Anal. Calcd for $C_4H_{11}O_3PS$: C, 28.23; H, 6.47; S, 18.82. Found: C, 28.33; H, 6.32; S, 19.25.

O,O'-Diisopropylthiophosphoric Acid.—The free acid was prepared directly by the addition of sulfur to diisopropyl hydrogen phosphite in dioxane according to the method of Kabachnik and Golubeva.[10] The yield (81%) of crude product was comparable to those reported (80–92%). However, nmr analysis of our product indicated 15–20% of impurities which could not be removed by distillation. Purification of the acid was accomplished through its sodium salt employing a method previously used in the case of dialkyldithiophosphoric acids.[14] The impurities removed by this procedure were of a "neutral" nature. Glpc analysis showed the starting hydrogen phosphite in addition to three unidentified components. The O,O'-diisopropylthiophosphoric acid obtained was essentially pure based on its nmr analysis and was used as such for the addition experiments. A sample was distilled for elemental analysis and other physical measurements: bp 79–81° (0.15 mm), $n^{20}D$ 1.4589 [lit.[10] 90° (1.5 mm), $n^{20}D$ 1,4600]. Nmr parameters are recorded in Table II.

Anal. Calcd for $C_6H_{15}O_3PS$: C, 36.35; H, 7.63; S, 16.17. Found: C, 36.29; H, 7.13; S, 15.91.

General Procedure for the Addition of O,O'-Dialkylthiophosphoric Acids to Olefins.—A magnetically stirred mixture of the thio acid and olefin in a sealed quartz tube was irradiated with a 100-w medium-pressure Hanau mercury immersion lamp for 30–40 hr in a water bath at 16 ± 3°. The liquid 1-pentene was allowed to react under a nitrogen atmosphere. The gaseous 1,3-butadiene and allene were condensed into Dry Ice cooled, evacuated tubes containing the thio acid and then allowed to react in the liquid phase under their own vapor pressures. After completion of the irradiation, the tubes were opened and the mixtures were sampled for semiquantitative analysis by nmr spectroscopy. Then the remaining material was diluted with ether and washed with 5% aqueous solution of sodium hydrogen carbonate to remove any unreacted acid. The ether phase was dried over anhydrous magnesium sulfate and then concentrated using a rotary evaporator at 10 mm and room temperature to remove the solvent. The residual crude product was then weighed and analyzed by a combination of glpc and nmr techniques. Part of the product was purified by fractional distillation at 0.1–0.25 mm for analyses. This was frequently accompanied by a partial decomposition yielding considerable amounts of undistillable residue.

Registry No.—$C_9H_{21}O_3PS$, 995-51-7; $C_{11}H_{25}O_3PS$, 10428-93-0; $C_8H_{17}O_3PS$, 10428-94-1; $C_{10}H_{21}O_3PS$, 10428-95-2; $C_7H_{15}O_3PS$, 10428-96-3; $C_9H_{19}O_3PS$, 10428-97-4; O,O'-diethylthiophosphoric acid, 2465-65-8; O,O'-diisopropylthiophosphoric acid, 10428-99-6; in Table II where R' = CH_2CH_3 and R = C_2H_5, 1186-09-0.

Acknowledgment.—The authors wish to thank Mr. W. C. Whitlock for excellent technical assistance and Dr. R. V. Moen for interpreting the nmr spectra.

Arylnorbornane Compounds. III. The 3-Phenyl-2-norbornanols and Derivatives. Preparation and Properties[1,2]

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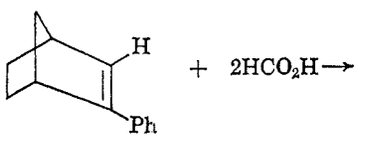
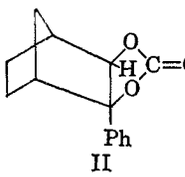
Preparations of the four isomeric 3-phenyl-2-norbornanols are described with particular emphasis on the routes to the more difficultly accessible *exo*-phenyl alcohols. Reduction of 3-*exo*-phenyl-2-norbornanone (VIII) appeared to be the best method for preparing these latter alcohols. Analyses of the infrared and nuclear magnetic resonance spectra are discussed in detail with emphasis on the observable effects of the 2 and 3 substituents.

Two possible mechanisms for the reaction of 2-phenylnorbornene (I) with performic acid to give the carbonate (II),[3] the result of a "*cis*" epoxide ring opening, involve (a) *endo*-phenyl participation at the 3 position followed by reaction of formic acid at C-3



+ $2HCO_2H \rightarrow$

I



+ HCO_2H + H_2O

II

from the *exo* side, a double-inversion process which leads to retention of C-3 configuration;[4] (b) stereoselective *exo* addition of formic acid to the tertiary carbonium ion at C-2, a mechanism similar to that offered by Brewster[5] for configurational retention in styrene-type epoxide openings.

In order to gain insight on the possibility of mechanism a and because we were interested in the geometrical requirements for aryl participation, we wished to find a norbornyl system whose solvolyses might involve a phenonium ion intermediate of the type postulated for acyclic systems. In addition, we desired to determine the relationship of dihedral angle between an aryl and another functional group on the spectral properties observed by infrared and nuclear magnetic resonance (nmr) spectroscopies. This present paper discusses the methods of preparation and characterization of the four 3-phenyl-2-norbornanols and their tosylate and *p*-nitrobenzoate derivatives.

Methods and Results

The two 3-phenyl-2-norbornanols with *endo*-phenyl substituents III and IV are readily available by hydroboration of I[6] and by hydride reduction of 3-*endo*-

(1) Grateful acknowledgment is made to the National Science Foundation for a research grant (NSF-GP-1574) which supported a large part of this work.

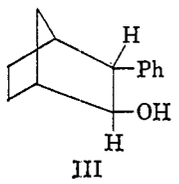
(2) For parts I and II, see (a) D. C. Kleinfelter and T. E. Dye, *J. Am. Chem. Soc.*, **88**, 3174 (1966); (b) D. C. Kleinfelter, E. S. Trent, J. E. Mallory, and T. E. Dye, *ibid.*, **88**, 5350 (1966).

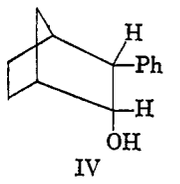
(3) D. C. Kleinfelter and P. von R. Schleyer, *ibid.*, **83**, 2329 (1961).

(4) For example, see R. C. Cookson and J. Hudec, *Proc. Chem. Soc.*, 24 (1957).

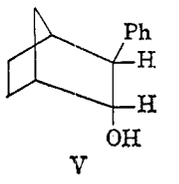
(5) J. Brewster, *J. Am. Chem. Soc.*, **78**, 4061 (1956).

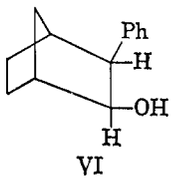
(6) C. J. Collins, Z. K. Cheema, R. G. Werth, and B. M. Benjamin, *ibid.*, **86**, 4913 (1964).


III

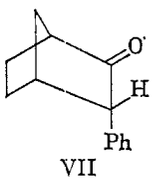

IV

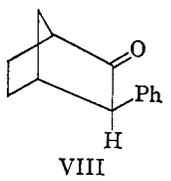
phenyl-2-norboranone,[2a,7] respectively. In contrast preparation of the two 3-*exo*-phenyl-2-norbornanols, V and VI, in respectable yields proved to be a far more difficult problem.


