in 50 mL of THF under argon at room temperature. The usual workup gave a brown polymeric powder from which no pure product could be isolated.

Attempted 2 + 2 Cycloadditions of DABT. LTA (3.1 g, 6.95 mmol) in 50 mL of dry THF was added in portions over 30 min to a stirred suspension of DABT (0.6 g, 3.16 mmol) and 1,1-dimethoxyethene[23] (0.62 g, 6.95 mmol) in 100 mL of THF (argon, room temperature). Lead diacetate was removed by filtration. Workup led to recovery of the unreacted 1,1-dimethoxyethene (0.57 g, 95%). Similar results were obtained with vinyl acetate.

Acknowledgment. We are indebted to the National Institutes of Health (GM15997) for financial support of this research.

Registry No. **3**, 91477-70-2; **6**, 42783-40-4; **8**, 54807-06-6; **9**, 7221-63-8; **10**, 100367-17-7; **11**, 100367-18-8; **12**, 100367-19-9; **13**, 100367-20-2; **14**, 110-00-9; *anti*-**15**, 87207-46-3; *syn*-**15**, 87248-22-4; **16**, 625-86-5; *anti*-**17**, 100367-21-3; *syn*-**17**, 100483-34-9; **18**, 955-83-9; **19**, 100430-68-0; **20**, 5471-63-6; **21**, 100367-22-4; **22**, 24956-46-5; **23**, 100367-23-5; **24**, 2406-01-1; **25**, 100367-24-6; **26**, 36439-78-8; *anti*-**27**, 100367-25-7; *syn*-**27**, 100483-35-0; **28**, 30614-77-8; **29**, 100367-26-8; **30**, 19434-69-6; **31**, 100430-69-1; **32**, 611-13-2; **33**, 91477-72-4; **34**, 1048-83-5; **35**, 91477-73-5; **36**, 22037-28-1; **37**, 91477-75-7; **38**, 3376-23-6; **39**, 91477-76-8; **40**, 41106-03-0; **41**, 100367-27-9; **42**, 479-33-4; **43**, 100367-30-4; **44**, 16691-79-5; **45**, 91477-71-3; **50**, 2960-97-6; **53**, 100367-28-0; **54**, 100367-29-1; mesitaldehyde, 487-68-3.

(23) Corey, E. J.; Bass, J. D.; LeMahieu, R.; Mitra, R. B. *J. Am. Chem. Soc.* **1964**, *86*, 5570.

Trapping Reactive Intermediate Carbanions Generated by Lithium Tetramethylpiperidide Treatment of 7-Oxabicyclo[2.2.1]heptenes in the Presence of Trimethylsilyl Chloride

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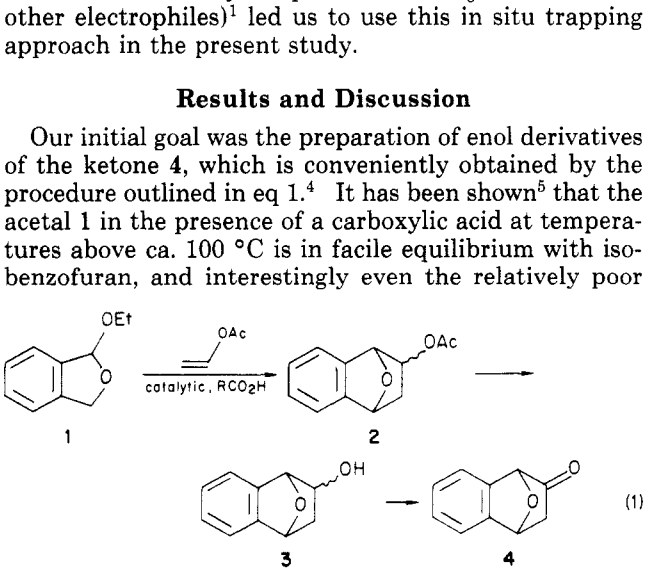
Received September 30, 1985

Standard strong base induced methods for preparing enol ether derivatives fail with oxabicyclic ketone **4**, giving instead an aldol product. The trimethylsilyl enol ether **5** can be prepared by addition of lithium tetramethylpiperidide (LTMP) to a mixture of **4** and trimethylsilyl chloride (Me_3SiCl) in THF solvent. Further reactions of **5** are observed under these conditions, leading to proximal bridgehead and vinyl trimethylsilylated products. These reactions appear to be general for benzannulated 7-oxabicyclo[2.2.1]heptenes; i.e., the enol ether function, while exerting a directing influence, is not needed for the reaction. Bridgeheads are somewhat more reactive than vinyl sites. Silylation of 9,10-dihydro-9,10-epoxyanthracene (**15**), which has $pK_a \geq 40$, occurs readily, demonstrating the utility of this in situ LTMP/Me_3SiCl approach for the trapping of very small equilibrium amounts of carbanions (reactive intermediates.) The benz[*a*]anthracene analogue **18** is similarly mono- and bis(trimethylsilylated), with a modest level of regioselection for the 7-position.

Some unusual reactions of substituted 7-oxabicyclo-[2.2.1]heptenes have been discovered by treatment of these substrates, *in the presence of trimethylsilyl chloride* (*Me_3SiCl*), with lithium tetramethylpiperidide (LTMP). The recent finding by Martin and co-workers that LTMP is at least moderately compatible with Me_3SiCl (and a few other electrophiles)[1] led us to use this in situ trapping approach in the present study.

Results and Discussion

Our initial goal was the preparation of enol derivatives of the ketone **4**, which is conveniently obtained by the procedure outlined in eq 1.[4] It has been shown[5] that the acetal **1** in the presence of a carboxylic acid at temperatures above ca. 100 °C is in facile equilibrium with isobenzofuran, and interestingly even the relatively poor dienophile vinyl acetate is efficiently trapped under these conditions (twofold exess of dienophile, PhCl solvent, sealed tube, 130 °C for 56 h) to afford **2** (85% endo, 15%



(1)

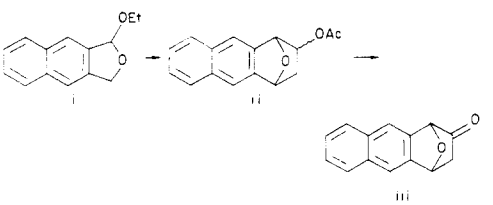
† Formerly known as Bagher Mir-Mohamad-Sadeghy.

