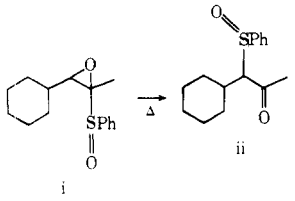
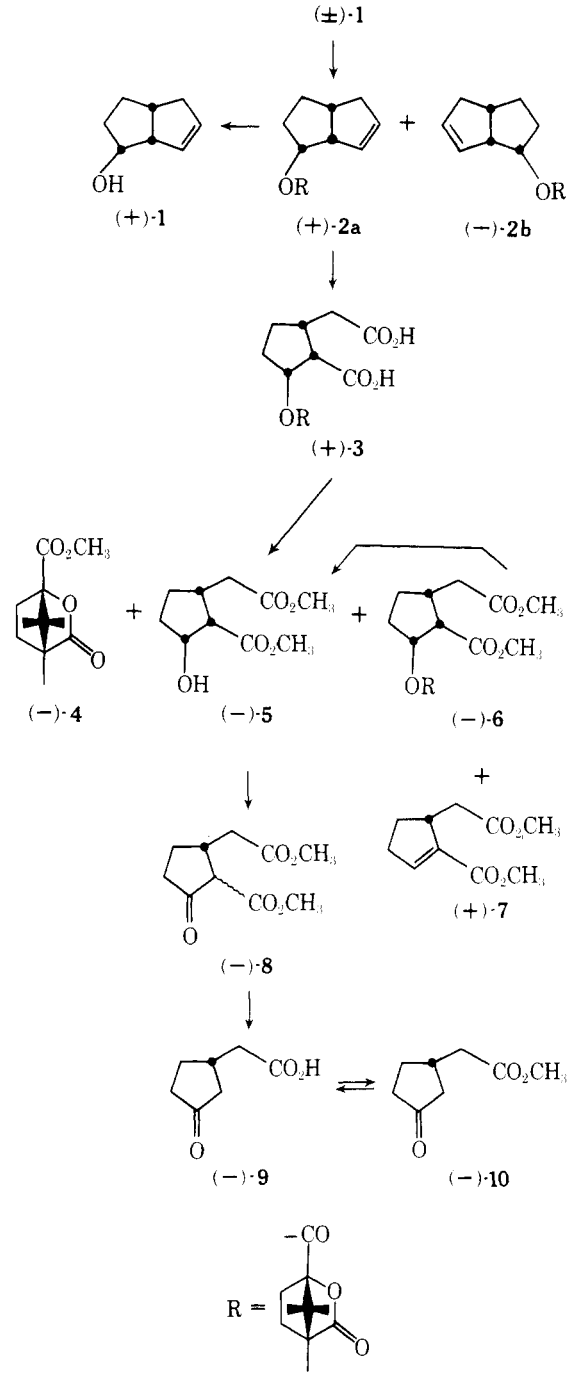
M. Kolb, and B.-T. Grobel, *Tetrahedron Lett.*, 3171 (1974); (c) H. Taguchi, S. Tanaka, Y. Yamamoto, and H. Nozaki, *ibid.*, 2465 (1973); (d) M. Charpentier-Morize and J. Sansoulet, *Bull. Soc. Chim. Fr.*, 331 (1977).
(2) B. M. Trost, T. N. Salzmann, and K. Hiroi, *J. Am. Chem. Soc.*, **98**, 4887 (1976).
(3) Durst[7] suggests a rather different mechanism. The intermediacy of the phenylsulfinyl ketone is supported by the isolation of sulfoxide ii (which has no low-energy elimination pathway available) on thermolysis of i.