V


VI

Reduction of Nef Reaction Products.—One of the most obvious routes involves hydride reduction of 3-*exo*-phenyl-2-norbornanone. This ketone has been prepared by the Nef reaction on 3-*exo*-phenyl-2-*endo*-nitronorbornane.[8] In our hands this reaction appeared to be much more complex than reported. We obtained a mixture of at least two ketones, 3-*endo*-phenyl-2-norbornanone (VII) and 3-*exo*-phenyl-2-norbornanone (VIII), and what appeared to be two hydroxy ketones formed presumably by oxidation of VII and VIII.

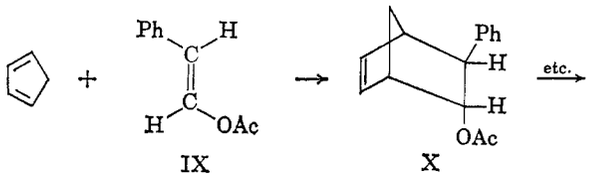

VII


VIII

The ketone mixture was reduced with lithium aluminum hydride, after which V was separated by adsorption chromatography. After fractional crystallization of IV, VI was obtained pure by formation of the *p*-nitrobenzoate, reduction to the *p*-aminobenzoate, and saponification. The yields of V and VI in a ratio of 4–5:1 based on the nitrobornane were *ca.* 8–10%.

Reduction of VII in Potassium Hydroxide–Ethylene Glycol Solution.—Since the preference of *exo* over *endo* substituents in the norbornyl system had been repeatedly demonstrated,[3,9] we attempted isomerization of VII to VIII in basic media. Heating of VII in a refluxing solution of potassium hydroxide in ethylene glycol afforded nearly a 70% yield of a mixture of alcohols IV, V, and VI in a ratio of 5:10:1. This reduction procedure[10] became our method of choice for preparing sufficient quantities of V and VI.

Production of VI *via* a Diels–Alder condensation of cyclopentadiene and *trans*-β-phenylvinyl acetate (IX)

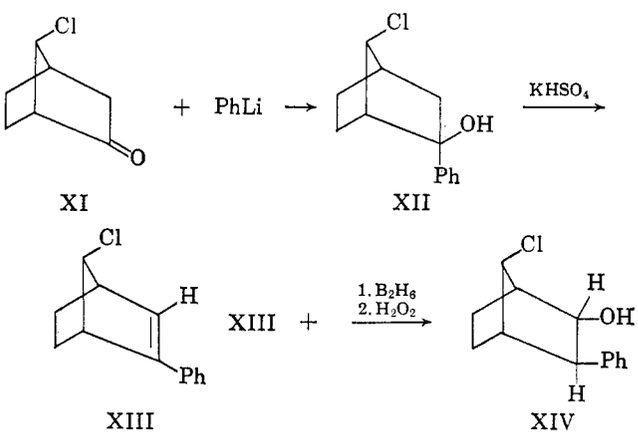

IX X

(7) B. M. Benjamin and C. J. Collins, *J. Am. Chem. Soc.*, **88**, 1556 (1966).
(8) W. C. Wildman and C. H. Hemminger, *J. Org. Chem.*, **17**, 1641 (1952).
(9) For references, see P. von R. Schleyer and M. M. Donaldson, *J. Am. Chem. Soc.*, **82**, 4645 (1960).
(10) D. C. Kleinfelter, *J. Org. Chem.*, **32**, 840 (1967).

was attempted. A search of the literature revealed that IX had never been utilized as a dienophile in a Diels–Alder condensation. A mixture of IV, VI, and III in a total yield of 35% was obtained after catalytic and hydride reductions. Unfortunately III was the predominant component of the alcohol products. Rearrangement of IX to the *cis* olefin[11] explains the eventual formation of IV.

A possible pathway to obtain larger amounts of VI by reduction of VIII with lithium in liquid ammonia by the method of Ourisson and Rassat[12] proved unsuccessful. Reduction of VII gave almost exclusive formation of III, but the best yields were obtainable on only small quantities of VII (*ca.* 2 g). From VIII a predominance of Birch reduction product formed,[13] perhaps due to the rate retardation of ketone reduction caused by the 3-*exo*-phenyl group.

We felt that the introduction of a 7-*syn*-chlorine substituent, which could be removed at a later stage by reduction, might alter the mode of addition to the norbornane system and afford the desired alcohols. The envisioned reactions are outlined below. Addition of phenyllithium to 7-*syn*-chloro-2-norbornanone (XI)


XI XII XIII XIV

gave 7-*syn*-chloro-2-*endo*-phenylnorbornanol (XII). The *exo* orientation of the hydroxyl group was confirmed by its OH–Cl intramolecularly hydrogen-bonded peak at 3572 cm^{-1} with an extremely weak shoulder at 3604 cm^{-1} ($\Delta\nu$ = 32 cm^{-1}). Dehydration of XII afforded 7-*syn*-chloro-2-phenylnorbornene (XIII) whose structure was confirmed by comparison of its spectral properties with those of 2-phenylnorbornene.

Hydroboration of XIII did not produce the desired alcohol XIV but instead gave the product of *exo* addition, 7-*syn*-chloro-3-*endo*-phenyl-2-*exo*-norbornanol (XV). The structure of XV was assigned from the OH–Cl intramolecularly hydrogen-bonded absorption at 3589 cm^{-1} and free peak at 3621 cm^{-1} ($\Delta\nu$ = 32 cm^{-1}), and from comparison of its nmr spectrum with that of III. XV as an uncrystallizable oil was converted to the tosylate XVa whose nmr spectrum was also compatible with the assigned structure.

Evidently our original goal of introducing the 7-*syn*-chloro substituent into the norbornyl system to cause diborane to add from the *endo* direction was not attained. Possibly, the 7-*syn*-chlorine may have co-

(11) J. Boeseken and H. L. Soesman, *Rec. Trav. Chim.*, **52**, 874 (1933).
(12) G. Ourisson and A. Rassat, *Tetrahedron Letters*, No. 21, 16 (1960).
(13) A. J. Birch, *Quart. Rev.* (London), **4**, 69 (1950).

TABLE I

Compd[c]	δ, ppm[a] 1	3 (tp)[d]	4	7a (tp)[d]	J', cps[b] 1, 3	1, 7a	3, 4	4, 7a	3, 7a
I	3.25	6.21	2.92	...	0.8	...	3.2	...	0.8
XIII	3.32	6.20	3.03	3.86	1.0	1.7	3.1	1.7	1.0
Compd[c]	1	2n (dp)[d]	3x (t)[d] 4	7a (tp)[d]	1, 7a	2n, 3x	2n, 7a	3x, 4	4, 7a
III	2.11	3.80	2.82 2.29	...	...	3.1	1.2	~3.5	...
XV	2.32	3.88	3.72 2.52	4.01	1.5	4.1	1.5	4.1	1.5
IIIa	2.45	4.68	3.08 2.42	...	...	3.4	1.2	~3.6	...
XVa	2.64	4.84	3.98 2.47	4.08	1.4	4.5	1.4	4.5	1.4

[a] δ values are correct to ±0.01 ppm. [b] J's are correct to ±0.1 cps except for those labeled ~, which are correct to ±0.2 cps. [c] Chemical shifts (δ) for the alcohols and alkenes are for *ca.* 10 mole % solutions in carbon tetrachloride; those for the tosylates are for *ca.* 10 wt % in chloroform-*d*. [d] dp = doublet pair; t = triplet; tp = triplet pair; q = quartet.

