tosylate.[20] Equally important, the convergent pattern for the 5-OBs data is consistent with the results obtained from the graphical analysis of the solvolysis data for 2-phenyl-1-propyl tosylate (see Figure 4), another primary substrate that is known[13c,21] to react by competitive k_Δ and k_s processes whose ratio varies with solvent nucleophilicity as well as solvent ionizing power.[22]

The above results obviously support our contention that delocalization of charge in solvolytic transition states by exhalted hyperconjugation can be differentiated from that by bridging by a graphical analysis of solvolysis rates in aqueous ethanol and acetic acid–formic acid solvent systems. Furthermore, it is clear from the analysis of dispersion patterns that the different response to solvent effect by a substrate solvolyzing with assistance by strained C–C bonds (such as those in the cycloproyl and cyclobutyl groups) from one solvolyzing with phenyl or alkyl assitance cannot be explained by simply invoking nucleophilic solvent assistance.

Experimental Section

Cyclobutylcarbinyl *p*-bromobenzenesulfonate (4-OBs) was prepared by a published procedure[6b] in 40% yield: mp 25 °C [after recrystallization from a 10:1 mixture of petroleum ether (bp 30–60 °C)–ethyl acetate] (lit.[6b] mp 25 °C).

Cyclopentylcarbinyl *p*-bromobenzenesulfonate (5-OBs) was also prepared by a published procedure[6b] in 60% yield: mp 49.5–50.0 °C [after recrystallization from petroleum ether (bp 30–60 °C)] (lit.[24] mp 49.5–50.0 °C).

Solvents were prepared as previously described.[1]

Rate Measurements. The rates of solvolysis were followed titrimetrically. Reaction solutions were 0.03 M with the exception of the 50% aqueous ethanol runs for 4-OBs and neophyl tosylate which were respectively, 0.02 and 0.01 M. Rate measurements were accomplished by the ampoule technique, again with the exception of the 50% aqueous ethanol runs for 4-OBs and neophyl tosylate where the volumetric flask technique[1] was employed. In a typical run, 5-mL aliquots of the reaction solution were sealed under nitrogen in 10-mL ampules, thermostated in a constant-temperature bath held to ±0.05 °C of the reaction temperature, and then, at appropriate times, titrated as previously described.[1]

Registry No. 4-OBS, 51108-24-8; 5-OBS, 38806-24-5.

(20) Plots of the log k_t values for solvolysis of 4-OBs against those of either 3-OPms or *exo*-2-norbornyl tosylate do indeed show good linearity.
(21) Raber, D. J.; Harris, J. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 4829.
(22) Both water and ethanol are of comparable nucleophilicity,[23] consequently, for aqueous ethanol, increasing ethanol content produces little change in nucleophilicity. This is also true for acetic acid–formic acid.[23] On the other hand, water has a much greater ionizing power than ethanol as does formic acid compared to acetic acid.[23] As a result, increasing either the water content in aqueous ethanol or formic acid in acetic acid–formic acid solvents produces a sharp increase in ionizing power.
(23) See Table I in ref 10b.
(24) Felkin, H.; LeNy, G. *Bull. Soc. Chim. Fr.* **1957**, 1169.

Cyclopentenones from γ-Lactones. Synthesis of 2-(6-Carboxyhexyl)cyclopent-2-en-1-one, an Intermediate in Prostaglandin Synthesis

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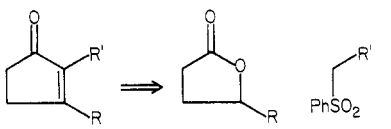
Received July 30, 1981

The most valuable methods for the construction of substituted cyclopentenones[1] are based on the transformation of compounds already possessing the carbocyclic framework,[2] or on the preliminary preparation of γ-dicarbonyl compounds, which successively undergo base-catalyzed cyclization.[3]

Scheme I



2 3

According to the latter approach we have recently developed a method to prepare cyclopentenones (1) from simple inexpensive γ-lactones (2) and alkyl phenyl sulfones (3), which contribute the C-2 ring carbon and the relative substituent R′ (Scheme I).

