Tetrahedron Vol. 43, No. 24, pp. 5769 to 5774, 1987
Printed in Great Britain.

0040-4020/87 $3.00+.00

THE OCTANT RULE. XXIII.[1] ANTIOCTANT EFFECTS IN γ,δ-UNSATURATED KETONES.

VIEN VAN TOAN AND DAVID A. LIGHTNER*

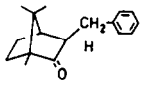
Department of Chemistry, University of Nevada,

Reno, Nevada 89557-0020

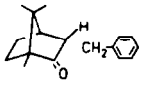
(*Received in USA* 31 *August* 1987)

Abstract. The exo and endo α-benzyl derivatives (1 and 2, respectively) of (+)-camphor have been synthesized and are found to exert a strong influence on the circular dichroism n→π* Cotton effects: 1: $\Delta\epsilon^{301}_{max}$ -0.36 (n-heptane) and 2: $\Delta\epsilon^{302}_{max}$ +3.22, relative to camphor: $\Delta\epsilon^{304}_{max}$ +1.8 (n-heptane). Evidence for electric dipole transition moment coupling in these γ,δ-unsaturated systems is found in the n→π* UV: 1: ϵ^{291}_{max} 84 (n-heptane) and 2: ϵ^{295}_{max} 303, relative to camphor: ϵ^{290}_{max} 25.

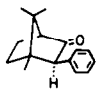
Although the potentially dominating effects of transition moment coupling on the ultraviolet (UV) and circular dichroism (CD) spectra have been well-recognized for β,γ-unsaturated ketones,[2,3] the influence of longer range electrostatic interaction between localized transitions of the chromophores, e.g., γ,δ-bis-homoconjugation and δ,ε-tris-homoconjugation, remains much less well known. Yet, examples of n→π* Cotton effect (CE) sign inversions can be found in comparing the CD spectra of 5α-cholest-6-ene-3-one [$\Delta\epsilon^{297}_{max}$ -0.47 (hexane)] and 5α-cholestan-3-one [$\Delta\epsilon^{297}_{max}$ +0.84 (hexane)], and CE exaltations can be found in comparing the CD spectra of 5α-cholest-2-ene-6-one [$\Delta\epsilon^{293}_{max}$ -2.72 (CF_3CH_2OH)] and 5α-cholestan-6-one [$\Delta\epsilon^{293}_{max}$ -1.55 (CF_3CH_2OH)].[4] In the few examples studied,[4] long range coupling of the C=O and C=C locally excited states through the σ-framework has been shown to exert a surprisingly strong influence on the CD CEs, in some cases an antioctant effect[5] sufficient to invert the sign predicted by the Octant Rule.[1,6] Yet in these cases, unlike the strong coupling of selected β,γ-unsaturated ketones, the UV n→π* transition remained essentially unaffected.



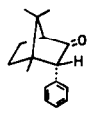
1



2



3



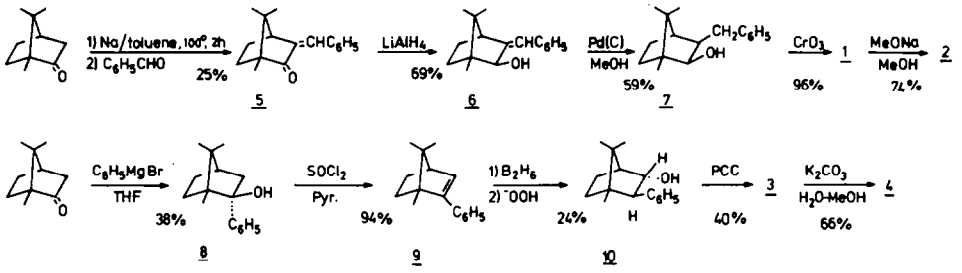
4

To investigate the influence of γ,δ remote conjugation further we prepared 3-exo- and 3-endo-benzylbornan-2-ones (1 and 2) and studied their UV and CD spectra. These data are contrasted with those from 2-exo and 2-endo-phenylbornan-3-ones (3 and 4), β,γ-unsaturated ketones whose CD spectra were reported earlier[7] and gave uncertain evidence for homoconjugation.

