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Single and Double Stereoselective Ring Expansion of 1,2,3,4-Tetrahydro-1,4-naphthalenedimethanol Ditosylates

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The formolysis of *cis*- and *trans*-ditosylates **7a** and **7b** yielded the mixed esters **13** (at 55 °C) or the diols **11** (at 100 °C, after LAH reduction) by single and double ring expansion, respectively. The reactions are stereoselective, occurring with retention of configuration, which points to the intermediacy of phenonium ions.

Einfache und doppelte stereoselektive Ringerweiterung der 1,2,3,4-Tetrahydro-1,4-naphthalindimethanol-ditosylate

Bei der Formolyse unter verschiedenen Bedingungen liefern die *cis*- und *trans*-Ditosylate **7a** und **7b** die Ester **13** (bei 55 °C) oder die Diole **11** (bei 100 °C, nach LAH-Reduktion). Die Produkte bilden sich durch einfache bzw. doppelte Ringerweiterung. Die Reaktionen verlaufen stereoselektiv unter Erhaltung der Konfiguration, was auf das intermediäre Auftreten von Phenonium-Ionen hindeutet.

In previous papers[1] the solvolysis of ditosylates *cis*-**1** and *trans*-**1** was reported, in which a one- or two-carbon expansion of the original carbocyclic ring may take place. The solvolysis in acetic acid buffered with sodium acetate yielded the doubly expanded acetate **3** as the product of kinetic control, whereas in the absence of buffer the mono-expanded, thermodynamically more stable **2** was obtained. The two systems are interconvertible (**2** ⇄ **3**).

Brown and *Sondheimer*[2] have shown that the acetolysis of ditosylate **4** under various conditions leads to the benzocycloheptatriene derivative **5**, together with a 1,4-disubstituted naphthalene, **6**.

As the ring size is the same in both cases, the different behaviour under the same reaction conditions is obviously due to particular structural features. It should also be mentioned that in the solvolysis of ditosylates **1** and **4** the stereochemical information stored in the starting materials is lost in the reaction products, since elimination reactions are favoured in both systems.

These facts prompted us to study the simpler system **7** which, unlike **1** or **4**, has only one benzene ring and no double bond.

It was hoped that in the ditosylates **7a** and **7b** the elimination would be less favoured than in the related compounds **1** and **4**, so that the solvolysis would afford diesters, the stereochemistry of which could provide new information about the intermediates involved in these rearrangements. A new synthetic entry into the benzocyclooctene system was also expected.

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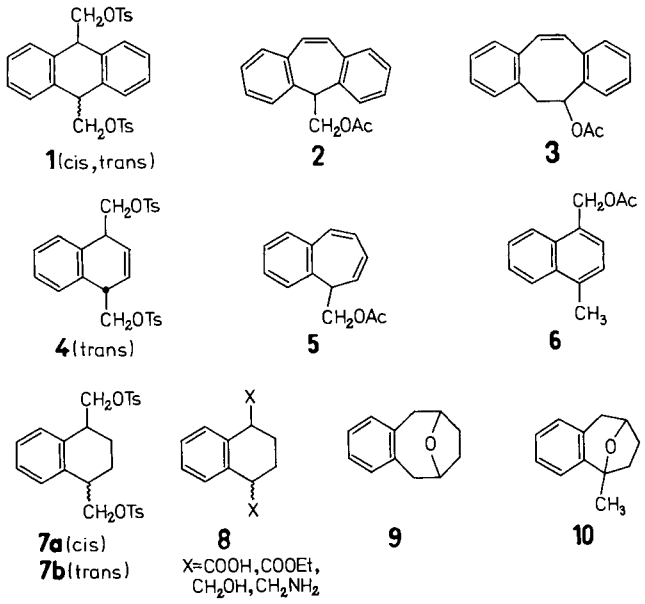


In an earlier paper from this laboratory[3], nitrous acid deamination of the related diamine **8**-CH_2NH_2 (*cis*-isomer) gave a very complex reaction mixture. Lack of physical instrumentation (NMR, preparative g.l.c.) at that time did not allow to purify the reaction products and to determine unambiguously their structures.

