# The Dehydration of 2-Phenyl-3-diphenylmethyleneisoborneol in Acid Media

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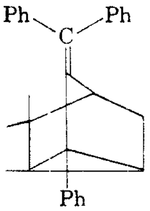
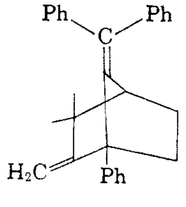
Dehydration of 2-phenyl-3-diphenylmethyleneisoborneol afforded 1-phenyl-7-diphenylmethylenecamphene and 2-phenyl-3-diphenylmethylenetricyclene as the respective kinetic and thermodynamically controlled products. This preference of tricyclene over camphene-type product, contrary to other observations in similar systems, may be explained from consideration of steric factors. Anisotropic effects of the phenyl substituents mutually operative and operating on other proximate hydrogens are used for phenyl orientational assignments.

A study of carbonium ions derived from substituted 3-methylenebicyclo[2.2.1]heptan-2-ols is presently being carried out in our laboratories. We have felt that such an investigation could be significant in relation to the emphasis on the tenets of classical and nonclassical carbonium ions. Rupe and Hagenbach[2] studied a rearrangement apparently involving a 3-substituted methylenebicyclo[2.2.1]heptyl cation before the nonclassical carbonium ion controversy had gained significant momentum. They reported that addition of phenyllithium to 3-diphenylmethylenecamphor (I) afforded a mixture of two isomeric hydrocarbons, one with mp 163–164°, and the other with mp 114–115°. The higher melting compound could be transformed into its lower melting isomer by heating in acetic acid solution in the presence of strong acids or by prolonged warming in acetic acid. The isomerization rate was studied spectrophotometrically since a deep amethyst red to bright yellow color change was involved in the transformation.

Since Meerwein and Van Emster[3] had demonstrated that tricyclene is changed into camphene by heating with acid, Rupe and Hagenbach reasoned that a similar change was involved with their hydrocarbons and assigned the tricyclene structure (II) to the higher melting hydrocarbon and the camphene structure (III) to the lower melting isomer. The work described herein involves a check of the account given by Rupe and Hagenbach and some further reactions of the rearrangement product. In addition, we wished to compare the nuclear magnetic resonance (nmr) spectral data of the obtainable compounds with the data already compiled in the arylnorbornyl system to determine the relative operative phenyl diamagnetic anisotropic shielding effects.



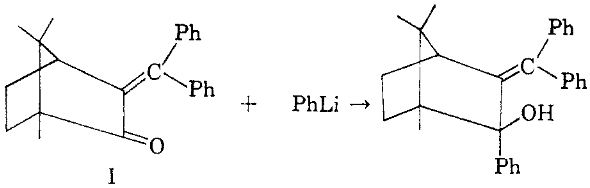
II



III

## Results

Contrary to what was reported,[2] phenyllithium addition to I gave the tertiary alcohol, 2-phenyl-3-diphenylmethyleneisoborneol (IV), not II and III. Apparently IV was dehydrated to II and III by Rupe and Hagenbach in their decomposition of the lithium salt in acid. The *exo* orientation of IV's hydroxyl group is assigned on the basis of the general rule of *endo* addition to norbornane compounds with 7-*syn* substituents.[4] In sufficiently dilute carbon tetrachloride solution in which no intermolecular association was present, the O–H-stretching vibration in the infrared appeared at 3574 cm$^{-1}$, which amounts to a $\Delta\nu$ (OH–$\pi$ type) of 30 cm$^{-1}$ when compared with the 3604-cm$^{-1}$ value for 2-*endo*-phenylnorbornanol.[5] An examination of molecular models reveals that the intramolecular hydrogen-bonding site may be the carbon–carbon double bond or a benzene ring.



I

IV

Dehydration of IV in acid media proceeds to the hydrocarbon mixture reported. The relative percentages of the two hydrocarbons depend on the acid strength and reaction time. Brief heating with trichloracetic–acetic acid mixtures gives largely the higher melting compound while the lower melting isomer predominates from heating of IV with potassium bisulfate. The initial solution color of wine red changes with time to yellow in trichloroacetic–acetic acids, but this change is apparently not an indication of the completion of the isomerization as a hydrocarbon mixture still can be obtained. As reported, refluxing of the higher melting compound in acetic acid converted it to the lower melting isomer.

Examination of the infrared and nmr spectra of the two hydrocarbons revealed that their structures were reversed from those assigned by Rupe and Hagenbach. The higher melting hydrocarbon is the camphene (III) and the lower melting isomer is the tricyclene (II). In the infrared spectra III showed strong absorption at 885 cm$^{-1}$ characteristic of the $C{=}CH_2$ system,[6] while II showed only medium absorption at 882 and 781

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[1] National Science Foundation Undergraduate Summer Research Participant, 1965.

[2] H. Rupe and R. Hagenbach, *Helv. Chem. Acta*, **28**, 81 (1945).

[3] H. Meerwein and K. Van Emster, *Ber.*, **53**, 1815 (1920).

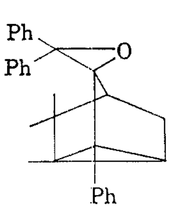
[4] K. Alder, G. Stein, and H. F. Rickert, *Ann.*, **525**, 221 (1956), and many subsequent examples.

