Although it contains no crystallographic symmetry element, the complex molecule, even including the three phenyl groups, comes close to displaying the 3*m* symmetry it would be expected to have in isolation (see the bond-length and -angle data in Figure 1). The coordination polyhedron about the molybdenum atom is distorted slightly from an ideal octahedron. For example, the three P–Mo–P angles are 86.8 (1), 88.5 (1), and 85.3 (1)° instead of the ideal 90°, probably as a necessary consequence of closing the rings of the cage.

The observed chemical and spectroscopic properties of the new chelate complex **1** can readily be reconciled with the structure found. Thus, elemental analyses[4] are consistent with the stoichiometry $P[N(C_6H_5)PF_2]_3Mo(CO)_3$. The proton-decoupled phosphorus-31 NMR spectrum in dichloromethane solution exhibits the following two resonances: (1) a resonance assigned to the three equivalent PF_2 groups, centered at δ 157.1 and split into a 1197-Hz triplet by the strong phosphorus–fluorine coupling; (2) a resonance assigned to the central phosphorus atom, centered at δ 101.3 with no major splitting. The infrared spectrum exhibits frequencies ν(CO) at 2041 and 1988 cm^{-1}, consistent with a *fac*-$L_3Mo(CO)_3$ complex containing relatively strong π-acceptor ligands.[5]

The Mo–P bond lengths, averaging 2.343 Å, and the Mo–C bond lengths, averaging 2.050 Å, provide striking evidence of the strong π-acceptor character of the PF_2 groups. The Mo–P bonds are among the shortest ever observed for trivalent phosphorus ligands bound to molybdenum, and the Mo–C bonds are among the longest ever observed for carbonyl groups similarly bound. These bond lengths are essentially identical within experimental error with the corresponding lengths 2.369 (10) and 2.063 (6) Å in $Mo(CO)_5PF_3$[6] and 2.063 (3) Å in $Mo(CO)_6$,[7] from gas-phase electron-diffraction analysis in each case. Some other relevant comparisons are available in ref 8. Since the Mo–C bond order in $Mo(CO)_6$ may be assigned[5,9] a value of 1.5, it follows then from the bond-length data that the Mo–C and Mo–P bond orders in $Mo(CO)_5PF_3$ and **1** must all be about 1.5. We conclude, then, that each ligating group of the tridentate ligand in **1** is about as strong a π acceptor as the CO or the PF_3 molecule.[10]

A few other features of the molecular structure deserve brief comment. The F–P–F angles, averaging only 94.0°, are remarkably small in comparison with the angle 97.8 (2)° in PF_3[11] and the angle 99.5 (5)° in $Mo(CO)_5PF_3$.[6] The average P–F bond length, 1.568 Å, is close to the lengths 1.570 (1) and 1.557 (4) Å in PF_3 and $Mo(CO)_5PF_3$, respectively. The average of the three P(4)–N bond lengths is greater by 0.060 Å than the average of the other three P–N bonds.

Acknowledgment. The portion of this research performed at the University of Georgia was partially supported by the U.S. Air Force Office of Scientific Research under Grant AFOSR-75-2869. The portion of this research performed at the Oak Ridge National Laboratory was sponsored by the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract W-7405-eng-26 with the Union Carbide Corporation.

Supplementary Material Available: Lists of atomic coordinates and thermal parameters (2 pages). Ordering information is given on any current masthead page.

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[4] Anal. Calcd for $C_{21}H_{15}F_6MoN_3O_3P_4$: C, 36.5; H, 2.2; N, 6.1; M_r, 691. Found: C, 35.8, 36.3; H, 2.0, 2.3; N, 6.0, 6.0; M_r, 659 in benzene.

[5] Cotton, F. A. *Inorg. Chem.* **1964**, *3*, 702. The related compound *fac*-$Mo(CO)_3(PCl_3)_3$ exhibits frequencies ν(CO) at 2040 and 1991 cm^{-1}.