(1) Krizan, T. D.; Martin, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 6155. Taylor, S. L.; Lee, D. Y.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4156. These authors noted NMR evidence for the rapid formation of a complex (−78 °C) of LTMP and Me_3SiCl, which was nonetheless suitable for the deprotonations described. The extent of compatibility of LTMP/Me_3SiCl (i.e., stability vs. self-destructive reactions) is not completely understood. One might expect deprotonation of Me_3SiCl to occur, based on a study of the course of the reaction of this material with *tert*-butyllithium.[2] The Martin group studies suggest somewhat more efficient utilization of the reagents when mixed at low temperature, but successful ambient temperature applications are also reported. Very recently, Eaton and Castaldi[3] have described the in situ use of $HgCl_2$ to trap LTMP-generated carbanionic species in a cubane derivative.

(2) Gornowicz, G. A.; West, R. *J. Am. Chem. Soc.* **1968**, *90*, 4478.

(3) Eaton, P. E.; Castaldi, G. *J. Am. Chem. Soc.* **1985**, *107*, 724.

(4) This approach is also useful for preparing the benzo[*f*]isobenzofuran analogue, viz;



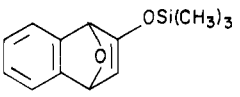
Cycloadduct ii (endo, exo mixture) was isolated in 79% yield, with subsequent methanolysis and Jones oxidation giving iii (74%); unpublished work of S. Mirsadeghi.

(5) Mir-Mohamad-Sadeghy, B.; Rickborn, B. *J. Org. Chem.* **1983**, *48*, 2237.

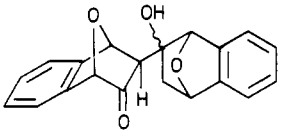
0022-3263/86/1951-0986$01.50/0

exo) in 94% yield. Hydrolysis to the mixture of alcohols[6] (KOH, methanol, 96%) followed by PDC oxidation (80%) gave 4.[7]

Several attempts were made to convert 4 to the trimethylsilyl enol ether 5 using conventional strong base procedures (addition of 4 to excess base, *followed* by addition of Me_3SiCl, with subsequent cold aqueous sodium bicarbonate workup). These led either to recovery of 4 or to the isolation of a dimeric (aldol condensation) product 6[8] (especially prominent when lithium diisopropylamide in ether was used).



5



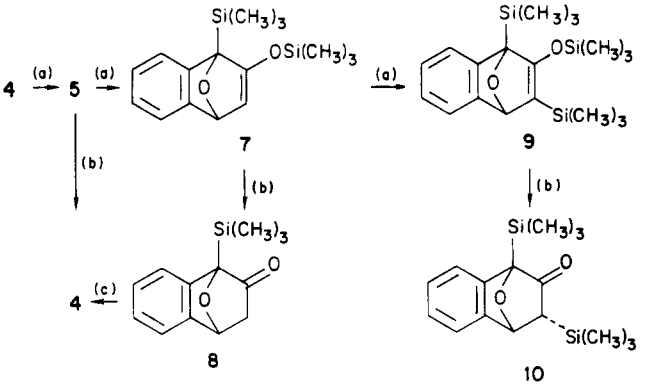
6

The formation of 6 shows that enolate is indeed generated but an abnormally facile aldol condensation with 4 prevents complete conversion to the anionic species. Even slow (syringe pump) addition of a solution of 4 to excess, well-stirred, LDA in ether failed to prevent formation of 6 as the major product. House and co-workers[9] have described a similar competitive aldol condensation in the preparation of the enolate from a long chain methyl ketone, but it appears that the conversion of 4 to 6 is unusually facile.

When a modest excess (1.5 equiv) of LTMP was employed with ketone added to the base at −78 °C and quenching at this temperature after 0.5 h by addition of D_2O, aldol product 6 was formed along with recovered ketone 4, which contained no deuterium as measured by integration of its ^1H NMR spectrum. A similar experiment in which Me_3SiCl was used to quench the reaction also gave aldol 6 (unsilylated) and recovered 4. These results indicate that deprotonation of 4 is relatively slow, and this offers a rational explanation for the formation of 6.

It was apparent that isolation of an enol ether derivative would require formation of the enolate *in the presence* of a reactive electrophile. Encouraged by the Martin group observations,[1] reactions involving either addition of 4 to LTMP/Me_3SiCl or of LTMP to solutions of 4/Me_3SiCl were examined. Both approaches were effective in causing complete loss of 4 without formation of 6 (as shown by direct examination of the reaction mixtures by NMR). However, a second unusual feature of the system became apparent when the standard bicarbonate workup was employed; this led to recovery of major amounts of 4. Further experimentation showed that in fact the enol trimethylsilyl ether 5 is formed, but it is remarkably sensitive to hydrolysis, the reaction being complete even on brief (two phase) contact with cold dilute bicarbonate solution. We eventually found that 5 could be isolated in nearly pure form by adding the mixture to a large volume of pentane and cold pH 7 buffer, but rapid treatment was required, since even these conditions caused slow hydrolysis of 5 to 4. As a control experiment, the enol Me_3Si ether of the carbocyclic model norbornanone was prepared and isolated in 71% distilled yield after washing with both bicarbonate and dilute HCl, with no special precautions taken. The extreme sensitivity of 5 to hydrolysis (also very rapid with a pH 5 wash) may be due to the oxa bridge playing a role in the delivery of acid/base to the reactive sites, and this may also be significant in the facile aldol condensation described above.

Scheme I[a]



[a] (a) LTMP, Me_3SiCl; (b) cold aqueous $NaHCO_3$ wash; (c) KOH, CH_3OH.

