Stereochemistry and Chiroptical Properties of the 3-Phenyl-2-norbornanones[1]

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Abstract: The optical purities and absolute configurations of 3-*exo*- and 3-*endo*-phenyl-2-norbornanone and several related 3-phenyl-2-norbornyl compounds were determined. Primary determination of optical purity in this series was achieved by comparison of relative signal intensities in the nmr spectrum of the O-methylmandelate of (−)-3-*endo*-phenyl-2-*exo*-norbornanol. The absolute configurations of both (+)-3-*exo*- and (−)-3-*endo*-phenyl-2-norbornanone were established as (1*S*) by the conversion of (−)-(1*R*)-norcamphor to (−)-(1*R*)-2-phenylnorbornene, whose configurational relationship to the other 3-phenyl-2-norbornyl compounds is known. Comparison of absorption and chiroptical (ORD and CD) characteristics of (+)-3-*exo*-phenyl-2-norbornanone, (−)-3-*endo*-phenyl-2-norbornanone, and (+)-norcamphor revealed only slight enhancement of the carbonyl n–π* transition due to α-phenyl substitution. However, the contribution of the α-phenyl groups to this transition cannot be rationalized simply on the basis of back octant effects but can be understood on the basis of transition moment coupling or front octant effects.

The n–π* transition in a variety of β,γ-unsaturated ketones exhibits enhanced absorption intensity[3] and rotatory power.[4–8] Consideration of the geometric and electronic factors involved in this intensification has led to the proposal of an extension of the octant rule, based on treatment of the composite carbonyl carbon π system as an inherently dissymmetric chromophore.[5–8] In their related work, Cookson, *et al.*,[3,4] found that α-phenylcholestanones in which the phenyl group is axial possess an intensified n–π* band, and that the position of the phenyl group of such phenylcholestanones determines the sign of the Cotton effect associated with the carbonyl n–π* transition.[4] By contrast, this intensification was not observed in the equatorial isomers. The key difference in structure between the axial and equatorial α-phenyl ketones studied by Cookson is the dihedral angle between the carbon–oxygen bond and the α-carbon–phenyl bond which is *ca.* 0° for the equatorial phenyl derivatives and *ca.* 120° for the axial phenyl derivatives. It therefore became of interest to study the absorption and chiroptical properties of isomeric α-phenyl ketones in which this angle assumes values intermediate between these extremes. A system which possesses the requisite structural features is 3-phenyl-2-norbornanone. The 3-*exo* and 3-*endo* isomers of this compound have dihedral angles which are nearly identical in magnitude (*ca.* 60°) *yet which are oppositely signed.* Naive expectation, based on the anticipated dominance of the benzene π-system interaction with the carbonyl group,[4,5,7,8] might therefore lead to the prediction that the 3-*exo*- and 3-*endo*-phenyl isomers derived from the same 2-norbornanone (of given chirality) would exhibit oppositely signed n–π* Cotton effects. The present work was undertaken in order to look into this question.

Syntheses, Optical Purities, and Absolute Configuration

Asymmetric hydroboration of racemic 2-phenylnorbornene provided a facile approach to the synthesis of the optically active 3-phenyl-2-norbornyl series. Treatment of the olefin with triisopinocampheyldiborane[9] prepared from (−)-α-pinene afforded (−)-3-*endo*-phenyl-2-*exo*-norbornanol (**1**), $[\alpha]^{19}\mathrm{D}$ −22 ± 1° (*c* 1, ethanol). Further transformations discussed in this work are outlined in Chart I. In series A is shown the route employed in the synthesis of optically active 3-*endo*-phenyl-2-norbornanone (**2**) and 3-*exo*-phenyl-2-norbornanone (**3**) from **1**. The absolute configurations of **2** and **3** were related to that of norcamphor (**4**) by the transformation shown in series C which gives 2-phenylnorbornene (**5**), whose configurational relation to **2** has been elucidated by Collins and coworkers as shown in series B.[10]

A quantitative discussion of chiroptical properties requires an accurate measure of the optical purity of the compounds to be investigated. Formation of diastereomeric O-methylmandelates allowed determination of the optical purity of **1** by application of an nmr method of proven reliability.[8,11–13] The feasibility of the nmr method was checked by preparation of racemic **1** (hydroboration–oxidation of racemic 2-phenylnorbornene) and reaction with the acid chloride[8] obtained from optically pure (−)-(*R*)-O-methylmandelic acid,[13] $[\alpha]^{23}\mathrm{D}$ −164° (water). The 100-MHz nmr spectrum of a benzene solution of the resulting

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[2] National Aeronautics and Space Administration Fellow, 1967–1969.

[3] R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956).

[4] R. C. Cookson and J. Hudec, *ibid.*, 429 (1962).

[5] A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Amer. Chem. Soc.*, 84, 1945 (1962).

[6] K. Mislow, *Ann. N. Y. Acad. Sci.*, 93, 457 (1962).

[7] E. Bunnenberg, C. Djerassi, K. Mislow, and A. Moscowitz, *J. Amer. Chem. Soc.*, 84, 2823, 5003 (1962); K. Mislow in "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," E. Snatzke, Ed., Heyden and Son, Ltd., London, 1967, Chapter 10.

[8] D. J. Sandman and K. Mislow, *J. Org. Chem.*, 33, 2924 (1968); D. J. Sandman, K. Mislow, W. P. Giddings, J. Dirlam, and G. C. Hanson, *J. Amer. Chem. Soc.*, 90, 4877 (1968).

[9] H. C. Brown, N. R. Ayyangar, and G. Zweifel, *ibid.*, **86**, 1071 (1964).