By this method we have synthesized target molecules such as *cis*-jasmone and dihydrojasmone from γ-valerolactone and the proper sulfones.[3a] We now report a new synthesis of 2-(6-carboxyhexyl)cyclopent-2-en-1-one (9),[4] a useful prostanoid synthon, using γ-butyrolactone and sulfone 4 as building blocks, on the basis of the retrosynthetic analysis in Scheme I. The protected hydroxyl group in 4 is liable to be converted to the carboxylic function in the last step of the synthetic sequence (Scheme II).

The sulfone 4 was prepared in 44.5% yield from 1,8-octanediol by routine transformations, which involve monoiodination with iodidric acid in continuous extraction conditions,[5] tetrahydropyranylization[6] of the residue hydroxyl group, and iodide ion displacement by polymer-supported sulfinate anion.[7] The sulfone 4 was treated with 2 equiv of *n*-butyllithium in anhydrous tetrahydrofuran, and then a small amount of hexamethylphosphoric triamide and 1 equiv of γ-butyrolactone were added at −78 °C to give, after quenching with ammonium chloride, extraction, and column chromatography, the expected product 5 in 55% yield (68.7% based on reacted starting sulfone).

Cleavage of the carbon–sulfur bond with aluminum amalgam[8] afforded 6 in 85% yield, on which we accomplished the oxidation of the free hydroxyl group to aldehyde.[9] The best reagent, for the product yield (67% of 7) and the easy workup, was found to be pyridinium

(1) Ellison, R. A. *Synthesis* **1973**, 397. Wenkert, E. *Acc. Chem. Res.* **1980**, *13*, 27.
(2) For recent examples, see (a) Novak, L.; Baan, G.; Marosfalvi, J.; Szantay, C. *Chem. Ber.* **1980**, *198*, 2839. (b) Bernady, K. F.; Poletto, J. F.; Nocera, J.; Mirando, P.; Schaub, R. F.; Weiss, M. J. *J. Org. Chem.* **1980**, *45*, 4702. (c) Zima, G.; Barnum, C.; Liotta, D. *Ibid.* **1980**, *45*, 2736. (d) Becker, D.; Birnbaum, D. *Ibid.* **1980**, *45*, 570. (e) Funk, R. L.; Vollhardt, K. P. C. *Synthesis* **1980**, 118. (f) Barco, A.; Benetti, S.; Baraldi, P. G.; Simoni, D. *Ibid* **1981**, 199. (g) Birch, A. J.; Dahler, P.; Narula, A. S.; Stephenson, G. R. *Tetrahedron Lett.* **1980**, 3817. Birch, A. J.; Narula, A. S.; Dahler, P.; Stephenson, G. R.; Kelly, L. F. *Ibid.* **1980**, 979.
(3) For recent examples, see (a) Mussatto, M. C.; Savoia, D.; Trombini, C.; Umani-Ronchi, A. *J. Org. Chem.* **1980**, *45*, 4002. (b) Matsuda, I.; Murata, S.; Izumi, Y. *Ibid.* **1980**, *45*, 237.
(4) (a) Sih, C. J.; Solomon, R. G.; Price, P.; Sood, R.; Peruzzotti, G. *J. Am. Chem. Soc.* **1975**, *97*, 857. (b) Bagli, J. F.; Bogri, T.; Deghenghi, R.; Wiesner, K. *Tetrahedron Lett.* **1966**, 465. For a recent synthesis of the methyl, ethyl, and butyl esters of the acid 9, see ref 2a, 2b, and 2f, respectively.
(5) We followed the experimental procedure described for the analogue monobromination of diols with HBr: Butenandt, A.; Hecker, E.; Hopp, M.; Koch, W. *Justus Liebigs Ann. Chem.* **1962**, *658*, 39.
(6) Bongini, A.; Cardillo, G.; Orena, M.; Sandri, S. *Synthesis* **1979**, 729.
(7) Manescalchi, F.; Orena, M.; Savoia, D. *Ibid.* **1979**, 445.
(8) Corey, E. J.; Chaykowsky, M. *J. Am. Chem. Soc.* **1971**, *87*, 1345.
(9) We have found more convenient to carry out the desulfonation on 5 prior to the oxidation step, since the aldehydic function is labile in the reducing conditions. The crude compound 6 obtained by desulfonation could be directly used in the oxidation step, but we obtained a slightly better yield by oxidizing the purified compound.

