Carbonium Ion–Silane Hydride Transfer Reactions.
V. *tert*-Alkyl Cations

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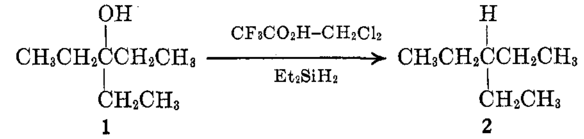
A number of *tert*-alkyl cations have been generated from alcohol or alkene precursors in methylene chloride-trifluoroacetic acid and their reactivity toward intermolecular hydride-transfer reactions with organosilicon hydride donors has been studied. In some cases this reaction could be synthetically useful: 3-methyl-5α-cholest-2-ene was converted to 3β-methyl-5α-cholestane, 3-ethyl-3-pentanol to 3-ethylpentane, and 2-methyl-2-admantanol to 2-methyladamantane. Rearrangements occurred faster than hydride transfer in the conversion of *cis,cis,trans*-perhydro-9b-phenalenol to *trans,trans,trans*-perhydrophenalene and the formation of an unidentified hydrocarbon from cholest-5-ene. The 9-decalyl cation yielded a decalin mixture in which the cis/trans ratio was 3:2.

Organosilicon hydrides have been shown to be quite reactive in intermolecular hydride transfer to carbonium ions. Stable carbonium ions of the arylmethyl type,[1,2] tropylium cation,[3] and ferrocenylmethyl cations[4] are all converted rapidly and in high yield to the corresponding hydrocarbons. Cyclopropylmethyl cations which form readily but rapidly undergo ring-opening reactions are converted to cyclopropylmethanes at rates competitive with and, in many cases, exceeding the rate of ring opening.[5] In a reaction which is potentially useful synthetically, Kursanov has reported that *tert*-alkyl cations generated by protonation of olefins also abstract hydride from organosilicon hydrides.[6] In order to explore these synthetic possibilities, we have examined a number of *tert*-alkyl cations as hydride acceptors. Our approach was not one of a thorough investigation of many representative *tert*-alkyl cations but rather that of choosing selected compounds of more general interest in which the information gained would be more useful than simply a report of yield data on structurally similar compounds.

Results

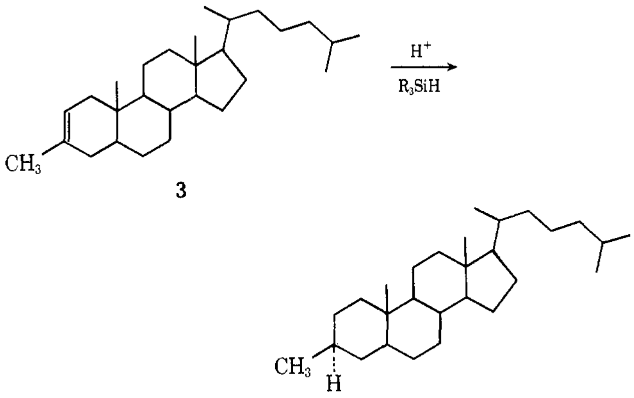
3-Ethyl-3-pentyl Cation.—Suitable experimental conditions for carrying out the hydride transfer reactions were determined using 3-ethyl-3-pentanol (1) and measuring its conversion to 3-ethylpentane (2) by gas chromatography. Using diethylsilane as the hydride donor in methylene chloride at 25° and trifluoroacetic acid as the proton source (0.5 *M*), conversion to 2 was complete to the extent of only about 19% in 0.5 hr. Increasing the trifluoroacetic acid concentration to 6 *M* in methylene chloride and the reaction time to 24 hr brought about the complete conversion of 1 to 2. It was determined by gas chromatography that 1 is not stable under these reaction conditions and is rapidly converted to 3-ethyl-2-pentene which is the actual species undergoing reaction. The experimental conditions can be varied within rather wide limits since in a reaction carried out on a preparative scale using triphenylsilane as the donor and a trifluoroacetic acid concentration of 1.5 *M* pure 2 was isolated in 78% yield.[7]



$$CH_3CH_2C(OH)(CH_2CH_3)CH_2CH_3 \xrightarrow[Et_2SiH_2]{CF_3CO_2H-CH_2Cl_2} CH_3CH_2CH(CH_2CH_3)CH_2CH_3$$

