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Bridged Polycyclic Compounds. LI. Selectivity in the Diels–Alder Synthesis of Some Janusene (5,5a,6,11,11a,12-Hexahydro-5,12:6,11-di-*o*-benzenonaphthacene) Derivatives[1]

STANLEY J. CRISTOL AND WENDEL Y. LIM

Department of Chemistry, University of Colorado, Boulder, Colorado 80302

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The preparation of a number of substituted janusenes (**4y** and **5y**) by Diels–Alder syntheses from dibenzobicyclo[2.2.2]octatriene (**2a**) and 2-substituted anthracenes (**3y**) or from substituted dibenzobicyclo[2.2.2]octatrienes (**2y**) and anthracene (**3a**) has been investigated. There appears to be no selectivity with a chlorine substituent (and none is possible with hydrogen), but there is substantial preference for the formation of "face" ring substituted products (**4y**) over "lateral" ring products (**5y**) with methyl and nitro substituents. The results are discussed briefly.

In the first paper[2] on the synthesis and properties of 5,5a,6,11,11a,12-hexahydro-5,12:6,11-di-*o*-benzenonaphthacene (**1**), which has been dubbed "janusene," the preparation *via* the Diels–Alder reaction between dibenzobicyclo[2.2.2]octatriene (**2a**) and anthracene (**3a**) was described. In that paper and in other work,[3] several electrophilic substitution reactions of janusene were reported, including nitration, bromination, and chlorination. In each case, electrophilic substitution occurred preferentially in the "face" (F) rings compared with that in the "lateral" (L) rings, and largely in the β positions on the rings. Thus, for example, nitration with acetyl nitrate led to about six times as much F_β-nitrojanusene (**4b**) as L_β-nitrojanusene (**5b**), in spite of the fact that the F rings suffer from steric hindrance. Bromination has a somewhat greater selectivity factor,[2] while aluminum chloride catalyzed chlorination of janusene gives a ratio of *ca.* 4.5 F_β:L_β. The greater reactivity of the F rings was rationalized in terms of transannular π-cloud interactions leading (a) to destabilization of the F rings by transannular electronic repulsion and (b) to stabilization of the transition state for F-ring substitution by transannular electronic delocalization.[2,4]

Nonbonding interactions appear to be of considerable importance in the transition states for Diels–Alder reactions.[6] It seemed possible that this might show up in the reaction between substituted anthracenes (**3y**) and dibenzobicyclo[2.2.2]octatriene (**2a**) or between substituted **2y** species and anthracene. Thus, if the transition state for the diene synthesis resembled the janusene product, and if the effect of the substituent on a ring was to increase attraction to another benzene ring, it might be anticipated that more F-ring product **4y** would be produced in the Diels–Alder reaction than L-ring product **5y**.

Reactions were carried out by heating mixtures of the two components under nitrogen in sealed glass tubes at 200–210° for 3–4 days. The product mixture compositions did not appear to change substantially with time, so that they were apparently kinetically controlled product mixtures. Analyses of methyljanusene and nitrojanusene mixtures were carried out by pmr analysis while those of chlorojanusenes were carried out by infrared analysis. The structures of the chlorojanusenes were confirmed by transformation of F_β-nitrojanusene[2] to F_β-chlorojanusene *via* a Sandmeyer procedure. The analytical data were confirmed in many cases by separation and isolation of the components. With chlorine and methyl substituents, we were able to carry out reactions in both fashions, *i.e.*, with **2a** and **3y** components and with **2y** and **3a** components, but the nitro reaction was run only with **2b** and **3a**, because of the difficulty of preparing β-nitroanthracene (**3b**). Table I gives the isomer distributions in the products of the Diels–Alder reactions.

With hydrogen substituents, the F_β and L_β isomers are, of course, identical, so that a 50:50 composition must be formed. With chlorine substituents, the mixture compositions were indistinguishable from equimolar by our analytical techniques (probably ±3%). However, methyl substitution favored F_β formation by 2:1 and nitro substitution by 3:1. The data corre-

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(1) Paper L: S. J. Cristol, G. O. Mayo, and R. M. Sequeira, *J. Amer. Chem. Soc.*, **90**, 5564 (1968).