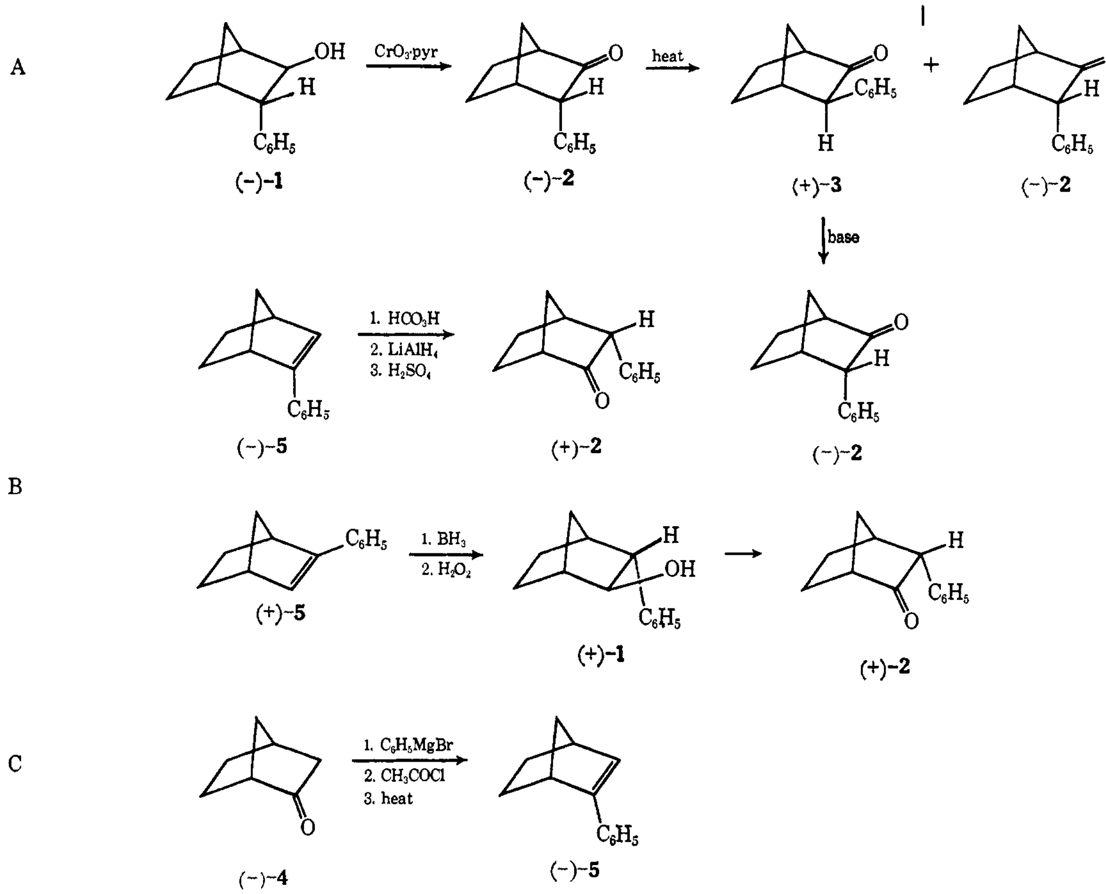
[10] C. J. Collins, Z. K. Cheema, R. G. Werth, and B. M. Benjamin, *ibid.*, 86, 4913 (1964).

[11] M. Raban and K. Mislow, "Topics in Stereochemistry," Vol. 2, N. L. Allinger, and E. L. Eliel, Ed., Interscience, New York, N. Y., 1967, p 216 ff.

[12] M. Raban and K. Mislow, *Tetrahedron Lett.*, 3961 (1966).

[13] J. Jacobus, M. Raban, and K. Mislow, *J. Org. Chem.*, 33, 1142 (1968).

Chart I



mixture of diastereomeric esters exhibited two signals of equal intensity at δ 4.77 and 4.81, due to the diastereotopic methoxymethine protons. A sample of (−)-**1** (prepared as above) was treated with the same reagent. The signal at δ 4.81 was more intense than that at 4.77 and integration of these signals indicated that the diastereomeric excess of the mixture and hence the optical purity of (−)-**1** was 26 ± 2%.[14] Accordingly, the absolute rotation of (−)-**1** is calculated to be $[\alpha]_D$ −85 ± 10° (*c* 1, ethanol). This value compares well with the value of $[\alpha]_D$ −95° (ethanol) which can be calculated from the work of Collins, *et al.*,[10] by assuming that the reported resolution of 3-*exo*-phenyl-2-*endo*-norbornylamine and subsequent transformations produced optically pure (−)-**5**.

Treatment of (−)-**1** with the Sarett reagent[10,15] afforded (−)-**2**, $[\alpha]^{21}_D$ −33.3 ± 1.7° (*c* 1, ethanol). Corrected to optical purity,[16] (−)-**2** has $[\alpha]^{21}_D$ −128 ± 15° (*c* 1, ethanol), which is in agreement with the highest rotation obtained by Collins and coworkers for (+)-**2**, $[\alpha]_D$ +141° (*c* 1, ethanol).[10]

In the course of subjecting (−)-**2** to preparative vpc (20 ft × $^3/_8$ in. FFAP, 243–246°) it was found that a mixture of (−)-**2** and (+)-**3** was produced under the conditions employed. The ratio of **3** to **2** was 47:53 by nmr. Separation of the epimeric ketones by column chromatography gave (+)-**3**, $[\alpha]^{27}_D$ +2.6° (*c* 0.3, isooctane), and (−)-**2** which appeared to have racemized to the extent of 15%. It was shown that an equilibrium was established between **2** and **3** since mixtures of composition identical with that from vpc treatment of **2** were obtained by repetition of the vpc treatment on both the epimerized mixture and a sample of **3**. The optical purity of this sample of (+)-**3** was accordingly taken to be 22 ± 2%, on the assumption that the same degree of racemization had been suffered by the produced (+)-**3**.

In order to adduce the relative configurations of (+)-**3** and (−)-**2** the base-catalyzed epimerization of (+)-**3** to (−)-**2** was investigated. After carrying out experiments on a mixture of racemic **2** and **3**, a procedure was chosen which compromised between completeness of epimerization and yield of material recovered. Epimerization of (+)-**3** was effected by treatment with 0.5 *N* methanolic sodium hydroxide for 1 hr and recovery (90%) of a mixture containing 65% of (−)-**2** by nmr. Isolation of (−)-**2** from this mixture afforded material whose optical purity was 14% less than that of (−)-**2** prior to vpc treatment. This result corroborates the degree of racemization suffered during the formation of (+)-**3** by vpc of (−)-**2**, and also indicates that (+)-**3** and (−)-**2** have the same relative configuration, differing only at C-3, as shown in Chart I, series A.[17]

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(14) The uncertainty in this value does not derive from a statistical treatment of data, but rather from an estimate of the instrumental limitations of the method.

(15) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Amer. Chem. Soc.*, **75**, 422 (1953).

(16) It is tacitly assumed that no change in optical purity occurred in transforming (−)-**1** into (−)-**2** so the value of 26% is used here.

(17) A reversible enolization mechanism could conceivably account for the observed epimerization during vpc. A likely alternative for the mechanism of epimerization under vpc conditions is homolytic scission–recombination, as shown in eq 1. Scission of the bond between C-2 and C-3 would give an intermediate diradical species in equilibrium with (−)-**2** and (+)-**3**. That homolytic scission should occur at the relatively low temperature of *ca.* 250° is not unreasonable since the indicated bond

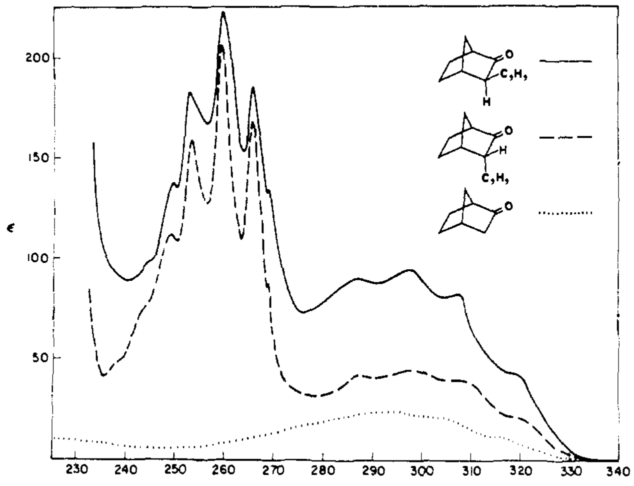


Figure 1. Ultraviolet absorption spectra (isooctane solution) of 3-*exo*-phenyl-2-norbornanone (**3**) (solid line), 3-*endo*-phenyl-2-norbornanone (**2**) (dashed line), and norcamphor (**4**) (dotted line).