An effort was made to circumvent the hydrolysis problem through the use of *tert*-butyldimethylsilyl chloride in place of Me_3SiCl. However, none of the enol silyl ether was detected; instead essentially complete conversion to the aldol 6 occurred. Clearly the same features which make the *tert*-butyldimethylsilyl group attractive as a protecting group have in this instance prevented rapid trapping of the enolate, allowing aldol condensation to intervene.

Before the hydrolytic instability of 5 was fully appreciated, we had initiated an examination of the reaction of 4, in the presence of excess Me_3SiCl, with LTMP added to the mixture at 0 °C. In an early experiment involving a bicarbonate wash, a Me_3Si-containing product was isolated, which proved to be an *isomer* of 5. The ^1H NMR spectrum of this material established that it has the bridgehead silylated ketone structure 8 (Scheme I).

Although in principle 8 could arise by direct deprotonation/silylation of the bridgehead position adjacent to the carbonyl group of 4 (there is precedent in H,D exchange studies of unrelated carbobicyclic ketones[10]), the cumulative evidence indicates that instead the first step is the conversion of 4 to 5. By variation in the reaction conditions, it was possible to establish some control over the relative amounts of 4, 5, 7, and more highly silylated materials. Thus, at −78 °C with 1.5 equiv of LTMP (2 equiv of Me_3SiCl) and quenching by addition of the cold mixture after 0.5 h to chilled pentane/buffer, 5 contaminated only with starting material 4 was obtained. Repetition of this experiment with a threefold increase in base and Me_3SiCl concentrations, with quenching after 2 h, gave a mixture containing no 4 or 8 but only 5 and 7 in nearly equal amounts. These observations support the view that enolate formation is relatively slow, that rapid silylation to form 5 then occurs, and that 5 is the precursor of 7. It is noteworthy that the bridgehead deprotonation occurs even at dry ice temperature. Treatment of 4 in the presence of Me_3SiCl at 0 °C with a limited amount of

(6) The exo alcohol has recently been described, prepared via hydroboration/oxidation (bulky hydroborating agents required to avoid oxa-ring cleavage) of 1,4-dihydro-1,4-epoxynaphthlene: Brown, H. C.; Vara Prasad, J. V. N. *J. Org. Chem.* **1985**, *50*, 3002.

(7) Ketone 4 has also been prepared (unpublished work with M. L. Chase) by cycloaddition of isobenzofuran with α-acetoxyacrylonitrile, followed by basic methanolysis. The latter step gave product in modest and variable yields, which in the light of the present study is presumably associated with facile aldol condensation of 4.

(8) The stereochemistry of the ketol 6 has not been fully determined, but NMR features show it to have the substituent exo on the carbonyl-containing ring as depicted (both bridgehead protons on this ring appear as singlets; see Experimental Section).

(9) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324.

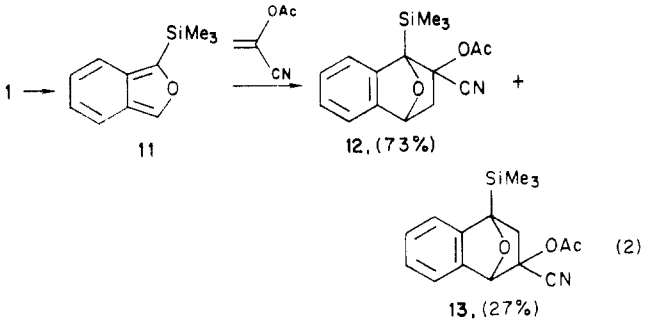
(10) See, for example: Chang, A. K.; Stothers, J.B. *Can. J. Chem.* **1978**, *56*, 1342.

LTMP also can be used to prepare **5** as the nearly exclusive product (see Experimental Section), indicating that this change in temperature does not cause a major alteration in the product-forming sequence.

As the relative amounts of electrophile, base, temperature, and/or reaction time are increased, the enol ether **5** is consumed, giving rise to the bis(trimethylsilylated) species **7**. Although not isolated in pure form, evidence for this structure was obtained by MS and NMR and by isolation of its hydrolysis product, ketone **8**, by column chromatography. Very interestingly, further silylation of **7** occurs (MS, NMR). Structure **9** is proposed for this material, based on the isolation of bis(trimethylsilylated) ketone **10** by chromatography. The structure of **10** is apparent from examination of its ^{1}H NMR spectrum. In the parent ketone **4**, a striking downfield shift of the bridgehead proton remote from the carbonyl group results in a doublet (J = 5 Hz, due to coupling with the exo methylene proton) at 5.61 ppm, while the adjacent bridgehead proton appears as a singlet at 4.90 ppm. In **10**, the remaining bridgehead proton appears as a doublet (J = 5 Hz) at 5.95 ppm; the vicinal coupling not only establishes the positional feature but also shows that the Me_3Si group has the endo configuration. Whether this stereochemical feature reflects kinetically controlled protonation or the equilibrium structure has not been determined.

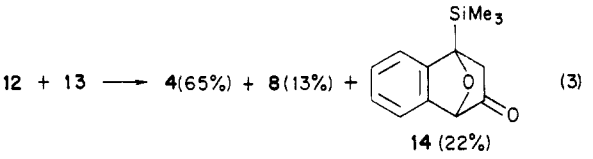
It is not obvious why the further deprotonation/silylation of **7** occurs preferentially at the vinyl position, as opposed to the remaining bridgehead site. While it is possible that the Me_3Si ether oxygen plays an important role, either through inductive or coordination effects, in establishing the order of reaction (**5** → **7** → **9**), evidence from another substrate discussed below suggests that this view may be an oversimplification.