In connection with the present work, the nitrous acid deamination of *cis*-**8**-CH_2NH_2 was reinvestigated. It was found that the structure of one of the products, believed[3] to be the ether **9**, was in error. The ether was isolated in pure state by preparative g.l.c. (m. p. 35 – 36 °C). The correct structure of this compound, 6,7,8,9-tetrahydro-5-methyl-5,8-epoxy-5*H*-benzocycloheptene (**10**), follows from its ^{1}H NMR spectrum (CCl_4): $\delta = 1.50 - 2.15$ (m; with superimposed singlet at 1.65; 7H, CH_2CH_2 and CH_3), 2.38 (dd, J = 16.5 and 0.5 Hz; 1H, benzylic H), 3.28 (dd, J = 16.5 and 5 Hz; 1H, benzylic H), 4.61 (m; 1H, CH – O), and 7.05 (s; 4H, aromat. H).

The symmetrical ether **9** was obtained in the acidolysis of diol **11b** reported in the present paper; ^{1}H NMR (CCl_4): $\delta = 1.10 - 2.00$ (m; 4H, CH_2CH_2), 2.62 (dd, J = 15.5 and 4.5 Hz; 2H, benzylic H), 3.29 (dd, J = 15.5 and 2 Hz, 2H, benzylic H), 4.43 (m; 2H, 2 CH), and 7.15 (s; 4H, aromat. H).

Results

1. Solvolysis of Ditosylates 7

The ditosylates **7a** and **7b**, obtained by conventional methods from *cis*- and *trans*-**8**-CH_2OH[3], were solvolyzed in formic acid in the presence of sodium formate. Using the "time ratio" method[4], k_1 and k_2 were determined for the two steps involved in the solvolysis (table 1) at 55 °C.

The kinetic data were used to calculate the time at which the concentration of the monotosylate formed in the first step of the solvolysis reaches a maximum; it was thus found that after 8 – 10 hours (2.5 half-lifes, approximately) the monotosylate represents 65 – 70% of the reaction mixture.

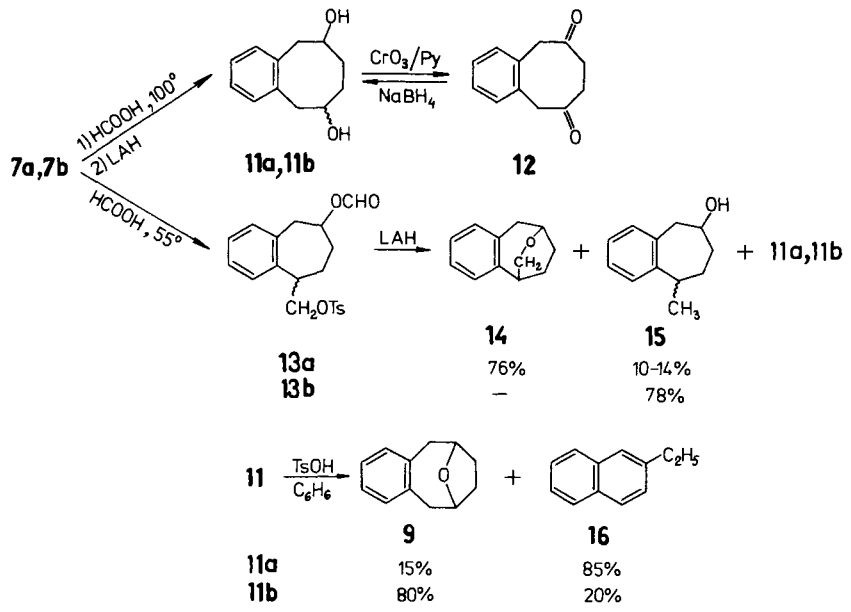
Table 1. Rate constants for the formolysis of tosylates **7** (55 °C)

Compound	$10^5 k_1 (s^{-1})$	$10^5 k_2 (s^{-1})$
7a	6.10	0.85
7b	5.65	1.30

The preparative formolyses of ditosylates **7** were performed a) at reflux (100 °C), for 24 hours, in order to obtain the final solvolysis products; b) at 55 °C for 8 hours, in order to isolate the intermediate monotosylates.