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

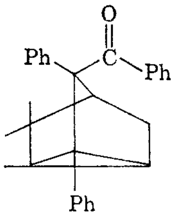
[6] L. J. Bellamy, "The infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 34.

$cm^{-1}$, probably associated with tricyclene absorption.[7] The olefinic methylene hydrogens of III appeared in the nmr as two nonequivalent sharp signals at 4.61 and 4.05 ppm. Only two methyl signals at 1.39 and 1.20 ppm were observed. The nmr spectrum of II showed three methyl signals at 1.27, 0.95, and 0.76 ppm.

Hydrogenation of II over platinum was unsuccessful but was accomplished by utilizing the catalyst system of rhodium on charcoal. The relative inaccessibility of the double bond of II was further demonstrated by its virtual inertness to oxidation with potassium permanganate. Peracid oxidations were successful, however, and the epoxide (V) and ketone (VI) were obtained with buffered peracetic acid and performic acid oxidations, respectively. That V was presumably an intermediate in the performic acid reaction was demonstrated by its conversion to VI with formic acid. The stereochemistry of the epoxide ring in V (oxygen "*anti*" to methyls) has been assigned from a consideration of the greater probability for attack of the double bond by the per acid from the "*anti*" direction. Rearrangements of styrene-type epoxides to ketones are common.[8] Backside attack by phenyl *via* a phenonium ion intermediate in the epoxide opening process would give the *anti*-ketone stereochemistry.



V



VI

## Discussion

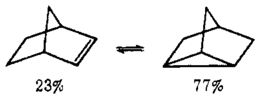
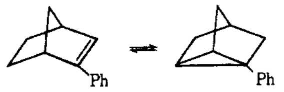
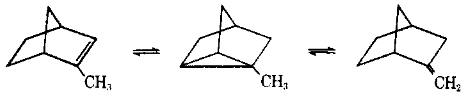
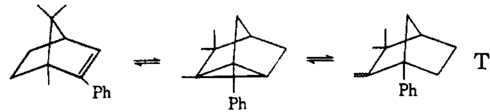
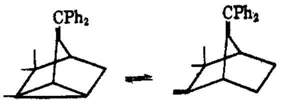
**Isomerization of Some Bicyclic Hydrocarbons.**—Apparently the camphene (III) is the product of kinetic control and the tricyclene (II) the thermodynamically preferred product. This result may be considered surprising in light of the previously acknowledged tricyclene to camphene rearrangement of Meerwein and Van Emster.[3] Data on some equilibrations of related bicyclic hydrocarbons reported previously along with those involved in our present work are summarized in Table I.

Table I reveals that a phenyl-conjugated or exocyclic methylenic system is preferred over a tricyclic system with the exception of system 6. In 6, phenyl conjugation without rearrangement to different hydrocarbon types is precluded, and only camphene- and tricyclene-type hydrocarbons are possible. The *ca.* 3:1 ratio of X:IX in system 7 demonstrates that the bridge diphenylmethylene system alone is not responsible for the preference of II over III. An argument for the stabilization of II attributed to phenyl conjugation with the cyclopropane type ring appears unfounded owing to the absence of 1-phenyltricyclene in system 5.

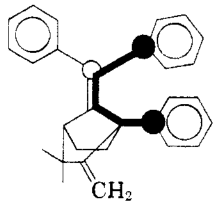
Evidently, the combination of the diphenylmethylene and the 1-phenyl substituents alters the thermodynamic stabilities of the bicyclic and tricyclic systems. This alteration may be due to differences in steric interactions between the benzene rings in II and III. In both hydrocarbons the $C_1$ carbon atoms of the 1-phenyl substituent and the 7-phenyl *syn* to it must lie nearly in a common plane. If there is sufficient decrease in steric interactions between these phenyls in III relative to II then the apparent lower energy of II would be understandable. Such a decrease can be envisioned owing to the change in bond angles caused by the three-membered ring. The *ca.* 60° internal bond angle requirement for the cyclopropane-type ring in II should cause a corresponding expansion of the external bond angles and a consequent bending of the 1-phenyl substituent away from the *syn*

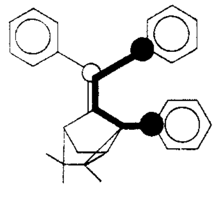
TABLE I

EQUILIBRATION OF BICYCLIC HYDROCARBONS WITH ACID CATALYST[a]

| System | | Ref |
|---|---|---|
| 1 |  23% ⇌ 77% | *b* |
| 2 |  95% ⇌ 5% | *c* |
| 3 |  21 ± 6% ⇌ 3.5 ± 1.5% ⇌ 75 ± 5% | *d* |
| 4 |  trace ⇌ 17% ⇌ 83% | *e* |
| 5 |  VII, 60% ⇌ <1% ⇌ VIII, 40% | This work[f] |
| 6 | II, 100% ⇌ III, 0% | This work |
| 7 |  IX, 26% ⇌ X, 74% | This work |

[a] Systems 2 and 5–7 involved reaction of alcohol precursors with $KHSO_4$. [b] Reflux on silica-alumina catalyst, P. von R. Schleyer, *J. Am. Chem. Soc.*, **80**, 1700 (1958). [c] D. C. Kleinfelter and P. von R. Schleyer, *J. Org. Chem.*, **26**, 3740 (1961). [d] Distillation of 2-*exo*- and 2-*endo*-methylnorbornanols over *p*-toluenesulfonic acid, R. Sauers, *J. Am. Chem. Soc.*, **81**, 4873 (1959). [e] Reflux over $TiO_2$ catalyst, G. Swann and F. J. Cripwell, *Ind. Chemist*, **24**, 573 (1948). [f] S. S. Nametkin, A. S. Kichkina, and D. N. Kursanov [*J. Prakt. Chem.*, **124**, 144 (1930)] reported that 2-phenylisoborneol is dehydrated with $KHSO_4$ to 1-phenylcamphene alone.