Norcamphor (**4**) offers a convenient reference for establishing absolute configurations in the 3-phenyl-2-norbornyl series, since its optical purity[20,21] and absolute configuration[22] are known. Treatment of norbornene with tetraisopinocampheyldiborane[23] (prepared from (−)-α-pinene) followed by Jones oxidation and extensive purification afforded (−)-**4**, $[\alpha]^{23}\mathrm{D}$ −9.74 ± 0.40° (*c* 2.8, chloroform), which was 31 ± 3% optically pure[20] and possessed the configuration (1*R*,4*S*),[20,22] as shown in Chart I, series C. Reaction of (−)-**4** with phenylmagnesium bromide gave optically active 2-*exo*-phenyl-2-*endo*-norbornanol, which was converted to the acetate without purification. Pyrolysis of the acetate by preparative vpc and subsequent purification afforded (−)-(1*R*,4*S*)-**5** (see Chart I, series C), $[\alpha]^{24}\mathrm{D}$ −63.6 ± 0.6° (*c* 1.6, ethanol). Corrected to optical purity (−)-**5** has $[\alpha]^{24}\mathrm{D}$ −204 ± 22° which is comparable with the value of $[\alpha]^{25}\mathrm{D}$ −180.3° observed by Collins, *et al.*[10] The absolute configurations of **1**, **2**, **3**, and **5** are thus established, and are as presented in Chart I. The absolute configurations of the other optically active intermediates utilized by Collins and coworkers[10] are also established by these transformations. Thus configurations are now assigned as (+)-(1*S*,2*S*,3*R*,4*R*)-3-*exo*-phenyl-2-*endo*-norbornylamine (and the derived hydrochloride), (+)(1*R*,2*R*,3*R*,4*S*)-2-*endo*-phenyl-2,3-*exo-cis*-norbornylene carbonate, and (−)-(1*R*,2*R*,3*R*,4*S*)-2-*endo*-phenylnorbornane-2,3-*exo-cis*-diol.

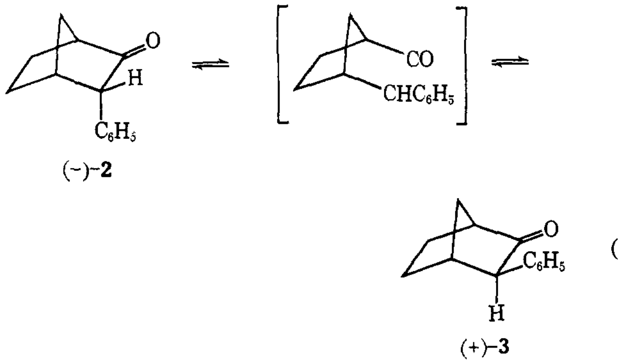
Following the completion of this work, reports appeared[24] in which the configuration of (+)-3-*exo*-phenyl-2-*endo*-norbornylamine hydrochloride was given as (2*S*), in agreement with the present work. The reported assignment[24] was based upon establishment of a new sector rule and application of this rule to one conformer of a conformationally labile system.

Absorption Spectra, Optical Rotatory Dispersions, and Circular Dichroic Spectra. The ultraviolet absorption spectra of (+)-**3**, (−)-**2**, and (−)-**4** are displayed in Figure 1.

The intensities of the n–π* transitions at *ca.* 295 mμ of all three compounds fall into the category of normal carbonyl absorptions as defined by Cookson and Wariyar ($\epsilon_{\max}$ 20–80),[3] with the possible exception of (+)-**3** ($\epsilon_{\max}$ 94).[25] However, it is important to note that the *endo*-phenyl group in **2** and the *exo*-phenyl group in **3** produce two- and fourfold enhancements, respectively, over the same transition in **4**.

The optical rotatory dispersions (ORD) and circular dichroic spectra (CD) of (+)-**3**, (−)-**2**, and (+)-**4**[26] are shown in Figures 2 and 3, respectively.[27] As shown in these curves, the long wavelength Cotton effects due to the carbonyl n–π* transitions are all of the same sign. Taken with the evidence of the low molar extinction coefficients, the chiroptical spectra indicate that (+)-**3** and (−)-**2** do not constitute inherently dissymmetric homoconjugated chromophores,[5,7] since the presence of the phenyl groups in these molecules fails to dominate the sign of the long wavelength Cotton effect. Closer examination of the chiroptical spectra in the light of the octant rule[28] (see Figure 4) reveals a rather more startling fact. In (+)-**3**, if the 3-*exo*-phenyl group is considered as occupying the upper left back octant it should give rise to a *positive* contribution relative to the Cotton effect of (+)-**4**. If in (−)-**2** the 3-*endo*-phenyl group is considered to lie in the lower left back octant, it should correspondingly produce a *negative* contribution.

opening would relieve considerable ring strain. The energy required for bond dissociation also should be lower than usual since the radical centers produced possess unusual stability, the one center because it is benzylic,[18] the other because it is an acyl radical.[19]



(−)-**2**

(1)

(+)-**3**

Speculation on the mechanism of racemization is not warranted at this time, except to note that reversible migration of two hydrogen atoms in the proposed diradical intermediate to give a configurationally labile ditertiary diradical represents one possible scheme to account for the observations.

(18) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed, Butterworths, London, 1958, p 183 ff.

(19) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, p 51 ff.

(20) K. Mislow and J. G. Berger, *J. Amer. Chem. Soc.*, **84**, 1956 (1962).

(21) J. A. Berson and S. Suzuki, *ibid.*, **81**, 4088 (1959).

(22) J. A. Berson, J. S. Walia, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff, and D. Willner, *ibid.*, **83**, 3986 (1961).

(23) H. C. Brown and G. Zweifel, *ibid.*, **83**, 486 (1961); H. C. Brown, N. R. Ayyanger, and G. Zweifel, *ibid.*, **86**, 397 (1964).

(24) H. E. Smith and T. C. Willis, *Chem. Commun.*, 873 (1969); *Tetrahedron*, **26**, 107 (1970).

(25) This ε is still far less than the absorptivities characteristic of molecules which possess "strong interaction" between the β,γ-unsaturation and the carbonyl group (ε 300–500),[3] although it approaches that of (+)-bicyclo[2.2.2]oct-5-en-2-one (ε 110) which has been discussed as an inherently dissymmetric homoconjugated chromophore.[5,7]

(26) The actual measurements were taken on (−)-4, but plotted as the enantiomeric curves, so as to display the chiroptical spectra for compounds of comparable configurations at C-1 (*i.e.*, (1*S*)). The sign of 4 refers to the sign of the D-line rotation in chloroform solution. This convention was adopted to maintain consistency with earlier work.[20-22]

(27) The [φ] and [θ] values are corrected to optical purity and are accurate to within ±10% of the given values.

(28) W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, *J. Amer. Chem. Soc.*, **83**, 4013 (1961).