1 2

3-Methyl-3-cholestanyl Cation.—Reduction of 3-methyl-5α-cholest-2-ene (3) by the two-step protonation–hydride transfer sequence was examined as a synthetic alternative to catalytic hydrogenation, as well as to observe the stereoselectivity of hydride transfer. Using triphenylsilane as the donor, the product was 3β-methyl-5α-cholestane (4) in 66% yield of purified product. This is the equatorial methyl epimer and is also the product of catalytic hydrogenation.[8]



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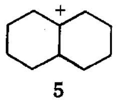
9-Decalyl Cation (5).—Examination of the stereoselectivity associated with hydride transfer to the 9-decalyl cation (5) was undertaken in view of the recent interest in tertiary carbonium ions at bridgeheads in condensed ring systems.[9] The stereoselectivity of capture of 5 by a number of reagents has been reported and



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

[2] T. A. Serebryakova, Z. N. Parnes, A. V. Zakharychev, S. N. Anachenko, and I. V. Tergov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 662 (1969).

[3] Z. N. Parnes, M. E. Volpin, and D. N. Kursanov, *Tetrahedron Lett.*, No. 21, 20 (1960).

[4] H. S. Tremper, Ph.D. Thesis, University of Virginia, 1969.

[5] F. A. Carey and H. S. Tremper, *J. Amer. Chem. Soc.*, **91**, 2967 (1969); Z. N. Parnes, G. A. Khotimskaya, M. Y. Lukina, and D. N. Kursanov, *Proc. Acad. Sci. USSR, Chem. Sect.*, **178**, 88 (1968).

[6] D. N. Kursanov, Z. N. Parnes, G. I. Bassova, N. M. Loim, and V. I. Zdanovich, *Tetrahedron*, **23**, 2235 (1967); D. N. Kursanov and Z. N. Parnes, *Russ. Chem. Rev.*, **10**, 812 (1969).

[7] For a study on the reactivity of various organosilicon hydrides as donors, see F. A. Carey and C. W. Hsu, *J. Organometal. Chem.*, **19**, 29 (1969).

[8] D. H. R. Barton, A. da S. Campos-Neves, and R. C. Cookson, *J. Chem. Soc.*, 3500 (1956).

[9] A review of the literature through 1965 may be found in the chapter by R. C. Fort, Jr., and P. v. R. Schleyer, *Adv. Alicyclic Chem.*, **1**, 283 (1966); R. C. Fort, Jr., and R. E. Hornish, *Chem. Commun.*, 11 (1969); A. F. Boschung, M. Geisel, and C. A. Grob, *Tetrahedron Lett.*, 5169 (1968).

found to be variable. Kinetically controlled carbonylation of **5** gives a mixture of *cis*-decalin-9-carboxylic acid (**6**) and *trans*-decalin-9-carboxylic acid (**7**) in ratio of 1:9. When carried out under conditions of thermodynamic control, the ratio of **6**:**7** is reversed.[10]

