**Registry No.**—**2**, 37759-72-1; **3**, 37759-73-2; **4**, 406-94-0; **5**, 37759-75-4; **6**, 37759-76-5; **7**, 25597-16-4; **8**, 37759-78-7; **9**, 37759-79-8; **10**, 37759-80-1; **11**, 37759-81-2; **12**, 37759-82-3; **13**, 37759-83-4; **17**, 37759-84-5; **15**, 37759-85-6; **16**, 37759-86-7; *cis*-**17**, 37759-87-8; *trans*-**17**, 37759-88-9; *endo*-**19** benzylthiouronium, 37746-47-7; *exo*-**19** benzylthiouronium, 37746-48-8; *endo*-**20**, 37746-49-9; *exo*-**20**, 37705-54-7; *endo*-**21**, 37746-50-2; *exo*-**21**, 37746-51-3; *endo*-**22**, 37746-52-4; *exo*-**22**, 37746-53-5; *endo*-**23**, 37746-54-6; *exo*-**23**, 37746-55-7; *endo*-**24**, 37746-56-8; *exo*-**24**, 37746-57-9; *endo*-**25**, 37746-58-0; *exo*-**25**, 37746-59-1; *endo*-**26**, 37746-60-4; *exo*-**26**, 37746-61-5; *endo*-**27**, 37705-55-8; *exo*-**27**, 37705-56-9; *endo*-**28**, 37746-62-6; *exo*-**28**, 37746-63-7; *endo*-**29**, 37746-64-8; *exo*-**29**, 37746-65-9; *endo*-**30**, 37746-66-0; *exo*-**30**, 37746-67-1; *endo*-**31**, 37746-68-2; *exo*-**31**, 37746-69-3; *endo*-**32**, 37746-70-6; *exo*-**32**, 37746-71-7; *endo*-**33**, 37746-72-8; *exo*-**33**, 37746-73-9; *endo*-**35**, 37746-74-0; *exo*-**35**, 37746-75-1; *endo*-**36** $\alpha$-naphthylurethane, 37705-57-0; *exo*-**36** $\alpha$-naphthylurethane, 37746-76-2; *endo*-**37**, 37705-58-1; *exo*-**37**, 37705-59-2; cyclopentadiene, 542-92-7; ethyl 4-fluorocrotonate, 37746-77-3; ethyl 4-bromocrotonate, 37746-78-4; 3-hydroxy-4,4-difluorobutyric acid, 37746-79-5; difluoroacetaldehyde, 430-69-3; ethyl 3-hydroxy-4,4-difluorobutanoate, 37746-81-9; ethyl *trans*-4,4-difluorocrotonate, 37746-82-0.

**Acknowledgment.**—The authors are grateful to the Hooker Chemical Company for partial financial support of this work.

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# Stereochemistry of Asymmetric Silicon. XXII. Preparation and Properties of Optically Active Perfluorophenyl Compounds[1,2]

LEO H. SOMMER* AND MICHAEL A. SILVERMAN

*Department of Chemistry, University of California, Davis, California 95616*

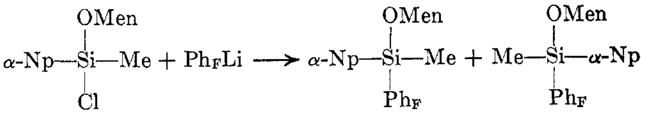
*Received February 14, 1972*

The synthesis and resolution of two new optically active organosilicon systems has been achieved. These are $\alpha$-naphthylperfluorophenylmethylsilanes, $\alpha$-NpPh$_F$MeSi*X, and phenylmethylpentafluorophenylsilanes, PhMePh$_F$Si*X. Synthesis and resolution of these compounds is of special significance for organosilicon stereochemistry and reaction mechanisms because of the highly electron-withdrawing polar effect of the pentafluorophenyl group. The available data relating to the magnitude of the electron-withdrawing effect of the $C_6F_5$ group indicate that it approximates Br.

