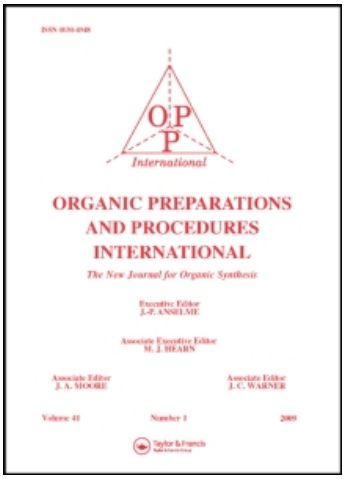



## Organic Preparations and Procedures International

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

# SYNTHESES OF TETRASUBSTITUTED CYCLOPENTANES

Kenichi Somekawa[a]; Masafumi Nomura[a]; Shoichi Aoki[a]; Shinji Noma[a]; Tetsuro Shimo[a]
[a] Department of Applied Chemistry and Chemical Engineering Faculty of Engineering, Kagoshima University, Korimoto, Kagoshima, JAPAN

**To cite this Article** Somekawa, Kenichi , Nomura, Masafumi , Aoki, Shoichi , Noma, Shinji and Shimo, Tetsuro(1993) 'SYNTHESES OF TETRASUBSTITUTED CYCLOPENTANES', Organic Preparations and Procedures International, 25: 4, 449 — 456
**To link to this Article: DOI:** 10.1080/00304949309457988
**URL:** http://dx.doi.org/10.1080/00304949309457988

ORGANIC PREPARATIONS AND PROCEDURES INT., 25 (4), 449-456 (1993)

# SYNTHESES OF TETRASUBSTITUTED CYCLOPENTANES

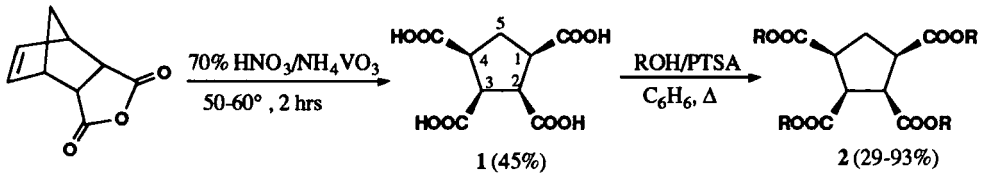
Kenichi Somekawa*, Masafumi Nomura, Shoichi Aoki, Shinji Noma, and Tetsuro Shimo

*Department of Applied Chemistry and Chemical Engineering*
*Faculty of Engineering, Kagoshima University*
*Korimoto, Kagoshima 890, JAPAN*



Recently it was reported that certain cycloalkanepolycarboxylic acids and some of its derivatives display several types of functions, e. g. antitumor activity,[1] binding ability with several metal ions,[2] selective interactions with some nucleic bases,[3] *inter alia*. Some cycloalkanepolymethylols bound with nucleic acids were also reported to have very potent antiviral activitity.[4] Our interest in a variety of functionalized polysubstituted cycloalkanes led us to synthesize some new basic tetrasubstituted cyclopentanes, such as all-*trans*-cyclopentanetetramethylol (**6**) and its tetraester **8**, a diester (**7**) of all-*cis*-tetramethylol **5**, and the tetra (bromomethyl)- (**10**) and tetra(aminomethyl)derivatives (**18**) of **6**. Direct iodination of **5** also provided the novel diiodide, 3-oxabicyclo[3.3.0]octane (**16**).

The starting material, all-*cis*-cyclopentanetetracarboxylic acid (**1**) was prepared from the Dieis-Alder adduct of cyclopentadiene with maleic anhydride by an improved, one-step method using fuming nitric acid and ammonium vanadate catalyst rather than by the previously described two-step method[5] (*Scheme 1*). Esterifications of **1** with methanol,[6] propanol, and long-chain alcohols using *p*-toluenesulfonic acid (PTSA) catalyst gave the corresponding esters **2** in high yields. The all-*cis*-configuration of **2** was confirmed from the similarity of peak-position of cyclo-pentane-hydrogens to those of **1**[6,7] in the $^1$H NMR spectra.