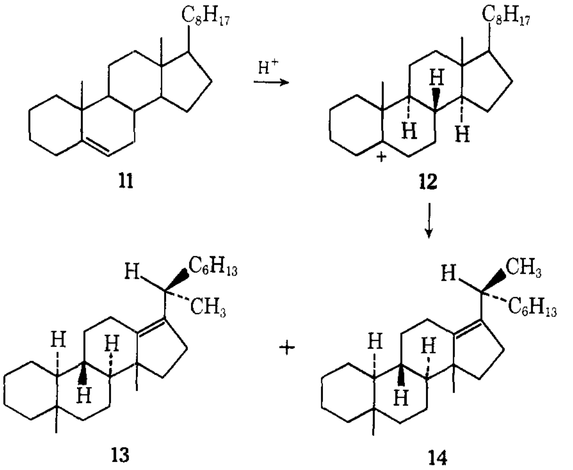
Addition of hydrogen chloride to $\Delta^{9,10}$-octalin (**8**) under conditions of kinetic control affords approximately equal amounts of *cis*- and *trans*-9-chlorodecalin (54% cis:46% trans).[11]

Hill and Carlson[12] have reported that hydride transfer to **5** from carbon donors gives mixtures of *cis*-decalin (**9**) and *trans*-decalin (**10**) in which the cis/trans ratio ranges from 4.5 to 6.5. This reaction is clearly kinetically controlled and the results were rationalized by proposing delivery of hydride to the less hindered face of the carbonium ion.

We have generated **5** by protonation of an octalin mixture containing 92% **8** and 8% the $\Delta^{1,9}$ isomer in methylene chloride–trifluoroacetic acid at 25° in the presence of triphenylsilane and determined the composition of decalins by gas chromatography. The ratio of **9** to **10** was substantially different from that observed for hydride transfer from carbon donors in that decalin composition was 61–64% cis:36–39% trans for three runs.

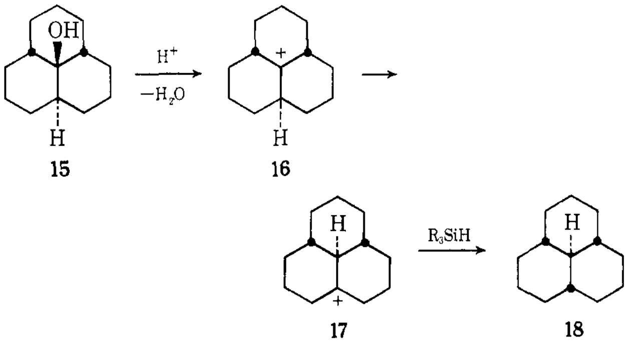
5-Cholestanyl Cation (12).—The steroidal olefin cholest-5-ene (**11**) was chosen as a model compound to investigate the effect of an angular methyl group in influencing the stereochemistry of attack in decalyl cations. Hydride transfer to carbonium ion **12** from the α face would yield 5α-cholestane while hydride transfer from the β face would yield 5β-cholestane.

When the reaction of **11** with either triethylsilane or triphenylsilane was carried out under the usual conditions it was found that the product was an uncrystallizable syrup, the nmr of which clearly indicated that it was neither 5α-cholestane nor 5β-cholestane. The parent peak in the mass spectrum of the product appeared at *m/e* 372 and thus corresponds to the addition of a proton and a hydride to the double bond. Intense peaks were also observed at *m/e* 259, 257, and 217 and were comparable in peak height to that of the molecular ion and were the most intense peaks in the mass spectrum. By way of comparison the most intense peak in the mass spectrum of cholestane is *m/e* 217. The failure to obtain either 5α- or 5β-cholestane can be attributed to the slowness of hydride transfer relative to the rate at which **12** undergoes the backbone rearrangement to **13** and **14**.[13]

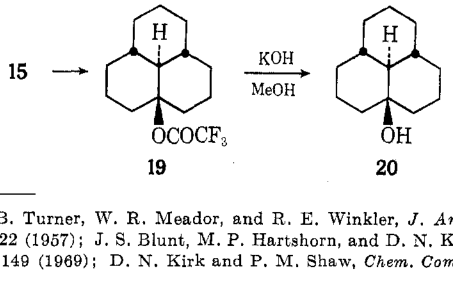


The product obtained is therefore formulated as a mixture of diastereomers derived from protonation of **13** and **14** followed by hydride transfer.[14] This experiment points out a serious limitation to the use of this reaction for synthetic purposes in that skeletal rearrangements may be faster than intermolecular hydride transfer.