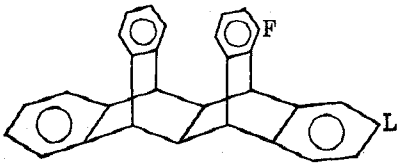
(2) S. J. Cristol and D. C. Lewis, *ibid.*, **89**, 1476 (1967).

(3) D. C. Lewis, Ph.D. Thesis, University of Colorado, 1965.

(4) The Dreiding model of janusene has the face rings parallel and *ca.* 2.5 Å apart. An X-ray analysis[5] of janusene-5a,11a-dicarboxylic anhydride shows that the face rings are not parallel (the fused bicyclooctane rings are distorted by the ring repulsions) and are *ca.* 3.1 Å apart at the fused atoms and *ca.* 4.0 Å apart at the β-carbon atoms.

(5) T. Fukunaga and Y. Iitaka, private communication.

(6) For a recent discussion, see A. Wassermann, "Diels–Alder Reactions," Elsevier Publishing Co., Amsterdam, The Netherlands, 1965, Chapter 5.



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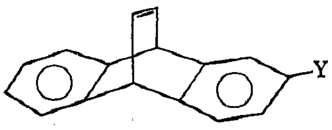

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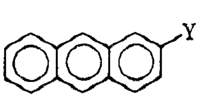

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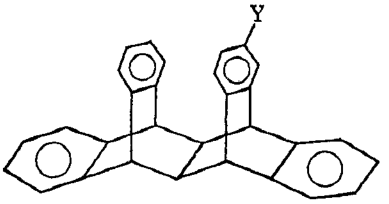

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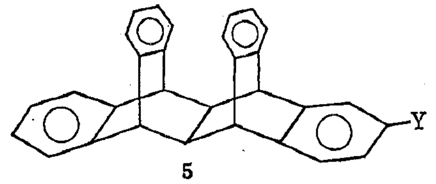

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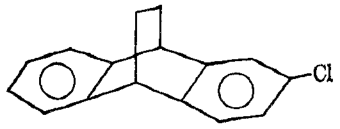

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a, Y = H
b, Y = NO_2
c, Y = Cl
d, Y = CH_3

Table I

Isomer Distributions in Diels–Alder Products from Anthracenes (**3y**) and Dibenzobicyclo[2.2.2]octatrienes (**2y**)

	Mode of reaction			
	3a + **2y**		**3y** + **2a**	
Substituent Y	% Fβ	% Lβ	% Fβ	% Lβ
H	50	50	50	50
Cl	50	50	50	50
CH_3	67	33	66	34
NO_2	75	25		

spond with the ideas[6] described above. One may assume that one of the rings acts as a π base or as a π acid, and the other in a conjugate fashion, in the nature of a π or charge-transfer complex,[7] in the transition state for janusene formation. The data suggest that a chlorobenzene ring (in which inductive effects and resonance effects are in the opposite sense[8]) is not perceptibly a π acid or a π base toward a benzene ring at the transition-state distance. However, the methylbenzene ring appears to have modestly strong basic character[7] compared with benzene and the nitrobenzene ring shows even stronger π-acid character. The results with the methylbenzene compounds imply that the transition state for the diene synthesis is reached before electron repulsions postulated for F-ring interactions in janusenes become critical.

