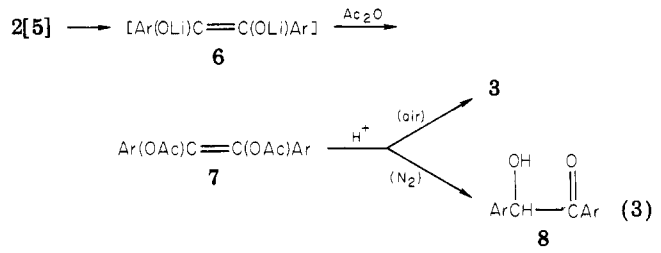

during the hydrolytic procedure. **8a** could only be obtained when special care was taken to avoid any air contamination. Similar properties are exhibited by 2,6-dimethylbenzoin (**8b**) formed in the reaction of **1b**.

Formation of the ketones **2a** and **2b** can be envisaged in the same way proposed for the production of benzophenone in the CO insertion reaction of phenyllithium, i.e., by oxidation of the dilithium dianion produced from the reaction of **5** with another molecule of aryllithium.[11] Again, the oxidation was proved to occur during the hydrolytic workup, with $CO-H_2O$ as the oxidant. When a mixture of **1a** and **1b** in THF at 0 °C is flushed with CO, a mixed benzil derivative [the (1-naphthyl)(2,6-dimethylphenyl)-glyoxal] is produced in addition to the expected products **2** and **3**; this provides further support to the intermediation of the acyl **5**.

Experimental Section

Proton NMR spectra were recorded on a Varian XL-100 spectrometer. Mass spectra were determined on a Varian MAT CH7 spectrometer at an ionization potential of 70 eV. IR spectra were recorded with a Perkin-Elmer 137. Melting points are uncorrected. 1-Bromonaphthalene was distilled at 118–120 °C (1 mmHg), and the distillate was passed under pressure through a basic alumina chromatographic column. All the solvents were purified as previously described and distilled from the dark blue solution of benzophenone ketyl under nitrogen immediately before use. Carbon monoxide was generated and purified as previously described.[7] **1a** was prepared by adding 1.1 mL (8 mmol) of 1-bromonaphthalene to a serum-capped test tube containing an hexane solution of butyllithium (8 mmol). The reacting mixture was heated at 70 °C for 20 min. The resulting white crystals were centrifuged and washed three times with hexane, and the remaining solvent was distilled under vacuum until a white dry powder was obtained. **1b** was prepared from 2,6-dimethyliodobenzene and butyllithium in hexane at 0 °C, the resulting white crystals were purified in the same way as **1a**. **1** prepared by these methods can be stored unaltered for several months if kept in a freezer and protected from light.

Reaction of 1a and 1b with Carbon Monoxide. The general procedure described for phenyllithium was followed.[11] In the present case, the absorption of CO was complete within 10 min at 0 °C. The reaction mixture was worked up as previously described and was analyzed by GLC on a 3% SE-30 Chromosorb W column. The reaction products were also isolated by column chromatography and fully characterized by their melting points and spectroscopic characteristics, as compared with those of authentic samples. When the reaction was carried out in the presence of 1.5 equiv of Dabco, no CO absorption occurs, thus confirming the previous finding that CO–lithium coordination is the first activation step for these reactions.[11]

1,1'-Dinaphthoyl- (3a) and Bis(2,6-dimethylphenyl)glyoxal (3b). Compound **3a** can be prepared from the reaction of CO with **1a** in a solution of HMPT/THF (20:80 v/v) at −78 °C and **3b** from the same reaction with **1b** in THF at room temperature. Under these conditions only **3** is formed, which can be easily isolated in 96.1% and 96.5% yields for **3a** and **3b**, respectively. **3a** was crystallized from hexane–ethyl acetate [mp 192–194 °C (lit.[15] mp 190–191 °C)] and of **3b** with hexane, gives yellow plates, mp 151–153 °C (lit.[16] mp 153–154 °C cor).

1,2-Diacetoxy-1,2-bis(1-naphthyl)ethene (7a) and 1,2-Diacetoxy-1,2-bis(2,6-dimethylphenyl)ethene (7b). Compound **7** can be isolated from the reaction mixture of **1** with CO quenched by acetic anhydride. Hexane (5 mL) was added, the mixture was washed three times with water and dried, and the solvent was distilled. By successive addition of hexane and evaporation, white crystals of **7** were obtained. Compound **7a** was recrystallized from a hexane-saturated solution of ethyl acetate: mp 249–251 °C; IR (Nujol) 1780 (C=O), 1590 (C=C) cm^{-1}; MS (70 eV), *m/e* (relative intensity 396 (M^+, 13), 354 (M^+ − ketene, 12), 312 (M^+ − 2 ketene, 100), 127 (Ar^+, 23); yield 65.2%. **7b** was recrystallized from hexane: mp 190–195 °C (lit.[16] mp 196–167 °C); yield 42.3%.

