A Simple Synthesis of a New Family of Polycyclic Oxygen Containing Heterocycles

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Benzocyclobutenols **1** were transposed by boron trifluoride etherate in the presence of triethylsilane into a new family of heterocycles **2**.

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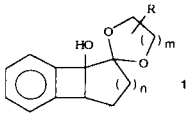
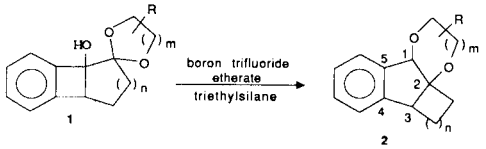
In the preceding papers [1,2] we showed that benzocyclobutenols **1** were easily obtained by simple arynic condensation of the corresponding 1,2-diketone monoketal enolates on bromobenzene in the presence of the Complex Base sodium amide-sodium *t*-butoxide.



Continuing our work on the chemical properties of benzocyclobutenols, we wish to describe the results obtained concerning the one-pot transformation of the alcohols **1** into a new family of polycyclic oxygen containing heterocycles **2**.

We found that **1** reacted with boron trifluoride etherate and triethylsilane to directly give transposed polycyclic heterocycles **2**.

Scheme 1



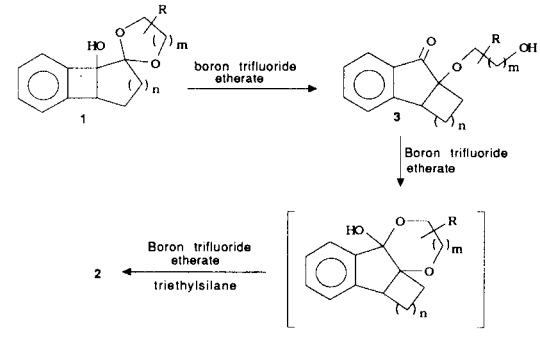
We have gathered the results obtained in Table I.

The transformations are actually multistep reactions. Indeed, we have previously shown [3] that under acidic anhydrous conditions, alcohols **1** are transposed into indanonols **3** (Scheme 2), the stereochemistry of which depends on the structure of the starting material **1**.

When such ketoalcohols **3** react with boron trifluoride etherate and triethylsilane, an ionic hydrogenation [4] occurs leading to **2**.

All the analyses of the isolated products are compatible with formula.

Scheme 2



The stereochemistry of compounds **2** was determined as described below.

Stereochemistry of C_2-C_3 Junction.

Starting from indanonol **3** which stereochemistry was previously determined without ambiguity [3] we performed the reaction described in Scheme 2. The products obtained were identical to the ones isolated during the one step reaction. Since no isomerization of the C_2-C_3 junction can take place during the cyclization the nature of the C_2-C_3 stereochemistry was thus determined. The X-ray diffraction data performed on a number of compounds **2** (*vide infra*) support our conclusion.

Stereochemistry of C_1-C_2 Junction.

Dreiding models show that **2g** (*trans,cis*) and **2i** (*trans,cis*) can only have a *cis* C_1-C_2 junction. Indeed in the *trans* isomer the two C-O bonds would be *trans* antiperiplanar.

Structure of **2b** (*cis,cis*), **2c** (*trans,cis*), **2d** (*cis,cis*), **2e** (*cis,cis*), **2f** (*cis,trans*). **2h** (*trans,cis*) and **2i** (*cis,cis*) were determined by X-ray diffraction data [5].

The stereochemistry of **2f** (*trans,cis*) was determined by comparison with an authentic sample prepared as given in Scheme 3.

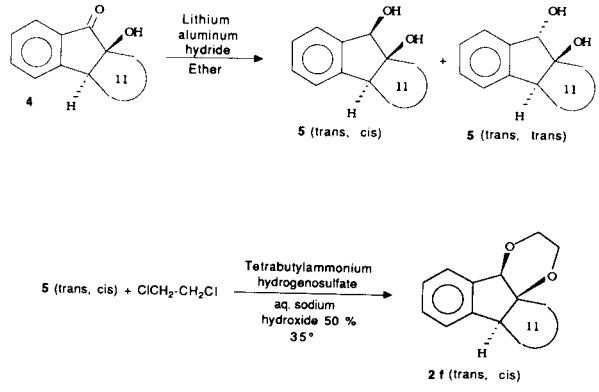
Table I

Compound 1	n	Reaction time (h)	2[a] Isolated yield %
a	2	3	50 (cis,cis)
b	3	1	75 (cis,cis)
c	4	0,5	80 (trans,cis)
d	5	5	77 (cis,cis)
e	7	16	84 (cis,cis)
f	8	4	58 (cis,trans) + 5 (trans,cis)
g	3	24	20[b] (trans,cis)
h	4	2	46[c] (trans,cis)
i	3	114	20[d] (trans,cis) + 35[d] (cis,cis)

