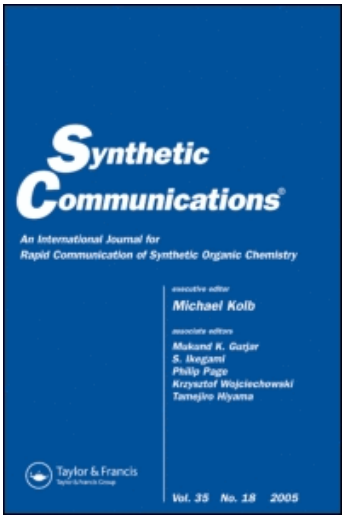

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1-Bromo-3,3-*bis*(2-bromoethyl)alkanes: Precursors to 4-Substituted Quinuclidines and 1-Phosphabicyclo[2.2.2]octanes

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1-BROMO-3,3-BIS(2-BROMOETHYL)ALKANES: PRECURSORS TO 4-SUBSTITUTED QUINUCLIDINES AND 1-PHOSPHA-BICYCLO[2.2.2]OCTANES

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Abstract

1-Bromo-3,3-bis(2-bromoethyl)octane has been synthesized from tetrahydro-4*H*-pyran-4-one in 6 steps and 18% overall yield. This method is more convenient, gives higher overall yields and is potentially more general than those previously reported for related tribromides.

Introduction

Tribromides **1** are potentially general precursors of a class of 4-alkyl-1-heterabicyclo[2.2.2]octanes such as quinuclidines **2** and 1-phosphabicyclo[2.2.2]octanes **3**. Indeed, it has been reported that tribromides **1a**

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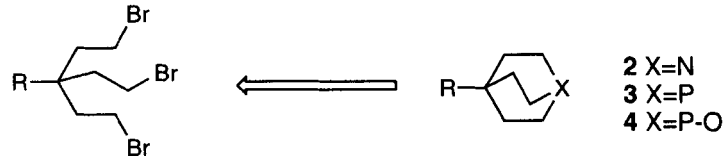
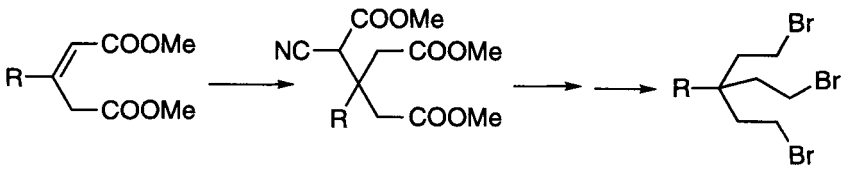
and **1b** each react with alcoholic ammonia to furnish the corresponding quinuclidines **2a**[1,2] and **2b**[3] in 29.5%[2] and 33%[3] yields respectively. Similarly, tribromide **1a** was converted into phosphine oxide **4a** in 1.5% yield.[4] Our interest in liquid crystalline materials based on these 4-alkyl-1-heterabicyclo[2.2.2]octanes (such as **2** and **3**) prompted us to develop a reliable and efficient synthetic procedure for the preparation of tribromides **1** with a variable chain-length alkyl group R. Halides **1** (R=alkyl) are seemingly simple to prepare yet surprisingly, are unknown in the literature other than the parent **1a**[1,2,4] and its methyl derivative **1b**.[3,5]



1 **a** R=H; **b** R=Me; **c** R=*n*-C_5H_{11}

The parent tribromide **1a** has been obtained by the ring opening reaction of 4-(2-hydroxyethyl)tetrahydropyran, which is itself synthesized in 10 steps from diethyl malonate and 2,2'-dichloroethyl ether in 1% overall yield.[1,6,7] The methyl derivative **1b** was prepared in a multistep procedure in which the base catalyzed Michael addition of methyl cyanoacetate to dimethyl 3-methylpentenedioate (**5b**) and the formation of cyanotriester **6b** is the critical step of the synthesis (see Scheme 1).[8] This reaction is reported to have worked well for both the methyl derivative (**5b**)[8] and the parent **5a**[9] giving **6b** and **6a** in 82% and 60% yields respectively. However, in our case, the addition reaction failed for **5c** (R=*n*-C_5H_{11}) presumably due to steric reasons. Thus, with the possibility of synthesizing **1c** via the corresponding cyanotriester removed and the only other potential route to **1c** allowing for the introduction of a long alkyl chain being

Scheme 1



5 **6** **1**

a R=H, **b** R=Me; **c** R=*n*-C_5H_{11}

impractically long[1,7] it was necessary to develop a new synthetic route to tribromides **1**.

