Oxidation of secondary alkanols with the system cerium ammonium nitrate—lithium bromide into ketones, α-bromo ketones, and α,α´-dibromo ketones

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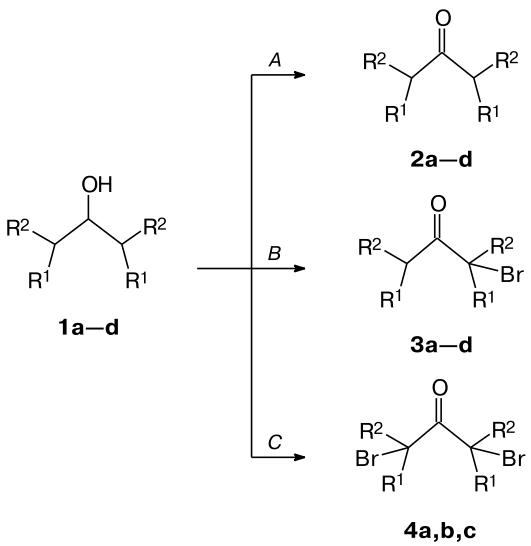
Oxidation of secondary alkanols with the system $Ce(NH_4)_2(NO_3)_6$—LiBr in aqueous acetonitrile gave ketones, α-bromo ketones, or α,α´-dibromo ketones. The selectivity of the reaction under standard conditions depends only on the molar ratio of the reagents (alkanol : Ce^{IV} : LiBr).

Key words: secondary alkanols, cerium ammonium nitrate, lithium bromide, oxidation, ketones, bromo ketones, dibromo ketones.

At present, cerium(IV) ammonium nitrate (CAN), $Ce(NH_4)_2(NO_3)_6$, is a common one-electron oxidant in various reactions of organic synthesis. The substrates to be oxidized are aromatic and aliphatic hydrocarbons and their numerous functionalized derivatives. Oxidation of alcohols with CAN was first mentioned in the 1960s. It was found that benzylic alcohols can be oxidized into aldehydes,[1] pentan-1-ol, into 2-methyltetrahydrofuran,[2] and cyclopropylmethanol, into cyclopropanecarbaldehyde.[3] Cyclic alcohols (cyclobutanol, 1-methylcyclobutanol,[4] 1-alkylcyclopentanols,[5] 1-alkylcyclohexanols,[6] and 1-methylcyclopropanol[7]) undergo oxidative decyclization leading to carbonyl compounds. Oxidation of 5-phenylpentan-1-ol and 4-phenylbutan-1-ol, as in the case of pentan-1-ol, yields 2-benzyl- and 2-phenyltetrahydrofurans, respectively.[8] Secondary alkyl phenyl carbinols react with CAN mainly with cleavage of the α-C—C bond to give benzaldehyde.[9] Secondary alkanols can be oxidized into ketones with the system CAN—$NaBrO_3$; alkan-1-ols are inert to these oxidants.[10] When studying organic reactions in the presence of Ce^{IV}, we found that alkan-1-ols are easily oxidized with the systems CAN—LiBr[11] and $Ce(SO_4)_2$—LiBr[12] into esters.

In the present work, we studied a selective oxidation of secondary alcohols (**1**) with the system CAN—LiBr into ketones (**2**), α-bromo ketones (**3**), or α,α´-dibromo ketones (**4**) (Scheme 1). Under the same conditions (65—70 °C, aqueous MeCN), a particular ketone (**2**, **3**, or **4**) can be selectively obtained by varying only one parameter of the process, *viz.*, the molar ratio of the reagents **1** : CAN : LiBr. The sensitivity of the yields of oxidation products to this parameter is shown in Table 1 for the transformation of nonan-5-ol (**1c**) into nonan-5-one (**2c**), 4-bromononan-5-one (**3c**), and 4,6-dibromononan-5-one (**4c**) as an example.

