Absolute Configuration of Dimethyl *tert*-Butylsuccinate and *tert*-Butyl-α-naphthylacetic Acid: Degradation of the Aromatic Ring with Ruthenium Tetroxide

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Received March 21, 1979

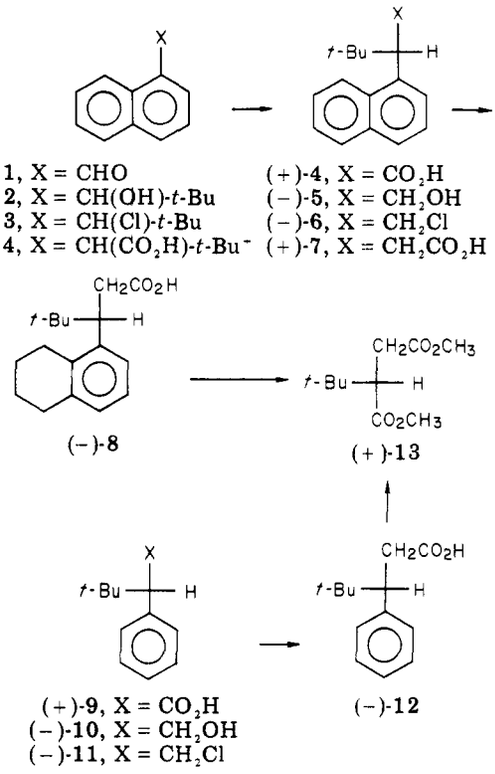
Recently we reported a modification of Horeau's method for the determination of the absolute configuration of aryl-*tert*-butylacetic acid, assigning the *S* configuration to (+)-*tert*-butyl-α-naphthylacetic acid (**4**).[1] To confirm the effectiveness of such an empirical method, a direct chemical correlation of **4** with a configurationally established compound seems to be necessary.

The chemical correlation of compounds with *tert*-butyl groups at the asymmetric center has been laborious because of the limited kinds of route to elaborate the *tert*-butyl group and because of few key compounds of known configuration having the *tert*-butyl group.[2-5] Similarly, very few chiral compounds with the naphthyl group at the chiral center have so far been correlated by the chemical route,[2] although the method of quasiracemates was utilized in some compounds.[6] In particular, degradation of the naphthalene ring to a carboxyl group by ozonolysis usually resulted in a very poor yield.[7]

In this paper, we report the establishment of the absolute configuration of hitherto unknown dimethyl *tert*-butylsuccinate (**13**), one of the most important key compounds for the configuration assignment of a chiral tertiary carbon atom attached by a *tert*-butyl group,[8] through its chemical correlation with *tert*-butylphenylacetic acid (**9**) of known configuration.[4] An unambiguous interrelation of naphthalene compound **4** to **13** has also been presented.

The correlation course is summarized in Scheme I. The key step for this correlation is the direct degradation of the aromatic ring into a carboxyl group by the use of ruthenium tetroxide.[9] After some unsuccessful trials, it was found that the presence of the carboxyl or carboxylate group in the substrate is a desirable requisite for obtaining satisfactory results[10] (see Table I). Furthermore, **4** needed to be converted into the tetralin compound **8** prior to the degradation since naphthalene compounds are known to resist complete oxidation.[9,11]

Scheme I



Optical resolution of **9** was much more easily achieved with brucine followed by cinchonine than by using the previous method,[12] giving both the enanthiomers in high yields (more than 70%). (*S*)-(+)-**9**, $[\alpha]_{589}$ +48.0° (ethanol), was converted successively into (*S*)-(−)-**10**, $[\alpha]_{589}$ −16.4° (ethanol), (*S*)-(−)-**11**, $[\alpha]_{589}$ −30.7° (*n*-hexane), and (*S*)-(−)-**12**, $[\alpha]_{589}$ −15.8° (ethanol),[13] according to Mosher's procedure[12] except for some modification in the method of preparation of **11** (triphenylphosphine and carbon tetrachloride).[14]

Oxidation of (*S*)-(−)-**12** with ruthenium dioxide and sodium periodate in aqueous acetone followed by esterification with diazomethane afforded (+)-dimethyl *tert*-butylsuccinate (**13**), $[\alpha]_{589}$ +12.4° (ethanol), in 63% yield. Thus the absolute configuration of **13** has been established as (*S*)-(+).

tert-Butyl-α-naphthylacetic acid (**4**) was prepared from α-naphthaldehyde (**1**)[15] via the carbinol **2** and the chloride

(1) Kuritani, H.; Imajo, S.; Shingu, K.; Nakagawa, M. *Tetrahedron Lett.* **1979**, 1697.