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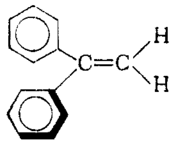
[7] H. Hart and R. A. Martin, *J. Org. Chem.*, **24**, 1267 (1959); D. C. Kleinfelter and P. von R. Schleyer, *J. Am. Chem. Soc.*, **83**, 2329 (1961).

[8] See, for example, R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959), and references therein.

bridge phenyl ring. This is an example of the Thorpe–Ingold effect of bond angle deviation.[9,10] A thorough examination of our ultraviolet and nmr data was carried out to learn if spectral evidence for such changes in steric interactions could be revealed.

**Consideration of Ultraviolet Spectral Data.**—Numerous examples of the effect of steric factors on electronic spectra are known.[11] Such effects depend on the principle that an essential requirement for maximum resonance is coplanarity of the resonating system. If one of the centers contributing to the resonance hybrid is displaced out of coplanarity, steric hindrance to resonance will be reflected in the system's absorption properties.[12] Jones[13] has studied the substitution of one or more of the ethylenic hydrogens of styrene and of *trans*-stilbene by phenyl groups. Such substitution does not necessarily produce a change in the chromophore, and the spectra of the compounds fall into two classes, depending on whether they exhibit a styrene or *trans*-stilbene spectral type. The similarity of the spectrum of 1,1-diphenylethene to that of styrene has been explained as owing to rotation of one of the phenyl groups out of the plane of the ethylenic system, resulting in a molecule (XI) with a styrene chromophore and a phenyl chromophore, the latter exhibiting no appreciable influence on the resultant spectrum.



XI

Systems 6 and 7 of this present work are those related to 1,1-diphenylethene and hence would be expected to exhibit spectra of the styrene type. Data on these and related systems are listed in Table II.

Table II

Ultraviolet Absorption Spectra for Some *unsym*-Diphenylethylenic Compounds[a]

| Compound | $\lambda_{max}$, m$\mu$ | Log $\epsilon$ |
|---|---|---|
| XI[b] | 251 | 4.07 |
| | 224 | 4.23 |
| 1,1-Diphenyl-1-heptene[c] | 248 | 3.78 |
| III | 240 | 4.14 |
| II | 253 | 4.20 |
| IX + X[d] | 239 | 4.14 |
| 3-Diphenylmethyleneisoborneol | 248 | 4.13 |

[a] All spectra except that for 1,1-diphenyl-1-heptene were determined in 95% ethanol. [b] Calculated from Figure 2 of ref 13. [c] The $\lambda_{max}$ and log $\epsilon$ for this compound were obtained from API Research Project 44 Publications, Ultraviolet Spectral Data, Serial No. 516. [d] The data are for the hydrocarbon mixture.

Significant comparisons are made among camphene and tricyclene compounds II, III, IX, and X, since in these the substitution and geometry about the ethylenic chromophore should be nearly equivalent. The bathochromic shift of 13 m$\mu$ and the slight hyperchromic shift in proceding from III to II are in line with expectations from consideration of steric factors presented previously. In the spectra of a series of $\alpha,\alpha'$-dialkyl-substituted derivatives of *cis*- and *trans*-stilbenes Suzuki[14] has noted that the long-wavelength band undergoes a hypsochromic shift of 7–8 m$\mu$ in proceding from the dimethyl to the more bulky diethyl substituents. There is also an accompanying hypochromic shift. The apparent equivalence of the absorption maxima for IX and X in which the bridgehead phenyl is absent adds some credulance to our arguments. However, the near equivalence of the absorption maxima for IX and X with III is somewhat disconcerting in that steric effects are presumably minimal in the former two compounds.

**Consideration of Nmr Spectral Data.**—The nmr spectra of the camphene and tricyclene-type compounds were thoroughly scrutinized in order to assign preferred phenyl orientational arrangements. Chemical shifts for these compounds are recorded in Table III.

Methylenic olefinic protons normally absorb at *ca.* 4.6–5.0 ppm.[15] When a bridgehead aryl group is substituted adjacent to the olefinic attachment in the camphene compounds, at least one of the two hydrogens is substantially shielded. Evidently the preferred 1-phenyl orientation is that in which the plane of the phenyl ring approaches an orthogonal arrangement with respect to the most proximate olefinic proton, placing it well within the diamagnetic shielding cone of the benzene ring.[16] The spectrum of III reveals that a proton signal with large *J* values is considerably deshielded and appears in the vicinity of the 4-methine hydrogen signal. If the bridgehead phenyl ring adopts an arrangement in which the shielding cone envelopes the most proximate olefinic hydrogen, then the 6-*exo* proton lies in the plane of the phenyl ring, and anisotropic deshielding will be experienced.