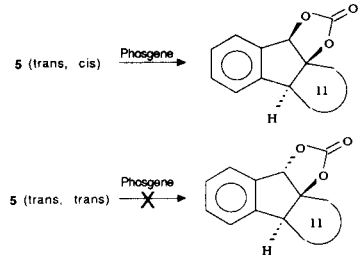
[a] For convenience, the stereochemistry of **2** is designed by naming in parenthesis first the nature of the C_2-C_3 junction and second the nature of the C_1-C_2 junction. [b] The transposed *cis*-glycol **3** intermediate (see text and Scheme 2) was recovered in 58% yield. [c] The transposed *trans*-glycol **3** intermediate was recovered in 40% yield. [d] The transposed *cis*-glycol **3** intermediate was recovered in 21% yield.

The stereochemistry of **5** (*trans,cis*) and **5** (*trans,trans*) was determined by reaction with phosgene. Indeed one of the isomers easily gave the corresponding carbonate while the second did not according to the Scheme 4.

Scheme 3



Scheme 4



Finally comparison of ^1H nmr data of **2a** (*cis,cis*) with those of **2b** (*cis,cis*) led us to conclude to the stereochemistry proposed for **2a**. Indeed the chemical shift of C_1 proton is very sensitive to the stereochemistry of the C_1-C_2 junction (see Table II) and it has been found that both compounds displayed a signal at 4.56 ppm for C_1 proton.

We are presently continuing our work by introducing heteroatoms other than oxygen in the heterocyclic ring.

EXPERIMENTAL

Melting points were determined on a Köfler melting point apparatus and are reported uncorrected. The ^{13}C nmr spectra were recorded on a Bruker AM 400 instrument and ^1H nmr spectra on a Bruker AW 80 spectrometer at 80 MHz and on a Bruker AM 400 spectrometer at 400 MHz with tetramethylsilane as internal standard. Ultraviolet spectra were obtained with methanol solutions on a Beckman model DK 2A instrument. Infrared spectra with sodium chloride film or potassium bromide pellets were recorded on a Perkin Elmer 580 instrument. Elemental analyses were performed by Mrs. François M. (Strasbourg). All experiments were carried out under a nitrogen atmosphere. Thin layer chromatography was performed by using Kieselgel G (Merck) with a hexane-ethyl acetate mixture as eluent. Kieselgel 0.063 (0.2 mm) (Merck) was used for liquid phase chromatography.

Benzocyclobutenols **1a-f**.

These compounds were prepared as previously reported in detail [1].

Benzocyclobutenols **1g-i**.

