Activation of Reducing Agents. Sodium Hydride Containing Complex Reducing Agents. 15.[1] Reduction and Selective Reduction of Organic Halides

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The reduction of alkyl and vinyl halides with a reducing system composed of NaH, alkoxides, and metal salts ("complex reducing agents", CRA) has been investigated. The reagent system efficiently converts primary, secondary, and tertiary alkyl iodides, bromides, and chlorides to the corresponding hydrocarbons. Alkyl tosylates are less readily attacked, and fluorides are inert. Benzyl, allyl, and vinyl halides are also reduced. The latter react stereospecifically without double bond isomerization. Selective reductions of mixtures of alkyl halides are possible with either Ni CRA or Zn CRA, and the reagents are inert toward a number of other functional groups, allowing selective reductions to be achieved. Finally, the reduction may be achieved by using catalytic amounts of nickel salts. Possible structures for the complex reducing agents are discussed, as well as suggested mechanisms for halide reductions.

The reduction of organic halides or tosylates to the corresponding hydrocarbons plays an important role in organic synthesis. In synthetic applications such conversions often must be accomplished in complex molecules containing other functional groups. Consequently, chemoselectivity is an important consideration. Moreover, it is also important that the reducing agent is readily and reproducibly prepared and, for large-scale reactions, inexpensive.

The importance of halide reductions has stimulated a considerable amount of investigations, and a number of successful approaches have been described especially with complex metal hydrides.[2] Recently, reviews on this topic have been published.[3]

Some years ago, we undertook the study of new reducing reagents composed of a combination of NaH, an alkoxide, and a metallic salt (NaH–RONa–MX_n).[4] These systems, which are termed complex reducing agents (CRA), have been shown to be efficient, inexpensive reagents for carbonylations,[5] catalytic hydrogenations,[6] and a variety of selective functional group reductions.[7,8]

One successful application involves the hydrogenolysis of aryl halides, including aromatic fluorides.[4] In addition, the reduction of alkyl halides to alkanes has been briefly described.[9] This report describes the scope, limitations, and synthetic usefulness of these latter reductions as well as the functional group selectivity possible.

Results and Discussion

Reduction of Primary Alkyl Halides. Our initial investigation on the ability of CRA to reduce carbon–halide bonds stemmed from our preliminary finding[9] which showed that the reducing ability of CRA strongly depends upon the nature of the metallic salt MX_n and that primary alkyl halides are more easily reduced than secondary or tertiary systems. Thus, it was decided to systematically investigate the reactivity of numerous M CRA, NaH–*t*-AmONa–MX_n, toward *n*-octyl bromide, selected as a representative alkyl halide. Reactions were performed in THF and 1,2-dimethoxyethane (DME) which were found to be the most adequate solvents.

Control experiments, illustrated in Table I, demonstrated that the reagents alone were not successful for efficient reductions and, as expected, that the bases NaH and *t*-AmONa gave substantial amounts of elimination products. As previously observed,[10] the combination of NaH and *t*-AmONa is a better reducing agent than NaH alone.

Complementary control experiments on the reactivity of NaH–MX_n systems were also performed. Indeed, it might be thought that the observed reductions by M CRA were due to NaH–MX_n combinations. Furthermore, it might also be believed that, in some cases, reductions were impeded by the presence of *t*-AmONa (leading to elimination to 1-octene) or by the formation of $(t\text{-AmO})_nM$[11] (preventing the reaction of NaH with M^{n+}). From these experiments (detailed in the Experimental Section), it appeared that, under simulated reaction conditions, all NaH–MX_n systems were poorly reactive toward *n*-octyl bromide. However, it is interesting to note that for much larger reaction times, some NaH–MX_n couples (MX_n = $FeCl_3$, $Ni(OAc)_2$, $Cu(OAc)_2$, $ZnCl_2$, $CdCl_2$) led to the formation of octane in 20–50% yields. These results may provide some information about the nature of M CRA and we shall discuss this point later. Thus, it is clearly evident that NaH, *t*-AmONa, and MX_n are all necessary for generating active CRA, although, in some cases, such systems are almost unreactive toward *n*-octyl bromide.

Depending upon which solvent was used, two different methods were used for the preparation of CRA. Thus, for

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(5) J. J. Brunet, C. Sidot, B. Loubinoux, and P. Caubere, *J. Org. Chem.*, **44**, 2199 (1979). See also part 14 of ref 1.
(6) J. J. Brunet, P. Gallois, and P. Caubere, *Tetrahedron Lett.*, 3955 (1977); J. J. Brunet, P. Gallois, and P. Caubere, *J. Org. Chem.*, **45**, 1937 (1980); P. Gallois, J. J. Brunet, and P. Caubere, *ibid.*, **45**, 1946 (1980)
(7) (a) J. J. Brunet, L. Mordenti, B. Loubinoux, and P. Caubere, *Tetrahedron Lett.*, 1069 (1977); (b) J. J. Brunet and P. Caubere, *ibid.*, 3947 (1977); (c) J. J. Brunet, L. Mordenti, and P. Caubere, *J. Org. Chem.*, **43**, 4804 (1978).
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(9) B. Loubinoux, R. Vanderesse, and P. Caubere, *Tetrahedron Lett.*, 3951 (1977).
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Table I. Reaction of NaH, *t*-AmONa and NaH-*t*-AmONa with *n*-Octyl Bromide[a]

mmol of NaH	mmol of *t*-AmONa	solvent[a]	reaction time, h	% recovered material[b]		
				$C_8H_{17}Br$	octane	1-octene
60	0	THF	50	85	5	8
60	0	DME	50	87	5	7
0	60	THF	50	10		85
0	60	DME	4	traces		90-95
40	20	THF	30	10	15	70
40	20	DME	5		5	85-90

[a] Reactions performed at 65 °C in 40 mL of solvent with 10 mmol of *n*-octyl bromide. [b] Determined by GLC analysis with internal standards.