Examination of the phenyl region of the nmr spectra of II and III reveals that the hydrogens of two phenyl groups are considerably shielded. Curtin and coworkers[17] in their study of the 1,2-diphenylcyclopentanes have shown that the *cis* isomer is shielded by 0.20 ppm with respect to the *trans* isomer. In the *cis* case the phenyl rings are presumably tilted and there is mutual shielding of the phenyl rings with the resultant phenyl pattern being a complex multiplet with outer peaks separated by 31 cps. Evidently the tilting of the phenyl rings causes different diamagnetic shieldings of the protons of one phenyl ring by the other; *i.e.*, the protons are not magnetically equivalent as they are in the *trans* isomer where a narrow absorption was observed.

The upfield shifts to 6.83 and 6.69 and 6.78 and 6.70 ppm for the phenyl protons of III and II, respectively, are presumably due to analogous mutual shielding between the bridgehead (B) and the "*syn*" (S)

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[9] R. M. Beesley, C. K. Ingold, and J. F. Thorpe, *J. Chem. Soc.*, **107**, 1080 (1915); C. K. Ingold, *ibid.*, **119**, 305 (1921).

[10] P. von R. Schleyer, *J. Am. Chem. Soc.*, **83**, 1368 (1961).

[11] E. A. Braude and E. S. Waight, *Progr. Sterochem.*, **1**, 126 (1954).

[12] A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold Ltd., London, 1957, p 267.

[13] R. N. Jones, *J. Am. Chem. Soc.*, **65**, 1818 (1943).

[14] H. Suzuki, *Bull. Chem. Soc. Japan*, **33**, 396 (1960).

[15] J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, p 85.

[16] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Ltd., London, 1959, p 126.

[17] D. Y. Curtin, H. Gruen, and B. A. Shoulders, *Chem. Ind.* (London), 1205 (1958); D. Y. Curtin, H. Gruen, Y. G. Hendrickson, and H. E. Knipmeyer, *J. Am. Chem. Soc.*, **83**, 4838 (1961).

TABLE III

CHEMICAL SHIFTS (PARTS PER MILLION) FOR SOME BICYCLIC HYDROCARBONS

| Compound[a] | $=CH_2$ | $CH_3$'s | 4 H | Tricyclene H | Phenyls[b] | | |
|---|---|---|---|---|---|---|---|
| | | | | | A | B | S |
| VIII | 4.54, 4.17 | 1.07, 1.11 | 2.13 | ... | ... | 7.20 | ... |
| III | 4.61, 4.05 | 1.20, 1.39 | 2.46 | ... | 7.22 | 6.83 | 6.69 |
| 1-*o*-Anisyl-7-diphenylmethylenecamphene | 4.44, 4.06 | 1.20, 1.41 | 2.45 | ... | 7.22 | ... | 6.70 |
| X | 4.82, 4.61 | 1.03, 1.10 | 2.35 | (1H = 3.22) | 7.18 | ... | ... |
| 1-Phenylnortricyclene | ... | ... | 2.17 | 1.49 | ... | 7.10 | ... |
| II | ... | 0.76, 0.95, 1.27 | 2.27 | 1.78 | 7.15 | 6.78 | 6.70 |
| 2-*o*-Anisyl-3-diphenylmethylenetricyclene | ... | 0.77, 0.92, 1.35 | 2.27 | 1.68 | 7.16 | ... | 6.71 |
| IX | ... | 0.84, 0.99, 1.21 | 2.07 | ... | 7.18 | ... | ... |

[a] $\delta$'s are for sufficiently dilute carbon tetrachloride solutions in which no change with further dilution was observed. [b] A = 7-*anti*-phenyl; B = 1-bridgehead phenyl; S = 7-*syn*-phenyl.

bridge phenyl rings. Assignments of the former signals to the B rings and the latter signals to the S rings were made by comparison with the *o*-anisyl analogs.

The B protons of III are shielded by 0.37 ppm when compared with the appropriate signal for VIII, while the same protons of II are shielded by 0.32 ppm when compared with the appropriate signal for 1-phenylnortricyclene. The S protons of III are shielded by 0.53 ppm compared to 0.45 ppm for II when both are referred to their respective A ring signals. However, the choice of appropriate reference signals for the S protons is a difficult one. (See discussion that follows.) At most, only a small difference in mutual shielding between II and III can be ascribed.

Apparently structures in which the benzene rings are aligned somewhat face to face are preferred. In II rings B and S are presumably orthogonally aligned with respect to the bridge ethylenic plane, an arrangement which places the hydrogens of ring T (7.15 ppm) in the shielding cone of the S ring. The 4-bridgehead hydrogen (2.27 ppm) lies primarily in the deshielding cone of ring A as can be seen by comparison with the corresponding signal (2.07 ppm) for IX. In the latter system, the A ring spends *ca.* 50% of its time in the plane of the bridge double bond (deshielding 4 H) and *ca.* 50% perpendicularly arranged (shielding 4 H) since both arrangements should be energetically equivalent.

Most of the phenyl signals in Table III are fairly narrow lines. Tiers[18] reports that the phenyl signal for 1,1-diphenylethene is a multiplet. We have found that the multiplicity disappears with dilution, and the resultant signal at 7.22 ppm is a sharp line with width at half-peak height of 1.2 cps. The sharp character of the lines with 1.2 cps width at half-peak height for rings S and B requires a face to face arrangement in that only then could a shielding cone, especially of S, affect all protons of the proximate ring to the same extent.