Since the electronegativity of the pentafluorophenyl group is approximately equal to that of Br[3] and is much greater than that of other "nonreactive" substituents previously bonded to asymmetric silicon,[4-7] it was of considerable interest to undertake the preparation and study of optically active compounds containing this group, in order to determine whether its presence would change the stereochemical course of substitution reactions at asymmetric silicon. The synthetic methods for preparation of $C_6F_5MgBr$[8,9] and $C_6F_5Li$[10,11] have been well established, and the coupling of either of these organometallic reagents with the appropriate chlorosilane has been shown to yield compounds containing the pentafluorophenyl group bonded to silicon.[12] The synthesis and properties of optically active perfluorophenylsilicon compounds is discussed in the next section.

**Optically Active Perfluorophenylsilicon Compounds.**—Two new monofunctional triorganosilicon systems incorporating the pentafluorophenyl group have been prepared by two methods and these are discussed below.

Reaction of $\alpha$-naphthylmagnesium bromide with methyltrimethoxysilane gave a 68% yield of $\alpha$-naphthylmethyldimethoxysilane, $\alpha$-NpMeSi(OMe)$_2$, bp 118–119° (1.0 mm). Lithium aluminum hydride reduction of $\alpha$-NpMeSi(OMe)$_2$ in refluxing ether gave an 88% yield of $\alpha$-naphthylmethylsilane, $\alpha$-NpMeSiH$_2$, bp 77–79° (0.35 mm). This substance was treated with chlorine in $CCl_4$ to give predominantly $\alpha$-naphthylmethylchlorosilane, $\alpha$-NpMeSiHCl. It is interesting that the electron-withdrawing effect of chlorine in $\alpha$-NpMeClSiH is sufficient to prevent the substitution of chlorine for the remaining hydrogen atom. Without purification, $\alpha$-NpMeSiHCl was then mixed with (−)-menthol in pentane to give a 78% yield of $\alpha$-naphthylmethyl-(−)-menthoxysilane, bp 118° (0.13 mm). $\alpha$-NpMeSi(H)-(−)-OMen was then treated with chlorine to give $\alpha$-naphthylmethyl-(−)-menthoxychlorosilane. Without purification, $\alpha$-NpMeClSi-(−)-OMen was treated with a previously prepared solution of pentafluorophenyllithium at −78° in ether (or tetrahydrofuran) to give a 69% yield of the desired diastereomeric mixture of (±)-$\alpha$-naphthylmethylpentafluorophenyl-(−)-menthoxysilane, bp 160–164° (0.1 mm).



$$\alpha\text{-Np}-\overset{\text{OMen}}{\underset{\text{Cl}}{\text{Si}}}-\text{Me} + \text{Ph}_\text{F}\text{Li} \longrightarrow \alpha\text{-Np}-\overset{\text{OMen}}{\underset{\text{Ph}_\text{F}}{\text{Si}}}-\text{Me} + \text{Me}-\overset{\text{OMen}}{\underset{\text{Ph}_\text{F}}{\text{Si}}}-\alpha\text{-Np}$$

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[1] For the preceding paper in this series, see L. H. Sommer, K. T. Rosborough, and J. McLick, *J. Amer. Chem. Soc.*, **94**, 4217 (1972).

[2] We thank National Science Foundation for vital support of this work.

[3] See M. C. Hays, *J. Inorg. Nucl. Chem.*, **26**, 2306 (1964); J. Dalton, I. Paul, and F. G. A. Stone, *J. Chem. Soc. A*, 1212 (1968); R. R. Schrieke and B. O. West, *Aust. J. Chem.*, **22**, 49 (1969).

[4] L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965.

[5] L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *J. Amer. Chem. Soc.*, **86**, 3271 (1964).

[6] L. H. Sommer, K. W. Michael, and W. D. Korte, *ibid.*, **89**, 868 (1967).

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[9] E. Nield, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 166 (1959).

[10] R. J. Harper, Jr., E. J. Soloski, and C. Tamborski, *J. Org. Chem.*, **29**, 2385 (1964).

