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CYCLIC α, β-EPOXYSILANES

ACID-CATALYSED REACTIONS OF 1-TRIMETHYLSILYLCYCLOOCTENE OXIDE

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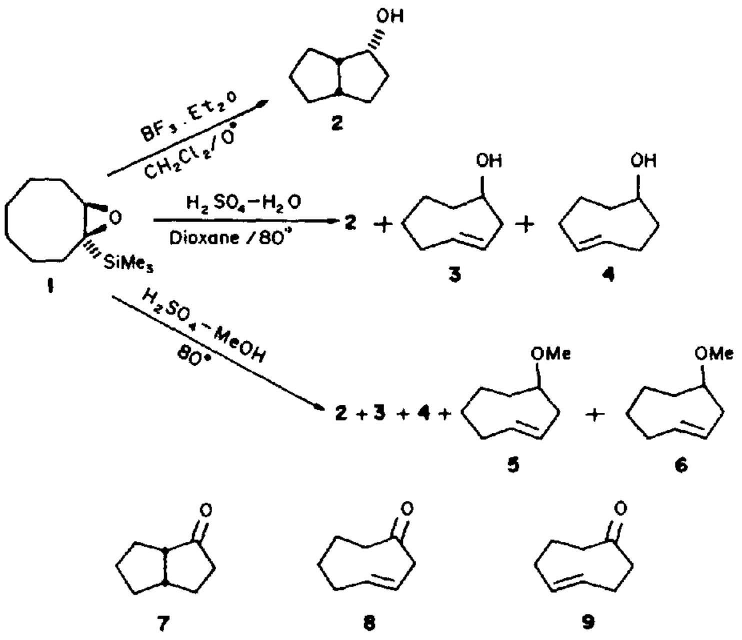
Abstract—The acid-catalysed reactions of medium ring α,β-epoxysilane 1 are described. The epoxide 1 gives exclusively the bicyclic alcohol 2 with boron trifluoride etherate. With aqueous sulphuric acid the products are due to both transannular ring closure, 2, and transannular hydride migration, 3 and 4. *trans*-Cyclooctene derivatives 3 and 4 are formed by the *trans*-elimination of trimethylsilanol from the likely intermediate β-hydroxysilanes 10 and 11. The results with methanolic sulphuric acid are similar. It is also noticed that the hydride migration is facilitated by the nucleophilic strength of the medium.

The reactions of medium ring compounds usually give products formed predominantly through the transannular participation of C–H bond or C=C double bond from across the ring.[1] The hydrolysis of the medium ring epoxides under both acidic and basic catalysis is the best studied transannular reaction. The influence of α-substituents, be it steric or electronic, on the epoxide ring has not been reported. Since the trimethylsilyl group is known to facilitate exclusive α-opening of the epoxide ring[2] and as the silicon is known to favour bimolecular displacement on the carbon α to it,[3] we expected that the silyl group would have some counter influence on the transannular participation. Thus, we anticipated that 1-trimethylsilylcyclooctene oxide (1) would give 'normal' product, 1-trimethylsilyl-*trans*-1,2-cyclooctanediol, which we needed in some other study,[4] in major amounts if not exclusively. But contrarily, 1 was found to yield solely transannular products with acid catalysts under various conditions. More interestingly, *trans*-cyclooctene derivatives were identified in major proportions of the product under certain conditions. The results are reported here.

RESULTS AND DISCUSSION

1-Trimethylsilylcyclooctene oxide (1) was prepared in excellent yield by the reaction of 1-trimethylsilylcyclooctene[5] with *m*-chloroperbenzoic acid. The results of the reactions of the epoxide 1 are summarised in Scheme 1.