Table II

Compound No.	Melting point (°) petroleum ether-ethyl acetate	Molecular formula	Analyses Calcd. % Found % C	H	^{1}H NMR (δ ppm) (deuteriochloroform)	^{13}C NMR (δ ppm) (deuteriochloroform)
2a (*cis,cis*)	–	$C_{14}H_{16}O_2$ (216.28)	77.75 77.72	7.46 7.51	1.18-2.19 (6 H, m, 3 x CH_2), 3.60-3.88 (5 H, m, benzylic >CH- and OCH_2CH_2O), 4.56 (1 H, s, benzylic >CH-O-) 7.15-7.39 (4 H, m, ArH)	(arom C) 146.18, 140.35, 129.23, 126.92, 125.15, 124.63, (aliph C) 90.44 (->C-O-), 79.72 (benzylic >CH-O-), 63.64, 62.04 (OCH_2CH_2O), 47.62 (benzylic >CH-), 37.03, 29.82, 23.49 (3 x CH_2)
2b (*cis,cis*)	57	$C_{15}H_{18}O_2$ (230.31)	78.23 78.11	7.88 7.75	1.25-1.97 (8 H, m, 4 x CH_2), 3.40 (1 H, t, J = 6 Hz, benzylic >CH-), 3.57-3.87 (4 H, m, OCH_2CH_2O), 4.56 (1 H, s, benzylic >CH-O-), 7.20-7.42 (4 H, m, ArH)	(arom C) 146.26, 139.83, 128.80, 126.80, 125.77, 124.01, (aliph C) 80.47 (->C-O-), 79.25, (benzylic >CH-O-), 62.64, 60.45 (OCH_2CH_2O), 42.99 (benzylic >CH-), 31.16, 26.50, 22.61, 22.01 (4 x CH_2)
2c (*trans,cis*)	87	$C_{16}H_{20}O_2$ (244.33)	78.65 79.01	8.25 8.50	1.41-1.86 (8 H, m, 4 x CH_2), 2.12-2.23 (1 H, m, 0.5 x CH_2), 2.80-2.90 (1 H, m, 0.5 x CH_2), 2.90-3.00 (1 H, m, benzylic >CH-), 3.28-3.92 (4 H, 2 m, OCH_2CH_2O), 4.78 (1 H, s, benzylic >CH-O-), 7.15-7.35 (4 H, m, ArH)	(arom C) 145.95, 140.11, 128.89, 127.25, 124.30, 124.21, (aliph C) 84.77 (->C-O-), 83.38 (benzylic >CH-O-), 60.91, 60.44 (OCH_2CH_2O), 50.77 (benzylic >CH-), 32.83, 27.64, 27.56, 26.08, 25.89 (5 x CH_2)
2d (*cis,cis*)	71-72	$C_{17}H_{22}O_2$ (258.36)	79.03 79.12	8.58 8.70	1.02-1.95 (11 H, m, 5.5 x CH_2), 2.51-2.65 (1 H, m, 0.5 x CH_2), 2.91-3.04 1 H, m, benzylic >CH-), 3.23-3.91 (4 H, m, OCH_2CH_2O), 4.80 (1 H, s, benzylic >CH-O-), 7.09-7.35 (4 H, m, ArH)	(arom C) 148.52, 137.55, 128.64, 127.67, 125.61, 123.74, (aliph C) 82.45 (benzylic >CH-O-), 82.09 (->C-O-), 60.25, 59.69 (OCH_2CH_2O), 55.14 (benzylic >CH-), 33.21, 32.11, 26.01, 24.72, 23.52, 23.27 (6 x CH_2)
2e (*cis,cis*)	148	$C_{19}H_{26}O_2$ (286.41)	79.68 79.57	9.15 9.20	1.45-2.05 (14 H, m, 7 x CH_2), 2.14-2.26 (1 H, m, 0.5 x CH_2), 2.59-2.67 (1 H, m, 0.5 x CH_2), 3.09-3.15 (1 H, m, benzylic >CH-), 3.39-4.04 (4 H, m, OCH_2CH_2O), 4.89 (1 H, s, benzylic >CH-O-), 7.29-7.45 (4 H, m, ArH)	(arom C) 149.07, 137.18, 128.30, 126.42, 124.36, 124.22, (aliph C) 84.19 (->C-O-), 81.93 (benzylic >CH-O-), 60.34, 59.47 (OCH_2CH_2O), 51.01 (benzylic >CH-), 29.90, 27.54, 27.48, 24.78, 23.73, 23.52, 22.53 (8 x CH_2)
2f (*cis,trans*)	115	$C_{20}H_{28}O_2$ (300.44)	79.96 79.79	9.39 9.37	1.10-1.95 (16 H, m, 8 x CH_2), 1.99-2.13 (1 H, m, 0.5 x CH_2), 2.30-2.49 (1 H, m, 0.5 x CH_2), 2.87-2.98 (1 H, m, benzylic >CH-), 3.57-4.13 (4 H, m, OCH_2CH_2O), 4.73 (1 H, s, benzylic >CH-O-), 7.10-7.33 (4 H, m, ArH)	(arom C) 141.46, 138.82, 126.99, 126.37, 123.28, 120.18, (aliph C) 88.91 (->C-O-), 86.45 (benzylic >CH-O-), 68.21, 61.48 (OCH_2CH_2O), 49.59 (benzylic >CH-), 27.55, 26.35, 26.07, 24.72, 23.94, 22.62, 20.31, 19.42, 16.41, (9 x CH_2)
2f (*trans,cis*)	122	$C_{20}H_{28}O_2$ (300.44)	79.96 79.88	9.39 9.54	1.40-2.48 (18 H, m, 9 x CH_2), 2.90-3.00 (1 H, m, benzylic >CH-), 3.31-3.94 (4 H, m, OCH_2CH_2O), 4.79 (1 H, s, benzylic >CH-O-), 7.19-7.37 (4 H, m, ArH)	(arom C) 146.16, 138.48, 128.04, 126.26, 123.46, 123.16, (aliph C) 84.00 (->C-O-), 80.91 (benzylic >CH-O-), 60.07, 59.69 (OCH_2CH_2O), 48.79 (benzylic >CH-), 29.40, 28.07, 27.54, 27.36, 26.68, 25.71, 23.81, 23.20, 21.77 (9 x CH_2)
2g (*trans,cis*)	120	$C_{16}H_{20}O_2$ (244.33)	78.65 78.73	8.25 8.32	1.47-2.12 (9 H, m, 4.5 x CH_2), 2.40-2.69 (2 H, m, 0.5 x CH_2 and benzylic >CH-), 3.54-3.96 (4 H, OCH_2-CH_2O), 4.93 (1 H, s, benzylic >CH-O-), 7.08-7.40 (4 H, m, ArH)	(arom C) 143.17, 140.36, 127.27, 125.86, 123.65, 121.88, (aliph C) 88.66 (->C-O-), 87.17 (benzylic >CH-O-), 61.52, 59.69 (OCH_2-CH_2O), 50.13 (benzylic >CH-), 33.28, 29.64, 25.53, 21.12, 20.96 (5 x CH_2)