1a. *The formolysis at reflux* was carried out in the presence of sodium formate. The reaction mixture was reduced with lithium aluminium hydride, then subjected to continuous extraction with ether. Each tosylate **7** afforded only one major product (in nearly 90% yield).

cis-Ditosylate **7a** yielded the diol **11a**, identical with the diol, obtained previously[3]. *trans*-Ditosylate **7b** led to another diol **11b**. By oxidation with chromium trioxide/pyridine both diols afforded the same diketone **12**, likewise known from previous studies[3], which shows that they are diastereomers. Sodium borohydride reduction of the diketone led to a mixture of **11a** and **b**. The NMR spectrum of **12** is in good agreement with the proposed structure, supporting also, indirectly, the skeleton of the diols **11a** and **b**. Unfortunately, the NMR spectra of the diols and of the corresponding acetates (obtained by treatment with acetyl chloride/pyridine) did not indicate the stereochemistry of the reaction products.



1b. *The formolysis at 55 °C* was interrupted after 8 hours, according to the kinetic indications, in order to isolate the products formed in the first part of the formolysis by loss of one of the two tosylate groups.

In the case of *cis*-ditosylate **7a** a crystalline compound was isolated (in 62% yield). Spectral and elemental analysis data indicated the structure of a formyloxy-tosylate **13a**. Due to its complexity the NMR spectrum could not be used to determine the configuration of ester **13a**.

Lithium aluminium hydride reduction of pure ester **13a** led exclusively to the liquid cyclic ether **14**. If the whole product resulting from the solvolysis of the ditosylate **7a** is reduced under the same conditions, a mixture of products is obtained in which, according to gas chromatographic analysis, the ether **14** predominates (76%). An alcohol with skeleton **15** and a small amount of diol **11a** were also identified. The compounds **14**, **15**, and **11a** were isolated by elution chromatography.

In the case of *trans*-ditosylate **7b** no formyloxy-tosylate could be isolated in a pure state, although the latter was identified in the mixture by spectral analysis. Lithium aluminium hydride reduction of the formolysis mixture afforded alcohol **15** as the main product (78%), together with small amounts of diol **11b** and a secondary benzylic alcohol, probably an isomer of **15**; ether **14** was not identified.

Alcohol **15**, which appears as a side product in the lithium aluminium hydride reduction of the formolysis product of the *cis*-isomer **7a**, arises very likely from an admixture by the *trans*-isomer as a result of an imperfect separation of the initial acids *cis*- and *trans*-**8**-CO_2H used for preparing *cis*- and *trans*-**8**-CH_2OH[3] (and therefore of the ditosylates **7**). This assumption is supported by the following observations: a) lithium aluminium hydride reduction of pure **13a** yielded only ether **14**; b) alcohol **15** obtained as a side product in the reaction of the *cis*-isomer was found to be identical with the major product from the *trans*-isomer (identical v.p.c. retention time and NMR).

2. Reactions of Diols 11a and 11b in Acid Medium

Treatment of diols **11** with *p*-toluenesulfonic acid in benzene, at reflux, yielded a cyclic ether **9** and 2-ethylnaphthalene (**16**) in different ratios.

The two compounds were separated as pure products by preparative gas-chromatography. The structure of hydrocarbon **16**, suggested by IR and UV spectra characteristic of 2-alkylnaphthalenes[5], was confirmed by comparison with an authentic sample. The structure of the second compound, ether **9**, which is the major product of the reaction of alcohol *trans*-**11**, was ascribed by means of IR and NMR spectra (see Exp. Part).

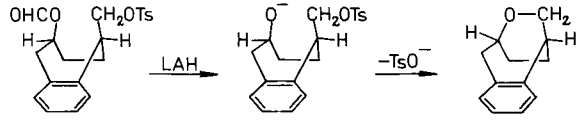
3. Configuration of Formolysis Products

As mentioned before the configuration of the mixed esters **13a** and **b** and of diols **11a** and **b** could not be elucidated by spectral means due to the complexity of their NMR spectra. However, useful indications were provided by the chemical behaviour of the two pairs of isomers **11** and **13**.