Here we describe a new, convenient synthetic procedure for 1-bromo-3,3-bis(2-bromoethyl)octane, **1c**, as a prototype of this class of tribromides (R=alkyl). Tetrahydro-4*H*-pyran-4-one (**7**) was chosen as starting material as its cyclic structure should help alleviate problems associated with steric congestion. We have used tribromide **1c** to synthesize 4-*n*-pentylquinuclidine (**2c**)[10] and quinuclidine-*closo*-boranes which will be published elsewhere.

Results and Discussion

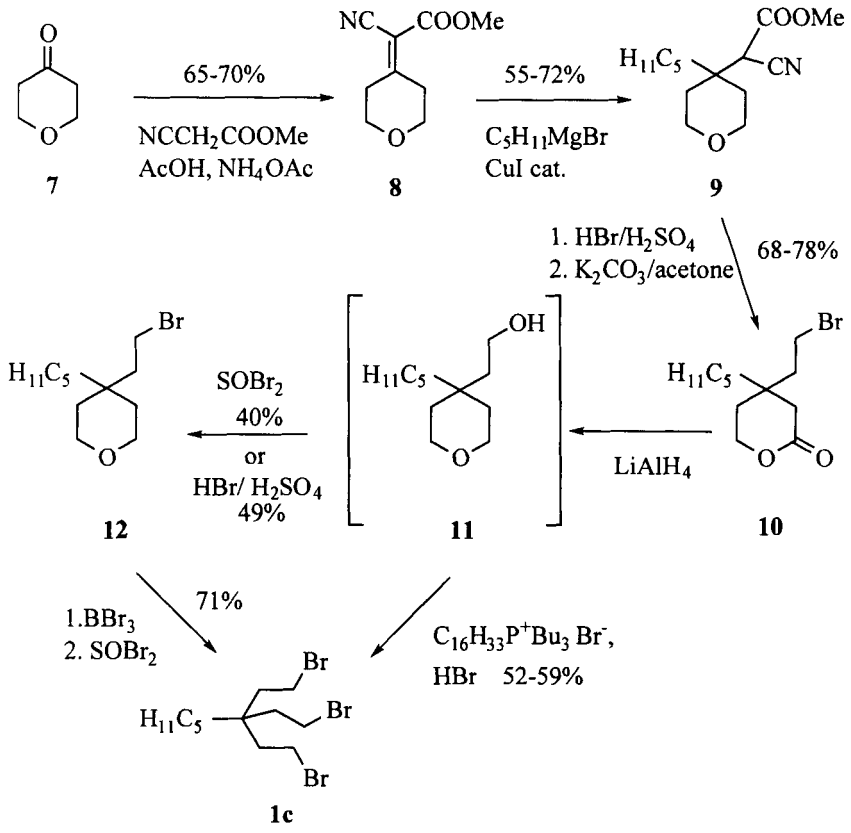
The synthetic route to tribromide **1c** is given in Scheme 2. The methyl (tetrahydropyran-4-ylidene)cyanoacetate (**8**) was readily synthesized in high yield from tetrahydro-4*H*-pyran-4-one (**7**) using the literature procedure.[11] Reaction of the olefin **8** with pentylmagnesium bromide in the presence of CuI allowed for the introduction of the alkyl chain and the formation of **9**. GC-MS analysis indicated that 2-(4-tetrahydro-4*H*-pyranyl)cyanoacetate was formed as a byproduct in this reaction. Treatment of the product **9** with a boiling mixture of HBr and sulfuric acid resulted in hydrolysis of the nitrile and ester groups, decarboxylation,

tetrahydropyran ring opening and partial lactonization to form **10**. The use of HBr/ H_2SO_4 is the literature method for opening a tetrahydropyran ring.[12] Esterification of the crude reaction mixture with diazomethane showed the lactone **10** to be the major reaction product and 3,3-bis(2-bromoethyl)octanoic acid to be the minor component (4:1 ratio by GC). Complete lactonization to **10** was effected by stirring the crude product mixture with potassium carbonate in acetone.