(2) Brewster, J. H. "Elucidation of Organic Structures by physical and Chemical Methods", Bently, L. W.; Kirby, G. W., Eds.; Wiley-Interscience: New York, 1972; Part III. Klyne, W.; Buckingham, J. "Atlas of Stereochemistry"; Chapman and Hall: London, 1974. Gros, J. J. C.; Bourcier, S. "Stereochemistry, Fundamentals and Methods", Kagan, H. B., Ed.; Georg Thieme: Stuttgart, 1977; Vol. 4.

(3) Jacobus, J.; Majerski, Z.; Mislow, K.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1969**, *91*, 1998.

(4) Clark, D. R.; Mosher, H. S. *J. Org. Chem.* **1970**, *35*, 1114.

(5) Bellucci, G.; Ingrosso, G.; Marsili, A.; Mastrorilli, E.; Morelli, I. *J. Org. Chem.* **1977**, *42*, 1079.

(6) Sjöberg, B. *Ark. Kemi* **1958**, *13*, 1.

(7) Nakazaki, K.; Arakawa, H. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 464. Cervinka, O.; Belovsky, O. *Z. Chem.* **1967**, *7*, 226. Hayashi, Y.; Lawson, W. B. *J. Biol. Chem.* **1969**, *244*, 4158.

(8) Numerous lower monoalkylsuccinic acids (except for alkyl = *tert*-butyl) were correlated with each other and with malic acid by the stepwise application of the quasiracemate technique. Fredga, A. *Tetrahedron* **1960**, *8*, 126, and references cited therein. The configuration of methylsuccinic acid has been unequivocally defined by the X-ray study of ergoflavin. Mc Phail, A. T.; Sim, G. A.; Asher, J. D. M.; Robertson, J. M.; Silverton, J. V. *J. Chem. Soc. B* **1966**, 18.

(9) Lee, D. G.; v. d. Engh, M. "Oxidation in Organic Chemistry"; Trahanovsky, W. S., Ed.; Academic Press: New York, 1973; p 1. Rylander, P. N. "Organic Synthesis with Noble Metal Catalyst"; Academic Press: New York, 1973; p 133.

(10) Another course of correlation (following scheme) gave an unsuccessful result on account of the low yield and the difficulties in purification of the degradation product.

aryl-CH(*t*-Bu)CO_2H → aryl-CH(*t*-Bu)CH_3 → HO_2CCH(*t*-Bu)CH_3

The points pertinent to the degradation reaction with ruthenium tetroxide we have achieved are listed in Table I.

(11) The identified products were usually phthalic acid derivatives.

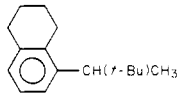
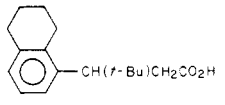
(12) Aaron, C.; Dull, D.; Schmiegel, J. L.; Jaeger, D.; Ohashi, Y.; Mosher, H. S. *J. Org. Chem.* **1967**, *32*, 2797.

(13) $[\alpha]_D^{25}$ −22.4° ($CHCl_3$) is reported. Almy, J.; Cram, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 4459. Incorrect stereochemical nomenclature was used.

(14) Downie, I. M.; Holmes, J. B.; Lee, J. B. *Chem. Ind. (London)* **1966**, 900. Lee, J. B.; Downie, I. M. *Tetrahedron*, **1967**, *23*, 359. When thionyl chloride was used as the reagent, the product was contaminated by a 20–30% amount of an olefin.

