described above to give 0.08 g (20%) of *cis*-diol **1** and 0.10 g (24%) of *trans*-diol **4**.

Preparation of Benzyl Ether 19.—A dispersion of 53% sodium hydride in mineral oil (3.24 g of sodium hydride, 0.135 mol) was washed with three 50-ml portions of dry pentane under nitrogen. After the final wash the residual pentane was evaporated *in vacuo* and 60 ml of dimethyl sulfoxide was added dropwise under nitrogen. The resulting solution was stirred at room temperature for 0.5 hr. To this solution was added dropwise over a period of 5 min a solution of 13.70 g (0.090 mol) of **16**[32] {$[\alpha]^{25}D$ −26.26° (*c* 2, $CHCl_3$)} in 40 ml of dimethyl sulfoxide, and the mixture was stirred at room temperature for 10 hr. To this mixture was added 17.0 g (0.135 mol) of benzyl chloride with stirring over a period of 0.5 hr. The reaction mixture was stirred for 1.0 hr, diluted with 350 ml of ice water, and extracted with pentane. The combined extracts were washed with brine, dried, and concentrated to give 26.87 g of a pale yellow oil from which crystallized 0.46 g of *trans*-stilbene. The remaining material was distilled to give 14.55 g (67%) of **19**: bp 115–116° (0.25 mm); $[\alpha]^{25}D$ −21.79° (*c* 3.5, $CHCl_3$); ir (CCl_4) 3090 (C=CH), 3050 (aromatic CH), 1640 (C=C), 1380 and 1360 (*gem*-dimethyl), 1055 (CO), 897 (C=CH_2), and 692 cm^{-1} (aromatic); nmr (CCl_4) δ 7.23 (s, 5, C_6H_5), 4.86 (s, 2, C=CH_2), 4.62 (d, 1, J = 12.0 Hz), 4.35 (d, 1, J = 12.0 Hz) (AB system, OCH_2Ph), 3.97 (m, 1, $CHOCH_2Ph$), 2.60–1.50 (m, 6), 1.30 (s, 3, CH_3), and 0.82 (s, 3, CH_3).

Anal. Calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found: C, 83.98; H, 9.31.

Preparation of Keto Benzyl Ether 20.—A solution of 14.31 g (59 mmol) of olefin **19** in 150 ml of absolute methanol was ozonized for 1.0 hr at −70°. The ozonized solution was stirred vigorously with a mixture of 55 ml of methanol, 15 ml glacial acetic acid, and 29.6 g, (0.198 mol) of sodium iodide under nitrogen at room temperature for 7.0 hr. The resultant iodine-colored solution was diluted with 450 ml of water and treated with 25 ml of saturated sodium bisulfite solution. The solution was made basic by addition of solid sodium bicarbonate and was extracted with ether. The combined ethereal extracts were washed with water and brine, dried, and concentrated to give 14.22 g of a pale yellow oil which was recrystallized from hexane to afford 5.64 g (39%) of colorless, crystalline keto ether **20**: mp 51–52°; $[\alpha]^{25}D$ +1.01° (*c* 3.5, $CHCl_3$); ir (CCl_4) 3040 (aromatic CH), 2950 (CH), 1715 (ketone C=O), 1385 and 1370 (*gem*-dimethyl), 1055 (CO), and 695 cm^{-1} (aromatic); nmr (CCl_4) δ 7.21 (s, 5, C_6H_5), 3.90 (d, 1, J = 12.0 Hz), 3.74 (d, 1, J = 12.0 Hz) (AB system, OCH_2Ph), 2.70–1.60 (m, 6), 1.35 (s, 3, CH_3), and 0.77 (s, 3, CH_3).

(32) J. K. Crandall and L. Chang, *J. Org. Chem.*, **32**, 435 (1967).

Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.87; H, 8.48.

Treatment of 20 with Methyllithium.—To 57 ml (38 mmol) of 0.67 *N* ethereal methyllithium cooled to −70° was added under nitrogen 4.20 g (17.2 mmol) of crystalline keto ether **20** in 30 ml of anhydrous ether. The solution was allowed to warm to room temperature and was stirred for 25 hr. The reaction mixture was poured into 300 ml of water and extracted with ether. The ethereal extracts were dried and concentrated to give 4.57 g of a mixture of alcohols **21** and **22** as a pale yellow oil. Without further purification the benzyl group was reductively cleaved as described below.