Table II. Reaction of Various CRA[a] with *n*-Octyl Bromide (10 mmol)

metal salt	solvent[b,c]	temp, °C	reaction time, h	% recovered material			
				$C_8H_{17}Br$[d]	C_8H_{18}[d]	C_8H_{16}[d,e]	$C_{16}H_{34}$[d]
Cp_2TiCl_2	THF	20	6-7		40-45		
	DME	65	0.083		30	traces	traces
VCl_3	THF	65	6		90-95	traces	traces
	DME	65	43	9	48	38[f]	
$FeCl_3$	THF	65	1.5		80	5-10	
	DME	65	1.5		76	24	
$Co(OAc)_2$	THF	65	0.5		77	7[g]	10-12
		20	9-10		98		
	DME	65	1		80	20[h]	
		20	27		65	25[i]	
$Ni(OAc)_2$	THF	65	0.083		98		
		20	2.5		95-100		
	DME	65	0.05		95		
		20	0.5		90-95		
$ZnCl_2$	THF	65	1		95-100		
		20	19		95		
	DME	65	0.5		92	8	
		20	13		95	5	
$CdCl_2$	THF	65	0.5		95	5	
	DME	65	2.5		66	34	
$ZrCl_4$	THF	65	65		45-50	30	10-15
$MoCl_5$	THF	65	75	20-25	55-60	9	
	DME	65	120	95-100			
WCl_6	THF	65	42	99			
	DME	65	45	98			

[a] In all cases, the NaH/*t*-AmONa/MX_n/$C_8H_{17}Br$ ratio 40/20/10/10 (in millimoles) was used. [b] 40 mL. [c] Preparation of CRA was achieved by method A in THF and method B in DME (see Experimental Section). [d] Determined by GLC analysis (squalene capillary column) with internal standards. [e] Unless otherwise specified, C_8H_{16} refers to 1-octene. [f] Traces of 2-octenes. [g] 1-Octene, 5%; *trans*-2-octene, 2%. [h] 1-Octene, 12%; *trans*-2-octene, 6%; *cis*-3-octene, 3%. [i] 1-Octene, 5%; 2-octenes, 20%.

reactions performed in THF, the metallic salt was added to the preformed NaH–*t*-AmONa mixture (method A), while for reactions in DME, *t*-AmOH was added to a suspension of NaH and MX_n (method B). (Full details of the procedures are given in the Experimental Section). In addition to the reagents reported in Table II, CRA prepared from $Cr(OAc)_3$, $Mn(OAc)_2$, and $Cu(OAc)_2$ were also tested toward *n*-octyl bromide, but these combinations afforded mainly 1-octene along with small amounts (5–20%) of octane.

Results reported in Table II deserve some comments. First, it may be noted that the largest amounts of 1-octene were observed for reactions performed in DME. With Cp_2TiCl_2, nonreproducible results were obtained, and, additionally, unidentified high-molecular-weight side products were produced. THF was more efficient than DME for reductions by Fe CRA. For both $FeCl_3$- and $Co(OAc)_2$-containing systems, at least part of the octane formed may be due to reduction of initially produced 1-octene by the reaction medium.[12] With $Ni(OAc)_2$ in THF, no intermediate formation of octenes was observed during the reaction, so that very little of the product octane was produced by alkene reduction.[13] On the contrary, for reductions performed in DME, formation of a maximum of 5–10% of 1-octene was observed, which slowly disappeared during the reaction.[12] Zn CRA and Cd CRA exhibited similar reactivities, with a larger propensity of Cd CRA to yield 1-octene. As these two CRA were found to be unreactive toward alkenes,[14] only direct reduction of *n*-octyl bromide to octane occurred with both systems. Zr CRA could be reproducibly prepared only in THF and gave mixtures of octane, 1-octene, and hexadecane upon reaction with octyl bromide. Mo CRA exhibited reactivity only in THF, while W CRA were completely unreactive in both solvents.

Once the reactivity order of M CRA had been determined, the influence of the nature of the halogen in the reduction by some CRA was studied. This point is very

(12) Indeed, it has been shown that Fe CRA (see ref 7b) and Co CRA (unpublished work) allow the reduction of alkenes to alkanes in such conditions. However, the reduction rate of alkenes by these systems appeared to be lower than the observed reduction rate of *n*-octyl bromide.

(13) It has been previously shown that Ni CRA is a good reducing agent for alkenes (see ref 7a). Further unpublished studies indicated that DME was the best solvent for such reactions. However, the reduction rate of 1-octene by Ni CRA is lower than the observed reduction rate of *n*-octyl bromide.

(14) J. J. Brunet, D. Besozzi, P. Jacob, and P. Caubere, to be submitted for publication.

Table III. Reaction of Some Selected CRA[a] with *n*-Octyl Halides

metal salt	X of $C_8H_{17}X$	solvent[b,c]	temp, °C	reaction time, h	% recovered material[d]			
					$C_8H_{17}X$	octane	1-octene	hexadecane
VCl_3	Cl	THF	65	18.5	92	7	traces	
	Br			6		90-95	traces	traces
	I			0.75		76	4	12
$FeCl_3$	Cl	THF	65	25	10	84	2	2
	Br			1.5		80	5-10	
	I			0.25		60	traces	39
$Ni(OAc)_2$	Cl	DME	20	15		90-95		
	Br			0.5		90-95		
	I			0.5		93	traces	traces
$ZnCl_2$	Cl	THF	20	16	90[e]	10		
	Br			19		95		
	I			0.75		95-100		
$CdCl_2$	Cl	THF	65	2.5		98		
	Br			0.5		95	5	
	I			0.33		83	11	

[a] In all cases, a NaH/*t*-AmONa/MX_n/$C_8H_{17}X$ ratio of 40/20/10/10 (in millimoles) was used. [b] 40 mL. [c] The preparation of CRA was achieved by method A in THF and method B in DME. [d] Determined by GLC analysis with internal standards. [e] At 65 °C, 1-chlorooctane was reduced to octane in 96% yield after 30 h.

Table IV. Reduction of Secondary and Tertiary Alkyl Halides by Ni CRA[a] in DME[b]

RX	temp, °C	reaction time, min	% recovd RX[c]	% reduction to RH[c]	% elimination[c]
2-bromooctane	20	20		95-100	
bromocyclohexane	20	30		95	traces
chlorocyclopentane	65	15		91	traces
chlorocyclopentane	20	90		90	traces
1-bromoadamantane	65	15		95 (90)	
1-bromoadamantane	20	60		95 (90)	
1-chloroadamantane	65	45		92 (90)	
1-chloroadamantane	20	240		95	
2-bromo-2-methyldodecane	65	2400	40	60	
2-chloro-2-methyldodecane	65	2880		90 (85)	
1-bromo-1-methylcyclohexane	65	3		66	33[d]
1-chloro-1-methylcyclohexane	20	120		60	40[d]

[a] NaH/*t*-AmONa/$Ni(OAc)_2$/RX ratio of 40/20/10/10 (in millimoles). [b] 40 mL. [c] Determined by GLC analysis with adequate internal standards. Isolated yields in parentheses. [d] 1-Methylcyclohexene.

important from both mechanistic and synthetic viewpoints.[15] Some of the most active M CRA were selected, and their reactivities were tested under optimum experimental conditions. The main results are summarized in Table III.

