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A Practical Synthesis of Polyhalomethyllithium-Carbonyl Adducts[1]

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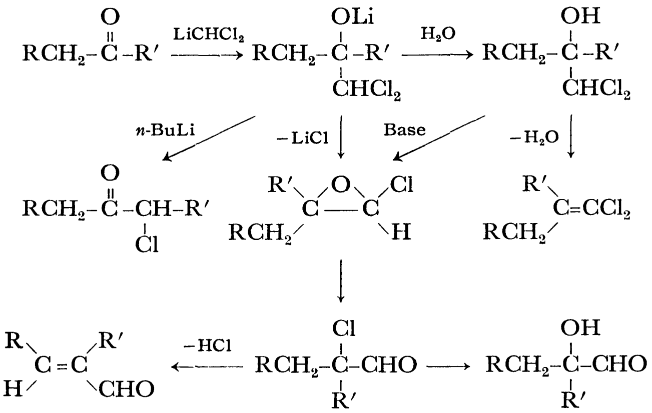
The title adducts are produced upon treatment of a mixture of polyhalomethane and a carbonyl compound with a hindered lithium amide. The kinetically controlled, selective lithiation of the halide enables us to avoid a troublesome procedure involving preformed lithium carbenoid. The halide components examined are dichloromethane, dibromomethane, diiodomethane, chloroform, and bromoform, while the carbonyl ones are ubiquitous ketones and nonanal. A *gem*-dichloroallyllithium is generated similarly from 3,3-dichloropropene and, furthermore, the procedure is successfully extended to the Darzens-type reaction of α-halo esters.

Polyhalomethyllithiums have proved to be extremely useful in organic synthesis as shown in the accompanying scheme.[2,3,4] For example, nucleophilic addition of dichloromethyllithium to ketones, followed by α-chloro aldehyde formation and dehydrochlorination, gives one carbon homologated α,β-unsaturated aldehydes.[4b]



Difficulties arise from the extreme thermolability of the carbenoids[2,3] in generating them on a large scale. Slow and constant addition of butyllithium under vigorous stirring of the halide solution is essential even at −78 °C in order to prevent the local heating, which causes the rapid decomposition of the resulting lithium reagent. The optimum reaction temperature, which is normally between −70 and −120 °C (internal temperature), is limited at the lower end of the range by the rate of formation, and the upper end by the tendency of the carbenoids to decompose.

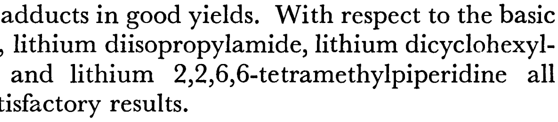
We have disclosed that the *in situ* reaction of a polyhalomethyllithium with carbonyl compounds offers a simple and direct solution to this problem. Treatment of a mixture of polyhalomethane and carbonyl component with an *N,N*-disubstituted lithium amide[5] results in the preferential formation of polyhalomethyllithium instead of the expected enolate. The carbenoid attacks instantaneously the carbonyl group prior to its thermal decomposition. With this new technique in hand, we can prepare dichloromethyllithium–cyclohexanone adduct even at the reaction temperature of 0 °C in an 89% isolation yield. Table 1 summarizes the fairly extensive scope of this technique.

1

Obvious side reaction is the formation of 2-halooxirane, whose rearrangement produces α-halo aldehyde. The extent of such consecutive reactions was not significant upon treatment of simple ketones or aldehydes with dichloro- or dibromomethyllithium. However, the rate of ring closure was found to be greatly enhanced in the reaction of dibromomethyllithium with carbonyl componenents having bulky group directly attached to C=O moiety, probably owing to the steric acceleration. Minimizing this pathway has been attained by performing the reaction in less polar solvents and at lower temperatures. Ether was found to be a favorable solvent for the isolation of hydroxylic adducts, while tetrahydrofuran (THF) gave poor yields. Although the safe upper limit of the reaction temperature was found to be −78 °C, the reaction of crowded carbonyl components should preferably be performed at −95 °C.