Hydrogenolysis of Alcohols 21 and 22. A. By Catalytic Hydrogenation.—In an alcoholic potassium hydroxide washed Paar hydrogenation bottle was placed 0.80 g (3.08 mmol) of the mixture of alcohols **21** and **22** contained above in 50 ml of absolute ethanol and 0.3 g of 5% palladium-on-charcoal catalyst. The mixture was shaken under a 60-psi atmosphere of hydrogen for 24 hr, filtered, and concentrated to give a 0.61 g of a colorless semisolid which was chromatographed through 24 g of neutral silica gel (100–200 mesh) contained in a 30 cm × 15.5 mm glass column. Elution with ether–hexane mixtures afforded in the earlier fractions 0.09 g (16.9%) of *cis*-diol **1**. Later fractions afforded 0.25 g (48.5%) of *trans*-diol **4**.

B. By Reduction with Sodium in Liquid Ammonia.—To 150 ml of liquid ammonia which had been distilled through a potassium hydroxide tower was added 1.00 g (3.9 mmol) of the mixture of alcohols **21** and **22** in 6 ml of absolute ethanol. To this solution was added 0.44 g (19 mg-atoms) of sodium in small pieces. When all of the sodium was added, the solution maintained a dark blue color for *ca.* 3 min and then spontaneously became colorless. The mixture was allowed to stir an additional 1 hr and the ammonia was allowed to evaporate. The residue was diluted with 150 ml of water and extracted with chloroform. The combined extracts were washed with water and brine, dried, and concentrated to give 0.41 g of a pale yellow semisolid which was chromatographed through 17 g of neutral silica gel (100–200 mesh) contained in a 38 cm × 11.5 mm glass column. Elution with petroleum ether–ether mixtures afforded in the early fractions 88 mg (13.5%) of *cis*-diol **1**. Later fractions afforded 150 mg (23%) of *trans*-diol **4**.

Registry No.—**1**, 18680-27-8; **2**, 21803-49-6; **3**, 29333-10-6; **4**, 20536-52-1; **6**, 1845-25-6; **10**, 29333-13-9; **12**, 29333-14-0; **13**, 29333-15-1; **14**, 22419-98-3; **15**, 29333-17-3; **18**, 22419-94-9; **19**, 29333-19-5; **20**, 29333-20-8; **23**, 29333-21-9.

An Efficacious Methyl-Labeled (±)-Camphor Synthesis[1]

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A nine-step (±)-camphor synthesis is reported which allows the individual labeling of each of the three methyl groups, all steps proceeding in high yield. Norcamphor is methylated, carboxylated, and then treated with methylmagnesium bromide, leading to 2-*endo*,3-*exo*-dimethyl-3-*endo*-hydroxy-2-*exo*-norbornanecarboxylic acid. This acid was rearranged in 85% sulfuric acid to 1,7-dimethylnorbornane-7-carbo-2-lactone, which was reduced with lithium aluminum hydride and monotosylated with tosyl chloride to give 8-tosyloxyisoborneol. Chromic acid–pyridine oxidation to 8-tosyloxycamphor, followed by tosyl group displacement with iodide ion and catalytic hydrogenolysis, led to (±)-camphor.

We wish to report a convenient synthesis of (±)-camphor which allows the specific labeling of each of the three methyl groups. The sequence approximates one reported earlier by Finch and Vaughan[3] with, however, some important variances (Chart I) and all steps proceeding in good yield.

The procedure commences from norcamphor (**1**), which was methylated essentially by the method described by Corey and coworkers,[4] yielding the exo methyl ketone **2**. This ketone was converted to the corresponding enolate anion using triphenylmethylsodium,