It is clearly evident from Table III that the general reactivity for primary alkyl halides followed the trend RI > RBr >> RCl. *n*-Octyl fluoride was completely inert under a variety of conditions.

Relative to other *n*-octyl halides, *n*-octyl chloride was only slowly reduced, suggesting that it should be possible to reduce an alkyl bromide or an alkyl iodide in the presence of an alkyl chloride. On the other hand, the difference of reactivity between *n*-octyl bromide and iodide strongly depended upon the nature of the metal. Thus, it may be conjectured that V CRA, Fe CRA, and especially Zn CRA may be used successfully to selectively reduce alkyl iodides in the presence of alkyl bromides. On the contrary, Cd CRA and particularly Ni CRA appeared to be much less promising for such selective reductions. Finally, it is noteworthy that Fe CRA and V CRA led to significant amounts of hexadecane, resulting from coupling. This reaction is currently being investigated.[16]

Reduction of Secondary and Tertiary Alkyl Halides. After considerable experimentation, the most efficient reducing system for secondary and tertiary halides was found to be Ni CRA. The zinc derivative, Zn CRA, was unreactive. Thus, Zn CRA may constitute a good reagent for the selective reduction of primary alkyl iodides or bromides in the presence of secondary or tertiary alkyl bromides or chlorides.

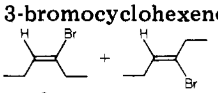
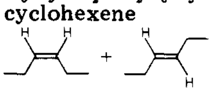
Reductions of secondary and tertiary alkyl halides by Ni CRA are summarized in Table IV. It appears from these experiments that Ni CRA is efficient for the reduction of both classes of halides. Comparison of the results reported in Table II shows that the general trend observed with Ni CRA is primary > secondary > tertiary. It must also be noted that elimination to alkenes is generally low. Even in unfavorable cases, such as 1-halo-1-methylcyclohexanes, 60–65% reduction is easily obtained.

Reduction of Benzyl, Allyl, and Vinyl Halides. Reduction of unsaturated organic halides may be accompanied by side reactions such as coupling of benzyl and allyl halides or hydrogenation or isomerization of carbon–carbon double bonds in allyl and vinyl halides. Thus, it was of interest to examine the behavior of CRA toward such substrates. The results with various examples are summarized in Table V. Several features of the reductions are evident from this table and are outlined below.

First, Zn CRA reduces benzyl bromide to toluene in 100% yield while some bibenzyl was formed with benzyl chloride. On the contrary, Ni CRA was less selective in both cases. In addition, Ni CRA selectively reduced 3-bromocyclohexene to cyclohexene without side reactions at low temperatures. Interestingly, it was observed that at longer reaction times, coupling to bis(2-cyclohexen-1-yl) occurred and became quantitative.[16] Zn CRA led to

(15) J. K. Kochi, "Oranometallic Mechanisms and Catalysts", Academic Press, New York, 1978, and references cited therein.
(16) J. J. Brunet, R. Vanderesse, and P. Caubere, to be submitted for publication.

Table V. Reduction of Some Benzyl, Allyl and Vinyl Halides with CRA[a]

compd	CRA prepared from MX_n	solvent[b]	temp, °C	reaction time, min	product	yield,[c] %
C_6H_5-CH_2Br	$Ni(OAc)_2$	DME	20	15	$C_6H_5CH_3$	50
					$C_6H_5CH_2C_6H_5$	(50)
C_6H_5-CH_2Br	$ZnCl_2$	THF	20	30	$C_6H_5CH_3$	100
C_6H_5-CH_2Cl	$Ni(OAc)_2$	DME	20	30	$C_6H_5CH_3$	80
					$C_6H_5CH_2CH_2C_6H_5$	(20)
C_6H_5-CH_2Cl	$ZnCl_2$	THF	65	180	$C_6H_5CH_3$	85
					$C_6H_5CH_2CH_2C_6H_5$	(10)
3-bromocyclohexene	$Ni(OAc)_2$	DME	−40	5	cyclohexene	90
	$Ni(OAc)_2$	DME	20	60	 [d]	90
9 1					2-hexenes	5
					hexane	4
1-bromocyclohexene	$Ni(OAc)_2$	DME	20	30	cyclohexene	98
					cyclohexane	2
1-chlorocyclohexene	$Ni(OAc)_2$	DME	45	25	cyclohexene	90
					cyclohexane	3
4-methyl-1-chlorocyclohexene	$Ni(OAc)_2$	DME	45	10	4-methylcyclohexene	97
					methylcyclohexane	3
1-bromocyclooctene	$Ni(OAc)_2$	DME	20	60	cyclooctene	95
					cyclooctane	5

[a] NaH/t-AmONa/$Ni(OAc)_2$/RX ratio of 40/20/10/10 (in millimoles). [b] 40 mL. [c] Determined by GLC analysis (on a squalene capillary column) with internal standards and comparison of retention times with those of authentic samples (isolated yields in parentheses). [d] Cis/trans ratio of 9.3:0.7.