Syntheses. The synthesis (Scheme 1) of 1, with the exo-benzyl configuration depends on a stereospecific catalytic hydrogenation step. Thus, the mixed aldol condensation of (+)-camphor enolate with benzaldehyde gave 3-benzylidene bornanone (5), which was reduced to alcohol 6 by $LiAlH_4$. Catalytic hydrogenation of the styrene C=C with Pd(C) in CH_3OH gave only one diastereomeric alcohol (7). Jones oxidation of 7 gave 1 in >99% purity. Base-catalyzed epimerization of 1 with $NaOCH_3$ /CH_3OH gave 2 in >95% epimeric purity. An alternative route to 1 involv-

&ing direct hydrogenation of 5 gave 1 contaminated with 2. Exo-phenyl ketone 3 was prepared from (+)-camphor first by conversion via 8 to 2-phenylbornylene (9) (Scheme 1) followed by hydroboration to give 10 then oxidation with pyridinium chlorochromate. Base-catalyzed epimerization of 3 led to 4.

SCHEME 1



UV Spectra. The UV spectra of the benzyl ketones 1 and 2 (Figs. 1 and 2) show unexpectedly intense n→π* transitions, but relatively unshifted λ_{max} compared to camphor. The intense n→π* transitions of 2 and (particularly) 1 are more intense than normal carbonyl absorptions (ϵ_{max} 20-80)[8], with the n→π* intensities of 1 approaching the values (ϵ_{max} 300-500)[8] of β,γ-unsaturated ketones where strong interchromophoric interaction has been noted. Enhanced ε values for γ,δ-unsaturated ketones have been recorded previously[9-11] (Fig. 3), but ε values have also been found to fall in the normal range (ϵ_{max} ~25) for the γ,δ-unsaturated steroidal ketones[4] described above and showing antioctant and enhanced CD effects. The markedly enhanced n→π* UV transitions of 1 and 2 provide evidence for, in the orbital formalism, a mixing in of the aromatic π→π* transition with the C=O n→π* transition, or for a coupling of the locally excited states of each component of the extended chromophore. The coupling is expected to be highly geometry-dependent (Fig. 3), and in other γ,δ-unsaturated ketones (Fig. 4)[12] with unfavorable orientations of the chromophores, no enhanced n→π* ε values are observed. Presumably, and as seen in Dreiding models, a conformation is available for 1 and 2, that lines up the C=O and aromatic ring transition dipoles in a parallel orientation. Unlike 1 and 2, the β,γ-unsaturated ketones 3 and 4 show much less intense n→π* transitions, with ε values not much larger than the parent ketone (Table 1).

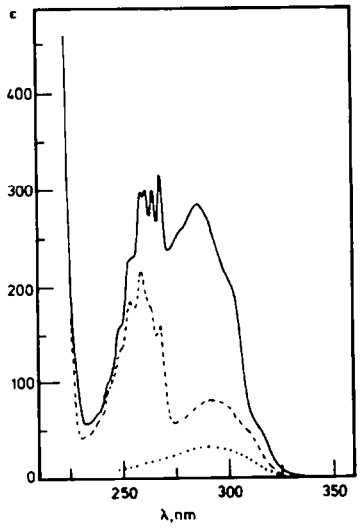


FIGURE 1. UV spectra of 3×10^{-3} M 1 (---), 2 (——) camphor (····) in n-heptane at 20° C

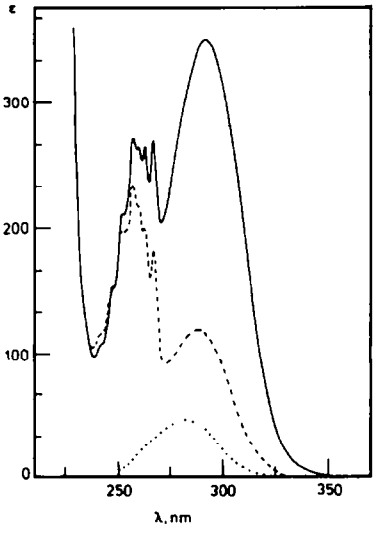


FIGURE 2. UV spectra of 3×10^{-3} M 1 (---), 2 (——) camphor (····) in 2,2,2 trifluoroethanol at 20° C