Reaction of 1 *with boron trifluoride etherate.* The reaction of the epoxide 1 with boron trifluoride etherate in dichloromethane at 0° resulted, within 30 min, in the formation of pure single *endo-cis*-bicyclo [3.3.0] octan-2-ol (2) in 96% isolated yield. Its structural identity was established by its spectral characteristics and converting to its phenylurethane derivative. Further, 2 was oxidised to the corresponding ketone 7 which in turn was identified by its spectral characteristics and converting to semicarbazone and 2,4-dinitrophenyl hydrozone derivatives. This sequence of reactions which gives



Scheme 1.

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excellent yields of **2**, could be a good source of **7** which has synthetic applications[6].

Reactions of **1** *with aqueous sulphuric acid in dioxane.* Treatment of **1** at 80° gave, within 1 hr, a product mixture, in 93% isolated yield, which showed two major peaks in gas chromatograph (GC) accounting for 90–95% of the product. The two components (in about 3:1 ratio) were separated by preparative GC. The first and the larger component was identified as **2**. The spectral characteristics of the second component indicated that it is *trans*-3-and/or *trans*-4-cyclooctenol (**3** and/or **4**). Further, the original product mixture was oxidised with chromium trioxide in pyridine and the resultant ketones were separated by preparative GC into two components. The first component was identified as the ketone **7**, and the second showed all the spectral characteristics indicating it to be a mixture of **8** and **9** (in the ratio of about 2:1 by NMR), thus confirming that the second alcoholic product component is a mixture of **3** and **4**.

Hydrogenation under normal pressure of the ketone mixture showed two peaks in GC. One of them was due to the ketone **7** and the other was a new peak which must have resulted from the hydrogenation of **8** and **9**. The two compounds were separated by the usual way. The new compound was identified as cyclooctanone by comparing its spectral data with those of an authentic sample and by melting and mixed m.ps of its semicarbozone derivative. These results establish the identities of **8** and **9** and therefore, those of **3** and **4**.

The ratio of the alcohols **2** to **3** and **4** in this reaction appears to depend on the proportion of the aqueous acid in relation to the epoxide. It was found that using higher proportion of acid increased the proportion of **3** and **4** and there was corresponding reduction in **2**. However, we have not established any quantitative relationship.

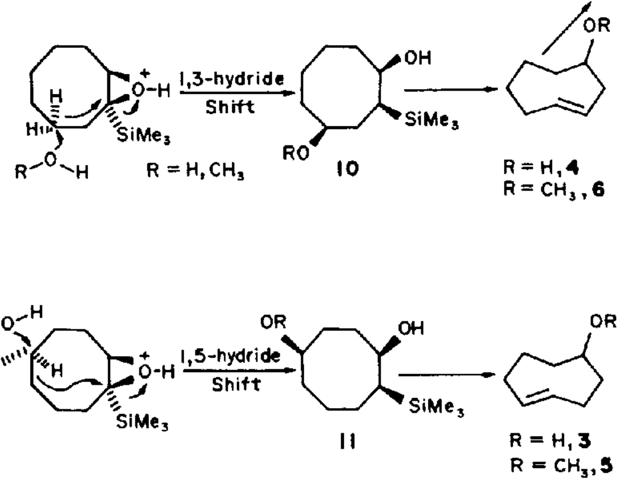
Reaction of **1** *in methanolic sulphuric acid.* The reaction of **1** at 80° gave a product mixture consisting of four major components in the ratio 5:40:46:5 as indicated by GC. The remaining 4% is due to several small peaks including that of unreacted epoxide **1** and no attempt was made to identify them. The first of the four peaks was identified as 1,3-cyclooctadiene (*cis, cis*-or *cis, trans*-) from its GC retention time and mass spectrum.[7] The fourth component was found to be due to **3** and **4** by its GC retention time and GC-MS. The remaining two major components were separated by preparative GC. The latter (46%) was identified as **2** by its spectral and chemical characteristics as described previously. The former (40%) is likely a mixture of **5** and **6** (in about 2:1 ratio) as indicated by its IR, NMR and MS characteristics which are similar to those of the mixture of **3** and **4** with appropriate modification due to methoxy group in place of OH group. Unfortunately, we were unable to separate **3** from **4** or **5** from **6**.