The nmr data for III require that the allignment of rings B and S cannot be as that proposed for II. Shielding parameters from the Johnson and Bovey tables[19] for the B ring alligned in a Dreiding model as suggested for II predicts negligible shielding of the methylene protons. Since at least one of the methylene protons is considerably shielded, the B ring is not aligned orthogonal to the bridge ethylenic system, but must be rotated clockwise toward this system. In order to maintain rings B and S in their parallel alignment, the S ring also rotates toward the bridge ethylenic plane, and the A protons (7.22 ppm *vs.* 7.15 ppm in II) fall within the deshielding cone of ring S.[20] Significantly, the phenyl signals for IX and X fall at 7.18 ppm, an intermediate value with respect to the A protons of II and III.

If the B and S rings in III are rotated as suggested, then the *para* hydrogens, at least, should experience a different degree of diamagnetic shielding from the other hydrogens. The widths at half-peak height for the B and S ring signals are 1.8 and 3.3 cps, respectively (A = 1.2 cps).

The nmr data of preferred phenyl sterochemistry may be interpreted to support the hypothesis that steric interactions alter the normal thermodynamic preference for camphene- over tricyclene-type products. If the $\pi$ orbitals in II are not severely opposing one another, then the rings may maintain their face-to-face allignment. However, if the mutual interactions between the $\pi$ orbitals of III are sufficiently severe, then partial relief of the stress may be achieved by rotation of the B and S rings. The proposed nmr assignments of preferred stereochemistry for II and III might also explain the differences in the ultraviolet data. If ring S is aligned more in the bridge ethylenic plane in III than II, the energy of the excited state of the A ring ethylene chromophore in III may be raised, with a resulting hypochromic shift in reference to II.

## Experimental Section

Melting points were determined in soft capillary tubes using a Mel-Temp apparatus (Laboratory Devices, Cambridge, Mass.) and are uncorrected. Infrared spectra were recorded on a Beckman IR-5 Model spectrometer, and also on a Perkin-Elmer Model 421 grating spectrometer for the 3-$\mu$ region of the alcohols. A Varian A-60 nmr spectrometer, calibrated with tetramethylsilane ($\delta$ = 0) and chloroform ($\delta$ = 436.5 cps), was used for the nmr determinations. Chemical shifts should be correct to ±0.01 ppm except for those indicated by $\simeq$ which should be correct to ±0.02 ppm; coupling constants are presumed correct to ±0.1 cps, except for those indicated by $\simeq$ which are assumed correct to ±0.2 cps. Microanalyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.

Unless otherwise specified, all ether and ligroin solutions of products were dried over anhydrous sodium sulfate prior to removal of solvent. Ligroin was distilled over potassium permanganate and had bp 40–55°.

**3-Diphenylmethylenecamphor (I).**—The procedure of Rupe and Hagenbach was employed with the following modification.

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[18] G. V. D. Tiers, "Tables of $\tau$-Values for a Variety of Organic Structures," Minnesota Mining and Manufacturing Co., St. Paul, Minn., 1958.

[19] C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958); J. W. Emsley, J. Feeney, and L. H. Sutcliff, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press Ltd., London, 1965, Vol. 1, pp 595–604.

[20] This rotation may in turn affect III's A phenyl alignment in that its 4-bridgehead hydrogen is deshielded by only 0.11 ppm relative to that of X.

The yellow oil that remained after steam distillation of the unreacted camphor partially crystallized upon standing. The semisolid material was dissolved in hot ethanol and gave pale yellow I (74.5% yield), mp 116–117° (lit.[4] mp 116–117°), after one further recrystallization.

The ultraviolet spectrum in 95% ethanol showed $\lambda_{max}$ 228 mμ (log ε 4.15) and 300 mμ (log ε 4.11). The nmr spectrum in deuteriochloroform showed the following: ten phenyl hydrogens centered at ≃7.25 ppm; 4 hydrogen, 2.78 ppm; methyl hydrogens, 0.99, 0.96, and 0.92 ppm; remaining four hydrogens, 1.5–2.1 ppm; $J_{4,5x}$ = 3.6 cps.

**2-Phenyl-3-diphenylmethyleneisoborneol** (IV).—To a phenyllithium solution made from 2.3 g (0.33 g-atom) of lithium wire, 20 g (0.13 mole) of bromobenzene, and 200–250 ml of anhydrous ether was added 19.8 g (0.0626 mole) of I dissolved in ether, The mixture was stirred under reflux for 6 hr and the adduct was decomposed with water. After removal of the aqueous layer the ether solvent was removed at reduced pressure.

The viscous tan residue was dissolved in the minimum amount of ligroin and poured onto a 4-ft chromatographic column (1-in. bore) packed with alumina (Alcoa, F-20) in ligroin. Chromatography afforded a total of 21.8 g (88.2%) of crude alcohol as a gummy oil that would not crystallize from a variety of solvents.