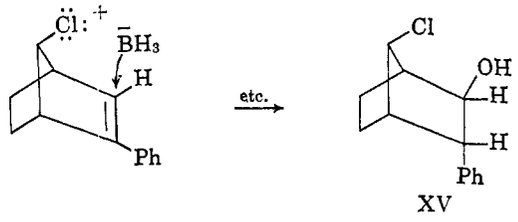
TABLE II

CHARACTERISTIC INFRARED ABSORPTION FREQUENCIES OF 3-ARYL-2-NORBORNYL COMPOUNDS[a]

Compd	Alcohols: O–H stretch, cm⁻¹[b]	Alcohols: 1000–1200-cm⁻¹ region		C_6H_5 C–H bending vibration region, cm⁻¹: Alcohol	*p*-Nitrobenzoate[c]	Tosylate
exo-Norbornanol	(3619)	1005 (s)			716 (s)	
		1082 (s)				
endo-Norbornanol	(3622)	1035 (s)	1120 (m)			
		1083 (s)	1150 (m)		716 (s)	
III	3600 (w), 3330 (m),	1007 (ms)	1060 (s)	695 (s)	695 (ms), 717 (s),	682 (w), 728 (w)
	(3616)	1032 (m)	1117 (ms)	733 (s)	735 (ms)	696 (s), 773 (s)
IV	3600 (w), 3400 (w),	1032 (m)	1090 (s)	704 (s)	702 (m), 715 (s),	680 (m), 752 (vw)
	(3612)[d]	1070 (m)	1130 (s)	748 (ms)	755 (m)	698 (s), 770 (m), 724 (ms)
				760 (w)		
V	3600 (w), 3370 (mw),	1048 (s)	1122 (m)	696 (s)	695 (ms), 717 (s),	693 (s)
	(3622)	1070 (ms)	1155 (m)	728 (w)	750 (w)	727 (vw)
				749 (ms)		748 (vw)
VI	3600 (w), 3450 (w),	1030 (m)	1075 (w)	697 (s)	697 (ms), 717 (s),	682 (s), 758 (s)
	(3589)[e]	1063 (s)	1145 (w)	727 (ms)	728 (m)	694 (s), 770 (s)

[a] Spectra for a series of compounds were run on solutions of *ca.* equal concentrations as checked by comparison of the intensities of the C–H stretching vibration at 2940 cm⁻¹ (Beckman IR-5 spectrometer). [b] Values in parentheses are those found in very dilute solutions where intermolecular association is relatively absent (Perkin-Elmer 21 spectrometer with lithium fluoride optics). [c] Since there is a strong peak at 716 cm⁻¹ in *exo*- and *endo*-norbornyl *p*-nitrobenzoate, the peaks at 716 ± 1 cm⁻¹ in the *p*-nitrobenzoates of III–VI are not due to C_6H_5 C–H bending vibrations. [d] $\Delta\nu$ = 10 cm⁻¹ relative to *endo*-norbornanol. [e] $\Delta\nu$ = 30 cm⁻¹ relative to *exo*-norbornanol.

ordinated with the boron atom, as shown below, and then reacted intramolecularly and stereospecifically to give XV.



XV

The pertinent chemical shifts and coupling constants for XIII, XV, and XVa are recorded in Table I and are compared with those for the analogous compounds without the *syn*-chlorine atom. The bridgehead and 2-*endo*-hydrogens are generally deshielded by *ca.* 0.1–0.2 ppm, but the 3-*exo*-hydrogen is deshielded by 0.90 ppm in both XV and XVa. A 3-*exo*-hydrogen is approximately parallel to the proximate 7-*syn*-carbon–chlorine bond. The large deshielding is presumably a consequence of the anisotropic effect of the chlorine substituent.[14]

Structural Assignments and Spectral Properties

Infrared Analysis.—Since structural assignments were made, in part, from the infrared absorption frequencies, and since structural effects are implicated to cause the chromatographic separation patterns of the alcohols, we have incorporated differences and similarities in Table II.

Alcohols IV and VI were those initially eluted. In these alcohols the hydroxy and phenyl groups are eclipsed, and the phenyl group can somewhat sterically block the OH group from adsorbing to the alumina more so than alcohols III and V in which the same two groups are *trans* oriented. The initially eluted alcohols both show essentially complete intramolecular hydrogen bonding, OH–π type, in very dilute solutions in comparison with *endo*- and *exo*-norbornanol. Both 7-*syn*-phenyl-2-*exo*-norbornanol and 1-phenyl-2-*exo*-norbornanol, which show OH–π bonding, are eluted prior to other alcohols with phenyl and hydroxyl *trans* oriented.[15] The energetically favorable intramolecular bond may also be involved with the lesser degree of adsorbability to alumina displayed by such *cis* alcohols. A decision as to what magnitudes of steric and hydrogen bonding effects are operative cannot be assigned. The spatial structure of the molecules to be adsorbed[16] and the diminished adsorbability attributed to hydrogen bonding[17] are well known facets of adsorption chromatography.

In some chromatographs where both III and V were present it was noted that V eluted before III. Pre-

(14) J. W. Emsley, J. Feeney, and L. H. Sutcliff, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. I, Pergamon Press, London, 1965, p 136; see P. Lazlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964).

(15) D. C. Kleinfelter and W. E. Wilde, unpublished observations.

(16) M. Kofler, *Helv. Chim. Acta*, **30**, 1053 (1947).

(17) H. Hoyer, *Kolloid-Z.*, **116**, 121 (1950).

TABLE III

NMR SPECTRAL DATA FOR 3-PHENYL-2-NORBORNANOLS AND DERIVATIVES[a]

	δ, ppm[b]				J', cps[c]				
Compd	2n	2x	3n	3x	2n, 3x	2n, 7a	3x, 4		
III	3.86 } dp[d]	...	...	2.87 } t[d]	3.1	1.2	~3.5		
IIIa	4.68 } dp[d]	...	...	3.08 } t[d]	3.4	1.2	~3.6		
IIIb	5.30 } dp[d]	...	...	3.43 } t[d]	3.2	1.1	~3.6		
					1, 2x	2x, 3x	3x, 4		
IV	...	4.36 } dp[d]	...	3.03 } dp[d]	4.5	9.8	3.7		
IVa	...	5.08 } dp[d]	...	3.12 } dp[d]	4.6	10.2	3.8		
IVb	...	5.61 } dp[d]	...	3.43 } dp[d]	4.5	10.2	3.7		
					1, 2x	2x, 3n	3n, 7a		
V	...	4.10 } t[d]	2.27 } dp[d]	...	~4.1	4.4	2.6		
Va	...	4.82 } t[d]	2.52 } dp[d]	...	~3.7	3.8	2.4		
Vb	...	5.47 } t[d]	2.82 } dp[d]	...	~4.2	4.2	2.6		
					1, 2n	2n, 3n	2n, 7a	3n, 4	3n, 7a
VI	3.87 } tp[d]	...	2.83 } 2dp[d]	...	1.1	6.8	1.1	~0.6	1.1
VIa	4.74 } tp[d]	...	2.86 } 2dp[d]	...	1.2	7.3	1.2	~0.5	1.1
VIb	5.35 } tp[d]	...	3.17 } 2dp[d]	...	1.1	7.3	1.1	~0.5	1.0