To rule out the possibility of formation of **5** and **6**, from **3** and **4** in methanol solvent, the latter were heated with methanolic sulphuric acid at 80°, that is under the same reaction condition under which **5** and **6** are formed from **1**. No trace of **5** and **6** was observed, however, even after 3 hr period. Therefore, **5** and **6** must have formed by direct attack of methanol on the epoxide **1**.

Since cyclooctanone is not formed by the acid catalysed reactions of **1**, it is conceivable that no nucleophilic attack takes place on silicon prior to the epoxide ring opening, though the converse does not hold good. The absence of cyclooctanone also shows that 1-trimethylsilyl-*trans*-1,2-cyclooctanediol is not formed as an intermediate.[2]

Thus it can be assumed that the epoxide ring is opening at considerably faster rate than the attack on silicon or α- or β-carbon followed by concerted transannular ring closure or hydride migration with simultaneous attack by the solvent. The formation of the olefinic products, **3**, **4**, **5** and **6** as well as 1,3-cyclooctadiene may be visualised as depicted in Scheme 2.

The Scheme 2 shows that the products are formed by an initial acid catalysed α-opening of the epoxide ring, for which there is overwhelming evidence in the literature,[2,8] with concerted 1,3- or 1,5-hydride migration to α-position taking place. Closely following this or simultaneously, an attack by the solvent on the carbon from which the hydride migration occurs results in the formation of the intermediate **10** or **11**. The steric requirement of the hydride migration has to be such that the intermediate **10** or **11** will have the trimethylsilyl group *cis* to the β-OH group. It is well known that the acid catalysed 1,2-elimination of trimethylsilanol takes place in a *trans* fashion.[8,9] Therefore, **11** and **10** must lead to *trans*-cyclooctene derivatives **3** or **5** and **4** or **6** respectively. In fact the IR spectra of these products exhibit a



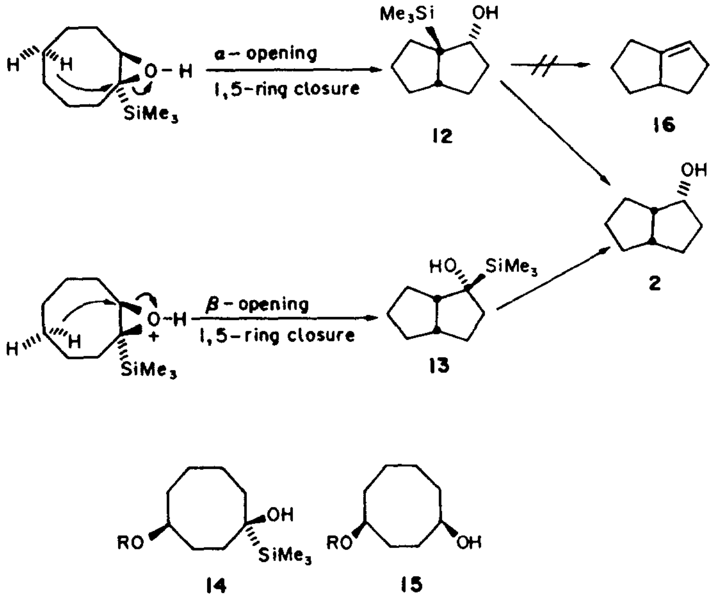
Scheme 2.

band at 985 cm^{-1} characteristic of a *trans* double bond.[10] This band is absent in the IR spectra of other compounds described here. We had not expected *trans*-cyclooctenes from these reactions as the conditions are not very favourable for the survival of the *trans* configuration of the double bond. But Wiberg and Pfeiffer have isolated 3-*trans*-cyclooctenol under more drastic conditions.[11] Therefore, it may not be unreasonable to assign *trans* geometry to the double bond in 3, 4, 5 and 6. This shows that *cis*-2-trimethylsilylcyclooctanols could be good starting compounds for the synthesis of *trans*-cyclooctene and its derivatives which are not very easy to synthesise,[12] but are of great theoretical interest.