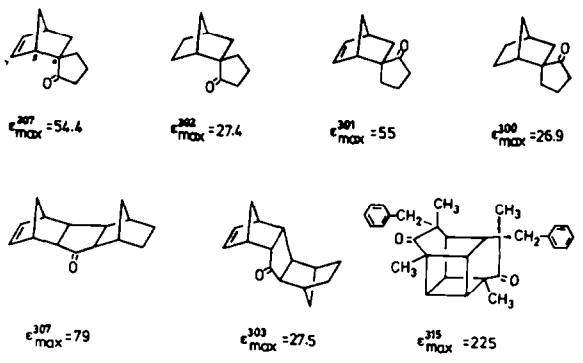


FIGURE 3. UV characteristics of γ,δ-unsaturated ketones and their saturated ketone analogs. (Data from refs. 9-11)

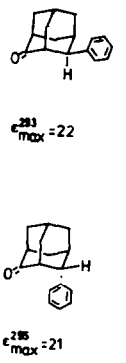
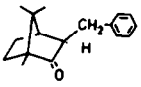
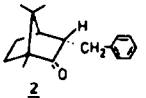
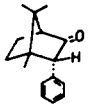


FIGURE 4. UV data for β-phenyladamantanones. (ref. 12)

TABLE 1. Circular Dichroism (CD) and Ultraviolet (UV) Data of Some Substituted Camphors and Epicamphors.[a]

Structure	n-Heptane		2,2,2-Trifluoroethanol	
	UV	CD	UV	CD
 1 $[\alpha]_D$ = +5.75°	298 (81.5)[b] 291 (84) 268 (159) 259 (218) 254 (182) 299 (134)[b]	324 (+0.030) 320 (0.000) 312 (-0.247) 301 (-0.362) 293 (-0.298) 267 (-0.238) 262 (-0.192) 255 (-0.102)	287 (111) 266 (183) 262 (200) 257 (237) 251 (196)[b]	313 (+0.123) 305 (0.000) 286 (-0.299) 267 (-0.212) 260 (-0.130) 255 (-0.066) 244 (0.000)
 2 $[\alpha]_D$ = +113.0°	285 (303) 268 (335) 264 (318) 261 (318) 259 (317) 253 (246)[b]	313 (+2.27)[b] 302 (+3.22) 295 (+2.81)[b] 268 (+0.73)[b] 261 (+0.41)[b]	292 (349) 267 (270) 263 (262) 260 (262) 257 (270) 252 (208)[b]	295 (+3.27) 269 (+0.85)[b] 262 (+0.48)[b] 255 (+0.23)[b]
 $[\alpha]_D$ = +44°	290 (27.3)	302 (+1.85)	282 (44.2)	288 (+1.95)
 3 $[\alpha]_D$ = +20.5°	294 (34.1) 266 (178) 259 (224) 244 (190)	299 (-1.39)	280 (73.5) 262 (184)[b] 257 (294)[b] 250 (405)[b] 242 (460)	292 (-1.81)
 4 $[\alpha]_D$ = -115.0°	321 (23.4) 310 (43.2) 300 (46.0) 264 (153) 258 (198) 252 (155) 248 (113)	322 (-1.20) 310 (-1.46) 300 (-1.06) 267 (-0.35) 260 (-0.41) 253 (-0.30)	287 (70.5) 263 (174) 257 (218) 251 (191)	297 (-1.31) 267 (-0.313) 260 (-0.395) 254 (-0.340)
 $[\alpha]_D$ = -46°	294 (26.1)		280 (48.6)	287 (-2.25)

[a] Values reported for UV are λ_{max} (ϵ) and for CD are λ_{max} ($\Delta\epsilon$). [b] Shoulder

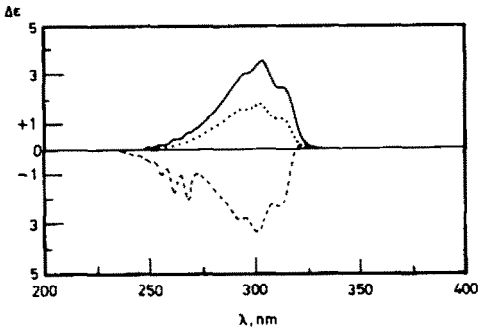


FIGURE 5. Circular dichroism spectra of $3x10^{-3}$ M solutions of exo-benzyl 1 (----), endo-benzyl 2 (——) and (+)-camphor (····) in n-heptane at 20° C. The enantromeric excess is the same (-100%) for all.