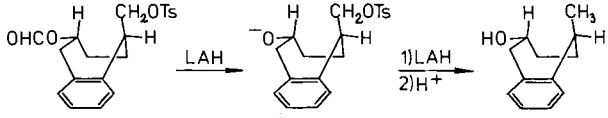
3a. On lithium aluminium hydride treatment of monotosylates **13**, the formate group is more easily reduced than the tosyloxy group, which leads to an intermediate alkoxide

17. The examination of models shows that *cis*-**13a** has conformations in which the two substituents are especially well placed for the closure of a six-membered ring leading to ether **14** (by an intramolecular Williamson reaction).

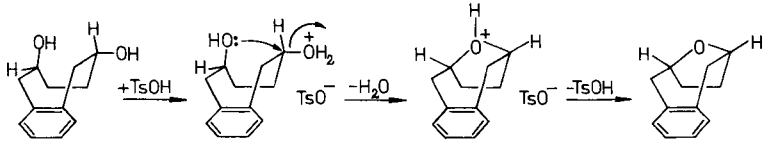
In the *trans*-**13b** isomer, the functional groups are too distant to allow the formation of the C–O bond. With an excess of lithium aluminium hydride the tosyloxymethyl group is reduced, as expected, to a methyl group, alcohol **15** being formed.



13a **17a** **14**



13b **17b** **15**



11b **18** **19** **9**

These reactions suggest a *cis*-configuration for the monotosylate **13a**, and *trans* for the isomer **13b**. Therefore, in the first ring enlargement, **7** → **13**, the configuration is retained: *cis*-ditosylate **7a** affords *cis*-monotosylate **13a**, as the major product, while *trans*-ditosylate **7b** is converted to *trans*-monotosylate **13b**.

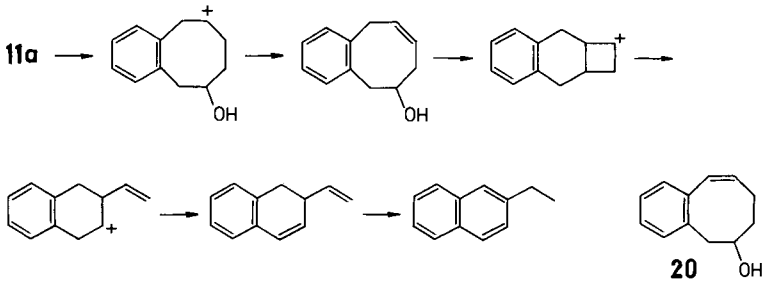
3b. The stereochemistry of the diols **11** is disclosed by their behaviour in acid medium.

As mentioned above, treatment of diol **11b** with toluenesulfonic acid in benzene leads to the cyclic ether **9**. Protonation of an OH group gives rise to the ion pair **18** which is not very open to solvent attack, but rather reacts intramolecularly (such transannular reactions in eight-membered rings are known to proceed with relative ease[6]). Examination of molecular models shows that for the *trans*-diol **11b** there are conformations in which one of the OH groups can assist the ionization of the other one in an S_N2-type transition state.

Elimination of a molecule of water (a concerted reaction) and of a proton (as TsOH) leads to ether **9**, the main product arising from alcohol **11b** in acid medium. Indirectly this supports the *trans*-configuration for **11b** and *cis* for **11a**, resp., suggesting that the second ring enlargement **13** → **11** likewise proceeds with retention of configuration.

Treatment of diol **11a** with toluenesulfonic acid in benzene leads to 2-ethylnaphthalene (see above); the OH groups cannot adopt a conformation favourable to interaction and react independently. However, the mechanism of this reaction is still unclear.

The following hypothesis may be proposed:



It should be mentioned that the isomeric alcohol **20**[7] is stable in acid medium.