The alcohol 2 can result through the intermediate 12 or 13 by concerted epoxide ring opening and transannular ring closure. The intermediate 12 would be the result of α-opening of the epoxide ring and 13 would result from β-opening of the epoxide ring. Scheme 3.

smooth elimination of trimethylsilanol, and direct substitution on silicon in 12 may become kinetically more important leading to 2. There are instances in literature of substitution on silicon being faster than elimination.[13]

We would like to point out another observation in this study, namely that the nucleophilic character of the medium appears to exert some influence on the ratio of the transannular ring closure product 2 to the products 3–6 resulting from the hydride migration. As one goes from dichloromethane through water to methanol, the proportion of 2 decreases considerably. This was evident even in the case of aqueous acid alone when different ratios of 1 to aqueous acid were used. As the proportion of the aqueous acid (same concentration) was increased the amount of 2 in the product mixture decreased in comparison with the amount of 3 and 4. From these results we could, at least qualitatively, say that the hydride migration is facilitated by a stronger nucleophile or a higher concentration of the same nucleophile. Some related observation is reported by Cope *et al.*,[14] who have demonstrated that as the solvent becomes relatively less nucleophilic the contribution of the migrating transannular hydride ion becomes more important.



Scheme 3.

Since, we have already explained other results as arising from α-opening of the epoxide, we favour in this case also the same direction of ring opening. Moreover, there is an indirect evidence that β-opening is not taking place, because no significant amount of 1,4-cyclooctanediol or 4-methoxycyclooctanol (15) was observed in the reaction of 1 with aqueous or methonolic sulphuric acid. If β-opening were taking place 14 would be formed leading ultimately to 15. However, the stereochemistry of transannular ring closure in this case requires that the trimethylsilyl and the OH groups on C_1 and C_2 of the bicyclic intermediate 12 are *trans* to each other (Scheme 3). When the geometry of the β-hydroxysilane is *trans* the elimination of trimethylsilanol in acid medium, especially in presence of BF_3-etherate, should be very facile.[9] Thus 12 should lead to 16 which, however, was not detected in any of the reactions. The reason for the absence of 16 may be as follows. The elimination of trimethylsilanol does not occur unless the silyl and the hydroxy groups are antiperiplanar.[2] In the case of 12, construction of molecular model indicates that the two groups may not aquire perfect antiperiplanarity for a

EXPERIMENTAL

The IR spectra were taken on Beckman Acculab 1 instrument. Unless otherwise noted, the IR spectra of the liquids were run as thin films between NaCl plates and those of solids in KBr pellets. The NMR spectra were recorded on Bruker Data System Model MTC-120 (60 MHz) instrument and the chemical shifts are reported in parts per million (δ) using TMS as internal standard unless otherwise stated. The qualitative GC analysis were carried out on Varian Aerograph 1400 with temp programme. For preparative GC Parkin-Elmer F-21 instrument was used. The GC-MS analyses were conducted on Varian Mat-111 instrument. Elemental analyses were carried out at Prof. Dipl-Ing. Dr. H. Malissa and G. Reuter Analytische Laboratorien, 5250 Engelskirchen, West Germany. All the preliminary experiments were monitored by GC to follow the progress and completion of the reactions. 1-Trimethylsilylcyclooctene was prepared by the procedure previously described.[5]