i ii

(4) (a) M. Hojo, R. Masuda, T. Saeki, and S. Uyeda, *Synthesis*, 697 (1976). (b) The crude chlorosulfoxides show a main spot on TLC (30% v/v EtOAc/hexane) at R_f ~0.2. They were purified by filtration through silica gel (CH_2Cl_2/EtOAc) followed by bulb-to-bulb distillation ($bp_{0.3}$ = 120–130 °C (bath temperature)). Chlorosulfoxides so purified were colorless oils indefinitely stable in the freezer. Development of dark yellow or brown color on addition to LDA/THF at −78 °C is an indication of insufficiently purified chlorosulfoxide.
(5) T. Durst, M. J. LeBelle, R. van den Elzen, and K.-C. Tin, *Can. J. Chem.*, **52**, 761 (1974).
(6) T. Durst, *J. Am. Chem. Soc.*, **91**, 1034 (1969).
(7) T. Durst and K.-C. Tin, *Tetrahedron Lett.*, 2369 (1970).
(8) V. Reuktrakul and W. Kanghae, *Tetrahedron Lett.*, 1377 (1977).
(9) As the application of this method to an aldehyde gives an enone more simply prepared by condensation of a ketophosphonate with the lower homologue of the aldehyde, additions to aldehydes were not extensively investigated. The preliminary indication is that aldehydes work as well as ketones.
(10) J. L. Pierre, H. Handel, and R. Perraud, *Tetrahedron Lett.*, 2013 (1977).
(11) I. Heilbron, E. R. H. Jones, R. W. Richardson, and F. Sondheimer, *J. Chem. Soc.*, 737 (1949).
(12) J. Klein, *Tetrahedron*, **20**, 465 (1964).
(13) D. V. Nightingale, E. C. Milberger, and A. Tomisek, *J. Org. Chem.*, **13**, 357 (1948).
(14) R. Jacquier and G. Maury, *Bull. Soc. Chim. Fr.*, 306 (1967).
(15) I. Heilbron, E. R. H. Jones, J. B. Toogood, and B. C. L. Weedon, *J. Chem. Soc.*, 1827 (1949).
(16) R. A. Cormier, W. L. Schreiber, and W. C. Agosta, *J. Am. Chem. Soc.*, **95**, 4873 (1973).
(17) P. A. Grieco, M. Nishizawa, N. Marinovic, and W. J. Ehmann, *J. Am. Chem. Soc.*, **98**, 7102 (1976).
(18) Refluxing for an hour was an arbitrary choice. An aliquot taken after 20 min showed the isomerization to be largely complete.
(19) T. Nagasawa, K. Umemoto, T. Tsuneya, and M. Shiga, *Nippon Nogei Kagaku Kaishi*, **49**, 217 (1975); *Chem. Abstr.*, **83**, 97589y (1975).
(20) L. J. Dolby and M. Debono, *J. Org. Chem.*, **29**, 2306 (1964).
(21) K. M. More and J. Wemple, *J. Org. Chem.*, **43**, 2713 (1978).
(22) Columbia Organic Chemical Co., Inc.
(23) (a) B. J. Hunt and W. Rigby, *Chem. Ind. (London)*, 1868 (1967); (b) W. C. Still, Columbia University, personal communication.
(24) B. M. Mitzner, V. J. Mancini, S. Lemberg, and E. T. Theime, *Appl. Spectrosc.*, **22**, 34 (1968).



Absolute Configuration of *endo-cis*-Bicyclo[3.3.0]oct-7-en-2-ol and Specific Rotation of 3-Oxocyclopentaneacetic Acid

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The *cis*-bicyclo[3.3.0]octane skeleton has often been found in natural products and proved to be a useful precursor for the synthesis of some monoterpenes,[1] yet the absolute configuration of its simplest asymmetric derivatives has not been established.[2]

In connection with our studies on optical activity of simple chromophores,[3] we report here the chemical correlation of *endo-cis*-bicyclo[3.3.0]oct-7-en-2-ol (**1**) to 3-oxocyclopentaneacetic acid (**9**). The specific rotation of the latter has also been determined.

(±)-*endo-cis*-Bicyclo[3.3.0]oct-7-en-2-ol (**1**)[4] was treated with (−)-camphanyl chloride[5] in pyridine. The resulting diastereomeric mixture of camphanates was separated by fractional recrystallization, or by column chromatography on silica gel, to give **2a**, $[\alpha]_{589}$ +129.0° (ethanol), and **2b**, $[\alpha]_{589}$ −139.8° (ethanol), each in pure form.[6] Hydrolysis of (+)-**2a** gave optically pure (+)-**1**, $[\alpha]_{589}$ +210.6° (methanol).

