

of the methyl signals gave the relative ratio of the L-methyl- to the F-methyljanusene.

**Preparation of Nitrojanusene.**—A well-ground deoxygenated mixture of 3 g (0.012 mol) of **2b** and 3 g (0.016 mol) of anthracene was introduced into a Pyrex tube flushed with nitrogen gas. The tube was sealed and heated at  $200 \pm 10^\circ$  for 3 days. A procedure similar to that utilized for the chlorojanusene work-up gave a product (0.61 g, 12% yield) which melted at  $278\text{--}286^\circ$ . A saturated solution of the product in Spectrograde carbon tetrachloride with few drops of dimethyl sulfoxide- $d_6$  showed a ratio of 3F:1L.<sup>1</sup>

*Anal.* Calcd for  $C_{20}H_{21}NO_2$  (mixture): C, 84.28; H, 4.95. Found: C, 84.07; H, 5.10.

**Registry No.**—**2a**, 2734-13-6; **2b**, 17604-37-4; **2c**, 17604-38-5; **2d**, 17604-39-6; **4b**, 17344-73-9; **4c**, 17604-04-5; **4d**, 17604-05-6; **5b**, 17522-63-3; **5c**, 17604-06-7; **5d**, 17604-07-8; **6**, 17604-40-9; *cis*-2,11,12-trichloro-9,10-ethano-9,10-dihydroanthracene, 17604-08-9; *trans*-2,11,12-trichloro-9,10-ethano-9,10-dihydroanthracene, 17604-23-8.

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## Carbonium Ion–Silane Hydride Transfer Reactions.

### II. The 2-Phenyl-2-norbornyl Cation

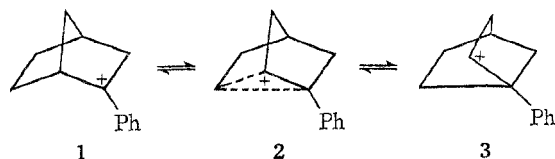
FRANCIS A. CAREY AND HENRY S. TREMPER

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

Received July 8, 1968

The 2-phenyl-2-norbornyl cation (**1**) was generated from *exo*-2-phenyl-*endo*-2-norbornanol (**4**), *endo*-2-phenyl-*exo*-2-norbornanol (**5**), and 2-phenylnorbornene (**8**) in methylene chloride–trifluoroacetic acid. Under these conditions **1** abstracted hydride from triethylsilane, triphenylsilane, and phenylsilane to give exclusively the product from *exo*-hydride transfer, 2-*endo*-phenylnorbornane (**6**). The results indicate that *exo* attack on classical norbornyl cations is preferred and is not a consequence of bridging. The preparations of **5** and **6** are described.

The extraordinary efficiency exhibited by  $\equiv\text{Si}\text{--H}$  compounds in donating hydride to carbonium ions in acid solution<sup>1,2</sup> offers interesting possibilities in both the areas of synthesis and carbonium ion reactions. Carbonium ions where the  $pK_{R^+}$  is more positive than  $-18$  abstract hydride from silanes under very mild conditions (0.3 M trifluoroacetic acid in methylene chloride at  $25^\circ$ ) to form the corresponding alkanes in high yield.<sup>2</sup> An examination of the 2-phenylnorbornyl cation (**1**,  $pK_{R^+} -13$ )<sup>3</sup> seemed in order because of the continuing interest in stabilized norbornyl cations as models for classical norbornyl cations.<sup>4</sup> The rationalization here is, because of the energy-lowering associated with delocalization of positive charge into the aromatic ring, that the 2-phenylnorbornyl cation has the classical structure **1** and that the bridged ion **2** is an approximation of the transition state for the equilibrium  $\mathbf{1} \rightleftharpoons \mathbf{3}$ .

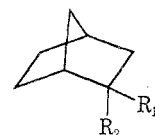


By observing the stereoselectivity associated with product formation from **1** in respect to the *exo/endo* capture ratio we can obtain information as to what this ratio should be for a classical norbornyl cation. Brown has found exclusive *exo* substitution at 2-arylnorbornyl cations by borohydride<sup>4a</sup> and hydroxide ion.<sup>5</sup> He concludes that, because *exo* attack is preferred in 2-arylnorbornyl cations where  $\sigma$  participation (bridging) is absent, the same preference for *exo* substitution in the

norbornyl cation is not sufficient grounds for bridging in this ion.

