Synthetic Photochemistry. XVII.[1] The Singlet-oxygen Oxidation of Vinylcyclopropane in the Presence of Diphenyl Sulfide. The Chemical Reduction of a Dioxetane to a *cis*-1,2-Glycol

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The singlet-oxygen oxidation of a spirocyclic vinylcyclopropane in the presence of diphenyl sulfide, a reducing agent, was shown to form a *cis*-glycol by the O–O cleavage of dioxetane. The determination of the stereochemistry of isomeric glycols obtained by chemical derivation led to a revision of the structure of the azido alcohol formed during the photosensitized oxygenation in a presence of the azide ion to the *trans*-derivative.

Previously, we have reported[2] a *cis*-glycol formation by a photoreductive O–O cleavage of the dioxetane (**A**) in the Rose Bengal (RB)-sensitized photooxidation of **1**, dispiro[cyclopropane-1,3′-tricyclo[5.2.1.$0^{2,6}$]deca-4′,8′-diene-10′,1″-cyclopropane], a spirocyclic vinylcyclopropane, which is a typical dioxetane-forming alicyclic olefin in the singlet-oxygen oxygenation. This new process has been verified by low-temperature experiments monitored by NMR spectroscopy,[13] and its generality has been demonstrated by experiments with indene[2] and thujopsene.[4] From a comparative point of view, it will be worthwhile to examine the chemical reduction of **A**. The results have in fact verified the O–O cleavage to give the *cis*-glycol (**2**) by the thioether-reduction which will be a subject of this paper. In literature, several investigations along the same line of a singlet-oxygen oxidation with a reducing agent are recorded; Kaneko *et al.*[5] used thiourea to reduce the endo-peroxide from cyclopentadiene, and Wassermann and Saito[6] showed the results of the thioether-reduction of a series of photooxygenation products. In this paper we will describe the reaction in a system of diphenyl sulfide (**3**) and Methylene Blue (MB) in chloroform. This selection was made out of consideration of the solubility as well as the moderate reactivity of **3** toward singlet oxygen compared with that of dialkyl sulfides.

When a chloroform solution of **1**, **3**, and MB was irradiated by means of a tungsten lamp under an oxygen atmosphere, a considerable rate retardation was recognized; the reaction was still not completed after 32 h. From the reaction mixture, **2**,[7] **4**, **5**, **6**, and **7** were isolated, along with large amounts of diphenyl sulfoxide and diphenyl sulfone, by silica-gel chromatography. The major product, **4** (41%), and another product, **5** (31%), were identified as the dioxetane-derived dialdehyde and the known vinyloxirane respectively.[8] In addition, a glycol, **2** (19%), was identical with the authentic sample of *cis*-glycol prepared by the RB-sensitized photooxidation of **1**[2] in respect to the NMR spectral analysis and the easy formation of the dioxolane derivative, **8**. **6** (3%) and **7** (3%) were a pair of isomeric ketones, and the NMR and IR spectra of **6** [δ:[9] 0.45 (4H, m), 0.75—1.35 (4H, m), 2.03 (1H, dd, J=19.5, −0.1 Hz*), 2.17 (1H, m), 2.42 (1H, dd, J=19.5, 13.5 Hz*), 2.53 (1H, m), 2.77—3.02 (2H, m), and 6.16 (2H, m). $\nu_{C=O}$: 1730 cm^{-1}] and of **7**[δ: 0.3—0.7 (8H, m), 1.95 (1H, dd, J=19.7, 1.5 Hz), 2.25 (1H, d, J=19.7 Hz),

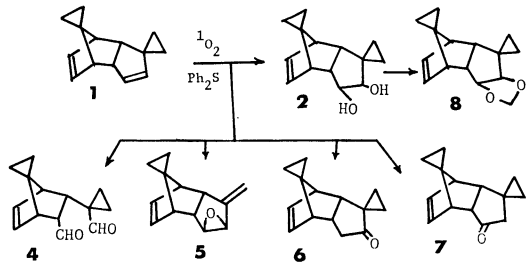

Chart 1.