Carbonium Ions Derived from *cis,cis,trans*-Perhydro-9b-phenalenol[15] **(15)**.—The *cis,cis,trans*-tercyclanol (**15**)[16] was converted in high yield and stereoselectively to *trans,trans,trans*-perhydrophenalene (**18**)[17] when allowed to react with either triethylsilane or triphenylsilane in methylene chloride–trifluoroacetic acid. The sequence of intermediates is believed to be as shown on the basis of this experiment and reactions carried out in the absence of hydride donors.



By monitoring the reaction of **15** with triethylsilane by gas chromatography, it was found that formation of **18** was relatively slow and that **15** was rapidly converted to another substance which decreased as **18** increased. This intermediate was identified as **19** by allowing **15** to react with a solution of trifluoracetic acid in methylene chloride for 30 min, quenching the reaction mixture, and cleaving the crude product which exhibited trifluoroacetate ester absorbance in the infrared with potassium hydroxide in methanol. The product obtained in 72% yield was identified as **20** by comparing its ir and melting point with those of authentic material.



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[10] R. E. Pincock, E. Grigat, and P. D. Bartlett, *J. Amer. Chem. Soc.*, **81**, 6332 (1959); P. D. Bartlett, R. E. Pincock, J. H. Rolston, W. G. Schindel, and L. A. Singer, *ibid.*, **87**, 2590 (1965); H. Christol and G. Solladie, *Bull. Soc. Chim. Fr.*, 1307 (1966).

[11] F. D. Greene and N. N. Lowry, *J. Org. Chem.*, **32**, 875 (1967).

[12] R. M. Carlson and R. K. Hill, *ibid.*, **34**, 4178 (1969).

[13] R. B. Turner, W. R. Meador, and R. E. Winkler, *J. Amer. Chem. Soc.*, **79**, 4122 (1957); J. S. Blunt, M. P. Hartshorn, and D. N. Kirk, *Tetrahedron*, **25**, 149 (1969); D. N. Kirk and P. M. Shaw, *Chem. Commun.*, 806 (1970).

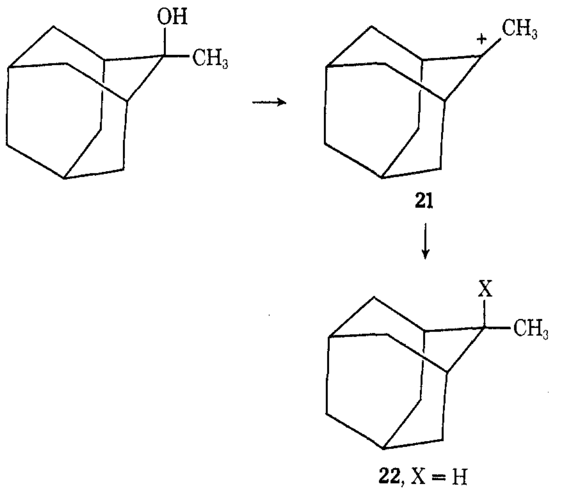
[14] Experiments carried out by Mr. D. S. Watt using a more reactive hydride donor (Et_2SiH_2) at −10° did not alter the product composition.

[15] We wish to acknowledge the invaluable assistance of Dr. W. C. Dickason and Professor H. C. Brown in this study. Dr. Dickason generously provided samples of **15** and **18** and copies of ir spectra as well as many timely and helpful suggestions.

[16] H. C. Brown and E. Negishi, *J. Amer. Chem. Soc.*, **89**, 5478 (1967); H. C. Brown and W. C. Dickason, *ibid.*, **91**, 1226 (1969).

[17] A. Schneider, R. W. Warren, and E. J. Janoski, *J. Org. Chem.*, **31**, 1617 (1966); *J. Amer. Chem. Soc.*, **86**, 5365 (1964).