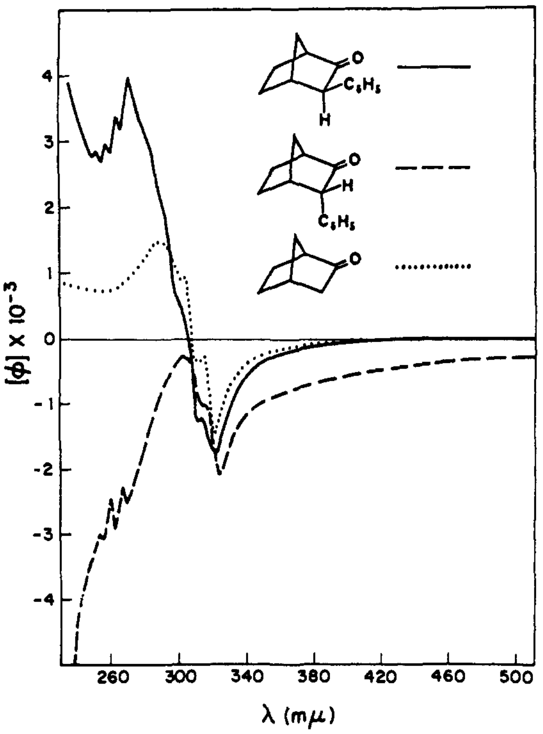


Figure 2. Optical rotatory dispersions (isooctane solution) of (+)-3-*exo*-phenyl-2-norbornanone (**3**) (solid line), (−)-3-*endo*-phenyl-2-norbornanone (**2**) (dashed line), and (+)-norcamphor (**4**)[26] (dotted line), corrected to optical purity.[27]

However, we see that the Cotton effect of (+)-**3** is *more negative* than that of (+)-**4**.[29] Thus this behavior cannot be rationalized simply on the basis of back octant effects, and constitutes an example of either front octant effects[28,30] or antioctant behavior.[31] The former effects are possible since certain rotational conformations of the phenyl ring situate atoms of the phenyl group in front octants.[30] It is not clear, however, whether the populations of such conformers and the magnitude of such an effect is sufficient to account for our observations. Accordingly, an additional rationalization was sought.

The theoretical treatments developed to account for the optical properties of β,γ-unsaturated ketones have undergone considerable development in recent years. Initial approaches involved mixing of carbonyl and carbon–carbon π-bond states by orbital overlap,[3,4,32-34] and predicted enhanced ultraviolet absorption and optical rotatory power for the n–π^* transition when conditions obtained for maximum overlap. Later de-

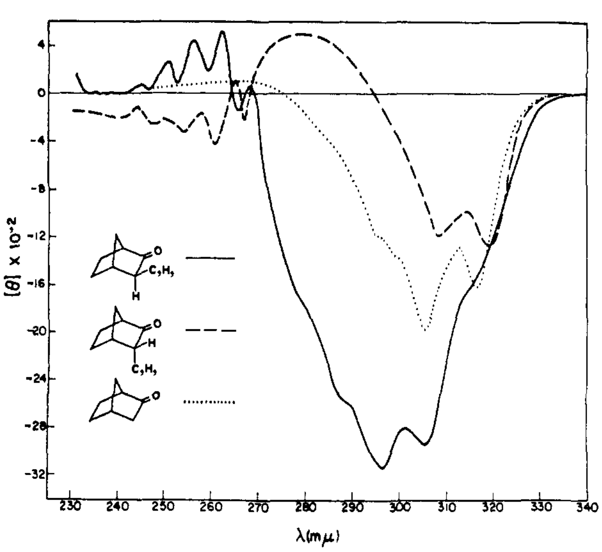


Figure 3. Circular dichroic spectra (isooctane solution) of (+)-3-*exo*-phenyl-2-norbornanone (**3**) (solid line), (−)-3-*endo*-phenyl-2-norbornanone (**2**) (dashed line), and (+)-norcamphor (**4**)[26] (dotted line), corrected to optical purity.[27]

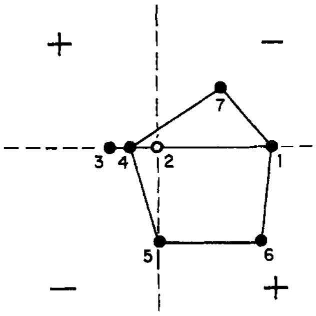


Figure 4. Back octant projection for (+)-(1*S*:4*R*)-norcamphor (**4**).

tailed calculations[35] showed that contribution by this mechanism of interaction is quite negligible, and demonstrated that electrostatic interaction between the localized transitions of the chromophores (transition moment coupling) is mainly responsible for the intensified spectral and chiroptical properties of the n–π^* band.[33-36] Both theories make similar predictions regarding sign and magnitude of the long wavelength Cotton effect for such compounds as dehydronorcamphor and axial α-phenylcholestanones, and both imply a Cotton effect equal in magnitude and opposite in sign to the n–π^* Cotton effect for the coupled transition (*e.g.*, olefinic) which is responsible for enhancing the n–π^* transition. In the chiroptical spectra of (−)-**2** and (+)-**3**, the highly structured Cotton effects of the respective benzene $^1B_{2u}$ transitions centered near 260 mμ have signs opposite to those of the partial contributions of the phenyl groups in (−)-**2** and (+)-**3** (relative to (+)-**4**) which are manifest in the n–π^* Cotton effects. This finding provides strong evidence for transition moment coupling between these two transitions.

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(29) The possibility that the CD of (−)-**2** in the region 265–330 mμ is a composite of overlapping strong positive (centered near 280 mμ) and negative (centered near 310 mμ) Cotton effects, resulting in effective cancellation of rotational strengths for both, is considered unlikely in the light of the low intensity of the corresponding region of the absorption spectrum.[40]

(30) C. Djerassi and W. Klyne, *J. Chem. Soc.*, 2390 (1963); T. D. Bouman and A. Moscowitz, *J. Chem. Phys.*, **48**, 3115 (1968). This possibility was first suggested to us by Professor A. Moscowitz.

(31) Y.-H. Pao and D. P. Santry, *J. Amer. Chem. Soc.*, **88**, 4157 (1966); G. Snatzke and G. Eckhardt, *Tetrahedron*, **24**, 4543 (1968); G. Snatzke, B. Ehrig, and H. Klein, *ibid.*, **25**, 5601 (1969).

(32) H. Labhart and G. Wagniere, *Helv. Chim. Acta*, **42**, 2219 (1959); R. C. Cookson and S. MacKenzie, *Proc. Chem. Soc., London*, 423 (1961); S. MacKenzie, S. F. Marsocci, and H. C. Lampe, *J. Org. Chem.*, **30**, 3328 (1965).

(33) D. E. Bays, G. W. Cannon, and R. C. Cookson, *J. Chem. Soc. B*, 885 (1966).

(34) R. C. Cookson, *Proc. Roy. Soc., Ser. A*, **297**, 27 (1967).

(35) A. Moscowitz, A. E. Hansen, L. S. Forster, and K. Rosenheck, *Biopolym. Symp.*, **1**, 75 (1964).