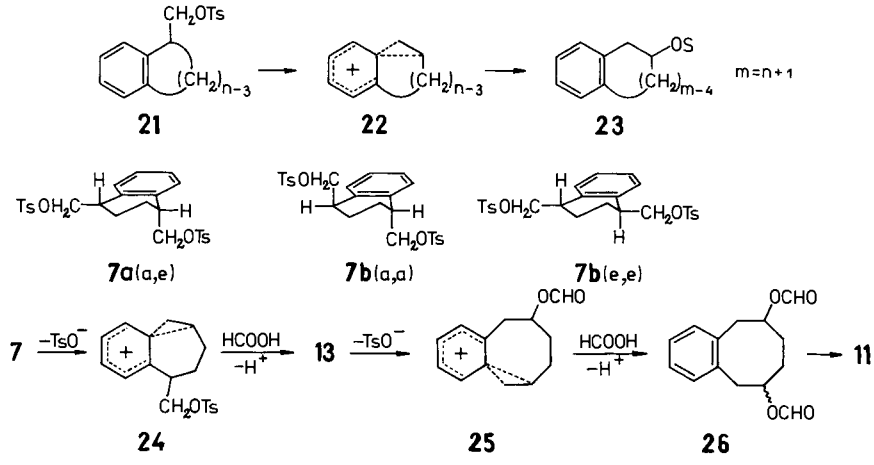
Discussion

As expected, the elimination reactions which accompany the solvolysis of ditosylates **7** are less favoured than in case of systems **1** and **4**. In the formolysis performed under mild conditions (55 °C, 8 hours), the seven-membered ring mixed esters **13**, formed by simple ring enlargement, were isolated or otherwise established. Under more energetic conditions (reflux, 24 hours) the eight-membered ring diols **11** (formates, respectively), formed by double ring enlargement, were obtained.

The identification of a mixed ester is a decisive proof in support of a stepwise mechanism. This mechanism has been demonstrated for the solvolysis of arylsulfonates of secondary 1,2-diols, studied by several authors[8].

The two steps of the solvolysis of ditosylates **7a** and **b** proceed with quantitative ring expansion and stereoselective formation of either a *cis*- or a *trans*-formyloxy tosylate **13** in the first step, and a *cis*- or a *trans*-diol **11** (after lithium aluminium hydride reduction) in the second step, depending on the configuration of the initial ditosylate.

This high stereoselectivity provides evidence for β-phenyl participation in the transition state and the intervention of a phenonium ion in the product-determining step.



The intermediacy of phenonium ions of type **22** in the solvolysis of monotosylates **21**, accompanied by ring enlargement to **23**, has been ingeniously demonstrated by *Huisgen* and collab.[9] in a series of investigations based on reaction rates and on retention of configuration of optically active compounds.

Since a single CH_2OTs group is involved in the first step of the solvolysis of ditosylates **7**, it can be assumed that the reaction occurs in a manner similar to that observed for **21** (n = 6). However, the presence of a second substituent in the molecule allows the direct analysis of the steric course of the reaction.

The steric requirements for phenyl participation, namely axial conformation of the CH_2OTs group involved, seem to be fulfilled by both ditosylates **7**. The tetralin ring probably adopts a half-chair conformation, similar to that of cyclohexene. In this case, the *cis*-ditosylate **7** has a single conformation with one substituent axial and the other equatorial (a, e). The *trans*-isomer **7b** may adopt two different conformations (a, a and e, e). Therefore in each stereoisomer there is at least one axial CH_2OTs group correctly placed for anchimeric assistance.

The ionization of a CH_2OTs group in **7**, assisted by the aromatic ring in β-position, leads to the phenonium ion **24** from which by solvent attack the mixed ester **13** results.

Since both closure and opening of the three-membered ring is accompanied by Walden inversion, the net result is retention of configuration, in accordance with experimental data. In the second step of the solvolysis, the monotosylate **13** undergoes a similar change, leading via phenonium ion **25** to diformates **26**, respectively diols **11**, again with retention of configuration.

The experimental data, which indicate high stereoselectivity of the formolysis of ditosylate *cis*- and *trans*-**7**, with retention of configuration in both steps of the solvolysis, are evidence for the intermediacy of phenonium ions in these reactions.

We are grateful to professor *R. Huisgen* for a careful reading of the manuscript and for helpful suggestions.