Table II (continued)

Compound No.	Melting point (°) petroleum ether-ethyl acetate	Molecular formula	Analyses Calcd. % Found % C	H	^{1}H NMR (δ ppm) (deuteriochloroform)	^{13}C NMR (δ ppm) (deuteriochloroform)
2h (*trans,cis*)	94	$C_{17}H_{22}O_2$ (258.36)	79.03 79.16	8.58 8.40	1.40-2.04 (10 H, m, 5 x CH_2), 2.14-2.25 and 2.64-2.73 (2 H, m, CH_2), 3.00-3.08 (benzylic >CH-), 3.55-3.95 (4 H, m, OCH_2--CH_2O), 5.02 (1 H, s, benzylic >CH-O-), 7.13-7.34 (4 H, m, ArH)	(arom C) 145.11, 139.31, 127.83, 126.07, 127.14, 122.84, (aliph C) 91.26 (->C-O-), 88.82 (benzylic >CH-O-), 61.35, 60.07 (OCH_2--CH_2O), 49.42 (benzylic >CH-), 35.66, 32.59, 26.59, 26.33, 25.94, 25.18 (6 x CH_2)
2i (*trans,cis*)	65	$C_{18}H_{24}O_2$ (272.39)	79.37 79.52	8.88 8.90	0.71 and 0.93 (6 H, 2 s, 2 x CH_3), 1.33-2.07 (7 H, m, 3.5 x CH_2), 2.57-2.72 (2 H, m, 0.5 x CH_2 and benzylic >CH-), 3.21, 3.28, 3.61 (4 H, 3 d, J = 12 Hz, OCH_2--CH_2O), 4.97 (1 H, s, benzylic >CH-O-), 7.11-7.32 (4 H, m, ArH)	(arom C) 143.71, 140.18, 127.46, 126.00, 124.80, 121.94, (aliph C) 88.21 (->C-O-), 87.80 (benzylic >CH-O-), 72.94, 71.46 (OCH_2--CH_2O), 50.86 benzylic >CH-), 39.24 (-$C(CH_3)_2$-), 30.36, 25.66, 21.28, 20.86 (4 x CH_2), 24.73, 24.43 (2 x CH_3)
2i (*cis,cis*)	88	$C_{18}H_{24}O_2$ (272.39)	79.37 79.26	8.88 8.53	0.72 and 1.20 (6 H, 2 s, 2 x CH_3), 0.86-2.20 (8 H, m, 4 x CH_2), 3.28-3.38 (2 H, m, benzylic >CH- and 0.5 x CH_2, OCH_2--CH_2O), 3.51-3.72 (3 H, m, 1.5 x CH_2, OCH_2--CH_2O), 4.20 (1 H, s, benzylic >CH-O-), 7.11-7.43 (4 H, m, ArH)	(arom C) 144.65, 140.81, 129.18, 126.88, 126.62, 122.74, (aliph C) 91.39 (benzylic >CH-O-), 85.12 (->C-O-), 83.77, 72.62 (OCH_2--CH_2), 46.52 (benzylic >CH-), 38.74 (-$C(CH_3)_2$-), 27.76, 22.65, 21.24, 20.74 (4 x CH_2), 22.81, 21.55 (2 x CH_3)

These alcohols were obtained in a similar manner.

