Experimental Section

Melting points are uncorrected and were determined on a Kofler hot stage microscope. NMR spectra were recorded on a Varian T-60 NMR spectrometer with Me_4Si as an internal standard. IR spectra were determined as Nujol mulls using a Beckman IR-20A spectrophotometer. MS were determined by a Finnigan 3100 GC–MS coupled to a D6000 data acquisition system. Thin-layer chromatograms were run on glass plates coated with Silica Gel F-254. Separated components were detected by UV fluorescence and iodine vapor.

2,3-Bis(trifluoroacetoxy)-2-methyl-1,4-oxathian-3-carboxanilide (2). A suspension of carboxin sulfoxide (**1**,[11] 510 mg) in benzene (10 mL) was treated with an excess of trifluoroacetic anhydride (0.5 mL) and stirred for 15 min at room temperature. Removal of the benzene and unreacted trifluoroacetic anhydride with a stream of dry N_2 yielded, after recrystallization from anhydrous diethyl ether, the bis(trifluoroacetate) **2** (793 mg), mp 98–100 °C: IR (Nujol) 3224, 1795, 1700, 1540 cm^{-1}; NMR ($CDCl_3$) δ 7.92 (1 H, s, NH), 7.35 (5 H, m, pH), 2.57–4.17 (4 H, m, ring H), 1.91 (3 H, s, CH_3); MS *m/e* 461 (M^+). Anal. Calcd for $C_{16}H_{13}O_6NSF_6$: F, 24.73. Found: F, 24.41.

2,3-Bis(methoxy)-2-methyl-1,4-oxathian-3-carboxanilide (3). A solution of **2** (300 mg) in 95% methanol (10 mL) was stirred overnight. After dilution with water (40 mL) the mixture was neutralized by the addition of sodium bicarbonate and then extracted with chloroform (2 × 60 mL). After drying (anhydrous sodium sulfate) the chloroform was removed under vacuum, and the residue was purified by preparative thin-layer chromatography (ethyl acetate–hexane, 1:1). Crystallization of the major component (119 mg) from diethyl ether–hexane gave the dimethoxy analogue **3**, mp 120–122 °C: NMR ($CDCl_3$) δ 8.14 (1 H, s, NH), 7.36 (5 H, m, Ph), 2.24–4.02 (4 H, m, ring H), 3.62 (3 H, s, OMe), 3.38 (3 H, s, OMe), 1.42 (3 H, s, Me); MS *m/e* 297 (M^+).

2-Methyl-1,3-oxathiolan-2-ketocarboxanilide (4). A solution of **2** (200 mg) in dimethylformamide (20 mL) and H_2O (5 mL) was stirred overnight. Removal of the solvents under vacuum yielded, after recrystallization from aqueous ethanol, the 1,3-oxathiolane **4** (78 mg), mp 130–131 °C: IR (Nujol) 3335, 1710, 1690, 1545 cm^{-1}; NMR ($CDCl_3$) δ 9.10 (1 H, s, NH), 7.40 (5 H, m, Ph), 3.01–4.44 (4 H, m, ring H), 2.12 (3 H, s, Me); MS *m/e* 251 (M^+) −103 (M^+ − 148).

***N*-Trifluoroacetyl-5,6-dihydro-2-trifluoroacetoxymethyl-1,4-oxathiin-3-carboxanilide (5).** A solution of **2** in benzene or alternately a solution of **1** in benzene plus an excess of trifluoroacetic anhydride refluxed for approximately 1 h or left to stir overnight afforded (after removal of solvents with a stream of N_2) a near quantitative yield of the 2-trifluoroacetoxymethyl derivative **5**, which did not crystallize but showed one spot on TLC (ethyl acetate–hexane, 3:2): IR (Nujol) 1795, 1745, and 1705 cm^{-1}; NMR ($CDCl_3$) δ 7.36 (5 H, m, Ph), 5.17 (2 H, s, CH_2O), 2.86–4.48 (4 H, m, ring H); MS *m/e* 443 (M^+). Anal. Calcd for $C_{16}H_{11}O_5NSF_6$: F, 25.74. Found: F, 25.84.

5,6-Dihydro-2-trifluoroacetoxymethyl-1,4-oxathiin-3-carboxanilide (6). A solution of **5** (250 mg) in chloroform (40 mL) in a separatory funnel was shaken with saturated sodium bicarbonate solution (25 mL) for several minutes. The chloroform layer was separated and dried over anhydrous sodium sulfate, and the chloroform was removed under vacuum. Recrystallization of the residue from hexane gave the monotrifluoroacetate **6** (174 mg), mp 92–93 °C: IR (Nujol) 3255, 1790, 1650, 1545 cm^{-1}; NMR ($CDCl_3$) δ 8.02 (1 H, s, NH), 7.38 (5 H, m, Ph), 5.36 (2 H, s, CH_2O), 2.98–4.45 (4 H, m, ring H); MS *m/e* 347 (M^+).