Reduction of lactone **10** with $LiAlH_4$ gave 4-(2-hydroxyethyl)-4-pentyltetrahydro-4*H*-pyran (**11**) as the major product which was used for subsequent transformations without further purification. In this reaction the lactone is converted to the bromodiolaluminate which, under the reaction conditions, undergoes intra- and intermolecular nucleophilic alkylations to form cyclic (**11**) or acyclic ethers respectively. Upon quenching the reaction produced a mixture containing mainly the alcohol **11**, the expected bromodiol and possibly other partially brominated and polymeric ethers which can all be converted to the tribromide **1c**. The yield of **11** could be increased by stirring and gently refluxing the quenched reaction mixture for 6 hr. In this case alcohol **11** was formed in 54% yield based on lactone **10**. It is worth noting that using reaction times of greater than 1 h for the reduction of **10** caused significant reduction of the carbon-bromine bond forming an alkane. Indeed, by reacting lactone **10** overnight with $LiAlH_4$ and then brominating, 3,3-bis(2-bromoethyl)octane (*vide infra*) could be isolated as the major product (33% based on **10**, bp 134-136°C/ 0.5 torr) to the tribromide **1c** (20% based on **10**).

The crude product from the lactone reduction was then converted into tribromide **1c** in 52-59% yield using the hexadecyltributylphosphonium bromide phase-transfer catalyst method for the cleavage of ethers described by Landini *et al.*[13] It was found

Scheme 2



in small scale reactions that if complete bromination did not occur then the addition of more HBr would suffice. On larger scales it was found necessary to extract the reactant mixture and catalyst and then resubmit this with fresh HBr in order to complete the transformation to **1c**. Running the reaction too long appears to reduce the yield of tribromide. For example, when the reaction was run for a total of 120 hours using 2 separate portions of HBr a yield of only 27% was obtained and extraction of the product was hindered by the presence of large amounts of black

slurry. In the absence of catalyst, 4-(2-bromoethyl)-4-pentyltetrahydro-4*H*-pyran (**12**) is formed as the major product accompanied by some **1c**. For example reacting crude **11** for four hours at 120°C with HBr/ H_2SO_4 produces 49% **12** and 13% **1c** based on **10**. 4-(2-Bromoethyl)-4-pentyltetrahydro-4*H*-pyran (**12**) has also been obtained from **11** in 40% yield (based on **10**) using thionyl bromide.[10] The bromide **12** was converted to tribromide **1c** in 71% yield using boron tribromide followed by thionyl bromide.[10]

Conclusions

1-Bromo-3,3-bis(2-bromoethyl)octane has been obtained from tetrahydro-4*H*-pyran-4-one in 6 steps giving, on average, 18% overall yield. This represents a considerable improvement over the previous method for the parent, 1-bromo-3,3-bis(2-bromoethyl)propane which required 10 steps and produced 1% overall yield. Additionally, by judicious choice of alkyl magnesium bromide this method should serve as a general route to other homologues in this series of 1-bromo-3,3-bis(2-bromoethyl)alkanes.

Experimental

Melting points were obtained on a Boetius PHMK 05 hot stage. NMR spectra were obtained using a Bruker 300 MHz instrument in $CDCl_3$ and referenced to residual $CHCl_3$. FTIR spectra of neat compounds between NaCl plates were recorded on a Nicolet Magna 500 instrument. Mass spectrometry was performed using a Hewlett-Packard 5890 GC-MS. Elemental analyses were provided by Atlantic Microlab, Norcross, GA.