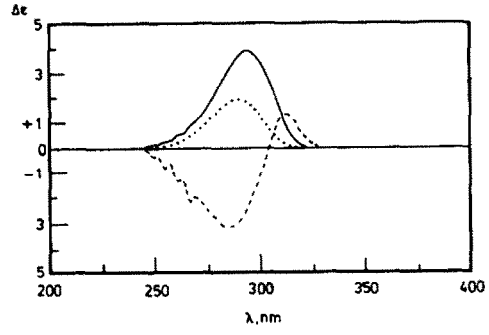


FIGURE 6. Circular dichroism spectra of $3x10^{-3}$ M solutions of exo-benzyl 1 (----), endo-benzyl 2 (——) and (+)-camphor (····) in 2,2,2-trifluoroethanol at 20° C. The enantromeric excess is the same (-100%) for all.

Circular Dichroism. The CD spectra of 1 and 2, shown in Figs. 5 and 6, indicate a powerful influence of the benzyl group. From the enhanced UV n→π* transitions, one should expect a contribution to the CE coming from orbital interaction as well as from octant contributions.[1,2,5,6] The exo-benzyl group is expected to lie in a front octant, adding its (+) front octant contribution to the (+) back octant contributions inherent to the camphor skeleton. If these were the only contributions to the CE, 1 would be expected to have a $\Delta\epsilon > +1.8$, not the extremely weak negative value, $\Delta\epsilon \approx -0.4$. The dominating influence of the benzyl groups is clearly evident through the mechanism of an inherently dissymmetric extended chromophore[3]--similar, apparently, to that seen for 5α-cholest-6-en-3-one (see above). The octant contribution of endo-benzyl group depends considerably on its orientation. If in a lower right or upper left back octant, it will make a (+) contribution to the n→π* CD CE. If the phenyl ring juts into a front octant, however, as seems probable from Dreiding models, the contribution could be weakly (-) or weakly (+). Considering the very large n→π* $\Delta\epsilon$ values for 2, it seems probable that the normal octant contributions of the camphor system are being augmented by the sort of homoconjugation effects described for the exo-benzyl group and noted earlier for 5α-cholest-2-en-6-one. In marked contrast, neither the exo nor the endo phenyl group show such a profound influence on the CDs of 3 and 4 (Table 1). Here, however, as with their des-methyl analogs,[13] a weaker transition moment coupling due to an unfavorable interchromophoric geometry has a far smaller influence on the n→π* CD $\Delta\epsilon$ values.

Acknowledgement. We thank the National Science Foundation (CHE 8218216) for generous support of this work and Dr. Donald Wijekoon for assistance in running the CD and UV spectra.

EXPERIMENTAL SECTION

General. Circular dichroism (CD) spectra were recorded on a JASCO J-600A or a J-40A instrument equipped with a photoelastic modulator and a J-DPY data processor, and a spectroscopic Dewar variable temperature CD measurements. Ultraviolet (UV) spectra were recorded on a Cary 219 spectrophotometer, and rotations were determined in 95% ethanol, unless otherwise indicated, on a Perkin-Elmer 141 polarimeter. All nuclear magnetic resonance (NMR) spectra were determined in $CDCl_3$ and reported in δ ppm downfield from tetramethylsilane unless otherwise indicated on an IBM NR80/AF or a JEOL FX-100 instrument. Infrared (IR) spectra were measured on a Perkin-Elmer Model 599 instrument. All melting points are uncorrected and were determined on a Mel-Temp capillary apparatus. Combustion analyses were performed by Desert-Analytics, Tucson, AZ. Analytical gas chromatography (GC) was performed on a Varian-Aerograph model 2400 F/I instrument on a 6 ft. x 1/8 in. diam. column packed with 12% QF-1 adsorbed on 80/100 Chromosorb WAW-DMCS. Spectral data were obtained using spectral grade solvents (Aldrich): 2,2,2-trifluoroethanol (TFE) and n-heptane. Other solvents were distilled and dried before use. They were used freshly distilled or stored over 4A molecular sieves (Linde). Column chromatography was accomplished on (0.05 - 0.20 mm) J.T. Baker silica gel.