Experimental Part

Melting points are uncorrected. – IR spectra: UR-20 spectrophotometer Carl Zeiss-Jena. – ^1H NMR spectra: Varian A-60A (TMS as internal standard). – G.l.c. analyses and preparative separations: Carlo Erba Fractovap D chromatograph (flame ionization detector), 1.5 m × 2 mm steel column of 20% ethyleneglycol adipate on 60 – 80 mesh Chromosorb P. Column temperature 190 °C followed by programmed rise of temperature until 225 °C with a range of 1.5°C/min. Carrier gas hydrogen 40 ml/min.

cis- and trans-1,2,3,4-Tetrahydro-1,4-naphthalenedimethanol ditosylates (**7a** and **b**) were obtained in 90% yield from the known[3] *cis*- and *trans*-1,2,3,4-tetrahydro-1,4-naphthalenedimethanols (**8**, X = CH_2OH) with *p*-toluenesulfonyl chloride in anhydrous pyridine.

cis-Ditosylate **7a**: m.p. 102 – 103 °C (methanol). – IR (CCl_4): 1192, 1178 cm^{-1} (OSO_2). – ^1H NMR ($DCCl_3$): δ = 1.60 – 1.80 (m; 4H, CH_2CH_2), 2.42 (s; 6H, 2 CH_3), 3.04 (m; 2H, 2 CH), 3.95 – 4.25 (m; 4H, 2 CH_2O), 7.00 (s; 4H, aromat. H), 7.15 – 7.80 (AA'BB' system; 8H, aromat. Ts-H).

trans-Ditosylate **7b**: m.p. 105°C (methanol or dioxane). – IR (CCl_4): 1184, 1176 cm^{-1} (OSO_2). – ^1H NMR ($DCCl_3$): 1.65 – 1.80 (m; 4H, CH_2CH_2), 2.42 (s; 6H, 2 CH_3), 3.01 (m; 2H, 2 CH), 3.80 – 4.15 (m; 4H, 2 CH_2O), 7.05 (s; 4H, aromat. H), 7.15 – 7.80 (AA'BB' system; 8H, aromat. Ts-H).

$C_{26}H_{28}O_6S_2$ (500.6) Calcd. C 62.36 H 5.64 S 12.81 **7a**: Found C 62.33 H 5.91 S 12.52
7b: Found C 62.56 H 5.93 S 12.47

Formolysis of the cis-ditosylate **7a** *at reflux temperature:* A solution of **7a** (5.0 g, 9.99 mmol) and anhydrous sodium formate (3.0 g, 44.1 mmol) in 200 ml 98% formic acid was refluxed for 24 h. After removing the formic acid in vacuo, the residue was diluted with water, neutralized with sodium carbonate, and extracted with diethyl ether. The solution was dried over magnesium sulfate and the solvent was removed. The viscous residue (2.4 g) was reduced with an excess of lithium aluminium hydride in etheral solution. After the usual working up 1.8 g (94%) of *cis-5,6,7,8,9,10-hexahydrobenzocyclooctene-6,9-diol* (**11a**), m.p. 169°C (ethyl acetate) (lit.[3] 167 – 169°C), was obtained. – IR (KBr): 3270 (OH), 1050, 1018 cm^{-1} (C – O).

Diacetate: m.p. 92 – 94°C (diethyl ether). – IR (CCl_4): 1736 (C = O), 1236 cm^{-1} (C – O).

$C_{16}H_{20}O_4$ (276.3) Calcd. C 69.54 H 7.30 Found C 69.66 H 7.58

Formolysis of the trans-ditosylate **7b** *at reflux temperature:* The reaction was carried out as described for the *cis*-isomer. From the crude reaction mixture *trans-5,6,7,8,9,10-hexahydrobenzocyclooctene-6,9-diol diformate* (**26**), m.p. 100°C (diethyl ether), was isolated in 95% yield.