An effort was made to substantiate the structure of **8** by an alternative synthesis, which while not successful for the intended purpose, provides further insights into the reactivity of this bicyclic system. The acetal **1** was converted to 1-(trimethylsilyl)isobenzofuran (**11**) by the RLi/catalytic LDA procedure described in previous work from this laboratory.[11] Treatment of this material with a solution of α-acetoxyacrylonitrile gave 70% of the regioisomers (endo, exo stereoisomers not distinguished by NMR) **12** and **13**, in the approximate ratio shown in eq 2. Identification is based on the NMR spectrum; the



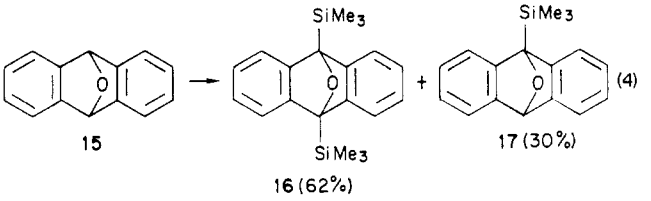
bridgehead proton of **12** appears as a doublet (J = 5 Hz), while in **13** the corresponding absorption is a singlet. The ratio of **12**/**13** indicates a modest level of regioselectivity imparted by the Me_3Si group in the cycloaddition reaction.

When this mixture was treated with KOH/MeOH (ice bath, 3.5 h), three products were isolated, in overall quantitative yield (eq 3). The major product was the unsilylated ketone **4**, which we believe arises from **8** by base-induced protiodesilylation. Indeed, a sample of **8**



prepared as described in Scheme I when subjected to these conditions gave **4** (75% isolated yield.) In contrast, **14** appears to be stable to this basic methanol treatment, since the amount isolated corresponds, within experimental error, to the amount of **13** present in the starting mixture. The greater reactivity of **8** (compared with **14**) toward base presumably reflects the stabilizing influence of the adjacent carbonyl dipole on the developing bridgehead carbanionic intermediate.

We were intrigued by the possibility that other 7-oxabicyclo[2.2.1]heptenes might exhibit related reactions. One interesting substrate is the anthracene derivative **15**, which has recently been prepared by protiodesilylation of compound **16**,[12] e.g., by treatment with KOH or KO-t-Bu in dimethyl sulfoxide (Me_2SO). When **15**, in the presence



of excess Me_3SiCl, was treated with LTMP (0 °C, 6 h required to consume **15**, TLC), products **16** and the new material **17** were isolated by column chromatography. These observations unmask a previously undetected acid/base reaction in this system.

When the bis(trimethylsilyl) material **16** was subjected to potassium *tert*-butoxide in Me_2SO-d_6, **15**-d_2 was formed rapidly in essentially quantitative yield with very high isotope incorporation (94% d_2). However, much longer treatment of **15** under these conditions gave recovered **15** containing no detectable (^{1}H and ^{2}H NMR) amount of deuterium. Similarly, when **15** was treated with excess LTMP (room temperature, THF, 24 h) and then quenched with D_2O, **15** was recovered (>80%) with no isotope incorporation.[12] The results of eq 4 show that the bridgehead anion is indeed being formed, at a rate sufficient to consume all of the starting material within 6 h, while the latter observation indicates that the equilibrium amount of anion is too small to measure by the techniques employed.[13] Fraser and co-workers[14] have established a pK_a = 37.3 for tetramethylpiperidine (lithium counterion, THF solution) and demonstrated that equilibration of LTMP with several weak acids of pK_a < 40 are rapid (laboratory time scale; slow on the NMR scale.) Although unknown rate factors preclude determining the pK_a value for **15** from our results, the data suggest a lower limit of ca. 40, and the actual value

(11) Crump, S.; Rickborn, B. *J. Org. Chem.* **1984**, *49*, 304.

(12) Crump, S.; Netka, J.; Rickborn, B. *J. Org. Chem.* **1985**, *50*, 2746.

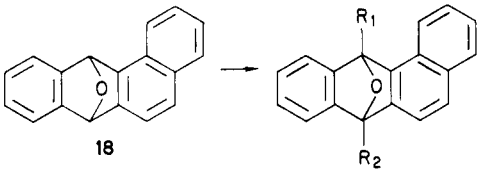
(13) A reviewer has pointed out that such quenching experiments may significantly underestimate the amount of carbanion present (see: Laube, T.; Dunitz, J. D.; Seebach, D. *Helv. Chim. Acta* **1985**, 1373 and references therein), due to complex formation between the R_2NH and anion. While we cannot discount this possiblity, it is not known that such complexes, which have been demonstrated especially with enolates, would be important for the bridgehead anion of **15**. In addition, the relatively slow in situ reaction with Me_3SiCl (6 h) described in the text does not argue for the presence of a large percentage of carbanion, since on the basis of common experience one expects such reactions to be quite rapid.

(14) Fraser, R. R.; Bresse, M.; Mansour, T. S. *J. Chem. Soc., Chem. Commun.* **1983**, 620.

may be several pK_a units higher (on the scale as defined by Fraser.)

The trimethylsilylation of **15** undoubtedly proceeds in a stepwise fashion, giving first **17** and then **16**. The formation of **16** is significant in demonstrating that the incorporation of the first Me_3Si group does not prevent reaction at the remaining bridgehead site (see below.)

Monotrimethylsilylation could be useful, particularly if the reaction could be controlled to stop at this stage, or if an unsymmetrical substrate exhibited regioselectivity. The latter point was briefly explored, by subjecting the benz[*a*]anthracene derivative **18**[12] to the Me_3SiCl/LTMP reaction conditions (eq 5). Halted when TLC indicated

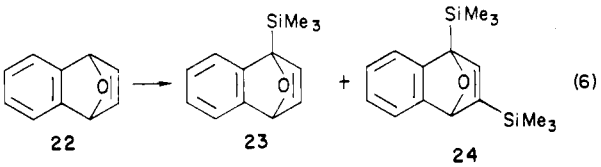


18 (5)

19, $R_1 = R_2 = SiMe_3$ (11%)
20, $R_1 = H$; $R_2 = SiMe_3$ (53%)
21, $R_1 = SiMe_3$; $R_2 = H$ (9%)

that all of **18** had been consumed, the three products **19–21** were formed, in the yields shown (the ratio of **20**/**21** was not changed by chromatography, which also failed to separate this pair). The bis(trimethylsilyl) derivative **19** was isolated in pure form, and its identity secured by comparison with an authentic sample.[12] The mixture (**20**/**21**) was assigned by comparison of the residual bridgehead proton and the Me_3Si signals, with the "bay region" substituent having the more downfield chemical shift (the shift values correspond closely to the related shifts for the protons of **18** and the Me_3Si groups of **19**[12]). The results show that an energetically modest level of regioselection (**20**/**21** = 85/15) is found for deprotonation/silylation at the more open face of the substrate.