Oxidation of (+)-**2a** with sodium metaperiodate in the presence of ruthenium dioxide gave the diacid **3**, $[\alpha]_{589}$ +3.2° (ethanol). Solvolysis of **3** with sulfuric acid in methanol proceeded only partially, affording the desired alcohol **5**, $[\alpha]_{589}$ −11.8° (ethanol), and methyl camphanate (**4**), $[\alpha]_{589}$ −124.4° (ethanol), as well as the esterification product **6**, $[\alpha]_{589}$ −4.87° (ethanol), and a small amount of the olefinic product **7**, $[\alpha]_{589}$ +54.1° (carbon tetrachloride). Methanolysis of **6** with hydrogen chloride gave (−)-**4** and (−)-**5** in 80% yield. (−)-**5** was oxidized with Jones' reagent to yield the ketone **8**, $[\alpha]_{589}$ −66.8° (methanol). Hydrolytic decarboxylation of (−)-**8** with concentrated hydrochloric acid gave the acid **9**, which was purified via the methyl ester **10**, $[\alpha]_{589}$ −121.0° (chloroform). The optical rotation of the regenerated acid **9**, $[\alpha]_{589}$ −115.5°

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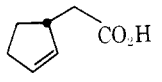
(chloroform), was nearly the same as that of the crude product.

Since every reaction used for the degradation of **2a** cannot affect the asymmetric center in **9**, the 1*R*,2*R*,5*R* absolute configuration has been assigned to (+)-**1** from the known *S* configuration of (−)-**9**[2,7] and from the established relative configuration of **1**.[4]

However, it should be noted that considerable discrepancy from the reported data was found concerning the optical rotation of **9**. Thus, according to Hill's work,[7] a maximum rotation of −63° can be estimated for **9** from a route of chemical correlation in which (*R*)-(−)-2-cyclopenteneacetic acid (**11**, 84.3% optically pure, based on Mislow's work[8]) was



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converted to (−)-**9**, $[\alpha]_D$ −53.1° (chloroform).[9] In our work, the observed rotation for (−)-**9** (−116°) should be regarded as the maximum value since the diastereomeric purity of (+)-**2a** was ascertained by LC.

We are currently investigating the chiroptical properties of *cis*-bicyclo[3.3.0]octane derivatives,[12] and the results will be reported in the near future.

Experimental Section

Melting and boiling points are uncorrected. Melting points were determined on a Mettler EP2 apparatus. IR spectra were measured with a Hitachi EPI-G3 grating infrared spectrophotometer on liquid films unless otherwise stated. ^{1}H NMR spectra were registered on a Varian A-60D spectrometer from $CDCl_3$ solutions and are reported in δ from tetramethylsilane as an internal standard. Optical rotations were obtained with a Union PM-71 polarimeter. UV spectra were recorded on a Hitachi EPS-3T spectrometer, and CD spectra were registered with a Jasco J-20 automatic recording spectropolarimeter. Silica gel for column chromatography refers to Merck Kieselgel 60 (70–230 mesh ASTM). Organic extracts were washed with saturated aqueous sodium chloride and dried over sodium sulfate before solvent removal.

Optical Resolution of *endo-cis*-Bicyclo[3.3.0]oct-7-en-2-ol (1) via Camphanates (2a and 2b). A solution of (±)-alcohol **1**[4] (6.18 g, 49.8 mmol) in dry pyridine (75 mL) was dropped into an ice-cold, stirred solution of (−)-camphanyl chloride[5] (15.0 g, 69.2 mmol) in dry pyridine (75 mL). The mixture was allowed to stand overnight, poured onto water (1 L), and extracted with benzene (3 × 150 mL). The organic layer was washed with 2 N hydrochloric acid (9 × 100 mL) and 5% aqueous sodium bicarbonate. Evaporation of solvent gave a colorless solid (14.36 g, 94.8%). Recrystallization from hexane (three times) and methanol (twice) gave 3.44 g of **2a**: mp 111.4–111.8 °C; $[\alpha]^{18}_{589}$ +129.0° (*c* 0.592, ethanol); IR (KBr disk) 3050, 1785, 1738 cm^{-1}; NMR δ 0.96, 1.04, 1.10 (3 H each, s each, methyls), 1.20–2.90 (12 H, m), 5.30 (1 H, q, *J* = 6 Hz, –CH–OCO), 5.44 (1 H, m, olefinic), 5.75 (1 H, m, olefinic).

Anal. Calcd for $C_{18}H_{24}O_4$: C, 71.02; H, 7.95. Found: C, 70.78; H, 8.02.