(36) A. Moscowitz, *Proc. Chem. Soc. London*, 60 (1964); D. E. Bays, R. C. Cookson, and S. MacKenzie, *J. Chem. Soc. B*, 215 (1967); A. Moscowitz, *Proc. Roy. Soc., Ser. A*, **297**, 40 (1967); C. W. Deutsche, D. A. Lightner, R. W. Woody, and A. Moscowitz, *Annu. Rev. Phys. Chem.*, **20**, 407 (1969).

For carbonyl n-π^* transitions, such coupling has been formulated as magnetic–electric[33,37,38] since electric dipole–electric dipole coupling is dominant only for strong transitions ($\epsilon > 10^3$).[37] Actually the perturbing electric transition moment does not interact directly with the magnetic moment of the n-π^* transition but rather with the large quadrupole moment associated with the allowed magnetic transition, thus generating the back quadrant of the octant rule.[37,38] However, the rotational strength arising from this coupling is proportional to $\vec{\mu}\cdot\vec{m}$, where $\vec{\mu}$ is the electric moment of the coupled transition and $\vec{m}$ is the magnetic moment of the n-π^* transitions.[37] For the $^1B_{2u}$ transition of monosubstituted benzene rings, $\vec{\mu}$ lies in the plane of the ring perpendicular to the phenyl-substituent bond,[29] and $\vec{m}$ for the n-π^* transition lies along the axis of the carbonyl group.[33,34,37,38,40] Consideration of a few representative types of cyclic α-phenyl ketones in light of the above treatment immediately offers qualitative insights, and provides an alternative explanation for the observed chiroptical behavior of (−)-**2** and (+)-**3**. The technique used is examination of Dreiding models to deduce sterically favored rotational conformers of the phenyl ring, followed by observation of the interaction of the axes containing $\vec{\mu}$ and $\vec{m}$. Since $\vec{\mu}\cdot\vec{m}$ has a cos ω dependence, the angle of interaction (ω) of these moments will be crucial in determining the rotational strength contribution due to this coupling. For an axial α-phenylcyclohexanone (a prototype for the axial α-phenylcholestanones of Cookson),[3,4] one sees that sterically favored rotamers have small values of ω, so that the contribution to the rotational strength will be maximal, in agreement with the observed domination of the sign of the long wavelength Cotton effect.[4] Equatorial α-phenylcyclohexanones have $\vec{\mu}$ essentially in the nodal plane of the electric quadrupole moment induced by the magnetic transition, so that interaction will be minimal, as in the case for equatorial α-phenylcholestanones.[3,4] Turning to the 3-phenyl-2-norbornanones examined in this study, one finds that $\vec{\mu}$ is well away from nodal planes, but that sterically favored rotamers appear to have values of ω near 90°. Not only does this explain the small contributions of these phenyl groups to the rotational strength of the n-π^* transition, but one can see that small changes in ω can change the sign of the rotational strength contribution as cos ω becomes either positive or negative. This may provide an alternative explanation to front octant effects.

The absence of strengthening of the n-π^* transition by the phenyl group in **2** and **3** is consistent with the observation that the extinction coefficient of the corresponding transition in 2-phenylcyclopentanone (**6**) is also normal.[41] Similarly, the lack of enhancement of the rotational strength of the same transition in **2** and **3** has its counterpart in the absolute rotation of **6**, whose value, $[\phi]_D$ 253°, is not abnormally high.[42] By the same token, the value of the absolute rotation of 2-methyl-2-phenylcyclopentanone, $[\phi]_D$ 166°,[44] may also be judged normal in magnitude.

Experimental Section[45]

(−)-3-*endo*-Phenyl-2-*exo*-norbornanol (1). Triisopinocampheyldiborane (0.046 mol) was prepared after the method of Brown[9] employing (−)-α-pinene[46] (from Oregon fir balsam, Meer Corp., New York, N. Y.). To this reagent was added a solution of 7.83 g of 2-phenylnorbornene (Aldrich). The reaction mixture was stirred for 3 hr at 0° and then subjected to oxidative work-up. The product mixture was chromatographed on Florisil. The fractions exhibiting an OH stretch in the ir were combined and subjected to preparative vpc (7 ft × $^3/_8$ in. FFAP, 225°). A white crystalline solid (3.14 g, 36.4%) was collected which vpc analysis showed to contain 1% isopinocampheol. After four recrystallizations from petroleum ether (bp 30–60°) the material had mp 53.5–55°, $[\alpha]^{19}{}_D$ $-22 \pm 1°$ (*c* 1, ethanol), $[\alpha]^{19}{}_D$ $-21 \pm 1.5°$ (*c* 1, 95% ethanol), ir and nmr spectra identical with those of an authentic sample prepared by a modification of the method of Collins and coworkers[10] (see below), with chemical shifts (δ) and assignments[48] as follows: five aromatic H, 7.12; 2-*endo*- and hydroxyl H, 3.50–3.87; 3-*exo*-H, 2.82; 4-bridgehead H, 2.35; 1-bridgehead H, 2.11; 7-*syn*-H, 1.85; five remaining H, 0.75–1.6 (lit.[48] five aromatic H, 7.13; 2-*endo*-H, 3.80; hydroxyl H, 3.60; 3-*exo*-H, 2.87; 4-bridgehead H, 2.29; 1-bridgehead H, 2.11; 7-*syn*-H, 1.83; remaining H, 0.8–1.6).

Racemic 3-*endo*-Phenyl-2-*exo*-norbornanol (1). This material was prepared by a modification of the method of Collins, *et al.*[10] Commercially available (Metal Hydrides, Inc.) borane in tetrahydrofuran solution was used as the hydride source and the product was purified after oxidative work-up by preparative vpc (7 ft × $^3/_8$ in. FFAP, 250°) to give a 60% yield of crystalline material which, after two recrystallizations from petroleum ether, had mp 52–53°. This material had ir and nmr spectra identical with those of (−)-**1**.

3-*endo*-Phenyl-2-*exo*-norbornyl O-Methylmandelate. Optically pure (−)-(*R*)-O-methylmandelic acid[13] (200 mg, 1.2 mmol) was refluxed gently with 1.5 ml of thionyl chloride for 30 min, then stripped on a rotary evaporator. Benzene (dried over molecular sieves) was added and stripped three times to remove traces of thionyl chloride, then 7 ml of benzene was added, followed by 1 ml of pyridine (dried over barium oxide, *ca.* 12 mmol) which formed a precipitate. After stirring for 5 min, 100 mg of **1** (0.53 ml) in 2 ml of benzene was added. The flask was fitted with a drying tube and the mixture was stirred for 40 hr. The reaction mixture was filtered and solvent was removed on a rotary evaporator. The residue was taken up in ether, washed with 1% hydrochloric acid, saturated sodium bicarbonate, and water, and dried over magnesium sulfate, and the solvent was removed by rotary evaporator. Analysis by vpc showed no unreacted alcohol and indicated that the ester was 97% pure. The 100-MHz nmr spectrum (benzene solution) of the mixture of diastereomers exhibited signals at δ 5.19 (1 H), 4.81 and 4.77 (1 H, methoxymethine), 3.27 and 3.03–3.30 (3 methoxy H, and 1 H), 2.29 (2 H), 0.8–1.85 (6 H). Electronic integration of the methoxymethine signals indicated the ratio of diastereomers derived from **1** to be 1.0:1.0.