0022-3263/79/1944-3587$01.00/0

Table I

starting material[a]	equiv of oxidant[b]	reaction[c] time, h	reaction products (yield, %)
$PhCH(t\text{-}Bu)CH_3$	4.2	65.0	$HO_2CCH(t\text{-}Bu)CH_3$ (13)
$PhCH(t\text{-}Bu)CO_2CH_3$	2.4	4.0	$HO_2CCH(t\text{-}Bu)CO_2CH_3$ (92)
$PhCH(t\text{-}Bu)CH_2CO_2CH_3$	3.8	46.5	I, $CH_3O_2CCH(t\text{-}Bu)CH_2CO_2CH_3$[d] (57) II, $CH_3O_2CCOCH(t\text{-}Bu)CH_2CO_2CH_3$[d] (12)
$PhCH(t\text{-}Bu)CH_2CO_2H$[e]	5.7	66.0	I (63), II (9)[d]
$PhCH(t\text{-}Bu)CH_2CH(CO_2CH_3)CH_2CH(t\text{-}Bu)Ph$	1.2	44.0	$HO_2CCH(t\text{-}Bu)CH_2CH(CO_2CH_3)CH_2CH(t\text{-}Bu)CO_2H$ (89)
$PhCH(t\text{-}Bu)CH_2CH(CO_2H)CH_2CH(t\text{-}Bu)Ph$[e]	3.0[f]	40.7	$CH_3O_2CCH(t\text{-}Bu)CH_2CH(CO_2CH_3)CH_2CH(t\text{-}Bu)COCO_2CH_3$[d] (15) $CH_3O_2CCOCH(t\text{-}Bu)CH_2CH(CO_2CH_3)CH_2CH(t\text{-}Bu)COCO_2CH_3$[d] (37)
	3.1	21.0	$HO_2CCH(t\text{-}Bu)CH_3$ (trace)
	7.4	70.5	$CH_3O_2CCH(t\text{-}Bu)CH_2CO_2CH_3$[d] (33)

[a] Racemates or diastereomeric mixtures were used unless otherwise noted. [b] $NaIO_4$ in water–acetone (1:1) was used unless otherwise noted. [c] All reactions were carried out at room temperature. [d] Esterified with diazomethane. [e] The optically active form was used. [f] $NaIO_4$–$HIO_4 \cdot H_2O$ (1:1) in water–*t*-BuOH (1:1) was used.

3. Its optical resolution via brucine salt also gave both antipodes in good yields.

(+)-3-*tert*-Butyl-3-α-naphthylpropionic acid (**7**), $[\alpha]_{589}$ +33.2° (ethanol), was prepared from (+)-**4**, $[\alpha]_{589}$ +119° (ethanol), by a similar route as **12** was prepared. (+)-**7** was hydrogenated over Adams catalyst to afford the tetrahydronaphthyl compound (−)-**8**, $[\alpha]_{589}$ −18.8° (ethanol). This was degraded with ruthenium tetroxide and esterified to give (+)-**13** (31% yield), which showed nearly the same optical rotation as the sample derived from (*S*)-(−)-**12**.

From this interrelation, the absolute configuration of the acid **4** was unequivocally established as (*S*)-(+), since any reaction involved in the correlation does not affect the asymmetric center. This result is consistent with the previously assigned configuration by the use of the kinetic resolution method,[1] whose effectiveness has therefore been corroborated. In addition, the degradation of the tetralin skeleton with ruthenium tetroxide we adopted here will provide an effective method of chemical correlation of naphthalene compounds.

Experimental Section

Melting and boiling points are uncorrected. Melting points were determined on a Mettler EP2 apparatus. IR spectra were obtained on KBr pellets or liquid films with a Hitachi EPI-G3 grating infrared spectrophotometer. ^1H NMR spectra were registered on a Varian A-60D spectrometer from $CDCl_3$ solutions, using tetramethylsilane as the internal standard. Optical rotations were measured with a Union PM-71 polarimeter in ethanol solutions unless otherwise stated. Silica gel for column chromatography refers to Merck Kieselgel 60 (70–230 mesh ASTM). Organic extracts were washed with saturated NaCl solution and dried over $MgSO_4$ before the solvent was removed.