Table VI. Selective Reductions of Alkyl Halides by CRA[a]

substrate(s), (amt, mmol)	reducing agent	solvent[b]	temp, °C	reaction time, min	products	yield,[c] %
n-octyl bromide (10)	Ni CRA	DME	65	3	n-octane	100
n-octyl chloride (10)					n-octyl chloride	100
n-octyl bromide (10)	Zn CRA	THF	65	60	n-octane	102
n-octyl chloride (30)					n-octyl chloride	98
1-chloro-4-bromobutane (10)	Zn CRA	THF	65	55	n-butyl chloride	93
1-chloro-4-bromobutane (10)	Ni CRA	DME	20	10	n-butyl chloride	60
n-octyl bromide (10)	Zn CRA	THF	65	60	n-octane	100
4-bromooctane (10)					4-bromooctane	95
n-octyl bromide (10)	ZnCRA	THF	40	45	n-octane	98
cyclohexyl bromide (10)					cyclohexyl bromide	85
					cyclohexane	15
n-octyl bromide (10)	Zn CRA	THF	65	90	n-octane	99
1-bromoadamantane (10)					1-bromoadamantane	100
n-octyl bromide (10)	Zn CRA	THF	65	75	n-octane	96
1-bromocyclooctene (10)					1-octene	2
					1-bromocyclooctene	99
1-bromocyclooctene (10)	Ni CRA	DME	20	45	cyclooctene	96
2-chloro-2-methyldodecane (10)					2-chloro-2-methyldodecane	99
n-octyl bromide (10)	Ni CRA	DME	20	30	n-octyl bromide	95
benzyl chloride (10)					toluene	85
					bibenzyl	15
4-chlorobenzyl chloride (10)	Zn CRA	THF	65	150	4-chlorotoluene	97
2-bromochlorobenzene (10)	Ni CRA	DME	20	60	chlorobenzene	96
					benzene	traces

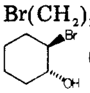
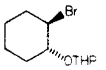
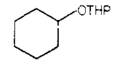
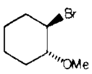
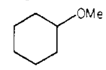
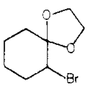
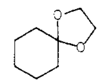
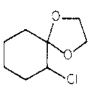
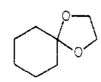
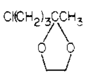
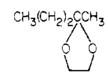
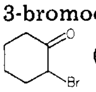
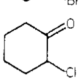
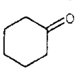
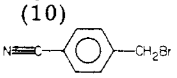
[a] NaH/t-AmONa/MX_n ratio of 40/20/10 (in millimoles). [b] 40 mL. [c] Determined by GLC analysis with adequate internal standards and on the basis of starting halides.

mixtures of cyclohexene and 1,3-cyclohexadiene. In this case no coupling was observed. Vinyl halides were readily reduced by Ni CRA and very little hydrogenation of the double bond occurred. Also, isomerization of the double bond did not occur, as evident from the quantitative reduction of 4-methyl-1-chlorocyclohexene to 4-methylcyclohexene. Moreover, the reaction is highly stereospecific, as indicated by the reduction of 3-bromo-3-hexenes. Interestingly, unreported experimental results indicated that Zn CRA was very poorly reactive toward vinyl halides and thus may be used for selective reductions.

Selective Reductions of Organic Halides. A new reagent for the reduction of organic halides is of some interest mainly if it is able to perform selective conversions. In order to investigate the ability of CRA to achieve such reactions, we undertook a brief study of the reduction of carbon–halogen bonds in the presence of another functional group.

First of all, the possibility of selective reduction of one C–X bond in the presence of another C–X′ bond was investigated. The main results are presented in Table VI. It is clearly evident that, for identical environments, an alkyl bromide may be reduced in the presence of an alkyl chloride by either Ni CRA or Zn CRA. However, Zn CRA is a milder reagent and allows the selective reduction of n-octyl bromide even in the presence of excess n-octyl chloride. Zn CRA also achieved the selective reduction of 1-chloro-4-bromobutane to n-butyl chloride in 93% yield, while Ni CRA led to only 60% n-butyl chloride. As expected, the selective reduction of primary halides in the

Table VII. Selective Reduction of Some Polyfunctional Alkyl Halides with CRA

substrates (amt, mmol)	reducing system[a]	solvent[b]	temp, °C	reaction time, min	products	yield,[c] %
$Br(CH_2)_{10}CH_2OH$ (10)	NaH-*t*-AmONa-$Ni(OAc)_2$	DME	65	5	undecanol	95 (90)
 (10)	NaH-*t*-AmONa-$Ni(OAc)_2$	DME	20	10	cyclohexene oxide	90
 (10)	NaH-*t*-AmONa-$Ni(OAc)_2$	DME	65	5		80
					cyclohexene	10
					cyclohexane	3
 (10)	NaH-*t*-AmONa-$Ni(OAc)_2$	DME	65	5		90
 (10)	NaH-*t*-AmONa-$Ni(OAc)_2$	DME	65	5		100
 (10)	NaH-*t*-AmONa-$Ni(OAc)_2$	DME	65	20		96
 (10)	NaH-*t*-AmONa-$Ni(OAc)_2$	DME	65	20		95
$C_6H_5C(O)CH_2Cl$ (10)	NaH-*t*-AmONa-$Ni(OAc)_2$	DME	65	15	$C_6H_5C(O)CH_3$	80
					$C_6H_5CHOHCH_3$	20
3-bromocamphor (10)	NaH-*t*-AmONa-$Ni(OAc)_2$	DME	20	20	camphor	98 (95)
 (10)	NaH-*t*-AmONa-$Ni(OAc)_2$-WCl_6 [d]	DME	20	240	cyclohexanone	75
 (10)	NaH-*t*-AmONa-$Ni(OAc)_2$-WCl_6 [d]	DME	20	180	cyclohexanone	80
 (10) *n*-octyl bromide (10)	NaH-*t*-AmONa-$ZnCl_2$	THF	40	30	*n*-octane	100
					cyclohexanone	98
cycloheptanone (10) cyclohexyl bromide (10)	NaH-*t*-AmONa-$Ni(OAc)_2$	THF	20	20	cyclohexane	100
					cycloheptanone	93
					cycloheptanol	7
ethyl 4-bromobutyrate (10)	NaH-*t*-AmONa-$Ni(OAc)_2$-WCl_6 [d]	DME	65	150	ethyl butyrate	82
 (10)	NaH-*t*-AmONa-$ZnCl_2$	THF/benzene (3/2)	20	120	4-tolunitrile	56
2-bromoundecanoic acid (10)	NaH-*t*-AmONa-$Ni(OAc)_2$	DME	20	2	undecanoic acid	(90)
11-bromoundecanoic acid (10)	NaH-*t*-AmONa-$Ni(OAc)_2$	DME	20	2	undecanoic acid	(86)
2-chlorobutyric acid (10)	NaH-*t*-AmONa-$Ni(OAc)_2$	DME	20	30	butyric acid	(90)
5-chloropentanoic acid (10)	NaH-*t*-AmONa-$Ni(OAc)_2$	DME	20	20	pentanoic acid	(90)

[a] NaH/*t*-AmONa/MX_n ratio of 40/20/10 (in millimoles). [b] 40 mL. [c] Determined by GLC analysis with internal standards. Isolated yields are given in parentheses. [d] NaH-*t*-AmONa/$Ni(OAc)_2$/WCl_6 ratio of 40/20/10/10 (in millimoles). See Experimental Section.

presence of secondary or tertiary ones was easily achieved by Zn CRA.