[11] P. L. Coe, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 3227 (1962).

[12] For a recent paper containing pertinent earlier references, see A. J. Oliver and W. A. G. Grahm, *J. Organometal. Chem.*, **19**, 17 (1969).

When this very viscous oil was dissolved in hexane and chilled at −5°, a white, crystalline material, identified as (+)-α-NpPh$_F$MeSi-(−)-OMen (the higher melting diastereomer), was deposited on the sides of the flask, mp 93–95°, [α]D −11° (*c* 1.6, pentane). If one assumes that the two diastereomers were formed in equal amounts, only 30–40% of the above diastereomer can be cleanly separated from the diastereomeric mixture. After removal of the above crystalline diastereomer and some hexane from the flask, further crystallization from the chilled hexane solution usually results in a mixture of diastereomers. Because crystals of the higher melting diastereomer are distinctly harder and different in appearance than the lower melting diastereomer, they can be physically separated and recrystallized. By such a process, (−)-α-NpPh$_F$MeSi-(−)-OMen (the lower melting diastereomer) was purified, mp 80–81°, [α]D −75° (*c* 2.0, pentane). With a great deal of patience, substantial quantities of both diastereomers can be isolated and recrystallized in this fashion.

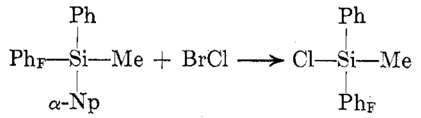
Recently it was shown that (−)-α-NpPhMeSi-(−)-OMen can be reduced with diisobutylalane in good yields in hexane and ether, at room temperature, in 2 and 14 hr, respectively.[13] Similarly, reduction of (+)-α-NpPh$_F$MeSi-(−)-OMen with diisobutylalane in hexane at 46° for 19 hr gave (+)-α-naphthylpentafluorophenylmethylsilane, (+)-α-NpPh$_F$MeSi*H, in 88% yield, mp 73.5–74°, [α]D +40° (*c* 0.88, pentane).

It is probable that the enantiomers of α-NpPh$_F$MeSi*H form a racemic mixture (not a racemic compound), since the melting point of racemic α-NpPh$_F$MeSi*H (mp 54–55°) is raised by the addition of either enantiomer, and since both enantiomers of α-NpPh$_F$MeSi*H of low optical purity can be recrystallized up to high optical purity. The enantiomers of α-NpPhMeSi*H behave similarly.

We turn now to the synthesis and resolution of phenylmethylpentafluorophenylsilane, PhMePh$_F$Si*H. A previously prepared solution of pentafluorophenyllithium in ether was mixed with α-NpPhMeSi*Cl, [α]D −6.3°, to give (after fractional distillation) a 74% yield of extremely viscous α-naphthylphenylmethylpentafluorophenylsilane, bp 175–178° (0.15 mm), [α]D +8.2° (*c* 1.6, pentane).

The cleavage of the naphthyl group from α-NpPhMeSi*Ph$_F$ proved to be the most difficult part of the synthesis of PhMePh$_F$Si*H, and was the prime factor in preventing more extensive stereochemical studies on this system. Although bromine in benzene has been successfully used in the cleavage of the naphthyl group from α-NpPhMeSi*-neo-$C_5H_{11}$ and α-NpPhMeSi*Et,[6] no optically active PhMePh$_F$Si*H (after reduction of the halosilane formed) could be obtained by this procedure. Cleavage attempts with $Br_2$ in carbon tetrachloride and chloroform, and BrCl in benzene and carbon tetrachloride at room temperature and at 0°, give, after reduction, some optically active PhMePh$_F$Si*H, but the yields were disappointingly low (20–30%).