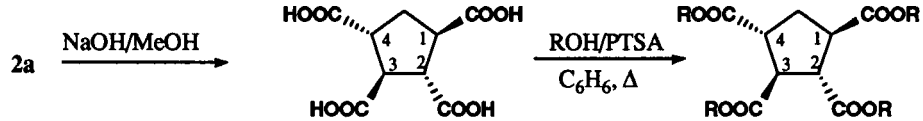

1 (45%) 2 (29-93%)

a) R = Me b) R = Pr c) R = *n*-$C_{12}H_{25}$ d) R = $(CH_2CH_2O)_2Et$

**Scheme 1**

All-*trans*-cyclopentanetetracarboxylic acid (**3**) derived from alkaline epimerization of **2a**[6] was similarly esterifid to **4**. The acid and esters were distinguished from the other configurational isomers *cis,trans,cis*-,[6] *trans,cis,trans*-cyclopentanetetracarboxylic acids as well as their esters, by their

melting points and spectral data. The 5-$CH_2$ signals in $^1H$ NMR spectra of the all-*trans*-configurations appeared as triplets, and the two 5-$CH_2$ protons of all-*cis*-isomers had nonequivalent signals. The esterification of **3** was more rapid and proceeded to give higher yields than those of **1**. This behavior is reasonable in view of their steric hindrance. Compounds **4c** and 4e are solids of low melting points and are stable up to 300°.

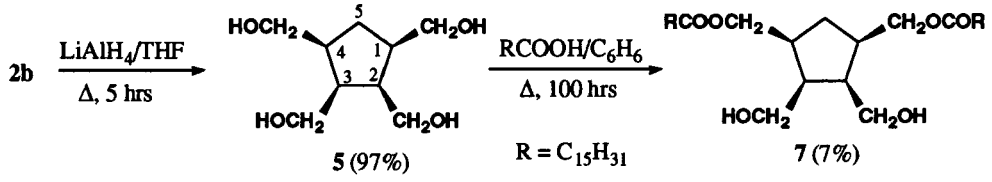



**3** (81%) **4** (37-95%)

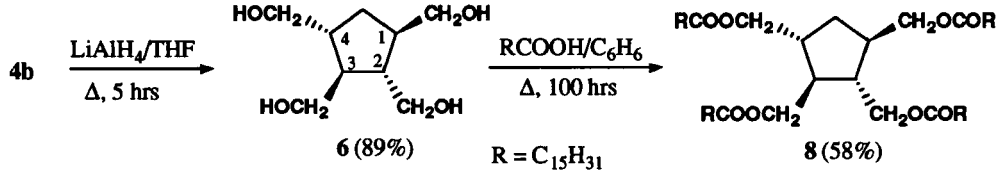
a) R = Me b) R = Pr c) R = *n*-$C_{12}H_{25}$ d) R = $(CH_2CH_2O)_2Et$ e) R = $C_{18}H_{37}$

**Scheme 2**

All-*cis*-cyclopentanetetramethylol (**5**)[7] was obtained in 97% yield by lithium aluminum hydride (LAH) reduction of **2b** in THF. Compound **5** was also obtained albeit in lower yield (16%) by direct reduction of **1** with LAH. All-*trans*-cyclopentane-tetramethylol (**6**), mp. 75-76.5°, was obtained by LAH reduction of **4b** in 95% yield. **5** and **6** are insoluble in chloroform and very soluble in water. The differences between **5** and **6** appear in the $^1H$ NMR spectral data and in their subsequent esterifications. The 5-$CH_2$ of **5** shows an unsymmetrical pattern and those of **6** appear a triplet.; they confirmed their structures. Esterification of **5** and **6** with palmitic acid gave different results as shown in *Scheme 3*; compound **5** gave the *cis*-1,4-diester (**7**) even under prolonged reaction time, but compound **6** gave the all-*trans*-1,2,3,4-tetraester **8**. The structures were confirmed by their spectral data. The difference in their reactivity are inferred from steric hindrance of the all-*cis*-configuration in **7**.