Experimental Section

All nuclear magnetic resonance spectra were taken on a Varian A-60 instrument as saturated solutions in carbon tetrachloride, using tetramethylsilane as an internal standard. All chemical shifts are reported in τ units (τ = 10.00 for tetramethylsilane). In cases where the compound was slightly soluble in carbon tetrachloride, a few drops of dimethyl sulfoxide-d_6 were added. The far-infrared spectra of the chlorojanusenes were taken on a Perkin-Elmer Infracord (KBr prism; 12.5–25 μ) in carbon tetrachloride. All elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

2-Chloroanthracene, mp 222–223°, was prepared by reduction of 2-chloroanthraquinone with zinc powder in ethanolic aqueous ammonia.[9] 2-Methylanthracene,[10] mp 204–205°, was prepared by a similar reaction (except that toluene was added to remove the tarry reduction side-reaction products which coat the zinc) from 2-methylanthraquinone.

Preparation of 2,11,12-Trichloro-9,10-ethano-9,10-dihydroanthracene Isomers.—To a mixture of 20 g (0.12 mol) of 2-chloroanthracene (**3c**) and 100 mg of hydroquinone in a Pyrex tube (19 × 600 mm) was added 125 g (1.66 mol, the excess amount acted as solvent) of *cis*- or *trans*-dichloroethylene. The tube was sealed and was heated at 190–200° for 3 days. After the 3-day period, the tube was opened and the solvent removed with the aid of a rotary evaporator. The residue was dissolved in 250 ml of xylene and heated at reflux with 21 g of maleic anhydride for 2 hr. Water (250 ml) was added and the mixture was neutralized with sodium carbonate. The xylene layer was separated and the xylene was removed by steam distillation. The crude product obtained was passed through a column packed with 80–200 mesh activated neutral alumina (Merck 71707). The column was eluted with Skellysolve B (petroleum ether, bp 60–70°) with increasing amounts of benzene or carbon tetrachloride. Colorless crystals were obtained for the *trans* adduct mixtures (17–29 g, 47–81% yield, mp 180–210°) or the *cis* adduct mixtures (31–34 g, 87–96% yield, mp 177–184°). The isomers in the corresponding adduct mixtures were not separated, but were used directly for the preparation of olefin **2c**.

Anal. Calcd for $C_{16}H_{11}Cl_3$: C, 62.06; H, 3.58. Found (*trans* adduct): C, 62.06; H, 3.58. Found (*cis* adduct): C, 62.16; H, 3.62.

Preparation of 2-Chloro-9,10-etheno-9,10-dihydroanthracene (2c).—To a warm solution containing 1.25 g (0.004 mol) of the trichloride in 125 ml of 95% ethanol was added 4 g (0.06 g-atom) of zinc dust (which was coupled with 2% copper sulfate solution; see below). The reaction mixture was brought to reflux and stirred for 6 hr.

The zinc was filtered and washed with several portions of hot ethanol or acetone. The combined washings and filtrate were poured into 1 l. of water. A light suspension of white solid was allowed to stand for several hours until the solids were filterable. The crude product (mp 123–125°) was recrystallized from 95% ethanol to give 0.79–0.82 g (84–89%) of pure **2c**, mp 125–126°.

Anal. Calcd for $C_{16}H_{11}Cl$: C, 80.50; H, 4.65. Found: C, 80.22; H, 4.55.

When a similar reduction was conducted for 40 hr, the crude product melted at 98–133°. The pmr spectrum of this material showed approximately 33% saturated compound, which was separated by recrystallization from 95% ethanol from the **2c** product. The pure substance, mp 95–96°, had analytical data and a pmr spectrum consistent with those anticipated[11] for the structure 2-chloro-9,10-ethano-9,10-dihydroanthracene (**6**). Aliphatic proton resonances were at τ 8.33 (4 H) and 5.80 (2 H).

Anal. Calcd for $C_{16}H_{13}Cl$: C, 79.83; H, 5.44. Found: C, 79.68; H, 5.42.

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[7] G. Briegleib, "Elektronen-Donator-Acceptor Komplexe," Springer-Verlag, Berlin, 1961, p 144 ff.

[8] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter 2.

[9] H. Schilling, *Ber.*, **46**, 1066 (1913).

[10] E. Bornstein, *ibid.*, **15**, 1820 (1882).

[11] S. J. Cristol, T. W. Rusell, J. R. Mohrig, and D. E. Plorde, *J. Org. Chem.*, **31**, 581 (1966).