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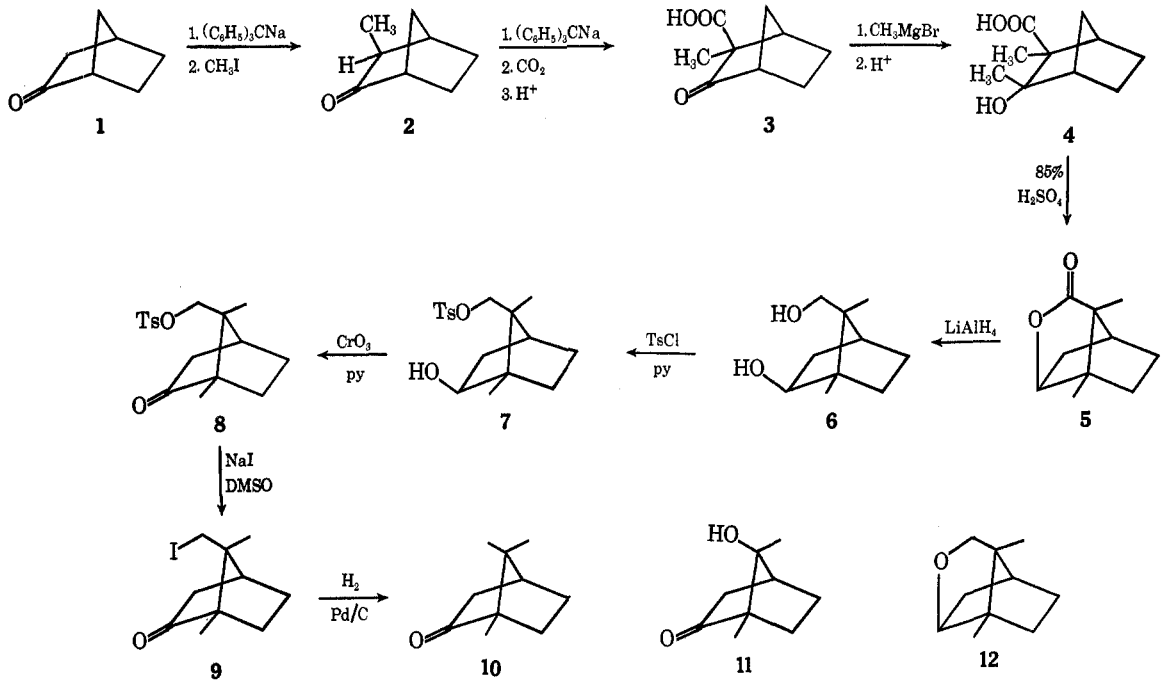
(2) Recipient of a National Science Foundation Traineeship, 1967–1971.

(3) A. M. T. Finch and W. R. Vaughan, *J. Amer. Chem. Soc.*, **87**, 5520 (1965); **91**, 1416 (1969).

(4) E. J. Corey, R. Hartmann, and P. A. Vatakencherry, *ibid.*, **84**, 2611 (1962); J. Wolinsky, D. R. Dimmel, and T. W. Gibson, *J. Org. Chem.*, **32**, 2087 (1967).

Chart I

The Synthesis of (±)-Camphor



which was allowed to react with carbon dioxide to give the 3-*exo*-carboxylic acid **3**.

The reaction of the keto acid **3** with methylmagnesium bromide gave the hydroxy acid **4**, the newly introduced methyl group having previously been assigned the exo configuration on the basis of the known direction of preferred attack on the norbornane enolate system.[3] The acid **4** was rearranged in 85% sulfuric acid to the lactone **5**,[3,5] which, in turn, was reduced with lithium aluminum hydride to 8-hydroxyisoborneol (**6**).[3,6] The previously reported selective oxidation of the secondary hydroxyl group in **6** yielding 8-hydroxycamphor (**11**) in relatively poor yield was also found to be the case in our hands, and we explored instead an alternate route to camphor.

Monotosylation of 8-hydroxyisoborneol was successfully accomplished at low temperature[7] and the hydroxy tosylate **7** was smoothly oxidized to 8-tosyloxycamphor (**8**) by the Sarett method.[7,8] The keto tosylate was readily converted to the iodo derivative **9** using sodium iodide in dimethyl sulfoxide, and catalytic hydrogenolysis of the iodide yielded (±)-camphor. In the present case, (±)-camphor-*8*-^{14}C and (±)-camphor-*9*-^{14}C were prepared by the described route.

Experimental Section

The melting points are uncorrected and were determined with a Thomas-Hoover melting point apparatus. The infrared spectra were recorded on a Perkin-Elmer Model 257 grating infrared spectrophotometer, nmr spectra were carried out on a Perkin-Elmer Hitachi R-20 spectrometer using tetramethylsilane as an internal standard, mass spectra were obtained using a Perkin-Elmer RMU-6E low-resolution mass spectrometer, and vapor phase chromatograms were carried out on a Varian Aerograph Series 200 instrument. Microanalyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, 5251 Elbach über Engelskirchen, West Germany, and by Spang Microanalytical Laboratory, Ann Arbor, Mich. The purity of the initially obtained reaction product was always checked by tlc (Merck silica gel F-254,[9] methanol, ether, *n*-heptane, 1:5:5) and/or by vpc (5% SE-30 on Chromosorb W). In all cases the product was found to contain not more than trace amounts of impurities, which were readily removed by the final recrystallization.