**5** (97%) **7** (7%)

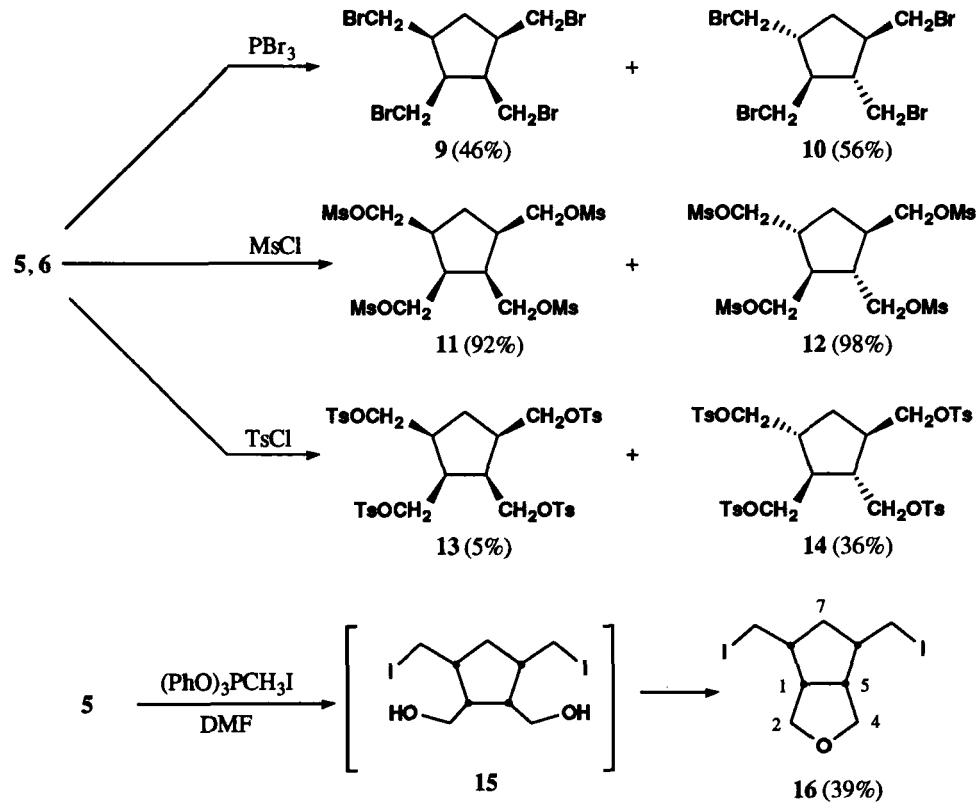



**6** (89%) **8** (58%)

**Scheme 3**

All-*cis*-(**9**) and all-*trans-tetra*(bromomethyl)cyclopentanes (**10**) were obtained in 46% and 56% yields respectively by bromination of **5** and **6** with $PBr_3$ at 180°. All-*cis*-(**11**)[7] and all-*trans*-

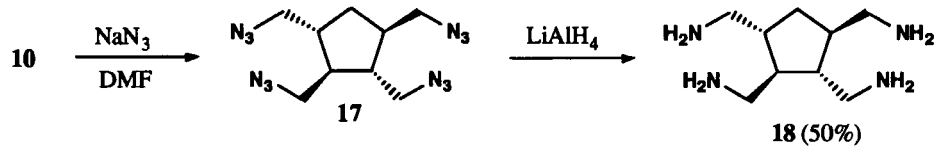
tetra(mesyloxymethyl)cyclopentanes (**12**) were obtained in quantitative yields by reactions of **5** and **6** with mesyl chloride in the presence of pyridine at 0° All-*cis*-(**13**) and all-*trans*-tetra(tosyloxymethyl)-cyclopentanes (**14**) were also obtained by reaction of **5** and **6** with tosyl chloride in the presence of pyridine under 0°, but the yields were 5% and 36%, respectively. The lower yields are probably the consequence of steric hindrance and the use of a less reactive reagent. Attempted direct iodination[8a] of **5** with methyltriphenylphosphonium iodide in DMF gave a novel product, 6,8-diiodomethyl-3-oxabi-cyclo[3.3.0]octane (**16**) in 39% yield after column chromatography on silica gel. The structure was determined from its $^1$H NMR and MS spectra. The reaction of **6** with the iodide gave a complex result. Reaction of **5** with trimethylchlorosilane and sodium iodide[8b] also gave **16** in 28% yield. The reaction is presumed to proceed *via* a diiodo intermediate **15** and subsequent dehydration as shown in *Scheme 4*. Iodine-exchange of all-*cis*-*tetra*-(chloromethyl)cyclopentane with sodium iodide did not occur. The chemical rational is under further consideration.