$C_{14}H_{16}O_4$ (248.3) Calcd. C 67.72 H 6.50 Found C 67.81 H 6.62

26 (2.3 g, 9.26 mmol) was reduced with an excess of LAH in etheral solution. The usual working up afforded 1.6 g (90%) of *trans-5,6,7,8,9,10-hexahydrobenzocyclooctene-6,9-diol* (**11b**), m.p. 148 – 150°C (benzene). – IR (KBr): 3380, 3310 (OH), 1020 cm^{-1} (C – O).

$C_{12}H_{16}O_2$ (192.3) Calcd. C 74.96 H 8.39 Found C 75.20 H 8.54

Diacetate: m.p. 83 – 84°C (diethyl ether). – IR (CCl_4): 1740 (C = O), 1237 cm^{-1} (C – O).

$C_{16}H_{20}O_4$ (276.3) Calcd. C 69.54 H 7.30 Found C 69.31 H 7.44

Formolysis of the cis-ditosylate **7a** *at 55°C:* A solution of **7a** (10 g, 19.98 mmol) in 800 ml 98% formic acid was heated at 55°C for 8 h. The reaction mixture was treated as above and the obtained viscous residue (6.8 g) was triturated with methanol yielding 4.6 g (62%) of crystalline *cis-8-formyloxy-6,7,8,9-tetrahydro-5H-benzocycloheptene-5-methanol tosylate* (**13a**), m.p. 95°C (methanol). – IR (CCl_4): 1721 (C = O), 1372 (CO_2), 1190, 1180 (OSO_2), 976 cm^{-1} (C – O). – ^1H NMR ($DCCl_3$): δ = 1.58 – 2.08 (m; 4H, CH_2CH_2), 2.43 (s; 3H, CH_3), 2.83 – 3.50 (m; 3H, benzylic CH_2 and CH), 4.45 (d, *J* = 7.5 Hz; 2H, CH_2O), 5.05 (m; 1H, CH – O), 6.85 – 7.85 (m at 6.85 – 7.20 and AA'BB' type subspectrum; 8H, aromat. H and Ts-H), 7.92 (s; 1H, CH = O).

$C_{20}H_{22}O_5S$ (374.4) Calcd. C 64.15 H 5.92 S 8.56 Found C 64.17 H 6.33 S 8.36

A solution of crude **13a** (6.8 g, 18.16 mmol) from another formolysis, in anhydrous diethyl ether (75 ml), was reduced with LAH (1.5 g, 39.47 mmol) in ether (100 ml) 8 h at reflux. After working up 3.2 g of an oily material was obtained, whose g.l.c. analysis indicated a mixture of 76% cyclic ether **14**, 14% alcohol **15**, 5% *cis*-diol **11a**, and 5 % unknown products. The oil (2.5 g) was separated by column chromatography on neutral alumina (100 g, grade II). By elution with petroleum ether/benzene (1 : 1.5) 1.8 g of *6,7,8,9-tetrahydro-8,5-(epoxymethano)-5H-benzocycloheptene* (**14**), colorless oil, was obtained. – IR (CS_2): 1118, 1063 cm^{-1} (C – O). – ^1H NMR (CCl_4): δ = 1.25 – 2.42 (m; 4H, CH_2CH_2), 2.65 – 3.15 (dd, *J* = 17 and 4 Hz at 2.95 and m at 2.70; 2H, 9- and 5-H), 3.47 (dd, *J* = 17 and 3 Hz; 1H, 9-H), 4.00 – 4.35 (d, *J* = 3.5 Hz at 4.05 and m at 4.17; 3H, CH_2OCH), 6.80 – 7.15 (m; 4H, aromat. H).

$C_{12}H_{14}O$ (174.2) Calcd. C 82.71 H 8.10 Found C 82.66 H 8.03

Further elution with benzene/diethyl ether (1:1) afforded 0.30 g of *6,7,8,9-tetrahydro-5-methyl-5H-benzocyclohepten-8-ol* (**15**), m.p. 60°C. – IR (CCl_4): 3620 (OH), 1032, 1021 cm^{-1} (C–O). – ^1H NMR (CCl_4): $\delta = 1.34$ (d, $J = 7$ Hz; 3H, CH_3), 1.50–2.10 (m; 4H, CH_2CH_2), 2.25 (s; 1H, OH), 2.70–3.30 (m; 3H, CH_2CHOH and $CHCH_3$), 3.57 (m; 1H, *CH*OH) and 7.05 (s; 4H, aromat. H).