3-*exo*-Methyl-2-norbornanone (2).—The methylation of norcamphor[10] was carried out by the method described by Corey, Hartmann, and Vatakencherry.[4] For the preparation of 3-*exo*-methyl-^{14}C-2-norbornanone, 0.10 mCi of methyl-^{14}C iodide (sp act. 5.54 mCi/mmol) was diluted with 28.40 g of nonradioactive methyl iodide and added to the sodium enolate prepared from 5.50 g (0.050 mol) of norcamphor as previously described.[4]

3-*endo*-Methyl-2-norbornanone-3-*exo*-carboxylic Acid (3).—A three-necked flask fitted with a rubber septum, a pressure-equalizing dropping funnel, and a nitrogen inlet system was filled with nitrogen, and 38 ml of a 0.53 *N* ethereal solution of triphenylmethylsodium[11] was added through the septum with the aid of a syringe. The stirred reagent was cooled in an ice bath and an ethereal solution of 3-*exo*-methyl-2-norbornanone (**2**) was added dropwise until the mixture turned bright yellow, occurring after 2.39 g (0.019 mol) of ketone had been introduced. The reaction mixture was transferred with a syringe to a flask containing 22 g (0.50 mol) of powdered Dry Ice and allowed to stir under a carbon dioxide atmosphere for 1 hr. Water was added and the ether was extracted with cold 10% potassium hydroxide solution. The combined basic extracts were washed with ether to remove any nonacidic material, cooled in an ice bath, and acidified with 6 *N* hydrochloric acid. The keto acid was removed by extraction with chloroform and the combined chloroform extracts were washed with water and dried. Removal of the solvent left 2.70 g (83%) of 3-*endo*-methyl-2-norbornanone-3-*exo*-carboxylic acid as a white solid, mp 94–96°. A small portion of the acid was recrystallized from pentane–ether, followed by sublimation (0.10 mm, 60°): mp 102.5–103.5°; ir (KBr) 1760 (ketone C=O) and 1690 cm^{-1} (acid C=O); nmr ($CDCl_3$) δ 8.75 [broad s (exchanged with D_2O), 1, COOH] and 1.36 ppm (s, 3,

(5) S. Beckmann and H. Geiger, *Ber.*, **92**, 2411 (1959).

(6) S. Beckmann, H. Geiger, and M. Schaber-Kiechle, *ibid.*, **92**, 2419 (1959).

(7) W. S. Johnson, J. C. Collins, Jr., R. Pappo, M. B. Rubin, P. J. Kropp, W. F. Johns, J. E. Pike, and W. Bartmann, *J. Amer. Chem. Soc.*, **85**, 1409 (1963).

(8) G. I. Poos, B. E. Arth, R. E. Beyler, and L. H. Sarett, *ibid.*, **75**, 425 (1953); J. R. Holum, *J. Org. Chem.*, **26**, 4814 (1961).

(9) EM Reagents Division, Brinkmann Instruments, Inc., Westbury, N. Y. 11590.

(10) Aldrich Chemical Co., Inc., Milwaukee, Wis. 53233.

(11) W. B. Renfrow, Jr., and C. R. Hauser, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 607.

CH_3); mass spectrum (70 eV) *m/e* (rel intensity, fragment ion) 168 (2, M^+), 124 (35, $M^+ - CO_2$), 44 (100, CO_2^+).

Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.19; H, 7.34.

When the ketone **2** was added to a suspension of sodium amide in ether and the resulting enolate carbonated with CO_2 gas or Dry Ice, the keto acid was isolated according to the procedure described above in only low yields. The use of sodium naphthalide also proved to be less satisfactory.

To prepare 3-*endo*-methyl-2-norbornanone-3-*exo*-carboxylic acid-^{14}C, gaseous carbon dioxide was generated in a 300-ml three-necked flask equipped with a magnetic stirrer, a dropping funnel, and a delivery tube which was connected through a drying tube to the flask containing the sodium enolate of 3-*exo*-methyl-2-norbornanone. Barium carbonate-^{14}C (1.0 mCi, sp act. 59.6 mCi/mmol), diluted with a tenfold molar excess of nonradioactive barium carbonate, was placed in the carbon dioxide generating flask as an aqueous slurry and concentrated sulfuric acid was used to liberate the carbon dioxide. This method gave a 70% yield of the labeled keto acid.