These systems undergo bridgehead silylation in the absence of the enol Me_3Si ether linkage, but both are formally doubly benzylic. The readily available 1,4-dihydro-1,4-epoxynaphthalene (**22**) offered structural features related to both these substrates and the enol Me_3Si ether **5** but without the dissymmetry of the latter. It gave an unexpected result, however, when subjected to the in situ silylation procedure at 0 °C with ca. 4 equiv of LTMP/Me_3SiCl (eq 6). We had anticipated that bride-



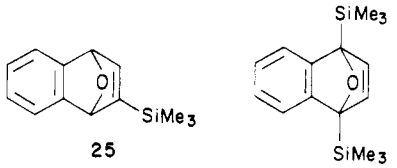
22 23 24 (6)

head reactions would dominate the process, and indeed the major product (ca. 50% in several experiments), isolated as an oil by chromatography, was a monotrimethylsilyl derivative (MS). This material was compound **23** of ca. 90% purity, with the remainder its isomer **25** (see below). The structure assigned is based on NMR comparisons with the parent **22**, which exhibits slightly broadened singlets at 5.6 (bridgehead protons) and 7.0 ppm (vinyl protons.)[15] The Me_3Si substituent in **23** perturbs the NMR spectrum very little, with the exception that the singlet at 5.6 ppm has a relative value of one proton.

The other product is also an oil (30%) and has two Me_3Si groups as demonstrated by MS analysis. Symmetrical structures (either both bridgehead or both vinyl substituents) are ruled out by the ^1H NMR spectrum, which exhibits singlets at 5.7 and 7.0 ppm (1 H each) and two distinct Me_3Si absorption (9 H each.) Again, with the exception of these changes, the spectrum closely resembles that of **22**, supporting the view that the parent bicyclic structure has been retained. This left two possible substitution patterns (1,2 or 1,3), and evidence supporting the latter was obtained by nuclear Overhauser enhancement difference spectroscopy. The downfield Me_3Si absorption (0.3 ppm) was assigned to the bridgehead substituent based on its close similarity to **23**; irradiation of this peak led to enhancement of the vinyl proton (13%) and to an aromatic proton (8%), supporting the bridgehead assignment and suggesting the 1,3-disubstitution pattern. Similarly, irradiation of the upfield (0.08 ppm) vinyl Me_3Si absorption caused enhancement of both the vinyl and bridgehead protons (10% each). These data strongly support structure **24** as shown in eq 6 for this bis(trimethylsilylated) product.

Compound **24** could arise in two ways, differing in the order of introduction of the two substituents. While the formation of **23** as the major product suggested that the bridgehead group was introduced first, this was by no means a secure conclusion.

Interestingly, **22** reacts with LTMP (1.5 equiv)/Me_3SiCl (2 equiv) even at −78 °C, although this reaction is much slower than that of the enol Me_3Si ether **5**. After 26 h, the mixture was quenched and monosilylated material (28%) was isolated by chromatography (the remainder was largely unreacted **22**). NMR analysis indicated that the monotrimethylsilyl fraction consisted of 84% **23** and 16% of the vinyl–trimethylsilyl product **25**. Thus competitive reac-



25 26

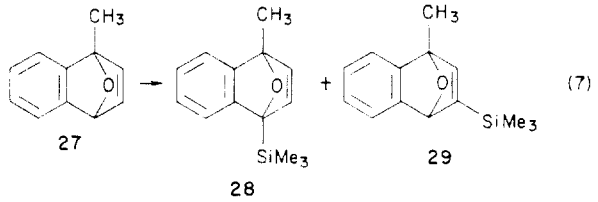
tions at the bridgehead and vinyl positions are occurring, with some preference for the former. This mixture (73 mg) of **23** + **25** was then subjected to a tenfold excess of LTMP/Me_3SiCl (ice bath, THF) for 1 h. TLC indicated complete loss of the monotrimethylsilyl materials. The product, isolated by chromatography (55%), was a mixture of **24** (ca. 65%) and another material which we believe to be the symmetrical derivative **26**. These results show that **23** can serve as a precursor to **24** and suggest that further reaction of **23** in fact occurs preferentially at the vinyl site (for reasons which are not obvious). It is likely on steric grounds that further reaction of **25** gives only **24**, although this could not be substantiated. The results of eq 6 are in keeping with (a) initial conversion of **22** to a mixture of **23** and **25**, with modest selectivity for the former (at 0 °C), and (b) more rapid reaction of **25** (to give **24**) than of **23** (to give predominantly **24**.)

Brief examination of the reaction of **22**/Me_3SiCl with LDA indicated that similar processes occur, but naphthalene (15%) was also formed in one experiment; hydride addition followed by elimination may explain the formation of this product.

Finally, the bridgehead methylated analogue **27** was examined and found to react readily with excess LTMP/Me_3SiCl at 0 °C (0.5 h). Only monosilylated

(15) The possibility that these assignments might be reversed is ruled out by the loss of the proton absorption at 5.7 ppm in 1,4-dideuterio-1,4-epoxynaphthalene, prepared by cycloaddition of 2,5-dideuteriofuran to benzyne (unpublished work of R. Moss.)

products were observed and isolated, with the bridgehead product **28** obtained in 54%, and vinyl–silylated isomer **29** in 24% yield. This result reinforces the conclusion that



(7)

competitive bridgehead/vinyl silylation is also involved in the reactions of **22**. The absence of bis(silylated) product in the reaction of **27** is likely due to steric hindrance to further reaction at a site adjacent to either the methyl or a Me_3Si group. This result also supports the conclusion initially reached by inspection of the NMR spectra, that the conditions employed in this study are insufficient to cause silylation of the aromatic ring in any of the substrates examined.