**Scheme 4**

A mixture of tetrabromide **10** and sodium azide in DMF was refluxed and worked up to give the crude tetraazide (**17**), which was reacted with LAH in diethyl ether to give the all-*trans*-*tetra*-(aminomethyl)cyclopentane (**18**) in 50% yield; **18** is very soluble in water and showed NH absorp-

tions at 3400-3300 $cm^{-1}$ and peaks at δ 3.85-4.00 ppm in the $^1H$ NMR. These sterically controlled, basic tetrasubstituted cyclopentanes may be good synthons of some functional materials.




**Scheme 5**

## EXPERIMENTAL SECTION

Melting points were determined on Yanagimoto's block and are uncorrected. $^1H$ NMR spectra were recorded on a JOEL JNM-GSX 400 (400 MHz) spectrometer with TMS, as an internal standard. IR and MS spectra were recorded on JASCO A-3 and JEOL JMSOISG spectrometers, respectively.

**All-*cis*-Cyclopentanetetracarboxylic Acid (1).**- *endo*-5-Norbornene-2,3-dicarboxylic anhydride (Tokyo Kasei Kogyo Co.) (100 g, 620 mmol) was oxidized with fuming $HNO_3$ (400 mL) and ammonium vanadate (343 mg, 2.93 mmol) for 2 hrs under 60°. The mixture was evaporated at 30° to reduce the volume to half and the resulting suspension was filtered. The precipitate was washed with acetones to give 68.6 g (45%) of all-*cis*-cyclopentanetetracarboxylic acid (**1**), mp. 197-200°. This one-step preparation of **1** was preferred over the two-step method, which used the hydroxylamine and subsequent oxidation of an intermediate (35% yield).[7] The all-*cis*-structure was confirmed by its mp. 195-197°, lit.[6] mp. 195° (dec.) and the 5-$CH_2$ pattern of $^1H$ NMR.

**All-*cis*-Tetraalkyl Cyclopentanetetracarboxylates (2). General Preparation. All-*cis*-tetra(n-Propyl)cyclopentanetetracarboxylate (2b).**- Acid **1** (94.6 g, 380 mmol) and PTSA (4.57 g, 22.4 mmol) were dissolved in *n*-propanol (470 mL) and benzene (600 mL). The mixture was refluxed for 18 hrs, while $H_2O$ formed was azetropically removed. The residue was washed with $H_2O$ and aqueous $NaHCO_3$ and dried ($MgSO_4$). The solvent was evaporated to give **2b** quantitatively (oil; yield 93%). IR (film): 2970, 2890, 1740 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): δ 0.90 (12H, t, $CH_3$), 1.60 (8H, m, $CH_2CH_3$), 2.40 (1H, dt, 5-H), 2.80 (1H, dt, 5-H), 3.05 (2H, m, 1,4-H), 3.40 (2H, dd, 2,3-H), 4.00 (8H, m, $OCH_2$).

*Anal.* Calcd for $C_{21}H_{34}O_8$: C, 60.85; H, 8.27. Found: C, 60.71; H, 8.18

Compound **2b** was also obtained by using conc. $H_2SO_4$, a catalyst used for the preparation of the all-*cis*-tetramethyltetracarboxylate (**2a**).[6] But the yield was not good.

The following all-*cis*-tetraalkyl tetracarboxylates were obtained similarly.

**2c**, mp. 45-50° (32%): 2960-2860, 1740 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 0.88 (12H, t, $CH_3$), 1.26 (72H, m, $CH_2$), 1.58 (8H, m, $CH_2$), 2.28-3.45 (6H, m, ring-H), 4.04 (8H, t, $OCH_2$).

*Anal.* Calcd for $C_{57}H_{106}O_8$: C, 74.46; H, 11.62. Found: C, 74.73; H, 11.62

**2d**, oil (29%): 2950-2880, 1740, 1100 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 1.21 (12H, t, $CH_3$) 2.3-3.5 (6H, m, ring-H), 3.60 (32H, m, 8 $CH_2$), 4.24 (8H, t, $OCH_2$).