2-Methyl-2-adamantyl Cation (21).—Recent interest has developed in 2-adamantyl cations as examples of carbonium ions which are formed with little, if any, solvent participation during the ionization process.[18] Ion **21** also has been reported to be converted to the 2-methyl-1-adamantyl cation in 95% sulfuric acid and so would provide further information as to the relative rates of hydride transfer and isomerization.[19] It was found by an nmr experiment that **21** was not converted to the 2-methyl-1-adamantyl cation under conditions (2.5 *M* trifluoroacetic acid in $CDCl_3$) where efficient hydride transfer takes place. In addition, the use of triphenyldeuteriosilane afforded **23** as evidenced by the fact that the methyl signal which appears as a doublet ($J = 7$ Hz) in **22** was a broadened singlet (triplet, $J = 1$ Hz on scale expansion) due to the smaller magnitude of the coupling constant to deuterium. These small-scale experiments performed in nmr tubes clearly showed the conversion to **22** and **23** to be quantitative. When the hydride transfer was carried out on a preparative scale using triethylsilane as the donor, **22** could be isolated in a yield of only 41%. The problems here appeared to be manipulative rather than inefficiency of reaction, since **22** is rather volatile and difficult to recrystallize without significant loss.



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22, X = H
23, X = D

Discussion

The carbonium ion to alkane conversions described here serve as examples of the synthetic possibilities of intermolecular hydride transfer reactions by extending the observations of Kursanov[6] to conditions of decreased acidity and also illustrate the present deficiencies of the reaction in that rearrangements often occur faster than hydride transfer. In favorable cases the reaction of a tertiary alcohol with an organosilicon hydride in 2.5–6 *M* trifluoroacetic acid in methylene chloride constitutes an excellent means of effecting the reduction of an alcohol to a hydrocarbon. Reduction of olefins capable of generating tertiary carbonium ions under these conditions offers the novel feature of allowing the introduction of protium at one end of the double bond and deuterium at the other through use of the appropriate combinations of CF_3CO_2H, CF_3CO_2D, R_3SiH, and R_3SiD.

The relatively direct approach allowing alcohols and organosilicon hydrides to react in trifluoroacetic acid media appears to be limited to reduction of those alcohols which can form carbonium ions at least as stable as tertiary.

Experimental Section

Nmr spectra were recorded on a Hitachi Perkin-Elmer R-20 spectrometer in $CDCl_3$, and chemical shifts are reported in ppm (δ) 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 used was a Varian Aerograph 90-P unit equipped with a Disc integrator. The mass spectra were obtained using a Hitachi Perkin-Elmer RMU-6E mass spectrometer at an ionizing potential of 70 eV.

Reduction of 3-Ethyl-3-pentanol.—To a solution of 2.0 g (17.4 mmol) of 3-ethyl-3-pentanol and 5.36 g (20.6 mmol) of triphenylsilane in 68 ml of methylene chloride was added 11.76 g (113 mmol) of trifluoroacetic acid. After 24 hr at room temperature solid sodium carbonate was added, the solution filtered, and the solvent removed by distillation. The residue was then chromatographed on 25 g of alumina and eluted with pentane (100 ml) to yield 1.34 g (78%) of 3-ethylpentane. The infrared and nmr spectra of the product matched those of an authentic sample, and analysis by glpc on a 10-ft 20% SE-30 on Chromosorb W column at 100° and 60 cc of helium per minute revealed a single peak having the same retention time as 3-ethylpentane.