In summary, the in situ electrophile/LTMP procedure not only allows the formation of an otherwise inaccessible enol derivative (**5**) but also unmasks acidity features of benzannulated 7-oxabicyclo[2.2.1]heptenes. The bridgehead position(s) are the most reactive sites. Presumably this reflects intrinsic acidity (pK_a) caused by the combined inductive effects of the aromatic ring(s), bridging oxygen, and/or double bond,[16] perhaps enhanced by rehybridization effects which may be important in stabilizing bridgehead carbanions.[17] In one system (**15**) it is clear that a very small amount of carbanion is present at equilibrium, and thus the silylation allows the trapping of a true reactive intermediate. We believe this to be the case for all the substrates examined (except for ketone **4**, where enolate formation must be exothermic). To the extent that the results mirror the pK_a's of the reaction sites, these must lie between a low of ca. 40 and an upper limit below the (unknown) value for an unactivated aromatic system, on this pK_a scale. These results extend the accessible pKa range for in situ LTMP/Me_3SiCl reactions beyound that already demonstrated[18] by Martin,[1] and numerous other possible applications can be envisaged.

Experimental Section

All reactions were carried out under N_2, and reagents were similarly protected. Solvents were purified before use as described earlier.[12] Tetramethylpiperidine was distilled from CaH_2, and trimethylsilyl chloride was distilled from dimethylaniline. LTMP was prepared at 0 °C by addition of *n*-butyllithium (in hexane) to the amine in the reaction solvent. All transfers were by syringe. The term "buffer" refers to Mallinckrodt potassium acid phosphate pH 7 solution, used without dilution. The instruments used in this work have been described previously.[12] Combustion analyses were performed by Galbraith Laboratories, Knoxville, TN. NMR spectra were all taken at 300 MHz in $CDCl_3$ solvent, using either methylene chloride or acetone as the internal standard for materials containing trimethylsilyl groups. The term "Skelly-solv" refers to commerical alkanes (petroleum ether), redistilled before use, bp 40–45 °C.

3,4-Dihydro-1,4-epoxy-2(1*H*)-naphthalenone (4). A sealed tube containing the acetal **1** (476 mg, 3.17 mmol), 0.60 mL of vinyl acetate (6.5 mmol), and 63 mg of mesitoic acid catalyst in 5 mL of chlorobenzene was heated at 130 °C for 56 h. The solvent was removed in vacuo, and the residue chromatographed on 20 g of silica gel using 1/1 CH_2Cl_2/Skelly-solv to give 595 mg (94%) of **2** (endo/exo = 85/15): MS/Cl cald for $C_{12}H_{13}O_3$ (P + H) 205.0864, found 205.0853. The isomers have the following NMR characteristics. *endo*-**2**: ^1H NMR δ 1.23 (dd, 1 H, J = 12, 3 Hz, endo methylene), 1.75 (s, 3 H), 2.2–2.6 (m, 1 H, exo methylene), 5.0–5.4 (m, 2 H, distal bridgehead and C*H*OAc), 5.50 (d, 1 H, J = 4 Hz, proximal bridgehead), 7.15 (br s, 4 H); *exo*-**2** (partial data): ^1H NMR δ 2.05 (s, 3 H), 4.8 (m, 1 H, C*H*OAc), 5.2–5.4 (m, 2 H, bridgehead), 7.15 (4 H.)

This reaction was repeated twice on a larger scale (20×), with the chromatography step omitted, to obtain material for the next step.

Hydrolysis of **2** (16.3 g) was effected by adding a methanol solution (50 mL) to 9 g of KOH in 50 mL of the same solvent, and stirring for 0.5 h. Ether/water workup gave 12.5 g (96%) of the alcohol **3**, which was not further purified.

Oxidation of **3** (8.0 g, 0.05 mol) in 80 mL of DMF (ice bath) was carried out by slow addition (portions) of pyridinium dichromate (35 g, 0.09 mol), with stirring for 4 h at 0 °C, followed by 12 h at room temperature. The mixture was then poured into water, extracted with ether, dried over K_2CO_3, and distilled to give 6.3 g (80%) of **4**, bp 90 °C (0.5 torr), which solidified on standing, mp 46–47 °C: IR (CCl_4) 1780 cm^{-1}; ^1H NMR δ 1.98 (d, 1 H, J = 17 Hz, endo methylene), 2.58 (dd, 1 H, J = 17, 5 Hz, exo methylene), 4.90 (s, 1 H, proximal bridgehead), 5.61 (d, 1 H, J = 5 Hz, distal bridgehead), 7.2 (s, 4 H); MS/Cl calcd for $C_{10}H_9O_2$ (P + H) 161.0613, found 161.0602. Anal. Calcd for $C_{10}H_8O_2$: C, 74.99; H, 5.03. Found: C, 74.83; H, 5.12.

LTMP/Me_3SiCl Reactions of 4. Because of the sequence of reactions involved, these were difficult to control to maximize a single product; representative examples are cited.

(a) Aldol Product (6). This material, identified by TLC and NMR, was formed in several reactions as a major or minor product, and as the essentially exclusive product of reactions carried out in diethyl ether solvent.