Both diiodomethyllithium and tribromomethyllithium are extremely unstable even at −110 °C.[6] The carbonyl adducts of these carbenoids could, however, be prepared in good to excellent yields by means of the present *in situ* technique at −78 °C (external cooling). Although cyclopentanone is known as one of the readily enolizable ketones, the generation of polyhalomethyllithium proceeded in preference of the enolate formation to afford the desired adducts in good yields. With respect to the basic reagent, lithium diisopropylamide, lithium dicyclohexylamide, and lithium 2,2,6,6-tetramethylpiperidine all gave satisfactory results.

Seyferth and co-workers previously prepared *gem*-dichloroallyllithium from $Ph_3PbCH_2CH=CCl_2$ by the action of butyllithium.[7] In extention of the present method, the carbenoid-carbonyl adduct was synthesized directly from 3,3-dichloropropene in a single step. Addition of lithium diisopropylamide to a mixture of cyclododecanone and the dichloride furnished 1-(3,3-dichloropropenyl)cyclododecanol **2** in 66% yield.



2

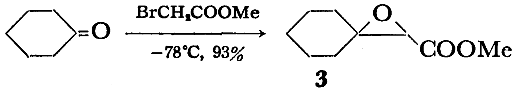
Attempts to obtain a carbonyl adduct of monohalomethyllithium derived from allyl bromide or methyl iodide failed to success. The halides containing -COOR moiety on the α-carbon afforded the desired adducts almost quantitatively. Treatment of a mixture of methyl bromoacetate and cyclohexanone with lithium

TABLE 1. PREPARATIONS OF POLYHALOMETHYLLITHIUM-CARBONYL ADDUCTS

Polyhalomethane	Carbonyl	Method[c)]	Temp, °C	% Yield[b)]
CH_2Cl_2	Cyclohexanone	A	−78	quant.
CH_2Cl_2	Cyclohexanone	B	0	89
CH_2Cl_2	Cyclohexanone	C	−78	86
CH_2Cl_2	Cyclopentanone	A	0	66
CH_2Cl_2	Cyclopentanone	A	−20	90
CH_2Cl_2	Cycloheptanone	A	−20	88
CH_2Cl_2	6-Methyl-5-hepten-2-one	A	0	84
CH_2Cl_2	Nonanal	C	0	73
CH_2Br_2	Cyclopentanone	C	−78	82
CH_2Br_2	Cyclohexanone	C	−78	91
CH_2Br_2	Cycloheptanone	C	−78	76
CH_2Br_2	Cyclooctanone	D	−78	70
CH_2Br_2	Cyclododecanone	E	−95	81
CH_2Br_2	2-Methylcyclohexanone	E	−78	75
CH_2Br_2	2-Methylcyclododecanone	E	−78	66
CH_2Br_2	2-Methylcyclotetradecanone	E	−78	78
CH_2Br_2	2-Cyclohexanone	D	−78	67
CH_2Br_2	2-Cycloheptanone	D	−78	75
CH_2Br_2	Nonanal	C	−78	77
CH_2I_2	Nonanal	C	−78	79
$CHCl_3$	Cyclopentanone	F	−78	91
$CHCl_3$	Cyclohexanone	C	−78	92
$CHCl_3$	Cyclohexanone	F	−78	94
$CHBr_3$	Cyclohexanone	C	−78	91

a) For details, see experimental part. b) Yields are based on material isolated by column or thin layer chromatography. c) *Method A*: Lithium dicyclohexylamide (2 equiv) was added to a polyhalomethane solution of carbonyl compound over a period of 1 h; *Method B*: Lithium dicyclohexylamide (2 equiv) was added to a polyhalomethane solution of carbonyl compound over a period of 10 min; *Method C*: Lithium dicyclohexylamide (2 equiv) was added to a THF solution of carbonyl compound and polyhalomethane (24 equiv) over 1 h; *Method D*: Lithium 2,2,6,6-tetramethylpiperidine (2.2 equiv) was added to a THF solution of carbonyl compound and polyhalomethane (2.2 equiv) over a period of 1 h; *Method E*: Lithium 2,2,6,6-tetramethylpiperidine (2.2 equiv) was added to an ether solution of carbonyl compound and polyhalomethane (2.2 equiv) over a period of 1 h; *Method F*: Lithium dicyclohexylamide (2 equiv) was added to a THF solution of carbonyl compound and polyhalomethane (2 equiv) over a period of 1 h.

dicyclohexylamide afforded a Darzens-type product, methyl α,β-epoxycyclohexylacetate **3**, in 93% yield.[8)] In contrast, ethyl dichloroacetate gave an aldol, ethyl dichloro(1-hydroxycyclohexyl)acetate **4**, in 91% yield. This variation provides a simple and efficient means of preparing two carbon homologated esters.



