REDUCTION.^{1a)}
K METAL-CROWN ETHER-TOLUENE SYSTEM FOR REDUCTIVE DEFLUORINATION

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ABSTRACT. Toluene radical anion, generated by dissolving potassium metal in toluene by the assistance of dicyclohexano-18-crown-6, has been proved to be especially effective for reductive removal of fluorine atom from unactivated alkyl fluorides that resist common reduction conditions. Stereochemical and mechanistic aspects of the present method is discussed. In connection with the preparation of substrates the effect of dipolar aprotic solvents on the nucleophilic fluorination with potassium fluoride/dicyclohexano-18-crown-6 system was also examined, and sulfolane or N,N-dimethylformamide was shown to be a solvent of choice.

1. INTRODUCTION

Most of the papers on cyclic polyethers are concerned with their complexation phenomena with common salts of alkali metal, alkaline earth metal or ammonium²⁾. Metal (M) itself can be regarded formally as a sort of salt, $M^+ M^-$ or $M^+ e^-$ (e: electron). Thus, as is already suggested in Pedersen's paper²⁾, cyclic polyethers have been revealed to form complexes with alkali metal or alkaline earth metal^{3a,c)}. Preparation of a single crystal of a complex of cryptand 2,2,2 with sodium metal and its structure determination by X-ray crystallography by Dye made an epoch in this field^{3b)}. Development of a method for generation of unusual chemical species as sodium or potassium anion stimulated us to study the chemical reactivity of these alkali metal anions. Generation of potassium or sodium anion in less polar organic solvents should provide a new scope in the chemistry of dissolving metal reduction, since the active entities of common dissolving metal reductions are believed to be solvated electrons⁴⁾. To our knowledge, papers on the application of the above principle to the organic synthesis seems to be quite limited⁵⁾.

Relatively stable radical anions are produced in high concentration when naphthalene and anthracene were allowed to contact with sodium metal in ether or dimethoxyethane and these species are widely used in synthetic organic chemistry⁶⁾. On the other hand, conversion of toluene

or xylene to the corresponding radical anion under the same conditions are rather difficult because of their low electron affinity. However, when crown ether was used as a co-reagent, formation of even the mesitylene radical anion, which had not been reported so far, was detected by electron spin resonance spectroscopy⁷⁾.

These curious chemical entities led us to study the reactivity of potassium anion (K^-) generated from K/crown ether/diglyme (or Et_2O , THF) system^{3a)} and toluene radical anion from K/crown ether/toluene system⁸⁾. The effectiveness of the former system for reductive cleavage of sulfonamide was reported elsewhere^{1b)}. In the present paper, reductive defluorination with the latter system is reported^{1a)}.

Alkyl fluorides were chosen as the substrates because the carbon-fluorine bond is known to be very strong⁹⁾ and resists common reduction conditions^{10,11)}.

In this paper, the application of crown ether to the preparation of primary alkyl fluorides was also examined. So called "naked fluoride" method of fluorination by Liotta¹²⁾ was modified by changing the solvent from acetonitrile to sulfolane^{13,14)} in order that this method could be applied for long chain alkyl halides or sulfonates.

2. MATERIAL AND METHOD

2.1. Analytical Methods and Materials

Melting points were recorded on a Kofler-type block and are uncorrected. Thin layer chromatography (TLC) for preparative purposes were carried out on Merck Kieselgel 60 PF₂₅₄. Infrared (IR) spectra were measured in CCl_4 or $CHCl_3$. Nuclear (proton) magnetic resonance (NMR) spectra were measured in $CDCl_3$ at 60 or 400 MHz vs. tetramethylsilane as an internal standard. Deuterium NMR (D-NMR) were measured at 50°C¹⁵⁾ in $CHCl_3$ [ca 5% (w/v) solution] at 61.44 MHz vs. $CDCl_3$ (natural abundance) as an internal standard (δ 7.26 ppm.) under proton noise decoupling, without lock. Fluorine NMR were measured in $CHCl_3$ (ca 2% solution) at 93.66 MHz vs. CF_3COOH as an external standard (δ 0.0 ppm). Gaschromatography-Mass (GC-MS) spectra were obtained by GC-column (2% OV-1, 3 mm ϕ x 1m) connected to a single focus mass spectrometer with an electron impact ionization (EI) system, unless otherwise stated, usually at 160-180°C and at 20 eV. High-resolution mass spectra were provided by a double-focusing instrument with EI at 20 eV. Commercial reagent grade dicyclohexano-18-crown-6 (DC-18-C-6)(1)¹⁶⁾ from Merck was used after being dried over P_2O_5 by a rotary pump at ambient temperature for 0.5-1.0 hr and toluene was dried over molecular sieves (3A). Commercial reagent grade potassium metal was cut into small pieces in dry hexane in nitrogen gas. Nitrogen gas of 99.9995% purity was used after being dried over molecular sieves (3A) and by a liquid nitrogen trap. Potassium fluoride (KF) was oven-dried at 120°C.