2.27 (1H, m), 2.58 (1H, m), 2.68 (1H, dd, J=8.5, 4 Hz), 3.25 (1H, ddm, J=8.5, 4.5 Hz), 6.12 (1H, ddd, J=6, 3, 1 Hz), and 6.25 (1H, J=6, 3, 1 Hz). $\nu_{C=O}$: 1740 cm^{-1}] were consistent with the depicted structures (Chart 1), which were themselves supported chemically by the selective derivation of **6** from a monotosylate of **2**.

It is noteworthy that the concomitant formation of **6** and **7** strongly suggests that an epoxide, **9**, is not likely to be their precursor. This can be checked experimentally: The epoxidation of **1** with *m*-chloroperbenzoic acid (MCPA) in dichloromethane yielded no **9**; alternatively, we obtained were isomeric epoxide (**10**), the cyclopropyl ketone (**7**), and two glycol mono-*m*-chlorobenzoates (**11a** and **12**). The **10** was identical with the sample obtained in the sensitized photooxygenation of **1** in the presence of sodium azide[10] or in the RB-sensitized photooxygenation.[1] On the basis of the NMR analysis, **12** was demonstrated to be a *m*-chlorobenzoate of the primary alcohol; it is probably formed by the solvolysis of the cyclopropane. On the other hand, **11a** was convertible to an isomer (**11b**) by prolonged standing at room temperature. The coupling patterns of the NMR spectra of **11a** and **11b** were quite similar and suggested an intact stereochemistry on the oxygen functions. Therefore, **11a** and **11b** must be derivatives of **2**, **11**, and **12** are secondary products of an intermediate epoxide, **9**. **11a** was indeed saponified to **2** in methanol, and **11b** was converted to **2** by an LAH reduction. The spontaneous formation of the *cis*-glycol derivatives during the epoxidation is remarkable, but not surprising; it can be explained in terms of an orbital asistance form the norbornene double bond of **1**.

Meanwhile, the MCPA-oxidation of **1** in a solvent containing methanol yielded predominantly methoxy derivatives, **13**, and its further epoxidized product, **14**, together with **10** and **7**. Again, the ionic cleavage of the cyclopropane ring is characteristic. Therefore,