7,8,9,9a-Tetrahydro-*cis*-spiro[5*H*-benzo[3,4]cyclobuta[1,2]cycloheptene-5,2'-[1,3]dioxinan]-4b(6*H*)-ol (**1g**).

This compound was obtained in a yield of 72%, mp 104° (petroleum ether-ethyl acetate); ir (potassium bromide): ν 3520 (OH) cm^{-1}; uv (methanol): λ nm (log ε) 272.5 (3.49), 266 (3.49), 260 (3.32); ^{1}H nmr (carbon tetrachloride): δ 1.06-2.35 (10 H, m, 5 x CH_2), 2.74-3.24 (1 H, m, OH, deuterium oxide-exchangeable), 3.24-4.15 (5 H, m, OCH_2--CH_2O and benzylic H), 6.75-7.26 (4 H, m, ArH); ^{13}C nmr (deuteriochloroform): δ (arom C) 146.31, 128.94, 127.30, 122.31, 122.08, (aliph C) 101.85 (...O->C-O...), 85.73 (COH), 59.76, 59.56 (OCH_2--CH_2O), 55.70 (benzylic C), 25.68, 25.46, 23.54 (5 x CH_2); ms: (m/e) 260 (M^+).

6,7,8,9,10,10a-Hexahydro-*cis*-spiro[benzo[3,4]cyclobuta[1,2]cyclooctene-5(4b*H*),2'-[1,3]dioxinan]-4b-ol (**1h**).

This compound was obtained in a yield of 74%, mp 112° (petroleum ether-ethyl acetate); ir (potassium bromide): ν 3460 (OH) cm^{-1}; uv (methanol): λ nm (log ε) 273 (3.39), 266 (3.38), 260 (3.21); ^{1}H nmr (carbon tetrachloride): 0.98-2.84 (13 H, m, 6 x CH_2 and OH deuterium oxide-exchangeable), 3.07-4.18 (5 H, m, OCH_2--CH_2O and benzylic H), 6.82-7.27 (4 H, m, ArH); ^{13}C nmr (acetone d_6): δ (arom C) 148.99, 148.47, 128.93, 127.42, 123.60, 121.55 (aliph C) 103.74 (...O->C-O...), 85.98 (COH), 59.92, 59.51 (OCH_2--CH_2O), 58.18 (benzylic C), 29.81, 29.24, 26.83, 26.18, 25.25, 20.11 (6 x CH_2).

Anal. Calcd. for $C_{17}H_{22}O_3$ (274.36): C, 74.72; H, 8.08. Found: C, 74.43; H, 7.99.

7,8,9,9a-Tetrahydro-*cis*-spiro[5*H*-benzo[3,4]cyclobuta[1,2]cycloheptene-5,2'-[(5,5 dimethyl)[1,3]dioxinan]]-4b(6*H*)-ol (**1i**).

This compound was obtained in a yield of 55%, mp 119° (petroleum ether-ethyl acetate); ir (potassium bromide): ν 3460 (OH) cm^{-1}; uv (methanol): λ nm (log ε) 272.5 (3.47), 266 (3.47), 260 (3.29); ^{1}H nmr (carbon tetrachloride): δ 0.5-2.30 (14 H, m, 4 x CH_2 with s at 0.67 and 1.12, 2 x CH_3), 2.92-3.80 (6 H, m, OCH_2--CH_2O, benzylic H and OH deuterium oxide-exchangeable), 6.80-7.27 (4 H, m, ArH); ^{13}C nmr (deuteriochloroform): δ (arom C) 146.45, 146.19, 128.81, 127.16, 122.01 (aliph C) 101.70 (...O->C-O...), 85.81 (COH), 70.09, 69.76 (OCH_2--CH_2O), 55.65 (benzylic C), 29.68, 24.71, 23.66 (5 x CH_2), 23.17, 22.23 (2 x CH_3).