The selective reduction of *n*-octyl bromide in the presence of 1-bromocyclooctene was also easily achieved by Zn CRA, while 1-bromocyclooctene could be selectively reduced to cyclooctene by Ni CRA in the presence of a tertiary alkyl chloride. Ni CRA also allowed the selective reduction of benzyl chloride in the presence of *n*-octyl bromide[9] and, as expected, Zn CRA allowed the reduction of 4-chlorobenzyl chloride to 4-chlorotoluene.

An interesting result was also obtained with 2-bromochlorobenzene. In spite of the propensity of this compound to give benzyne,[17] reaction with Ni CRA led to chlorobenzene in 96% yield. Under the same conditions, 1,2-dichlorobenzene (unreported experiments) led to 42% chlorobenzene, 45% benzene, and 10% unreacted dihalide after 3 h at 20 °C. This result shows that even with such dihalides some selectivity was maintained.

It was then decided to further extend the application field of CRA to the selective reduction of C–X bonds in the presence of other different functional groups. Thus, Ni CRA and Zn CRA were reacted with some representative substrates, and the results are reported in Table VII.

Although isolated hydroxyl groups do not influence the reduction of alkyl halides, 2-bromocyclohexanol quantitatively afforded cyclohexene oxide. This could be prevented by protection of the OH group via tetrahydropyranyl or methyl ether. In the same way, reduction of glycol acetals of halogenated ketones was easily performed with Ni CRA. Reduction of unprotected α-halo ketones

(17) See, for example, R. W. Hoffman, "Dehydrobenzene and Cycloalkynes", Verlag Chemie, Weinheim/Bergstr., Germany, Academic Press, New York, 1967.

led to desirable results in only a few cases. However, it was found that formation of such side products could be considerably lowered by adding WCl_6 to Ni CRA before addition of the ketonic compound (see Experimental Section). The possibility thus offered by Ni CRA–WCl_6 systems is well exemplified for the reduction of 2-bromo- and 2-chlorocyclohexanones. The same feature was observed with ethyl 4-bromobutyrate which led to ethyl butyrate in 82% yield with Ni CRA–WCl_6 whereas Ni CRA alone promoted cyclization to ethyl cyclopropylcarboxylate in 100% yield.

When the C–X bond and the carbonyl group are isolated from each other (as in the reduction of a mixture of an alkyl halide and a ketone), Ni CRA readily achieved the selective reduction of the C–X bond. This was exemplified by the selective reduction of primary or secondary alkyl bromides in the presence of cyclic ketones. However, it must be noted that when alkyl chlorides were used, mixtures of the alkanes and alcohols were obtained (unreported experiments).

Generally speaking, most reactive CRA destroy nitriles. However, with sufficiently reactive C–X bonds, such as in benzyl bromide, Zn CRA led to selective reduction in acceptable yields. Finally, Ni CRA very easily reduced halo acids to the corresponding acids in quantitative yields.

Catalytic Reduction of Alkyl Halides. One interesting point was also the determination of whether reductions by CRA reagents could be achieved with catalytic amounts of metallic salt. Both Ni CRA and Zn CRA were investigated in this way. The main results are summarized in Scheme I. It is clearly evident from reactions 1–3 that reductions with Ni CRA are catalytic with respect to the nickel salt. Yields up to 3000% (based on $Ni(OAc)_2$) may be obtained by adding *n*-octyl bromide (10 mmol) every 2 h (time necessary for reduction of 10 mmol of octyl bromide; reaction 4). Side reactions (mainly elimination to alkene) may occur with secondary alkyl bromides (reaction 5) but are excluded with secondary alkyl chlorides (reaction 6). Finally, reaction 5 shows that reductions with Zn CRA, although somewhat catalytic with respect to $Zn(OAc)_2$, cannot be conveniently achieved with catalytic amounts of metallic salt.

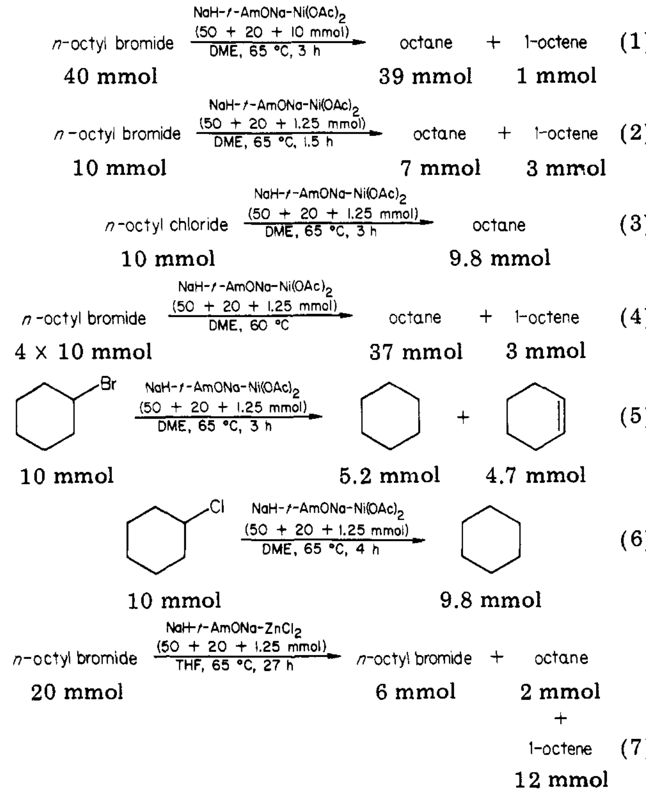
Some Information Concerning the Reaction Mechanism. The exact nature of the active entities in CRA reagents, as well as the exact mechanism of their reactions, is still somewhat obscure. However, the available information concerning these reagents provides some clues as to their nature and mode of action.[4-10]

It has been shown[6] that Ni CRA are insoluble in both THF and DME. Indeed, no nickel could be detected (atomic absorption) in the liquid phase obtained after centrifugation of the reaction medium. Note that, generally speaking, CRA reagents appeared to be of poor solubility in THF or DME.