In very dilute carbon tetrachloride solution IV showed absorption at 3574 cm$^{-1}$ in the infrared. The nmr spectrum in deuteriochloroform solution (*ca.* 10 mole %) showed the following: 15 aromatic hydrogens as multiplets, 6.7–7.6 ppm; 4-bridgehead hydrogen, 2.68 ppm; hydroxyl hydrogen, 2.05 ppm; nine methyl hydrogens, 1.37, 0.90, and 0.88 ppm; four remaining hydrogens, 1.0–2.0 ppm; $J_{4,5x}$ = 2.6 cps.

**Isolation of 1-Phenyl-7-diphenylmethylenecamphene** (III).—In 250 ml of acetic acid was dissolved 55.0 g of crude, tan, unchromatographed IV. Approximately 20 g of trichloroacetic acid was added, and the resulting solution was heated at 90–95° for *ca.* 20 min. The purple color that formed initially was changed to wine red as time progressed. The solution was poured into ice water and a yellow-white solid formed. The solid was filtered with suction and then added to *ca.* 250 ml of ethanol with heating and stirring. Very little solution was attained, but the crystallinity of the material was improved considerably. Cooling and filtration gave 36.2 g of product, mp 144–150°. Seven recrystallizations from ethyl acetate gave pure III, mp 163–164°.

By use of shorter reaction time, relatively smaller amounts of trichloroacetic acid, or a few drops of concentrated sulfuric acid in place of trichloroacetic acid, it was possible to obtain material with initial mp 159–161°.

*Anal.* Calcd for $C_{29}H_{28}$: C, 92.51; H, 7.49. Found: C, 92.23; H, 7.61.

The ultraviolet spectrum in 95% ethanol showed $\lambda_{max}$ 240 mμ (log ε 4.14). Pertinent signals for the nmr spectrum of III are recorded in Table III; $J_{4,5x}$ ≃ 3.8 cps.

**2-Phenyl-3-diphenylmethylenetricyclene** (II). **A. Potassium Bisulfate Method.**—A mixture of 8.70 g (0.221 mole) of crude chromatographed IV and 10 g of potassium bisulfate was heated to *ca.* 160° for 0.5 hr. Water was added to the cooled mixture and the contents were washed out with ether and water. The water layer was removed and the ether solution was washed with sodium carbonate prior to solvent removal. Crystallization from ethanol gave 5.25 g of II. An additional 0.70 g was obtained by chromatography of the filtrate in ligroin over alumina. The 5.95 g (71.5%) of II gave mp 111–112° after one recrystallization from ethanol. The nmr spectrum of the filtrate showed it to be devoid of III.

*Anal.* Calcd for $C_{29}H_{28}$: C, 92.51; H, 7.49. Found: C, 92.65; H, 7.76.

The ultraviolet spectrum in 95% ethanol showed $\lambda_{max}$ 253 mμ (log ε 4.20). Pertinent signals for the nmr spectrum of II are recorded in Table III. In addition the 5-methylene hydrogens came at *ca.* 1.76 ppm with $J_{AB} = 12.6 \pm 0.3$ cps. The 4-bridgehead and tricyclene-ring hydrogens showed some splitting, but no coupling constants could be obtained.

**B. From II–III Mixture.**—A solution of 13.4 g of II–III mixture (mp 138–144°), 50 g of trichloroacetic acid, and 150 ml of acetic acid was heated at 70 ± 2° for 1.5 hr and then poured into ice water. Work-up in a manner similar to that for the isolation of III gave 10.5 g of II from ethanol, mp 109–111°. Pure II could also be obtained in comparable amount by refluxing the II–III mixture in acetic acid for 72 hr.

**Performic Acid Oxidation of II.**—To a solution of 4 ml (0.040 mole) of 30% hydrogen peroxide in 100 ml of 98% formic acid stirred at 10° was added dropwise 3.00 g (7.98 mmoles) of II dissolved in 35 ml of chloroform. The reaction mixture was stirred overnight at room temperature, and then added to 200 ml of water. Extraction with ether, washing with aqueous sodium carbonate, and evaporation of the ether solvent left a semisolid material which was crystallized from ethanol to give 3.10 g (95.0%) of ketone (VI), white flakes with mp 138–139°. Two further recrystallizations gave mp 142.0–142.5°.

*Anal.* Calcd for $C_{29}H_{28}O$: C, 88.73; H, 7.19. Found: C, 88.63; H, 7.20.

The infrared spectrum of VI in carbon disulfide showed a strong carbonyl band at 6.00 μ (1670 cm$^{-1}$) for the benzoyl group. The nmr spectrum in deuteriochloroform solution (*ca.* 10 mole %) showed the following: 15 aromatic hydrogens as multiplets, 6.7–7.6 ppm; 4-bridgehead hydrogen, 2.96 ppm; 5-methylene hydrogens, 2.10 and 1.88 ppm, with $J_{AB}$ = 11.8 cps; tricyclene-ring hydrogen, 1.20 ppm; nine methyl hydrogens, 1.06, 1.01, and 0.88 ppm.

**Epoxidation of II.**—A mixture of 5.0 g (0.013 mole) of II, 50 ml of chloroform, 6.8 g (0.080 mole) of sodium acetate, and 15 g (0.16 mole) of 40% peracetic acid was stirred with heating at 45–50° for 7 days. The excess peracetic acid was neutralized with 40% aqueous sodium hydroxide, and the chloroform layer was separated and dried. Evaporation of the solvent afforded 3.8 g (75%) of V which melted at 126–129°. Recrystallization from ethanol gave mp 129–130°.