A solution of 1.25 mmol of **4** in 10 mL of ether at 0 °C was treated with 1.37 mmol of LTMP (prepared in 5 mL of ether, using methyllithium). After being stirred for 4 h, the mixture was washed three times with cold buffer, dried over Na_2SO_4, and vacuum evaporated to give crude **6** in essentially quantitative yield. (Interestingly, **6** is also the nearly exclusive product when LTMP was added to **4** plus 1 equiv of Me_3SiCl, *in ether*.) Recrystallization from chloroform/hexane gave 76% of colorless solid **6**, mp 220–221 °C (presumably **6** forms as a single diasteromer; the NMR features were unchanged after recrystallization). Pure **6**: IR (CCl_4) 3480, 1760 cm^{-1}; ^1H NMR δ 1.53 (d, 1 H, J = 12 Hz), 2.51 (s, 1 H), 2.57 (dd, 1 H, J = 12, 5 Hz), 2.87 (br s, O*H*), 5.07 (s, 1 H), 5.34 (d, 1 H, J = 5 Hz), 5.62 (s, 1 H), 5.84 (s, 1 H), 7.2–7.5 (m, 8 H); MS/Cl calcd for $C_{20}H_{16}O_4$ (P) 320.1048, found 320.1036.

(b) Enol Me_3Si Ether (5). A THF solution containing 182 mg (1.13 mmol) of **4** and 3 equiv of Me_3SiCl in an ice bath was treated with 2.6 equiv of LTMP (presumably some base is consumed by moisture or side reactions); after the mixture was stirred for 1 h, rapid quenching (cold buffer and pentane), drying (Na_2SO_4), and vacuum evaporation gave **5** as an oil, in essentially quantitative yield and estimated >90% purity. Attempts to chromatograph similar preparations invariably led to hydrolysis. **5**: ^1H NMR δ 0.03 (s, 9 H), 4.99 (s, 1 H, proximal bridgehead), 5.35 (d, 1 H, J = 2 Hz, vinyl or distal bridgehead), 5.52 (br s, 1 H, vinyl or distal bridgehead), 6.8–7.2 (m, 4 H); MS calcd for $C_{13}H_{16}O_2Si$ (P) 232.0919, found 232.0892.

(c) Bis- and Tris(trimethylsilyl) Derivatives 7 and 9. These materials are very sensitive and hydrolyze or otherwise decompose on standing; it was necessary to carry out analyses rapidly after formation to avoid these complications. For the reasons discussed earlier, it was not possible to form or isolate pure **7** or **9**. Milder conditions led to **7** contaminated mostly by **5**, while more forcing conditions gave mixtures of **7** and **9** (30% maximum of the latter.) This result was general for reactions carried out in THF solvent at 0 °C. Evidence for the formation of **7** and **9** is derived from the MS of such mixtures (parent peaks

(16) The dihydro analogue of **22**, 1,4-epoxy-1,2,3,4-tetrahydronaphthalene, also appears to undergo bridgehead silylation under the in situ THF conditions, but this reaction has not been fully characterized.

(17) So, S. P.; Wong, M. H.; Luh, T. *J. Org. Chem.* **1985**, *50*, 2632.

(18) For example, Martin[1] has shown that benzonitrile is efficiently *o*-trimethylsilylated by the in situ LTMP/Me_3SiCl procedure. Fraser et al. have derived a pK_a = 38.1 (at −78 °C) for benzonitrile based upon conversion by LTMP to a substantial amount (36%) of the anionic form.[19] In this instance, the anion must be viewed as a reactive intermediate mainly because it decomposes by routes other than simple reprotonation.

(19) Fraser, R. R.; Bresse, M.; Mansour, T.S. *J. Am. Chem. Soc.* **1983**, *105*, 7790.

for both observed), the NMR data cited here, and particularly the identification of the hydrolysis products described below. In a typical experiment, 293 mg (1.83 mmol) of **4** and 18 mmol of Me_3SiCl in 35 mL of THF (ice bath) was treated with 9.2 mmol of LTMP in 10 mL of THF. After 1.5 h, the mixture was added to ice-cooled Skelly-solv and buffer soltuion. The separated and dried organic phase was rotary evaporated to remove most of the solvent, and the residue was examined by ^1H NMR, which showed absorptions at δ 5.34 and 5.53 (2 d, 1 H each, J = 2 Hz) attributed to the vinyl and bridgehead protons of **7** and a singlet at δ 5.55 attributed to the bridgehead proton of **9**. The ratio of **7**/**9** based on integration of these peaks was 70/30, and the combined yield, as shown by the isolation of the derived ketones discussed below, was in excess of 70%.

(d) 3,4-Dihydro-1,4-epoxy-1-(trimethylsilyl)-2(1*H*)-naphthalenone (8). To an ice bath cooled THF (35 mL) solution of 293 mg (1.83 mmol) of **4** and 7 equiv (1.6 mL) of Me_3SiCl was added 5 equiv of LTMP. Analysis (NMR) of an aliquot taken after 1 h indicated that all of **4** had been consumed, leading to **7** and **9** in a ratio of ca. 70/30. After the usual buffer workup, the residue from vacuum evaporation was chromatographed on 30 g of silica gel, with 10% CH_2Cl_2 in Skelly-solv, containing 1% of triethylamine. Two fractions were obtained, the second being 212 mg of **8** (oil, 51%): IR (CCl_4) 1750 cm^{-1}; ^1H NMR δ 0.65 (s, 9 H), 2.30 (d, 1 H, J = 16 Hz, endo methylene), 3.90 (dd, 1 H, J = 16, 5 Hz, exo methylene), 5.95 (d, 1 H, J = 5 Hz, bridgehead), 7.5 (br s, 4 H); MS/Cl calcd for $C_{13}H_{17}O_2Si$ (P + H) 233.0997, found 233.1003. Anal. Calcd for $C_{13}H_{16}O_2Si$: C, 67.20; H, 6.94. Found: C, 66.93; H, 7.13.

A sample (59 mg) of **8** in 20 mL of methanol containing 30 mg of KOH was stirred at 0 °C for 2 h. Normal extraction, drying, and evaporation gave 30 mg (75%) of ketone **4**.