Preparation of Zinc–Copper Couple.[12]—To 10 g of reagent grade powdered zinc (0.15 g-atom) was added 50 ml of 2% (by weight) copper sulfate solution with constant stirring. The zinc turned gray and the aqueous layer became decolorized. This process was repeated until the decantate retained a slight blue coloration (after four to five washings).

Preparation of 9,10-Etheno-9,10-dihydroanthracene (2a).—To a stirred warm solution containing 15 g (0.05 mol) of 11,12-dichloro-9,10-ethano-9,10-dihydroanthracene[13] in 500 ml of 95% ethanol was added 32.6 g (0.5 g-atom) of coupled zinc. Following the same procedure as for compound **2c**, a pure product (91–98% yield), which melted at 119–120°, was obtained. This is an improvement over the original procedure.[13]

Preparation of 2-Methyl-11,12-dichloro-9,10-ethano-9,10-dihydroanthracene Isomers.—To 5 g (0.02 mol) of 2-methylanthracene (**3d**) in a Pyrex tube was added 62 g of *trans*-dichloroethylene. The tube was flushed with nitrogen, sealed, and then heated at 190–200° for 3 days. The work-up was the same as that performed on the trichloro compounds. The isomer mixture was obtained in 60–80% yield (3.5–4.6 g, mp 135–140°).

Preparation of 2-Methyl-9,10-etheno-9,10-dihydroanthracene (2d).—Into a warm stirred solution of 1.5 g (0.005 mol) of the dichloride mixture in 150 ml of 95% ethanol was added 5 g of copper-activated zinc. The reaction mixture was heated at reflux for 4 hr. A work-up similar to that with **2c** gave the pure olefin **2d** (0.97 g) in 90% yield (mp 89–90°).

Anal. Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.45; H, 6.54.

2-Nitro-9,10-etheno-9,10-dihydroanthracene (2b), mp 183–184°, was prepared by the treatment of **2a** with acetyl nitrate in acetic anhydride according to the procedure described by Mohrig.[14]

Preparation of Chlorojanusene. A.—An intimately ground mixture of 5 g of ethenodihydroanthracene (**2a**, 0.024 mol), 5 g of 2-chloroanthracene (**3c**, 0.024 mol), and 0.05 g of hydroquinone (optional provided the tube was flushed with nitrogen gas) was introduced into a 19 × 300 mm Pyrex tube. After being flushed with nitrogen gas, the tube was sealed and heated at 200 ± 10° for 3–4 days. After being cooled in an acetone–Dry Ice bath, the tube was opened and the contents were poured into a flask. The liquid was evaporated and the residue was taken up in a small amount of benzene. The benzene solution was passed through a neutral alumina column and eluted with Skellysolve B with increasing amounts of carbon tetrachloride. The mixture of isomeric chlorojanusenes were separated from the starting material. The mixture had a variable melting point (ranged from 207 to 226°, 45% yield).

Higher yields (63–89%) were obtained by prolonging the reaction time to 1 week. Average composition data (±3%) are given in Table I.

Anal. Calcd for $C_{30}H_{21}Cl$ (mixture): C, 86.42; H, 5.08. Found: C, 86.31; H, 5.13.

B.—A well-ground mixture of 1 g (0.004 mol) of **2c**, 2.5 g (0.014 mol) of anthracene, and 0.05 g of hydroquinone (optional) was introduced into a Pyrex tube and sealed after flushing with nitrogen gas. The tube was heated at 200 ± 10° for 3–4 days. The normal work-up gave a mixture of chlorojanusenes (mp 216–227°) in 63% yield. Longer reaction periods at 220–230° increased the yield to 89%.

Anal. Calcd for $C_{30}H_{21}Cl$ (mixture): C, 86.42; H, 5.08. Found: C, 86.67; H, 5.24.

Separation of F_β- and L_β-Chlorojanusenes.—Preliminary thin layer chromatography showed that the isomeric chlorojanusenes were separable with the use of silica gel but not with alumina.