(1R,4S)-3-Benzylidene-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (3-Benzylidene bornanone[14]) (5): This reaction was performed under nitrogen until hydrolysis of the product. Sodium (3.5 g, 0.15 moles) was cut into small pieces and suspended in 120 mL of dry toluene. To this stirred suspension were added 30.0 g (0.20 moles) of (+)-camphor [Aldrich, $[\alpha]_D^{20}$ = +44.0° (c 1, ethanol)]. The mixture was heated at 100°C until all the sodium pieces were dissolved (2 hours). After cooling to 0°C, toluene was pumped out by suction and the crystals of the Na-salt of camphor were washed with toluene (2 x 20 mL) and finally suspended in 120 mL of dry toluene. To this stirred suspension, was added dropwise at 0°C, a solution of 6.0 g (0.15 moles) of benzaldehyde in 10 mL of toluene. An exothermic reaction was observed. At the end of the addition, the mixture was kept at 50°C for 1 hour, cooled to 0°C and hydrolyzed by addition to a solution of 2N HCl (150 mL). The hydrolysate (water phase) was extracted with ether (100 mL). The combined organic solution was washed with 5% $NaHCO_3$ (100 mL), saturated brine and dried ($MgSO_4$). The solvent was removed (rotovap) and the excess of benzaldehyde and camphor were eliminated by distillation at 120-150°C/1mm. The residue was recrystallized in the ether-pentane to give 11.9 g (25%) of a mixture of anti and syn 3-benzylidene bornanone (5) as colorless prisms, m.p. 68-78°C [Lit.[14] mp 95-96° for the anti isomer and 72-73° for the syn isomer,[15]] and $[\alpha]_{589}^{20}$ = +446°C, (c = 1.0). It had UV (n-heptane): ϵ_{max}^{286} = 21,800, ϵ_{max}^{227} = 7080, ϵ_{max}^{221} = 8900, ϵ_{sh}^{215} = 7450; CD (n-heptane): $\Delta\epsilon_{max}^{278}$ = +17.8; IR (KBR) ν: 3060, 3030, 2960, 2880, 1725, 1650, 1450, 1330, 1260, 1060, 1010, 750, 700, 550, 520 cm^{-1}; ^{1}H-NMR δ: 0.80 (s, 3H), 0.99 (s, 3H), 1.03 (s, 3H), 1.10-2.30 (m, 4H), 3.10 (d, 1H, J=4 Hz), 7.24 (s, 1H), 7.10-7.60 (m, 5H) ppm; ^{13}C-NMR δ: 9.25 (q), 18.26 (q), 20.49 (q), 25.87 (t), 30.61 (t), 46.58 (s), 49.15 (d), 56.99 (s), 127.37 (d), 128.54 (d), 129.65 (d), 135.62 (d), 142.05 (s), 207.9 (s) ppm.

(1R,4S)-anti-3-Benzylidene-exo-1,7,7-trimethyl-bicyclo[2.2.1]heptan-2-exo-ol. (16)[15]: A solution of 2.40 g (10 mmoles) of unsaturated ketone 5 in 10 mL of ether was added to a solution of 0.40 g (10 mmoles) of $LiAlH_4$ in 50 mL of ether. After 1 hour at reflux, the solution was quenched by successive addition of 0.40 mL of water, 0.40 mL of 15% NaOH and 1.20 mL of water. After stirring for 30 min, the white precipitate was filtered and the filtrate evaporated. Recrystallization of the residue in petroleum ether (50 mL) gave 1.64 g (69%) of the exo alcohol (6) as colorless prisms, m.p. 89-93°C (lit.[15] m.p. 82.5-93.5°C). It was reduced directly in the next step.

(1R,4R)-exo-3-Benzyl-exo-1,7,7-trimethyl-bicyclo[2.2.1]heptan-2-ol (7): Alcohol 6 (1.20 g, 5 mmoles) was dissolved in 30 mL of methanol and hydrogenated at 1 atm. hydrogen in the presence of 100 mg of 15% Pd-C (t = 12 hrs, room temp.). After filtration of the catalyst, the crude product was chromatographed on a silica gel column, (ø = 2 cm, h = 30 cm), eluant: pet. ether-ether (85:15). The main fraction gave 0.70 g (59%) of alcohol 7 as a colorless oil. It was oxidized directly to ketone 1.