The results reported here tend to support Brown's conclusions and are complementary in that the reaction conditions and nature of the attacking reagent are rather different. Cation **1** may be generated in methylene chloride–trifluoroacetic acid at  $25^\circ$  from *exo*-2-phenyl-*endo*-2-norbornanol (**4**), *endo*-2-phenyl-*exo*-2-norbornanol (**5**), or 2-phenylnorbornene (**8**). The hydride donors, triethylsilane and triphenylsilane, are stable in this dilute acid medium. Brown's studies were performed in basic, ionizing solutions (diglyme–water) since he was using borohydride ion to trap the carbonium ion. He was also limited to studying only one epimer, the *endo*-2-aryl-*exo*-chloronorbornanes, as efficient routes to the *endo*-chlorides are not available.

The necessary starting material for our work, **4** and **5**, and the possible products, *endo*-2-phenylnorbornane (**6**) and *exo*-2-phenylnorbornane (**7**), were either previously known compounds or readily available by straightforward routes.



- 4**,  $R_1 = \text{Ph}$ ;  $R_2 = \text{OH}$   
**5**,  $R_1 = \text{OH}$ ;  $R_2 = \text{Ph}$   
**6**,  $R_1 = \text{H}$ ;  $R_2 = \text{Ph}$   
**7**,  $R_1 = \text{Ph}$ ;  $R_2 = \text{H}$

Thus **4** was prepared by addition of phenyllithium to norecamphor<sup>6</sup> and **7** by alkylation of benzene with norbornene in sulfuric acid.<sup>7</sup> While *exo*-alcohol **5** has been previously reported as a hydrolysis product from the corresponding chloride,<sup>5</sup> we chose to prepare it by

(1) D. N. Kursanov, Z. N. Parnes, G. I. Bassova, N. M. Loim, V. I. Zdanovich, *Tetrahedron*, **23**, 2234 (1967).

(2) F. A. Carey and H. S. Tremper, *J. Amer. Chem. Soc.*, **90**, 2578 (1968).

(3) N. C. Deno, P. R. Schleyer, and D. C. Kleinfelter, *Tetrahedron Lett.*, No. 12, 414 (1961).

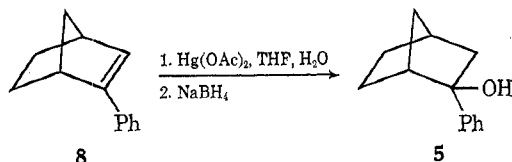
(4) (a) H. C. Brown and K. Takeuchi, *J. Amer. Chem. Soc.*, **90**, 2691, 2693 (1968); (b) T. G. Traylor and C. L. Ferrin, *ibid.*, **88**, 4934 (1966).

(5) H. C. Brown, F. J. Chloupek, and M-H Rei, *ibid.*, **86**, 1246 (1964).

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

(7) L. Schmerling, U. S. Patent 2,480,267 (1949); *Chem. Abstr.*, **44**, 1136 (1950).

hydration of 2-phenylnorbornene (**8**) using the oxymercuration procedure.<sup>3</sup> Thus treatment of **8** with mercuric acetate in aqueous tetrahydrofuran for 1 hr followed by decomposition of the organomercury intermediate with sodium borohydride afforded **5** in 90% yield.



Catalytic hydrogenation of **8** proceeded readily to give a single product in 50% yield after purification. Since hydrogenation of **8** should occur from the less hindered, *exo* direction, **6** would be the expected product from this reaction. The nmr spectrum of the product (Figure 1) was consistent with this expectation. Comparison of the nmr spectra of **6** and **7** (Figure 2) is interesting and important in that this constitutes the only practical way that we have found for distinguishing the epimers and analyzing the product mixtures from the hydride transfer reactions.

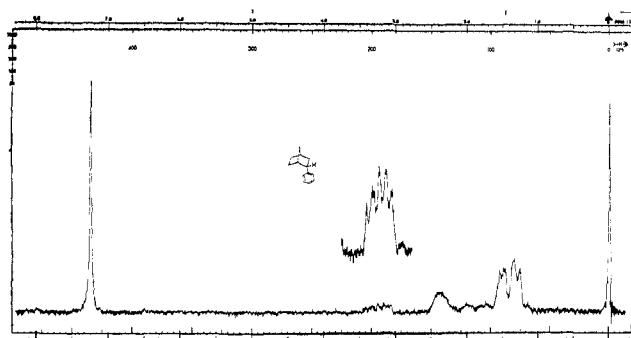


Figure 1.—Nmr spectrum of *endo*-2-phenylnorbornane (**6**), 60 MHz.