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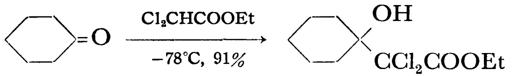

4

Experimental

The IR spectra were determined on a Shimadzu IR-27-G spectrometer; the mass spectra, on a Hitachi RMU-6L mass spectrometer; and the NMR spectra, on a JEOL C-60-H or a Varian EM-360 spectrometer. The chemical shifts are given in δ, with TMS as the internal standard. The analyses were carried out by the staff at the Elemental Analyses Center of Kyoto University. All the experiments were carried out under an atmosphere of dry nitrogen, by preparative thin-layer chromatography (PLC) on silica gel PF-254 plates (Merck) with benzene as an eluent, and by preparative column chromatography on silica gel Wakogel C-100 (Wako).

Preparation of Polyhalomethylcarbinols. *Method A*: Lithium dicyclohexylamide (50 mmol) was prepared from dicyclohexylamine (9.05 g, 50 mmol) in dry THF (50 ml) with butyllithium (50 mmol, 33 ml of 1.5 M hexane solution) at 0 °C. This solution was added dropwise into a well-stirred polyhalomethane (50 ml) solution of carbonyl compound (25 mmol) under a nitrogen atmosphere over a period of 1 h at the low temperature described in Table 1. The mixture was then allowed to stand for 1 h at the same low temperature. After hydrolysis at that temperature, the resulting organic layer was extracted with ether, and the extract was washed with water and dried over anhydrous Na_2SO_4. The solution was condensed under reduced pressure, and the residue was purified by column chromatography using benzene as an eluent.

Method B: A well-stirred solution of carbonyl compound (1.0 mmol) in polyhalomethane (2.0 ml) was cooled to the temperature listed in Table 1. To the mixture was added a THF solution of lithium dicyclohexylamide (2.0 mmol) dropwise over a period of 10 min, and the resulting solution was stirred for 5 min at the same temperature. After extractive work up, polyhalomethylcarbinol was obtained by PLC using benzene as an eluent.

Method C: A well-stirred solution of polyhalomethane (50 mmol) and carbonyl compound (25 mmol) in dry THF (50 ml) was cooled to the temperature described in Table 1. To the mixture was added a THF solution of lithium dicyclohexylamide (50 mmol) dropwise over a period of 1 h. The mixture was stirred for 1 h at that temperature. After extractive work up, polyhalomethylcarbinol was obtained by column chromatography using benzene as an eluent.

Method D: A THF solution of lithium 2,2,6,6-tetramethylpiperidide (2.2 mmol) was added to a stirred solution of polyhalomethane (2.2 mmol) and carbonyl compound (1.0 mmol) in dry THF over a period of 1 h at low temperature. Polyhalomethylcarbinol was obtained according to the similar procedure.

Method E: To an ether solution of polyhalomethane (2.2 mmol) and carbonyl compound (1.0 mmol) was added a THF solution of lithium 2,2,6,6-tetramethylpiperidine (2.2 mmol) mmol) over a period of 1 h at low temperature, and the solution was stirred for 1 h at the same temperature. Polyhalomethylcarbinol was obtained according to the similar procedure.

Method F: A well-stirred solution of polyhalomethane (24 mmol) and carbonyl compound (1 mmol) in dry THF was cooled to low temperature. To the mixture was added a THF solution of lithium dicyclohexylamide (2 mmol) over a period of 1 h and the resulting solution was stirred for 1 h at the same temperature. After extractive work up, polyhalomethylcarbinol was obtained by PLC using benzene as an eluent.

1-Dichloromethylcyclopentanol: Bp 110 °C (bath temp 14 Torr); IR (neat) 3450, 790, 760 cm^{-1}; NMR (CCl_4) δ 1.46—2.15 (m, 8H), 2.25 (s, 1H), 5.65 (s, 1H); MS: *m/e* (%) 139 (11), 85 (100). Found: C, 42.9; H, 6.2%. Calcd for $C_6H_{10}Cl_2O$: C, 42.6; H, 6.0%.