2-*endo*,3-*exo*-Dimethyl-3-*endo*-hydroxy-2-*exo*-norbornanecarboxylic Acid (4).—A solution of 4.90 g (0.029 mol) of 3-*endo*-methyl-2-norbornanone-3-*exo*-carboxylic acid (**3**) in 90 ml of dry ether was added to a three-necked flask equipped with a magnetic stirrer, reflux condenser, pressure-equalizing dropping funnel, and nitrogen inlet system. The reaction flask was placed under nitrogen and 24 ml of 2.95 *M* methylmagnesium bromide[12] in ether was added dropwise with stirring. Stirring was continued at room temperature for 2 hr and the mixture was acidified with dilute hydrochloric acid. The aqueous phase was separated and extracted with chloroform. The combined organic layers were washed with water and dried, and the solvent was removed by distillation under reduced pressure. There remained 5.35 g (100%) of the hydroxy acid **4** as a white solid, mp 157–161°. For analysis a sample from another run was recrystallized from pentane–ether: mp 160–164°; ir (KBr) 3420 and 3315 (OH), 1700 cm^{-1} (C=O); nmr ($CDCl_3$) δ 6.55 [broad s (exchanged with D_2O), 2, COOH and OH], 1.39 (s, 3, CH_3), and 1.24 ppm (s, 3, CH_3); mass spectrum (70 eV) *m/e* (rel intensity, fragment ion) 166 (5, $M^+ - H_2O$), 138 (100, 166 − C_2H_4), 123 (28, 138 − CH_3), 116 (49).

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.09; H, 8.68.

1,7-Dimethylnorbornane-7-carbo-2-lactone (5).—This substance was prepared by an adaptation of the method of Finch and Vaughan.[3] A cold aqueous sulfuric acid solution, prepared from 23 ml of concentrated sulfuric acid and 7.5 ml of water, was added dropwise to a flask containing 5.35 g (0.029 mol) of 2-*endo*,-3-*exo*-dimethyl-3-*endo*-hydroxy-2-*exo*-norbornanecarboxylic acid (**4**), cooled in an ice bath. The solution was stirred at room temperature for 17 hr, poured over 30 g of ice, and extracted with ether. The combined ether extracts were washed with 5% aqueous potassium hydroxide and brine and dried, and the solvent was removed *in vacuo*, yielding 4.25 g (88%) of the lactone **5** as a white solid. A small portion of the product was recrystallized from heptane–ether: mp 192–194° (lit.[5] mp 192–194°); ir (KBr) 1770 cm^{-1} (C=O); nmr ($CDCl_3$) δ 4.31 (d, 1, H at C-2), 1.10 (s, 3, CH_3), and 1.07 ppm (s, CH_3); mass spectrum (70 eV) *m/e* (rel intensity, fragment ion) 138 (73, $M^+ - C_2H_4$), 123 (36, 138 − CH_3), 105 (73), 79 (82), 44 (100, CO_2^+).

8-Hydroxyisoborneol (6).—A solution of 4.21 g (0.025 mol) of 1,7-dimethylnorborane-7-carbo-2-lactone (**5**) in 20 ml of dry ether was added slowly *via* a pressure-equalizing dropping funnel to a magnetically stirred slurry of 0.96 g (0.025 mol) of lithium aluminum hydride in 65 ml of dry ether under a nitrogen atmosphere in a three-necked flask also equipped with a reflux condenser. The reaction mixture was stirred at room tmperature for 4.5 hr and at reflux for 1 hr. The reaction mixture was worked up as previously described,[3] yielding 3.98 g (92%) of 8-hydroxyisoborneol (**6**) as a white solid. The diol was recrystallized from ethyl acetate and then sublimed (0.15 mm, 100°): mp 273–275° (lit.[3] 275–276°); ir (KBr) 3320 cm^{-1} (broad, OH); nmr ($CDCl_3$) δ 2.79 [s (exchanged with D_2O), 2, OH], 0.97 (s, 3, CH_3), and 0.92 ppm (s, 3, CH_3); mass spectrum (70 eV) *m/e* (rel intensity, fragment ion) 152 (22, $M^+ - H_2O$), 137 (26, 152 − CH_3), 124 (26, 152 − C_2H_4), 108 (79), 67 (100), 31 (40, $CH_2{=}{}^+OH$).