[a] Chemical shifts (δ) for the alcohols are for dilute solutions (less than 1 mole %) in carbon tetrachloride; those for the tosylates and *p*-nitrobenzoates are for *ca.* 10 wt % in chloroform-*d*. [b] δ values are correct to ±0.01 ppm. [c] *J*'s are correct to ±0.1 cps except for those labeled ~, which are correct to ±0.2 cps. [d] dp = doublet pair; t = triplet; tp = triplet pair.

sumably steric effects in the *endo* alcohol (V) cause some diminution in its adsorbability relative to III. The wide medium weak (mw) absorption at 3370 cm^{-1} in V is to be contrasted with the medium (m) absorption at 3330 cm^{-1} in III. Greater intermolecular association in the alcohol molecules leads to a decrease in the energy required for the O–H stretching vibration[18] as reflected by the longer wavelength shift in III compared with V. The intensity of the longer wavelength absorption in III is greater as anticipated. It follows then that the greater the ease of intermolecular association, the greater the adsorbability to alumina.

Nmr Analysis.—The nmr spectra of the four 3-phenyl-2-norbornanols (III–VI), their tosylates (IIIa–VIa), and their *p*-nitrobenzoates (IIIb–VIb) were all critically analyzed in the region of the 2- and 3-hydrogen signals. The spectra are summarized in Table III.

Discussion of Chemical Shifts.—The δ values for the alcohols underwent a downfield shift upon dilution, consistent with a decrease in the anisotropic effect of phenyl which operates intermolecularly causing diamagnetic shielding of the hydrogen atoms. The extent of this shift varied from one alcohol to another. For example, 2x of IV appeared at 4.14 ppm at *ca.* 10 molar %, and this was shifted to 4.36 ppm with dilution to below 1 molar %. The corresponding dilution of V caused a 2x shift from 4.00 to 4.10 ppm. Intermolecular hydrogen bonding may affect the magnitude of this downfield shift. If the arrangement of the benzene ring in the intermolecular association is such that it is brought close to the shielded hydrogen, then a comparatively larger effect will be observed. The δ values for the 3x and 3n hydrogens of IV and V are shifted downfield only 0.07 and 0.05 ppm, respectively, upon dilution, consistent with a greater distance separating the benzene rings from the shielded hydrogens. At most the δ values for the tosylates and *p*-nitrobenzoates underwent a paramagnetic shift of 0.03 ppm with infinite dilution.

The 2x and 2n signals for *endo*- and *exo*-norbornanol appear at 4.15 and 3.66 ppm, respectively.[19] That most *exo* protons are deshielded relative to the *endo* protons is a recognized observation.[20] All of the 2x and 3x protons of the 3-phenyl-2-norbornanols and derivatives also appear at lower field strengths than the respective 2n and 3n signals. However, no apparent constant difference exists between an *exo*- and *endo*-hydrogen on the same carbon atom in a given series. This inconsistency is obviously due to anisotropic effects of the benzene rings and to the oxygen atoms in positions eclipsed with the hydrogen atoms.

The effect that one might expect from the inductive effect of phenyl on the chemical shift of a 2-hydrogen about which anisotropic effects would presumably be minimal can be obtained from the *cis* alcohols IV and VI, where the dihedral angles between the 2-hydrogen and the adjacent phenyl attachment are *ca.* 120°. The inductive effect of phenyl causes a deshielding of 0.21 and 0.22 ppm in IV and VI, respectively. Similarly, a 3-hydrogen should also be deshielded by a noneclipsed hydroxyl group. If one compares the 2n position of 2.71 ppm for 2-*exo*-phenylnorbornane[3] with that observed for 3n of VI, 2.83 ppm, one obtains an approximate deshielding contribution of 0.12 ppm for a noneclipsed hydroxyl group.

The effect of eclipsing a phenyl or an oxygen function in the *exo* and *endo* positions with a hydrogen atom can be gathered by comparison with the noneclipsed analogs. For convenience, these shielding contributions are calculated below in the form of Table IV.

Table IV reveals that a 3-*exo*-phenyl group diamagnetically shields an eclipsed 2-*exo* proton, but that a 3-*endo*-phenyl has relatively little effect on its eclipsed hydrogen. Evidently the 2-*exo*-hydrogen prefers to lie almost perpendicular to the plane of the benzene

(18) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 99.

(19) E. W. C. Wong and C. C. Lee [*Can. J. Chem.*, **42**, 1245 (1964)] report values of 4.17 and 3.66 ppm, respectively.

(20) J. I. Musher, *J. Mol. Phys.*, **6**, 93 (1963).

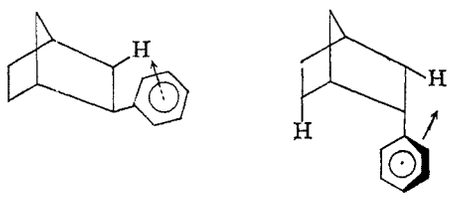
TABLE IV

SHIELDING CONTRIBUTIONS (PARTS PER MILLION) FOR ECLIPSED PHENYL AND OXYGEN FUNCTIONS (O–X)

exo-Phenyl			*endo*-Phenyl		
Alcohol	Tosylate	*p*-Nitrobenzoate	Alcohol	Tosylate	*p*-Nitrobenzoate
IV 4.36	IVa 5.08	IVb 5.61	VI 3.87	VIa 4.74	VIb 5.35
V 4.10	Va 4.82	Vb 5.47	III 3.86	IIIa 4.68	IIIb 5.30
0.26	0.26	0.14	0.01	0.06	0.05

exo-O–X			*endo*-O–X		
Alcohol	Tosylate	*p*-Nitrobenzoate	Alcohol	Tosylate	*p*-Nitrobenzoate
IV 3.03	IVa 3.12	IVb 3.43	VI 2.83	VIa 2.86	VIb 3.17
III 2.87	IIIa 3.08	IIIb 3.43	V 2.27	Va 2.52	Vb 2.82
0.16	0.04	0.00	0.56	0.34	0.35

ring, with the π cloud significantly oriented toward the hydrogen atom. A similar effect has been observed in *trans*-1,2-diphenylcyclopentane in which the 1- and 2-hydrogens are shielded 0.40 ppm relative to the *cis* isomer.[21] A 3-*endo*-phenyl group is then so fixed that the π cloud is oriented only slightly toward the 2-*endo*-hydrogen. If the plane of the *endo*-benzene ring were oriented as in the *exo* arrangement, a serious steric interaction would be created between an *ortho*-hydrogen and the 5-*endo*-hydrogen. Consequently, the benzene ring prefers a position somewhat removed from this interaction in which the 2-*endo*-hydrogen is only slightly shielded by the π cloud. Pictorial representations of the effects attributed to *exo*- and *endo*-phenyls are shown below. (The arrow indicates the point-dipole maximum directional effect.)



Oxygen functional groups, whether *exo* or *endo*, shield their corresponding eclipsed hydrogens, with the shielding effect being significantly greater for the *endo* orientation. A similar effect by *exo*- and *endo*-hydroxyl groups has been demonstrated by Davis and Van Auken[22] in the nmr spectra of *endo*- and *exo*-norbornene derivatives. The need to remove an unfavorable interaction between the oxygen atom and the 5-*endo* bond may affect the orientation of the oxygen atom relative to the 3-*endo*-hydrogen atom in a manner that leads to greater shielding of the eclipsed hydrogen. Whether *exo* or *endo*, the hydroxyl group leads to a greater shielding contribution than either of the other functional groups.