Anal. Calcd. for $C_{18}H_{24}O_3$ (288.39): C, 74.97; H, 8.39. Found: C, 75.00; H, 8.27.

Heterocyclic Compounds **2a-i**.

General Procedure.

To a magnetically stirred solution of the alcohol **1** (2 mmoles) and triethylsilane (2.2 mmoles, 0.35 ml) in dry dichloromethane (15 ml), maintained at 0° and under a nitrogen atmosphere, was added dropwise boron trifluoride etherate (2.2 mmoles, 0.28 ml) diluted in dichloromethane (5 ml). At the end of the addition, the mixture was allowed to warm to room temperature. At the completion (monitored by tlc, eluent: 30% ethyl acetate in hexane) a saturated solution of sodium hydrogenocarbonate was added and the stirring maintained for 15 minutes. After extraction with dichloromethane, drying over magnesium sulfate and removal of the solvents under vacuum, the oily residue was chromatographed on silica gel with eluent: 5% ethyl acetate in petroleum ether to afford compound **2** and with eluent 30-40% ethyl acetate in petroleum ether for recovering the unreacted intermediate indanonol. Reaction times and yields are reported in Table I and physical, analytical and spectral data of the heterocyclic compounds **2** are given in Table II.

Recovered Unreacted Intermediate Indanonols **3**.

1,2,3,4,4a,9a-Hexahydro-9a-(3-hydroxypropoxy)-*cis*-cyclohex[a]inden-9-one (**3g** *cis*).

This compound was obtained in a yield of 58%; ir (sodium chloride): ν 1715 (C=O), 3200-3660 (OH) cm^{-1}; uv (methanol): λ nm (log ε) 295 (3.49), 249 (4.17); ^{1}H nmr (carbon tetrachloride): δ 1.11-2.20 (10 H, m, 5 x CH_2), 2.51 (1 H, br s, OH, deuterium oxide-exchangeable), 3.20-3.86 (5 H, m,

benzylic H and OCH_2--CH_2O), 7.16-7.76 (4 H, m, ArH); ^{13}C nmr (deuteriochloroform): δ 206.92 (C=O) (arom C) 153.78, 135.28, 134.28, 127.64, 124.57, 124.41, (aliph C), 84.99 (-*C*OCH_2--CH_2OH), 62.19, 59.88 (O*C*H_2--*C*H_2OH), 40.17 (benzylic C), 32.76, 30.67, 24.46, 20.92, 20.55 (5 x CH_2); ms: (m/e) 260 (M^+).

2,3,4,5,5a,10a-Hexahydro-10a-(3-hydroxypropoxy)-*trans*-cyclohept[*a*]-inden-10(1*H*)-one (**3h** *trans*).

This compound was obtained in a yield of 40%; ir (sodium chloride): ν 1720 (C=O), 3200-3600 (OH) cm^{-1}; uv (methanol): λ nm (log ε) 295 (3.51), 249.5 (4.13); ^1H nmr (carbon tetrachloride): δ 0.75-2.80 (12 H, m, 6 x CH_2), 2.80-3.80 (6 H, m, benzylic H, OCH_2--CH_2O and OH, deuterium oxide-exchangable), 6.71-8.22 (4 H, m, ArH); ^{13}C nmr (deuteriochloroform): δ 202.64 (C=O), (arom C) 155.57, 135.20, 134.52, 127.41, 124.20, (aliph C) 84.31 (-*C*OCH_2--CH_2OH), 61.43, 61.21 (O*C*H_2--*C*H_2OH), 47.59 (benzylic C), 32.51, 28.48, 26.84, 25.93, 25.74, 24.38 (6 x CH_2); ms: (m/e) 274 (M^+).

1,2,3,4,4a,9a-Hexahydro-9a-(2,2 dimethyl-3-hydroxypropoxy)-*cis*-cyclohex[*a*]inden-9-one (**3i** *cis*).