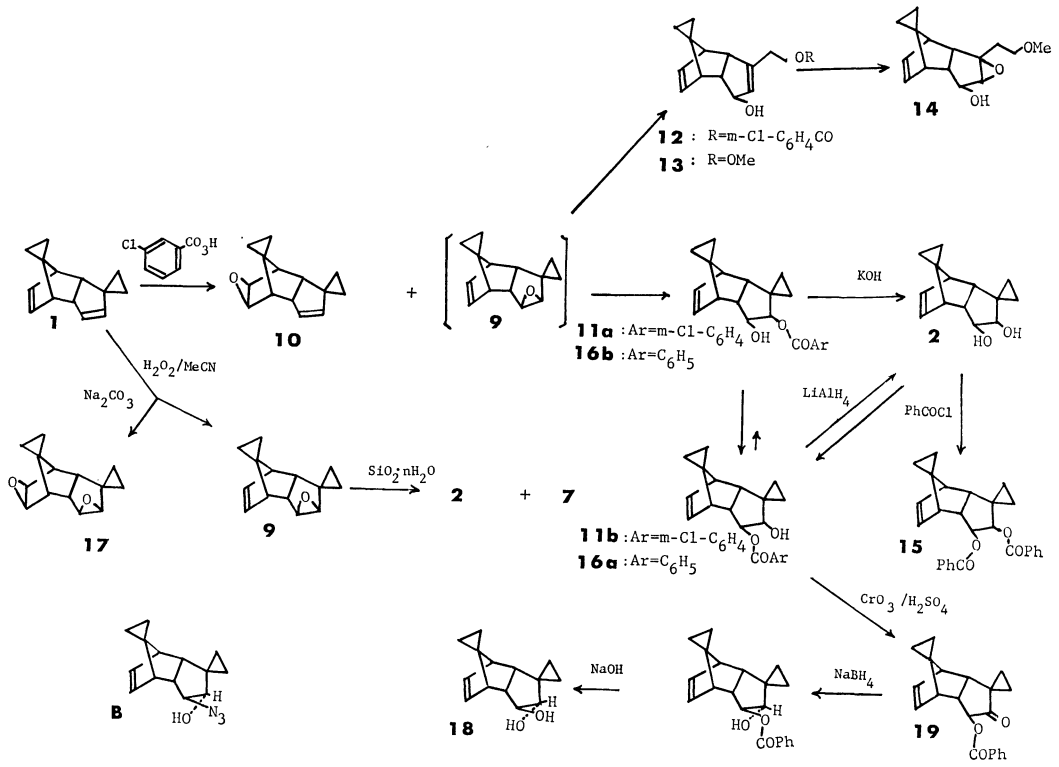

Chart 2.

the absence of the ketone (**6**) in the chemical oxidation is clear evidence of the involvement of independent precursors in chemical and photochemical oxidations.

In this regard, the benzoylation products of **2** were a dibenzoate (**15**) and a monobenzoate (**16**) [δ: 0.40 (7H, m), 0.90 (1H, m), 1.83 (1H, br., OH), 2.04 (1H, m), 2.40 (1H, m), 2.82 (1H, dd, J=9.5, 4 Hz), 3.07 (1H, ddd, J=9.5, 4.5, 3.5 Hz), 3.90 (1H, d, J=4.5 Hz), 5.03 (1H, dd, J=4.5, 3.5 Hz), 6.35 (2H, m), 7.28—7.55 (3H, m), and 7.99 (2H, m) for the **a**-isomer; 4.06 (1H, dd, J=4.5, 4 Hz), and 4.98 (d, J=4 Hz) for the **b**-isomer (**a**:**b**=85:15)]. Again, the monobenzoate showed acyl-migration.

After extensive investigations, we have found a method to obtain this acid-sensitive epoxide, **9**. By the mild oxidation of **1** with the acetonitrile–hydrogen peroxide adduct under weakly basic conditions,[11,12] two epoxides, **9** and **17**, were obtained; they were subsequently purified by fractional recrystallization. **9** (colorless needles, from methanol) was highly reactive, as expected; *i.e.*, a brief treatment with silica gel in chloroform caused a facile conversion into **2** and **7**, but not to **6**. On the other hand, crystalline bisepoxide (**17**), lacking the norbornene C–C bond, was relatively stable.

These findings have established that the precursor of **2** in the photooxygenation must be the dioxetane, **A**. The following points are particularly important: i) There is a difference in the selectivity of the reaction site between the chemical epoxidation and the photooxygenation, ii) there is no incorporation of the solvent nucleophile into the photooxygenation products, iii) there is no cleavage product of the cyclopropane ring in the photooxygenation, and iv) the compositions of the ketones formed in the different reactions differ. Should **2** be derived by the oxidation of **1** by some active species like a complex of diphenyl sulfide and oxygen, the observed reactivity, an overwhelming oxidation at the spiroheptene moiety, must be rather controversial.[10]

At the same time, we wish to make an additional point as to the effect of the reducing agent on the relative yields of **4** and **5** in this sensitized photooxygenation. Upon the addition of **3**, although the yield of **5** was almost unaffected, the yield of **4** decreased considerably, from 85 to 41%. This certainly suggests that the precursor of **5** is not interconvertible with the dioxetane, being parallel to the previous results on the solvent and temperature dependences for the occurrence of **5**.[2,3] Therefore, the precursor of **5**, if any, must be very short-lived to be trapped by a bimolecular process.