Discussion of Coupling Constants.—The coupling constants and spectral patterns observed (Table III) are in line with the proposed structures for all the 3-aryl-2-norbornanols and derivatives. The agreement between the alcohols and their derivatives precludes any possible rearrangement taking place during derivative formation. The unequal splitting of the 2-*endo*-hydrogen of III with its 3-*exo*- and 7-*anti*-hydrogens leads to the expected doublet pair, while the approximate equal splitting of the 3-*exo*-hydrogen with the 2-*endo*- and 4-hydrogens leads to the triplet. In V it is the 2-*exo*-hydrogen which appears as the triplet and the 3-*endo*-hydrogen as the doublet pair, due to approximately equal $J_{1,2x}$ and $J_{2x,3n}$ but unequal $J_{3n,7a}$.

For both the 2x and 3x protons of IV the spectral pattern is that of a doublet pair due to $J_{2x,3x}$ being greater than coupling with an adjacent bridgehead proton. Under conditions of excellent resolution one can discern some further finer splitting of 2x and 3x, apparently due to coupling with the respective 6x and 5x protons.[23] One might initially expect the 2n and 3n protons of VI also to appear as doublet pairs resulting from coupling with each other and with the 7-*anti*-hydrogen. However, the pattern for 2n is quite clearly a triplet pair which presumably is the result of an additional coupling with the 1-bridgehead hydrogen, the coupling constant of which is practically identical with that of the 7-*anti* coupling. Coupling between bridgehead and *endo*-hydrogens is generally not observed.[22,23] The 3n-hydrogen spectral pattern is even more complex with two doublet pairs resulting, due apparently to unequal coupling with the 4-bridgehead and 7-*anti*-hydrogens. The larger J was intuitively assigned to the 3n,7a interaction.

Consistent with prior investigations,[24] the *exo-exo-vic* coupling constants are greater than *endo-endo-vic* coupling constants. Presumably interactions between the *exo* substituents cause some change in molecular geometry which leads to the unexpected coupling between bridgehead and adjacent *endo*-hydrogens. The 3-*endo*-hydrogen of 2-*endo*-phenyl-2,3-*cis*-*exo*-norbornylene carbonate (II) is coupled with the 4-bridgehead hydrogen by 0.8 cps. Such coupling may be due to change in the HC_3C_4H dihedral angle caused by the incorporation of the five-membered ring carbonate structure.

All *endo-anti* coupling constants are 1.1 ± 0.1 cps except for the $J_{3n,7a}$ values for V and its derivatives, which are 2.5 ± 0.1 cps. These latter J's are more in line with what have been previously reported,[24] although not much data is available for compounds with both C-2 and C-3 substituents. Evidently such substitution can affect the magnitude of *endo-anti* coupling constants.

Experimental Section

Melting points were determined in soft capillary tubes using a Mel-Temp apparatus (Laboratory Devices, Cambridge Mass.) and are corrected. All boiling points are uncorrected. Infrared spectra were recorded on a Beckman IR-5 spectrometer except

(21) 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).

(22) J. C. Davis, Jr., and T. V. Van Auken, *ibid.*, **87**, 3900 (1965).

(23) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).

(24) Reference 32, p 3903, and reference therein.

for the 3-μ region where a Perkin-Elmer Model 21 spectrometer with lithium fluoride optics was also used. A Varian A-60 nmr spectrometer, calibrated with tetramethylsilane (TMS) (δ = 0 cps) and chloroform (δ = 436.5 cps), was used for the nmr determinations. Chemical shifts should be correct to $\pm$0.01 ppm and coupling constants to $\pm$0.1 cps, except those indicated by $\cong$ which should be correct to $\pm$0.2 cps. Microanalyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn., and Weiler and Strauss Microanalytical Laboratory, Oxford, England.

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°.

The alcohols were recrystallized from ligroin. All tosylates were prepared by reaction with a 1 molar excess of *p*-toluenesulfonyl chloride in pyridine for 3–5 days. Addition of the solution to ice water with stirring gave the solid tosylate, which was washed with water, dilute hydrochloric acid, dilute sodium carbonate, and water again. The tosylates were recrystallized from an ether–ligroin solvent mixture. The *p*-nitrobenzoates were prepared by the method of Shriner, Fuson, and Curtin,[25] and recrystallized from ethanol. Melting points and analytical data for the 3-phenyl-2-norbornanols and derivatives are recorded in Table V.

TABLE V

3-PHENYL-2-NORBORNANOLS AND DERIVATIVES

Compd	Mp, °C	Formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H
III	52–53	$C_{13}H_{16}O$	82.93	8.57	82.99	8.41
IV	71–72				82.67	8.41
V	42.5–43.5				82.80	8.39
IIIa	95–96	$C_{20}H_{22}O_3S$	70.16	6.48	69.97	6.30
IVa	111–112				70.23	6.58
Va	96–97				70.04	6.46
VIa	102–103				70.03	6.60
IIIb	94–95	$C_{20}H_{19}NO_4$	71.20	5.68	71.20	5.80
IVb	98–99				71.06	5.82
Vb	92.5–93.5				71.00	5.66
VIb	110.5–111.5				71.01	5.80

2-Phenylnorbornene (I).—The procedure was similar to that employed by Kleinfelter and Schleyer[26] with the following exception. Potassium bisulfate and 2-*exo*-phenylnorbornanol in a *ca.* 1:2 ratio were heated for about 1 hr at 110–120° instead of distilling the alkene from the reaction mixture at water pump pressure. The light yellow mixture was poured into ice water, and the product was extracted with ether. Distillation gave I (95% yield) whose infrared spectrum showed no significant absorption at 11.9–11.95 μ characteristic of 1-phenylnortricyclene.

The nmr spectrum in carbon tetrachloride solution showed the following: five aromatic hydrogens as a multiplet centered at 7.2–7.3 ppm; 3-hydrogen, 6.21 ppm; 1-bridgehead hydrogen, 3.25 ppm; 4-bridgehead hydrogen, 2.92 ppm; remaining hydrogens, 1.0–2.0 ppm; $J_{3,4}$ = 3.1 cps; $J_{1,3} = J_{3,7a}$ = 1.0 cps.

2-*endo*-Phenyl-2,3-*cis*-*exo*-norbornylene Carbonate (II).—The procedure was similar to that previously employed[3] with the following exception. The formic acid–product oil mixture was poured into ice water, and the solid that formed was filtered and washed repeatedly with water and aqueous sodium carbonate. Recrystallization from ethanol gave essentially pure carbonate in *ca.* 67% yield.

The nmr spectrum in deuteriochloroform solution showed the following: five aromatic hydrogens, 7.35 ppm; 3-*endo*-hydrogen, 4.83 ppm; 1-bridgehead hydrogen, 2.71 ppm; 4-bridgehead hydrogen, 2.55 ppm; 7-*syn*-hydrogen, 2.04 ppm; remaining hydrogens, 0.9–1.8 ppm; $J_{3n,4}$ = 0.8 cps; $J_{3n,7a}$ = 1.5 cps.