1-*Trimethylsilylcyclooctene oxide* (1). To a mixture of 12.51 g of 85% (61.60 mmol) *m*-chloroperbenzoic acid and 8.94 g (62.92 mmol) of disodium hydrogen phosphate in 120 ml dry CH_2Cl_2 (distilled over P_2O_5), stirred in an ice-water bath under N_2, was added a soln of 9.53 g (52.36 mmol) of *cis*-1-trimethylsilylcyclooctene in 50 ml dry CH_2Cl_2 over a period of 30 min. The reaction was almost instantaneous. However, the mixture was stirred for 1 hr more. The solids were then filtered off and washed with 10 ml CH_2Cl_2. The filtrate and washings were combined and stirred with 100 ml of 5% Na_2SO_3 aq. The layers were separated, the organic layer was washed successively with 5% NaOH aq (100 ml), 5% $NaHCO_3$ aq sn (100 ml), water (2 × 100 ml) and sat NaCl aq sn (100 ml). After drying over Na_2SO_4, the soln was concentrated on rotary evaporator and the residue was distilled to get 8.78 g (84.7%) of 1 of more than 98% purity, b.p. 59–60°/0.5 torr. (Found: C, 66.51; H, 11.20; $C_{11}H_{22}OSi$. Requires: C, 66.66; H, 11.11%), IR (cm^{-1}), 2960 (sh), 2930, 2860. 1470, 1450, 1250, 840. NMR ($CDCl_3$; $CHCl_3$ as internal standard), δ 0.12 (s, 9H), 1.27–1.87 (m, 10H), 1.87–2.43 (m, 2H), 2.53–3.03 (m, 1H). MS, *m/e* (intensity, %), 198 (1.6, M^+), 183 (5.2), 169 (6.8), 155 (10.0), 143 (17.5), 130 (8.4), 129 (6.3), 115 (13.3), 108 (6.8), 79 (7.1), 75 (54.8), 73 (100), 67 (5.5), 59 (11.7).

Reaction of 1 *with* BF_3*-etherate.* To a soln of 0.78 g (3.94 mmol) of 1 in 15 ml of dry CH_2Cl_2, stirred in an ice-water bath, under N_2, was added 1.0 ml of freshly distilled BF_3-etherate. After stirring for 30 min, the mixture was neutralized with 5% $NaHCO_3$ aq. The layers were separated, the organic layer was washed with water (10 ml) and sat NaCl aq (10 ml), and dried over Na_2SO_4. After concentrating the soln on a rotary evaporator, the residue was distilled (bulb-to-bulb; bath temp 95°; pressure 5.0 torr) to give 0.48 g (96.5%) of 2 which was homogenous in GC (3 m 5% carbowax column; temp programme, 60–160° at 4°/min). IR (cm^{-1}), 3360 (broad), 2950, 2870, 1460, 1075, 1010, 975. NMR (CCl_4), δ 0.96–2.06 (m, 11H), 2.06–2.73 (m, 2H), 3.97–4.43 (m, 1H). MS, *m/e* (intensity, %), 126 (1.3, M^+), 124 (2.9), 109 (3.3), 108 (15.5), 98 (4.4), 97 (9.0), 95 (6.7), 93 (13.3), 91 (3.3), 83 (13.3), 82 (42.2), 81 (10.0), 80 (35.5), 79 (21.0), 68 (16.6), 67 (100). 58 (25.5), 55 (24.4). Phenylurethane, m.p. 88–89° (lit[15] m.p. 86.4–87°). (Found: C, 73.39; H, 7.79; N, 5.74; $C_{15}H_{19}NO_2$. Requires C, 73.44; H, 7.80; N, 5.74%).