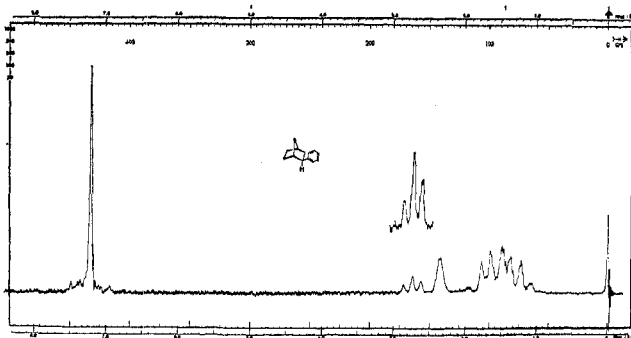


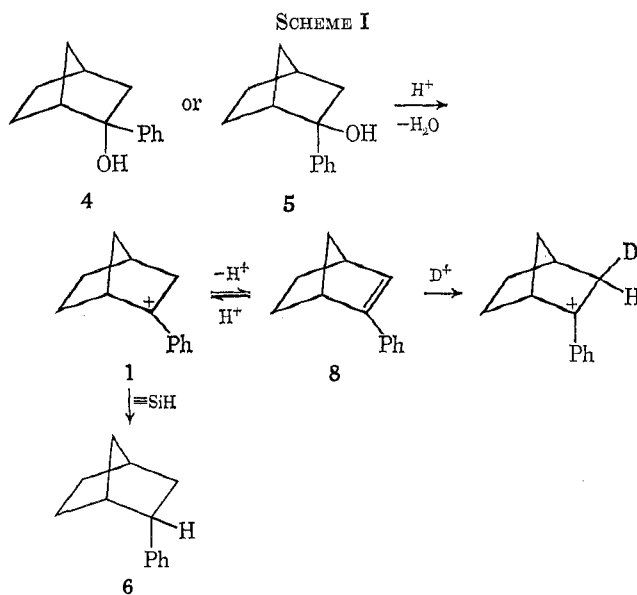
Figure 2.—Nmr spectrum of *exo*-2-phenylnorbornane (**7**), 60 MHz.

The benzylic proton signals for **6** and **7** differ both in respect to multiplicity and position. In **6** (*endo*-phenyl) the signal due to the proton at C-2 appears as a complex multiplet from  $\delta$  3 to 3.5 while in **7** (*exo*-phenyl) the corresponding signal appears as a skewed triplet from  $\delta$  2.6 to 2.9. This dependence of multiplicity and band position on the stereochemistry at C-2 in bornanes has been

well studied by Flautt and Erman<sup>9</sup> and applied to the quantitative analysis of 2-*p*-anisylbornanes by Brown.<sup>4</sup> By examining known mixtures by nmr at 100 MHz, we found that as little as 2% **7** in **6** could be detected. This method of analysis proved to be extremely useful since we were unable to separate **6** and **7** by gas chromatography on any of the equipment available to us.

As had been observed with other benzylic alcohols,<sup>1</sup> both **4** and **5** readily underwent rapid hydride transfer reactions with triethylsilane and triphenylsilane in methylene chloride-trifluoroacetic acid (30 min, 25°). In each case the product from hydride transfer was the only product formed as shown by gas chromatography using conditions under which both **8** and 1-phenylnorbornene would have been detected. Nmr analysis of the products at 100 MHz showed that the hydride transfer product was exclusively (>98%) **6**. In a preparative experiment in which the hydrocarbon product was separated from triphenylsilanol by chromatography on alumina **6** was isolated in 65% yield.

Since in previous work involving 1-phenylcyclohexanols, the products from hydride transfer were invariably accompanied by olefins formed by elimination the absence of **8** in the reaction product seemed unusual and raised the possibility that any **8** which did form was converted into **6** by protonation followed by hydride transfer. This possibility was further indicated when it was found that **8** was completely converted into **6** under the reaction conditions. Moreover, when the reaction of **4** with triphenylsilane was carried out using trifluoroacetic acid-*d* as the acid, the resulting **6**, isolated in 59% yield, had incorporated deuterium as shown both by its infrared spectrum which exhibited a weak band at 2170  $\text{cm}^{-1}$  (C-D stretch) and its mass spectrum which indicated approximately equal amounts of deuterated and undeuterated **6** (Scheme I).