This compound was obtained in a yield of 21%; ir (sodium chloride): ν 1715 (C=O), 3100-3700 (OH) cm^{-1}; uv (methanol); λ nm (log ε) 295 (3.44), 250 (4.04); ^1H nmr (carbon tetrachloride): δ 0.77 and 0.82 (6 H, 2 s, 2 x CH_3), 1.10-2.20 (8 H, m, 4 x CH_2), 2.70-3.65 (6 H, m, benzylic H, OCH_2--CH_2OH and OH, deuterium oxide-exchangeable), 7.20-7.80 (4 H, m, ArH); ^{13}C nmr (deuteriochloroform): δ 207.75 (C=O), (arom C) 153.44, 135.35, 134.22, 127.67, 124.50, 124.25, (aliph C) 85.16 (-*C*OCH_2--CH_2OH), 71.52, 69.76 (OCH_2--CH_2OH), 39.32 (benzylic C), 36.52 (-C(CH_3)$_2$-) 31.25, 23.95, 20.97, 20.73 (4 x CH_2), 21.87 (2 x CH_3); ms: (m/e) 288 (M^+).

Preparation of an Authentic Sample of **2f** (*trans,cis*).

The indanonol **4** was obtained as previously reported [3], by hydrolyzing the corresponding benzocyclobutenol **1f** dissolved in acetone with concentrated hydrochloric acid. The keto alcohol **4** (1.06 g, 3.90 mmoles) dissolved in ether (20 ml) was reduced with lithium aluminum hydride (150 mg, 3.95 mmoles) at ambient temperature. After 1 hour, the reaction was quenched by the cautious addition of ethyl acetate. Ether and 5% hydrochloric acid were added, the layers were separated and the organic layer was dried (magnesium sulfate). Solvent removal gave a residue which was chromatographed (20% ethyl acetate-petroleum ether) to afford **5** (*trans,cis*) (450 mg, 42% yield), mp 85° (petroleum ether-ethyl acetate); ir (sodium chloride): ν 3100-3700 (OH) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.12-3.28 (21 H, m, 9 x CH_2, benzylic H and 2 x OH, deuterium oxide-exchangeable), 4.62 (1 H, s, benzylic -CHOH-), 7.02 -7.44 (4 H, m, ArH) and **5** (*trans,trans*) (460 mg, 43% yield), mp 148° (petroleum ether-ethyl acetate); ir (potassium bromide): ν 3100-3600 (OH) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.18-2.40 (20 H, m, 9 x CH_2 and 2 x OH, deuterium oxide-exchangeable), 3.13-3.42 (1 H, m, benzylic H), 4.51 (1 H, s, benzylic CHOH-), 7.13-7.44 (4 H, m, ArH).

To the diol **5** (*trans,cis*) (274 mg, 1 mmole) and tetrabutylammonium hydrogenosulfate (50 mg, 0.147 mmole) dissolved in 4 ml of dichloroethane, were added 4 ml of 50% aqueous sodium hydroxide. The mixture was magnetically stirred at 35° for 24 hours. After cooling to room temperature, water was added and aqueous phase was extracted twice with ether. Organic layer was dried (magnesium sulfate) and evaporated *in vacuo* to give a mixture which was subjected to chromatography. Elution with 5% ethyl acetate-petroleum ether afforded the compound **2f** (*trans,cis*) (80 mg, 27%), mp 122° (petroleum ether-ethyl acetate), then with 25% ethyl acetate-petroleum ether the unreacted diol **5** (*trans,cis*) (178 mg, 65%).

Preparation of the Cyclic Carbonate of **5** (*trans,cis*).

To the diol **5** (*trans,cis*) (350 mg, 1.28 mmoles) and pyridine (0.5 ml) dissolved in toluene (10 ml) at 0° was slowly added a 20% solution (2.5 ml) of phosgene in toluene. At the completion of the reaction [15 minutes, monitored by tlc (25% ethyl acetate-hexane)] dilute hydrochloric acid was added and the mixture extracted with ether. The organic layer was dried (magnesium sulfate) and evaporated under reduced pressure to give an oil which was rapidly chromatographed on silica gel (15% ethyl acetate-petroleum ether) to afford the carbonate (370 mg, 96%); ir (sodium chloride): ν 1795 (-O-CO-O-) cm^{-1}; ^1H nmr (carbon tetrachloride): δ 1.16-2.64 (18 H, m, 9 x CH_2), 3.30-3.62 (1 H, m, benzylic H), 5.30 (1 H, s, benzylic ->CH-O-), 7.13-7.53 (4 H, m, ArH).

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