*Anal.* Calcd for $C_{29}H_{28}O$: C, 88.38; H, 7.42. Found: C, 88.67; H, 7.34.

The nmr spectrum in deuteriochloroform solution (*ca.* 10 mole %) showed the following: 15 aromatic hydrogens as multiplets, 6.7–7.7 ppm; 5-methylene hydrogens, ≃ 2.13 and 1.80 ppm, with $J_{AB}$ = 10.6 cps; 4-bridgehead and tricyclene-ring hydrogens, 1.32 or 1.25 ppm; nine methyl hydrogens, 1.34, 1.01, and 0.80 ppm.

Compound V was converted to VI in 85.0% yield by stirring with formic acid in chloroform solution overnight.

**Hydrogenation of II.**—A mixture of 1.00 g (2.66 mmoles) of II, 3.0 g of 5% rhodium on charcoal, 50 ml of acetic acid, and 10 ml of ethyl acetate was shaken in a Paar bomb hydrogenation reactor for 10 days at an initial pressure of 43 psi. The catalyst was removed by filtration and the filtrate was poured into 100 ml of ice water. The resultant milky mixture was extracted with ether, the ether extracts were washed with aqueous sodium carbonate, and the ether was removed at reduced pressure, giving 0.69 g (69%) of colorless oil which could not be crystallized from a variety of solvents.

The ultraviolet spectrum in 95% ethanol showed no absorption in the 253-mμ region. An attempted performic acid oxidation of the oil, in the same manner as that employed on II, proved unsuccessful. No further characterization of the oil was attempted.

**2-*o*-Anisyl-3-diphenylmethyleneisoborneol.**—The *o*-anisyllithium was prepared by the method of Gilman, Zoellner, and Selby.[21] The quantities of material used were 2.8 g (0.40 mole) of lithium, 30.0 g (0.160 mole) of *o*-bromoanisole, and 150 ml of anhydrous ether. To this reagent was added 30.0 g (0.0948 mole) of I dissolved in 150 ml of ether. The mixture was stirred under reflux for 2 hr and worked up as done with IV. Ether removal left a yellow-brown oil. From ligroin 21.5 g (53.3%) of white solid (mp 145–146°) was obtained.

*Anal.* Calcd for $C_{30}H_{32}O_2$: C, 84.87; H, 7.60. Found: C, 84.67; H, 7.47.

In very dilute carbon tetrachloride solution the alcohol showed absorption at 3562 cm$^{-1}$ (OH-π bond) and 3523 cm$^{-1}$ (OH-O bond) in the infrared. The former absorption was a shoulder on the much more intense latter band. The nmr spectrum in deuteriochloroform solution (*ca.* 10 mole %) showed the following: 14 aromatic hydrogens, 6.4–7.6 ppm; hydroxyl hydrogen, 5.30 ppm; methoxymethyl, 3.40 ppm; 4-bridgehead hydrogen, 2.54 ppm; nine methyl hydrogens, 1.37, 0.96, and 0.84 ppm.

**Preparation of 1-*o*-Anisyl-7-diphenylmethylenecamphene-2-*o*-Anisyl-3-diphenylmethylenetricyclene Mixture.**—A solution of 10.0 g of 2-*o*-anisyl-3-diphenylmethyleneisoborneol, 50 g of trichloroacetic acid, and 250 ml of acetic acid was heated at

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[21] H. Gilman, E. A. Zoellner, and W. M. Selby, *J. Am. Chem. Soc.*, **54**, 1957 (1943).

70 ± 2° for 5 min. Work-up as in II (B) gave a yellow oil from which 8.1 g (85%) of white solid (mp 120–123°) was obtained from ethanol.

The ultraviolet spectrum in 95% ethanol showed $\lambda_{max}$ 241 mμ. The nmr spectrum in carbon tetrachloride solution showed the solid to be *ca.* 50:50 mixture of camphene and tricyclene isomers. Pertinent signals for the nmr spectrum of the camphene compound are recorded in Table III.

**2-*o*-Anisyl-3-diphenylmethylenetricyclene.**—A solution of 7.0 g (0.017 mole) of the hydrocarbon mixture (*vide supra*) in 160 ml of acetic acid was refluxed for 48 hr. The yellow solution was poured into ice water, and the creamy semisolid material that formed was dissolved in ether. The ether solution was washed with aqueous sodium carbonate, and the ether was removed at reduced pressure leaving a tan oil. From 95% ethanol 5.8 g (70% based on the alcohol) of white solid (mp 122–123°) was obtained.

*Anal.* Calcd for $C_{30}H_{30}O$: C, 88.63; H, 7.44. Found: C, 88.45; H, 7.37.

The ultraviolet spectrum in 95% ethanol showed $\lambda_{max}$ 253 mμ (log ε 4.20). Pertinent signals for the nmr spectrum of the tricyclene compound are recorded in Table III.

**Dehydration of 2-Phenylisoborneol.**—The dehydration with potasium bisulfate and subsequent work-up were identical with that employed for the preparation of II. A mixture of 19.8 g (0.0859 mole) of 2-phenylisoborneol [bp 159–171° (13–14 mm)] and 15 g of potassium bisulfate was heated at 160–170° for 0.5 hr. After work-up in the usual manner and chromatography over alumina using ligroin solvent, 14.1 g (77.3%) of a mixture of 2-phenylbornene (VII) and 1-phenylcamphene (VIII) as a light yellow oil was obtained.