8-Tosyloxyisoborneol (7).—To a solution of 1.02 g (0.006 mol) of 8-hydroxyisoborneol (**6**) in 6.0 ml of dry pyridine was added 1.20 g (0.0063 mol) of *p*-toluenesulfonyl chloride with stirring. The solution was stirred at −10° (cold room) under nitrogen for 19 hr, water was added, and the mixture was extracted with ether. The combined ether extracts were washed with 6 *N* hydrochloric acid and brine and dried, and the solvent was removed under reduced pressure, leaving 1.67 g (86%) of the 8-tosyloxyisoborneol (**7**) as a white solid. The tosylate was recrystallized from hexane–ether: mp 97–98°; ir (KBr) 3515 (OH), 1181 and 1174 cm^{-1} (tosylate); nmr ($CDCl_3$) δ 7.88 (d, 2, ArH), 7.41 (d,2, ArH), 4.70 (d, 1, H at C-2), 3.90 (d, 2, CH_2OTs), 2.56 (s, 3, $ArCH_3$), 1.97 [s (exchanged with D_2O), 1, OH], 0.91 (s, 3, CH_3), and 0.88 ppm (s, 3, CH_3).

Anal. Calcd for $C_{17}H_{24}O_4S$: C, 62.93; H, 7.46; S, 9.88. Found: C, 62.91; H, 7.54; S, 9.82.

8-Tosyloxycamphor (8).—A solution of 1.39 g (0.0043 mol) of 8-tosyloxyisoborneol (**7**) in 14 ml of dry pyridine was added in one portion to an ice-cold slurry of 1.29 g (0.013 mol) of anhydrous chromium trioxide in 13 ml of dry pyridine. The mixture was placed under a nitrogen atmosphere and stirred at room temperature for 5 hr, poured into water, and extracted with ether. The combined ether extracts were washed successively with 6 *N* hydrochloric acid and brine and dried, and the solvent was removed under reduced pressure to yield 1.30 g (94%) of the ketotosylate (**8**) as a pale yellow oil. Crystallization occurred in pentane–ether to give a colorless solid: mp 73–74°; ir (neat) 1745 (C=O), 1191 and 1180 cm^{-1} (tosylate); nmr ($CDCl_3$) δ 7.83 (d, 2, ArH), 7.41 (d, 2, ArH), 3.69 (s, 2, CH_2OTs), 2.44 (s, 3, $ArCH_3$), 1.01 (s, 3, CH_3), and 0.82 ppm (s, 3, CH_3); mass spectrum (70 eV) *m/e* (rel intensity, fragment ion) 322 (5, M^+), 167 (100, M^+ − Ts), 108 (64), 107 (95), 95 (80), 91 (48, $C_7H_7^+$).

Anal. Calcd for $C_{17}H_{22}O_4S$: C, 63.33; H, 6.88; S, 9.95. Found: C, 63.06; H, 7.40; S, 9.73.

8-Iodocamphor (9).—A solution of 0.720 g (0.0022 mol) of 8-tosyloxycamphor (**8**) in 17 ml of dimethyl sulfoxide containing 1.68 g (0.0112 mol) of sodium iodide was heated at 120° under nitrogen for 24 hr. The reaction mixture was cooled to room temperature, diluted with water, and extracted with pentane. The combined pentane extracts were washed with sodium thiosulfate solution and brine and dried, and the solvent was removed under reduced pressure to give 0.534 g (86%) of 8-iodocamphor (**9**) as a pale yellow oil. Crystallization occurred in pentane to yield the product as a colorless solid: mp 40–42° (lit.[13] mp 79°); ir (KBr) 1740 cm^{-1} (C=O); nmr ($CDCl_3$) δ 3.01 (s, 2, CH_2I), 1.15 (s, 3, CH_3), and 0.96 ppm (s, 3, CH_3); mass spectrum (70 eV) *m/e* (rel intensity, fragment ion) 278 (30, M^+), 151 (58, M^+ − I), 109 (74), 107 (100), 94 (21), 81 (79).