Crystals from the mother liquor of the first recrystallization were recrystallized from methanol (twice) to give 0.88 g of **2b**: mp 78.8–80.6 °C; $[\alpha]^{20}_{589}$ −139.8° (*c* 0.661, ethanol); IR (KBr disk) 3060, 1780, 1740 cm^{-1}; NMR δ 0.97, 1.04, 1.10 (3 H each, s each, methyls), 1.30–2.90 (12 H, m), 5.25 (1 H, q, *J* = 6 Hz, –CH–OCO), 5.46 (1 H, m, olefinic), 5.76 (1 H, m, olefinic).

Anal. Calcd for $C_{18}H_{24}O_4$: C, 71.02; H, 7.95. Found: C, 71.10; H, 8.01.

All mother liquors were combined and concentrated to give a crude diastereomeric mixture which was chromatographed on silica gel (200 g) with benzene–ethyl acetate (100:1, 200-mL fraction). The ratio of **2a** and **2b** in each fraction was checked by LC (Merk SI-100, 8 × 500 mm; 10:3 *n*-hexane–ether solvent. Retention time: **2a**, 19 min; **2b**, 17 min.), and the crystals from each fraction were again fractionally recrystallized to give **2a** or **2b**, according to its diastereomeric content.

(+)-3-(Camphanyloxy)-2-(oxycarbonyl)cyclopentaneacetic Acid (3). (+)-**2a** (3.0 g, 9.86 mmol) was treated with sodium metaperiodate (11.4 g) and ruthenium dioxide (0.15 g) by the procedure reported elsewhere.[13] The crude product was passed through a silica gel column (20 g) with ether to give 3.42 g (94.2%) of a colorless solid, which was recrystallized from ethyl acetate–benzene (3:8) to yield colorless prisms of **3** (2.50 g): mp 157.0–157.4 °C; $[\alpha]^{15}_{589}$ +3.16°, $[\alpha]^{15}_{405}$ +7.77° (*c* 1.65, ethanol); IR (KBr disk) 1780, 1742, 1710 cm^{-1}; NMR δ 0.95, 1.06, 1.11 (3 H each, s each, methyls), 1.50–2.50 (4 H, m), 2.53 (3 H, br s, methine and –CH_2CO), 3.33 (1 H, m, –CH–CO), 5.58 (1 H, q, *J* = 5.5 Hz, –CH–OCO), 11.56 (2 H, s, COOH).

Anal. Calcd for $C_{18}H_{24}O_8$: C, 58.69; H, 6.57. Found: C, 58.84; H, 6.59.

(−)-Methyl 3-Hydroxy-2-(methoxycarbonyl)cyclopentaneacetate (5). A solution of (+)-**3** (2.35 g, 6.38 mmol) in absolute methanol (150 mL) and concentrated sulfuric acid (1 mL) was refluxed for 20 h. Sodium bicarbonate (5.5 g) was added, and after stirring the solid was filtered off. The filtrate was concentrated under reduced pressure, diluted with saturated aquous sodium chloride (50 mL), and extracted with ether (3 × 50 mL). The ether layer was washed with saturated aqueous sodium bicarbonate. Solvent removal left an oil (2.62 g) which was chromatographed on silica gel (90 g). Elution with benzene (100-mL fractions) gave, successively, **7** [34 mg; $[\alpha]^{24}_{589}$ +54.1° (*c* 0.821, carbon tetrachloride); IR 3070, 1743, 1726, 1630 cm^{-1}; NMR δ 1.50–3.70 (7 H, m), 3.73, 3.80 (3 H each, s each, OCH_3), 6.90 (1 H, m, olefinic)], **4** (516 mg), **6** [2.1 g; $[\alpha]^{15}_{589}$ −4.87° (*c* 1.85, ethanol); IR 1780, 1730 cm^{-1}; NMR δ 0.96, 1.06, 1.12 (3 H each, s each, methyls), 1.60–2.50 (4 H, m, –CH_2–), 2.58 (3 H, m, –CH– and –CH_2CO–), 3.30 (1 H, t, *J* = 6.5 Hz, –CH–CO), 3.71 (6 H, s, OCH_3), 5.53 (1 H, q, *J* = 6.5 Hz, –CH–OCO)], and **5** (439 mg).