The infrared spectrum in carbon disulfide showed absorption at 885 cm$^{-1}$ for the C=CH$_2$ system of VIII and 826 cm$^{-1}$ for the alkene C–H-bending vibration of VII.[6] Pertinent signals for the nmr spectrum of VIII are recorded in Table III. Compound VII showed the following: phenyl hydrogens, 7.18 ppm; 3-olefinic hydrogen, 5.93 ppm, 4-bridgehead hydrogen, 2.33 ppm, nine methyl hydrogen, 0.79, 0.89, and 1.11 ppm.

Integration of the phenyl signals, the 3-hydrogen signal of VII, and the olefinic methylene signals of VIII gave a ratio of 5.0:0.60:0.80, which calculates for a 60%:40% mixture of VII: VIII. The ultraviolet spectrum in 95% ethanol showed $\lambda_{max}$ 251 mμ (log ε 3.91) for VII, assuming 60% purity.

**Dehydration of 3-Diphenylmethyleneisoborneol.**—The dehydration with potassium bisulfate and subsequent work-up was identical with that employed for the preparation of II. A mixture of 9.40 g (0.0295 mole) of 3-diphenylmethyleneisoneol[22] and 12 g of potassium bisulfate was heated at 150–160° for 0.5 hr. After work-up in the usual manner and chromatography over alumina using ligroin solvent, 7.60 g (85.8%) of a mixture of 7-diphenylmethylenecamphene (X) and 3-diphenylmethylenetricyclene (IX) as a colorless oil was obtained.

The infrared spectrum in carbon disulfide showed absorption at 876 cm$^{-1}$ for the C=CH$_2$ system of X.[6] Pertinent signals for the nmr spectrum of X and IX are recorded in Table III. Integration of the phenyl signals, and the 1- and 4-bridgehead hydrogens' signals gave a ratio of 5.0:0.74:0.74, which calculates for a 74%:26% mixture of X:IX. The ultraviolet spectrum in 95% ethanol showed $\lambda_{max}$ 239 mμ (log ε 4.14).

**Registry No.**—I, 14164-35-3; II, 14164-36-4; III, 14164-37-5; IV, 14164-38-6; V, 14164-39-7; VI, 14164-40-0; VII, 7070-09-9; VIII, 7070-29-3; IX, 14164-42-2; X, 14271-25-1; XI, 530-48-3; 3-diphenylmethyleneisoborneol, 14164-43-3; 1-phenylnortricyclene, 461-86-9; 2-*o*-anisyl-3-diphenylmethyleneisoborneol, 14164-44-4; 1-*o*-anisyl-7-diphenylmethylenecamphene, 14164-45-5; 2-*o*-anisyl-3-diphenylmethylenetricyclene, 14164-46-6.

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[22] S. Yuan, M.S. Thesis, University of Tennessee, 1967.

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# Aryl Norbornane Compounds. V. Intramolecular Diamagnetic Shielding in Some Phenylnorbornyl *p*-Nitrobenzoates and Tosylates[1,2]

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Those *p*-nitrobenzoates which approach a *cis* relationship with their phenyl groups show greater shielding of one *p*-nitrobenzoyl proton pair than another in the nuclear magnetic resonance (nmr) spectrum, while other *p*-nitrobenzoyl protons are magnetically equivalent. Greater anisotropic shielding by phenyl of one proton pair and correlation between degrees of shielding and measured shielding parameters explain the results. Only the *p*-tosyl group of 7-*anti*-phenyl-2-*exo*-norbornyl tosylate shows no diamagnetic shielding by phenyl. Differences between the tosylate and *p*-nitrobenzoate shielding values are attributed to conformational differences.

Recently we reported initial results on the acetolyses of the 3-phenyl-2-norbornyl tosylates[3] in which the unexpected rate retardation attributed to a 3-*exo*-phenyl group was demonstrated. In order to understand better the chemistry of the arylnorbornyl system, we felt that a detailed study of the magnitudes of interaction between the aryl group and an adjacent or other proximately situated substituent was in order. Presumably nuclear magnetic resonance (nmr) spectroscopy could assist in this evaluation since the response of hydrogen nuclei to the orientational dependent diamagnetic anisotropic shielding of a benzene ring is well established.[4,5] Data in this present paper should assign the preferred phenyl orientations for the *cis*-positioned isomers and further demonstrate a technique introduced previously[2] for conformational assignments.

## Results and Discussion

The norbornyl derivatives involved in this investigation were *exo*- and *endo*-norbornyl *p*-nitrobenzoates

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[2] For part IV, see D. C. Kleinfelter, *J. Am. Chem. Soc.*, **89**, 1734 (1967).

[3] D. C. Kleinfelter, E. S. Trent, J. E. Mallory, and T. E. Dye, *ibid.*, **88**, 5350 (1966).

[4] L. M. Jackman, "Applications of a Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Ltd., London, (1959), p 126.

[5] D. Y. Curtin, H. Gruen, and B. A. Shoulders, *Chem. Ind.* (London), 1205 (1958); D. Y. Curtin, H. Gruen, Y. G. Hendrickson, and H. E. Knipmeyer, *J. Am. Chem. Soc.*, **83**, 4838 (1961).