[6] Bridges, D. M.; Holywell, G. C.; Rankin, D. W. H.; Freeman, J. M. *J. Organomet. Chem.* **1971**, *32*, 87.

[7] Arnesen, S. P.; Seip, H. M. *Acta Chem. Scand.* **1966**, *20*, 2711.

[8] Cotton, F. A.; Darensbourg, D. J.; Ilsley, W. H. *Inorg. Chem.* **1981**, *20*, 578.

[9] Cotton, F. A.; Wing, R. M. *Inorg. Chem.* **1965**, *4*, 314.

[10] Cotton[5] has concluded from an approximate calculation of the force constant of the C–O bond in *fac*-$Mo(CO)_3(PF_3)_3$ that PF_3 is a considerably stronger π acceptor than CO. A similar conclusion has been reached from analysis of photoelectron spectra of PF_3, $Ni(PF_3)_4$, and $Pt(PF_3)_4$ by: Green, J. C.; King, D. I.; Eland, J. H. D. *J. Chem. Soc., Chem. Commun.* **1970**, 1121.

[11] Morino, Y.; Kuchitsu, K.; Moritani, T. *Inorg. Chem.* **1969**, *8*, 867.

Synthesis of Nitrogen-Containing Polycycles on the Basis of a New Method of *o*-Quinone Methide Imine Generation

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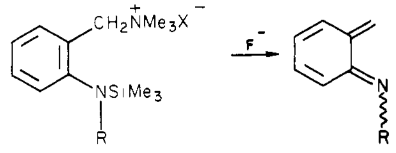
Received April 1, 1981

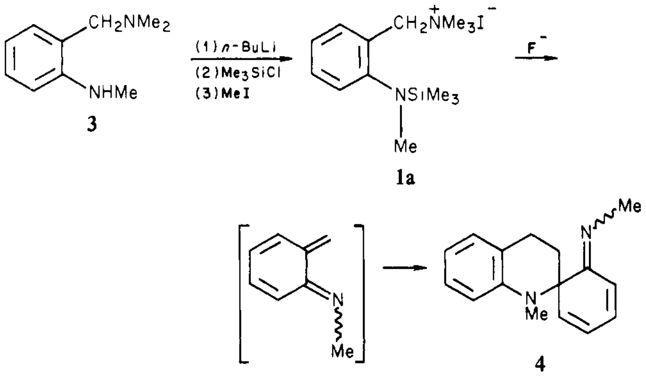
Intramolecular Diels–Alder reactions have been widely used for syntheses of polycyclic ring systems with stereocontrol.[1] Recently, we reported[2] a stereoselective synthesis of steroid frameworks on the basis of the mild generation of *o*-quinodimethanes, in which [*o*-[α-(trimethylsilyl)alkyl]benzyl]trimethylammonium halides are treated with fluoride anion at room temperature.

It was now found that [*o*-[(trimethylsilyl)alkylamino]benzyl]trimethylammonium halide (**1**) also underwent the fluoride anion induced 1,4-elimination under mild conditions to generate *o*-quinone methide *N*-alkylimine intermediate (**2**).[3] Described



1 **2**

herein are the syntheses of nitrogen-containing polycycles based on this methodology for the generation of N-substituted *o*-quinone methide imine (**2**). When [*o*-[(trimethylsilyl)methylamino]benzyl]trimethylammonium iodide (**1a**),[4] prepared by N-silylation via lithiation at the nitrogen of [*o*-(methylamino)benzyl]dimethylamine (**3**) followed by quaternization with methyl iodide, was treated with CsF or tetrabutylammonium fluoride in acetonitrile at room temperature, spirotetrahydroquinoline derivative **4** was isolated as a yellow liquid (chromatography on silica gel) in 77% yield. The structural assignment of **4**[5] is based on the spectral data [IR (neat) 1650, 1610, 1585 cm^{-1}; NMR ($CDCl_3$ with Me_4Si) δ 2.0 (m, 2 H), 2.62 (s, 3 H), 2.8 (m, 2 H), 3.30 (s, 3 H), 6.0–7.4 (m, 8 H)] and hydrogenolysis of **4** on Pd/C affording 1,2-bis[*o*-(methylamino)phenyl]ethane.[6]



3 **1a** **2a** **4**

Spirotetrahydroquinoline derivative **4** may be derived from [4 + 2] cyclodimerization of the *o*-quinone methide imine (**2a**).[3b]

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[1] Oppolzer, W. *Synthesis* **1978**, 793.

