A Facile Synthesis of 2,2-Dihalogenated Aliphatic Aldehydes

R. Verhé, N. De Kimpe*, L. De Buyck, N. Schamp

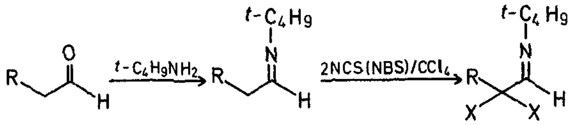
Laboratory of Organic Chemistry, Faculty of Agricultural Sciences, State University of Ghent, Coupure 533, B-9000 Gent, Belgium

In the course of studies on *N*-1-(2,2-dichloroalkylidene)-*t*-butylamines, we found a convenient method for the preparation of 2,2-dihalogenated aldehydes. Little work has been reported for effecting 2,2-dihalogenation of aldehydes. Chlorination of aliphatic aldehydes with chlorine has been shown to result in the formation of the corresponding acyl halides[1]; except for propanal where the chlorination in aqueous hydrogen chloride could be controlled in such a manner as to produce 2-chloro- or 2,2-dichloropropanal[2]. 2,2-Dibromoaldehydes cannot be obtained by direct bromination because of oxidation and side reactions[3], although the synthesis of 2,2-dibromobutanal has been described by bromination of butanal with bromine in chloroform[4]. Bromination of methyl acetals with dibromotrichlorophosphorane gave the α,α-dibromoaldehydes in low yields[3], while bromination of aldehydes with *N*-bromosuccinimide resulted in the formation of acid bromides[5,6].

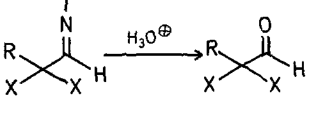
The only generally applicable route to 2,2-dihalogenated aldehydes involved the laborious synthesis of β-halogenoenamines from α-halogenated aldehydes or α-halogen immonium salts followed successively by halogenation and hydrolysis[7].

Our technique is based on the masking of the aldehyde function as its Schiff base. Thus, aliphatic aldehydes (**1**) were transformed into the corresponding *N*-1-(alkylidene)-*t*-butylamines (**2**) and then converted directly to *N*-1-(2,2-dihalogenalkylidene)-*t*-butylamines (**3**) by 2 equivalents of *N*-chloro- or *N*-bromosuccimide.

Hydrolysis of **3** in hydrochloric acid at room temperature gave the 2,2-dihalogenated aldehydes **4** in high yields.



1 **2** **3a** X = Cl
b X = Br



3a,b **4a** X = Cl
b X = Br

The reaction can be carried out in one step without isolating and purifying the crude intermediates **2** and **3**. Although compounds **2** and **3** could be obtained in excellent yields by distillation[8].

General Procedure for the Synthesis of 2,2-Dihalogenated Aliphatic Aldehydes:

A mixture of the aldehyde (0.25 mol) and *t*-butylamine (0.25 mol) was cooled (10°) and stirred for 10 minutes, followed by tritu-

Table. 2,2-Dihalogenated Aliphatic Aldehydes

Product **4**		Yield (%)	B.p.	^{1}H-N.M.R. δ ppm (—C$\underline{H}$=O)	I.R. ν cm^{-1} (C=O)	Elemental Analysis			
R	X								
C_2H_5	Cl	65	45–46°/12 torr[a]	9.16	1751	$C_4H_6Cl_2O$	calc.	C 34.07	H 4.29
							found	34.13	4.19
C_2H_5	Br	72	55–56°/12 torr[b]	9.17	1738	$C_4H_6Br_2O$	calc.	C 20.90	H 2.63
							found	20.35	2.54
n-C_3H_7	Cl	80	45–46°/20 torr	9.13	1753	$C_5H_8Cl_2O$	calc.	C 38.74	H 5.20
							found	38.68	5.03
n-C_3H_7	Br	58	73–74°/12 torr	9.17	1738	$C_5H_8Br_2O$	calc.	C 24.62	H 3.31
							found	24.58	3.19
n-C_4H_9	Cl	67	77°/25 torr	9.17	1753	$C_6H_{10}Cl_2O$	calc.	C 42.63	H 5.96
							found	42.30	5.72
n-C_4H_9	Br	57	88–94°/12 torr	9.13	1738	$C_6H_{10}Br_2O$	calc.	C 27.93	H 3.91
							found	27.60	3.78
n-C_5H_{11}	Cl	70	93–95°/25 torr	9.13	1753	$C_7H_{12}Cl_2O$	calc.	C 45.92	H 6.61
							found	45.62	6.52
n-C_5H_{11}	Br	88	101–105°/12 torr[c]	9.13	1738	$C_7H_{12}Br_2O$	calc.	C 30.91	H 4.45
							found	30.48	4.42

[a] Lit.[3]: b.p. 53°/17 torr.
[b] Lit.[4]: b.p. 85°/40 torr.
[c] Lit.[3]: b.p. 96°/11 torr.

ration with tetrachloromethane (200 ml). To the dried solution ($MgSO_4$) was added portionwise N-halosuccinimide (0.52 mol) and the suspension was stirred for 12 h at room temperature. After filtration of the succinimide and evaporation of the solvent, the residue was stirred with concentrated aqueous hydrogen chloride (200 ml) for 12 h at room temperature. The 2,2-dihalogenated aldehydes were extracted with dichloromethane and distilled.

Received: February 24, 1975

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* N. De Kimpe is indebted to the Belgian "Nationaal Fonds voor Wetenschappelijk Onderzoek" for his aspirant fellowship.

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