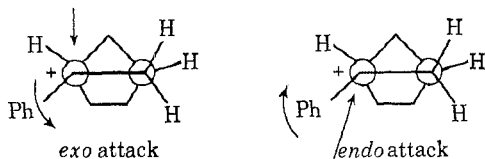


These results are accommodated by the reaction sequence shown. It is especially significant that here again *exo* substitution is observed exclusively even though the ion is classical. This and Brown's results<sup>4</sup>

(8) H. C. Brown and P. Geoghegan, Jr., *J. Amer. Chem. Soc.*, **89**, 1523 (1967); H. C. Brown and W. J. Hammar, *ibid.*, **89**, 1524 (1967); H. C. Brown, J. W. Kawakami, and S. Ikegami, *ibid.*, **89**, 1525 (1967).

(9) T. J. Flautt and W. F. Erman, *ibid.*, **85**, 3212 (1963); W. F. Erman, *ibid.*, **86**, 2887 (1964).

cast doubt on the conclusion that *exo* attack at norbornyl cations is a consequence of bridging.<sup>10</sup> The explanation provided by Schleyer<sup>11</sup> that at least part if not all of the stereoselectivity observed in reactions of this type results from torsional interactions is attractive. In cation **1** the phenyl substituent at C-2 and the bridgehead hydrogen are staggered with a dihedral angle of about 20° between them. *exo* Attack causes the phenyl and bridgehead hydrogen to move apart in the transition state while *endo* attack leads to eclipsing of these two substituents in going to the transition state. On this basis, it is clear that *exo* attack should be preferred.



This explanation, while it provides a satisfactory qualitative explanation for the observed stereoselectivity, should be taken as tentative because, as Schleyer has pointed out, we know little about conformational preferences in carbonium ions and the magnitude of their rotational barriers. In addition, the problem of steric hindrance in the attacking reagent is a matter of some consequence since *exo* attack will also be favored by bulky hydride donors. We have some evidence that this is not a factor of overriding importance in this reaction in the observation that phenylsilane (PhSiH<sub>3</sub>) also gives only **6** under these conditions. This result contrasts with our observations made on hydride transfers to the 4-*t*-butyl-1-phenylcyclohexyl cation where on changing from triethyl or triphenylsilane to phenylsilane an increase in the ratio of axial/equatorial transfer of hydride occurred.<sup>2</sup>

### Experimental Section

Nmr spectra were recorded on Varian Associates A-60 and HA-100 spectrometers as ca. 20% solutions in CDCl<sub>3</sub> or CCl<sub>4</sub> and chemical shifts are reported in parts per million ( $\delta$ ) from internal tetramethylsilane. Infrared spectra were measured on a Perkin-Elmer 337 grating instrument as KBr disks for solids and pressed films for neat liquids. Melting points are corrected and were determined on a Thomas-Hoover apparatus. The gas chromatograph was a Varian Aerograph 90-P unit fitted with a 10-ft 15% Carbowax 20M on Chromosorb P column at 195° column temperature and a flow rate of 60 ml of He/min. Under these conditions the retention time of **6** was 18.2 min; that of **8** was 21.8 min. **6** and **7** were not separable under any of the conditions we examined. The mass spectra were obtained using a Hitachi-Perkin-Elmer RMU-6E mass spectrometer at an ionizing potential of 70 ev.

Triethylsilane and triphenylsilane were purchased from Pierce Chemical Co. and the triphenylsilane was recrystallized from hexane before use.

*exo*-2-Phenyl-*endo*-2-norbornanol<sup>6</sup> (**4**) and *exo*-2-phenylnorbornane<sup>7</sup> (**7**) were prepared according to the literature methods and had physical constants consistent with those reported.

*endo*-2-Phenyl-*exo*-2-norbornanol.—To a solution of 3.59 g (12.4 mmol) of mercuric acetate in 25 ml of 50% aqueous tetrahydrofuran was added 2.10 g (12.4 mmol) of 2-phenylnorbornene.<sup>12</sup> The solution was stirred magnetically at 25°.

(10) G. D. Sargent, *Quart. Rev.* (London), **20**, 319 (1966).

(11) P. von R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 701 (1967).