1-Dichloromethylcyclohexanol: Bp 118 °C (20 Torr); IR (neat) 3460, 980, 785, 750 cm^{-1}; NMR (CCl_4) δ 1.10—2.10 (m, 10H), 2.20 (s, 1H), 5.49 (s, 1H); mass *m/e* (%) 149 (1), 139 (4), 99 (100). Found: C, 46.0; H, 6.9%. Calcd for $C_7H_{12}Cl_2O$: C, 45.9; H, 6.6%.

1-Dichloromethylcycloheptanol: Bp 155 °C (bath temp 14 Torr); IR (neat) 3460, 805, 780, 732 cm^{-1}; NMR (CCl_4) δ 1.35—2.30 (m, 12H), 2.18 (s, 1H), 5.54 (s, 1H); mass *m/e* (%) 173 (trace), 113 (100). Found: C, 48.9; H, 7.4%. Calcd for $C_8H_{14}Cl_2O$: C, 48.8; H, 7.2%.

1,1-Dichloro-2,6-dimethyl-5-hepten-2-ol: Bp 110 °C (bath temp 2 Torr); IR (neat) 3470, 796, 770 cm^{-1}; NMR (CCl_4) δ 1.36 (s, 3H), 1.58 (s, 3H), 1.64 (s, 3H), 1.70—2.45 (m, 4H), 5.07 (m, 1H); mass *m/e* (%) 212 (3), 210 (5), 109 (68). Found: C, 51.3; H, 7.8%. Calcd for $C_9H_{16}Cl_2O$: C, 51.2; H, 7.6%.

1,1-Dichloro-2-decanol: Bp 130 °C (bath temp 2 Torr); IR (neat) 3500, 780 cm^{-1}; NMR (CCl_4) δ 0.75—1.10 (m, 3H), 1.10—1.85 (m, 14H), 2.65 (m, 1H), 3.75 (m, 1H), 5.54 (d, *J*=4, 1H); mass *m/e* (%) 143 (18), 83 (45). Found: C, 52.6; H, 9.0%. Calcd for $C_{10}H_{20}Cl_2O$: C, 52.9; H, 8.9%.

1-Dibromomethylcyclopentanol: Bp 140 °C (bath temp 2 Torr); IR (neat) 3450, 745, 688 cm^{-1}; NMR (CCl_4) δ 1.55—2.25 (m, 8H), 2.30 (s, 1H) 5.68 (s, 1H); mass *m/e* (%) 137 (6), 135 (6), 85 (100). Found: C, 28.0; H, 3.7%. Calcd for $C_6H_{10}Br_2O$: C, 27.9; H, 3.9%.

1-Dibromomethylcyclohexanol: Bp 74 °C (2 Torr); IR (neat) 3570, 974, 745 cm^{-1}; NMR (CCl_4) δ 1.30—2.20 (m, 10H), 1.98 (s, 1H), 5.59 (s, 1H); mass *m/e* (%) 231 (trace), 229 (trace), 227 (trace), 99 (100). Found: C, 31.0; H, 4.5%. Calcd for $C_7H_{12}Br_2O$: C, 30.9; H, 4.5%.

1-Dibromomethylcycloheptanol: Bp 152 °C (bath temp 2 Torr); IR (neat) 3460, 800, 720 cm^{-1}; NMR (CCl_4) δ 1.30—2.27 (m, 12H), 2.31 (s, 1H), 5.62 (s, 1H); mass *m/e* (%) 288 (trace), 286 (trace), 284 (trace), 113 (100). Found: C, 33.8; H, 4.9%. Calcd for $C_8H_{14}Br_2O$: C, 33.6; H, 4.9%.

1-Dibromomethylcyclooctanol: Bp 150 °C (bath temp 1 Torr); IR (neat) 3460, 787, 688 cm^{-1}; NMR (CCl_4) δ 1.10—2.23 (m, 14H), 2.33 (s, 1H), 5.68 (s, 1H); mass *m/e* (%) 302 (1), 300 (2), 298 (1), 127 (100). Found: C, 36.3; H, 5.4%. Calcd for $C_9H_{16}Br_2O$: C, 36.0; H, 5.4%.