Di-1-naphthyl Ketone (2a). A solution of **1a** (3.6 mmol) in THF was added at 0 °C to a THF solution of 1-naphthonitrile (500 mg) prepared by standard methods.[17] The mixture was allowed to warm to room temperature and stirred for 30 min. Concentrated sulfuric acid (10 mmol) in water (5 mL) was added, and the mixture was heated under reflux for 30 min and added dropwise to ice–water. Extraction with ethyl ether and solvent distillation give a noncrystallizable oil that was passed through a silica gel H column by pressurized hexane elution. Distillation of the solvent gives white crystals, mp 100–101 °C (lit.[18] mp 103–104 °C cor).

2,2',6,6'-Tetramethylbenzophenone (2b). Ethyl formate (0.081 mL, 1 mmol) in hexane (1 mL) was added dropwise to a suspension of **1b** (2.5 mmol in 10 mL of hexane), and the mixture was stirred for 30 min at room temperature. Water (2 mL) was added and the hexane distilled at reduced pressure. A solution of potassium dichromate (0.33 mmol) in acetic acid (10 mL) plus a few drops of sulfuric acid was added to the resulting mass, and the mixture was stirred 10 min at room temperature, added dropwise to ice–water, and extracted with hexane. The Cr^{VI} oxidation procedure was repeated to complete the reaction. After the workup white crystals of compound **2b** [mp 133–134 °C (lit.[19] mp 134 °C)] are obtained.

Acknowledgment. We thank the National Research Council and the Science and Technology Secretariat (Argentine) for financial support. UMYMFOR (FCEN-CONICET) is acknowledged for the spectroscopic determinations.

Registry No. **1a**, 14474-59-0; **1b**, 63509-96-6; **2a**, 605-78-7; **2b**, 14252-21-2; **3a**, 3457-41-8; **3b**, 1225-22-5; **7a**, 82679-07-0; **7b**, 82679-08-1; CO, 630-08-0.

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Syntheses of the 5,6-Trimethylene-*exo*- and -*endo*-9-norbornanols

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Received March 30, 1982

During our studies of the metabolism of the jet fuel JP-10 [*exo*-5,6-trimethylenenorbornane (**1**)], it was necessary to synthesize *exo*-5,6-trimethylene-*exo*-9-norbornanol (**2**) and exo-5,6-trimethylene-*endo*-9-norbornanol (**3**). Both sodium borohydride ($NaBH_4$) reduction and catalytic hydrogenation (platinum on carbon) of *exo*-5,6-trimethylene-9-norbornanone[1] (**4**) yielded only one product

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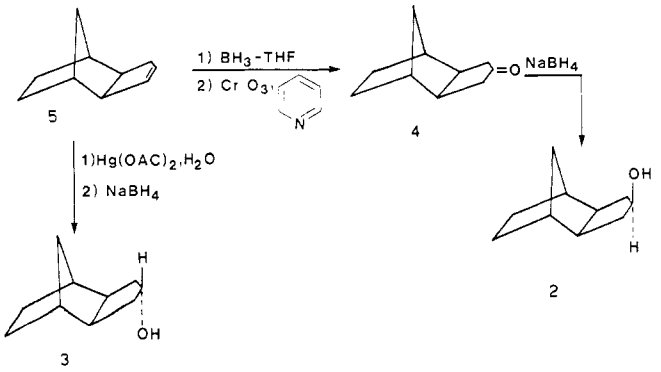
Scheme I. Preparation of *exo*-5,6-Trimethylene-*exo*-9-norbornanol and *exo*-5,6-Trimethylene-*endo*-9-norbornanol



as indicated by GC (Scheme I). The reduction product gave the elemental analysis and infrared and nuclear magnetic resonance spectra, which indicated that the compound could be either **2** or **3**. Previously reported hydride reductions of both *endo*- and *exo*-5,6-trimethylenenorbornanones proceeded with a high degree of product stereospecificity which was attributed to steric accessibility of the ketone by the reducing agent.[2,3] A Dreiding model of **4** indicated that the more sterically accessible position for attack via either $NaBH_4$ or catalytic hydrogenation would be from the underside of the molecule. Thus, we have assigned the structure **2** to the reduction product.

An attempted preparation of **3** via the hydroboration of *exo*-5,6-trimethylene-8-norbornene (**5**) using borane (BH_3) gave a mixture of various stereoisomeric *exo*-5,6-trimethylene-8- and -9-norbornanols, with the 8-norbornanols being formed in greater predominance. Oxymercuration–demercuration of **5**, however, gave only one product (**3**) in 89% yield. This was in marked contrast to the total unreactivity of *endo*-5,6-trimethylene-8-norbornene with mercuric acetate.[4] The elemental analysis and the spectral data of the oxymercuration reaction of **5** supported the structure **3**. Gas chromatographic results of the oxymercuration–demercuration reaction of **5** indicated that the product had a retention time similar to but not identical with the other *exo*-5,6-trimethylene-8- and -9-norbornanols. Lastly, mass spectrometric data indicated similar fragmentation patterns for **2** and the oxymercuration–demercuration product **3** which were different from the fragmentation patterns of the *exo*-5,6-trimethylene-8-norbornanols (Table I).