Reduction of 3-Methyl-5α-cholest-2-ene (3) by Hydride Transfer.—To a solution containing 150 mg (0.39 mmol) of **3**[8] and 0.5 ml of triethylsilane in 5 ml of methylene chloride was added 1.0 ml of trifluoroacetic acid, and the solution allowed to stand at room temperature for 16 hr. The reaction mixture was then shaken with 20 ml of methylene chloride and 30 ml of saturated sodium bicarbonate solution, and the organic layer was separated and dried over magnesium sulfate. Evaporation of the solvent and recrystallization of the residue from ethanol afforded 99.1 mg (66%) of 3β-methyl-5α-cholestane, mp 90.5–92°, $[\alpha]^{25}\text{D}$ +27.9° ($CHCl_3$). The nmr and ir spectra were identical with those of an authentic sample,[20] mp 99–100°, $[\alpha]^{25}\text{D}$ +23.3°.

Hydride Transfer to 9-Decalyl Cation.—An octalin mixture composed of 92% $\Delta^{9,10}$-octalin and 8% $\Delta^{1,9}$-octalin was prepared from decahydro-2-naphthol by the procedure of Campbell and Harris.[21] Trifluoroacetic acid (0.648 g, 6.0 mmol) was added to 1 ml of methylene chloride containing 0.136 g (1.0 mmol) of the octalin mixture and 1.2 mmol of triphenylsilane. After 24 hr solid sodium carbonate was added, and the solution was analyzed by glpc[22] using a 10-ft 20% Carbowax 20M on Chromosorb W column at 145° and a flow rate of 60 cc of He/min. Conversion of the octalin mixture to decalins was on the order of 90% under these conditions. *cis*- and *trans*-decalin were identified by comparing their retention times (2.9 and 2.2 min, respectively) with those of standard samples. In a typical experiment triphenylsilane yielded a mixture of 32% *trans*-decalin, 57% *cis*-decalin, and 11% octalins.

Attempted Reduction of Cholest-5-ene (11) by Hydride Transfer.—A solution containing 740 mg (2 mmol) of **11**[23] and 598 mg (2.3 mmol) of triphenylsilane in 8 ml of methylene chloride and 2 ml of trifluoroacetic acid was allowed to stand 50 hr at room temperature. Methylene chloride (30 ml) was added and the solution was extracted with three 30-ml portions of sodium bicarbonate. The organic phase was dried over magnesium sulfate, concentrated, and chromatographed on 40 g of Woelm silica gel. Elution with pentane (90 ml) and evaporation yielded 667 mg of a clear syrup which resisted all attempts at crystallization. The nmr spectrum of the product was similar to that of a saturated

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[18] J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2538 (1970); J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, **92**, 2540 (1970); J. A. Bone and M. C. Whiting, *Chem. Commun.*, 115 (1970).

[19] M. A. McKervey, J. R. Alford, J. F. McGarrity, and E. J. F. Rea, *Tetrahedron Lett.*, 5165 (1968).

[20] G. Just and V. DiTullie, *Can. J. Chem.*, **42**, 2695 (1964). We are grateful to Professor Just for providing a sample of **4** for comparison.

[21] W. P. Campbell and G. C. Harris, *J. Amer. Chem. Soc.*, **63**, 2721 (1941).

[22] For gas chromatographic data on octalins and decalins, see J. W. Powell and M. C. Whiting, *Tetrahedron*, **12**, 163 (1961).

[23] W. G. Dauben and K. H. Takemura, *J. Amer. Chem. Soc.*, **75**, 6302 (1953).

steroid but was clearly neither 5α- nor 5β-cholestane.[24] The infrared spectrum indicated the absence of any functional groups such as OH or carbonyl. The molecular weight of the material was 372 by mass spectrometry.