1-Dibromomethylcyclododecanol: Mp 61 °C; IR (Nujol) 3450, 693 cm^{-1}; NMR ($CDCl_3$) δ 0.77—2.00 (m, 22H), 2.08 (s, 1H), 5.73 (s, 1H); mass *m/e* (%) 279 (3), 277 (3), 183 (100). Found: C, 43.9; H, 6.8%. Calcd for $C_{13}H_{24}Br_2O$: C, 43.8. H, 6.8%.

1-Dibromomethyl-2-methylcyclohexanol: Bp 156 °C (bath temp 15 Torr); IR (neat) 3560, 737, 684 cm^{-1}; NMR (CCl_4) δ 0.90 (d, *J*=6, 3H), 1.07—2.36 (m, 9H), 2.47 (s, 1H), 5.70 (s, 1H); mass *m/e* (%) 288 (1), 286 (2), 284 (1), 95 (100); Found: C, 33.8; H, 5.0%. Calcd for $C_8H_{14}Br_2O$: C, 33.6; H, 4.9%.

1-Dibromomethyl-2-methylcyclododecanol: Mp 61 °C; IR (Nujol) 3500, 958, 700 cm^{-1}; NMR ($CDCl_3$) δ 5.73 (s, $C\underline{H}Br_2$ of major isomer), 5.81 (s, $C\underline{H}Br_2$ of minor isomer); mass *m/e* (%) 380 (2), 197 (100). Found: C, 45.6; H, 7.3%. Calcd for $C_{14}H_{26}Br_2O$: C, 45.4; H, 7.1%.

1-Dibromomethyl-2-methylcyclotetradecanol: Bp 190 °C (bath temp 2 Torr); IR (neat) 3580, 978, 702 cm^{-1}; NMR (CCl_4) δ 5.78 (s, $C\underline{H}Br_2$ of major isomer), 5.86 (s, $C\underline{H}Br_2$ of minor isomer); mass *m/e* (%) 398 (trace), 225 (51), 55 (100). Found: C, 48.1; H, 7.6%. Calcd for $C_{16}H_{30}Br_2O$: C, 48.3; H, 7.6%.

1-Dibromomethyl-2-cyclohexenol: Bp 110 °C (bath temp 2 Torr); IR (neat) 3450, 850, 736 cm^{-1}; NMR (CCl_4) δ 1.52—2.30 (m, 6H), 2.38 (m, 1H), 5.63 (s, 1H), 5.70—6.16 (m, 2H); mass *m/e* (%) 272 (1), 270 (2), 268 (1), 97 (100). Found: C, 31.1; H, 3.9%. Calcd for $C_7H_{10}Br_2O$: C, 31.1; H, 3.7%.

1-Dibromomethyl-2-cycloheptenol: Bp 125 °C (bath temp 1 Torr); IR (neat) 3450, 861, 757 cm^{-1}: NMR (CCl_4) δ 1.30—2.50 (m, 8H), 1.62 (s, 1H), 5.69 (s, 1H), 5.60—6.20 (m, 2H); mass *m/e* (%) 286 (trace), 284 (trace), 282 (trace), 111 (100). Found: C, 33.9; H, 4.4%. Calcd for $C_8H_{12}Br_2O$: C, 33.8; H, 4.3%.

1,1-Dibromo-2-decanol: Bp 165 °C (bath temp 4 Torr); IR (neat), 3450, 708 cm^{-1}; NMR (CCl_4) δ 0.66—1.06 (m, 3H), 1.06—1.97 (m, 14H), 2.77 (m, 1H), 3.75 (m, 1H), 5.64 (d, *J*=4, 1H); mass *m/e* (%) 205 (trace), 203 (1), 201 (trace), 143 (40), 69 (100). Found: C, 38.2; H, 6.6%. Calcd for $C_{10}H_{20}Br_2O$: C, 38.0; H, 6.4%.