***tert*-Butyl-α-naphthylcarbinyl Chloride (3).** To a stirred solution of *tert*-butylmagnesium chloride prepared from magnesium (110.6 g), *tert*-butyl chloride (514 g), and absolute ether (2 L) was added at 0 °C a solution of α-naphthaldehyde[15] (259.2 g) in absolute ether (1.5 L) over a 6-h period. The reaction mixture was stirred overnight at room temperature and hydrolyzed with 6 N HCl. After the usual workup, the product was distilled under high vacuum to give 206.9 g of oil, bp 120–130 °C (5×10^{-3} mm), which was added over a 4-h period to thionyl chloride (629 g) cooled with an ice bath. After the solution had been left to stand overnight, most of the excess thionyl chloride was evaporated, and the residue was poured onto ice, extracted with ether, and worked up in the usual way. The resulting brown oil was chromatographed three times on silica gel (800 g), eluting with *n*-hexane. Evaporation and high vacuum distillation of the eluate yielded the colorless oil of **3** (100.6 g, 26%): bp 119–121 °C (5×10^{-3} mm); NMR δ 1.06 (s, *tert*-butyl), 5.80 (s, methine), 7.23–8.18 (m, aromatic).

Anal. Calcd for $C_{15}H_{17}Cl$: C, 77.40; H 7.36; Cl, 15.23. Found: C, 77.38, H, 7.35; Cl, 15.13.

(±)-*tert*-Butyl-α-naphthylacetic Acid (4). The chloride (**3**) (78.0 g) was converted to the Grignard reagent in THF (700 mL) with magnesium sands (8.3 g). The reaction was conducted under dry N_2 gas at 40 °C and initiated by the addition of ethylene dibromide (3.2 g). The Grignard solution was stirred vigorously under dry CO_2 atomsphere for 3 h at a temperature below 15 °C. Water and 6 N HCl were added, and the organic layer was separated, washed, and extracted with 4% NaOH. The aqueous layer was acidified with HCl and extracted with ether, and the ether layer was washed, dried, and evaporated. The crystalline residue was washed with benzene–*n*-hexane (1:1) and recrystallized from benzene to give colorless prisms of **4** (39.9 g, 49%): mp 202.0–203.1 °C; NMR δ 1.06 (s, *tert*-butyl), 4.53 (s, methine), 7.27–7.91 (m, 6 H, aromatic), 8.03–8.25 (m, 1 H, aromatic); IR 1700 cm^{-1} ($\nu_{C=O}$).

Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.34; H, 7.46.

Resolution of *tert*-Butyl-α-naphthylacetic Acid (4). A mixture of (±)-**4** (70 g), brucine dihydrate (124.5 g), and methanol (1.85 L) was heated, and 0.85 L of methanol was removed by distillation. The solution was allowed to cool slowly to give 91.65 g of salt, which was recrystallized twice from methanol to yield 76.65 g of pure salt: mp 108 °C dec; $[\alpha]_{589}$ +11.5° (*c* 0.511). Regeneration with 3 N HCl in the cold gave, after recrystallization from benzene–*n*-hexane, colorless leaflets of (+)-**4** (24.65 g): mp 170.1–172.2 °C; $[\alpha]_{589}$ +119°, $[\alpha]_{405}$ +330° (*c* 0.295).

The mother liquor of the first crop of resolution was concentrated to 400 mL, and 100 mL of hot water was added. The crystals deposited on standing at room temperature were filtered off, and the noncrystalline residue obtained on evaporating the filtrate was treated with 3 N HCl, giving 25.8 g of (−)-**4**, $[\alpha]_{589}$ −114°, which was recrystallized from benzene–*n*-hexane to afford 18.8 g of (−)-**4**; $[\alpha]_{589}$ −118° (*c* 0.677).