(+)-(1R,4R)-exo-3-Benzylbornanone (1): Alcohol 7 (0.70 g 2.9 mmoles) in 40 mL of dry acetone and $MgSO_4$ (2.0 g) was treated with Jones reagent[16] until the orange color persisted (~1mL). After 20 min, with stirring, the excess chromium oxide was destroyed by addition of a few drops of 2-propanol. The solution was filtered and the filtrate evaporated. The residue was redissolved in ether (50 mL) washed with sat. brine and dried ($MgSO_4$). The solvent was removed, and kugelrohr distillation gave 0.67 g (96%) of ketone 1 as a colorless oil, b.p. 170-180°C/1mm. It was >99% pure by analytical GC and had $[\alpha]_{589}^{20}$ = +5.75°; $[\alpha]_{578}^{20}$ = +5.75°; $[\alpha]_{546}^{20}$ = +6.50°; $[\alpha]_{436}^{20}$ = +6.55°; $[\alpha]_{365}^{20}$ = -8.70° (c = 1.36). UV and CD in Table 1 and Figs. 5 and 6; IR (film) ν: 3020, 2960, 1740, 1600, 1450, 1390, 1020, 760, 730, 700 cm^{-1}; ^{1}H-NMR δ: 0.95 (s, 9H), 1.10-2.40 (m, 6H), 2.70 (d, J=10 Hz, 1H), 3.30 (dd, J=12Hz, 3Hz, 1H), 7.25 (s, 5H) ppm; ^{13}C-NMR δ: 9.33 (q), 20.43 (q), 21.83 (q), 29.32 (t), 37.22 (t), 46.68 (d), 56.64 (d), 57.55 (s), 125.92 (d), 128.41 (d), 12848 (d), 141.31 (s), 219.87 (s) ppm.

Anal. Calcd for $C_{17}H_{22}O$ (242.37): C, 84.25; H, 9.15
Found: C, 84.02; H, 9.13.

(+)-(1R,4R)-endo-3-Benzylbornan-2-one (2): A solution of 0.80 g (3.3 mmoles) of exo ketone (1) and 1.0 g of CH_3ONa in 20 mL of methanol was heated at 140°C for 20 hours in a pressure bottle. After cooling, the solution was poured into water (300 mL), extracted with ether (100 mL) and

dried ($MgSO_4$). The solvent removal and kugelrohr distillation of the residue gave 0.59 g (74%) of the endo ketone 2 as a colorless oil, b.p. 180°C/1 mm, (purity >95%, estimated by ^{13}C-NMR and analytical GC). It had $[\alpha]^{20}_{589}$ = +113°; $[\alpha]^{20}_{578}$ = +118.8°; $[\alpha]^{20}_{546}$ = +140.0°; $[\alpha]^{20}_{436}$ = +296.2°; $[\alpha]^{20}_{365}$ = +695° (c 1.06); UV and CD data in Table 1 and Figs. 5 and 6; IR (film) ν: 3030, 2920, 2880, 1740, 1605, 1500, 1450, 1370, 1050, 760, 740, 710 cm^{-1}; ^{1}H-NMR δ: 0.87 (s, 3H), 0.97 (s, 6H), 1.17-2.97 (m, 7H), 3.20 (d, J=10 Hz, 1H), 7.27 (s, 5H) ppm; ^{13}C-NMR δ: 9.47 (q), 19.22 (q), 20.27 (q), 31.04 (t), 32.75 (t), 45.62 (s), 45.96 (t), 51.81 (d), 58.66 (s), 125.96 (d), 128.43 (d), 128.53 (d), 140.35 (s), 219.74 (s) ppm.

Anal. Calcd for $C_{17}H_{22}O$ (242.37): C, 84.25; H, 9.15
Found: C, 84.15; H, 9.10.

(+)-(1R,4S)-exo-2-Phenylbornan-3-one (3): This ketone was prepared from (+)-camphor as described previously.[7] It had mp 90-91° (lit.[17] mp 88-89°), $[\alpha]^{20}_{589}$ = +20.5° (c 1.26); UV and CD in Table 1; IR (KBr) ν: 3010, 3000, 2960, 2880, 1740, 1600, 1500, 1450, 1160, 750, 710 cm^{-1}; ^{1}H-NMRδ: 0.93 (s, 3H), 0.96 (s, 3H), 0.99 (s, 3H), 1.50-2.40 (m, 5H), 3.35 (s, 1H), 7.23 (s, 5H) ppm; ^{13}C-NMR δ: 14.05 (q), 19.78 (q), 20.78 (q), 21.77 (t), 38.86 (t), 47.75 (s), 50.61 (s), 59.74 (d), 62.61 (d), 128.20 (d), 127.78 (d), 130.24 (d), 136.78 (s), 217.29 (s) ppm.