5,6-Dihydro-2-hydroxymethyl-1,4-oxathiin-3-carboxanilide (7). A solution of **6** (150 mg) in benzene (10 mL) containing pyridine (5 mL) was stirred for 1 h. The solution was then taken up in chloroform (50 mL) and shaken with water (2 × 30 mL) in a separatory funnel. After separation, drying (anhydrous sodium sulfate), and removal of the chloroform and traces of pyridine under vacuum, washing the crystalline residue with hexane afforded the alcohol **7** (82 mg), mp 87–89 °C: IR (Nujol) 3360, 3295, 1650, 1535 cm^{-1}; NMR ($CDCl_3$) δ 8.22 (1 H, s, NH), 7.42 (5 H, m, Ph), 4.28 (2 H, s, CH_2O), 2.98–4.52 (4 H, m, ring H); MS *m/e* 251 (M^+).

2-Acetoxymethyl-5,6-dihydro-1,4-oxathiin-3-carboxanilide (8). A solution of **7** (140 mg) in acetic anhydride (5 mL) and pyridine (3 mL) was stirred for 3 h at room temperature and then neutralized by decantation into a cold saturated solution of sodium bicarbonate. After extraction of the neutral solution with chloroform (2 × 50 mL), the chloroform extracts were dryed and concentrated under vacuum. Any residual pyridine was removed with a stream of N_2, and the residue was crystallized from hexane to yield the acetate **8** (113 mg), mp 90–91 °C: IR (Nujol) 3255, 1730, 1650, 1545 cm^{-1}; NMR ($CDCl_3$) δ 8.98 (1 H, s, NH) 7.40 (5 H, m, Ph), 4.97 (2 H, s, CH_2O), 3.00–4.37 (4 H, m, ring H), 2.92 (3 H, s, OAc); MS *m/e* 337 (M^+).

5,6-Dihydro-2-(hydroxymethyl)-1,4-oxathiin-3-carboxylic Acid γ-Lactone (9). **5**, **6**, or **7** in benzene and pyridine stirred overnight after workup inevitably yielded the α,β-unsaturated-γ-lactone **9**, which after crystallization from hexane had mp 117–118 °C: IR (Nujol) 1750 cm^{-1}; NMR ($CDCl_3$) δ 4.74 (2 H, s, CH_2O), 3.04–4.65 (4 H, m, ring H); MS *m/e* 158 (M^+). Anal. Calcd for $C_6H_6O_3S$: C, 45.56; H, 3.82. Found: C, 45.75; H, 3.73.

***N*-Methyl-2,3-bis(trifluoroacetoxy)-2-methyl-1,4-oxathian-3-carboxanilide (10).** A suspension of *N*-methylcarboxin sulfoxide[11] (200 mg) in benzene (5 mL) was treated with an excess of trifluoroacetic anhydride and stirred for 15 min. Benzene and unreacted trifluoroacetic anhydride were removed with a stream of N_2. Recrystallization of the residue from anhydrous diethyl ether furnished the *N*-methylbis(trifluoroacetoxy) compound **10**, mp 190 °C dec: IR (Nujol) 1795, 1645 cm^{-1}; NMR ($CDCl_3$) δ 7.34 (5 H, m, Ph), 2.18–5.14 (4 H, m, ring H), 4.38 (3 H, s, N–Me), 1.88 (3 H, s, Me).

A solution of **10** in benzene with or without trifluoroacetic anhydride on refluxing for several hours or after stirring at room temperature for up to 3 days did not produce any change in the compound.

Acknowledgment. The authors wish to thank R. B. Gibb for the NMR determinations and S. Skinner for the mass spectral data.

Registry No.—**1** (Ar = Ph), 17757-70-9; **2** (Ar = pH), 64754-69-4; **3** (Ar = Ph), 64754-70-7; **4** (Ar = Ph), 64754-74-1; **5** (Ar = Ph), 64754-72-9; **6** (Ar = Ph), 64754-73-0; **7** (Ar = Ph), 64754-75-2; **8** (Ar = Ph), 42825-80-9; **9**, 64754-76-3; **10** (Ar = Ph), 64754-71-8; trifluoroacetic anhydride, 407-25-0; acetic anhydride, 108-24-7; *N*-methylcarboxins sulfoxide, 17757-81-2.