Scheme 1



Compound	R^1	R^2	Method	**1** : CAN : LiBr
1a, **2a**, **3a**, **4a**	Me	H		
1b, **2b**, **3b**, **4b**	Et	H	*A*	1 : 2 : 0.05
1c, **2c**, **3c**, **4c**	Pr	H	*B*	1 : 4 : 1
1d, **2d**, **3d**	Me	Me	*C*	1 : 10 : 4

For **1c** : CAN : LiBr = 1 : 2 : 0.05, ketone **2c** was virtually the sole product (the reaction time is 30 min; the conversions of alkanol **1c** and CAN are 94 and 100%, respectively). Lithium bromide acts as a redox catalyst greatly promoting the reaction. In the absence of LiBr or

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Table 1. Oxidation of nonan-5-ols **1c** with the system CAN—LiBr[a]

Entry	Molar ratio **1c** : CAN : LiBr	*t*/h	Conversion **1c** (%)	Yield[b] (%)		
				2c	**3c**	**4c**
1	1: 2 : 0	1	11	91	—	—
2	1 : 2 : 0.01	1	10	90	—	—
3	1 : 2 : 0.05	0.5	94	95	~1	—
4	1 : 2 : 0.1	0.5	95	86	10	—
5	1 : 4 : 1	4	100	~1	97	—
6	1 : 4 : 2	48[c]	99	~1	95	—
7	1 : 4 : 2	6	100	—	59	25[d]
8	1 : 6 : 4	7	100	—	35	53[d]
9	1 :10 :4	10	100	—	~1	93[d]

[a] Reaction conditions: **1c** (1 mmol), $T = 65$—70 °C, 80% aqueous MeCN (15 mL) as a solvent. The conversion of CAN is 100%.
[b] Determined by GLC with an internal standard with respect to the consumed compound **1c**.
[c] The reaction temperature is 20 °C.
[d] The ratio of the diastereomers *meso* : *rac* is 1 : 1.

its adequate amount (see Table 1, entries *1*, *2*), the oxidation rate of alkanol **1c** is low: for the complete conversion Ce^{IV}—Ce^{III}, the yield of ketone **2c** was ~10% (reaction time 1 h). With an increase in the fractions of the oxidant and LiBr (**1c** : CAN : LiBr = 1 : 4 : 1), α-bromo ketone **3c** was obtained in 97% yield; *i.e.*, the H atom in one α-CH_2 group of intermediate ketone **2c** is selectively replaced by a Br atom. In the oxidation of alkanol **1c** into both ketone **2c** and α-bromo ketone **3c**, the use of stoichiometric amounts of CAN was sufficient (two and four moles per mole of alkanol **1c**, respectively).

To introduce two Br atoms into ketone **2c**, the amount of the oxidant should be increased from six (see Table 1, entry *8*) to ten moles per mole of compound **1c** (see Table 1, entry *9*). A high yield of dibromo ketone **4c** was attained for **1c** : CAN : LiBr = 1 : 10 : 4. The sole regioisomer, α,α′-dibromo ketone **4c**, was obtained as an equimolar mixture of two diastereomers. A possible regioisomer containing two Br atoms at the same α-C atom, 4,4-dibromononan-5-one, was not detected. The oxidation of alkanol **1c** into bromo ketone **3c** and dibromo ketone **4c** proceeds more slowly than the oxidation into ketone **2c**; the conversion of CAN and alkanol **1c** is completed in 4 and 10 h, respectively. The conditions for the selective oxidation of alkanol **1c** into ketones **2c**, **3c**, and **4c** were applied to other secondary alkanols. Starting from pentan-3-ol (**1a**), heptan-4-ol (**1b**), and 2,4-dimethylpentan-3-ol (**1d**), we easily obtained the corresponding ketones **2a**, **2b**, and **2d** and bromo ketones **3a**, **3b**, and **3d**. In addition, the oxidation of the former two alcohols gave α,α′-dibromo ketones **4a** and **4b**. The yields of these eight ketones vary from 90 to 98% (see Scheme 1, Table 2).