Although the *endo*-dicyclopentadiene molecule has been reported to undergo oxymercuration–demercuration in a highly stereospecific manner[3,5,6] without carbon skeleton rearrangement, it was surprising to note the absolute regiospecificity and stereospecificity of the reaction of **5** with mercuric acetate. Although the formation of an intermediate acetoxymercurium cation intermediate has been proposed,[7] the mechanism of the oxymercuration–demercuration reaction has not been fully delineated. However, it is accepted that steric considerations are important regarding the final stereochemistry of the product. In the case of the oxymercuration–demercuration of **5**, the attack of the H_2O molecule is rigidly controlled by the steric problems inherent in the mercurium ion so that not only the stereochemical outcome is controlled but also only attack at the 9-position is allowed.

Table I. Relevant Mass Spectral Fragmentations and the Relative Abundancies for *exo*-5,6-Trimethylene Compounds

	rel abundance of exo-5,6-trimethylene			
m/z	*exo*-8-norbornanol	*endo*-8-norbornanol	*exo*-9-norbornanol	*endo*-9-norbornanol
134	16	9	68	56
119	14	13	65	50
108	81	65	35	43
95	100	100	29	46
93	34	40	100	100
91	28	32	67	50

Experimental Section

Melting points were determined with an electrothermal apparatus and are uncorrected. ^1H NMR were recorded with a Varian EM-360A spectrometer. IR were recorded with a Perkin-Elmer 735B spectrophotometer. The 70-eV mass spectra were obtained on a Hewlett-Packard 5985 quadropole mass spectrometer with a source temperature of 200 °C. The samples were introduced into the mass spectrometer through the attached Hewlett-Packard 5480 gas chromatograph (10% SE-30 column). GC was performed on a Hewlett-Packard 5880 A using a 9-ft 10% SE-30 column. Elemental analyses were carried out on a Perkin-Elmer 240-B elemental analyzer.

***exo*-5,6-Trimethylene-*exo*-9-norbornanol (2).** To a solution of *exo*-5,6-trimethylene-9-norbornanol[1] (10.0 g, 75 mmol) in 100 mL of absolute ethanol at 5 °C was added sodium borohydride (1 g, 30 mmol). After being stirred at room temperature for 1 h, the solution was refluxed for 2 h. Water (20 mL) was added, and the solution was stirred at 60 °C for 30 min. Upon cooling, the solution was extracted with hexane. The hexane layer was dried over sodium sulfate. Distillation yielded **2**: 9.3 g (60 mmol, 80%); bp 88–90 °C (0.1 mm); IR (film) 3400 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–2.3 (m, 14 H), 2.8 (s, 1 H,), 3.9 (m, 1 H). Anal. Calcd for $C_{10}H_{16}O$: C, 78.88; H, 10.61. Found: C, 79.14; H, 10.67.

***exo*-5,6-Trimethylene-*endo*-9-norbornanol (3).** *exo*-5,6-Trimethylene-8-norbornene[1] (5 g, 40 mmol) was converted by following the oxymercuration–demurcuration procedure of Brown et all.[6] to **3**: 5.4 g (35 mmol, 89%); mp 30–32 °C; IR (film) 3250 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–2.4 (m, 14 H), 2.8 (s, 1 H), 4.3 (m, 1 H). Anal. Calcd for $C_{10}H_{16}O$: C, 78.88; H, 10.61. Found: C, 78.96; H, 10.46.

Catalytic Hydrogenation of *exo*-5,6-Trimethylene-8-norbornene (5). A solution 2 g (15 mmol) of **5** in 75 mL of ethanol was hydrogenated at 5 atm of H_2 at room temperature for 16 h over 5% Pd/C. After the catalyst was filtered off, **2** was isolated in 93% yield. GC (10% SE-30 column) showed the presence of only **2** and no other alcohols.

Reaction of *exo*-5,6-Trimethylene-8-norbornene (5) with Borane (BH_3). A solution of **5** (5 g, 36 mmol) in 100 mL of tetrahydrofuran (THF) was added to a 1 M solution of BH_3–THF (40 mL). The solution was stirred for 2 h. Water (10 mL) was added, followed by 25 mL of 3 N sodium hydroxide and 25 mL of 30% hydrogen peroxide at 0 °C. After ice–water (100 mL) was added, the solution was extracted with two 100-mL portions of methylene chloride. The organic layer was separated and dried over sodium sulfate. GC analysis (10% SE-30 column) indicated the presence of *exo*-5,6-trimethylene-*endo*-8-norbornanol, *exo*-5,6-trimethylene-*exo*-8-norbornanol, **2**, and **3** in a ratio of 6:1:3:2.

Registry No. **2**, 82752-61-2; **3**, 82752-62-3; **4**, 77845-77-3; **5**, 3129-29-1; *exo*-5,6-trimethylene-*endo*-8-norbornanol, 82752-63-4; *exo*-5,6-trimethylene-*exo*-8-norbornanol, 82752-64-5.

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