$C_{12}H_{16}O$ (176.1) Calcd. C 81.77 H 9.15 Found C 82.06 H 8.95

By elution with methanol/diethyl ether (2:1) *cis*-diol **11a** (0.10 g) was obtained.

The reduction of pure **13a** (0.10 g, 0.27 mmol) with LAH (0.40 g, 10.50 mmol) in anhydrous diethyl ether (15 ml) 8 h at reflux afforded, after usual working up, 0.040 g (85%) of pure **14** with IR and ^1H NMR spectra identical with those of the above described product.

Formolysis of the trans-ditosylate **7b** *at 55 °C:* After formolysis as described for **7a**, the *trans*-formyloxy tosylate **13b** could not be separated from the crude product. Sulfur determination corresponds to 55–60% tosyloxy formate in the crude product. After LAH reduction, g.l.c. analysis indicates 78% alcohol **15**, 6% *trans*-diol **11b**, 4% 1,2,3,4-tetrahydro-1,4-dimethylnaphthalene, and 12% unidentified compounds. The main product, alcohol **15**, and the diol **11b** were separated in pure state by elution chromatography on neutral alumina (grade II).

Oxidation of the diols **11a** *and* **b**: A solution of **11a** (0.60 g, 3.12 mmol) in anhydrous pyridine (6 ml) was added with stirring to a suspension of chromium trioxide/pyridine complex (from 6 g CrO_3 and 20 ml pyridine) and left at room temperature for 24 h. Water was added, the reaction product was extracted with ether, and the solution washed with 5% hydrochloric acid and water. After evaporation 0.50 g (85%) of *7,8-dihydrobenzocyclooctene-6,9(5H,10H)-dione* (**12**) resulted (m.p. 75°C and spectra identical with those of the previously described one[3]). From the *trans*-diol **11b** the same diketone was obtained similarly.

Reduction of diketone **12**: A solution of **12** (0.30 g, 1.59 mmol) in methanol (10 ml) was reduced with $NaBH_4$ (0.10 g, 2.64 mmol) in methanol (2 ml), water (1 ml), and 2 N NaOH (0.2 ml). The usual working up afforded 0.25 g (82%) of a crystalline mixture of **11a** and **b** (identification by IR).

Reaction of the cis-diol **11a** *with p-toluenesulfonic acid in benzene:* **11a** (1.5 g, 7.80 mmol) and anhydrous *p*-toluenesulfonic acid (2.7 g, 15.70 mmol) in benzene (100 ml) were refluxed for 24 h. Benzene (100 ml) was added, and after washing with 5% sodium carbonate solution and water, the solution was dried and benzene removed in vacuo. The oily residue (1.2 g) was distillated over sodium at 96–100°C/1 Torr. G.l.c. analysis indicated a mixture of two compounds (85 and 15%, respectively). The pure main product, obtained by preparative g.l.c., showed to be identical with a sample of 2-ethylnaphthalene (**16**) (IR, ^1H NMR spectra, retention time). The minor product was found to be the cyclic ether **9** by comparison with the main product of the reaction of *trans*-diol **11b** with *p*-TsOH (see below).

Reaction of the diol **11b** *with p-toluenesulfonic acid in benzene:* The reaction was carried out as described for the *cis*-isomer. After working up followed by distillation over sodium (100°C/1 Torr), g.l.c. analysis showed a two-component mixture (80 and 20%). The minor product was found to be 2-ethylnaphthalene (**16**) (by g.l.c.). The major product, *5,6,7,8,9,10-hexahydro-6,9-epoxybenzocyclooctene* (**9**), was separated by preparative g.l.c. as an oily product. – IR (CCl_4): 1113, 1067 cm^{-1} (C–O). – ^1H NMR spectrum: See introduction.

$C_{12}H_{14}O$ (176.2) Calcd. C 82.71 H 8.10 Found C 82.74 H 8.13

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