Furthermore, although *t*-AmONa is soluble in THF, no *t*-AmOH could be detected after hydrolysis of the liquid phase obtained after centrifugation. Tertiary sodium alkoxides are known to react with nickel salts to yield insoluble tertiary nickel alkoxides.[18] It may be concluded then that nickel *tert*-amyl oxides were formed (*t*-AmOH was recovered by hydrolysis of the insoluble part of Ni CRA). On the other hand, monitoring hydrogen gas evolution during the preparation of NaH–RONa–$Ni(OAc)_2$ (40/20/10 mmol) in DME (method B) (see Experimental Section) led to the hypothesis that electrons were transferred from H^- to an acceptor reagent which may only be

(18) B. P. Baranwal and R. C. Mehrotra, *Aust. J. Chem.*, **33**, 37 (1980). See also ref 11.

Scheme I



nickel(II) derivatives. Indeed, the quality of hydrogen evolved was always larger[19] than the 20 mmol obtained for reaction of 20 mmol of ROH with excess NaH in the absence of nickel salt. Finally, it has been shown that Ni CRA was able to reduce double and triple carbon–carbon bonds, suggesting the intermediacy of nickel hydrides.[7]

Thus, although we cannot give a definite structure for the Ni CRA, it appears that the material is a high polymer and has alkoxide bridges which possibly serve to hold the electron-rich nickel centers together. Moreover, some of these metal centers must bear hydrides, so that Ni CRA may be considered as anionic transition metal hydride species.

As shown above, the NaH–$ZnCl_2$ couple exhibited some reducing properties toward *n*-octyl bromide. One possible interpretation is that a Lewis acid–base association of the type (NaH, $ZnCl_2$) enhanced the reducing properties of NaH. In Zn CRA, the presence of alkoxy groups on the metal center could further enhance the reducing power of the system.

As far as the reducing properties of CRA toward organic halides are concerned, the following observations can be made.

CRA reagents are able to reduce aryl halides, even aromatic fluorides. The reactivity order is ArI > ArBr > ArCl ≫ ArF.[4a] As evidenced in the present work, the same reactivity order is obtained for alkyl halides, i.e., RI > RBr ≫ RCl (alkyl fluorides were not reduced). As to the nature of the alkyl group, the general trend primary > secondary > tertiary was observed. These last observations are in agreement with a S_N2-type mechanism.[15,20] However, tertiary alkyl halides, and especially adamantyl halides, are reduced by Ni CRA, so that, at least for such halides, a pure S_N2 mechanism is ruled out. Moreover, reduction

(19) Depending on the nature of the alcohol ROH, 25–30 mmol of hydrogen gas was evolved.

(20) See, for example, R. G. Pearson and P. E. Figdore, *J. Am. Chem. Soc.*, **102**, 1541 (1980).

of *n*-octyl tosylate by Ni CRA was found to be very slow (less than 50% reduction was observed after 30 h at 65 °C in DME). As alkyl tosylates are very reluctant to react by free-radical paths,[20] such reductions must be considered to occur via an S_N2-type mechanism, then suggesting that Ni CRA has poor nucleophilic properties.

Overall, Ni CRA behave as anionic transition-metal species[15] and may be best described as acting as both weak nucleophilic hydride transfer reagents and as electron transfer reagents.

Taking into account the complexity of CRA as well as the complexity of the numerous possible reaction mechanisms for alkyl halide reductions, it is difficult, at the present time, to discuss these reactions in more depth. Current studies in our laboratory are directed toward a more accurate description of reduction by CRA.

Conclusion

The present work emphasizes the versatility of complex reducing agents for converting alkyl halides to hydrocarbons and shows the utility they may have for selective reductions.

However, the reactivity of CRA raises the intriguing and still unanswered question of the actual nature of CRA. Indeed, these reagents are prepared from essentially basic reagents and exhibit rather low basic but high reducing properties.

Experimental Section

Materials. Sodium hydride (55–60% in oil) was obtained from Fluka and was washed several times with the solvent under nitrogen. Badische Anilin reagent grade THF was freshly distilled from benzophenone–sodium couple prior to use. DME (Fluka) was distilled from sodium under nitrogen and stored over sodium wires. For both solvents, the absence of peroxides was checked before each experiment. *tert*-Amyl alcohol was distilled from sodium. Except for Cp_2TiCl_2, VCl_3, $ZrCl_4$, $MoCl_5$, and WCl_6, all metallic salts were dried in vacuo for 8–12 h at 80–110 °C. All reactions were carried out under nitrogen R. All studied organic halides either were commercial (Fluka or Aldrich) or were prepared by described procedures (2-bromo-2-methyldodecane,[21] 2-chloro-2-methyldodecane,[21] 3-bromocyclohexene,[22] 3-bromo-3-hexene,[23] 1-bromocyclohexene,[24] 1-chlorocyclohexene,[25] 4-methyl-1-chlorocyclohexene,[25] 1-bromocyclooctene,[26] 11-bromoundecanol,[27] 2-bromocyclohexanol,[28] 1-bromo-2-methoxycyclohexane[29]). Protection of the OH group of α-bromocyclohexanol was achieved by following the procedure described by Robertson,[30] and protection of the carbonyl group of halo ketones was achieved according to the procedure of Walker.[31] Silica column chromatographies were performed by using Kieselgel (Merck, 0.063–0.200 mm).

General Methods. GLC analyses were performed on either a Carlo Erba GI 452 or a Girdel 3000 equipped with 5-m, 15% Carbowax 20M, 15% UCON 50 HB 2000, 15% QF_1, or 15% SE-30 columns or with a squalene capillary column.

IR spectra were recorded with a Perkin-Elmer 457 spectrophotometer. NMR spectra were recorded with a Perkin-Elmer R-12-B instrument.

Preparations of CRA. General Procedures. CRA were prepared according to either of the following methods.

Method A. This method was used for all reactions performed in THF. *t*-AmOH (20 mmol) in THF (10 mL) was added at 60–65 °C to a vigorously stirred suspension of NaH (60 mmol) in THF (10 mL), and the mixture stirred for 2 h. The temperature was then decreased, if necessary (to 0 °C for $FeCl_3$, $MoCl_5$, and WCl_6 and to 20 °C for VCl_3, $Mn(OAc)_2$, $ZrCl_4$, $ZnCl_2$, and $CdCl_2$), and the metallic salt (10 mmol) was added, followed by 10 mL of THF. After being refluxed for 4 h, the reagent was ready for use.