Cleavage of the naphthyl group *was accomplished* by the formation of a BrCl–chloroform solution at −78°, followed by addition of α-NpPhMeSiPh$_F$. A vigorous, exothermic reaction indicated that cleavage was occurring. However, the presence of $Br_2$ in equilibrium with the reagent BrCl possibly results in some formation of bromosilane.



$$\mathrm{Ph_F{-}\overset{\displaystyle Ph}{\underset{\displaystyle \alpha\text{-}Np}{Si}}{-}Me + BrCl \longrightarrow Cl{-}\overset{\displaystyle Ph}{\underset{\displaystyle Ph_F}{Si}}{-}Me}$$

The halosilane was not isolated but was promptly reduced with $LiAlH_4$ at room temperature.

Purification of the silane gave a 53% yield of phenylmethylpentafluorophenylsilane, (+)-PhMePh$_F$Si*H, [α]D + 3.2 (*c* 5.31, pentane), bp 75–79° (0.3 mm). PhMePh$_F$Si*H can be obtained with a specific rotation as high as +4.3° at the sacrifice of reasonable yields.

## Experimental Section

**α-Naphthylmethyldimethoxysilane.**—A Grignard reagent was prepared from 3.3 mol of α-bromonaphthalene and 4.5 g-atoms of magnesium chips in a solvent mixture containing ether (300 ml), tetrahydrofuran (100 ml), and benzene (200 ml).

The Grignard reagent was then added to 3 mol of methyltrimethoxysilane (supplied by Dow Corning Corp.) which was dissolved in ether (250 ml) and tetrahydrofuran (250 ml). Stirring overnight at room temperature was followed by extraction of the organic layer with pentane (3 l.), filtration to remove suspended salts, and subsequent removal of solvents. Distillation gave 461 g (68% yield) of α-naphthylmethyldimethoxysilane, bp 118–119° (1.0 mm).

*Anal.* Calcd for $SiC_{13}H_{16}O_2$: C, 67.20; H, 6.94. Found: C, 67.45; H, 6.80.

The infrared spectrum has all the characteristic absorbances of the $CH_3OSi$, α-$C_{10}H_7Si$, and $CH_3Si$ moieties.

**α-Naphthylmethylsilane.**—To a solution of lithium aluminum hydride (2.2 mol) and ether (500 ml) was added α-naphthylmethyldimethoxysilane (2 mol) in an ether solvent (500 ml). Refluxing for 20 hr was followed by treatment with concentrated hydrochloric acid and pentane at 0°, washing with water, drying the organic phase (sodium sulfate), and subsequent removal of the solvent. Distillation gave 303 g (88% yield) of α-naphthylmethylsilane, bp 77–79° (0.35 mm).

*Anal.* Calcd for $SiC_{11}H_{12}$: C, 76.68; H, 7.02. Found: C, 76.38; H, 6.92.

The infrared spectrum provided positive proof of structure, since it showed absorption bands characteristic of the α-NpMeSi– group as well as the strong band at 2130 cm$^{-1}$ characteristic of the Si–H stretch.

**α-Naphthylmethyl-(−)-menthoxysilane.**—A solution of carbon tetrachloride (600 ml) and 1.76 mol of α-naphthylmethylsilane maintained at 0° was treated with chlorine gas until the solution was distinctly yellow. Nitrogen was then used to purge the reaction mixture of excess hydrogen chloride and chlorine gas until the solution became colorless. Removal of the solvent under reduced pressure yielded α-naphthylmethylchlorosilane. The chlorosilane is characterized by its infrared spectrum, exhibiting all the characteristics of the α-NpMe(H)Si– group and in addition containing an absorbance at 505 cm$^{-1}$ (s) characteristic of Cl–Si. Without further purification, a solution of 1.7 mol of α-naphthylmethylchlorosilane and pentane (700 ml) was added to a filter flask fitted with an addition funnel and gas inlet tube. A solution of pentane (500 ml) and 1.9 mol of (−)-menthol was then slowly added to the stirred chlorosilane–pentane solution while a continuous stream of nitrogen was bubbled through the reaction mixture to remove the hydrogen chloride which had formed. After the addition, the reaction mixture was warmed to room temperature, stirred for 0.5 hr with continuous nitrogen purging, concentrated, and distilled to give 432 g (78% yield) of α-naphthylmethyl-(−)-menthoxysilane, bp 118° (0.13 mm).