2.2. Preparation of Alkyl Fluorides

Except primary alkyl fluorides commented in the later section, following

alkyl fluorides were synthesized by the known procedures and all of the structures were confirmed by the analytical methods stated above: (2)¹⁷, (3)¹⁷, (4)^{17,18}, (5)^{17,18}, (6)¹⁹, (10)²⁰.

2.3. Crown Ether for Nucleophilic Fluorination with Naked Fluoride

Reagents for fluorination are usually labile and toxic and the reaction conditions are difficult to control and sometimes dangerous²¹). Therefore, the nucleophilic fluorination (Finkelstein reaction) with "naked fluoride" generated from metal fluoride by the aid of crown ether reported by Liotta¹²) is highly advisable. KF/18-crown-6/acetonitrile system was successfully used in the conversion of short chain alkyl bromides to the corresponding fluorides. However, in cases of long chain alkyl bromides, only unsatisfactory results were obtained. Thus, modification of the reaction conditions were undertaken.

Examination of Solvent Effect on Nucleophilic Fluorination with KF/dicyclohexano-18-crown-6. Using 1-bromodocosane (12) as substrate and KF/DC-18-C-6 as reagent system, solvent effect was examined. Solvents were chosen from common dipolar aprotic solvent [acetonitrile, hexamethylphosphoric triamide (HMPT), dimethylsulfoxide (DMSO), diglyme], from weakly basic dipolar aprotic solvents (sulfolane, ethylene carbonate, propylene carbonate)²²) and from acid amide solvents [N,N-dimethylformamide (DMF), N,N-diethylacetamide (DEA), N-methylpyrrolidone (NMP), tetramethylurea]²³).

A typical procedure is as follows: A solution of KF (168 mg, 2.9 mmol) and DC-18-C-6 (574 mg, 1.54 mmol) in MeOH (14 ml) was refluxed for 30 min²⁴). The resulting homogeneous solution of KF/DC-18-C-6 complex was divided into 14 equal portions and the solvent was stripped off. A solution of 1-bromodocosane (546 mg, 1.4 mmol) in dry benzene (14 ml) was divided into 14 equal portions and combined with the above complex. The solvent was removed and the residue was dried in vacuo. After the addition of the solvents, each mixture was heated at 150°C in argon atmosphere for 2 h. Pentane extract (4 ml) of each reaction mixture was chromatographed on silica gel (Wako C-300, 0.7 g) to remove the crown ether complex, and was subjected to GC (2% OV-1, 200°C). The yield of alkyl fluoride was expressed by per cent of the peak area.

Table I. Nucleophilic Fluorination of 1-Bromodocosane with KF/dicyclohexano-18-crown-6 at 150°C for 2 h

solv.	DMF	DEA	NMP	SL	NEP	PC	DMSO	HMPT	TMU	EC	AN	DG
yield	82	82	80	80	77	76	75	59	54	37	15	2
	%											

DMF=N,N-dimethylformamide, DEA=N,N-diethylacetamide, NMP=N-methylpyrrolidone, SL=sulfolane, NEP=N-ethylpyrrolidone, PC=propylene carbonate, DMSO=dimethylsulfoxide, TMU=tetramethylurea, HMPT=hexamethylphosphoric triamide, EC=ethylene carbonate, AN=acetonitrile, DG=diglyme.

The results shown in Table I indicate that sulfolane, DMF, NMP and DEA gave high yields. Considering the relatively high cost of the latter two solvents, the use of the former two solvents were examined in the preparative sense.