*Anal.* Calcd for $C_{33}H_{58}O_{16}$: C, 55.76; H, 8.22. Found: C, 55.46; H, 7.93

**All-*trans*-Cyclopentanetetracarboxylic Acid (3) and the Tetraalkyl Esters 4.**- Acid **3** was derived by alkaline epimerization of **2b** in high yield (81%) rather than from the all-*cis*-tetramethyl analog.[6]

**General Procedure. All-*trans*-tetra(n-Propyl)cyclopentanetetracarboxylate (4b).**- A mixture of **3** (5.03 g, 20 mmol) , PTSA (0.21 g, 1.1 mmol), *n*-propanol (50 mL) and benzene (70 mL) was refluxed for 15 hrs and worked up similarly to the case of **2b** to give **4b**, oil (95%).

**4b**: 2970, 2890, 1755-1730 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 0.90 (12H, t, $CH_3$), 1.60 (8H, m, $CH_2$), 2.30 (2H, t, 5-H), 3.25 (2H, m, 1,4-H), 3.48 (2H, dd, 2,3-H), 4.00 (m, 8H, $OCH_2$).

*Anal.* Calcd for $C_{21}H_{34}O_8$: C, 60.85; H, 8.27. Found: C, 60.74; H, 7.99

**4c**, oil (41%): 2960-2860, 1740, 1470 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 0.88 (12H, t, $CH_3$), 1.26 (72H, m, $CH_2$), 1.55 (8H, m, $CH_2$), 2.29 (2H, t, 5-H), 3.20-3.50 (4H, m, 1-4-H), 4.09 (8H, t, $OCH_2$).

*Anal.* Calcd for $C_{57}H_{106}O_8$: C, 74.46; H, 11.62. Found: C, 74.35; H, 11.69

**4d**, oil (37%): 2950-2880, 1740, 1100 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 1.21 (12H, t, $CH_3$), 2.30 (2H, t, 5-H), 3.2-3.6 (36H, m, 1-4-H, $OCH_2$), 4.28 (8H, t, $CO_2CH_2$).

*Anal.* Calcd for $C_{33}H_{58}O_{16}$: C, 55.76; H, 8.22. Found: C, 55.58; H, 8.29

**4e**, mp. 48-50° (59%): 2960-2860, 1740, 1470 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 0.88 (12H, t, $CH_3$), 1.26 (72H, m, $CH_2$), 1.55 (8H, m, $CO_2CH_2CH_2$), 2.29 (2H, t, J = 8 Hz, 5-H), 3.20-3.50 (4H, m, 1-4-H), 4.09 (8H, t, $CO_2CH_2$).

*Anal.* Calcd for $C_{81}H_{154}O_8$: C, 77.45; H, 12.36. Found: C, 77.69; H, 12.25

**All-*cis*-1,2,3,4-Cyclopentanetetramethylol (5).**- Böhme *et al.* obtained **5** in 82% yield by $LiAlH_4$ reduction of the all-*cis*-tetraethylcyclopentanetetracarboxylate.[7] We prepared **5** in 97% yield by LAH reduction of **2b**. The data of an all-*cis*-structure of **5** were as follows.

**5**, oil: 3300, 2950-2850, 1020 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$): δ 1.08 (1H, dt, J = 12.8 and 10.4 Hz, 5-H), 1.79 (1H, dt, J = 12.8 and 8.4 Hz, 5-H'), 2.09 (2H, m, 1,4-H), 2.19 (2H, m, 2,3-H), 3.30-3.50 (8H, m, $OCH_2$), 4.50 (2H, t, OH), 4.80 (2H, t, OH).

**All-*trans*-1,2,3,4-Cyclopentanetetramethylol (6).**- A solution of **4b** (29 g, 70 mmol) in dry THF (100 mL) was added dropwise to a suspension of LAH (11 g, 30 mmol) in dry THF (130 mL), and the mixture was refluxed for 5 hrs. To the mixture was added THF-$H_2O$ (1:1) (50 mL) and continuous $H_2O$ (50 mL). A white precipitate was filtered and washed with ethanol, and the mixture between the filtrate and ethanol solution was evaporated *in vacuo*. The residue was column chromatographed on weakened silica gel ($CHCl_3$/EtOH) to give **6** as a viscous oil (79%).

