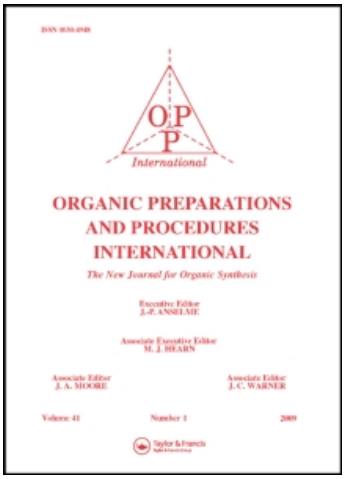

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

SYNTHESIS OF BRANCHED LONG CHAIN ALIPHATIC PRIMARY ALKYL BROMIDES

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To cite this Article Katritzky, Alan R. , Bieniek, Adam and Chiang, Long(1989) 'SYNTHESIS OF BRANCHED LONG CHAIN ALIPHATIC PRIMARY ALKYL BROMIDES', Organic Preparations and Procedures International, 21: 2, 129 — 133
To link to this Article: DOI: 10.1080/00304948909356357
URL: http://dx.doi.org/10.1080/00304948909356357

ORGANIC PREPARATIONS AND PROCEDURES INT. 21(2), 129-133 (1989)

SYNTHESIS OF BRANCHED LONG CHAIN ALIPHATIC PRIMARY ALKYL BROMIDES

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Recently the need arose in our laboratory to prepare the four previously unknown primary alkyl bromides $R_2CH(CH_2)_3$-Br, where R = n-C_5H_{11}, n-C_6H_{13}, n-C_8H_{17} or n-$C_{10}H_{21}$. The compounds were made from the corresponding secondary bromides R_2CHBr(1) the synthesis of which had previously been achieved in our laboratory.[1] We utilized a three-step approach with each step based on a literature analogy. The reaction between the secondary bromide 1 and allylmagnesium chloride gave[2] the terminal olefin 2, which, on sequential treatment with diborane and H_2O_2, afforded[3] the corresponding alcohol 3. The latter was then converted into the primary bromide 4 by reaction with tetrabromomethane and triphenylphosphine.

$$R_2CHBr \xrightarrow[THF]{ClMgCH_2-CH=CH_2} R_2CH-CH_2-CH=CH_2 \xrightarrow[2)\ NaOH\ H_2O_2]{1)\ B_2H_6}$$

1 2

$$R_2CH-CH_2-CH_2-CH_2OH \xrightarrow[PPh_3]{CBr_4} R_2CH-CH_2-CH_2-CH_2Br$$

3 4

a)R = n-C_5H_{11}, b)R = n-C_6H_{13}, c)R = n-C_8H_{17}, d)R = n-$C_{10}H_{21}$

Reaction of 7-bromotridecane (1b) with allylmagnesium chloride in diethyl ether under reflux for 36 hrs. gave only traces amounts of 2b as monitored by ^{1}H-NMR analysis. However, using THF as a solvent and excess of allylmagnesium chloride (molecular ratio 1:2), we obtained the desired compounds 2 in good yields, after refluxing for 24 hours. Reaction of the primary alcohols 3 with carbon tetrabromide and triphenylphosphine gave the bromides 4 in good yields.

EXPERIMENTAL SECTION

^{1}H NMR, and ^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer. IR spectra were recorded on a Perkin-Elmer 283B spectrophotometer. All boiling points were uncorrected.

Preparation of Olefins (2). General Procedure.- To a boiling 2M solution of the allylmagnesium chloride (0.2 mol) in THF (100 ml) was added the secondary bromide 1 (0.10 mol) in 20 ml THF and the mixture refluxed for 24 hrs. After cooling, it was decomposed by pouring onto 300 g of crushed ice and the resulting precipitate dissolved by addition of 10% sulfuric acid (75 ml). The product was extracted with diethyl ether (3 x 75 ml) and the combined ethereal extracts were dried over magnesium sulfate. Removal of the ether and distillation of the residue gave the compounds described in Tables I, II and III.

Preparation of Alcohols (3). General Procedure.- The reaction was carried out under nitrogen. To a stirred solution of 0.45 g (0.012 mol) of sodium borohydride in 12 ml of dry diglyme, was added a solution of 0.04 mole of the olefin 2 in 6.6 ml of dry diglyme. Next, a solution of 2.27 g (0.016 mol) freshly distilled boron trifluoride-etherate in 3.75 ml of dry diglyme was added over 15 min., while the temperature was held at 20-25°.

Table I. Physical properties of compounds 2 - 4

Compound	Yield [%]	b.p.[°C/mmHg]	Analyses[%] Calcd. C	Calcd. H	Found C	Found H
2a	91	92-96/1.3	85.39	14.30	(85.63)	(14.37)
2b	88	122-127/1.8	85.63	14.37	(85.57)	(14.31)
2c	82	155-162/0.8	85.63	14.37	(85.54)	(14.33)
2d	90	212-216/3.0	85.63	14.37	(85.57)	(14.27)
3a	68	125-130/0.5	78.43	14.10	(78.28)	(14.00)
3b	86	142-145/4.0	79.27	14.14	(79.29)	(14.08)
3c	75	175-185/1.6	80.46	14.18	(80.35)	(14.12)
3d	82	205-215/2.7	81.28	14.21	(81.45)	(14.14)
4a	85	132-135/0.8	60.64	10.54	(60.56)	(10.58)
4b	91	-	62.94	10.89	(63.01)	(10.93)
4c	87	-	66.46	11.43	a	
4d	69	-	69.04	11.83	(69.19)	(11.81)

[a]Characterized spectrally and by GC-MS; M^+ at 361 in chemical ionization MS.