(−)-2-*tert*-Butyl-2-(α-naphthyl)ethanol (5). To a mixture of $LiAlH_4$ (15 g) and absolute ether (250 mL) cooled in an ice bath was added dropwise a solution of (+)-**4** (13.0 g) in absolute THF (150 mL). The mixture was refluxed with stirring for 22.5 h, and water (50 mL) was added by portions to decompose excess $LiAlH_4$. The white precipitates were filtered, and the filtrate was dried and evaporated. The resulting colorless crystals of **5** (12.1 g, 98%) were used for further preparation without purification. Re-

(15) Angyal, S. J.; Tetraz, J. R.; Wilson, J. G. "Organic Synthesis"; Wiley: New York, 1963; Collect. Vol. IV, p 690.

crystallization of the crude alcohol from *n*-hexane gave colorless prisms of (-)-**5**: mp 78.3–79.9 °C (racemate; oil); $[\alpha]_{589}$ -39.9° (*c* 0.490); NMR δ 0.87 (s, *tert*-butyl), 1.33 (s, hydroxyl), 3.57–4.10 (m, methylene and methine), 7.23–7.88 (m, 6 H, aromatic), 8.05–8.33 (m, 1 H, aromatic); IR 3550, 3370 cm^{-1} (ν_{OH}).

Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.06; H, 8.82.

(-)-2-*tert*-Butyl-1-chloro-2-(α-naphthyl)ethane (6). A mixture of (-)-**5** (10.7 g), triphenylphosphine (14.8 g), and CCl_4 (300 mL, previously dried over molecular sieves 3A) was refluxed with stirring for 70 h. Methanol (5 mL) was added, and the mixture was refluxed for 3 h to decompose excess triphenylphosphine. The solvent was evaporated, *n*-hexane was added, and the precipitates were filtered. The residue obtained on evaporating the filtrate was dissolved in *n*-hexane and passed through a column of silica gel (80 g). The eluate was concentrated to yield crystals of **6** which were recrystallized from methanol to give colorless prisms (8.8 g, 76%): mp 79.0–80.4 °C (racemate; mp 61.8–63.5 °C); $[\alpha]_{589}$ -7.9° (*c* 1.414, isooctane); NMR δ 0.96 (s, *tert*-butyl), 3.78–4.26 (m, methylene and methine), 7.32–7.97 (m, 6 H, aromatic), 8.08–8.30 (m, 1 H, aromatic).

Anal. Calcd for $C_{16}H_{19}Cl$: C, 77.87; H, 7.76; Cl, 14.37. Found: C, 77.86; H, 7.84; Cl, 14.15.

(+)-*tert*-Butyl-3-(α-naphthyl)propionic Acid (7). A mixture of (-)-6 (2.997 g), ethylene dibromide (0.428 g), well-dried magnesium sands (0.350 g), and absolute THF (40 mL) was refluxed with stirring for 32 h under dry N_2 gas. The Grignard reagent was carboxylated in a similar manner as that used in the case of **4**. Recrystallization of the resulting acid from *n*-hexane yielded colorless rods of **7** (2.201 g, 71%): mp 99.4–100.7 °C (racemate; mp 179.8–180.4 °C); $[\alpha]_{589}$ +33.2° (*c* 0.849); NMR δ 0.88 (s, *tert*-butyl), 2.80, 2.87 (AB part of ABX pattern, $|J_{AB}|$ = 15.8 Hz, $|J_{AX}|$ = 12.2 Hz, $|J_{BX}|$ = 3.5 Hz, methylene), 4.02 (X part of ABX pattern, $|J_{AX} + J_{BX}|$ = 15.7 Hz, methine), 7.28–7.88 (m, 6 H, aromatic), 8.08–8.38 (m, 1 H, aromatic), 9.50 (bs, carboxyl).

Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.65; H, 7.87.