Furthermore, since the formation of **6** can not be explained in terms of a simple hydrolysis of **9**, an alternative pathway should be provided. To explain the reaction of the diphenyl-sulfide reduction of dioxetanes, the involvement of dipolar S–O-linked intermediate has been suggested by Wassermann and Saito.[6] In fact, they have identified a *trans*-glycol *via* an epoxide, which is shown to be derived by complicated rearrangements, but have failed to detect a *cis*-glycol. The present study can well be explained also in terms of an S–O-intermediate; otherwise, the direct isolation of **2**, a *cis*-glycol, together with **6** and **7**, isomeric ketones, is difficult to explain. Thus, Chart 3 is provided to interpret all the results.

The coupling patterns in the NMR spectra of the *cis*-glycol derivatives disclosed a discrepancy from those

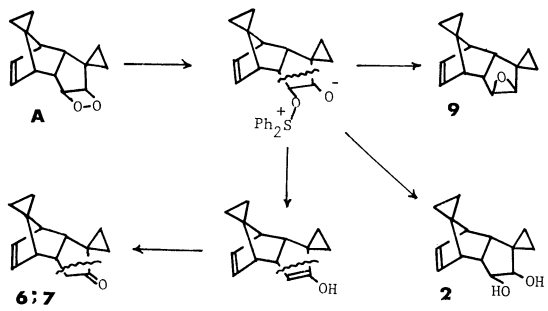

Chart 3.

of the azido alcohol (**B**), which was formed in the sensitized photooxidation of **1** in the presence of sodium azide.[10] The stereochemistry of **17** was identified as *cis* on the basis of the observed $^3J_{CH-OH}$ splittings due to a slow exchange of the hydroxyl proton, and this phenomenon was interpreted in terms of the hydrogen-bonding of the hydroxyl group to the azido group. To solve the problem, we should take the isomeric *trans*-glycol (**18**) for an NMR comparison. Thus, **15** was converted into a keto ester (**19**) by chromium(VI) oxide oxidation; the subsequent reduction of **19** with sodium borohydride yielded another glycol, which must be **18**. Indeed, the spin-spin splitting patterns of the NMR spectrum of **18** were similar to those of **B**. Therefore, the orginal assignment, a *cis*-orientation for the substituents of **B**, must be revised to *trans*.[13] Nevertheless, the conclusion of our previous work, *i.e.*, that the dioxetanes or peroxiranes are not responsible for the formation of azido alcohols, is still valid.

Experimental

*MB-Sensitized Photooxygenation of **1** in the Presence of Diphenyl Sulfide (**3**).* A chloroform solution (15 cm³) of **1** (460 mg), MB (60 mg), and **3** (3.73 g) was irradiated by means of a 500-W tungsten lamp under an oxygen stream at room temperature for 110 h. Subsequent silica gel column chromatography of the mixture gave recovered **1** (170 mg, 37%) and **3** (3.3 g) from the hexane fractions. Subsequently, a vinyloxirane (**5**, 90 mg, 31%), a ketone (**6**, 9 mg, 3%), a colorless oil [Found: M. W., 200.1170. Calcd for $C_{14}H_{16}O$: 200.1201], another ketone (**7**, 8 mg, 3%; colorless prisms; mp 76—77 °C [Found: M. W., 200.1170]), a dialdehyde (**4**, 109 mg, 41%), and a glycol (**2**, 54 mg, 19%; colorless needles, mp 56—57 °C)[7] were eluted from hexane–ether (4:1). From the most polar fractions (hexane–ether=1:1), considerable amounts of diphenyl sulfoxide and diphenyl sulfone were obtained.

*Preparation of a Dioxolane Derivative (**8**).* A benzene solution (1 cm³) of **2** (11.6 mg) and dimethoxymethane (0.5 cm³) containing TsOH (1 mg) was kept at room temperature for 18 h. The mixture was then extracted with benzene, and the extracts were purified on a silica-gel column to give **8** (a colorless oil, 56 mg (45%) [Found: M.W., 230.1334. Calcd for $C_{15}H_{18}O_2$: 230.1307. δ: 0.08—0.75 (7H, m), 0.90 (1H, m), 2.05 (1H, m), 2.36 (1H, m), 2.74 (1H, dd, J=9, 5 Hz), 3.07 (1H, dd, J=9, 5 Hz), 4.08 (2H, s), 4.88 (1H, s), 4.90 (1H, s), 6.22 (1H, ddd, J=6, 3, 1 Hz), and 6.32 (1H, ddd, J=6, 3, 1 Hz). ν: 2950, 1090 cm⁻¹]).