(±)-Camphor (10).—A solution containing 0.380 g (0.0014 mol) of 8-iodocamphor (**9**) in 20 ml of ethanol was added to a slurry of 0.760 g of 5% palladium on charcoal in 2.0 ml of water containing 0.090 g (0.0014 mol) of potassium hydroxide (85%). The mixture was shaken under 46 psi of hydrogen for 6 hr on a Parr apparatus, the catalyst then removed by filtration, water added, and the solution extracted with pentane. The combined pentane extracts were washed with brine and dried, and the solvent was removed under reduced pressure. There remained 0.160 g (77%) of (±)-camphor (**10**) as a white solid which was sublimed (18 mm, steam bath): mp 177–178° (lit.[14] mp 178–178.5°); ir (KBr) 1740 cm^{-1} (C=O); nmr[15] ($CDCl_3$) δ 0.98 (s, 3, H_3 at C-9), 0.93 (s, 3, H_3 at C-10), and 0.85 ppm (s, 3, H_3 at C-8); mass spectrum[16] (70 eV) *m/e* (rel intensity, fragment ion) 152 (36, M^+), 137 (9, M^+ − CH_3), 110 (18, M^+ − C_2H_2O), 109 (41, $C_8H_{13}^+$), 108 (55, $C_8H_{12}^+$), 95 (100, $C_7H_{11}^+$), 83 (23, $C_6H_{11}^+$), 81 (82, $C_6H_9^+$).

Purification of (±)-Camphor Using Girard Reagent T.—In several runs using larger amounts of materials, the (±)-camphor obtained contained some 2,8-epoxybornane (**12**), identified by comparing its vpc retention times on 5% SE-30 on Chromosorb W (95°) and 5% Apiezon L, 5% KOH on Chromosorb G (170°) columns with those of an authentic sample. This cyclic ether, reported as a product in the attempted reduction of 8-tosyloxyisoborneol (**7**) with lithium aluminum hydride,[3] was prepared by

(12) Alfa Inorganics, Inc., Beverly, Mass. 01915.

(13) H. Nishimitsu, M. Nishikawa, and H. Hagiwara, *Proc. Jap. Acad.*, **27**, 285 (1951); *Chem. Abstr.*, **46**, 6112*a* (1952). M. Nishikawa, *J. Pharm. Soc. Jap.*, **72**, 303 (1952); *Chem. Abstr.*, **47**, 2145*i* (1953).

(14) J. Simonsen, "The Terpenes," Vol. III, 2nd ed, Cambridge University Press, London, 1949, p 384.

(15) J. D. Connolly and R. McCrindle, *Chem. Ind. (London)*, 379 (1965); C. C. Hinckley, *J. Org. Chem.*, **35**, 2834 (1970).

(16) D. S. Weinberg and C. Djerassi, *ibid.*, **31**, 115 (1966).

us in this manner in high yield (see below). In the camphor synthesis it was presumably formed in the tosylation and/or oxidation step(s) and could be effectively removed by employing the following procedure.[17]

A solution of 790 mg of impure product (consisting of 90% camphor and 10% 2,8-epoxybornane), 863 mg (5.20 mmol) of Girard Reagent T,[9] and 0.80 ml of acetic acid in 8.0 ml of 95% ethanol was heated at reflux for 48 hr. The reaction mixture was cooled, diluted with equal volumes of water and brine, and extracted with pentane.

Purified camphor was recovered by treating the aqueous layer with 1.5 ml of concentrated hydrochloric acid and heating for 2 hr to effect hydrolysis of the Girard derivative. After cooling the camphor was removed by extraction with pentane; the combined pentane extracts were dried, and the solvent was removed under vacuum to yield 513 mg of (±)-camphor of >99% purity as determined by vpc analysis using a 5% SE-30 on Chromosorb W column.

The combined pentane extracts from the initial work-up of the reaction mixture were dried and the solvent was removed under reduced pressure to yield 215 mg of a white solid consisting of 41% camphor and 59% 2,8-epoxybornane (vpc). This mixture was recycled as described above, yielding an additional 108 mg of purified camphor. The combined weights of isolated camphor represent a recovery of 87% of purified product which was sublimed (18 mm, steam bath) to yield a white solid, mp 177–178°. Synthetically prepared (±)-camphor-*8*-^{14}C and (±)-camphor-*9*-^{14}C were both purified in this manner.