(-)-3-*tert*-Butyl-3-(1′,2′,3′,4′-tetrahydro-5′-naphthyl)-propionic Acid (8). A mixture of (+)-**7** (1.245 g), platinum dioxide (0.3 g), ethyl acetate (24 mL), and acetic acid (6 mL) was stirred vigorously under a hydrogen atomsphere for 19.5 h. The catalyst was removed, and the oil obtained on evaporating the solvent was chromatographed on silica gel (10 g). Benzene and benzene–ether (1:1) eluates were concentrated to give an oil which crystallized on trituration with *n*-pentane. Recrystallization from *n*-pentane afforded colorless rods of **8** (1.072 g, 85%): mp 104.3–106.0 °C (racemate; mp 161.0–163.6 °C); $[\alpha]_{589}$ -18.8° (*c* 0.821); NMR δ 0.92 (s, *tert*-butyl), 1.55–1.90 (m, 4 H, methylenes), 2.58–2.97 (m, 6 H, methylenes), 3.42 (dd, $|J_{AX} + J_{BX}|$ = 15 Hz, methine), 6.90–7.03 (m, aromatic), 8.75 (bs, carboxyl); IR 1705 cm^{-1} ($\nu_{C=O}$).

Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.17; H, 9.27.

Resolution of *tert*-Butylphenylacetic Acid (9). (±)-**9**[12] (80 g) was mixed with brucine dihydrate (124.5 g) in warm methanol (2.15 L), and 0.85 L of methanol was removed by distillation. The salt deposited on cooling (126.8 g) was recrystallized twice from methanol to afford 115.4 g of pure salt: mp 110 °C dec; $[\alpha]_{589}$ -58.7° (*c* 0.358). Regeneration with 2 N HCl and recrystallization from *n*-hexane afforded 31.7 g of colorless needles: mp 140.8–141.5 °C; $[\alpha]_{589}$ -48.2° (*c* 2.351).

The mother liquor of the first crop of resolution was concentrated and acidified with HCl to give 39.8 g of crude (+)-**9**, $[\alpha]_{589}$ +43.4° (*c* 2.478), which was mixed with 60.9 g of cinchonine in warm methanol (0.8 L), and 0.25 L of hot water was added. The salt deposited on cooling was recrystallized from methanol–water (5:2), giving 72.5 g of pure crystals: mp 198 °C dec; $[\alpha]_{589}$ -142.8° (*c* 1.094). Regeneration with HCl and recrystallization from *n*-hexane gave 28.75 g of (+)-**9**: $[\alpha]_{589}$ + 48.0° (*c* 2.279), lit.[12] $[\alpha]_{589}$ +47.7°.

(-)-**10** (mp 96.8–98.1 °C, $[\alpha]_{589}$ -16.4° (*c* 2.216)), (-)-**11** (bp 76–78 °C (1 mm), $[\alpha]_{589}$ -30.7° (*c* 2.215, *n*-hexane)), and (-)-**12** (mp 95.8–96.8 °C, $[\alpha]_{589}$ -15.8° (*c* 0.820))[13] were prepared starting from (+)-**9** according to Mosher's procedure.[12]

(+)-Dimethyl *tert*-Butylsuccinate (13). A. From (-)-8. To a yellow solution of ruthenium tetroxide prepared from ruthenium dioxide (307 mg), sodium periodate (2 g), acetone (50 mL), and water (12 mL) was added a solution of (-)-**8** (507 mg) in acetone (30 mL) at room temperature. The mixture was stirred for 66 h, during which time sodium periodate (28 g) in water (140 mL) and acetone (140 mL) was added portionwise to keep the reaction mixture light yellow whenever darkening occurred. After the precipitates were removed on a Celite column, most of the acetone was evaporated, and the residue was extracted with ether. The acidic materials were isolated in the usual manner to give 642 mg of crude acid, which was treated with an excess amount of ethereal diazomethane. The resulting ester was chromatographed twice on silica gel (20 g), eluting with *n*-hexane–ethyl acetate (9:1). The eluate was concentrated to afford 123 mg (31%) of pure ester (NMR and TLC), $[\alpha]_{589}$ +12.3° (*c* 1.108), which was distilled to give an analytical sample of **13**: bp 120 °C (bath temperature, 2 mm); $[\alpha]_{589}$ +12.4°, $[\alpha]_{405}$ +36.8° (*c* 0.582); NMR δ 0.99 (s, *tert*-butyl), 1.96–2.93 (m, methylene and methine), 3.69, 3.72 (s each, methyls); IR 1740 cm^{-1} ($\nu_{C=O}$).

Anal. Calcd for $C_{10}H_{18}O_4$: C, 59.38; H, 8.97. Found: C, 59.29; H, 9.04.