2-Phenylnorbornane-2,3-*cis*-*exo*-diol.—The procedure was similar to that previously employed[3] with the following exception. After distillation of the ethanol solvent required for the saponification, the residue was poured into ice water. The viscous oil solidified after stirring for *ca.* 1 hr. The solid was filtered and dried. A small portion was recrystallized from ligroin–ether solvent mixture and gave mp 57–58°. The literature[3] records the diol to be a gummy solid.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.63; H, 8.07.

The nmr spectrum in deuteriochloroform solution showed the following: five aromatic hydrogens as a multiplet centered at 7.35 ppm; two hydroxyl hydrogens, 4.20 ppm; 3-*endo*-hydrogen, 3.98 ppm; 1-bridgehead hydrogen, 2.45 ppm; 4-bridgehead and 7-*syn*-hydrogens, *ca.* 2.1 ppm; remaining hydrogens, 0.8–1.5 ppm; $J_{3n,7a}$ = 1.6 cps.

3-*endo*-Phenyl-2-norbornanone (VII).—The procedure was identical with that employed by Collins, Cheema, Werth, and Benjamin.[6]

The nmr spectrum in carbon tetrachloride solution showed the following: five aromatic hydrogens, 7.18 ppm; 3-*exo*-hydrogen, 3.32 ppm (lit.[6] 3.27 ppm); $J_{3x,4}$ = 4.4 cps (lit.[6] $J_{3x,4}$ = 4.5 cps).

3-*endo*-Phenyl-2-*endo*-norbornanol (IV).—A flask was charged with 33.0 g (0.177 mole) of VII [bp 131–132° (1.4 mm), lit.[3] bp 166–174° (15–17 mm)], dissolved in 200 ml of methanol. Water was added until the solution became turbid. To the stirred solution held at ice-bath temperature was added 8.8 g (0.12 mole) of sodium borohydride, and stirring was continued at room temperature for 24 hr. The solution was added to 1500 ml of ice water, and the white solid that formed was filtered and dried to give 33.0 g (99.4% yield).

In very dilute carbon tetrachloride solution, IV showed absorption at 3612 cm^{-1} in the infrared spectrum. The nmr spectrum in carbon tetrachloride solution (*ca.* 10 mole %) showed the following: five aromatic hydrogens, 7.14 ppm; 2-*exo*-hydrogen, 4.16 ppm; 3-*exo*-hydrogen, 2.93 ppm; 1- and 4-bridgehead hydrogens, 2.33 ppm; 7-*anti*-hydrogen, 1.88 ppm; hydroxyl hydrogen, 1.68 ppm; remaining hydrogens, 1.1–1.8 ppm; $J_{1,2x}$ = 4.5 cps; $J_{2x,3x}$ = 9.8 cps; $J_{3x,4x}$ = 3.7 cps. Further finer splitting of each line in the two doublet pairs was observed.

Reduction of VII with lithium aluminum hydride in ether gave comparable yields of alcohol, but the melting point was generally lower, indicative of the presence of an impurity, presumably III. Apparently the sodium borohydride procedure is more selective.

3-*endo*-Phenyl-2-*exo*-norbornanol (III).—The procedure employed was similar to that of Collins, Cheema, Werth, and Benjamin[6] with the following exception. The product mixture was chromatographed on florisil. After a small forerun of what the infrared spectrum indicated was 2-*endo*-phenylnorbornanol (III) was collected as an oil which solidified upon standing. The average yield of III was 69%.

In very dilute carbon tetrachloride solution III showed absorption at 3616 cm^{-1} in the infrared. The nmr spectrum in carbon tetrachloride solution (*ca.* 10 mole %) showed the following: five aromatic hydrogens, 7.13 ppm; 2-*endo*-hydrogen, 3.80 ppm; hydroxyl hydrogen, 3.60 ppm; 4-bridgehead hydrogen, 2.29 ppm; 1-bridgehead hydrogen, 2.11 ppm; 7-*syn*-hydrogen, 1.83 ppm; remaining hydrogens, 0.8–1.6 ppm; $J_{2n,3x}$ = 3.1 cps; $J_{2n,7a}$ = 1.2 cps; $J_{3x,4} \cong$ 3.5 cps.

3-*exo*-Phenyl-2-norbornanone (VIII).—A typical reaction employed a solution of 11.0 g (0.478 mole) of sodium metal in absolute ethanol to which was added 41.2 g (0.190 mole) of 2-*exo*-phenyl-3-*endo*-nitronorbornane [bp 125–127° (1 mm)] in 100 ml of absolute ethanol, and a solution of 300 ml of concentrated hydrochloric acid, 500 ml of water, and 3000 ml of ethanol. Work-up in the usual manner involving extensive extraction with ether, "salting out" with sodium chloride, and washing with aqueous sodium carbonate, gave 18.2 g of yellow oil.

Column chromatography on Florisil of a small portion of this oil gave in order of elution with ligroin and ligroin–ether eluting solvents (1) a mixture of VII and VIII, (2) a mixture of VIII and a small amount of what the infrared spectrum indicated to be hydroxy ketone, and (3) a mixture of hydroxy ketones. The nmr spectrum of 2 in carbon tetrachloride solution showed a doublet at 2.93 ppm, J = 3.1 cps, characteristic of VIII.[6]

3-*exo*-Phenyl-2-*endo*-norbornanol (V).—Reduction of impure Nef reaction product was carried out with lithium aluminum hydride in the standard manner.[27] A typical reaction involved 28.4 g of Nef product, 5.8 g (0.15 mole) of lithium aluminum hydride, and 500 ml of ether. A saturated sodium sulfate solution was used to destroy the excess hydride and to decompose the

(25) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, John Wiley and Sons, Inc., New York, N. Y., 1964, p 246.

(26) D. C. Kleinfelter and P. von R. Schleyer, *J. Org. Chem.*, **26**, 3740 (1961).

(27) W. G. Brown, *Org. Reactions*, **6**, 469 (1951).

lithium salts. Removal of the ether at reduced pressure left 27.6 g of a clear yellow oil.

Chromatography of 16.5 g of this oil was carried out on Alcoa F-20 alumina. (Alumina was found to be superior to florisil for the separation of the alcohols.) A clear oil, 1.5 g of unknown hydrocarbon, was eluted with ligroin, after which 5.7 g of a mixture of IV–VI was eluted with 10–20% ether–80–90% ligroin. Finally, 7.6 g of what the infrared spectra indicated to be diols by the strong broad absorption at 2.8–3.1 μ was obtained. In a later experiment the initially eluted alcohol fraction was distilled and bp 114–118° (0.75–0.80 mm) was obtained. The 7.6 g of diol gave bp 126–130° (0.30–0.35 mm).

The 5.7-g alcohol mixture was rechromatographed on alumina using ligroin and ligroin–ether as eluting solvents. The first material eluted was almost pure IV (1.10 g) followed by a mixture of IV and V (1.40 g), and finally in a nearly clean separation VI (2.55 g, 12% from nitroalkane) as a viscous oil. The oil solidified with vigorous scratching in an ice bath.