Determination of the Optical Purity of (−)-3-*endo*-Phenyl-2-*exo*-norbornanol (1). A mixture of diastereomers of 3-*endo*-phenyl-2-*exo*-norbornyl O-methylmandelate was prepared from (−)-**1**

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(40) S. F. Mason, *Quart. Rev. Chem. Soc.*, **17**, 20 (1963).

(41) K. Mislow and A. K. Lazarus [*J. Amer. Chem. Soc.*, **77**, 6383 (1955)] report an ϵ value of *ca.* 50 at 293 mμ.

(42) H. B. Hopps, Ph.D. Dissertation, Purdue University, 1962. We are greatly indebted to Dr. Hopps and to Professor J. H. Brewster for bringing our attention to this work, which corrects an earlier report[43] on the absolute rotation of **6**.

(43) K. Mislow and C. L. Hamermesh, *J. Amer. Chem. Soc.*, **77**, 1590 (1955).

(44) T. D. Hoffman and D. J. Cram, *ibid.*, **91**, 1000 (1969).

(45) Reagents and solvents were obtained from commercial sources and used without further purification, except as noted below. Nuclear magnetic resonance spectra were recorded on Varian Model A-60A and HA-100 spectrometers. Ultraviolet spectra were taken with a Cary 14 recording spectrophotometer and ORD's and CD's with a Cary Model 60 ORD with the Model 6001 CD attachment. Melting points are uncorrected.

(46) The sample used was *ca.* 93% pure by vpc and had $[\alpha]^{23}{}_D$ $-41.1°$ (*c* 5, ethanol), $[\alpha]^{20}{}_D$ $-38.2°$ (neat). The sample was thus *ca.* 75% optically pure based on the highest reported rotation, $[\alpha]^{20}{}_D$ $+51.1°$ (neat).[47]

(47) F. H. Thurber and R. C. Thielke, *J. Amer. Chem. Soc.*, **53**, 1030 (1931).

(48) D. C. Kleinfelter and T. E. Dye, *ibid.*, **88**, 3174 (1966).

and optically pure (−)-O-methylmandelic acid[13] exactly as described above with the exception that after the alcohol–acid chloride–pyridine–benzene mixture had been stirred for 20 hr an additional 100 mg of the acid was converted to the acid chloride and added to the reaction mixture, which was subsequently stirred for another 20 hr. Following work-up, the product was purified by preparative vpc (4 ft × 0.25 in. GE XE-60, 240°). The 100-MHz nmr spectrum (benzene solution) of the mixture of diastereomers was identical with that derived from racemic **1** except that the methoxymethine signal at δ 4.81 was more intense than that at 4.77. The diastereomeric excess and hence the optical purity of (−)-**1** were determined to be 26 ± 2% by integration of these signals.[14]

(−)-3-*endo*-Phenyl-2-norbornanone (2). A solution of 2.0 g of (−)-**1** (10.6 mmol) in *ca.* 0.5 ml of pyridine was added at 0° to a 500-ml round-bottomed flask containing Sarett reagent[5,13] prepared by *carefully* adding 2.0 g of chromium trioxide (Baker and Adamson) to 20 ml of pyridine (dried over barium oxide) vigorously stirred and cooled in an ice bath. After being stirred for 2 hr at room temperature, the reaction mixture was quenched by the addition of 400 ml of water. The aqueous mixture was extracted four times with 200-ml portions of ether. The extracts were combined and washed first with dilute hydrochloric acid, then with water, and dried over magnesium sulfate. After distillation (kugelrohr, *ca.* 100°, 0.05 mm), analysis by nmr indicated the ratio of unreacted alcohol to product ketone to be 0.19:0.81. Separation of the ketone from the alcohol was affected by chromatography on silica gel, eluting with up to 20% ether in petroleum ether (bp 30–60°). After distillation (kugelrohr, 95°, 0.07 mm), 0.82 g (41.4%) of a low-melting white solid was obtained with $[\alpha]^{21}_{\mathrm{D}}$ −33.3 ± 1.7° (*c* 1, ethanol). The material had ir and nmr spectra identical with those of an authentic sample prepared by the method of Collins and coworkers[10] (see below) with chemical shifts (δ) and assignments[10,48,49] as follows: five aromatic H, 7.17 (lit.[49] 7.18); 3-*exo*-H doublet, 3.30, *J* = 4.3 Hz (lit. 3.27, *J* = 4.5 Hz;[10] 3.32, *J* = 4.2 Hz;[48] 3.32, *J* = 4.4 Hz[49]); 1- and 4-bridgehead H, 2.49–2.87; six remaining methylene H, 1.20–1.93. The ultraviolet absorption spectrum in isooctane solution exhibited the following features: $\lambda_{\max}$ mμ (ε) 321 (20), 308.4 (38.5), 298.3 (44), 273.5 (36.6), 269 (81.6), 265.7 (168), 259.4 (206), 253.5 (159), 248.7 (111), 243.5 (75.5). The ORD characteristics in isooctane solution (*c* 0.3240), corrected to optical purity, were $[\varphi]_{\mathrm{D}}$ −214°, $[\varphi]_{324}$ −2100°, $[\varphi]_{315}$ −1065°, $[\varphi]_{302}$ −287°, $[\varphi]_{269}$ −2565°, $[\varphi]_{266.5}$ −2300°, $[\varphi]_{262.5}$ −2925°, $[\varphi]_{259.4}$ −2475°, $[\varphi]_{255}$ −3095°, $[\varphi]_{253.5}$ −3005°. Biot's law was obeyed through the first extremum. The CD in isooctane (*c* 0.3240), corrected to optical purity, had $[\theta]_{340}$ 0, $[\theta]_{319.3}$ −1273, $[\theta]_{314.5}$ −993, $[\theta]_{308.5}$ −1200, $[\theta]_{294.6}$ 0, $[\theta]_{279}$ +494, $[\theta]_{268.8}$ 0, $[\theta]_{267}$ −238.5, $[\theta]_{265}$ +100, $[\theta]_{260.5}$ −435, $[\theta]_{257.8}$ −169, $[\theta]_{253.8}$ −338, $[\theta]_{250}$ −215, $[\theta]_{248}$ −269, $[\theta]_{244}$ −116.7, $[\theta]_{241}$ −215. All of the spectral determinations on this material, ir, nmr, uv, ORD, and CD, were made within 24 hr after the kugelrohr distillation since crystalline **2** is known to decompose to a yellow oil on standing for a few weeks under nitrogen in a refrigerator.[50]