A solution of 2 g of unseparated F_β- and L_β-chlorojanusenes in benzene was diluted with Skellysolve B to approximately 10% (benzene) solution. This solution was passed through a silica gel (Baker 3405) column and eluted with Skellysolve B with increasing amounts of benzene or carbon tetrachloride. Several 200-ml fractions were collected and monitored by observing the small change in the aromatic pattern of the pmr spectra (at this point it was not yet discovered that the two chlorojanusenes have different far-infrared C–Cl stretching absorptions). The fractions which did not show apparent change in the intensity of the F aromatic pattern were combined and recrystallized from ethanol–acetone (1:1). The pure L_β isomer melted at 214–215°. The fractions that showed some change in the intensity of the F_β aromatic signal were combined in the same manner and recrystallized from ethanol–acetone. The pure F_β isomer melted at 247–248°. The ratio of the L_β to the F_β from product isolation was 52:48%.

Anal. Calcd for $C_{30}H_{21}Cl$: C, 86.42; H, 5.08. Found (F_β isomer): C, 86.17; H, 5.14. Found (L_β isomer): C, 86.46; H, 5.20.

Quantitative Determination of L_β- and F_β-Chlorojanusenes.—A solution of 100 mg of L_β- or F_β-chlorojanusene in 4 ml of Spectrograde carbon tetrachloride was made. The known mixtures used as standards for comparison were obtained from this solution. The crude products obtained above were made up to approximately the same concentration as the standard solutions. The far-infrared spectrum of each run was compared with the spectra obtained from the standards.

Chlorination of Janusene.—To a stirred acetic acid solution of 1 g of janusene (0.003 mol) was added 26 mmol of dry chlorine gas in slow controlled bubbles. A trace of aluminum chloride was used. After 10 min, the reaction mixture was poured into 100 ml of cold water. The product crystallized after neutralization of the solution with 25% sodium hydroxide. The filtered precipitate (1.2 g) was recrystallized from ethanol–acetone solvent mixture and gave 1.04 g (96% yield) of material which melted at 230–237°. Careful column chromatography showed that the mixture was composed of the following monochlorojanusene isomers: F_α 6%, L_β 17%, and F_β 74%. The basis for identification of the F_α isomer was by comparison with F_α-bromojanusene.[2]

Conversion of F_β-Aminojanusene to F_β-Chlorojanusene (4c).—To a solution of 150 mg (0.0005 mol) of F_β-aminojanusene[3] in 100 ml of 28% hydrochloric acid at 0° was added an aqueous solution of 280 mg (0.004 mol) of sodium nitrite (also at 0°). After 15 min the above mixture was added slowly to a cooled solution of cuprous chloride. The reaction mixture was stirred for 2 more hr at room temperature and then heated on a steam bath for several minutes. The precipitate was filtered and passed through an alumina column. The **4c** was obtained pure (51 mg, 24%) and melted at 246–248°.

Anal. Calcd for $C_{30}H_{21}Cl$: C, 86.42; H, 5.08. Found: C, 86.61; H, 5.21.

Preparation of Methyljanusene. A.—An intimately ground mixture of 13 g (0.06 mol) of **2a** and 13 g (0.07 mol) of 2-methylanthracene (**3d**) was deoxygenated and introduced into a Pyrex tube flushed with nitrogen gas. After the tube was sealed, it was heated for 3 days at 200 ± 10°. After the 3-day period, the tube was opened and the contents were worked up following the same procedure as that used for chlorojanusene. The methyljanusene isomers were separated from the starting material by column chromatography using silica gel (yield 18.3 g, 77%; mp 182–194°).

Anal. Calcd for $C_{31}H_{24}$ (mixture): C, 93.90; H, 6.10. Found: C, 94.05; H, 6.06.