**6**: 3300, 2950-2800, 1060, 1020 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$): δ 1.40 (2H, m, 1,4-H), 1.45 (2H, t, 5-H), 1.75 (2H, m, 2,3-H), 3.35-3.40 (8H, m, $CH_2O$), 4.60 (2H, t, OH), 4.80 (2H, t, OH). Mass spectrum m/z 191 ($M+1^+$, 0.3%); 93 ($C_7H_9^+$, 100%).

*Anal.* Calcd for $C_9H_{18}O_4$: C, 56.82; H, 9.54 . Found: C, 56.80; H, 9.48

**All-*cis*-1,4-bis(Hexadecanoyloxymethyl)-2,3-bis(hydroxymethyl)cyclopentane (7).**- A mixture of **5** (2.45 g, 12.9 mmol), palmitic acid (25.0 g, 97.5 mmol), PTSA (0.20 g, 1.0 mmol), and benzene (100 mL) was refluxed for 100 hrs, while the $H_2O$ was removed azeotropically. The residue was washed

with $H_2O$ and evaporated up to 150°/12 mmHg to remove palmitic acid, and recrystallized from benzene to give **7**, mp. 30-35° (7%).

**7**: 3350, 1740 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 0.90 (6H, t, $CH_3$), 1.10-1.40 (52H, m, $CH_2$), 1.40-1.80 (6H, m, ring-H), 2.20-2.40 (4H, m, $OCOCH_2$), 2.80 (2H, bs, OH), 3.70 (4H, m, $CH_2OH$), 4.00-4.20 (8H, m, $CO_2CH_2$).

*Anal.* Calcd for $C_{41}H_{78}O_6$: C, 73.87; H, 11.71. Found: C, 74.14; H, 11.50

**All-*trans*-1,2,3,4-tetra(Hexadecanoyloxymethyl)cyclopentane (8)**.- A mixture of **6** (2.16 g, 11.4 mmol), palmitic acid (11.7 g, 45.6 mmol), PTSA (0.20 g, 1.0 mmol), and benzene (100 mL) was refluxed for 100 hrs and similarly worked up to give **8**, mp 48-50° (58%).

**8**: 2950-2850, 1740 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 0.90 (12H, t, $CH_3$), 1.10-1.14 (104H, m, $CH_2$), 1.40-1.80 (6H, m, ring-H), 2.20 2.40 (8H, m, $OCOCH_2$), 4.00-4.20 (8H, m, $CH_2CO0$).

*Anal.* Calcd for $C_{73}H_{138}O_8$; C, 76.65; H, 12.16. Found; C, 76.51; H, 12.20

**All-*cis*-1,2,3,4-tetra(Bromomethyl)cyclopentane (9)**.- A mixture of **5** (4.49 g, 23.5 mmol) and $PBr_3$ (6.0 mL, 64.0 11 mmol) was heated for 5 hrs at 170-180°, then poured into cold water, and extracted with $CHCl_3$. After drying ($MgSO_4$) the extract was evaporated *in vacuo* to give a residue, which was column chromatographed ($SiO_2$) eluting with Hexane/EtOAc to give **9**, viscous oil (46%).

**9**: 2980-2860, 640 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$): δ 1.50 (1H, m, 5-H), 2.30 (1H, m, 5-H), 2.50-2.90 (4H, m, 1-4-H), 3.30-3.70 (gH, m, $CH_2Br$). Mass spectrum: m/z 441 ($M^+$, 0.1%); 119 ([M-4Br]$^+$, 100%).

*Anal.* Calcd for $C_9H_{14}Br_4$: C, 24.47; H, 3.19. Found: C, 24.37; H, 3.29

**All-*trans*-1,2,3,4-tetra(Bromomethyl)cyclopentane (10)**.- The preparation of **10** from **6** was similar to that of **9**, column chromatography gave **10** viscous oil (56%). 10: 2960- 2880, 600 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 1.90 (2H, t, J = 8, 5-H), 2.00-2.60 (4H, m, 1-4-H), 3.30-3.60 (gH, m, $CH_2Br$). Mass spectrum: m/z 441 ($M^+$, 0.1%); 119 ([M-4Br]$^+$, 100%).