(−)-**6** (1.7 g) was refluxed for 7 days with anhydrous methanol (200 mL) saturated with hydrogen chloride. After evaporation of solvent, the reaction mixture was treated in the usual manner to give 1.6 g of an oil which was chromatographed (silica gel, 80 g) to yield 597 mg of **4** and 626 mg of **5**. Recrystallization of **4** from benzene–*n*-hexane (1:5) afforded colorless rods: mp 108.4–108.5 °C; $[\alpha]^{15}_{589}$ −12.4° (*c* 2.17, ethanol); IR (KBr disk) 1783, 1730 cm^{-1}; NMR δ 0.98, 1.08, 1.13 (3 H each, s each, methyls), 1.60–2.80 (4 H, m, –CH_2–), 3.88 (3 H, s, OCH_3).

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.22; H, 7.57.

Distillation of **5** at 120 °C (bath temperature) under reduced pressure (3 mmHg) gave a colorless oil: $[\alpha]^{15}_{589}$ −11.8° (*c* 2.09, ethanol); IR 3500, 1735 cm^{-1}; NMR δ 1.70–3.10 (8 H, m), 3.70, 3.75 (3 H each, s each, OCH_3), 3.58 (1 H, br s, OH), 4.45 (1 H, m, –CH–O).

Anal. Calcd for $C_{10}H_{16}O_5$: C, 55.54; H, 7.46. Found: C, 55.51; H, 7.50.

(−)-Methyl 2-(Methoxycarbonyl)-3-oxocyclopentaneacetate (8). A 1.1-mL amount of Jones' reagent (CrO_3, 10 g; H_2SO_4, 10 mL; H_2O, 25 mL) was added dropwise to an ice-cold solution of (−)-**5** (810 mg, 3.75 mmol) in acetone (30 mL). After stirring for 3 min, the reaction mixture was diluted with benzene (300 mL), passed through a Celite column, and concentrated. The product was chromatographed on silica gel (30 g) eluting with benzene–ether (15:1) to yield 628 mg of **8** (78%) and recovered **5** (147 mg, 18% recovery). **8** was distilled at 130 °C (bath temperature) under 4 mmHg to give a colorless oil: $[\alpha]^{18}_{589}$ −66.8° (*c* 1.42, methanol); IR 1730–1770 cm^{-1}; NMR δ 1.10–3.40 (4 H, m), 3.72, 3.80 (3 H each, s each, OCH_3); UV (methanol) λ_{max} 290 sh (ε 54.5), 252 (490), 237 sh (398) nm; CD (methanol) Δε (nm) −1.65 (295), +0.028 (237).

Anal. Calcd for $C_{10}H_{14}O_5$: C, 56.07; H, 6.59. Found: C, 56.13; H, 6.70.

(−)-3-Oxocyclopentaneacetic Acid (9) via (−)-Methyl 3-Oxocyclopentaneacetate (10). The ester **8** (579 mg, 2.7 mmol) was mixed with concentrated hydrochloric acid (130 mL) and refluxed for 5 h. Removal of hydrochloric acid by repeated azeotropic distillation with benzene under reduced pressure gave a brown oil of **9** (400 mg), $[\alpha]^{20}_{589}$ −116.5° (*c* 6.99, chloroform). Crude acid **9** was mixed with methanol (50 mL) containing 1 mL of concentrated hydrochloric acid and refluxed overnight. The reaction mixture was worked up in the usual way to give 333 mg of a colorless oil, which was chromatographed on silica gel (30 g) with benzene–ether (10:1, 30-mL fractions). Fractions 6–10 gave 304 mg of **10** in 72% yield from the ketone **8**. Vacuum distillation (3 mmHg) of **10** at 100 °C (bath temperature) afforded 268 mg of a colorless oil: $[\alpha]^{18}_{589}$ −115.4° (*c* 1.13, methanol), $[\alpha]^{18}_{589}$ −121.0° (*c* 1.47, chloroform); IR 1740 cm^{-1}; NMR δ 1.40–2.80 (9 H, m), 3.73 (3 H, s, OCH_3); UV (methanol) λ_{max} 286.5 (ε 23.0), 205 sh (99.2) nm; CD (methanol) Δε (nm) −1.82 (291), −0.022 (207.5).

Anal. Calcd for $C_8H_{12}O_3$: C, 61.59; H, 7.75. Found: C, 61.80; H, 7.84.