*MCPA-Oxidation of **1** in Dichloromethane: Formation of **7**, **10**, **11**, and **12**.* **1** (900 mg) was dissolved in dichloromethane (15 cm³), after with MCPA (500 mg) was added in portions. After 1 h, an aqueous sodium carbonate was added and then extracted into dichloromethane. Silica gel column chromatography of the extracts gave recovered **1** (440 mg, from hexane–ethyl acetate (98:2)), **10**[2] (130 mg, 26%, from hexane–ethyl acetate (95:5)), **7** (14 mg, 3%, from hexane–ethyl acetate (9:1)), **11** (438 mg, 49%, from hexane–ethyl acetate (8:2 to 7:3) [Found: M.W., 356.1143. Calcd for $C_{21}H_{21}O_3Cl$: 356.1179. δ: 0.28—0.7 (7H, m), 0.88 (1H, m), 2.00 (1H, OH), 2.0 (1H, m), 2.36 (1H, m), 4.04 (1H, t, J=4.5 Hz), 4.95 (1H, d, J=4.5 Hz), 6.33 (2H, m), 7.2—7.6 (2H, m), and 7.7—8.0 (2H, m). ν: 3600, 3480, 1730, 1260 cm⁻¹], a colorless oil), and **12** (174 mg, 20%, from hexane–ethyl acetate (6:4)) [Found: M.W., 356.1184. δ: 0.43 (4H, s), 1.69 (1H, br., OH), 2.25 (1H, m), 2.44 (3H, m), 2.74 (1H, ddd, J=8, 5, 2 Hz), 3.48 (1H, m), 4.12 (1H, br., s), 4.44 (2H, t, J=7 Hz), 5.41 (1H, br., s), 5.99 (2H, m), 7.25—7.55 (2H, m), and 7.8—8.0 (2H, m). ν: 3430, 1735, 1260 cm⁻¹].

*MCPA-Oxidation of **1** in Methanol and Dichloromethane.* **1** (1010 mg) was dissolved in a mixture of methanol (30 cm³) and dichloromethane (8 cm³) and was then oxidized by MCPA (420 mg) at room temperature for 2.5 h. The mixture was treated with $NaHCO_3$ and extracted with dichloromethane. Silica gel chromatography of the extracts afforded, at first, recovered **1** (700 mg), and then **10** (92 mg (28%)), **7** (8 mg (2%)), and a mixture of methoxy derivatives (265 mg (**13**, *ca.* 44%, and **14**, *ca.* 20%)), which were later fractionated by the use of a pre-packed silica gel column (Merck) to give two colorless oils, **13** [Found: M.W., 232.1481. Calcd for $C_{15}H_{20}O_2$: 232.1463. δ: 0.41 (4H, br. s), 1.71 (1H, br., OH), 2.20 (1H, m), 2.24 (2H, t, J=7 Hz), 2.40 (1H, m), 2.69 (1H, ddd, J=7.5, 4.5, 2 Hz), 3.32 (3H, s), 3.4 (1H, m), 3.50 (2H, t, J=7 Hz), 4.08 (1H, m), 5.32 (1H, m), 5.91 (1H, ddd, J=6, 3, 1 Hz), and 6.01 (1H, ddd, J=6, 3, 1 Hz). ν: 3400 cm⁻¹] and **14** [Found: M. W., 248.1381. Calcd for $C_{15}H_{20}O_3$: 248.1413. δ: 0.39 (4H, br. s), 1.75 (1H, dt, J=15, 7 Hz), 2.05 (1H, dt, J=15, 7 Hz), 2.24 (1H, m), 2.32 (1H, br. s, OH), 2.4 (2H, m), 3.12 (1H, m), 3.31 (3H, s), 3.34 (1H, dm, J=2 Hz), 3.43 (2H, tm, J=7 Hz), 3.81 (1H, t, J=2 Hz), and 6.22 (2H, m). ν: 3610, 3500 cm⁻¹].