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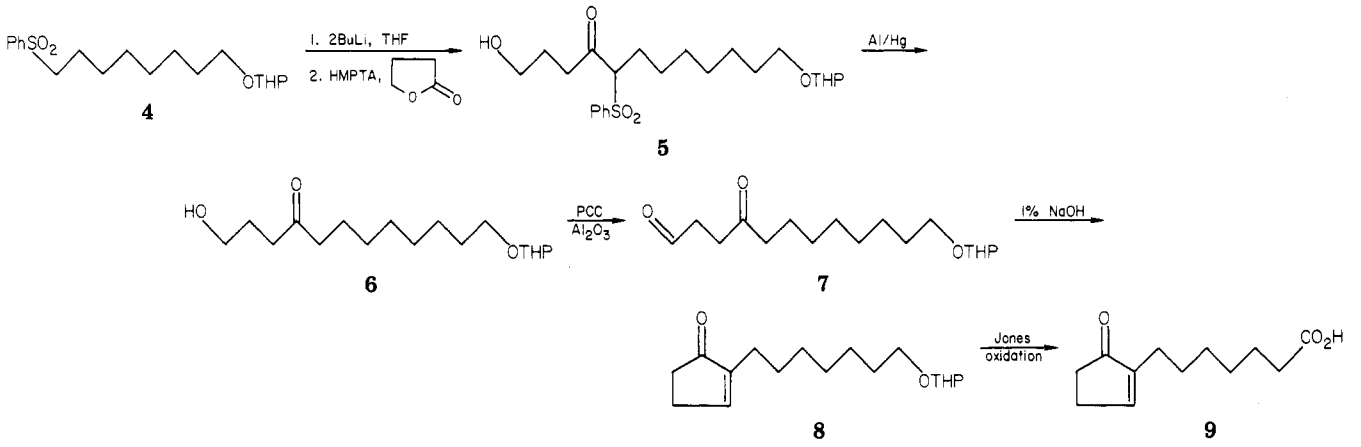
Scheme II



chlorochromate (PCC) supported on alumina,[10] which neutralizes the acidic character of the reagent, so preserving the other protected alcoholic function. Satisfactory yields (63% and 60%, respectively) were also obtained, using the chromic anhydride–pyridine complex[11] and pyridinium dichromate[12] in methylene chloride.

Different basic conditions have been employed in the literature to achieve the ring closure of γ-keto aldehydes.[13] In our hands the best yield of the cyclized compound **8** (60%) was obtained by stirring **7** at 70 °C for 1 h in 1% aqueous sodium hydroxide.[13a] The conversion of **7** was never complete even after several hours and at higher temperatures, and the concomitant occurrence of intermolecular reactions could not be suppressed. Added tetrahydrofuran or methanol lowered the yield of **8** and produced more tarry materials. Less effective bases were 1% NaOH in the phase-transfer catalyzed system H_2O–ether,[13b] alkali metal fluorides[14]–crown ether and polymer-supported fluoride ion[15] in toluene, and basic alumina[3a] in benzene.

Finally, the protected alcoholic function in the side chain was directly converted to carboxylic group by means of the Jones reagent[16] in acetone. Hydrolysis and oxidation of the protective group also produce glutaric acid, from which the acid **9** was separated by preparative thin-layer chromatography in 70% yield.

Experimental Section

IR spectra were recorded on a Perkin-Elmer 710B spectrophotometer. ^1H NMR spectra were determined in $CDCl_3$ with tetramethylsilane as the internal reference on a Perkin-Elmer R12B instrument (60 MHz). Mass spectra (MS) were obtained at 70 eV with a Varian MAT 111 spectrometer.