1-Bromo-3,3-bis(2-bromoethyl)octane (1c). A dry 500 mL 3-necked round-bottom flask equipped with a mechanical stirrer, reflux condenser and addition funnel was charged with 95% $LiAlH_4$ powder (4.08 g, 0.108 mol) and dry ether (100 mL). After stirring for 15 min a solution of 3-(2-bromoethyl)-3-(2-hydroxyethyl)octanoic acid lactone (**10**, 39.7 g, 0.14 mol) in ether (250 mL) was added dropwise at a rate maintaining a gentle reflux. The mixture was then stirred a further 1 h and the reaction quenched by the careful, sequential addition of ether saturated with water (20 mL), water (4 mL), 15 % NaOH (4 mL), and water (12 mL). Stirring was continued for 45 min and then the mixture was filtered and solids washed with ether (200 mL). Removal of the solvent yielded a crude yellow oil. 4-(2-hydroxyethyl)-4-pentyltetrahydro-4*H*-pyran (**11**): bp 110-120 °C 0.01 torr; EI MS, *m/e* 200 (M, 1), 155 (45), 140 (45), 111 (57), 99 (55), 93 (53), 83 (82), 81 (100).

The crude mixture, aqueous HBr (48%, 225 mL, 3.7 mol) and hexadecyltributylphosphonium bromide (8.25 g, 0.016 mol) were placed in a 500 mL round-bottom 3-necked flask equipped with a mechanical stirrer and reflux condenser. The mixture is then vigorously stirred and heated at 140°C in an oil bath causing the reaction mixture to darken and become more viscous. After 48 hours the mixture was cooled and extracted into methylene chloride. The methylene chloride was washed with water and after removing the solvent the mixture was then resubmitted for reaction with fresh HBr. Upon completion of the reaction (around 72 hr, monitored by GC) the organic phase was separated, the aqueous phase extracted with hexanes (3 x 100 mL), and the combined organics dried over $MgSO_4$. The solution was then passed through a silica gel plug and solvents evaporated to afford a brown oil which was distilled (bp 138-142 °C / 0.3 torr) to give the 1-bromo-3,3-bis(2-bromoethyl)octane as a viscous, colorless oil which

slowly crystallizes. Yields were in the range 52-59%. An analytical sample was prepared by recrystallization from pentane: mp 42-44 °C; ^{1}H NMR δ 0.88 (t, J=6.9 Hz, 3H), 1.19-1.35 (m, 8H), 1.82-1.87 (m, 6H), 3.26-3.32 (m, 6H); ^{13}C NMR δ 14.0, 22.5, 22.6, 27.0, 32.3, 36.1, 40.0, 42.2; IR 2928, 457 cm^{-1}; EI MS, *m/e* 329(M-80, 5), 327(M-80, 8), 325(M-80, 5), 301(23), 299(49), 297(24), 255(19), 219(14), 217(14), 137(68), 67(100). Anal. Calcd for $C_{12}H_{23}Br_3$: C, 35.41; H, 5.70; Br, 58.89. Found: C, 35.28; H, 5.62; Br, 58.70.

Dimethyl 3-pentyl-2-pentenedioate (5c). The ester was prepared from dimethyl 3-chloro-2-pentenedioate[14] using a method adapted from that described by Negishi *et al*.[15] An oven-dried 50 mL, 3-necked round-bottom flask equipped with a magnetic stirring bar, rubber septum outlet, septum for addition, and gas inlet was charged with a 1M solution of $ZnCl_2$ in ether (2 mL, 2 mmol) and dry THF (1 mL). A solution of $C_5H_{11}MgBr$ in ether (2M, 1 mL, 2 mmol) and dry THF (2.5 mL) was then added by syringe. The resulting mixture was stirred for 1.5 h at room temperature under nitrogen. This solution of $C_5H_{11}ZnCl$ was then added to a mixture of tetrakis(triphenylphosphine) palladium (0.0232 g, 0.02 mmol), dry THF (2 mL) and the dimethyl 3-chloro-2-pentenedioate (0.39 g, 2 afford 55-72% yield of the product (bp 126-130 °C / 0.1 torr): ^{1}H NMR δ 0.88 (t, J=6.8 Hz, 3H), 1.25-1.30 (m, 6H), 1.57-1.63 (m, 4H), 1.77-1.85 (m, 2H), 3.62-3.73 (m, 5H), 3.78 (s, 3H); ^{13}C NMR δ 13.9, 22.36, 22.43, 32.2, 32.9, 33.0, 33.5, 38.2, 45.8, 53.1, 63.02, 63.08, 115.4, 165.4; IR 2975, 2865, 2238, 1753, 1610, 1439, 1289, 1262, 1228, 1098, 1044, 743 cm^{-1}; EI MS, *m/e* 253(M, 4), 221(16), 182(17), 153(100), 122(28), 100(33), 95(35), 83(95), 69(61), 55(53). Anal. Calcd for $C_{14}H_{23}NO_3$: C, 66.37; H, 9.15; N, 5.53. Found: C, 66.43; H, 9.10; N, 5.56.