A solution of (−)-**10** (122 mg, 0.783 mmol) in methanol (5 mL) and water (1 mL) with potassium hydroxide (100 mg) was allowed to stand for 3 h and diluted with water (20 mL). After washing with ether, the aqueous layer was acidified with concentrated hydrochloric acid (5

mL) and extracted five times with ether. After the usual workup, solvent removal gave 72 mg of the acid **9**: $[\alpha]^{23}_{589}$ −115.5° (*c* 1.42, chloroform); IR 3400–2400, 1740 cm^{-1}; NMR δ 1.00–3.00 (9 H, m), 10.96 (1 H, s, COOH).

(1*R*,2*R*,5*R*)-(+)-Bicyclo[3.3.0]oct-7-en-2-ol (1). A solution of (+)-**2a** (3.0 g, 9.86 mmol) in ethanol (150 mL) was mixed with a solution of potassium hydroxide (1.5 g) in water (20 mL) and refluxed for 1.5 h. After the usual workup, the reaction product was chromatographed on silica gel (10 g) with benzene–ether (2:1) to give a colorless oil of **1** (1.14 g, 92.7%): bp 50 °C at 3 mmHg; $[\alpha]^{20}_{589}$ +210.6° (*c* 0.729, methanol); IR 3350, 3045 cm^{-1}; NMR δ 1.00–3.50 (9 H, m), 4.23 (1 H, m, –CH–O), 5.78 (2 H, m, olefinic); UV (methanol) ε 4300 (197 nm);[14] CD (methanol) Δε +11.4 (195 nm).[14]

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.00; H, 9.85.

Registry No.—(+)-**1**, 68366-26-7; (±)-**1**, 68317-62-4; **2a**, 68317-63-5; **2b**, 68422-21-9; **3**, 68317-64-6; **4**, 54200-35-0; **5**, 68366-27-8; **6**, 68317-65-7; **7**, 68317-66-8; **8**, 68366-28-9; **9**, 2630-37-7; **10**, 2630-38-8; (−)-camphanyl chloride, 39637-74-6.

References and Notes

(1) J. K. Whitesell and A. M. Helbling, *J. Chem. Soc., Chem. Commun.*, 694 (1977); J. K. Whitesell and R. S. Matthews, *J. Org. Chem.*, **43**, 1650 (1978).
(2) W. Klyne and J. Buckingham, "Atlas of Stereochemistry", Chapman and Hall, London, 1974. The absolute configuration of *trans*-bicyclo[3.3.0]-octan-3-one has already been established.
(3) H. Kuritani, F. Iwata, M. Sumiyoshi, and K. Shingu, *J. Chem. Soc., Chem. Commun.*, 542 (1977); H. Kuritani, M. Sumiyoshi, F. Iwata, and K. Shingu, *ibid.*, 543 (1977); M. Sumiyoshi, H. Kuritani, and K. Shingu, *ibid.*, 812 (1977).
(4) J. K. Crandall and L. Cheng, *J. Org. Chem.*, **32**, 532 (1967).
(5) H. Gerlach, *Helv. Chim. Acta*, **51**, 1587 (1968).
(6) Diastereomeric purity was ascertained by LC; see Experimental Section.
(7) R. K. Hill and A. G. Edwards, *Tetrahedron*, **21**, 1501 (1965).
(8) K. Mislow and I. V. Steinberg, *J. Am. Chem. Soc.*, **77**, 3807 (1955).
(9) According to Mislow's work,[8] 47% optically pure 3-(oxycarbonyl)adipic acid was obtained by the ozonolysis of **11** (98% optically pure), which was attributed to the racemization during the oxidation.[10] However, from Hill's work,[7] this result seems to be attributable to the incomplete resolution of **11**.[11]
(10) Footnotes 41 and 43 in ref 8.
(11) Recently, an unsuccessful attempt was reported to obtain optically pure **11** by the resolution via brucine salt: O. L. Chapman, K. C. Mattes, R. S. Sheridan, and J. A. Klun, *J. Am. Chem. Soc.*, **100**, 4878 (1978).
(12) The referee kindly informed us that he has also resolved the alcohol **1** via the α-methylbenzylamineurethane and that (−)-**1** ($[\alpha]^{23}_D$ −123.7°, chloroform) correlates to (−)-*cis*-bicyclo[3.3.0]octan-2-one ($[\alpha]^{25}_D$ −105.2°, chloroform) with a negative Cotton effect in the n → π* region, which predicts 2*S* configuration for (−)-**1** on the basis of the octant rule. He suggests that his work and our result confirm that the octant rule correctly predicts the absolute configuration in the *cis*-bicyclo[3.3.0]octane series. We would like to thank him for providing his unpublished result and for his helpful suggestions.
(13) S. W. Pelletier, K. N. Iyer, and C. W. J. Cheng, *J. Org. Chem.*, **35**, 3535 (1970).
(14) The shortest wavelength reached, not maximum.