TLC assays were made with hexane–ether or hexane–ethyl acetate on 0.2-mm Baker 1B2-F silica gel sheets. Preparative TLC plates of silica gel 60 F_{254} (20 × 20 cm) were purchased from Merck. Column chromatography was performed with Merck silica gel (70-230 mesh).

Tetrahydrofuran (THF) was obtained anhydrous and oxygen-free by distillation over sodium benzophenone ketyl under argon. Hexamethylphosphoric triamide (HMPTA) was distilled over calcium hydride under a reduced pressure of argon.

1,8-Octanediol, 3,4-dihydro-2*H*-pyran, sodium benzenesulfinate, *n*-butyllithium, and γ-butyrolactone were purchased from Fluka.

1-(Phenylsulfonyl)-8-[(tetrahydro-2*H*-pyran-2-yl)oxy]-octane (4). In a suitable apparatus for the continuous extraction of biphasic systems were placed 1,8-octanediol (25g, 0.17 mol) and 57% aqueous HI[5] (34 mL, 0.25 mol), and the aqueous phase was covered with the required amount of 2,2,4-trimethylpentane. After heating for 4h, the organic phase was concentrated to about 150 mL and washed with 10% aqueous $Na_2S_2O_3$, 10% aqueous $NaHCO_3$, and saturated brine and finally dried over Na_2SO_4. The solvent was distilled in vacuo and the residue was chromatographed on a silica gel column, eluting with hexane–ether (85:15) to obtain 1,8-diiodooctane (6.42 g, 17 mmol, 10%) and successively 8-iodo-1-octanol (30.25 g, 0.118 mol, 69%): IR (neat) 3300 (s), 1190 (s), 1050 cm^{-1} (s); NMR δ 3.9 (s, 1 H, OH), 3.5 (t, 2 H, CH_2OH), 3.15 (t, 2H, CH_2I), 1.2–2.0 (m, 12 H).

Amberlyst H-15, H^+ form (1 g), was added to a cooled solution of 8-iodo-1-octanol (28.16 g, 0.11 mol) and 3,4-dihydro-2*H*-pyran (13.9 g, 0.16 mol) in CH_2Cl_2 (200 mL).[6] After the mixture was stirred for 3 h at room temperature, the resin was taken away by decantation and the residue was chromatographed on a silica gel column, eluting with hexane–ether (95:5), to obtain 2-(8-iodooctyl-1-oxy)tetrahydropyran (28.05 g, 82 mmol, 75%): IR (neat) 2950 (s), 1130 (s), 1030 cm^{-1} (s); NMR δ 4.6 (s, 1 H, OCHO), 3.5 (m, 4 H, CH_2O), 3.2 (m, 2 H, CH_2I), 1.0–2.0 (m, 18 H).

A mixture of the last compound (27.2 g, 80 mmol) and Amberlyst A-26, benzenesulfinate form[7] (40 g, 0.14 equiv) in benzene (200 mL) was stirred at reflux for 6 h. Then the resin was filtered and washed with CH_2Cl_2. The solvent was evaporated and the residue was chromatographed on a silica gel column, eluting with hexane–ethyl acetate (8:2). First recovered was a small amount of the sulfinate ester (1.27 g, 3.6 mmol, 4.5%) derived from O-alkylation of the ambident sulfinate anion: IR (neat) 1130 (s), 1070 (s), 1030 (s), 750 cm^{-1} (s); NMR δ 7.6 (m, 5 H, aromatic), 4.6 (s, 1 H, OCHO), 3.2–4.2 (m, 6 H, CH_2O), 1.1–2.0 (m, 18 H). At the same polarity we successively eluted the sulfone **4** (24.07 g, 68 mmol, 85%): IR (neat) 1590 (w), 1310 (s), 1150 (s), 1080 (s), 1030 (s), 790 (s), 750 cm^{-1} (s); NMR δ 7.4–8.0 (m, 5 H, aromatic), 4.5 (s, 1 H, OCHO), 3.2–3.9 (m, 4 H, CH_2O), 3.05 (t, 2 H, CH_2SO_2), 1.1–2.0 (m, 18 H); mass spectrum, *m/e* 354(M^+), 253 (M^+–THPO). Anal. Calcd for $C_{19}H_{30}O_4S$: C, 64.38; H, 8.53; S, 9.03.