Oxidation of 2 *to* 7. To a soln of 2.83 g (35.85 mmol) of pyridine (distilled over BaO) in 30 ml of dry CH_2Cl_2 was added 1.93 g (19.30 mmol) of Cr(VI) oxide (washed with CH_2Cl_2 and dried over P_2O_5 under oil pump vacuum). After stirring the mixture for 10 min 0.30 g (2.38 mmol) of 2 was added and the stirring continued for another 30 min. Then water (25 ml) was added and the solids were filtered off. The organic layer was separated and washed successively with water (2 × 25 ml), dil. HCl (2 × 25 ml) to remove pyridine, 5% $NaHCO_3$ aq (25 ml), water (25 ml) and finally dried (Na_2SO_4). The product was concentrated. Bulb-to-bulb distillation gave 0.26 g (87.8%) of 7 homogenous on GC. Semicarbazone, m.p. 179–180° (Lit[16] m.p. 178.8–180.2°). 2,4-Dinitrophenylhydrezone, m.p. 108–109° (lit[14] m.p. 110–113°). IR (cm^{-1}), 2960, 2880, 1740. NMR ($CDCl_3$), three overlapping multiplets between δ 1.10–3.03. MS, *m/e* (intensity, %), 125 (5.3), 124 (42.5, M^+), 106 (5.3), 96 (18.0), 95 (58.5) 83 (8.5), 82 (25.5), 81 (14.9), 80 (56.4), 79 (8.5), 69 (6.4), 68 (36.2), 67 (100), 66 (8.5), 56 (9.6), 55 (21.1), 54 (13.8), 53 (9.6).

Reaction of 1 *with aqueous* H_2SO_4. A mixture of 3.54 g (17.87 mmol) of 1 and 4 ml of 0.8 M H_2SO_4 in 18 ml dioxane was stirred at 80° for 1 hr. After cooling to room temp the rn mixture was neutralized by carefully adding saturated $NaHCO_3$ aq. The mixture was then extracted with CH_2Cl_2 (3 × 20 ml). The combined organic extracts were successively washed with water (3 × 30 ml), sat NaCl aq (30 ml) and dried ($MgSO_4$). After removing the solvent on rotary evaporator, the remaining liquid was distilled at 67–69°/3.0 torr to get 2.10 g (93%) of a product which showed two peaks in GC (3 m 5% carbowax column; temp programme from 60–160° at 4°/min) in the ratio of 79.6:20.4. The two components were separated by preparative GC and the first (major) component was identified to be 2 by its spectral characteristics (IR, MNR and MS) and its phenylurathane derivative as described earlier.

The second (minor) component exhibited the following spectral characteristics. IR (cm^{-1}), 3350, 3010, 2920, 2850, 1645, 1465, 1450, 1045, 985, 975, 720. NMR (CCl_4), two complex overlapping multiplets between δ 1.23–2.60 (11H), 3.57–4.07 (m, 1H), 5.40–6.00 (m, 2H). Decoupling of the second peak does not change the character of the olefinic proton peak (third peak). MS, *m/e* (intensity, %), 126 (2.2), 124 (3.7), 111 (7.5), 109 (10.7), 108 (30.0), 107 (3.7), 99 (9.0), 98 (43.7), 97 (33.7), 96 (7.5), 95 (12.0), 94 (7.5), 93 (57.3), 91 (17.5), 84 (35.0), 83 (42.5), 82 (35.0), 81 (17.5), 80 (72.5), 79 (85.0), 78 (11.2), 77 (21.2), 71 (30.0), 70 (28.7), 69 (22.5), 68 (42.5), 67 (100), 66 (15.0), 65 (11.2), 59 (10.0), 58 (40.0), 57 (45.0), 56 (13.7), 55 (47.5), 54 (62.5), 53 (21.2). Therefore, this component is *trans*-3- and/or *trans*-4-cycloocten-1-ol (3 and/or 4). But it could not be separated on 3 m 5% carbowax column.