Table 2. Oxidation of secondary alkanols **1a**—**g** with the system CAN—LiBr[a]

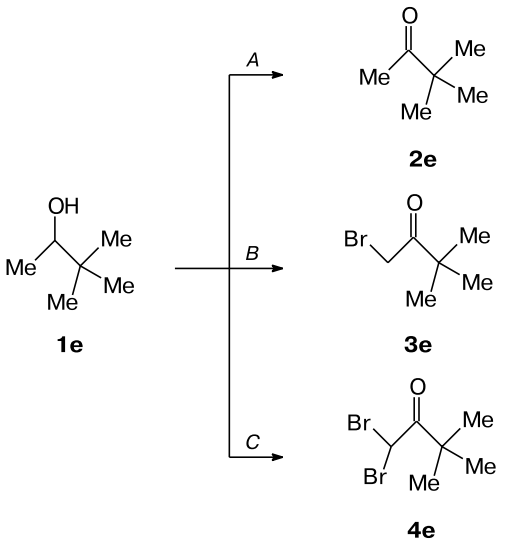
Entry	Compound	Reaction conditions	*t*/h	Conversion **1** (%)	Yield[b] (%)		
					2	**3**	**4**
1	Et_2CHOH (**1a**)	*A*	0.5	96	**2a** (98)	—	—
2		*B*	4	99	**2a** (~1)	**3a** (95)	—
3		*C*	10	100	—	**3a** (~1)	**4a** (93)[c]
4	Pr_2CHOH (**1b**)	*A*	0.5	92	**2b** (97)	**3b**	—
5		*B*	4	99	**2b** (~1)	**3b** (92)	—
6		*C*	10	100	—	**3b** (~1)	**4b** (91)[c]
7	Bu_2CHOH (**1c**)	*A*	0.5	94	**2c** (96)	**3c** (~1)	—
8		*B*	4	100	**2c** (~1)	**3c** (97)	—
9		*C*	10	100	—	**3c** (~1)	**4c** (93)[c]
10	Pr^i_2CHOH (**1d**)	*A*	1	95	**2d** (95)	**3d** (~1)	—
11		*B*	5	91	**2d** (~1)	**3d** (93)	—
12	$MeCH(OH)Bu^t$ (**1e**)	*A*	0.5	97	**2e** (96)	**3e** (~1)	—
13		*B*	3	100	—	**3e** (97)	—
14		*C*	10	100	—	**3e** (~1)	**4e** (92)
15	EtCH(OH)Ph (**1f**)	*A*	5	91	**2f** (93)	**3f** (~1)	—
16		*B*	7	98	**2f** (41)	**3f** (54)	—
17		*D*	9	97	**2f** (~1)	**3f** (94)	—
18	$C_5H_{11}CH(OH)Ph$ (**1g**)	*A*	5	99	**2g** (95)	**3g** (~1)	—
19		*B*	7	100	**2g** (39)	**3g** (57)	—
20		*D*	9	98	**2g** (~1)	**3g** (93)	—

[a] Reaction conditions: **1a**—**g** (1 mmol), $T = 65$—70 °C, 80% aqueous MeCN (15 mL) as a solvent. The molar ratio of **1** : CAN : LiBr is 1 : 2 : 0.05 (*A*), 1 : 4 (*B*) : 1, 1 : 10 : 4 (*C*), and 1 : 4 : 2 (*D*); the conversion of CAN is 100%.
[b] Determined by GLC with an internal standard with respect to the consumed compounds **1a**—**g**.
[c] The ratio of the diastereomers *meso* : *rac* is 1 : 1.

In contrast to unbranched carbinols **1a**—**c**, branched carbinol **1d** cannot be oxidized with the system CAN—LiBr into the corresponding α,α′-dibromo ketone. Apparently, the steric effect of the $BrMe_2C$ group in monobromo ketone **3d** precludes introduction of a Br atom into the other isopropyl group of 2,4-dimethylpentan-3-one (**2d**).