The L_β-methyljanusene was separated from the F_β isomer by several fractional crystallizations using acetone–ethanol (1:50 by volume) mixed solvent. The F_β isomer was easily separated from the mixture. The L_β isomer was difficult to isolate as it tended to cocrystallize a mixture with F isomer left in the mixture. The L_β isomer melted at 214–215° while the F_β isomer melted at 219–220°.

Anal. Calcd for $C_{31}H_{24}$: C, 93.90; H, 6.10. Found (F isomer): C, 93.77; H, 6.26.

B.—A well-ground mixture of 600 mg (0.003 mol) of compound **2d** and 500 mg (0.003 mol) of anthracene was deoxygenated and introduced into a Pyrex tube. The tube was sealed and heated at 200 ± 10° for 3 days. The same work-up as utilized for chlorojanusene gave a product (475 mg) which melted at 175–199° (40% yield).

Anal. Calcd for $C_{31}H_{24}$ (mixture): C, 93.90; H, 6.10. Found: C, 94.05; H, 6.06.

Quantitative Determination of Methyljanusene Isomers.—After maleic anhydride treatment of the crude product (to remove excess anthracene or methylanthracene) a saturated solution in spectrograde carbon tetrachloride was made. This was used for the pmr analysis. The pmr spectrum showed four distinct signals: aromatic absorption at τ 2.83–3.50 (15 H); benzohydrylic hydrogen absorption at 5.90 (4 H); nonbenzohydrylic hydrogen absorption at 7.50 (2 H); and methyl absorption at 7.83 (for L_β) and 8.00 (for F_β) (both integrated for three hydrogens with reference to the aromatic signal which integrated for 15 protons). The methyl signal at τ 8.00 was assigned to the F isomer owing to shielding effects of the F rings. The integration

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[12] J. H. Gladstone and A. Tribe, *J. Chem. Soc.*, 31, 561 (1877).

[13] S. J. Cristol and N. L. Hause, *J. Amer. Chem. Soc.*, **74**, 2193 (1952).

[14] J. R. Mohrig, Ph.D. Thesis, University of Colorado, 1963.

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 ± 10° 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 278–286°. A saturated solution of the product in Spectrograde carbon tetrachloride with few drops of dimethyl sulfoxide-d_6 showed a ratio of 3F:1L.[1]

Anal. Calcd for $C_{30}H_{21}NO_2$ (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.

Acknowledgment.—The authors are indebted to the Institute of General Medical Sciences (Public Health Service Grant GM-12139) for support of this work.

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

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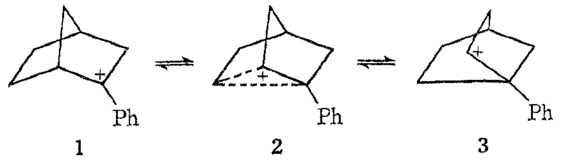
The 2-phenyl-2-norbornyl cation (1) was generated from *exo*-2-phenyl-*endo*-2-norbornanol (4), *endo*-2-phenyl-*exo*-2-norbornanol (5), and 2-phenylnorbornene (8) in methylene chloride–trifluoroacetic acid. Under these conditions 1 abstracted hydride from triethylsilane, triphenylsilane, and phenylsilane 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 ≡Si—H compounds in donating hydride to carbonium ions in acid solution[1,2] 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°) to form the corresponding alkanes in high yield.[2] An examination of the 2-phenylnorbornyl cation (**1**, pK_{R^+} −13)[3] seemed in order because of the continuing interest in stabilized norbornyl cations as models for classical norbornyl cations.[4] 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 **1** ⇌ **3**.

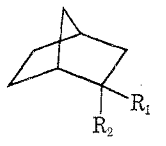


1 2 3

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[4a] and hydroxide ion.[5] He concludes that, because *exo* attack is preferred in 2-arylnorbornyl cations where σ 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° 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, $R_1 = Ph$; $R_2 = OH$
5, $R_1 = OH$; $R_2 = Ph$
6, $R_1 = H$; $R_2 = Ph$
7, $R_1 = Ph$; $R_2 = H$

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

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

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