(+)-3-*exo*-Phenyl-2-norbornanone (3). A sample of (−)-**2**, 0.82 g (4.4 mmol), was subjected to preparative vpc (20 ft × $^3/_8$ in. FFAP, 243–246°, retention time 69 min, with the preparative runs eluting for *ca.* 20 min). An estimate of the composition of the epimerized mixture was obtained by integrating the signals at δ 2.95 and 3.30 in the nmr spectrum of the crude eluate, due to the 3-*endo*-H of **3** and the 3-*exo*-H of **2**, respectively. The ratio of **3** to **2** was 47:53. Chromatography on Florisil, eluting with up to 15% ether in petroleum ether (bp 30–60°), gave pure **3** followed by a mixture of **3** and **2**, and finally a trace of pure **2**. The fractions containing pure **3** were combined and distilled (kugelrohr, 90°, 0.03 mm) to give 0.27 g (1.45 mmol, 33%) of a clear viscous oil. The ir spectrum (neat, sodium chloride plates) exhibited a strong ketone absorption at 1747 cm^{-1} and a phenyl absorption at 1600 cm^{-1}, and was generally similar to that of **2**. The nmr spectrum had signals at the following resonances (δ): five aromatic H, 7.19; 3-*endo*-H, 2.95, *J* = 3.1 Hz (lit.[10,49] 2.93, *J* = 3.1 Hz); 1- and 4-H, 2.51 and 2.81; six remaining H, 1.2–2.1. The ultraviolet absorption spectrum in isooctane solution exhibited the following features: $\lambda_{\max}$ mμ (ε) 320 (41.4), 308 (82), 298 (94.3), 287 (89.2), 269 (133), 265.7 (185), 259.9 (222), 254.3 (182), 249.5 (137). The ORD characteristics in isooctane solution (*c* 0.3098), corrected to optical purity,[51] were $[\varphi]_{\mathrm{D}}$ +12, $[\varphi]_{460}$ 0, $[\varphi]_{321.3}$ −1790, $[\varphi]_{314}$ −1250, $[\varphi]_{311.6}$ −1267, $[\varphi]_{305}$ 0, $[\varphi]_{270}$ +3935, $[\varphi]_{266}$ +3170, $[\varphi]_{263.6}$ +3360, $[\varphi]_{260}$ +2827, $[\varphi]_{257}$ +2950, $[\varphi]_{254.5}$ +2665, $[\varphi]_{251}$ +2827, $[\varphi]_{249}$ +2760. Biot's law was obeyed through the first extremum. The CD in isooctane (*c* 0.3098), corrected to optical purity,[51] had $[\theta]_{340}$ 0, $[\theta]_{315}$ −1647, $[\theta]_{306}$ −2955, $[\theta]_{301.6}$ −2805, $[\theta]_{296.5}$ −3140, $[\theta]_{269}$ 0, $[\theta]_{268}$ +51, $[\theta]_{265.7}$ −153, $[\theta]_{262}$ +513, $[\theta]_{259}$ +179, $[\theta]_{256}$ +434, $[\theta]_{252.5}$ +72, $[\theta]_{250.5}$ +255, $[\theta]_{246.5}$ +25, $[\theta]_{245}$ +68.

Recovery of (−)-3-*endo*-Phenyl-2-norbornanone (2) from Vpc Epimerization. All the fractions containing (−)-**2** from the chromatography described above were combined and rechromatographed on Florisil, eluting with up to 15% ether in petroleum ether (bp 30–60°). The fractions containing (−)-**2** were combined and distilled (kugelrohr, 90°, 0.03 mm) to give 270 mg of a low-melting white crystalline solid. The ir and nmr spectra were identical with those obtained above for pure (−)-**2**. The ORD characteristics through the first extremum showed only 85% of the molecular rotation of the starting (−)-**2**, and the CD showed 86% of the molecular ellipticity of the starting (−)-**2**.

Racemic 3-*endo*-Phenyl-2-norbornanone (2). Sarett oxidation[10,15] of racemic **1**, as described above for (−)-**2**, gave a mixture containing starting alcohol and product ketone **2** in the ratio 0.28:0.72 (nmr). Chromatography on silica gel followed by kugelrohr distillation (95°, 0.07 mm) gave 55% of a low-melting white solid whose ir, nmr, and uv spectra were identical with those for (−)-**2**.

Racemic 3-*exo*-Phenyl-2-norbornanone (3). Racemic **2** was epimerized by preparative vpc (20 ft × $^3/_8$ in. FFAP, 250°) to give a mixture in which the ratio of **3** to **2** was 47:53 by nmr. Repetition of the vpc treatment gave the same ratio of **3** to **2**. Pure **3** was obtained by chromatography on Florisil followed by kugelrohr distillation (90°, 0.03 mm). The resulting clear viscous oil had ir, nmr, and uv spectra identical with those for (+)-**3**. Epimerization of this material by preparative vpc (20 ft × $^3/_8$ in. FFAP, 245–248°) gave a mixture in which the ratio of **3** to **2** was 47:53 by nmr.

Base-Catalyzed Epimerization of 3. A mixture of racemic **3** and **2**, 47:53 by nmr, was subjected to base-catalyzed epimerization by three different methods.

Method A. The mixture of diastereomers was taken up in ether and washed four times with 1 *N* sodium hydroxide.[5] The material recovery was >90% but the ratio of epimers was unchanged by this treatment.

Method B. When the mixture was placed in 0.5 *M* methanolic sodium hydroxide for periods of 15 min, 1 hr, and 3 hr, the material recovery was >80% after quencing with water and extracting with ether, and the ratio of the epimers was 37:63 for each reaction time.

Method C. The mixture was taken up in a solution of 1 ml of 1 *N* sodium hydroxide in 20 ml of dimethyl sulfoxide. The reaction mixture immediately turned bright yellow, darkening to red-orange during 30 min stirring, after which it was taken up in water and extracted with ether. After drying with magnesium sulfate and removing solvent on a rotary evaporator, less than 40% of a yellow oil was obtained. This material showed no signals for **3** in the nmr spectrum.

Base-Catalyzed Epimerization of (+)-3. A sample of (+)-**3**, 220 mg, was taken up in 20 ml of 0.5 *N* methanolic sodium hydroxide and stirred for 1 hr. The reaction was quenched by addition of 100 ml of water, and extracted with ether. The extracts were combined and dried over magnesium sulfate, and solvent was removed on a rotary evaporator to give 200 mg (90%) of a slightly yellow oil. This material was shown to contain 65% **2** by nmr. After chromatography on Florisil and kugelrohr distillation, pure (−)-**2** was isolated as a white, crystalline, low-melting solid having an nmr spectrum identical with that reported above for (−)-**2**. The sample has $[\varphi]^{27}_{\mathrm{D}}$ −48° (*c* 0.3246, isooctane), 86% of that of (−)-**2** prior to vpc epimerization.

(−)-Norcamphor (4). Tetraisopinocampheyldiborane (0.215 mol) was prepared employing (−)-α-pinene,[46] according to the method of Brown.[23,52] This reagent was used in the hydroboration of 40.5 g of norbornene (Aldrich, 0.43 mol) which yielded a mixture of optically active norborneol and isopinocampheol after oxidative work-up and codistillation with *n*-decane. This mixture of alcohols was taken up in 250 ml of acetone and oxidized by titration with Jones reagent[53] at 15–20° with constant stirring until the orange

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(49) D. C. Kleinfelter, T. E. Dye, J. E. Mallory, and E. S. Trent, *J. Org. Chem.*, 32, 1734 (1967).