*Isomerization of **11a** to **11b**.* **11a** (neat liquid, 45 mg) was kept at room temperature for a month. The NMR analysis disclosed the formation of **11b** [δ: 0.42 (4H, m), 0.88 (4H, m), 1.94 (1H, OH), 2.04 (1H, m), 2.38 (1H, m), 2.92 (1H, dd, J=9.5, 4 Hz), 3.08 (1H, dt, J=9.5, 4 Hz), 3.89 (1H, d, J=4.5 Hz), 5.00 (1H, dd, J=4.5, 4 Hz), 6.34 (2H, m), 7.2—7.6 (2H, m), and 7.8—8.0 (2H, m). ν: 3620, 3500, 1728, 1255 cm⁻¹] (**a**:**b**=15:85).

*Saponification of **11a**: Formation of **2**.* **11a** (42 mg) was dissolved in a methanolic KOH solution (0.2 M (1 M= 1 mol dm⁻³), 10 cm³) and then kept at room temperature for 24 h. The mixture was subsequently acidified by dil HCl, and extracted with ether. Silica gel chromatography of the extracts gave a colorless oil, **2** (15 mg, 58%).

*LAH Reduction of **11b** to **2**.* An anhydrous ether solution (3 cm³) of **11b** (77 mg), containing *ca.* 13 mg of **11a**, was treated with LAH (30 mg) for 15 h. The mixture was then chromatographed on a silica gel column to give **2**, 28 mg (51%).

*Benzoylation of **2**: Formation of a Dibenzoate (**15**) and a Monobenzoate (**16**).* A benzene solution (8 cm³) of **2** (290 mg) was treated with benzoyl chloride (262 mg) and pyridine (0.4 cm³) for 48 h. Extractions by dichloromethane and water and subsequent silica gel column chromatography of the extracts gave **15** (colorless prisms, mp 155—156 °C

(from ethanol)) [Found: C, 78.67; H, 6.08%. Calcd for $C_{28}H_{26}O_4$: C, 78.85; H, 6.14%. δ: 0.44 (4H, m), 0.55—0.75 (3H, m), 0.95 (1H, m), 2.06 (1H, m), 2.44 (1H, m), 3.18 (2H, m), 5.20 (2H, m), 6.48 (1H, m), 7.1—7.6 (6H, m), and 7.8—8.0 (2H, m). ν: 1725 cm^{-1}], 42 mg (11%) and **16** (a colorless oil, 236 mg (80%), which consisted of an inseparable mixture (**15a**:**15b**=85:15) [Found: C, 78.07; H, 6.95%. Calcd for $C_{21}H_{22}O_3$: C, 78.23; H, 6.88%]).