1-Hydroxy-5-(phenylsulfonyl)-12-[(tetrahydro-2*H*-pyran-2-yl)oxy]dodecan-4-one (5). *n*-Butyllithium (1.8 M, 57.5

(10) Cheng, Y. S.; Lin, W. L.; Chen, S. *Synthesis* **1980**, 223.
(11) Ratcliffe, E.; Rodehorst, R. *J. Org. Chem.* **1970**, *35*, 4000.
(12) Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, 399.
(13) The commonly employed methods are as follows: (a) 1% aqueous NaOH, by heating for a brief time (Meyers, A. I.; Nazarenko, N. *J. Org. Chem.* **1973**, *38*, 175; Kondo, K.; Tunemoto, D. *Tetrahedron Lett.* **1975**, 1397); (b) 1% aqueous NaOH in the phase-transfer catalyzed two-phase system H_2O–ether, by stirring at room temperatures for 3 days (Stork, G.; Ozorio, A.; Leong, A. Y. W. *Tetrahdedron Lett.* **1978**, 5175); (c) 2–10% NaOH in alcoholic or hydroalcoholic media at different temperatures (Cookson, R. C.; Parsons, P. J. *J. Chem. Soc., Chem. Commun.* **1976**, 990; Oshima, K.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc* **1973**, *95*, 4446; Nakai, T.; Wada, E.; Okawara, M. *Tetrahedron Lett.* **1975**, 531); (d) 5% KOH in H_2O–THF–Et_2O (1:1:2), by refluxing for 48 h (Tsuji, J.; Kobayashi, Y.; Shimizu, I. *Tetrahedron Lett.* **1979**, *39*; see also ref 3b); (e) anhydrous K_2CO_3 in methanol at room temperature (Ide, J.; Sakai, K.; Yura, Y. *Bull. Chem. Soc. Jpn* **1978**, *51*, 939); (f) 5% Na_2CO_3 in hot aqueous methanol (Larcheveque, M.; Valette, G.; Cuvigny, T. *Tetrahedron* **1979**, *35*, 1745).
(14) The use of fluoride ion as a base has been recently reviewed: Clark, J. H. *Chem. Rev.* **1980**, *80*, 429.
(15) Cainelli, G.; Manescalchi, F.; Panunzio, M. *Synthesis* **1976**, 472.
(16) Bowden, K.; Heilbron, I. M.; Jones, E. R. H.; Weedon, B. C. L. *J. Chem. Soc.* **1946**, 39.

mL, 103 mmol) was added at 0 °C to a stirred solution of the sulfone 4 (17.7 g, 50 mmol) in dry THF (100 mL) under argon. After 30 min, HMPTA (5 mL) and γ-butyrolactone (4.3 g, 50 mmol) were added at −78 °C. The reaction mixture was stirred for 3 h and then allowed to reach room temperature and quenched with aqueous NH_4Cl. The organic phase was extracted with ethyl acetate, washed with brine, dried over Na_2SO_4, and evaporated in vacuo. The crude residue was chromatographed on a silica gel column, eluting with hexane–ethyl acetate (70:30), to separate the unreacted sulfone 4 (3.56 g, 20%) and then the sulfone 5 (12.1 g, 28.3 mmol, 55%): IR (neat) 3400 (m), 1720 (s), 1310 (s), 1070 (s), 1030 cm^{-1} (s); NMR δ 7.5–8.0 (m, 5 H, aromatic), 4.6 (s, 1 H, OCHO), 4.15 (t, 1 H, $CHSO_2$), 3.2–4.0 (m, 6 H, CH_2O), 2.9 (m, 2 H, $CH_2C{=}O$), 2.5 (s, 1 H, OH), 1.0–2.1 (m, 20 H); mass spectrum, *m/e* 339 (M^+ − THPO), 197 (339 − H − $PhSO_2$). Anal. Calcd for $C_{23}H_{36}O_6S$: C, 62.71; H, 8.24; S, 7.26. Found: C, 62.86; H, 8.24; S, 7.21.