References and Notes

(1) R. Pummerer, *Ber. Dtsch. Chem. Ges.*, **43**, 1401 (1910).
(2) L. Horner and P. Kaiser, *Justus Liebigs Ann. Chem.*, **62**, 19 (1959).
(3) J. Kitchin and R. J. Stoodley, *J. Chem. Soc., Chem. Commun.*, 959 (1972).
(4) H. Kosugi, H. Uda, and S. Yamagiwa, *J. Chem. Soc., Chem. Commun.*, 71 (1976).
(5) L. S. Reamour and W. I. O'Sullivan, *J. Chem. Soc., Chem. Commun.*, 642 (1976).
(6) H. Kosugi, H. Uda, and S. Yamagiwa, *J. Chem. Soc., Chem. Commun.*, 192 (1975). However, we believe on the basis of our present work that involvement of an additive Pummerer rearranged intermediate is quite possible.
(7) R. Greenhalgh, W. D. Marshall, and R. R. King, *J. Agric. Food Chem.*, **24**, 266 (1976).
(8) B. von Schmeling and M. Kulka, *Science*, **152**, 659 (1966).
(9) W. E. Parham and M. O. Bhavsar, *J. Am. Chem. Soc.*, **85**, 2686 (1963).
(10) W. E. Parham, J. Heberling, and H. Wynberg, *J. Am. Chem. Soc.*, **77**, 1169 (1955).
(11) Uniroyal Research Laboratory Ltd., Guelph, Ont., Can.

Transition Metal Catalyzed Reactions of Lithium Aluminum Hydride with Alkyl and Aryl Halides

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Received July 18, 1977

The reduction of organic halides to the corresponding hydrocarbons is an important transformation in organic synthesis. Recently, $2LiAlH(OCH_3)_3$–CuI[1] and LiCuHR[2] compounds (where R = alkyl and alkynyl) were evaluated as reagents for removal of halo and mesoloxy groups. $TiCl_3$–Mg[3] and $(\pi\text{-Cp})_2TiCl_2$–Mg[4] have been used for the same purpose at almost the same time by different research groups. More recently, we have been able to synthesize complex metal hydrides of copper and have demonstrated their ability to remove the halo and tosylate group from alkyl and aryl halides and tosylates.[5] We wish to report here that $LiAlH_4$ in the presence of first row transition-metal halides is a powerful and convenient reagent for the removal of halo and tosylate groups.

$LiAlH_4$ is not as effective a reagent for the removal of halo

0022-3263/78/1943-1263$01.00/0

Table I. Reduction of Halides by $LiAlH_4$–Transition-Metal Chlorides at Room Temperature in THF Solvent[a]

Expt	Halide substrate[d]	Registry no.	Transition-metal chloride[b]	Reaction time, h	Product	Yield, %
1.	1-Chlorodecane[e]	1002-69-3	None	24	*n*-Decane	68
2.			VCl_3			75
3.			$CrCl_3$			90
4.			$MnCl_2$			19
5.			$FeCl_3$			100
6.			$FeCl_2$			95
7.			$FeCl_2$[c]			85
8.			$CoCl_2$[c]			100
9.			$NiCl_2$[c]			100
10.			$TiCl_3$[c]			100
11.	1-Bromodecane[e]	112-29-8	None	1	*n*-Decane	92
12.			VCl_3			40
13.			$CrCl_3$			65
14.			$MnCl_2$			43
15.			$FeCl_3$			50
16.			$FeCl_2$			100
17.			$FeCl_2$[c]			90
18.			$CoCl_2$			98
19.			$CoCl_2$[c]			98
20.			$NiCl_2$			100
21.			$NiCl_2$[c]			100
22.			$TiCl_3$			96
23.			$TiCl_3$[c]			98
24.	1-Iododecane	2050-77-3	None		*n*-Decane	98
25.			$FeCl_2$			98
26.			$CoCl_2$[c]			98
27.			$NiCl_2$[c]			98
28.			$TiCl_3$[c]			100
29.	1-Fluorodecane	334-56-5	None	24	*n*-Decane	0
30.			$FeCl_2$			16
31.			$CoCl_2$[c]			10
32.			$NiCl_2$[c]			7
33.			$TiCl_3$[c]			9
34.	*n*-Octyltosylate	3386-35-4	None	24	*n*-Octane	92
35.			$FeCl_2$			25
36.			$CoCl_2$[c]			100
37.			$NiCl_2$[c]			98
38.			$TiCl_3$[c]			54
39.	3-Bromooctane	999-64-4	None	24	*n*-Octane	75
40.			$FeCl_2$			90
41.			$CoCl_2$			98
42.			$NiCl_2$			92
43.			$TiCl_3$			88
44.	Bromocyclohexane	108-85-0	None	24	Cyclohexane	0
45.			$FeCl_2$			97
46.			$CoCl_2$			99
47.			$NiCl_2$			99
48.			$TiCl_3$			100
49.	Chlorocyclohexane	542-18-7	None	24	Cyclohexane	0
50.			$FeCl_2$			98
51.			$CoCl_2$			92
52.			$CoCl_2$[c]			3
53.			$NiCl_2$			95
54.			$NiCl_2$[c]			5
55.			$TiCl_3$			95
56.			$TiCl_3$[c]			95
57.	1-Bromoadamantane	768-90-1	None	24	Adamantane	70
58.			$FeCl_2$			100
59.			$CoCl_2$			100
60.			$NiCl_2$			100
61.			$TiCl_3$[c]			100
62.	Chlorobenzene	108-90-7	None	24	Benzene	0
63.			$FeCl_2$			72
64.			$CoCl_2$			25
65.			$CoCl_2$[c]			0
66.			$NiCl_2$			100
67.			$NiCl_2$[c]			0
68.			$TiCl_3$[c]			45
69.	Bromobenzene	108-86-1	None	24	Benzene	0
70.			$FeCl_2$			80
71.			$CoCl_2$			74