B. From (*S*)-(-)-12. (*S*)-(-)-**12** (377 mg) was degraded by the action of ruthenium tetroxide reagent, and the resulting acid was esterified in a similar manner as that used in A. Purification by chromatography yielded 234 mg (63%) of pure **13** (NMR and TLC), $[\alpha]_{589}$ +12.7° (*c* 2.339), which was distilled to afford 112 mg of an analytical sample: $[\alpha]_{589}$ +12.4° (*c* 1.213).

Registry No. **1**, 66-77-3; **2**, 57573-88-3; **3**, 71185-36-9; (±)-**4**, 71185-37-0; (*S*)-(+)-**4**, 71214-34-1; (*S*)-(+)-**4** brucine salt, 71214-41-0; (*R*)-(-)-**4**, 71214-35-2; (*S*)-(-)-**5**, 71185-38-1; (*S*)-(-)-**6**, 71185-39-2; (±)-**6**, 71214-42-1; (*S*)-(+)-**7**, 71185-40-5; (±)-**7**, 71214-43-2; (*S*)-(-)-**8**, 71185-41-6; (±)-**9**, 13490-70-5; (+)-**9**, 13490-71-6; (-)-**9** brucine salt, 71185-51-8; (*R*)-(-)-**9**, 13491-16-2; (*S*)-(-)-**10**, 54321-15-2; (*S*)-(-)-**11**, 54321-14-1; (*S*)-(-)-**12**, 24425-68-1; (*S*)-(+)-**13**, 71185-42-7; brucine, 357-57-3; *tert*-butyl chloride, 507-20-0; 1-*tert*-butyl-1-phenylethane, 71214-36-3; methyl α-*tert*-butylphenylacetate, 71214-37-4; methyl β-*tert*-butylphenylpropanoate, 71214-38-5; 1,3-bis(*tert*-butylphenylmethyl)-3-(methoxycarbonyl)propane, 71185-43-8; 1,3-bis(*tert*-butylphenylmethyl)-2-carboxypropane, 71185-44-9; 1,2,3,4-tetrahydro-5-(1-*tert*-butylethyl)naphthalene, 71185-45-0; 3-*tert*-butyl-3-(1′,2′,3′,4′-tetrahydro-5′-naphthyl)propionic acid, 71214-39-6; 2-*tert*-butylpropionic acid, 19910-29-3; monomethyl 2-*tert*-butylpropanedioate, 71185-46-1; dimethyl 2-*tert*-butylbutanedioate, 71214-40-9; dimethyl 3-*tert*-butyl-2-oxopentanedioate, 71185-47-2; 2,6-di-*tert*-butyl-4-(methoxycarbonyl)heptanedioic acid, 71185-48-3; dimethyl 2,6-di-*tert*-butyl-4-(methoxycarbonyl)-7-oxooctanedioate, 71185-49-4; dimethyl 2,6-di-*tert*-butyl-4-(methoxycarbonyl)heptanedioate, 71185-50-7; ruthenium tetraoxide, 20427-56-9.

Quantitative Studies in Stereochemistry. 16. The Ratio of Diastereomeric Pinacols Produced in the Aluminum Amalgam Bimolecular Reduction of Acetophenone

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Received February 16, 1979

A report of the almost stereospecific bimolecular reduction of acetophenone employing aluminum amalgam in refluxing methylene chloride has appeared.[1] An earlier series of studies from the present authors' laboratory

(1) A. P. Schriebmann, *Tetrahadron Lett*, 4271 (1970). The author reports yields of 21–38% of this pinacol of which less than 1% is the meso form. An unspecified amount of *trans*-α,α′-dimethylstilbene was also found; no simple carbinol was observed (both items in contrast to the present study). Since experimental details for the methylene chloride studies did not include amounts or reaction times, it is not possible to offer any reasonable rationale for the discrepancies between the present and the earlier reports. It can only be assumed that some combination of reagent sources, reagent amounts, or reaction conditions could account for the observed differences. No report subsequent to this communication appears to have been made by this author.

0022-3263/79/1944-3589$01.00/0