1,1-Diiodo-2-decanol: Bp 180 °C (bath temp 0.1 Torr); IR (neat) 3440, 758, 677 cm^{-1}; NMR (CCl_4) δ 0.65—1.05 (m, 3H), 1.05—2.00 (m, 14H), 2.96 (m, 1H), 3.05 (m, 1H), 5.22 (d, *J*=4, 1H); mass *m/e* (%) 410 (M^+, 1), 283 (10), 268 (15), 170 (15).

1-Trichloromethylcyclopentanol: Bp 135 °C (bath temp 14 Torr); IR (neat) 3470, 886, 830, 786 cm^{-1}; NMR (CCl_4) δ (1.50—2.80 (m, 8H), 2.58 (s, 1H); mass *m/e* (%) 186 (1), 85 (100). Found: C, 35.6; H, 4.7%. Calcd for $C_6H_9Cl_3O$: C, 35.4; H, 4.5%.

1-Trichloromethylcyclohexanol: Mp 56 °C; IR (Nujol) 3480, 812, 780 cm^{-1}; NMR (CCl_4) δ 1.30—2.50 (m, 10H), 2.06 (s, 1H); mass *m/e* (%) 198 (3), 99 (46).

1-Tribromomethylcyclohexanol: Mp 74 °C; IR (Nujol) 3450, 760, 696 cm^{-1}; NMR (CCl_4) δ 1.40—2.80 (m, 10H), 2.13 (s, 1H); mass *m/e* (%) 273 (1), 271 (3), 269 (1). 99 (100). Found: C, 24.0; H, 3.2%. Calcd for $C_7H_{11}Br_3O$: C, 23.9; H, 3.0%.

Preparation of Methyl α,β-Epoxycyclohexylideneacetate. To a solution of methyl bromoacetate (168 mg, 1.1 mmol) and cyclohexanone (98 mg, 1.0 mmol) in dry THF (2 ml) was added dropwise a solution of lithium dicyclohexylamide (2.0 mmol) in THF over a period of 30 min at −78 °C. The reaction mixture was then stirred for 1 h at the same temperature, and for 3 h at room temperature. After extractive work-up 158 mg (93%) of methyl α,β-epoxycyclohexylacetate was obtained by preparative TLC using benzene as an eluent.

Preparation of Ethyl Dichloro(1-hydroxycyclohexyl)acetate. To a stirred solution of cyclohexanone (98 mg, 1.0 mmol) and ethyl dichloroacetate (0.246 ml, 2.0 mmol) was added dropwise lithium dicyclohexylamide (2.0 mmol) over a period of 30 min at −78 °C, and the reaction mixture was stirred for 30 min at the same temperature. According to the usual procedure 234 mg (92%) of ethyl dichloro(1-hydroxycyclohexyl)acetate was obtained by PLC using benzene as an eluent: Bp 165 °C (bath temp 5 Torr); IR (neat) 3475, 872, 694, 666 cm^{-1}; NMR (CCl_4) δ 1.36 (t, *J*=8, 3H), 1.20—2.20 (m, 10H), 3.71 (s, 1H), 4.03 (q, *J*=8, 2H); mass *m/e* (%) 218 (10), 98 (100). Found: C, 47.4; H, 6.6%. Calcd for $C_{10}H_{16}Cl_2O_3$: C, 47.1; H, 6.3%.

Preparation of 1-(3,3-Dichloropropenyl)cyclododecanol. To a solution of cyclododecanone (3.64 g, 20 mmol) and 3,3-dichloropropene (2.42 g, 22 mmol) in dry THF (40 ml) was added dropwise lithium diisopropylamide (30 mmol) at −78 °C over a period of 30 min, and stirred for 30 min at the same temperature. After extractive work-up 3.83 g (66%) of 1-(3,3-dichloropropenyl)cyclododecanol was obtained by column chromatography using benzene as an eluent: Mp

89 °C; IR (Nujol) 3480, 840, 794 cm^{-1}; NMR (CCl_4) δ 1.20—2.00 (m, 22H), 2.08 (s, 1H), 5.26 (d, J=10, d, J=1, 1H), 5.76 (d, J=16, d, J=1, 1H), 6.30 (d, J=16, d, J=10, 1H); mass m/e (%) 292 (4), 243 (32). Found: C, 61.7; H, 9.2%. Calcd for $C_{15}H_{26}Cl_2O$: C, 61.4; H, 8.9%.

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