Reduction of *cis,cis,trans*-Perhydro-9b-phenalenol (15) by Hydride Transfer.—Alcohol **15** (1.94 g, 10 mmol) was dissolved in 40 ml of methylene chloride along with 2.99 g (11.5 mmol) of triphenylsilane and 7.3 ml (11.2 mg, 100 mmol) of trifluoroacetic acid. After 48 hr the solution was poured in 250 ml of saturated sodium bicarbonate, the layers separated, and the aqueous layer was extracted with 50 ml of methylene chloride. The combined organic extracts were washed with 50 ml of saturated sodium bicarbonate, dried over magnesium sulfate, concentrated, and chromatographed on 40 g of silica gel (Woelm). Elution with 120 ml of pentane yielded 1.63 g (92%) of **18**. The reaction product was identical with respect to ir, nmr, and retention time (10-ft 15% Carbowax on firebrick at 188°) with an authentic sample. Analysis by glpc under these conditions indicated that the product was 90% pure.

Reaction of 15 with Trifluoroacetic Acid.—To 300 mg (1.55 mmol) of **15** in 10 ml of methylene chloride was added 2.5 ml of trifluoroacetic acid, and the solution was allowed to stand 30 min and then poured into 50 ml of saturated sodium bicarbonate solution. The organic layer was dried over magnesium sulfate and evaporated. Previous experiments had indicated that the product at this point was a trifluoroacetate ester which was difficult to purify directly. For identification purposes the product was taken up in 10 ml of methanol containing 1 g of KOH, allowed to stand 48 hr, then quenched with 50 ml of water, and extracted with four 25-ml portions of pentane. The pentane layers were washed twice with 5-ml portions of water, dried ($MgSO_4$), and evaporated to leave 216 mg (72%) of white solid, mp 81–84°. The infrared spectrum was identical with that of *trans,trans,trans*-perhydrophenalen-3a-ol (**20**). A small amount was recrystallized from pentane to yield material melting at 87.5–88.5°.

Conversion of 2-Methyl-2-adamantanol to 2-Methyladamantane (22).—Trifluoroacetic acid (7.3 ml) was added to a solution of 1.66 g (10 mmol) of 2-methyl-2-adamantanol and 2.0 ml of triethylsilane in 40 ml of methylene chloride. The combined extracts were dried over magnesium sulfate and evaporated, and the residue was recrystallized from ethanol–water to afford 613 mg (41%) of **22** as white crystals, mp 144–146° (reported[25] 143.8–146°). The nmr spectrum of the product provided confirmation of the supposed structure in that it exhibited a three-proton doublet (J = 7 Hz) at 1.05 ppm (reported[26] 1.04 ppm).

To check for completeness of the reaction, because of the low yield realized in the preparative experiment and to ensure that no rearrangment of the carbonium ion was occurring under these reaction conditions, 50 mg of 2-methyl-2-adamantanol and 85 mg of Ph_3SiD were dissolved in 0.4 ml of $CDCl_3$ in an nmr tube and 0.075 ml of trifluoroacetic acid was added. After 48 hr at 25° the nmr spectrum of this solution showed that **23** was formed quantitatively. The methyl signal appeared at 1.05 ppm as a broadened singlet which was found to be a triplet on scale expansion due to vicinal coupling of the methyl protons with one deuterium nucleus (J = 1 Hz).

Registry No.—**1**, 597-49-9; **4** (cation), 27390-89-2; **5**, 23373-80-0; **12**, 27390-90-5; **16**, 27390-91-6; **20**, 27390-92-7; **21**, 27411-03-6; diethylsilane, 542-91-6; triphenylsilane, 789-25-3; triethylsilane, 617-86-7.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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[24] 5α-Cholestane was purchased from Applied Science Laboratories, State College, Pa. 5β-Cholestane was obtained from Chemical Procurement Laboratories, College Point, N. Y.

[25] P. v. R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, **83**, 182 (1961).

[26] R. C. Fort, Jr., and P. v. R. Schleyer, *J. Org. Chem.*, **30**, 785 (1965).