Oxidation of the above alcohol mixture. The above mixture of alcohols was oxidised by Cr(VI) oxide-pyridine complex as described earlier for the oxidation of 2. The product ketone mixture showed two peaks in GC, the first peak having the same retention time as 7. Part of the mixture was separated by preparative GC. The first component was confirmed as 7 by its spectral characteristics. The second component has the following spectral properties. IR (cm^{-1}), 3030, 2950, 2875, 1705, 1650 (sh), 1465, 1450, 1350, 1230, 1105, 1085, 970, 885, 840, 735, 725. NMR ($CDCl_3$), δ 1.33–1.90, 1.90–2.33, 2.33–2.76 (three overlapping complex multiplets), 3.16 (d) (all four peaks together 10H), 5.46–6.06 (m, 2H). The doublet is likely to be due to the protons on C_2 in 3-cyclooctenone[17] (8) and since it integrates to about 1/3 the area of the olefinic peak, the ketones 8 and 9 must be in the ratio of about 1:2. MS, *m/e* (intensity, %), 124 (34.7, M^+), 109 (25.3), 96 (53.3), 95 (49.3), 83 (10.6), 82 (20.0), 81 (32.0), 80 (68. 0), 79 (36.0), 68 (62.7), 67 (100), 55 (61.3), 54 (82.7), 53 (24.0).

Hydrogenation of the above ketone mixture. A soln of 0.15 g of the mixture of ketones in 10 ml EtOAc was hydrogenated on 5% Pd–C at atmospheric pressure until complete saturation. After filtering off the catalyst, the filtrate was concentrated on rotary evaporator. There was no change in the GC retention time of the first component (i.e., unchanged 7). However, the retention time of the other component had changed and was now identical to that of cyclooctanone. To further confirm the identity of this it was separated from the other ketone (7) by GC. Semicarbazone, m.p. 168°, mixed m.p. 166–167° (lit.[18] m.p. 167–168°).

Reaction of 1 *in methanolic* H_2SO_4. A soln of 0.52 g (2.62 mmol) of 1 in 10 ml of MeOH containing 0.7 ml conc H_2SO_4 was stirred at 80° under N_2 for 20 min. The mixture was then cooled, 10 ml water was added, carefully neutralized with sat $NaHCO_3$ aq, and extracted with CH_2Cl_2 (3 × 10 ml). The combined organic extracts were washed with water (2 × 20 ml), sat NaCl aq (20 ml) and dried ($MgSO_4$). After concentrating the soln on rotary evaporator, the remaining liquid was distilled (bulb-to-bulb; pressure, 5.0 torr; bath temp, 95°) to obtain 0.31 g (94%) of product. The product showed four peaks in GC (3 m 5% carbowax column, temp programme 60–160° at 4°/min) in the ratio 5:40:46:5. The remaining 4% consists of several small peaks including that of unreacted 1. The last peak was identified as 3 + 4 by its retention time and GC-MS. The first peak was identified as 1,3-cyclooctadiene (*cis*, *cis*- or cis, trans-) by comparing its mass spectrum[6] [GC-MS, *m/e* (intensity, %) 108 (35.2, M^+), 93 (46.3), 91 (25.9), 80 (57.4), 79 (100), 77 (50), 75 (66.6), 67 (90.7), 66 (25.9), 54 (35.2), 51 (18.5)] and GC retention time with those of an authentic sample of *cis*, *cis*-1,3-cyclooctadiene. The two major components were separated by preparative GC. The third component (46%) was identified as 2 by its IR, NMR and MS and its phenylurethane derivative. The second component (40%) showed IR bands at 3020, 2980 (sh), 2930, 2860, 2820, 1650, 1470, 1450, 1100, 985, 970, 880, 750, 720 cm^{-1}. NMR ($CDCl_3$), δ 1.16–2.53 (m, 10H), 3.26 (s) and 3.36 (s) (in about 2:1 ratio) overlapping on 3.03–3.50 (m) (three peaks together 4H), 5.50–5.90 (m, 2H). Decoupling of the olefinic proton peak did not change the peak at δ 3.03–3.50. MS, *m/e* (intensity, %), 140 (4.2, M^+), 125 (5.0), 112 (22.5), 111 (32.5), 108 (26.2), 97 (47.5), 93 (45.0), 85 (62.5), 80 (57.5), 79 (62.5), 72 (57.5), 71 (100), 67 (80.0), 59 (65.0), 58 (67.5), 55 (28.8), 54 (31.2).

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