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

After 7 min the yellow color disappeared and a milky solution formed. After a further 70 min 12.4 ml of a 0.5 *M* sodium borohydride in 3 *M* sodium hydroxide was added and the solution filtered through Celite. Ether extraction, drying of the ether layer (Na<sub>2</sub>SO<sub>4</sub>), and evaporation left 2.23 g of crude product. This material was washed through a column of 20 g of alumina with methylene chloride and the solvent removed to leave 1.91 g (90%) of **5** as a clear syrup which crystallized readily. The analytical sample was purified by sublimation: mp 62.5–64° (lit.<sup>6</sup> mp 61–62°).

*Anal.* Calcd for C<sub>13</sub>H<sub>16</sub>O: C, 82.94; H, 8.57. Found: C, 82.90; H, 8.55.

*endo*-2-Phenylnorbornane (**6**).—A 1.50-g sample of 2-phenylnorbornene in 75 ml of absolute ethanol was hydrogenated over 0.5 g of 10% palladium-on-charcoal catalyst in a Parr apparatus at 27 psi for 16 hr. The solution was filtered through Celite and the ethanol removed to leave a clear liquid which was purified by evaporative distillation (Kugelrohr) at 115° (oil bath) and 0.4 torr. The purified product (0.755 g) was shown to be homogeneous by glpc and had *n*<sub>D</sub><sup>20</sup> 1.5445. The ir spectrum differed from **7** in that **6** had a peak of moderate intensity at 1161 cm<sup>-1</sup> as well as a weak peak at 930 cm<sup>-1</sup> not present in **7**.

*Anal.* Calcd for C<sub>13</sub>H<sub>16</sub>: C, 90.64; H, 9.36. Found: C, 90.71; H, 9.39.

Reactions of **4** and **5** with Silanes.—The standard method used was to dissolve 188 mg (1.0 mmol) of **4** or **5** in 4 ml of methylene chloride containing 1.2 mmol of the appropriate silane at 25° and add 0.15 ml (2.0 mmol) of trifluoroacetic acid. The solutions were allowed to stand for 0.5 hr, then neutralized with solid sodium carbonate, filtered, and evaporated; the residue was taken up in 0.3 ml of carbon tetrachloride and analyzed by nmr on the 100-MHz instrument. By inspection of known mixtures, it was found that as little as 2% **7** in **6** could be detected by this method.

In all experiments (**4** + triethylsilane, **4** + triphenylsilane, **4** + phenylsilane, **5** + triethylsilane, and **5** + triphenylsilane), the exclusive product was *endo*-2-phenylnorbornane (**6**). Analysis by glpc indicated that the reaction mixtures contained no **8**.

Preparative Reaction of **4** with Triphenylsilane.—To a solution of 1.0 g (5.3 mmol) of **4** in 21 ml of methylene chloride containing 1.66 g (6.36 mmol) of triphenylsilane was added 0.80 ml (10.6 mmol) of trifluoroacetic acid. After 0.5 hr at 25°, solid sodium carbonate was added and the solution filtered and evaporated. The residue was taken up in pentane and chromatographed on 25 g of alumina. Elution with pentane (60 ml) afforded 602 mg (65%) of clear liquid which was further purified by evaporative distillation and shown to be >98% *endo*-2-phenylnorbornane by its nmr and ir spectra.

When the experiment was repeated using trifluoroacetic acid-*d* (freshly prepared from trifluoroacetic anhydride and D<sub>2</sub>O), 544 mg (59%) of product was obtained which exhibited absorption at 2170 cm<sup>-1</sup> in its ir spectrum which could be due to C–D stretching. This band does not result from a triphenylsilane impurity since the Si–H frequency is at 2135 cm<sup>-1</sup>. The mass spectrum of this product indicated approximately equal amounts of deuterated and undeuterated material. The nmr spectrum of this material again indicated only *endo*-2-phenylnorbornane was formed.

Reaction of 2-Phenylnorbornene with Triethylsilane.—Trifluoroacetic acid (0.51 ml, 2.0 mmol) was added to a solution of 170 mg (1 mmol) of **8** and 139 mg (1.2 mmol) of triethylsilane in 4 ml of methylene chloride. After 0.5 hr sodium carbonate was added and the solution analyzed by glpc. No residual **8** was detected and the only material present (other than silicon compounds) was **6**.

Registry No.—**1**, 18026-67-0; **5**, 17989-93-4; **6**, 17989-94-5; **7**, 17989-95-6.

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