3-(2-Bromoethyl)-3-(2-hydroxyethyl)octanoic acid lactone (10). A 250 mL round-bottom flask equipped with condenser and stirring bar was charged with the methyl 4-*n*-pentyl-tetrahydro-4*H*-pyran-4-ylidene cyanoacetate (**9**, 16.16 g, 63.8 mmol) and a mixture of 48% HBr (44 mL) and H_2SO_4 conc. (10.5 mL). The black homogeneous mixture was refluxed for 4 hrs at 160-165 °C in an oil bath. This was accompanied with the formation of a black tar. The reaction mixture was poured into water (300 mL) and then extracted with ether (3x150 mL). The combined organic phases were dried over magnesium sulfate and filtered through a glass frit with a thin layer of celite. The solvent was evaporated to give 17.68 g of a brown oil. A sample of this crude material reacted with diazomethane and then analyzed showed the ratio of bromolactone to derivatized dibromoacid to be 4:1 (by GC). Methyl 3-bis(2-bromoethyl)octanoate: EI-MS *m/e* 343(M-31, 3), 341 (M-31, 5), 339 (M-31, 3), 293 (13), 291 (13), 109 (33), 74 (100).

A 500 mL round-bottom flask equipped with a stirring bar and condenser was charged with a solution of most of this mixture (16.72 g) in dry acetone (300 mL), then anhydrous Na_2CO_3 (3.0 g, 28.3 mmol) was added and the suspension stirred at room temperature under nitrogen for 4 hrs. The inorganic salts were filtered off mmol) placed in a 50 mL flask setup as described above and immersed in a water bath. The reaction mixture was stirred at room temperature for 2 h under a flow of nitrogen, and then for 13.5 h without nitrogen. The reaction mixture was poured onto a mixture of ether (2 mL) and ice-cold 3 M HCl (6 mL), and several mL of hexanes. The organic layer was separated, and the aqueous layer was extracted with ether (2x20 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. The aqueous layer became yellow-brown after washing with $NaHCO_3$, whilst the organic layer remained yellowish. The mixture was passed through a silica gel plug, the solvent was evaporated and the crude

product short-path distilled (bp 82-96 °C / 0.2-0.3 torr) to afford a colorless mixture of E- and Z-isomers (about 1:2 ratio by NMR) in 32% yield. Based on general trends,[16] NMR signals were assigned to each of the isomers. **5c-E**: ^{1}H NMR δ 2.63 (t, *J*=7.8 Hz, 2H), 3.10 (s, 2H), 3.65 (s, 3H), 3.66 (s, 3H), 5.72 (s, 1H). **5c-Z**: ^{1}H NMR δ 2.18 (t, *J*=7.6 Hz, 2H), 3.64 (s, 3H), 3.65 (br s, 5H), 5.80 (s, 1H). The remaining butyl group in both isomers absorbs at 0.84 (t, *J*=6.7 Hz, 3H), 1.20-1.29 (m, 4H), 1.38-1.48 (m, 2H). EI MS, *m/e* 196(M-32, 64), 168(80), 153(88), 140(57), 121(68), 108(100), 95(90), 79(29). Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.14; H, 8.83. Found: C, 63.04; H, 8.75.