(50) C. J. Collins, private communication.

(51) Since the (−)-**2** recovered from the vpc epimerization was 15% racemized (see below), it was assumed that the (+)-**3** also suffered 15% racemization so that its optical purity was 22 ± 2%.

(52) H. C. Brown, N. R. Ayyangar, and G. Zweifel, *J. Amer. Chem. Soc.*, 86, 397 (1964).

(53) J. Meinwald, J. Crandall, and W. E. Hymans, *Org. Syn.*, 45, 77 (1965).

color persisted for 30 min. A few drops of 5% sodium bisulfite solution was added to discharge most of the brown color. The reaction mixture was separated and the organic layer was washed with saturated potassium carbonate solution and dried over magnesium sulfate. The acetone solution was concentrated by distillation, followed by the addition of *n*-decane and codistillation of norcamphor on a spinning band column. After *ca.* 50% of the norcamphor had distilled, it was separated from the hydrocarbon by chromatography on Florisil, while additional norcamphor was separated from the pot residue by preparative vpc (20 ft × 3/8 in. FFAP). Both samples of norcamphor were combined and repeatedly sublimed until the melting point was unchanged at 90.5–93.0 (lit.[54] mp 97–98° (racemic)) to yield 7.5 g (16%) of white crystals. The ir and nmr spectra were identical with those of a commercially obtained sample (Aldrich). Analysis by vpc showed no discernible impurity. The material had $[\alpha]^{23}\text{D}$ −9.74 ± 0.40° (*c* 2.8, chloroform). Comparing this rotation to that obtained by Mislow and Berger,[20] this material is 31.2% optically pure. The ultraviolet absorption spectrum in isooctane solution exhibited $\lambda_{\max}$ 295 mμ (ε 23) (lit.[20] 295 (29)). The ORD characteristics in isooctane (*c* 0.3174), corrected to optical purity, were $[\varphi]_{320.5}$ −896°, $[\varphi]_{314}$ +294°, $[\varphi]_{312.5}$ +356°, $[\varphi]_{307}$ 0°, $[\varphi]_{302.5}$ −922°, $[\varphi]_{301.5}$ −895°, $[\varphi]_{289}$ −1450°, $[\varphi]_{255}$ −704°, $[\varphi]_{230}$ −850° (lit.[20] $[\phi]_{320}$ +1480, $[\phi]_{283}$ −1360). Biot's law was obeyed near 380 mμ. The CD in isooctane (*c* 0.3174), corrected to optical purity, had $[\theta]_{340}$ 0, $[\theta]_{316.5}$ +1628, $[\theta]_{313}$ +1302, $[\theta]_{305.4}$ +1986, $[\theta]_{300}$ +1387, $[\theta]_{295}$ +1202, $[\theta]_{275}$ 0, $[\theta]_{265}$ −80, $[\theta]_{250}$ −45 (lit.[55] (cyclohexane) $[\theta]_{340}$ 0, $[\theta]_{318}$ −1165, $[\theta]_{313}$ −983, $[\theta]_{306}$ −1463, $[\theta]_{274}$ 0, $[\theta]_{269}$ +33). The ORD and CD spectra of this compound are multiplied by −1 and plotted as its enantiomer in Figures 2 and 3.

(−)-2-Phenylnorbornene (5). Phenylmagnesium bromide (20 mmol) was prepared in ether solution, filtered, and slowly added to a solution of 2.20 g (20 mmol) of the (−)-norcamphor described above. Routine work-up afforded an oil which was treated with a tenfold excess of acetyl chloride–pyridine complex in benzene for 17 hr. The crude acetate was pyrolyzed by preparative vpc (20 ft × 3/8 in. FFAP, 250°) to give 0.76 g (22%) of a slightly yellow liquid containing *ca.* 4% of an impurity. Purification was effected by rechromatography on a new FFAP column, column chromatography on Florisil, and kugelrohr distillation to give 0.16 g of clear viscous liquid, homogeneous by vpc. The ir and nmr spectra were identical with those of a commercial sample of racemic 2-phenylnorbornene (Aldrich). The material had $[\alpha]^{24}\text{D}$ −63.6 ± 0.6° (*c* 1.6, ethanol). Corrected to optical purity, (−)-2-phenylnorbornene had $[\alpha]^{24}\text{D}$ −204 ± 22°.

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[54] D. C. Kleinfelter and P. von R. Schleyer, *Org. Syn.*, **42**, 79 (1962).

[55] P. Witz, H. Herrmann, J.-M. Lehn, and G. Ourisson, *Bull. Soc. Chim. Fr.*, 1101 (1963).

Thermal Decomposition of Tetramethyl-2-tetrazene. Reactivity of the Dimethylamino Radical

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Abstract: The reaction of the dimethylamino radical with toluene and substituted toluenes has been measured and the relative rates are correlated with σ^+ values. The ρ value for the abstraction reaction is −1.08. The deuterium isotope effect was found to be 4.0. The kinetics of the thermal decomposition of tetramethyl-2-tetrazene (TMT) in benzene solution have been measured. A comparison with gas-phase kinetics is made. It was found that at concentrations of TMT greater than 0.2 *M* induced decomposition becomes important.

Tetraalkyl-2-tetrazenes are convenient sources of dialkylamino radicals. The compounds decompose smoothly either thermally or photochemically. It is a little surprising that since the pioneering work of Wieland[1] relatively little work has been published on the chemistry of 2-tetrazenes or the amino radicals derived from them. Rice and Gerlecki[2] showed that when tetramethyltetrazene (TMT) in the gas phase was passed over a hot wire (1300°) the dimethylamino radicals could be trapped at −196°. Several workers studied the thermal decomposition kinetics of TMT in the gas phase. The most complete study was by Gowenlock and his coworkers[3] who examined the decomposition in a flow system over a wide temperature range. The energy of activation was 36.1 ± 1 kcal/mol and the preexponential factor was $10^{14.4 \pm 0.5}$. Watson and Waring[4] examined the decomposition in a static system, over a more limited temperature range, and found $E_a = 31.9 \pm 3$ kcal/mol and $\log A = 11.4 \pm 1.65$. Recently the static system decomposition of TMT was reexamined[5] over a wider temperature range (127–175°); the activation parameter values reported, $E_a = 34.6$ kcal/mol and $\log A = 13.83$, are more in line with Gowenlock's values.

The kinetics of the thermal decomposition of TMT in solution apparently have escaped attention except for the report of a rate constant from a single run at one temperature in cumene solution ($k = 0.56 \times 10^{-4}$ sec^{-1} at 145°).[6]

This paper reports a study of the kinetics of decomposition of TMT in benzene solution, the effect of induced decomposition, the reactivity of the dimethylamino radical toward toluene and substituted toluenes, and the deuterium isotope effect for the abstraction reaction.

Experimental Section

Ultraviolet spectra were obtained with a Cary Model 14 spectrophotometer and the ir spectra were obtained with Perkin-Elmer Model 237 and 621 instruments. The nmr spectra were recorded

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