Table I (*Continued*)

Expt	Halide substrate[d]	Registry no.	Transition-metal chloride[b]	Reaction time, h	Product	Yield, %
72.			$CoCl_2$[c]			23
73.			$NiCl_2$			100
74.			$NiCl_2$[c]			87
75.			$TiCl_3$[c]			91
76.	Iodobenzene	591-50-4	None	24	Benzene	38
77.			$FeCl_2$			98
78.			$CoCl_2$			98
79.			$NiCl_2$			100
80.			$TiCl_3$[c]			92

[a] All reactions were carried out in THF at −78 °C for 10 min and then warmed to room temperature by removing the cooling bath. The reaction time was counted beginning with the period at −78 °C. Yields were determined by GLC using a suitable internal standard. [b] Molar ratio of $LiAlH_4$ to transition-metal chloride is 1:1, except when noted. [c] Used 10% molar equivalent. [d] Halide substrate was used in equivalent molar amount to $LiAlH_4$ except when noted. [e] Halide substrate was one-half equivalent with respect to $LiAlH_4$.

or tosylate groups from organic molecules as the reagent $LiAlH_4$–transition-metal halide. For example, $LiAlH_4$ reduces 1-iododecane, 1-bromodecane, and *n*-octyl tosylate to the corresponding hydrocarbon in 92–98% yields, but reduces 1-chlorodecane in only 68% yield and exhibits no effect at all in the reduction of bromocyclohexane and bromobenzene under the same reaction conditions (room temperature, 24 h, stoichiometric 1:1 molar ratio of $LiAlH_4$–halide substrate). The admixture of $LiAlH_4$–transition-metal chloride (VCl_3, $CrCl_3$, $MnCl_2$, $FeCl_2$, $FeCl_3$, $CoCl_2$, $NiCl_2$, and $TiCl_3$) in stoichiometric or catalytic amount was allowed to react with alkyl or aryl halides in order to compare the reactivity of these mixed reagents with $LiAlH_4$ itself. The results are shown in Table I.

In the reactions of 1-chlorodecane and 1-bromodecane, $FeCl_2$, $CoCl_2$, $NiCl_2$, and $TiCl_3$ (stoichiometric or catalytic) show superior reducing ability compared to the other catalysts evaluated (i.e., VCl_3, $CrCl_3$, $MnCl_2$, and $FeCl_3$). The admixture of $LiAlH_4$–VCl_3, –$CrCl_3$, –$MnCl_2$, and –$FeCl_3$ (stoichiometric) reduced 1-chlorodecane and 1-bromodecane to *n*-decane in only low yields compared to the reactions involving $FeCl_2$, $CoCl_2$, $NiCl_2$, and $TiCl_3$ under the same reaction conditions. Furthermore, $LiAlH_4$ with 10 mol % $FeCl_2$, $CoCl_2$, $NiCl_2$, and $TiCl_3$ reduced 1-chlorodecane in 85, 100, 100, and 100% yields, respectively. These results reveal the relative catalytic ability of transition-metal chlorides; i.e., $CoCl_2$, $NiCl_2$, and $TiCl_3$ are more effective catalysts than $FeCl_2$.