Under similar conditions with variation in the ratio of the reagents and the reaction time, oxidation of asymmetric 3,3-dimethylbutan-2-ol (**1e**) afforded 3,3-dimethylbutan-2-one (**2e**), 1-bromo-3,3-dimethylbutan-2-one (**3e**), and 1,1-dibromo-3,3-dimethylbutan-2-one (**4e**) in 92—97% yields (see Table 2, entries *12*—*14*; Scheme 2).

Scheme 2

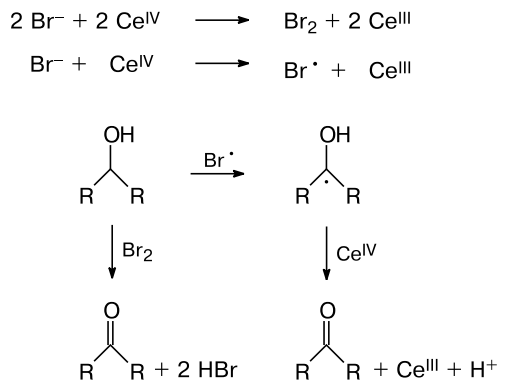


In this case, bromine atoms replace two H atoms at the same α-C atom of ketone **2e**, which was not observed for ketones **2a**—**c** containing no tertiary alkyl substituents.

Phenylalkanols (1-phenylpropan-1-ol (**1f**) and 1-phenylhexan-1-ol (**1g**)), like aliphatic alkanols, are easily oxidized into alkyl phenyl ketones **2f** and **2g** in the presence of a catalytic amount of LiBr (see Table 2, method *A*, entries *15*, *18*). Their oxidation into α-bromo ketones according to method *B* suitable for alkanols **1a**—**e** is not selective, giving a mixture of a ketone and an α-bromo ketone with slight domination of the latter (see Table 2, entries *16*, *19*). With an increase in the amount of LiBr (method *D*), 2-bromo-1-phenylpropan-1-one (**3f**) and 2-bromo-1-phenylhexan-1-one (**3g**) were obtained in preparative yields (~90%) (see Table 2, entries *17*, *20*). The corresponding α,α′-dibromo ketones were not obtained from phenylalkanols **1f,g**; their oxidation (method *C*) mainly yields monobromo ketones **3f,g**.

Thus, in the oxidation of secondary alkanols with the system CAN—LiBr, the initial step seems to follow the pattern described earlier[12] for the oxidation of primary alkanols with the system $Ce(SO_4)_2$—LiBr. In aqueous MeCN, cerium ammonium nitrate oxidizes the bromide anion and the generated atomic and molecular bromine serves, in combination with Ce^{IV}, to oxidize the hydroxy group into an oxo group (Scheme 3).

Scheme 3



Therefore, the anion Br^- (LiBr, HBr) acts as a redox catalyst (mediator) involved in repeated redox cycles alkanols→ketones. At next steps, the redox catalyst functions as a stoichiometric reagent. Bromine liberated from LiBr brominates the ketone according to a classic scheme.

Direct oxidation of secondary alkanols with CAN alone (despite the presence of LiBr in the reaction mixture) virtually does not occur or contributes only slightly to the net process. Otherwise, the formation of considerable amounts of oxidation products as a result of cleavage of the α-C—C bond (especially in alkanols) should be expected, as observed for ethyl, isopropyl, and *tert*-butyl phenyl carbinols.[9] The absence of such products can be evidence that oxidation of secondary alkanols with CAN does not proceed through generation of alkoxy radicals susceptible to characteristic β-decomposition with cleavage of the α-C—C bond.

To sum up, we proposed to use the system CAN—LiBr for oxidation of secondary alkanols into the corresponding ketones, α-bromo ketones, or α,α′-dibromo ketones. The selective formation of a particular ketone depends only on the molar ratio of the reagents (alkanol : CAN : LiBr). The reaction can be suitable as a preparative method for the synthesis of mono- and dibromo ketones from secondary alkanols.