*Anal.* Calcd for $C_9H_{14}Br_4$: C, 24.47; H, 3.19. Found: C, 24.67; H, 3.28

**All-*trans*-1,2,3,4-tetra(Mesyloxymethyl)cyclopentane (12)**.- In the similar way of **11** from **5**,[7] a solution of **6** (6.7 g, 35.2 mmol) with dry pyridine (25 mL) was added to a cold solution of mesyl chloride (7.2 g, 150 mmol) with dry pyridine (50 mL) under 0° and was stirred for 3 hrs. The mixture was poured into 4N HCl aqueous solution (200 mL) and extracted with $CH_2Cl_2$. The organic layer was dried and evaporated to give **12**, oil (98%).

**12:** 2940, 1350, 1170 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 1.84 (2H, t, J = 12 7.7 Hz, 5-H), 2.14 (2H, m, 1,4-H), 2.38 (2H, m, 2,3-H), 3.06 (6H, s, $CH_3$), 3.08 (6H, s, $CH_3$), 4.22 (4H, m, $OCH_2$), 4.32 (4H, m, $OCH_2$).

*Anal.* Calcd for $C_{13}H_{26}O_{12}S_4$: C, 31.06; H, 5.21. Found: C, 30.76; H, 5.12

**All-*cis*-1,2,3,4-tetra(Tosyloxymethyl)cyclopentane (13)** .- To a cold solution of tosyl chloride (11.0 g, 57 mmol) with dry pyridine (30 mL) a solution of **5** (2.0 g, 11 mmol) with dry pyridine (7 mL) was added under 0° and the mixture was stirred for 19 hrs at 25°. The mixture was poured into a cold 6N-HCl solution (100 mL) and extracted with $CH_2Cl_2$. The organic layer was dried and evaporated to give a residue, which was column chromatographed eluting with $CH_2Cl_2$ to give **13**, mp. 144-145° (5%).

**13**: 2990-2900, 1600, 1500, 1370, 1195, 1180 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 1.05 (1H, dt, J = 10.2, 13.2 Hz, 5-H), 1.88 (1H, m, 5-H), 2.35-2.55 (4H, m, 1-4-H), 2.45 (6H, s, $CH_3$), 2.47 (6H, s, $CH_3$), 3.79-4.03 (8H, m, $OCH_2$), 7.36 (8H, dd, arom.), 7.7 2 (8H, dd, arom.).

*Anal.* Calcd for $C_{37}H_{42}O_{12}S_4$: C, 55.07; H, 5.25. Found: C, 55.02; H, 5.27

**14**, mp. 33-34° (37%): 2950, 2900, 1600, 1500, 1300, 1200, 1180 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 1.52 (2H, t, 5-H), 1.75 (2H, m, 1,4-H), 2.04 (2H, m, 2,3-H), 2.46 (6H, s, $CH_3$), 2.47 (6H, s, $CH_3$), 3.70-3.85 (8H, m, $OCH_2$), 7.37 (8H, dd, J = 8.4, 3.3 Hz, arom.), 7.7 2 (8H, dd, arom.).

*Anal.* Calcd for $C_{37}H_{42}O_{12}S_4$: C, 55.07; H, 5.25. Found: C, 55.05; H, 5.27

**All-*cis*-6,8-bis(Iodomethyl)-3-oxabicyclo[3.3.0]octane (16).** A solution of 5 (1.9 g, 10 mmol) , methyltriphenylphosphonium iodide (41 g, 92 mmol) and dry DMF (300 mL) was stirred for 4.5 hrs at 25°. After evaporation *in vacuo*, the residue was column chromatographed ($SiO_2$) eluting with hexane/EtOAc) to give **16** as an oil (39%).

**16**: 2950, 2850, 1180 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 1.09 (1H, dt, J = 11.9, 12.5 Hz, 7-H), 2.05 (1H, dt, J = 11.9, 5.7 Hz, 7-H), 2.46 (2H, m, 6,8-H), 2.88 (2H, m, 1,5-H), 3.07 (2H, dd, J = 9.5, 5.9 Hz, CHI), 3.28 (2H, dd, J = 9.5, 6.8 Hz, CHI), 3.63 (2H, dd, J = 9.9, 6.7 Hz, CHO), 3.74 (2H, dd, J = 9.9, 2.9 Hz, CHO). $^{13}C$ NMR ($CDCl_3$): δ 6.4 ($CH_2I$), 38.5 (7-C), 44.9 (6,8-C) , 46.4 (1,5-C) , 68.1 ($OCH_2$). Mass spectrum: m/z 392 ($M^+$, 2%), 265 ([M-I]$^+$, 100%).