*Anal.* Calcd for $SiC_{21}H_{30}O$: C, 77.24; H, 9.26. Found: C, 77.36; H, 9.37.

The infrared spectrum is consistent with the presence of the α-NpMe(H)Si– group, and in addition contains the following absorption bands attributed to the $C_{10}H_{19}OSi$ moiety: 2930 (s), 2870 (s), 1460 (m), 1370 (m), 1180 (w), 1085 (s), 1070 (s), 1055 (s), 1000 (m), 930 (m), 855 cm$^{-1}$ (m).[4]

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(13) Unpublished results of L. H. Sommer and J. McLick.

**Preparation of Diastereomeric α-Naphthylmethylpentafluorophenyl-(−)-menthoxysilane.**—A solution of carbon tetrachloride (400 ml) and 0.46 mol of α-naphthylmethyl-(−)-menthoxysilane was treated with chlorine gas by the same procedure used to chlorinate α-naphthylmethylsilane. Disappearance of the strong infrared absorbance at 2120 cm$^{-1}$ (SiH) and appearance of the peak at 505 cm$^{-1}$ verified formation of α-naphthylmethyl-(−)-menthoxychlorosilane.

Pentafluorophenyllithium (0.5 mol in tetrahydroduran) was then prepared by the procedure of Harper, Soloski, and Tamborski. While the pentafluorophenyllithium solution was maintained at −75°, a solution of α-naphthylmethyl-(−)-menthoxychlorosilane (0.45 mol) and tetrahydrofuran (200 ml) was added over a 1-hr period and then warmed to room temperature over a 16-hr period.

The majority of the solvent was then removed under reduced pressure and the reaction mixture was treated with concentrated hydrochloric acid and pentane at 0°, washed with water, dried (sodium sulfate), and concentrated. Distillation of the diasteromeric mixture gave 90 g (39% yield) of an extremely viscous, clear pale yellow fraction, bp 155–160° (0.1 mm), and 70 g (30% yield) of a second fraction, bp 160–164° (0.1 mm), which was clear and colorless.

The infrared spectrum of each fraction is the same and contains the absorption bands attributed to the α-naphthylmethyl-(−)-menthoxysilyl group, and in addition contains the following bands attributed to the $C_6F_5Si$ moiety: 1645 (s), 1520 (s), 1470 (vs), 1380 (s), 1292 (s), 1140 (w), 1098 (s), 1030 (m), 977 cm$^{-1}$ (s).

**Crystallization of (+)-α-Naphthylmethylpentafluorophenyl-(−)-menthoxysilane, the Higher Melting Diastereomer.**—Separation of the mixed diastereomers was achieved with fractions 1 and 2 described in the distillation above. For simplification, however, the separation procedure will be described only for fraction 2. The clear, colorless, viscous liquid of fraction 2 was diluted to approximately twice its volume with purified *n*-hexane, and chilled in a cold room (−5°). After 24 hr, 14.5 g (mp 88–90°) of a hard, flat, rectangular crystalline material was obtained from the flask. Recrystallization of this material at at −5° to a constant melting point, in twice its volume of pentane, gave 9.8 g of (+)-α-naphthylmethylpentafluorophenyl-(−)-menthoxysilane, mp 93–95°, $[\alpha]_D$ −11° (*c* 1.6, pentane).

*Anal.* Calcd for $SiC_{27}H_{29}F_5O$: C, 65.83; H, 5.93. Found: C, 65.82; H, 5.98.