Experimental

The reaction mixtures were analyzed by GLC on a LKhM-80 chromatograph (flame ionization detector, metallic columns 2000×3 mm, 5% SE-30 and 5% FFAP on Chromaton N-AW-HMDS, 0.16—0.20 mm). The yields of the products were determined by the internal standard method (with pentan-2-one as an internal standard) and corrected using experimental correction

factors. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-250 spectrometer in $CDCl_3$ under standard conditions. GC-MS analysis was carried out on a Finnigan MAT ITD-700 spectrometer (EI, 70 eV, ionic source—ionic trap temperature 220 °C) and a Carlo Erba 4200 chromatograph fitted with an Ultra-1 column (Hewlett-Packard, 2500×0.2 mm, polymethylsiloxane stationary phase, layer thickness 0.33 μm, helium as a carrier gas). The starting secondary alcohols (pentan-3-ol (**1a**), heptan-4-ol (**1b**), nonan-5-ol (**1c**), 2,4-dimethylpentan-3-ol (**1d**), 3,3-dimethylbutan-2-ol (**1e**), 1-phenylhexan-1-ol (**1f**), and 1-phenylpropan-1-ol (**1g**)) and cerium ammonium nitrate (Acros) were used as purchased. Freshly distilled acetonitrile (high-purity grade) was used. Lithium bromide (high-purity grade) was calcined before use.

Oxidation of alcohols (1a—f) with the system CAN—LiBr in MeCN—H_2O. A mixture of alkanol **1**, CAN, and LiBr (their ratios are specified in Tables 1 and 2) in 80% aqueous MeCN (15 mL) was vigorously stirred with a magnetic stirring bar at 65 °C until the oxidant was completely consumed (this was indicated by a color change from orange to light yellow). The product was extracted with ether (3×25 mL). The combined extracts were washed with a saturated solution of $NaHCO_3$ and water, dried over $MgSO_4$, and concentrated. The yields of the products and the conversions of alkanol **1** were determined by GLC (see Tables 1, 2). The products were isolated by column chromatography on silica gel (L 40/100 μm) with hexane—ethyl acetate as an eluent.

Ketones (pentan-3-one (**2a**), heptan-4-one (**2b**), nonan-5-one (**2c**), 2,4-dimethylpentan-3-one (**2d**), 3,3-dimethylbutan-2-one (**2e**), 1-phenylpropan-1-one (**2f**), and 1-phenylhexan-1-one (**2g**)) were identified by IR and NMR spectroscopy and by comparison with authentic samples.

2-Bromopentan-3-one (3a) (*cf.* Ref. 13). ^{1}H NMR ($CDCl_3$), δ: 1.12 (t, 3 H, CH_3, J = 7.3 Hz); 1.75 (d, 3 H, C<u>H</u>$_3$CHBr, J = 6.8 Hz); 2.59 (m, 2 H, CH_2); 4.42 (m, 1 H, CHBr). ^{13}C NMR ($CDCl_3$), δ: 8.29 (CH_3); 20.26 (<u>C</u>H_3CHBr); 32.04 (CH_2); 47.39 (CHBr); 205.13 (CO). MS, *m/z*: 165 $[M + H]^+$ (^{79}Br), 167 $[M + H]^+$ (^{81}Br).

3-Bromoheptan-4-one (3b) (*cf.* Ref. 14). ^{1}H NMR ($CDCl_3$), δ: 0,91 (t, 3 H, CH_3, J = 7.5 Hz); 1.00 (t, 3 H, CH_3, J = 7.5 Hz); 1.61 (m, 2 H, CH_2); 1.99 (m, 2 H, C<u>H</u>$_2$Br); 2.34 (t, 2 H, C<u>H</u>$_2$CO, J = 7.3 Hz); 4.16 (m, 1 H, CHBr). ^{13}C NMR ($CDCl_3$), δ: 11.94 (CH_3); 13.65 (CH_3); 17.35 (CH_2); 26.86 (<u>C</u>H_2Br); 40.90 (<u>C</u>H_2CO); 55.47 (CHBr); 204.16 (CO). MS, *m/z*: 193 $[M + H]^+$ (^{79}Br); 195 $[M + H]^+$ (^{81}Br).