In very dilute carbon tetrachloride solution V showed absorption at 3622 cm^{-1} in the infrared. The nmr spectrum in carbon tetrachloride solution (*ca.* 10 mole %) showed the following: five aromatic hydrogens, 7.15 ppm; 2-*exo*-hydrogen, 4.00 ppm; hydroxyl hydrogen, 3.10 ppm; 1- and 4-bridgehead hydrogens, 2.2–2.3 ppm; 3-*endo*-hydrogen, 2.22 ppm (superimposed on bridgehead hydrogens, but discernible); remaining hydrogens, 1.0–2.0 ppm; $J_{1,2x} \cong 4.1$ cps; $J_{2x,3n} = 4.4$ cps; $J_{3n,7a} = 2.6$ cps.

Isolation of 3-*exo*-Phenyl-2-*exo*-norbornanol (VI).—From the 1.40-g mixture of IV and V (see previous preparation), 0.60 g of IV was obtained by crystallization from ligroin at Dry Ice–acetone bath temperatures. The filtrate was converted to the *p*-nitrobenzoate mixture of IV and V in the usual manner. Recrystallization from ethanol gave 1.10 g of the *p*-nitrobenzoate of V. (This represents a yield of 2.8% of V, based on nitroalkane. The total per cent yield of V and VI of *ca.* 15% represents the best achieved. Generally the yields were 8–10%.)

Purified *p*-nitrobenzoate of V (2.30 g) was catalytically reduced in ethyl acetate solution[28] to the *p*-aminobenzoate, which was saponified with potassium hydroxide in ethanol. After distillation of the ethanol, extraction with ether, and ether removal at reduced pressure, 1.26 g of VI was obtained as a colorless oil.

In very dilute carbon tetrachloride solution VI showed absorption at 3589 cm^{-1} in the infrared with a possible extremely weak shoulder at 3625 cm^{-1}. The nmr spectrum in carbon tetrachloride solution (*ca.* 10 mole %) showed the following: five aromatic hydrogens, 7.18 ppm; 2-*endo*-hydrogen, 3.81 ppm; 3-*endo*-hydrogen, 2.79 ppm; 4-bridgehead hydrogen, 2.40 ppm; 1-bridgehead hydrogen, 2.23 ppm; 7-*syn*-hydrogen, 1.99 ppm; hydroxyl hydrogen, 0.88 ppm; remaining hydrogens 1.05–1.70 ppm; $J_{1,2n} = J_{2n,7a} = J_{3n,7a} = 1.1$ cps, $J_{2n,3n} = 6.8$ cps; $J_{3n,4} \cong 0.6$ cps.

Reduction of 3-*endo*-Phenyl-2-norbornanone with Potassium Hydroxide in Ethylene Glycol to give IV–VI.—The exact details of the experimental procedure employed are recorded elsewhere.[10] From 18.6 g (0.100 mole) of VII there was obtained 13.9 g of colorless oil, bp 132–138° (1.3–1.8 mm). Chromatography on alumina gave 0.35 g of VII and VIII, 4.11 g (21.9% yield) of IV, 0.87 g (4.6% yield) of VI, and 8.12 g (43.2% yield) of V. The total amounts of IV and VI present were determined as follows. Crystallization from ligroin gave 3.78 g of IV. The filtrate from this crystallization (1.20 g) was shown to be composed of 0.33 g of IV and 0.87 g of VI by integration of the 2-*exo*-hydrogen signal of IV and the 2-*endo*-hydrogen signal of VI (see Table II). The total yield of IV–VI was 69.7%.

Diels–Alder and Further Reactions to Produce the Mixture of III–V. 1. β-Phenylvinyl Acetate (IX).—The procedure was similar to that employed by Boeseken and Soesman.[11] Compound IX [bp 87–92° (0.50 mm)] was collected as a clear colorless liquid in a yield of 77.2%. The liquid solidified in an ice bath (lit.[11] mp 33–34°).

2. Diels–Alder Reaction of Cyclopentadiene and β-Phenylvinyl Acetate.—A mixture of 25.0 g (0.145 mole) of IX, 28.7 g (0.435 mole) of freshly distilled cyclopentadiene, and a few crystals of hydroquinone was heated in a pressure bomb at 190–195° for 24 hr. The apparatus was cooled to room temperature, the reaction mixture was washed out with ether, and the ether and some excess cyclopentadiene (probably dicyclopentadiene) were removed at reduced pressure. The residual oil, 38.6 g, was treated as described in part 3.

3. Hydrogenation of Diels–Alder Reaction Mixture.—The viscous oil (38.6 g) was dissolved in 150 ml of ethyl acetate, 0.20 g of platinum oxide was added, and the mixture was reduced in a Paar bomb with hydrogen at 35–45 psi until hydrogen consumption had ceased. The reaction mixture was filtered to remove the catalyst and solid material, after which the ethyl acetate was removed at reduced pressure. The residual oil (35.0 g) was treated as described in part 4.

4. Preparation and Isolation of III–V.—The 35.0 g of oil was reduced with 7.6 g (0.20 mole) of lithium aluminum hydride in ether in the standard manner.[27] Ethyl acetate was used to destroy the excess hydride, and dilute hydrochloric acid was added until the reaction mixture separated into two layers. The ether layer was washed with a dilute aqueous sodium carbonate solution and then the ether was removed at reduced pressure. Distillation of the residual oil gave a forerun of hydrocarbon and β-phenylethanol, and then 10.0 g of a mixture of III–V, bp 135–155° (3.5–4.0 mm).

The 10.0-g mixture was chromatographed on alumina using ligroin and ligroin–ether mixtures as eluting solvents. With *ca.* 3:1 ligroin–ether (v/v) 0.90 g of IV was obtained; with *ca.* 2:1 ligroin–ether (v/v) 1.2 g of V was obtained; with *ca.* 1:1 ligroin–ether (v/v) 2.1 g of III was obtained. Small amounts of a mixture of IV and V as an oil and larger amounts of a mixture of III and V were also obtained as overlapping mixtures between isolation of the *ca.* pure compounds. Infrared analysis of the latter mixture indicated a greater amount of III relative to V. The yield of the alcohol mixture based on β-phenylvinyl acetate was 36.7%.

7-*syn*-Chloro-2-norbornanone (XI).—To a solution of 40.0 g (0.272 mole) of crude 7-*syn*-chloro-2-*exo*-norbornanol[29] [bp 95–115° (25 mm)] in 250 ml of acetone (reagent grade) maintained at 30–35° was added dropwise 110 ml of 6 *N* chromic acid. The orange-red mixture was stirred at room temperature for 2 hr, after which sodium bisulfite was added to reduce the excess oxidant. Inorganic solids were removed by filtration, and the acetone was evaporated by a current of air. The residual brown oil was dissolved in 200 ml of ether and washed with aqueous sodium bicarbonate, and the ether was removed at reduced pressure. Distillation of the brown oil gave 27.0 g (68.7% yield) of XI [bp 110–120° (26 mm)] obtained as a pasty white solid. After three recrystallizations from an ethanol–ethyl acetate solvent mixture the semicarbazone derivative gave mp 183–185°, (lit.[29] mp 183.5–185°).

7-*syn*-Chloro-2-*endo*-phenylnorbornanol (XII).—To a stirred solution of 27.0 g (0.186 mole) of 7-*syn*-chloro-2-norbornanone (XI) in 100 ml of ether under a nitrogen atmosphere was added dropwise 120 ml of 1.7 *N* phenyllithium. The stirred reaction solution was refluxed for 2 hr, cooled, and then poured slowly into 100 ml of ice water. The ether layer was separated, the ether was removed at reduced pressure, and the residual oil was distilled to give, after a forerun of XI, 18.3 g (44.0% yield) of XII [bp 130–136° (1.4 mm)] which solidified upon standing. Recrystallization from ligroin gave mp 45–45.5°.