**Crystallization of (−)-α-Naphthylmethylpentafluorophenyl-(−)-menthoxysilane, the Lower Melting Diastereomer.**—The volume of fraction 2, now enriched in the (−)-α-naphthylmethylpentafluorophenyl-(−)-menthoxysilane (*vide supra*), was reduced in volume by 30 ml of the steam bath and again placed in the cold room (−5°). After several days, 11 g (mp 65–85°) of white solid was removed from the flask. After it was dried under reduced pressure, close examination of the solid revealed two different crystalline layers. The upper layer, deposited in the flask, consisted of soft, small, needlelike crystals, which were very dissimilar to the crystals previously isolated. The lower layer (permeated in spots by the layer above) was hard and resembled (+)-α-naphthylmethylpentafluorophenyl-(−)-menthoxysilane. With a spatula, the soft crystals were scraped from the hard crystals, giving 5.4 g (mp 71–75°) and leaving 5.6 g (mp 91–93°) of the hard crystalline diastereomer. Subsequent recrystallization of the soft, lower-melting diastereomer at 4°, in twice its volume of hexane, gave 1 g of the needle crystals of (−)-α-naphthylmethylpentafluorophenyl-(−)-menthoxysilane (mp 80–81°), $[\alpha]_D$ −75° (*c* 2.0, pentane).

*Anal.* Calcd for $SiC_{27}H_{29}F_5O$: C, 65.83; H, 5.93. Found: C, 65.70; H, 6.01.

The subsequent crystallization from the flask containing the remaining 46 g of mixed diastereomer gave 14 g of a soft, white, flocculent solid, which was literally poured onto a large filter paper fitted over a watch glass, and air dried (mp 71–74°). Several recrystallizations with at least 80% loss of solid diastereomer to the various mother liquors gave crystalline (−)-α-naphthylpentafluorophenyl-(−)-menthoxysilane (mp 80–81°).

**Diisobutylalane Reduction of the Diastereomeric (+)-α-Naphthylmethylpentafluorophenyl-(−)-menthoxysilane.**—A solution of purified hexane (180 ml) and 29 g (59 mmol) of (+)-α-naphthylmethylpentafluorophenyl-(−)-menthoxysilane, $[\alpha]_D$ −11° (*c* 2.3, pentane), was placed in a 500-ml, three-necked flask equipped with a dropping funnel and condenser. Diisobutylalane, 33.3 ml (180 mmol), was syringed into 80 ml of purified hexane and then poured into the addition funnel. The diisobutylalane–hexane solution was added slowly over a 15-min period, under an inert atmosphere, to the stirred (+)-α-naphthylmethylpentafluorophenyl-(−)-menthoxysilane. During the addition, the flask temperature increased from 28 to 32°. After the addition was completed, the flask was heated to 47° and maintained at that temperature for 19 hr. When the reaction mixture had cooled down, it was cautiously added to a 2-l. separatory funnel and washed in ice water, concentrated hydrochloric acid (30 ml), and pentane (500 ml). After the aqueous layer was discarded, a second washing with concentrated hydrochloric acid was necessary to remove the remaining suspended aluminum salts from the organic layer. Following the second washing with acid, the organic phase was washed four times with distilled water, dried over sodium sulfate, and partially concentrated on the steam bath. The remaining organic layer was transferred to a sublimator, where heating for 5 hr at 80° (0.3 mm) removed the remaining volatile solvent by distillation and 7.4 g (80%) of the (−)-menthol by sublimation.

After cooling to room temperature the remaining solid (+)-α-naphthylmethylpentafluorophenylsilane–menthol mix was removed from the sublimator, dissolved in pentane (60 ml), and poured onto a wet (pentane) 1.8 × 46 cm column of silica gel. Elution with 650 ml of 30% benzene (by volume) in pentane gave 17.6 g (88%) of (+)-α-naphthylmethylpentafluorophenylsilane (mp 54–64°). Repeated crystallizations to a constant melting point gave 13.2 g of α-naphthylmethylpentafluorophenylsilane (mp 73.5–74°), $[\alpha]_D$ +40° (*c* 0.88, pentane).

*Anal.* Calcd for $SiC_{17}H_{11}F_5$: C, 60.34; H, 3.28. Found: C, 60.04; H, 3.49.