4-Bromononan-5-one (3c) (*cf.* Ref. 15). ^{1}H NMR ($CDCl_3$), δ: 0.89 (t, 3 H, CH_3, J = 6.4 Hz); 0.94 (t, 3 H, CH_3, J = 6.4 Hz); 1.36 (m, 2 H, CH_2); 1.49 (m, 2 H, CH_2); 1.62 (m, 2 H, CH_2); 1.92 (m, 2 H, CH_2CHBr); 2.68 (t, 2 H, CH_2CO, J = 7.0 Hz); 4.25 (t, 1 H, CHBr, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 1.75 (CH_3); 14.82 (CH_3); 20.86 (CH_2); 22.50 (CH_2); 25.92 (CH_2); 34.40 (<u>C</u>H_2CHBr); 43.85 (<u>C</u>H_2CO); 54.08 (CHBr); 207.93 (CO). MS, *m/z*: 221 $[M + H]^+$ (^{79}Br); 223 $[M + H]^+$ (^{81}Br).

2-Bromo-2,4-dimethylpentan-3-one (3d) (*cf.* Ref. 16). ^{1}H NMR ($CDCl_3$), δ: 1.23 (d, 6 H, 2 CH_3, J = 6.5 Hz); 1.88 (s, 6 H, 2 CH_3); 3.46 (m, 1 H, C<u>H</u>CO). ^{13}C NMR ($CDCl_3$), δ: 18.75 (CH_3); 18.80 (CH_3); 29.35 (CH_3); 29.47 (CH_3); 34.62 (<u>C</u>H(CH_3)$_2$); 64.66 (<u>C</u>Br(CH_3)$_2$); 210.08 (CO). MS, *m/z*: 193 $[M + H]^+$ (^{79}Br); 195 $[M + H]^+$ (^{81}Br).

1-Bromo-3,3-dimethylbutan-2-one (3e) (*cf.* Ref. 17). ^{1}H NMR ($CDCl_3$), δ: 1.21 (s, 9 H, CH_3); 4.16 (s, 2 H, C<u>H</u>$_2$BrCO). ^{13}C NMR ($CDCl_3$), δ: 26.42 (3 CH_3); 31.84 (CH_2Br); 44.26 (<u>C</u>(CH_3)$_3$); 206.16 (CO). MS, *m/z*: 179 $[M + H]^+$ (^{79}Br); 181 $[M + H]^+$ (^{81}Br).

2-Bromo-1-phenylpropan-1-one (3f) (*cf.* Ref. 18). ^{1}H NMR ($CDCl_3$), δ: 1.89 (d, 3 H, CH_3, J = 7.0 Hz); 5.29 (m, 1 H, CHBr); 7.48 (d, 2 H, H(2), H(4), J = 9.0 Hz); 7.62 (m, 1 H, H(3)); 8.02 (d, 2 H, H(2), H(1), H(5), J = 9.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 19.25 (CH_3); 41.20 (CHBr); 127.94 (C(1); C(5)); 128.10 (C(2); C(4)); 133.93 (C(6)); 134.05 (C(3)); 192.64 (CO). MS, *m/z*: 213 $[M + H]^+$ (^{79}Br); 215 $[M + H]^+$ (^{81}Br).

2-Bromo-1-phenylhexan-1-one (3g) (*cf.* Ref. 19). ^{1}H NMR ($CDCl_3$), δ: 0.92 (m, 3 H, CH_3); 1.43 (m, 2 H, CH_2); 1.53 (m, 2 H, CH_2); 2.18 (m, 2 H, CH_2); 5.15 (t, 1 H, CHBr, J = 7.5 Hz); 7.50 (d, 2 H, H(2), H(4), J = 9.0 Hz); 7.61 (m, 1 H, H(3)); 8.03 (d, 2 H, H(1); H(5), J = 9.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 13.90 (CH_3); 22.26 (CH_2); 29.64 (CH_2); 33.30 (CH_2); 47.32 (CHBr); 128.15 (C(1), C(5)); 128.85 (C(2), C(4)); 133.67 (C(3)); 134.60 (C(6)); 193.35 (CO). MS, *m/z*: 255 $[M + H]^+$ (^{79}Br); 257 $[M + H]^+$ (^{81}Br).