1-Hydroxy-12-[(tetrahydro-2*H*-pyran-2-yl)oxy]dodecan-4-one (6). Aluminum amalgam (10 g of Al, 0.37 mol), prepared according to Corey,[8] was added to the solution of sulfone 5 (10.7 g, 25 mmol) in THF–H_2O (9:1, 600 mL), and the mixture was stirred at reflux for 3 h and then cooled and filtered. The solid phase was washed with THF. Most of the solvent was removed in vacuo, ether was added, the aqueous phase was separated, and the organic phase was dried over Na_2SO_4 and concentrated. The crude product 6 was purified by chromatography on a silica gel column, using hexane–ether (7:3), to obtain 6.75 g (22.5 mmol, 85%): IR (neat) 3400 (m), 1715 (s), 1135 (s), 1120 (s), 1075 (s), 1030 cm^{-1} (s); NMR δ 4.6 (s, 1 H, OCHO), 3.1–4.0 (m, 6 H, CH_2O), 2.1–2.8 (m, 5 H, OH and $CH_2C{=}O$), 1.1–2.0 (m, 20 H); mass spectrum, *m/e* 299 (M^+ − H), 283 (M^+ − OH), 199 (M^+ − THPO). Anal. Calcd for $C_{17}H_{32}O_4$: C, 67.96; H, 10.74. Found: C, 68.05; H, 10.72.

4-Oxo-12-[(tetrahydro-2*H*-pyran-2-yl)oxy]dodecanal (7). Pyridinium chlorochromate on alumina[10] (57 g, 45 mmol) was added to a solution of 6 (4.5 g, 15 mmol) in CH_2Cl_2 (80 mL) distilled from P_2O_5. After the mixture was stirred for 3 h at room temperature, the solvent was evaporated, ether was added, and the solid phase was filtered and washed with ether. The organic phase was concentrated and the residue was chromatographed on a silica gel column, eluting with hexane–ether (7:3), to obtain the pure compound 7 (3.0 g, 10 mmol, 67%): IR (neat) 1720 (s), 1030 cm^{-1} (s); NMR δ 9.8 (s, 1 H, CHO), 4.55 (s, 1 H, OCHO), 3.1–4.0 (m, 4 H, CH_2O), 2.2–2.9 (m, 6 H, $CH_2C{=}O$), 1.2–2.0 (m, 18 H); mass spectrum, *m/e* 298 (M^+), 255 (M^+ − CH_2CHO), 197 (M^+ − THPO). Anal. Calcd for $C_{17}H_{30}O_4$: C, 68.42; H, 10.13. Found: C, 68.70; H, 10.10.

2-[7-[(Tetrahydro-2*H*-pyran-2-yl)oxy]heptyl]cyclopent-2-en-1-one (8). The γ-keto aldehyde 7 (2.53 g, 8.5 mmol) was added to 1% aqueous NaOH (100 mL) and the mixture was stirred at 70 °C for 1 h. The organic phase was extracted with ether, dried (Na_2SO_4), and evaporated. The crude residue was chromatographed on a silica gel column, eluting with hexane–ether (8:2), to obtain the pure cyclized compound 8 (1.43 g, 5.1 mmol, 60%): IR (neat) 1710 (s), 1630 (m), 1130 (s), 1070 (s), 1030 cm^{-1} (s); NMR δ 7.4 (s, 1 H, vinylic), 4.6 (s, 1 H, OCHO), 3.3–4.0 (m, 4 H, CH_2O), 2.0–2.8 (m), 6 H, $CH_2C{=}O$), 1.2–1.8 (m, 16 H); mass spectrum, *m/e* 280 (M^+), 179 (M^+ − THPO). Anal. Calcd for $C_{17}H_{28}O_3$: C, 72.82; H, 10.06. Found: C, 72.80; H, 10.07.