Stirring was continued at room temperature for 1 hr. and then 3.5 ml of water was added dropwise. When hydrogen evolution had ceased (5 min), 7.0 ml of 3.0 M aqueous sodium hydroxide was added, followed by dropwise addition of 7.0 ml of 30% hydrogen peroxide, while the temperature was maintained at 30-50 °C. After 1 hr. the reaction was poured into 30 ml of water at 0 °C. The reaction vessel was washed with 17 ml of water. The combined water solutions were extracted with diethyl ether (2 x 25 ml). The combined ethereal extracts were washed with water (5 x 5 ml). The ethereal extracts were dried over magnesium sulfate, the ether removed in vacuo, and the residue distilled to give the alcohol 3 (see Table I, II and III).

Preparation of Primary Bromides (4). General Procedure.- To a stirred solution of the alcohol (3) (0.01 mol) and 6.62 g

(0.02 mol) of carbon tetrabromide in 50 ml of anhydrous diethyl ether was added 5.24 g (0.02 mol) of triphenylphosphine at 20° C. The mixture was stirred 3 hrs. at room temperature, during which time it turned yellow.

Table II. ^{1}H NMR and IR spectra of compounds 2 - 4

Compound	^{1}H NMR[a] δ [ppm]	IR[b] [cm^{-1}]
2a	5.9-5.6(m,1H); 5.1-4.8(m,2H); 2.1-1.9(m,2H); 1.5-1.0(m,17H); 1.0-0.6(m,6H).	3080; 1640; 990; 905.
2b	5.9-5.7(m,1H); 5.2-4.8(m,2H); 2.1-1.9(m,2H); 1.5-1.1(m,21H); 1.0-0.8(m,6H).	3080; 1640; 990; 905.
2c	5.9-5.6(m,1H); 5.1-4.8 2.05-1.95(m,2H); 1.6-1.0(m,29H); 1.0-0.8(m,6H).	3080; 1640; 990; 905.
2d	5.9-5.6(m,1H); 5.1-4.8(m,2H); 2.1-1.9(m,2H); 1.4-1.0(m,37H); 1.0-0.7(m,6H).	3080; 1640; 990; 905.
3a	3.6(t,2H,J=6Hz); 2.8(m,1H); 1.65-1.1(m,21H); 1.0-0.8(m,6H).	3320; 1050.
3b	3.7(br s,1H); 3.6-3.5(m,2H); 1.6-1.0(m,25H); 0.95-0.7(m,6H).	3300; 1050.
3c	3.6(t,2H,J=6Hz); 2.0(m,1H); 1.6-1.1(m,33H); 0.95-0.8(m,6H).	3310; 1055.
3d	3.6-3.4(m,2H); 3.4-3.1(m,1H); 1.6-0.6(m).	3310; 1050.
4a	3.37(t,2H,J=7Hz); 1.9-1.65(m,2H); 1.5-1.1 (m,19H); 1.0-0.75(m,6H).	
4b	3.4(t); 2.1(m); 1.8(m); 1.25(m); 0.9(m).	
4c	3.37(t,2H); 1.8(m,2H); 1.4-1.1(m); 0.86(m).	
4d	3.4(t); 1.8(m); 1.25(m); 0.9(m).	

[a] in $CDCl_3$, tetramethylsilane was used as internal standard. [b] neat.

Filtration and removal of the solvent under vacuum, gave a residue which was dissolved in 100 ml of n-hexane. The solution was filtered and the hexane removed in vacuo. The residue was kept under vacuum for three days, after which time

it was purified by column chromatography (silica - petroleum ether, see Tables I, II and III).

Table III. ^{13}C-NMR[a] Chemical Shifts of Compounds 2-4

Comp.	-CH= or CH_2X	CH_2=	-CH<	CH_2 groups								-CH_3
2a	137.6	115.4	37.5	38.2	33.4					32.3	26.4	22.7	14.1
3a	63.1		37.2	33.5	32.3	29.8				29.6	26.3	22.6	14.1
4a	36.9		34.2	33.5	32.3	32.2				29.2	26.3	22.7	14.1
2b	136.7	115.4	37.4	38.1	37.4	33.1				29.7	26.7	22.7	14.1
3b	62.0		36.5	32.9	31.2	29.3	29.1			28.7	25.9	21.9	13.4
4b	36.8		34.4	33.5	32.1	31.8	30.1			29.6	26.5	22.6	14.0
2c	137.6	115.4	37.5	38.2	37.5	33.5	32.0	30.1	29.8	29.5	26.8	22.8	14.1
3c	63.4		37.2	33.6	31.9	30.1	20.9	29.7	29.6	29.4	26.6	22.7	14.1
4c	36.9		34.3	33.5	32.2	31.9	30.2	30.1	20.7	29.4	26.6	22.7	14.1
2d	137.6	115.3	37.4	38.1	33.4	31.9	30.0	29.7		29.2	26.7	22.7	14.1
3d[b]	62.4		36.8	33.1	31.4	29.6	29.6	29.3	29.2	28.8	26.1	22.1	13.6
4d[c]	36.9		34.4	33.6	32.2	31.9	30.2	30.1	29.7	29.4	26.6	22.7	14.3

[a]in $CDCl_3$. [b]peaks at 29.1 and 28.9 ppm are also present. [c]peaks at 29.6 and 29.5 ppm are also present.

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(Received July 15, 1988; in revised form October 18, 1988)