The infrared spectrum contains the absorbance bands attributed to α-$C_{10}H_7Si$, $C_6F_5Si$, and $CH_3Si$, and in addition contains a band at 2190 cm$^{-1}$ attributed to the Si–H moiety.

**Preparation of α-Naphthylphenylmethylpentafluorophenylsilane.**—A solution of ether (100 ml) and 0.2 mol of α-NpPhMeSi*Cl, $[\alpha]_D$ −6.3° (*c* 4.5, pentane),[4] was added to a chilled (−78°) solution of pentafluorophenyllithium (0.2 mol in ether) over a 2-hr period. While being continuously stirred, the reaction mixture was allowed to warm to room temperature overnight, and was then treated with concentrated hydrochloric acid and pentane at 0°, washed with water, dried (sodium sulfate), and concentrated. Distillation gave 50 g (74% yield) of an extremely viscous, colorless liquid, characterized as (+)-α-naphthylphenylmethylpentafluorophenylsilane (α-NpPhMeSi*-$Ph_F$), bp 175–178° (0.15 mm), $[\alpha]_D$ +8.2° (*c* 1.6, pentane).

The infrared spectrum is completely consistent with the structural assignment.

**Preparation of Phenylmethylpentafluorophenylsilane.**—A solution of 0.075 mol of (+)-α-NpPhMeSi*$Ph_F$, $[\alpha]_D$ +8.2° (*c* 1.40, pentane), and chloroform (25 ml) was added rapidly to a solution of chloroform (15 ml) and 0.08 mol of BrCl (prepared from 0.04 mol of $Br_2$ and 0.04 mol of $Cl_2$) maintained at −60°. The immediate ensuing exothermic reaction caused the reaction mixture to warm up to room temperature. The mixture was stirred for 30 min and then syringed from the reaction flask into a flask containing ether (150 ml) and lithium aluminum hydride (0.600 equiv) chilled to 0°.

Stirring the hydride solution at room temperature for 15 min, was followed by treatment with aqueous 10% HCl and pentane at 0°, washing with water, drying (sodium sulfate), and subsequent removal of the solvents. Distillation gave 11.4 g (53% yield) of (+)-phenylmethylpentafluorophenylsilane (PhMe-$Ph_F$Si*H), bp 75–79° (0.3 mm), $[\alpha]_D$ +3.2° (*c* 5.31, pentane). (A specific rotation of 4.3° for PhMe$Ph_F$Si*H was obtained by a procedure which gave significantly lower yields.)

*Anal.* Calcd for $SiC_{13}H_9F_5$: C, 54.16; H, 3.15. Found: C, 54.02; H, 3.31.

The infrared spectrum is completely consistent with the above structure and contains ir maxima ($C_6H_5Si$) at 1430, 1120, 700 cm$^{-1}$; $CH_3Si$ at 1265 cm$^{-1}$; $C_6F_5Si$, same as for α-NpMe$Ph_F$Si-(−)-OMen; SiH at 2180 cm$^{-1}$.

**Registry No.**—α-Naphthylmethyldimethoxysilane, 37787-14-7; α-bromonaphthalene, 90-11-9; methyltrimethoxysilane, 1185-55-3; α-naphthylmethylsilane, 37787-15-8; α-naphthylmethylchlorosilane, 17998-65-1; (−)-menthol, 2216-51-5; α-naphthylmethyl-(−)-menthoxysilane, 37787-17-0; α-naphthylmethylpentafluorophenyl-(−)-menthoxysilane, 37787-18-1; pentafluoro-

phenyllithium, 1076-44-4; α-naphthylmethyl-(−)-menthoxychlorosilane, 37787-19-2; (+)-α-naphthylmethylpentafluorophenyl-(−)-menthoxysilane, 37787-20-5; (−)-α-naphthylmethylpentafluorophenyl-(−)-menthoxysilane, 37787-21-6; (+)-α-naphthylmethylpentafluorophenylsilane, 36411-23-1; (+)-α-naphthylphenylmethylpentafluorophenylsilane, 37781-10-5; (+)-phenylmethylpentafluorophenylsilane, 36358-49-3.