[2] Ito, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1981**, *103*, 476.

[3] (a) Burgess, E. M.; McCullagh, L., *J. Am. Chem. Soc.*, **1966**, *88*, 1580. (b) Fisher, M.; Wagner, F. *Chem. Ber.* **1969**, *102*, 3486. (c) Mao, Y.-I.; Boekelheide, V. *J. Org. Chem.* **1980**, *45*, 1547. (d) Lancaster, M.; Smith, D. J. H. *J. Chem. Soc., Chem. Commun.* **1980**, 471.

[4] **1a**: NMR ($CDCl_3$ with Me_4Si) δ 0.08 (s, 9 H), 2.87 (s, 3 H), 3.13 (s, 9 H), 4.66 (s, 2 H), 7.2–7.8 (m, 4 H).

[5] Compound **4** turns brown and decomposes on standing in air.

[6] 1,2-Bis[*o*-(methylamino)phenyl]ethane: mass spectrum, *m/e* (relative intensity) 240 (M^+, 20), 172 (7), 121 (11), 120 (100), 118 (9), 93 (7), 91 (37), 77 (13), 65 (20); high-resolution mass spectrum, *m/e* 240.1628 (calcd 240.1626).

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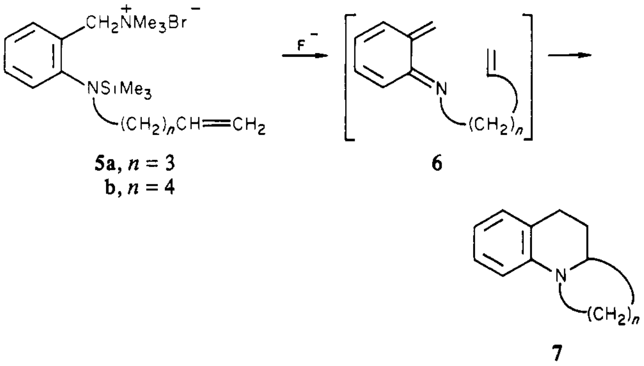
J. Am. Chem. Soc. **1981**, *103*, 5251–5253

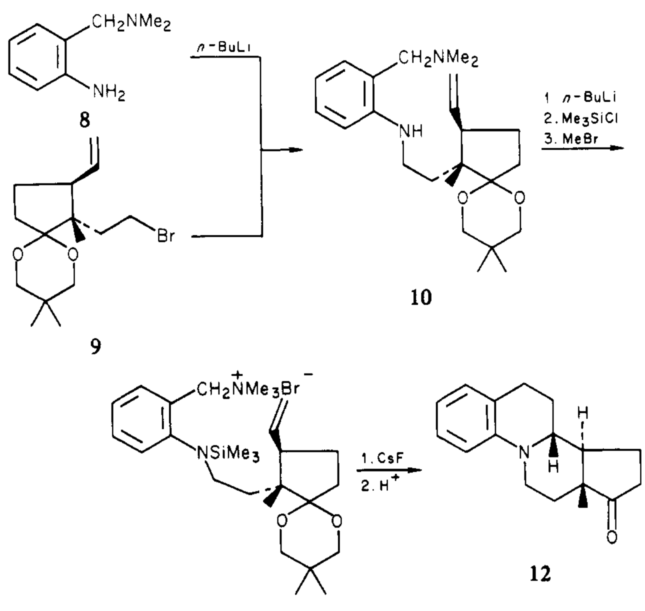
However, attempts to trap the *o*-quinone methide imine (**2a**) with dienophiles such as acrylate, fumarate, acetylenedicarboxylate, and *N*-phenylmaleimide all failed, resulting in the formation of **4** as the sole isolable product. However, intramolecular Diels–Alder reaction of *o*-quinone methide *N*-alkenylimine intermediates (**6**) provided a useful synthetic method for construction of nitrogen-containing polycycles as shown in the following scheme.