2,8-Epoxynorbornane (12).—A solution of 200 mg (0.60 mmol) of 8-tosyloxyisoborneol (**7**) in 5.0 ml of dry ether was added dropwise to a slurry of 23 mg (0.60 mmol) of lithium aluminum hydride in 6.0 ml of dry ether. The reaction mixture was stirred under nitrogen for 1 hr and then heated at reflux for an additional hour. The mixture was cooled, acidified with 10% sulfuric acid, and extracted with ether. The combined ether extracts were washed with 5% aqueous sodium bicarbonate and dried, and the solvent was removed under reduced pressure to yield 89 mg (95%) of 2,8-epoxynorbornane (**12**) as a white solid which was sublimed (16 mm, 50°): mp 172–174° (lit.[3] mp 164–167°); the infrared spectrum showed no peaks characteristic of hydroxyl or tosyl groups; mass spectrum (70 eV) *m/e* (rel intensity, fragment ion) 152 (7, M^+), 108 (100, $M^+ - C_2H_4O$ or $- C_3H_8$), 93 (70, 108 − CH_3), 79 (30), 67 (30).

Registry No.—**3**, 29908-22-3; **4**, 29908-23-4; **7**, 29908-24-5; **8**, 29908-25-6; **10**, 21368-68-3.

(17) D. J. Pasto and C. R. Johnson, "Organic Structure Determination," Prentice-Hall, Englewood Cliffs, N. J., 1969, p 393.

Addition of Active Methylene and Methine Compounds to 9-Nitroanthracene[1]

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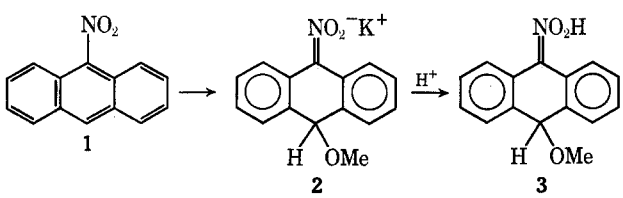
Addition of 9-nitroanthracene to solutions of sodio malonic ester, sodio methylmalonic ester, sodium 2-propanenitronate, and sodio malononitrile in dimethyl sulfoxide and subsequent dilution with water and acidification afford 10-dicarbethoxymethyl-, 10-(1,1-dicarbethoxyethyl)-, 10-(2-nitro-2-propyl)-, and 10-dicyanomethyl-9-nitro-9,10-dihydroanthracenes (**7a–d**), respectively. The results of nmr studies of **7a** are consistent only with the diaxially substituted cis isomer. Addition of benzyl halide to dimethyl sulfoxide solutions of the sodium salts of adducts **7a–c**, followed by aqueous work-up, produces 10-substituted 9-anthrone oximes **10a–c**. Treatment of adducts **7a** and **7b** with acid causes loss of the elements of nitrous acid with the formation of diethyl (9-anthryl)malonate (**12a**) and diethyl methyl(9-anthryl)malonate (**12b**), respectively.

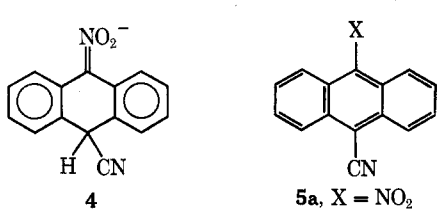
The stable σ complexes formed by nucleophilic attack of certain alkyl nitroaryl ethers by alkoxide ion are known as Jackson–Meisenheimer complexes.[3] These complexes, and structurally similar species, are of theoretical interest because they are possible intermediates in nucleophilic aromatic substitution.[3,4] In some cases the intermediacy of the complex may be shown by spectrometric methods, and some of the complexes are sufficiently stable to permit isolation.[5]

Acidification of Jackson–Meisenheimer complexes (and structurally similar species) normally causes regeneration of the aromatic system; the only exception of which we are aware is reported in the work of Meisenheimer.[6] Complex **2** was prepared by treatment of 9-nitroanthracene (**1**) with methanolic potassium hydroxide. Acidification produced a material for which Meisenheimer suggested structure **3**. It is the purpose of this paper to report the preparation, characterization, and reactions of a series of conjugate acids of anions which structurally resemble Jackson–Meisenheimer complexes.



1 2 3

Landolt and Snyder[7] examined the reaction of 9-nitroanthracene with cyanide ion in dimethylformamide. Isolated reaction products included 9-nitro-10-cyanoanthracene (**5a**) and 9,10-dicyanoanthracene (**5b**).



4 **5a**, X = NO_2; **b**, X = CN

Dicyanoanthracene **5b** is produced upon treatment of **5a** with cyanide ion under the conditions of the reaction.[7] The mechanism which was proposed for the formation of **5a** involves one-electron transfer from ini-

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(2) NSF Predoctoral Fellow, 1967–1971.

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