In the conversion of 24-chlorocholane (16), the corresponding fluoride (17), was obtained in 49% and 43% isolation yields, respectively, with sulfolane and DMF. Because of better solubility in water, sulfolane was mostly used for the preparation of primary alkyl fluorides.

In the conversion of 24-tosyloxycholane (14), the corresponding fluoride was obtained in 12% yield under Liotta conditions (KF/18-crown-6/acetonitrile, reflux)¹²⁾ and 78% yield under the present reaction conditions [KF/DC-18-C-6 (1.1 mol eq.)/sulfolane, 150°C, 19 h.]. Furthermore, the yield of fluoride from the corresponding mesylate (15) was 76% and no significant difference in the yield was found between DC-18-C-6 and cryptand 2,2,2.

1-Fluorodocosane (13) was synthesized analogously from the bromide (12) in 79% yield. 6-Fluoro-1-hexene (19) was obtained in 77% yield from 5-hexen-1-ol tosylate (18) under the standard conditions, followed by distillation at 4 mmHg.

2.4. Standard Procedure for the Reductive Defluorination

A solution of alkyl fluoride (0.5 mmol) and DC-18-CR-6 (1.0 mmol) in dry toluene (20 ml) was degassed by means of a rotary pump for 1-3 min in a two-necked cylindrical vessel (35 mm ϕ x 100 mm) connected to a vacuum line and a nitrogen gas line and equipped with a rubber septum. Dry nitrogen gas was introduced at atmospheric pressure. Then, a lump of K metal (ca. 7 mm cube), previously cut and washed in hexane (or toluene), was added under a stream of nitrogen gas through the side arm by removing the septum. Once again, the vessel was slightly evacuated and nitrogen gas was introduced and the mixture was magnetically stirred for 3 h. In cases of reductions of volatile substrates, such as 6-fluoro-1-hexene, the solution was simply flushed with nitrogen gas for 5 min. Quenching was done by transfer of the mixture to a round-bottomed flask containing iPrOH by means of a long syringe needle through the septum. Generally, the products were isolated by TLC after usual work-up.

As for 6-fluoro-1-hexene, the reaction mixture was filtered by a short column of silica gel and the filtrate was directly analyzed by capillary GC and 400 MHz NMR.

3. RESULTS

3.1. Reductive Defluorination of Alkyl Fluoride

The results of the reduction of $^3\beta$ -fluorocholestane (2) under various conditions (solvent, metal, crown ether, H^+) are shown in Table II. Alkyl fluorides (primary, secondary, tertiary) were reduced under standard conditions [K/DC-18-C-6 (2 mol eq.)/toluene at ambient temperature], and the results are shown in Table III.