2-(6-Carboxyhexyl)cyclopent-2-en-1-one (9). Aqueous 8 N chromic acid[16] was slowly nadded to a solution of compound 8 (1.29 g, 4.6 mmol) in acetone (10 mL), freshly distilled from $KMnO_4$, under stirring. When the reaction was complete, 2-propanol (1 mL) was added, and the solid was filtered and washed with acetone. Most of the solvent was evaporated in vacuo, aqueous 10% NaOH was added, and the neutral organic materials were extracted with ether. The aqueous phase was acidified with HCl, and the organic acids were extracted with ethyl acetate. The organic phase was dried (Na_2SO_4) and concentrated. The acid 9 was isolated by preparative TLC on silica gel, eluting with hexane–ethyl acetate (1:1), collecting 0.676 g of product (3.2 mmol, 70%): mp, 37–38 °C (lit.[4a] mp 37–38 °C); IR (Nujol mull) 1735 (s), 1710 (s), 1670 (s), 1620 (s), 1220 (s), 1165 cm^{-1} (s); NMR δ 10.9 (s, 1 H, CO_2H), 7.3 (s, 1 H, vinylic), 2.0–3.0 (m, 8 H), 1.5–2.0 (m, 8H); mass spectrum, *m/e* 210 (M^+), 192 (M^+ − H_2O). Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.41; H, 8.61.

Registry No. 2 (R = H), 96-48-0; **4**, 79918-30-2; **5**, 79918-31-3; **6**, 79918-32-4; **7**, 79918-33-5; **8**, 79918-34-6; **9**, 5239-43-0; 1,8-octanediol, 629-41-4; 1,8-diiodooctane, 24772-63-2; 8-iodo-1-octanol, 79918-35-7; 2-(8-iodooctan-1-oxy)tetrahydropyran, 53596-83-1; 8-[(tetrahydropyran-2-yl)oxy]octane benzenesulfinate, 79918-36-8.

Homoallylic Coupling in 1,4-Dihydronaphthalenes. 3. Crystal Structure of 1,4-Dihydronaphthoic Acid

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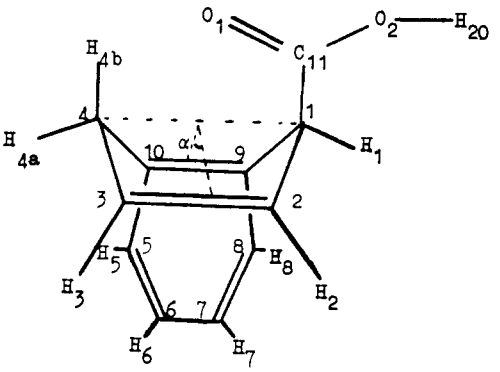
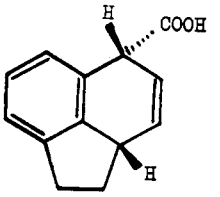
Received July 29, 1981

The precise conformations of simple dihydronaphthalenes in solution remain uncertain despite much discussion[1-9] of the interpretation of their solution NMR data. Marshall and co-workers originally suggested[1,2] that 1,4-dihydronaphthoic acid adopts a flattened boat geometry (1) in which the carboxyl group is placed pseudoaxially, whereas a more puckered conformation (α = ca. 150°) was initially suggested by Rabideau.[3] A subsequent study of ^{13}C–^{13}C and ^{13}C–^{1}H couplings about ^{13}C-labeled dihydro aromatic acids provided clear evidence that the conformation of 1 lies somewhere between the effectively planar 1,4-dihydrobenzoic acid and the highly puckered (α = 145°) 9,10-dihydroanthroic acid.[4] In the meantime, we had prepared a rigid, highly puckered dihydronaphthalene (2)[5] and had determined its conformation (α = 146.5°) by X-ray crystallography.[6] This work clearly established a



(1)



(2)

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