A representative procedure for the intramolecular Diels–Alder reaction of *o*-quinone methide *N*-alkenylimine intermediate (**6**) is exemplified by the synthesis of benzo[*c*]quinolizidine (**7b**). To a refluxing suspension of 304 mg (2 mmol) of CsF in 10 mL of acetonitrile, a solution of 400 mg (1 mmol) of [*o*-[(trimethylsilyl)hex-5-enylamino]benzyl]trimethylammonium bromide (**5b**)[7] in 10 mL of acetonitrile was added dropwise over 1 h and then heated at reflux for 1 h. The reaction mixture was filtered to remove insoluble materials and evaporated in vacuo. The residue was subjected to preparative thin layer chromatography on silica gel with benzene solvent to furnish benzo[*c*]quinolizidine (**7b**)[9] as a yellow liquid (R_f = 0.66) in 58% yield[10] [**7b**: ^{1}H NMR (CDCl$_3$ with Me$_4$Si) δ 1.1–2.2 (m, 8 H), 2.3–3.3 (m, 4 H), 3.89 (dm, 1 H, $J_{\text{H-H}}$ = 12.2 Hz), 6.4–7.7 (m, 4 H); ^{13}C NMR (CDCl$_3$ with Me$_4$Si) δ 24.43, 25.69, 26.95, 30.23, 33.29, 47.94, 56.70, 112.62, 117.12, 124.62, 126.78, 128.80, 146.78].

Similarly, the fluoride anion induced intramolecular Diels–Alder reaction of [*o*-[(trimethylsilyl)pent-4-enylamino]benzyl]trimethylammonium bromide (**5a**) afforded benzo[*e*]indolizidine (**7a**)[11] in 53% isolated yield.

Finally, the successful synthesis of nitrogen-containing polycycles mentioned above has been extended to the stereoselective synthesis of 9-azaestra-1,3,5(10)-trien-17-one (**12**). The requisite precursor (**11**) for construction of **12** was prepared by the reaction of (*o*-aminobenzyl)dimethylamine (**8**) and bromide (**9**)[2] followed by N-silylation and quaternization. On treatment of **11** with CsF in a refluxing acetonitrile according to the procedure described above, 8,14-*anti*-13,14-*trans*-9-azaestra-1,3,5(10)-trien-17-one (**12**)[12] was selectively produced in 60% yield based on **10** after preparative thin layer chromatography on silica gel with hexane–ethyl acetate (2:1) (R_f = 0.63) [**12**: mp 122.5–123 °C; IR (KBr disk) 1740 cm^{-1}; ^{1}H NMR (CDCl$_3$ with Me$_4$Si) δ 0.94 (s, 3 H), 0.5–2.6 (m, 9 H), 2.6–3.4 (m, 4 H), 3.70 (ddd, 1 H, $J_{\text{H-H}}$ = 12.8, 5.1, 2.6 Hz), 6.4–7.3 (m, 4 H); ^{13}C NMR (CDCl$_3$ with Me$_4$Si) δ 12.52, 20.70, 26.86 (2C), 31.35, 35.35, 42.36, 45.96, 48.88, 54.86, 112.49, 117.52, 123.81, 127.10, 129.25, 146.47, 219.20]. The stereochemistry and stereochemical homogeneity of **12** were established by the coupling constant of the ^{1}H NMR signal at 3.70 ppm and from the set of ^{13}C NMR absorptions (16 different C, thus one degeneracy).



Further studies of stereoselective synthesis of heterocyclic natural products on the basis of the present methodology are now in progress in our laboratory.

Acknowledgment. We are grateful to Shin-etsu Chemical Industry Co., Ltd., for a generous gift of trimethylchlorosilane.