Methyl (tetrahydro-4*H*-pyran-4-ylidene)cyanoacetate (8). A 50 mL round-bottom flask equipped with a Dean-Stark distillation setup and condenser was charged with tetrahydro-4*H*-pyran-4-one (**7**, 4.63 g, 46.2 mmol), methyl cyanoacetate (5.43 g, 54.8 mmol), ammonium acetate (0.93 g, 12.1 mmol), acetic acid (0.57 g, 9.5 mmol) and benzene (25 mL). The mixture was refluxed until no more water collected in the Dean-Stark (approximately 1 h), cooled, benzene (50 mL) was added and the organics washed with water (200 mL). The aqueous phase was extracted with methylene chloride (3x50 mL). The combined organic phase was washed with a saturated solution of $NaHCO_3$ (300 mL) and then brine (300 mL). After drying over anhydrous $MgSO_4$ and filtering through a silica gel plug the solvent was evaporated to afford the crude material. Kugelrohr distillation (bp 120-122°C, 1 torr) gave the product as a colorless liquid which slowly crystallized to a white solid. Yields were in the range of 65-70%. An analytical sample was further purified by recrystallization from petroleum ether: mp 43-44 °C (lit.[11] 42 °C); ^{1}H NMR δ 2.77 (t, J=5.5 Hz, 2H), 3.16 (t, J=5.5 Hz, 2H), 3.76 (t, J=5.6 Hz, 2H), 3.81 (s, 3H), 3.84 (t, J=5.6 Hz, 2H); ^{13}C NMR δ 32.4, 36.7, 52.6, 68.0, 68.2,

103.0, 114.9, 162.0, 173.9; IR 2975, 2865, 2238, 1753, 1098, 1044 cm^{-1}; EI MS, *m/e* 181(M, 22), 151(100), 136(44), 93(19), 65(28). Anal. Calcd for $C_9H_{11}NO_3$: C, 59.66; H, 6.12; N, 7.73. Found: C, 59.52; H, 6.05; N, 7.68.

Methyl (4-*n*-pentyl-4-tetrahydro-4*H*-pyranyl)cyanoacetate (9). A 2 L 3-necked round-bottom flask equipped with a mechanical stirrer, condenser, addition funnel and rubber septum with nitrogen inlet was charged with a solution of $C_5H_{11}MgBr$ in ether (2.0 M, 168 mL, 336 mmol) and CuI (0.63 g, 3.3 mmol). Methyl tetrahydro-4*H*-pyran-4-ylidene cyanoacetate (**8**, 54.0 g, 298 mmol) in 500 mL of dry ether was added dropwise over 2 hrs whilst cooling the reaction flask in an ice bath. The mixture became pink and viscous. More dry ether (50 mL) was added and the mixture was stirred for a day at room temperature. Then it was poured into 200 g of an ice/HCl mixture (5% overall concentration of HCl) and the organic phase was separated. The aqueous phase was extracted with ether (2x100 mL). The combined organic extracts were washed with water (200 mL), brine (200 mL) and dried over $MgSO_4$. The solution was filtered through a silica gel plug and the solvent evaporated to give a crude brown oil which was short-path distilled to and rinsed with acetone (100 mL). The solvent was removed and then the crude product redissolved in methylene chloride which was then washed with water (3 x 50 mL), brine (2 x 50 mL) and water again (2 x 50 mL). After filtration through a silica gel plug eluted with methylene chloride the solvent was removed. The lactone product was purified by short-path distillation (bp 140-146 °C / 0.3 torr). Yields were in the range 68-78% based on **9**. An analytical sample was prepared by Chromatotron separation and short-path distillation: ^1H NMR δ 0.87 (t, J=6.8 Hz, 3H), 1.24-1.33 (m, 8H), 1.72 (t, J=6.0 Hz, 2H), 1.94-2.0 (m, 2H), 2.34 (s, 2H), 3.26-3.32 (m, 2H), 4.28 (t, J=5.8 Hz, 2H); ^{13}C NMR δ 14.0, 22.5, 22.8, 26.5, 32.2, 32.8, 36.5, 38.4, 40.9, 42.4, 65.7, 171.2; IR 2955, 2930, 2860, 1742,

1456, 1259, 1230, 1081, 478, 464, 437 cm^{-1}; EI MS, *m/e* 207(M-71, 65), 205(M-71, 66), 169(100), 83(20), 81(49), 69(78), 55(49). Anal. Calcd for $C_{12}H_{21}BrO_2$: C, 52.00; H, 7.64; Br, 28.83. Found: C, 52.18; H, 7.64; Br, 28.66.