Anal. Calcd for $C_{13}H_{15}ClO$: C, 70.10; H, 6.80. Found: C, 70.05; H, 6.73.

In very dilute carbon tetrachloride solution XII showed absorption at 3572 cm^{-1} with extremely weak absorption at 3604 cm^{-1}.

The nmr spectrum of XII in carbon tetrachloride solution showed the following: five aromatic hydrogens as a multiplet centered at 7.3 ppm; 7-*anti*-hydrogen, 4.07 ppm; hydroxyl hydrogen, 3.36 ppm; 1- and 4-bridgehead hydrogens, 3-*exo*- and 3-*endo*-hydrogens, all as one peak at 2.37 ppm; remaining four 5- and 6-hydrogens, 0.8–1.6 ppm.

7-*syn*-Chloro-2-phenylnorbornene (XIII).—A mixture of 16.1 g (0.0720 mole) of XII and 11.0 g of potassium bisulfate was heated on a steam bath for 0.5 hr and then poured into ice water. The light yellow solid that formed was filtered to give 14.0 g (94.7% yield) of alkene, mp 43–44° after recrystallization from ethanol.

Anal. Calcd for $C_{13}H_{13}Cl$: C, 76.22; H, 6.41. Found: C, 76.03; H, 6.32.

The infrared spectrum in carbon disulfide showed strong absorption at 822 cm^{-1}, characteristic of trisubstituted alkenes.[30]

(28) Compare R. Adams and F. L. Cohen, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p 240.

(29) J. D. Roberts, F. O. Johnson, and R. A. Carboni, *J. Am. Chem. Soc.*, **76**, 5692 (1954).

(30) Reference 18, p 51.

The ultraviolet spectrum in 95% ethanol showed λ_{max} 262 mμ (log ε 4.07); λ_{max} 262.5 mμ (log ε 4.03[3] and 4.10[31]) for I.

Some of the signals and coupling constants for the nmr spectrum of XIII are recorded in Table I. In addition there were five aromatic hydrogens as a multiplet centered at *ca.* 7.25 ppm and the remaining four hydrogens at 1.0–2.0 ppm.

7-*syn*-Chloro-3-*endo*-phenyl-2-*exo*-norbornanol (XV).—The procedure was similar to that employed by Collins, Cheema, Werth, and Benjamin[6] for the preparation of III. From 7.20 g (0.0352 mole) of XIII there was obtained 3.24 g (42.8% yield) of a colorless oil [bp 148–152° (1.6 mm)] which could not be crystallized from a variety of solvents.

In very dilute carbon tetrachloride solution XV showed absorption at 3589 and 3621 cm^{-1} in the infrared with relative intensities of *ca.* 2:1.

Some of the signals and coupling constants for the nmr spectrum of XV are recorded in Table I. In addition there were five aromatic hyrogens (7.17 ppm), hydroxyl hydrogen (2.91 ppm), and remaining four hydrogens (0.9–1.7 ppm).

The tosylate (XVa) was prepared in the usual manner in 94% yield and gave mp 108–108.5°.

Anal. Calcd for $C_{20}H_{21}ClO_3S$: C, 63.74; H, 5.58. Found: C, 63.24; H, 5.86.

(31) The presence of some 1-phenylnortricyclene impurity reduces the absorption intensity. The log ε of 4.10 is for a sample practically devoid of 1-phenylnortricyclene.

The pertinent signals and coupling constants for the nmr spectrum of XVa are recorded in Table I.

Registry No.—I, 4237-08-5; II, 953-59-3; III, 944-56-9; IIIa, 10561-82-7; IIIb, 10561-83-8; IV, 10381-59-6; IVa, 10472-58-9; IVb, 10472-59-0; V, 10561-84-9; Va, 10561-85-0; Vb, 10561-86-1; VI, 10472-45-4; VIa, 10472-63-6; VIb, 10472-44-3; VIII, 10472-46-5; XII, 10472-47-6; XIII, 10472-48-7; XV, 10472-49-8; XVa, 10472-41-0; *exo*-norbornanol, 497-37-0; *exo*-norbornanol *p*-nitrobenzoate, 10472-43-2; *endo*-norbornanol, 497-36-9; *endo*-norbornanol *p*-nitrobenzoate, 10472-51-2; 2-phenylnorbornane-2,3-*cis*-*exo*-diol, 1135-59-7.

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Perhydroindan Derivatives. VII. Stereochemistry of Bridgehead Alkylation[1a]

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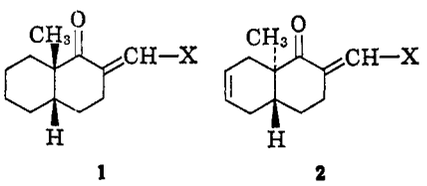
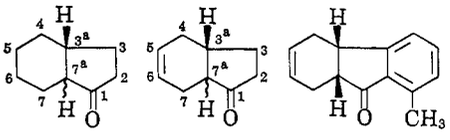
Solutions of the lithium enolate anions **8** (from **4**) and **9** (from **3**) were prepared from the corresponding enol acetates and then were alkylated with methyl bromoacetate. The monoalkylated product from the saturated ketone **3** contained more than 98% of the stereoisomer **17a** with a *cis* ring fusion. The corresponding ketone **4** with a $\Delta^{5,6}$ double bond gave monoalkylated product which contained 96% of the *cis* fused isomer **14a** and 4% of the *trans* fused isomer **15**. A comparable mixture of stereoisomers (mainly **14a**) was obtained from alkylation of the unsaturated ketone **6** and subsequent cleavage of the blocking group.

Earlier studies[2,3] demonstrated that the normal predominance of a *cis* fused product (*e.g.*, **1**) from the methylation of a suitably blocked 1-decalone derivative could be altered by the introduction of $\Delta^{6,7}$ double bond so that the major alkylated product became the *trans* fused isomer (*e.g.*, **2**). The introduction of an analogously located $\Delta^{5,6}$ double bond into the perhydroindanone system increased the equilibrium concentration of the *trans* isomer from 25% for the saturated ketone **3** to 47% for the olefinic ketone **4**.[4] These two observations suggested that the synthetic problem of obtaining a *trans* fused perhydroindan derivative from the alkylation of the ketone **3** at position 7a might be solved by alkylation of the unsaturated ketone **4**. We have explored this possibility earlier by alkylating the enolate anion derived from the tetrahydrofluorenone **5** with methyl bromoacetate;[4b]



1 **2**



3 **4** **5**

in this case the major alkylated product was found to be the *cis* isomer but a minor, uncharacterized product (possibly the *trans* isomer) was also obtained. However, this result did not provide an unambiguous answer to our question because the fused aromatic ring present in ketone **5** altered the relative stabilities of the two modes of ring fusion so that the *cis* fused isomer **5** was substantially more stable than the corresponding *trans* isomer.[4b]

To explore the question of alkylation stereochemistry further, we have now studied the alkylation with methyl bromoacetate of the appropriate enolate anions derived from the unsubstituted ketones **3** and **4** as well as the derivative **6** of the ketone **4** substituted with a thiobutylmethylene blocking group.[2b]

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