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(7) **5b** was prepared by the reaction of [*o*-[(trimethylsilyl)hex-5-enylamino]benzyl]dimethylamine [bp 95–100 °C (0.1 mmHg)], which was prepared by N-lithiation and subsequent silylation of [*o*-(hex-5-enylamino)benzyl]dimethylamine,[8] with methyl bromide in acetonitrile at 0–15 °C for 5 h [**5b**: NMR (CD$_3$CN with Me$_4$Si) δ 0.01 (s, 9 H), 0.9–2.2 (m, 6 H), 3.20 (s, 9 H), 2.9–3.4 (m, 2 H), 4.71 (s, 2 H), 4.6–5.9 (m, 3 H), 6.8–7.8 (m, 4 H)].

(8) Attempts to generate *o*-quinone methide imine intermediate (**6b**) by the reaction of [*o*-(hex-5-enylamino)benzyl]trimethylammonium bromide with *n*-BuLi have not led to the formation of **7b**.

(9) Fozard, A.; Davies, L. S.; Bradsher, C. K. *J. Chem. Soc. C* **1971**, 3650. **7b**: mass spectrum, *m/e* (relative intensity) 187 (M$^+$, 97), 186 (100), 172 (45), 158 (51), 146 (35), 144 (45), 131 (75), 130 (79), 117 (24), 91 (31), 77 (35). Anal. Calcd for C$_{13}$H$_{17}$N: C, 83.37; H, 9.15; N, 7.48. Found: C, 83.19; H, 9.17; N, 7.48.

(10) The yield based upon [*o*-[(trimethylsilyl)hex-5-enylamino]benzyl]dimethylamine was not optimized.

(11) **7a**: ^{1}H NMR (CDCl$_3$ with Me$_4$Si) δ 0.9–2.3 (m, 6 H), 2.5–3.6 (m, 5 H), 6.2–7.2 (m, 4 H); ^{13}C NMR (CDCl$_3$ with Me$_4$Si) δ 24.02, 27.57, 28.29, 33.28, 46.99, 58.14, 110.06, 114.91, 121.38, 127.32, 128.58, 145.03. Mass spectrum, *m/e* (relative intensity) 174 (13), 173 (M$^+$, 100), 172 (78), 145 (13), 144 (7), 117 (6). Anal. Calcd for C$_{12}$H$_{15}$N: C, 83.19; H, 8.73; N, 8.08. Found: C, 83.41; H, 8.60; N, 7.99.

(12) **12**: Anal. Calcd for C$_{17}$H$_{21}$NO: C, 79.96; H, 8.29; N, 5.49. Found: C, 80.12; H, 8.35; N, 5.53.

Effect of the Silicon Site on the Cyclization of Sila-5-hexen-1-yl Radicals. The Unusual Effect of α-Silicon

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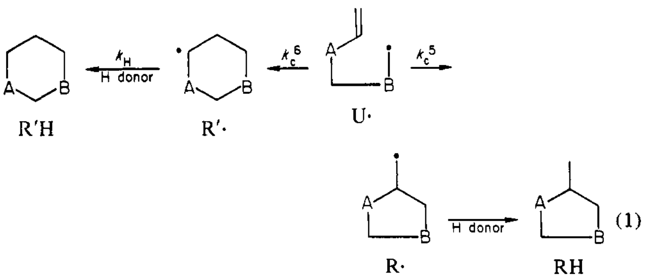
Received April 27, 1981

The cyclization of 5-hexen-1-yl radicals to cyclopentylcarbinyl and cyclohexyl radicals (reaction 1, A = B = CH$_2$) is one of the best-known radical rearrangements. It is very well documented and examples abound even in heteroatom analogues.[1] The process



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(1) For a recent and comprehensive review, see: Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground and Excited States"; deMayo, P., Ed.; Academic Press: New York, 1980; Vol. 1. I thank Professor Beckwith and Dr. Ingold for a preprint of their chapter.

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