Rate Decelerations in the Acetolysis of Substituted Cyclopentyl Tosylates

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A comparison of the acetolysis rates of geminally polymethylated secondary cyclopentyl tosylates to cyclopentyl tosylate showed a small rate deceleration in each case.[1] Two factors were considered to be responsible for the rate decelerations: (a) nonbonded repulsions in the transition state greater than in the ground state, and (b) a steric inhibition of effective solvation at the back side of the departing tosyloxy group at the transition state.

In an attempt to separate these factors, it was of interest to study the acetolysis rates of 2-indanyl tosylate (III) and 1,1,3,3,-tetramethyl-2-indanyl tosylate (IV). In this model indanyl system, the importance of factor (a) is greatly reduced (if not eliminated entirely) and the five-membered ring is probably in an envelope conformation of limited mobility.[2] More importantly, inspection of a model of IV suggests that the methyl substituents exert an "umbrella" effect in shielding the approach of solvent to the rear or the front of the carbon bearing the leaving group. The purpose of this paper is to present some data on these systems and discuss them in the light of solvolyses which are limiting (k_c) and/or nucleophilically solvent assisted (k_s).[3,4]

Inspection of the data in Table I reveals that a decrease in the acetolysis rate results when geminal dimethyl groups are adjacent to the reaction site. This rate retardation is most striking in the case of IV. Compound IV undergoes acetolysis 14 250 times slower than I. Moreover, despite similar conformational requirements and the same rate-retarding inductive effect of the benzene ring, IV undergoes acetolysis 299 times slower than III at 25 °C.

In general, increasing the conformational rigidity of the five-membered ring results in a decrease in the solvolysis rates of cyclopentyl derivatives. Meinwald[8] noted that the tosylate of *trans*-bicyclo[3.2.0]heptan-3-ol (half-chair conformation) solvolyzed 55 times slower than cyclopentyl tosylate at 75 °C. Winstein and Sonnenberg[9] subjected Δ^3-cyclopentenyl tosylate and *trans*-3-bicyclo[3.1.0]hexyl tosylate (envelope conformation) to acetolysis conditions at 50 °C and found the rates to be 8.3 and 16 times slower than cyclopentyl tosylate, respectively. The methanolysis of 2-indanyl tosylate has been reported to proceed 20 times slower than the methanolysis of cyclopentyl tosylate at 50 °C.[10]

In the results reported here, it is suggested that the effect of methyl participation is not of importance in system IV. If this were the case, methyl bridging should lead to a rate enhancement by formation of the methyl-substituted 1-indanyl cation as the first intermediate. A rate accelerating inductive effect due to the methyl groups should also be operative. Conformational effects and the effect of π-participation would also not seem to be of primary importance in the rate comparisons of III and IV. The relevant carbonyl stretching frequencies (measured in dilute carbon tetrachloride solution with a calibrated Perkin-Elmer Model 21 spectrophotometer) for the ketones corresponding to III and IV are 1755 and 1751 cm^{-1}—a trend of predicted faster acetolysis for IV compared to III based on the angle effect.[11]

Recently, Schleyer and co-workers carried out a detailed study of secondary systems without participating neighboring groups. The key compound in this work was 2-adamantyl tosylate for which nucleophilic participation by the solvent was expected to be a minimum. Support was convincing for a highly destabilized transition state resulting from severe steric interaction between the entering and leaving groups and the axial hydrogen atoms of the ring system.[3,4] Once nucleophilic solvent assistance was shown to be small for 2-adamantyl derivatives, it became possible to use the adamantyl system as a standard against which solvent assistance in the solvolysis of other secondary derivatives could be compared.[4]

Arguments similar to these proposed by Schleyer and coworkers for the slow rate of solvolysis of 2-adamantyl tosylate are applicable to the slow acetolysis rate of IV. Indeed, models of this system suggest that IV might even more severely inhibit solvent approach to the incipient electropositive carbon than 2-adamantyl tosylate. Hence, it appears that the main factor influencing the observed rate deceleration of IV (299 times

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