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# Photochemistry of 2-Acetylbenzonorbornenes

Ronald R. Sauers* and Anneli Mirja De Paolis

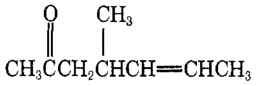
*School of Chemistry, Rutgers University, New Brunswick, New Jersey 08903*

*Received July 12, 1972*

The synthesis and photochemistry of *exo*- and *endo*-2-acetylbenzonorbornenes (**8** and **9**) is described. The exo isomer yields benzonorbornene upon irradiation at 310 nm, conditions under which the endo isomer is inert.

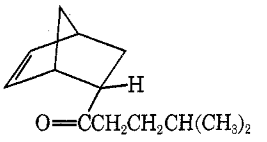
The presence of proximate n electrons is known to significantly modify the reactivity of photoexcited carbonyl groups. Examples include reactions of amino ketones,[1,2] alkoxy ketones,[3] and thiaketones.[4] In one of these studies,[2] the magnitude of the effect was shown to be a function of the distance between the interacting centers.

Similarly, the presence of π electrons can modify the excited-state behavior of ketones. Thus, neither ketone **4** or **5** undergoes appreciable type II photoelimination.[4,5] Rapid exciplex formation between the carbonyl singlet state and the double bond has been postulated to rationalize the diminished reactivities. In a related study, Cowan and Baum[6] have shown that intramolecular energy transfer was the principal mode of deactivation of the carbonyl triplets in systems **6a–c**.

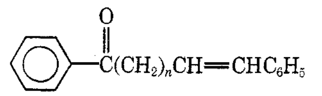


$CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{CH_3}{\overset{|}{C}}HCH{=}CHCH_3$

**4**

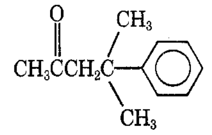


**5**



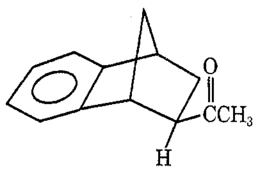
**6a**, $n = 2$
**b**, $n = 3$
**c**, $n = 4$

Lastly, several groups[7,8] have recently reported on the diminished reactivity of certain α- and β-phenyl ketones toward photoreduction and/or type II eliminations. Thus, ketone **7** undergoes photoelimination with unusually low efficiency, $\Phi = 0.02$.[8]

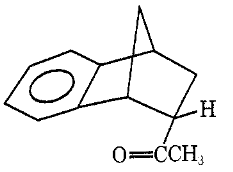


**7**

The foregoing results may be summarized with the statement that the presence of electrons in n or π orbitals significantly shortens the excited state lifetimes of nearby carbonyl groups. Although varied mechanisms may prevail, a common feature would appear to require significant overlap of the orbitals on the two interacting groups. In view of the fact that this orientational factor has not been tested, we wished to investigate the behavior of rigid analogs of **7** in which the relative positions of the two functions were more restricted. To this end, we synthesized *exo*- and *endo*-2-acetylbenzonorbornenes (**8** and **9**, respectively), and initiated photochemical studies which were designed to evaluate their relative excited state lifetimes.

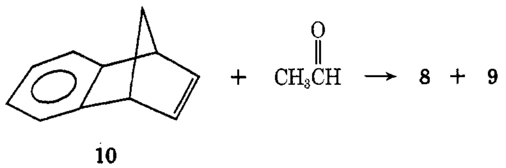


**8**



**9**

**Syntheses.**—A mixture of **8** and **9** was produced by the addition of acetaldehyde to benzonorbornadiene (**10**) as catalyzed by azobisisobutyronitrile.[9] By



**10**

analogy with norbornene,[9] it was assumed that the major product (*ca.* 90%) was the exo isomer and this supposition was supported by spectral evidence presented below. For example, the chemical shifts of the methyl protons in the two isomers were found in the expected relative positions (δ 2.15 and 1.87 for **8** and **9**, respectively) if it is assumed that the

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