4-(2-Bromoethyl)-4-pentyltetrahydro-4*H*-pyran (12). The crude mixture obtained from reduction of the lactone **10** (12.3 g) was dissolved in chloroform (20 mL), cooled to 0°C and 5 drops of anhydrous pyridine followed by $SOBr_2$ (5.4 mL, 69.7 mmol) were added. The mixture was stirred at room temperature overnight and then refluxed for 8 hrs. Water (100 mL) was added, the organic phase separated and the aqueous phase extracted with hexanes (2x100 mL). The combined organics were washed with a saturated solution of $NaHCO_3$ (100 mL), brine (100 mL), and water (100 mL). After drying over $MgSO_4$ the solvent was evaporated to give a brown oil which was eluted with methylene chloride through a silica gel plug. The crude material was purified by distillation to give a total of 4.94 g (40% overall yield based on **10**) of bromide **12** (bp 80-81 °C / 0.05 torr). The analytical sample was purified by Chromatotron separation: ^1H NMR δ 0.88 (t, J=6.9 Hz, 3H), 1.18-1.33 (m, 8H), 1.40-1.44 (m, 4H), 1.93-1.99 (m, 2H), 3.34-3.38 (m, 2H), 3.61-3.65 (t, J=5.4, 4H); ^{13}C NMR δ 13.9, 22.3, 22.5, 28.0, 32.5, 34.5, 35.6, 36.2, 40.6, 63.3; IR 2930, 2858, 1454, 1390, 1228, 1112, 1016, 841, 655, 448 cm^{-1}; EI MS, *m/e* 193(M-71, 8), 191(M-71, 9), 183(100), 155(49), 111(13), 83(49), 81(73), 79(20), 69(38), 55(43). Anal. Calcd for $C_{12}H_{23}BrO$: C, 54.76; H, 8.81; Br, 30.36. Found: C, 54.62; H, 8.77; Br, 30.49.

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References

(1) Prelog, V., Kohlbach, D., Cerkovnikov, E., Rezek, A. and Piantanida, M. *Ann. Chem.* **1937**, *532*, 69.

(2) Lukes, R., Strouf, O. and Ferles, M., *Collect. Czech. Chem. Commun.* **1957**, *22*, 1173.

(3) Lukes, R. and Ferles, M. *Collect. Czech. Chem. Commun.* **1953**, *18*, 818.

(4) Wetzel, R. B. and Kenyon, G. L. *J. Am. Chem. Soc.* **1974**, *96*, 5189.

(5) Quast, H. and Berneth, C.-P. *Chem. Ber.* **1983**, *116*, 1345.

(6) Prelog, V. and Cerkovnikov, E. *Ann. Chem.* **1936**, *525*, 292.

(7) Hanousek, V. and Prelog, V. *Collect. Czech. Chem. Commun.* **1932**, *6*, 259.

(8) Kohler, E. P. and Reid, G. H. *J. Am. Chem. Soc.* **1925**, *47*, 2803.

(9) Phillips, D. D., Acitelli, M. A. and Meinwald, J. *J. Am. Chem. Soc.* **1957**, *79*, 3517.

(10) Bairamov, K. A. *M. Phil.* Vanderbilt University, 1997.

(11) Vartanyan, S. A., Zhamagortsyan, V. N. and Grigoryan, L. G. *Arm. Khim. Zh.* **1966**, *19*, 619; *Chem. Abs.* **1957**, *66*, 65364d.

(12) Andrus, D. W. *Org. Synth. Collect. Vol. III* **1955**, 692. Drake, N.L. and Eaker, C.M. checkers.

(13) Landini, D., Montanari, F. and Rolla, F. *Synthesis* **1978**, 771.

(14) Bryson, T. A. and Dolak, T. M. *Org. Synth. Collect. Vol. VI* **1988**, 505; Shapiro, R. and Buchi, G. checkers.

(15) Negishi, E., Takahashi, T. and King, A. O. *Org. Synth. Collect. Vol VIII* **1993**, 430. Kawai, K. and Noyori, R. checkers.

(16) Silverstein, R. M., Clayton Bassler, G. and Morrill, T. C. "Spectrometric identification of organic compounds;" fifth ed., Wiley, **1991**, chap. 4.

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