2,4-Dibromopentan-3-one (4a) (*cf.* Ref. 20). <u>*meso*-Isomer.</u> ^{1}H NMR ($CDCl_3$), δ: 1.77 (d, 6 H, 2 CH_3, J = 6.0 Hz); 4.76 (m, H, CHBr). ^{13}C NMR ($CDCl_3$), δ: 19.72 (2 CH_3); 43.21 (2 CHBr); 196.06 (CO). <u>*rac*-Isomer.</u> ^{1}H NMR ($CDCl_3$), δ: 1.81 (d, 6 H, 2 CH_3, J = 6.0 Hz); 4.98 (m, 2 H, CHBr). ^{13}C NMR ($CDCl_3$), δ: 21.78 (2 CH_3); 44.35 (2 CH); 198.34 (CO). MS, *m/z*: 244 $[M + H]^+$ (^{79}Br); 246 $[M + H]^+$ (^{81}Br).

3,5-Dibromoheptan-4-one (4b) (*cf.* Ref. 21). <u>*meso*-Isomer.</u> ^{1}H NMR ($CDCl_3$), δ: 1.05 (t, 6 H, 2 CH_3, J = 6.0 Hz); 1.97 (m, 4 H, 2 CH_2); 4.52 (t, 2 H, CHBr, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 9.59 (2 CH_3); 26.47 (2 CH_2); 51.69 (2 CHBr); 194.27 (CO). <u>*rac*-Isomer.</u> ^{1}H NMR ($CDCl_3$), δ: 1.05 (t, 6 H, 2 CH_3); 2.09 (m, 4 H, 2 CH_2); 4.65 (t, 2 H, CHBr, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 9.77 (2 CH_3); 28.16 (2 CH_2); 52.30 (2 CHBr); 197.50 (CO). MS, *m/z*: 272 $[M + H]^+$ (^{79}Br); 274 $[M + H]^+$ (^{81}Br).

4,6-Dibromononan-5-one (4c) (*cf.* Ref. 22). <u>*meso*-Isomer.</u> ^{1}H NMR ($CDCl_3$), δ: 1.01 (t, 6 H, 2 CH_3, J = 6.0 Hz); 1.48 (m, 4 H, 2 CH_2); 1.96 (m, 4 H, 2 CH_2); 4.60 (t, 2 H, CHBr, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 13.41 (2 CH_3); 20.61 (2 CH_2); 35.00 (2 CH_2); 50.13 (2 CHBr); 194.36 (CO). <u>*rac*-Isomer.</u> ^{1}H NMR ($CDCl_3$), δ: 1.01 (t, 6 H, 2 CH_3, J = 6.0 Hz); 1.51 (m, 4 H, 2 CH_2); 1.98 (m, 4 H, 2 CH_2); 4.73 (t, 2 H, CHBr, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 13.51 (2 CH_3); 20.91 (2 CH_2); 36.35 (2 CH_2); 53.58 (2 CHBr); 197.75 (CO). MS, *m/z*: 300 $[M + H]^+$ (^{79}Br); 302 $[M + H]^+$ (^{81}Br).

1,1-Dibromo-3,3-dimethylbutan-2-one (4e) (*cf.* Ref. 20). ^{1}H NMR ($CDCl_3$), δ: 1.38 (s, 9 H, 3 CH_3); 6.35 (s, 1 H, $CHBr_2$). ^{13}C NMR ($CDCl_3$), δ: 26.56 (3 CH_3); 37.44 (CHBr); 44.08 (<u>C</u>(CH_3)$_3$); 201.63 (CO). MS, *m/z*: 258 $[M + H]^+$ (^{79}Br); 260 $[M + H]^+$ (^{81}Br).

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