Method B. This method was used for all reactions performed in DME. The metallic salt (10 mmol) was added at room temperature or below (see method A) to a stirred suspension of NaH (60 mmol) in DME (20 mL). The temperature was raised to 60–65 °C; *t*-AmOH (10 mmol) in DME (10 mL) was added dropwise. After the mixture was heated for 1 h at 65 °C, the reagent was ready for use.

Bimetallic systems (Table VII) were prepared as follows. WCl_6 (10 mmol) was added in small portions at 20 °C to Ni CRA prepared as described above (method B). After the reaction mixture was heated for 2 h at 65 °C, the bimetallic reagent was ready for use.

Reduction of *n*-Octyl Halides. General Procedure (Tables II and III). To the reagents prepared as described above were added the *n*-octyl halide (10 mmol) and the internal standard in 10 mL of solvent. The reductions were monitored by GLC analysis (squalene capillary column and UCON 50 HB 2000 for octane and octenes, QF_1 for octyl halides) of small aliquots periodically syringed from the reaction flask through a septum cap.

Control Experiments. Control experiments reported in Table I were conducted by reacting 10 mmol of *n*-octyl bromide with either NaH (60 mmol), *t*-AmONa (60 mmol), or NaH–*t*-AmONa (40–20 mmol). *t*-AmONa was prepared by reacting *t*-AmOH with an equimolecular quantity of NaH for 2 h at 60 °C in the desired solvent. NaH–*t*-AmONa was prepared as described above for method A.

Control experiments on the reactivity of NaH–MX_n systems (60–10 mmol) against *n*-octyl bromide were conducted as follows.

NaH (60 mmol) and the metallic salt (10 mmol) in THF (30 mL; MX_n = $FeCl_3$, $Co(OAc)_2$, $Cu(OAc)_2$, $ZnCl_2$, $ZrCl_4$, $MoCl_5$, and $CdCl_2$) or in DME (30 mL; MX_n = Cp_2TiCl_2, VCl_3, $Cr(OAc)_3$, $Mn(OAc)_2$, $Ni(OAc)_2$, and WCl_6) were heated for 2 h at 65 °C. Then, *n*-octyl bromide (10 mmol) was added together with the internal standard, and the reaction was monitored by GLC analysis of small aliquots, as described above.

For MX_n = Cp_2TiCl_2, VCl_3, $Cr(OAc)_3$, $Mn(OAc)_2$, $Co(OAc)_2$, $ZrCl_4$, $MoCl_5$, and WCl_6, more than 90% of the starting halide was recovered unchanged after 20 h at 65 °C. For the other metallic salts, the following results were obtained (MX_n, reaction time, percent recovered *n*-octyl bromide, percent octane, percent 1-octene): $FeCl_3$, 18 h, 28, 42, 16; $Ni(OAc)_2$, 13 h, 75, 20, 2; $Cu(OAc)_2$, 18 h, 30, 50, 20; $ZnCl_2$, 18 h, 50, 45, 3; $CdCl_2$, 13 h, 55, 40, 2.

Reduction of Secondary and Tertiary Alkyl Halides (Table IV). These reductions were conducted as described above for the reduction of *n*-octyl halides. Preparative experiments were conducted without internal standard. At completion, the reaction medium was cooled, and ethanol (20 mL) was added, followed by water. After acidification with dilute HCl, a classical workup yielded the reduction product which was purified by column chromatography on silica columns with petroleum ether–ether mixtures and identified by comparison with an authentic sample.

Reduction of Benzyl, Allyl, and Vinyl Halides (Table V). These reactions were conducted as described above for the reduction of *n*-octyl halides. The course of the reaction was followed by GLC analysis of small aliquots, and reduction products were identified by comparison of their retention times with those of authentic samples on several columns (squalene capillary column, UCON 50 HB 2000, Carbowax 20M).

Selective Reductions (Tables VI and VII). Selective reductions were conducted by the general procedure described above, both substrates being added simultaneously to the reducing agent. In most cases the reduction products were identified by GLC analysis by comparison, on several columns, of their retention times with those of authentic samples.

Catalytic Reductions of Alkyl Halides (Scheme I). All these reactions were performed and monitored by the general procedures described above. For reaction 4 the 40 mmol of *n*-octyl

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(26) P. Caubere and G. Coudert, *Bull. Soc. Chim. Fr.*, 3067 (1973).
(27) R. F. Nystrom, *J. Am. Chem. Soc.*, 81, 610 (1959).
(28) C. O. Guss and R. Rosenthal, *J. Am. Chem. Soc.*, 77, 2549 (1955).
(29) K. L. Erickson and K. Kim, *J. Org. Chem.*, **36**, 2915 (1971).
(30) D. N. Robertson, *J. Org. Chem.*, **25**, 931 (1960).
(31) G. N. Walker, *J. Am. Chem. Soc.*, 75, 3393 (1953).

bromide were added 10 mmol at a time every 2 h.

Acknowledgment. This work was supported by the Centre National de la Recherche Scientifique, France, which is gratefully acknowledged for financial aid. The authors are very grateful to one of the referees for helpful suggestions for improvement of the manuscript.