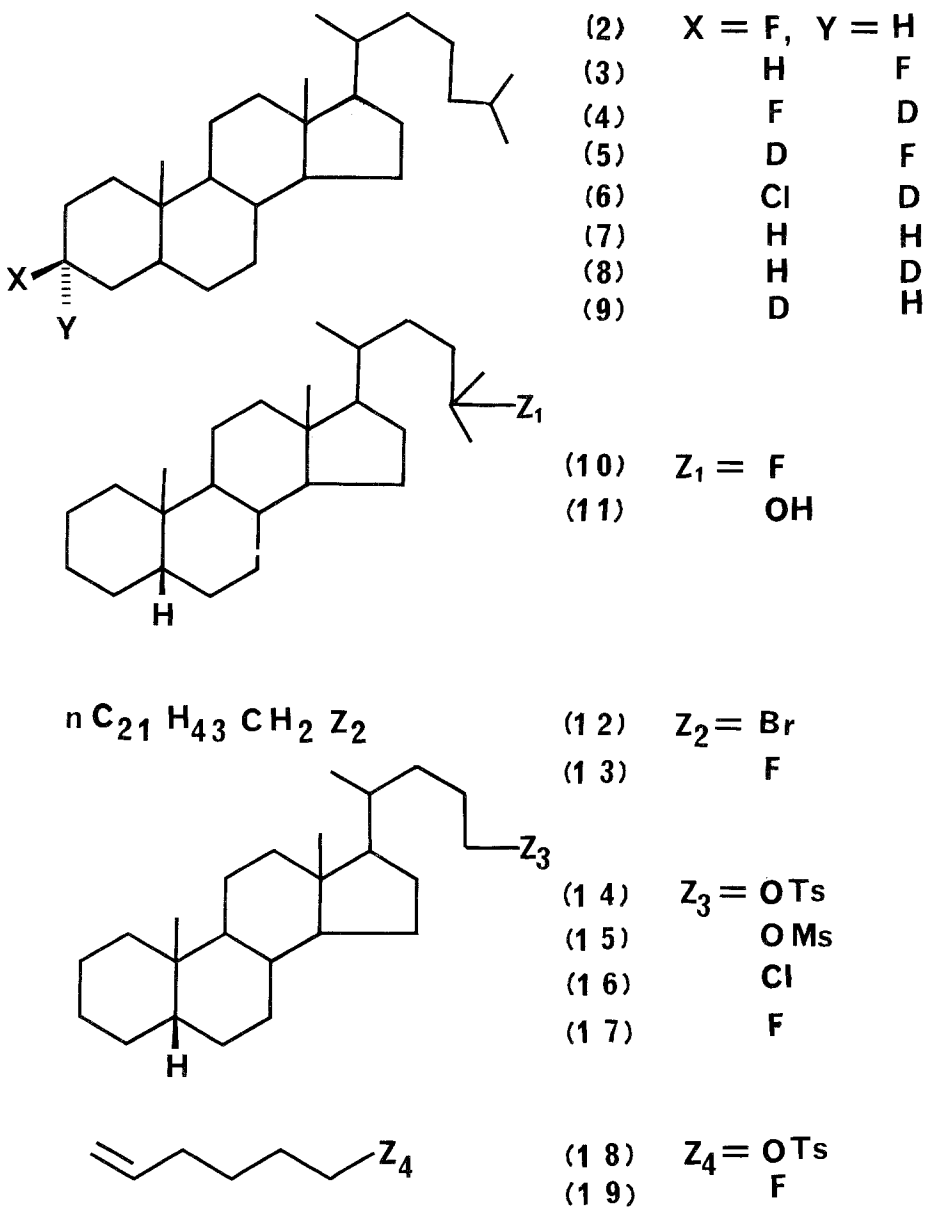


Figure 1.

Table II. Effect of the Reaction Condition on the Reductive Defluorination of 3β -Fluorocholestane (2).^{a)}

Entry	Solvent	Metal	Crown Ether ^{b)}	iPrOH ^{c)}	Yield % ^{d)}	
1	diglyme	K	-	-	RH 11	RF 87
2	"	"	-	+	18	81
3	"	"	+	-	33	65
4	"	"	+	+	19	74
5	"	Na-K ^{e)}	+	-	62	28
6	"	"	++	-	76	--
7	toluene	K	-	-	14	83
8	"	"	-	+	11	83
9	"	"	+	-	74	24
10	"	"	++	-	88 ^{f)}	7
11	"	"	+	+	16	84

a) 0.5 mmol of (2) was reduced at ambient temp. for 3 hrs.

b) +, ++ = dicyclohexano-18-crown-6, 2 or 4 mol equiv., respectively; - = no crown ether added.

c) + = iPrOH (0.5 ml); - = no alcohol added.

d) Isolated yield by TLC on silica gel.

e) Na-K (44 : 56 w/w) alloy²⁶⁾.

f) Averaged value; maximum was 99%.

Table III. Reductive Dehalogenation of Alkyl Halides*

Entry	Alkyl Halides	Yield of Hydrocarbon %
1	1-F-docosane (13)	87
2	24-F-choleane (17)	97
3	3β -F-cholestane (2)	99
4	24,24-diMe-24-F-choleane (10)	100
5	3α -F- 3β -D-cholestane (5)	100
6	3β -Cl- 3α -D-cholestane (6)	> 86

* Alkyl halides were treated with excess K metal /dicyclohexano-18-crown-6 (2 mol eq.) /toluene at ambient temperature for 3 hrs.