*Epoxidation of **1** under Weakly Basic Conditions: Formation of a Bisepoxide (**17**) and a Monoepoxide (**9**).* To an acetonitrile solution (10 cm^3) of **1** (320 mg) and one drop of aqueous 1 M KOH, hydrogen peroxide (30%, 0.7 cm^3) was added under ice-cooling. At once, an evolution of oxygen gas occurred, after which an aqueous 10% sodium carbonate solution was added, drop by drop, until the gas evolution ceased. The mixture was then warmed to 40 °C. After 1 h, the mixture was extracted with dichloromethane and water, and dried on magnesium sulfate. The subsequent evaporation of the solvent *in vacuo* left a crystalline solid (258 mg), which was indicated to be a mixture of **9** and **17** (4:3 according to the NMR spectrometry). Upon fractional recrystallizations from hexane, it gave **17** (colorless prisms, mp 121—122 °C [Found: C, 77.85; H, 7.38%. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46%. δ: −0.05—0.25 (2H, m), 0.4—0.75 (4H, m), 0.8—1.05 (2H, m), 1.70 (1H, d, J= 4.5 Hz), 2.08 (1H, d, J=4.6 Hz), 2.40 (1H, dd, J=8.5, 4.5 Hz), 2.94 (1H, dd, J=8.5, 4.6 Hz), 2.99 (1H, d, J= 2.7 Hz), 3.42 (1H, dd, J=3.7, 1 Hz), 3.52 (1H, d, J=2.7 Hz), and 3.59 (1H, dd, J=3.7, 1 Hz)]). Then, recrystallizations of the residue from methanol gave **9** (colorless prisms, mp 80.5—82 °C [Found: M. W., 200.1182. Calcd for $C_{14}H_{16}O$: 200.1201. δ: 0.3—0.8 (8H, m), 2.01 (1H, m), 2.32 (1H, m), 2.50 (1H, dd, J=7.7, 4.2 Hz), 2.79 (1H, d, J=2.4 Hz), 3.17 (1H, dd, J=7.7, 4.3 Hz), 3.28 (1H, d, J=2.4 Hz), and 6.20 (2H, m)]).

*Treatment of **9** with Silica Gel.* A dichloromethane solution (2 cm^3) of **9** was mixed with a silica gel (Merck, Kieselgel 60). The products, as characterized on thin-layer plates, were **7** and **2**.

*Chromium(VI) Oxide Oxidation of **16**: Formation of a Keto Ester (**19**).* An acetone solution (10 cm^3) of **16** (90 mg) was oxidized by chromium(VI) oxide and sulfuric acid for 5 min. A colorless oil, **19** (86 mg, 96%) [Found: C, 78.72; H, 6.29%. Calcd for $C_{21}H_{20}O_3$: C, 78.72; H, 6.29%. δ: 0.45 (4H, m), 0.90—1.55 (4H, m), 2.18 (1H, m), 2.68 (1H, m), 3.05 (2H, m), 4.83 (1H, d, J=3.7 Hz), 6.33 (2H, m), 7.3—7.6 (3H, m), and 8.00 (2H, m). ν: 1740, 1730, 1265 cm^{-1}] was obtained after silica gel chromatography.

*Sodium Borohydride Reduction of **19**: Formation of a* trans*-Glycol (**18**).* A methanol solution (5 cm^3) of **19** (81 mg) was reduced by $NaBH_4$ (52 mg) for 4 h. An aqueous alkaline solution was then added to the mixture, and it was hydrolyzed for 24 h. By silica gel column chromatography of the mixture, the desired glycol (**18**), as a single product, was isolated as colorless crystals (mp 85—86 °C, 42 mg (76%) [Found: M. W., 218.1297. Calcd for $C_{14}H_{18}O_2$: 218.1307. δ: 0.0—0.7 (8H, m), 1.8 (2H, OH), 1.95 (1H, m), 2.32 (1H, m), 2.70 (1H, ddd, J=10, 7, 4 Hz), 2.88 (1H, dd, J=10, 4 Hz), 3.43 (1H, dd, J=8, 7 Hz), 3.86 (1H, d, J=8 Hz), and 6.27 (2H, m). ν: 3320, 1100 cm^{-1}]).

*Conversion of **2** into **6**.* An anhydrous benzene solution (3 cm^3) of **2** (135 mg) was treated with TsCl (150 mg) at room temperature for 15 h and subsequently at 80 °C for 4 h. The mixture was then diluted with dil HCl and extracted with ether, and the extract was purified on a silica-gel column to give a colorless oil, **6** (30 mg, 52%), and some recovered **2** (70 mg, 52%).

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13) Previously, we have isolated three *vic*-azidoalcohols, two of which carry the functional groups on the norbornane moiety, and there was no problem in deducing the orientation. The third isomer (**17**) now turned out to be *trans*, rather surprisingly revealing a spin-spin splitting of the hydroxyl proton, ^3J=8 Hz, which is probably attributable to a sterical reason.