Ferrocene Studies. XVIII. Identification and Stereochemistry of Nine Bimolecular Clemmensen Reduction Products of Benzoylferrocene[1a–d]

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In addition to the normal reduction product, benzylferrocene, Clemmensen reduction of benzoylferrocene is shown to give nine bimolecular reduction products: achiral and chiral 1,2-diferrocenyl-1,2-diphenylethanes (**3** and **4**), *trans*-1,2-diferrocenyl-1,2-diphenylethene (**5**), 2,2-diferrocenyl-1,2-diphenylethanone (**6**), 1,2-diferrocenyl-2,2-diphenylethanone (**7**), achiral and chiral 1,2-diferrocenyl-1,2-diphenyl-1,2-ethanediols (**8** and **9**), and achiral and chiral 1,2-diferrocenyl-1,2-diphenylethanols (**10** and **11**). Rigorous stereochemical assignments to the achiral and chiral diastereomers of the ethanes, **3** and **4**, and the diols, **8** and **9**, are based on independent preparations of each pair in the presence of (+)-(*S*)-1-methoxy-2-methylbutane (**12**). These successful procedures of asymmetric selection give an optically active form (chiral) along with an optically inactive partner (achiral) in each case. The olefinic Clemmensen product is shown to consist of only the trans or *E* isomer **5** by its conversion, *via* overall syn addition of hydrogen, to the chiral ethane **4**. Stereochemical assignments to the alcohols, **10** and **11**, are mainly but tentatively based on the relative rates with which these highly unstable compounds undergo fragmentation to benzyl- and benzoylferrocene.

Although the Clemmensen reduction[2] is generally used in the conversion of ketones to $-CH_2-$ groups, bimolecular reduction products are sometimes formed.[3] The present work is concerned with the reduction of benzoylferrocene for which bimolecular products are known to predominate.[4] We have carried out a large

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[1] (a) First part of a subseries concerned with Clemmensen reductions of ferrocenyl ketones. Portions of this work have been presented in preliminary form.[1b–d] (b) 19th Southeastern Regional Meeting of the American Chemical Society, Atlanta, Ga., Nov 1967, Abstracts, p 308. (c) S. I. Goldberg and W. D. Bailey, *J. Amer. Chem. Soc.*, **91**, 5113 (1969). (d) S. I. Goldberg and W. D. Bailey, *J. Chem. Soc. D*, 1059 (1969). (e) A part of the experimental work is from the Ph.D. dissertation of M. L. McGregor, University of South Carolina Graduate School, 1969, and the work contributed by W. D. Bailey is to be included in his Ph.D. dissertation.

[2] E. Clemmensen, *Ber.*, **46**, 1838 (1913).

[3] For accounts of much of this work, see E. L. Martin, *Org. React.*, **1**, 155 (1942); J. H. Brewster, *J. Amer. Chem. Soc.*, **76**, 6361, 6364 (1954); D. Staschewski, *Angew. Chem.*, **71**, 726 (1959); T. Nakabayashi, *J. Amer. Chem. Soc.*, **82**, 3900, 3906, 3909 (1959).

[4] The claim[5] that the unidentified material obtained from Clemmensen reductions of benzoylferrocene (Rausch, Vogel, and Rosenberg[6] and Nesmeyanov and Kritskaya[5]) was 2,2-diferrocenyl-1,2-diphenylethane has been refuted.[7] It is likely that those isolations, as well as the unidentified material reported by Weliky and Gould,[8] consisted of various combinations of the bimolecular products incompletely accounted for earlier[1b,9] but more fully recognized in the present work.

[5] A. N. Nesmeyanov and I. I. Kritskaya, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 352 (1962).

[6] M. Rausch, M. Vogel, and H. Rosenberg, *J. Org. Chem.*, **22**, 903 (1957).

[7] S. I. Goldberg and M. L. McGregor, *ibid.*, **33**, 2568 (1968).

[8] N. Weliky and E. S. Gould, *J. Amer. Chem. Soc.*, **79**, 2742 (1957).

[9] M. D. Rausch and D. L. Adams, *J. Org. Chem.*, **32**, 4144 (1967).