Since $FeCl_2$, $CoCl_2$, $NiCl_2$, and $TiCl_3$ admixed with $LiAlH_4$ were found to be the most effective catalysts for reduction of 1-chlorodecane and 1-bromodecane, only these catalysts were used in further studies of other halides. Decyliodide was reduced to *n*-decane in nearly quantitative yield by the above transition-metal halides; however, fluorodecane was reduced in only 7–16% yield. *n*-Octyl tosylate was reduced to *n*-octane in 98–100% yield by $LiAlH_4$ and a catalytic amount (10 mol %) of $NiCl_2$ and $CoCl_2$, but in significantly lower yields by $FeCl_2$ and $TiCl_3$. The secondary halide, 3-bromodecane, was also reduced in high yield (88–98%) when the transition-metal halides were used in stoichiometric amount. Bromocyclohexane and chlorocyclohexane, which are inert to $LiAlH_4$, can be reduced by $LiAlH_4$ with stoichiometric amounts of $FeCl_2$, $CoCl_2$, and $NiCl_2$, or a catalytic amount (10 mol %) of $TiCl_3$, to produce cyclohexane in excellent yields (92–100%). However, a catalytic amount (10 mol %) of $CoCl_2$ or $NiCl_2$ was not effective in the reduction of bromocyclohexane. Also, 1-bromoadamantane was reduced to adamantane in quantitative yield by all four catalysts.

Phenyl halides (X = I, Br, and Cl) were also allowed to react with these new reagents. The substrates were reduced in the order I > Br > Cl, and the superior reagent for the reduction of aromatic halides was found to be $LiAlH_4$–$NiCl_2$ (1:1), which reduced iodo-, bromo-, and chlorobenzene to benzene in 100% yield.

In conclusion, admixtures of $LiAlH_4$ with stoichiometric or catalytic amounts of $FeCl_2$, $CoCl_2$, $NiCl_2$, and $TiCl_3$ have been found to be powerful reagents for removal of the halo or tosylate group in organic substrates. Especially, the reagent $LiAlH_4$–$NiCl_2$ can reduce primary, secondary, cyclic, and even aromatic halides (X = I, Br, and Cl) in essentially quantitative yield in each case.

Experimental Section

Apparatus. Reactions were performed under nitrogen at the bench using Schlenk tube techniques.[6] ^1H NMR spectra were obtained at 60 MHz using a Varian T-60 NMR spectrometer. Mass spectra were obtained on a Varian Model M-66 mass spectrometer. GLC analyses were performed on F & M Models 700 and 720 gas chromatographs.

Materials. Tetrahydrofuran (Fisher Certified Reagent Grade) was distilled under nitrogen over $NaAlH_4$. Transition-metal chlorides and organic substrates were purchased commercially and used without further purification.

General Reactions. A 10-mL Erlenmeyer flask with a Teflon-coated magnetic stirring bar was dried in an oven and allowed to cool under a nitrogen flush. The transition-metal chloride (ca. 0.2 mmol for stoichiometric and ca. 0.02 mmol for catalytic reactions) was transferred to the flask in a drybox, sealed with a rubber septum, removed from the drybox, and connected by means of a needle to a source of nitrogen. The calculated amount of organohalide in THF solution was syringed into the transition-metal halide in the flask at −40 °C (controlled by a dry-ice bath). The designated amount of $LiAlH_4$ in THF solution was added slowly. On addition a black color was immediately produced with gas evolution. After 10 min the reaction vessel was warmed to room temperature. After an indicated reaction time the reaction mixture was quenched with a minimum of distilled water and the resultant solution dried over $MgSO_4$. Analysis of the product was obtained by GLC using a 20 ft 8% Apiezon L column. Products were identified by comparing the retention times with authentic samples. In some cases, melting points, NMR specta, and mass spectra were also employed for identification of the products. Yields were corrected by using internal standards for GLC analyses.

Acknowledgment. We are indebted to the National Science Foundation, Grant No. MPS 7504127, for support of this work.

Registry No.—$LiAlH_4$, 16853-85-3.

References and Notes

(1) S. Masamune, P. A. Russy, and G. S. Bates, *J. Am. Chem. Soc.*, **95**, 6452 (1973).
(2) S. Masamune, G. S. Bates, and P. E. Georghiou, *J. Am. Chem. Soc.*, **96**, 3686 (1974).
(3) S. Tyrlik and I. Wolochowicz, *J. Chem. Soc., Chem. Commun.*, 781 (1975).
(4) T. R. Nelsen and J. J. Tufariello, *J. Org. Chem.*, **40**, 3159 (1975).
(5) E. C. Ashby, J. J. Lin, and A. B. Goel, *J. Org. Chem.*, in press.
(6) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.