*Anal.* Calcd for $C_9H_{14}O_{12}$: C, 27.57; H, 3.57; I, 64.78. Found: C, 27.31; H, 3.57; I, 64.45

**All-*trans*-1,2,3,4-tetra(Aminomethyl)cyclopentane (18)**.- A mixture of all-*trans*-tetrabromide **10** (5.0 g, 11.3 mmol) and $NaN_3$ (14.7 g, 226 mmol) in DMF (250 mL) was refluxed for 7 hrs. After cooling and filtrating the precipitate, the filtrate was evaporated *in vacuo*, and water (200 mL) was added. The $CHCl_3$ extract (100 mL x 4) was dried with $MgSO_4$ and evaporated *in vacuo* at 25° for getting out of danger to give all-*trans*-tetraazide (**17**) (2.0 g) (**CAUTION!**). The crude compound had the specific signals on the IR and NMR spectra, and was reduced with $LiAlH_4$. **17** (2.0 g, 6.9 mmol) in $Et_2O$ (20 mL) was slowly added to $LiAlH_4$ (2.28 g, 60 mmol) in $Et_2O$ (130 mL) and the solution was refluxed for 3 hrs. After adding $Et_2O$ (100 mL), EtOAc (40 mL) and water (10 mL), the precipitate was separated. The filtrate was evaporated and the residue was extracted with $H_2O/Et_2O$. The water layer was extracted with $Et_2O$ and the combined $Et_2O$ layer was evaporated *in vacuo* to give **18** as an oil (50%).

**18**: 3400-3300, 2950, 2880 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 1.00 (2H, t, 5-H), 1.33 (2H, m, 1,4-H), 1.44 (2H, m, 2,3-H), 2.40-2.60 (gH, m, $CH_2$-N), 3.85-4.00 (8H, bs, $NH_2$). Mass spectrum: m/z 186 ($M^+$, 0.5%), 30 ($CH_2{=}NH_2^+$, 100%).

*Anal.* Calcd for $C_9H_{22}N_4$: C, 58.02; H, 11.91; N, 30.08. Found: C, 57.77; H, 12.03; N, 29.82

## REFERENCES

1. M. Schmidt-Dunker and M. Potokar, *Ger. Offen.*, 2553964 (1977); *Chem. Abs.*, **87**, 90741 (1977).

2. A. K. Misra and K. J. Srinivasulu, *Indian Chem. Soc.*, **63**, 341 (1986); J. H. Price and J. R.

Pilbrow, *J. Chem. Soc. (A)*, 968 (**1970**).

3. J. Rebek, B. Askew, M. Killoran, D. Nemeth and F.-T. Lin, *J. Am. Chem. Soc.*, **109**, 2426 (1987); J. Rebek, *Angew. Chem. Int. Ed. Engl.*, **29**, 245 (1990).

4. T. Maruyama, Y. Sato, T. Horii, K. Nitta, T. Shirasaka, H. Mitsuya and M. Honjo, *Chem. Pharm. Bull. Jpn*, **38**, 2719 (1990); N. Katagiri, H. Sato and C. Kaneko, *ibid.* **38**, 3184 (1990).

5. H. Kawachi, Y. Komori and S. Fujiki, Japanese Patent, 7239103 (1972); *Chem. Abs.*, **78**, 3803 (1973); K. Alder and S. Schneider, Ann., **524**, 189 (1936).

6. K. Alder, H.-H. Moils and R. Reeber, *ibid.*, **611**, 7 (1958); H. Oka, S. Shimazaki and T. Yoshida, Japanese Patent, 84118741 (1984); *Chem. Abs.*, **102**, 24176 (1984).

7. H. Böhme and G. Seitz, *Chem. Ber.*, **101**, 1689 (1968); G. Seitz, H. Hoffmann and G. Kromeke, *Arch. Pharm.*, **309**, 930 (1976).

8. a) J.-H. Kim, G.-H. Jeon and K. A. Watanabe, *J. Org. Chem.*, **53**, 5046 (1988); b) G. A. Olah, S. C. Narang, B. G. B. Gupta and R. Malhotra, *ibid.*, **44**, 1247 (1979).

***(Received January 19, 1993; in revised form April 6, 1993)***