Table IV. Defluorination of 3β -Fluorocholestane (2)

Entry	Reducing System	Yield	%
1	K-CR-toluene	RH 99	RF --
2	Li-liq ammonia ^{10a)}	4	85
3	K-HMPT-THF-tBuOH ²⁷⁾	8	92
4	K-HMPT-THF	22	45
5	K-HMPT	58	41
6	Na-naphthalene-DME ²⁵⁾	7	80

For comparison, 3β -fluorocholestane was subjected to common reduction conditions as is shown in Table IV.

3.2. Reductive Defluorination of 6-Fluoro-1-hexene

Reduction of 6-fluoro-1-hexene (19) with K/DC-18-C-6/toluene was then carried out. Capillary GC of toluene solution of the product from K/DC-18-C-6/toluene reduction revealed two peaks at 5.4 min (relative intensity, 76%) and at 6.0 min (24%), beside the strong peak of toluene at 10.2 min. The retention time of the first and the second peak were identical with that of 1-hexene and cyclohexene, respectively. NMR spectrum of the above toluene solution clearly shows the existence of 1-hexene as the major component beside toluene. However, assignment of the signals of cyclohexene was difficult because of overlap and low intensity of signals, and furthermore, of poor resolution. Thus, there still remains some ambiguity in the assignment of cyclohexene.

3.3. Stereochemistry of Reductive Defluorination

Stereoisomeric fluorides, 3α -F- 3β -D-cholestane (5), and 3β -F- 3α -D-cholestane (4) and also the corresponding chloride, 3β -Cl- 3α -D-cholestane (6) were reduced under K/DC-18-C-6/toluene conditions to give mixtures of 3α - and 3β -D-cholestane, (8) and (9). Deuterium NMR spectrum of each gave a signal of 3α -D at δ 1.20 ppm (half-height width 3.7 Hz) and that of 3β -D at δ 1.66 ppm (h.b.w. 7.4 Hz), which were identified by the comparison with those of the authentic samples of them³⁰. The ratio of peak intensities of 3α -D and 3β -D were 64% : 36%, 63% : 37% and 64% : 36%, respectively.

4. DISCUSSION

4.1. Reductive Defluorination in General

It can be reasonably stated from the result in Table II that i) toluene is a better solvent than diglyme, proving the effectiveness of toluene radical anion for this type of reduction, ii) the presence of protic solvent depressed the reduction and iii) slightly more than one molar equivalent amount of crown ether is required for the completion of the reduction.

Conclusively, K/DC-18-C-6/toluene was confirmed to be a stronger reducing system for this type of reduction than Li/liq NH_3 , K/HMPT (with or without H^+ and/or THF) or Na naphthalenide in dimethoxyethane. The interesting point is that the rather stable radical anion system (Na naphthalenide) is weaker than the labile counterpart (toluene radical anion).

4.2. Reductive Defluorination of 6-Fluoro-1-hexene

The production of 1-hexene as the major product shows the chemoselectivity in the reduction between fluorine and vinyl group under the

present condition²⁸). If the assignment of cyclohexene is correct, its formation is quite exceptional because 6-halo-1-hexenes usually afford methylcyclopentane beside 1-hexene as the cyclic product from intramolecular radical trap reaction²⁹). Confirmation of the presence of cyclohexene is now undertaken. Cyclohexane, methylcyclopentane or n-hexane could not be detected.

4.3. Stereochemistry of Reductive Defluorination

The results of D-NMR analysis lead to the following conclusion: Irrespective of the stereochemistry of the fluorine atom or of species of halogen atoms, the ratio of 3 α -D- and 3 β -D-cholestane in the product of K/DC-18-C-6/toluene reduction is the same (64% : 36%). The feature of the present reduction differs from Li, Na or K-liq. ammonia reduction, which proceeds with predominating retention of configuration³¹), and also differs from nucleophilic reduction which proceeds with inversion of configuration as is observed with LiAlH₄ reduction³²). The ratio of 3 α -D/3 β -D shows that the majority of hydrogen atoms, no matter what the actual form (H⁺, H \cdot) or origin³³), attacked the carbon concerned from the less hindered side of steroidal skeleton.

5. ACKNOWLEDGEMENT

The authors wish to thank Dr. Jun Uzawa for NMR measurement. Thanks are also due to Takashi Takagaki, Akihiko Haneda, Atsumi Takeda, Tsuyoshi Shimazaki, Takao Kobayashi and Yoshiko Hirashima (née Yamanaka).

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