Registry No. Sodium hydride, 7646-69-7; *tert*-amyl alcohol, 75-85-4; sodium *tert*-amyl alcohol, 14593-46-5; octyl bromide, 111-83-1; 1-octene, 111-66-0; Cp_2TiCl_2, 1271-19-8; VCl_3, 7718-98-1; $FeCl_3$, 7705-08-0; $Co(OAc)_2$, 71-48-7; $Ni(OAc)_2$, 373-02-4; $ZnCl_2$, 7646-85-7; $CdCl_2$, 10108-64-2; $ZrCl_4$, 10026-11-6; $MoCl_5$, 10241-05-1; WCl_6, 13283-01-7; octane, 111-65-9; octyl chloride, 111-85-3; octyl iodide, 629-27-6; 2-bromooctane, 557-35-7; bromocyclohexane, 108-85-0; chlorocyclopentane, 930-28-9; 1-bromoadamantane, 768-90-1; 1-chloroadamantane, 935-56-8; 2-bromo-2-methyldodecane, 76402-83-0; 2-chloro-2-methyldodecane, 4325-53-5; 1-bromo-1-methylcyclohexane, 931-77-1; 1-chloro-1-methylcyclohexane, 931-78-2; cyclohexane, 110-82-7; cyclopentane, 287-92-3; adamantane, 281-23-2; 2-methyldodecane, 1560-97-0; methylcyclohexane, 108-87-2; benzyl bromide, 100-39-0; benzyl chloride, 100-44-7; 3-bromocyclohexene, 1521-51-3; (*E*)-3-bromo-3-hexane, 42843-52-7; (*Z*)-3-bromo-3-hexene, 16645-01-5; 1-bromocyclohexene, 2044-08-8; 1-chlorocyclohexene, 930-66-5; 4-methyl-1-chlorocyclohexene, 31053-83-5; 1-bromocyclooctene, 4103-11-1; methylbenzene, 108-88-3; diphenylmethane, 101-81-5; cyclohexene, 110-83-8; (*Z*)-3-hexene, 7642-09-3; (*E*)-3-hexene, 13269-52-8; 4-methylcyclohexene, 591-47-9; cyclooctene, 931-88-4; 1-chloro-4-bromobutane, 6940-78-9; 4-bromooctane, 999-06-4; 4-chlorobenzyl chloride, 104-83-6; 2-bromochlorobenzene, 694-80-4; butyl chloride, 109-69-3; 4-chlorotoluene, 106-43-4; chlorobenzene, 108-90-7; 11-bromo-1-undecanol, 1611-56-9; *trans*-2-bromocyclohexanol, 2425-33-4; *trans*-2-[(2-bromocyclohexyl)oxy]tetrahydro-2*H*-pyran, 76402-84-1; *trans*-1-bromo-2-methoxycyclohexane, 5927-93-5; 6-bromo-1,4-dioxaspiro[4.5]decane, 1724-15-0; 6-chloro-1,4-dioxaspiro[4.5]decane, 6954-16-1; 2-(3-chloropropyl)-2-methyl-1,3-dioxolane, 5978-08-5; 2-chloro-1-phenylethanone, 532-27-4; 3-bromocamphor, 76-29-9; 2-bromocyclohexanone, 822-85-5; 2-chlorocyclohexanone, 822-87-7; cyclohexanone, 108-94-1; cycloheptanone, 502-42-1; ethyl 4-bromobutyrate, 5969-81-5; 4-(bromomethyl)benzonitrile, 17201-43-3; 2-bromoundecanoic acid, 2623-84-9; 11-bromoundecanoic acid, 2834-05-1; 2-chlorobutyric acid, 4170-24-5; 5-chloropentanoic acid, 1119-46-6; cyclohexene oxide, 286-20-4; 2-(cyclohexyloxy)tetrahydro-2*H*-pyran, 709-83-1; methoxycyclohexane, 931-56-6; 1,4-dioxaspiro[4.5]decane, 177-10-6; 2-methyl-2-propyl-1,3-dioxolane, 4352-98-1; 1-phenylethanone, 98-86-2; camphor, 76-22-2; ethyl butyrate, 105-54-4; 4-tolunitrile, 104-85-8; undecanoic acid, 112-37-8; butyric acid, 107-92-6; pentanoic acid, 109-52-4; $Cr(OAc)_3$, 1066-30-4; $Cu(OAc)_2$, 142-71-2.

Reaction of *N*-Chloro-*N*-fluoroperhaloalkylamines with Mercury. Facile Synthesis of *N*-Fluoro Imines and *N*-Fluoro Amines

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The reaction of *N*-chloro-*N*-fluoroalkylamines with mercury has been studied with $ClCF_2NClF$, CF_3NClF, CF_3CF_2NClF, $CF_3CF_2CF_2NClF$, and $(CF_2NClF)_2$. In the absence of solvents, all but CF_3NClF undergo dehalogenation to form the corresponding *N*-fluoro imines in good yield. Only the syn isomers of $CF_3CF{=}NF$, $CF_3CF_2CF{=}NF$, and $(CF{=}NF)_2$ are observed. With trifluoroacetic acid as a solvent, the reactions with mercury yield the corresponding *N*-fluoro amines $ClCF_2NHF$, CF_3NHF, CF_3CF_2NHF, and $CF_3CF_2CF_2NHF$ in excellent yields except with $(CF_2NClF)_2$. For the latter, the amine $(CF_2NHF)_2$ eliminates HF under the reaction conditions, and only $(CF{=}NF)_2$ is isolated. With trifluoroacetic anhydride as a solvent, $ClCF_2NClF$ is dehalogenated with mercury to give excellent yields of $CF_2{=}NF$ in the first practical synthesis of this simplest perfluoro imine. Details of these reactions and the characterization of the new compounds $ClCF_2NHF$, CF_3CF_2NHF, $CF_3CF_2CF_2NHF$, and $CF_3CF_2CF{=}NF$ are presented.

Highly fluorinated organonitrogen compounds encompass a broad range of materials, whose synthesis, properties, and chemical reactions are of continuing interest.[1] The variety and number of fluorinated compounds are far less than hydrocarbon analogues, due in part to the lack of suitable preparative methods for their synthesis. The latter consideration also limits the investigation of the chemistry of some known fluorinated compounds.

Two related classes of compounds illustrative of the above are the *N*-fluoro imines, $R_fCF{=}NF$, and *N*-fluoro amines, R_fNHF. Several imines are known[2] but not easily prepared, and only one example of an amine, CF_3NHF,[3] has been isolated. These two classes of compounds are, of course, related and in principle interconvertible by the addition or elimination of hydrogen fluoride (eq 1).

$$R_fCF{=}NF \underset{-HF}{\overset{HF}{\rightleftharpoons}} R_fCF_2NHF \qquad (1)$$

Recently a general and preparatively useful method for the synthesis of *N*-chloro-*N*-fluoro amines has been found[4] (eq 2). This paper reports the conversion of these compounds to the corresponding *N*-fluoro imines and *N*-fluoro amines.[5]

$$R_fCN + F_2 + ClF \rightarrow R_fCF_2NClF \qquad (2)$$

Experimental Section

General Methods. All compounds were handled in Pyrex or stainless-steel vacuum systems equipped with glass–Teflon valves or Teflon-packed, stainless-steel valves. Pressures were measured with a Wallace and Tiernan differential pressure gauge (Series

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