(-)-(1R,2S)-2-endo-Phenylbornan-3-one (4): The exo phenyl epimer (3) (300 mg, 1.3 mmoles) in 20 mL of methanol was treated with a solution of 0.80 g (5.8 mmoles) of K_2CO_3 in 15 mL of water. The stirred solution was kept at 50°C for 3 hours then cooled, diluted with water (150 mL) and extracted with ether (80 mL). After drying ($MgSO_4$) the solvent was removed (rotavap) and recrystallization of the residue in ether-pentane at -50°C gave 200 mg (66%) of the endo-phenyl ketone 4 as colorless needles, m.p 95-98°C. It had $[\alpha]^{20}_{589}$ = -115° (c 1.38), (lit[18] m.p. 95-96°C); UV and CD in Table 1; IR (KBr) ν: 3040, 2960, 1745, 1600, 1500, 1480, 1450, 1370, 1170, 750, 720, 700, 590, 530 cm^{-1}; ^{1}H-NMR δ: 0.98 (s, 3H), 1.04 (s, 3H), 1.08 (s, 3H), 1.15-2.20 (m, 4H), 2.35 (d, J=7 Hz, 1H), 3.47 (s, 1H), 6.85-7.45 (m, 5H) ppm; ^{13}C-NMR δ: 13.93 (q), 18.09 (q), 22.36 (t), 27.81 (t), 46.05 (s), 51.08 (s), 60.68 (d), 61.73 (d), 126.78 (d), 128.19 (d), 129.89 (d), 136.15 (s), 217.46 (s) ppm.

REFERENCES

1. For part 22 see D.A. Lightner, T.D. Bouman, B.V. Crist, S.L. Rodgers, M.A. Knobeloch and A.M. Jones, J. Am. Chem. Soc., in press (1987).
2. For leading references see D.N. Kirk, Tetrahedron, 42, 777 (1986).
3. D.A. Lightner, D.E. Jackman and G.D. Christiansen, Tetrahedron Lett., 4467 (1977).
4. G.P. Powell, R.N. Totty and J. Hudec, J. Chem. Soc. Perkin I, 1015 (1975).
5. D.A. Lightner, B.V. Crist, N. Kalyanam, L.M. May and D.E. Jackman, J. Org. Chem., 50, 3867 (1985).
6. W. Moffitt, R.B. Woodward, A. Moscowitz, W. Klyne and C. Djerassi, J. Am. Chem. Soc., 83, 4013 (1961).
7. R.F.J. Cole, J.M. Coxon and M.P. Hartshorn, J. Chem. Soc. Perkin I, 351 (1972).
8. R.C. Cookson and N.S. Wariyar, J. Chem. Soc., 2302 (1956).
9. R.R. Sauers and T.R. Henderson, J. Org. Chem., 39, 1850 (1974).
10. R.R. Sauers and A.M. DePaolis, J. Org. Chem., 38, 639 (1973).
11. H-D. Becker, B.W. Skelton and A.H. White, J. Chem. Soc. Perkin II, 442 (1981).
12. W.M.D. Wijekoon and D.A. Lightner, J. Org. Chem., in press (1987).
13. H.T. Thomas and K. Mislow, J. Am. Chem. Soc., 92, 6292 (1970).
14. A. Haller, C.R. Acad. Sci. Paris, 113, 22 (1891).
15. J. Kossanyi, B. Furth and J.P. Morizur, Tetrahedron, 26, 395 (1970).
16. E.J. Eisenbraun, Org. Synth Coll Vol 5, 310 (1973).
17. J.M. Coxon, M.P. Hartshorn and A.J. Lewis, Austral. J. Chem., 24, 1009 (1971).
18. J.M. Coxon, M.P. Hartshorn and A.J. Lewis, Austral. J. Chem., 24, 1017 (1971).