(e) 3,4-Dihydro-1,4-epoxy-1,3-*endo*-bis(trimethylsilyl)-2-(1*H*)-naphthalenone (10). The first fraction collected from the preceding chromatography was **10** (oil, 100 mg, 19%): ^1H NMR δ 0.1 (s, 9 H), 0.65 (s, 9 H), 2.63 (d, 1 H, J = 5 Hz, exo proton), 5.95 (d, 1 H, J = 5 Hz, bridgehead), 7.4–7.7 (m, 4 H); MS/Cl calcd for $C_{16}H_{24}O_2Si_2$ (P) 304.1314, found 304.1296. Anal. Calcd: C, 63.10; H, 7.94. Found: C, 63.24; H, 7.90.

3,4-Dihydro-1,4-epoxy-4-(trimethylsilyl)-2(1*H*)-naphthalenone (14). A solution of the acetal **1** (2.05 g, 12.5 mmol) and catalytic diisopropylamine (0.15 mL) in 40 mL of THF at 0 °C was treated with 26 mmol of methyllithium (in 18 mL of ether.) After 45 min this mixture was added rapidly to a solution of 38 mmol (4.8 mL) of Me_3SiCl in 20 mL of ether. After a few minutes, 12.4 mmol (1.3 mL) of α-acetoxyacrylonitrile in 10 mL of ether was added and the mixture stirred at room temperature for 3 h. The solution was washed with 10% $NaHCO_3$ (3×) and brine, dried over K_2CO_3, and vacuum evaporated to give 70% of **12**/**13** in a ratio of 73/27 (by NMR integration of the bridgehead proton signals, doublets and singlets, respectively).

This product, without further purification, was treated with KOH (1.8 g) in 30 mL of methanol, at 0 °C for 3.5 h. Normal workup and chromatography (neutral alumina, 10% ether/Skelly-solv) gave three products, in order of elution: **8** (0.37 g, 13%); **14** (0.63 g, 22%); **4** (1.34 g, 65%.) Compound **14**: oil; ^1H NMR δ 0.35 (s, 9 H), 1.95 (d, 1 H, J = 16 Hz, endo methylene), 2.45 (d, 1 H, J = 16 Hz, exo methylene), 4.95 (s, 1 H, bridgehead), 7.3 (br s, 4 H); MS/Cl calcd for $C_{13}H_{17}O_2Si$ (P + H) 233.0997, found 233.1005.

Reaction of 15 with LTMP/Me_3SiCl: Formation of 16 and 9,10-Dihydro-9,10-epoxy-9-(trimethylsilyl)anthracene (17). The reaction of **15**[12] (92 mg) and 5 equiv (0.3 mL) of Me_3SiCl with 4 equiv of LTMP in 15 mL of THF at 0 °C was monitored TLC and showed no remaining **15** after 6 h. The buffer workup was used and the crude product chromatographed on silica gel (20% ether/Skelly-solv). The first fraction, 96 mg (62%) was the bis(trimethylsilyl) derivative **16**, identical with material reported previously.[12] Further elution gave 35 mg (30%) of **17**, which was recrystallized from aqueous methanol, mp 123–124 °C. **17**: ^1H NMR δ 0.44 (s, 9 H), 6.03 (s, 1 H), 7.0 and 7.3 (2 m, symmetrical AA'BB' pattern, 8 H); MS calcd for $C_{17}H_{18}OSi$ (P) 266.1127, found 266.1099. Anal. Calcd: C, 76.64; H, 6.81. Found: C, 76.13; H, 6.95.

Reaction of 18 with LTMP/Me_3SiCl: Formation of 19 and (20 + 21). The reaction of 86 mg of **18**,[12] 0.36 mL of Me_3SiCl, and 4 equiv of LTMP in 5 mL of THF (ice bath) was complete (loss of **18**) within 1 h. The usual workup followed by chromatography on silica gel (20% CH_2Cl_2/Skelly-solv with 1% triethylamine) gave two fractions. The first, 14 mg (11%) was **19**, identified by comparison with authentic material.[12] The second was a mixture of isomers **20** + **21** (85/15), with relative amounts determined by integration of pertinent NMR signals and identification base on comparison with the spectra of **18** and **19**. The major isomer **20** had ^1H NMR signals at δ 0.45 (s, 9 H) and 6.51 (s, 1 H), while the minor **21** had the analogous absorptions at δ 0.50 (s, 9 H) and 6.21 (s, 1 H); the mixture displayed the expected complex pattern[12] between δ 6.90–7.88 for the aromatic protons: MS calcd for $C_{21}H_{23}OSi$ (P) 316.1283, found 316.1333.

Reactions of 22 with LTMP/Me_3SiCl. Numerous runs were made with this substrate, at dry ice, ice bath, and room temperature, with various amounts of base and Me_3SiCl, including up to tenfold excesses. Competing reactions and similar chromatographic behavior of the products made it difficult to control for, or isolate, pure samples of some of the materials.

1,4-Dihydro-1,4-epoxy-1-(trimethylsilyl)naphthalene (23). This material was isolated in ca. 90% purity (remainder **25**) from several reactions carried out in THF at −78 °C to room temperature, with 4–8 equiv each of LTMP and Me_3SiCl, by chromatography as the second fraction eluted (after **24**). In a representative experiment, 166 mg (1.15 mmol) of **22** and 4.6 mmol of Me_3SiCl in 8 mL of THF (dry ice/acetone bath) was treated with 4.6 mmol of LTMP dissolved in 2 mL of THF. TLC indicated that all of **22** had been consumed after 1 h. The usual workup and chromatography gave 100 mg of **23** (50%, some losses may be due to volatility). Bridgehead silylated **23**: oil; ^1H NMR δ 0.30 (s, 9 H), 5.60 (br s, 1 H, bridgehead), 6.8 (m, 2 H, Ar), 7.06 (br s, 2 H, vinyl), 7.2 (m, 2 H, Ar); MS calcd for $C_{13}H_{16}OSi$ 216.0969, found 216.0955.

1,3-Bis(trimethylsilyl)-1,4-dihydro-1,4-epoxynaphthalene (24). The first fraction isolated by chromatography (oil, 45 mg, 30%) was a bis(trimethylsilyl) derivative: MS calcd for $C_{16}H_{24}OSi_2$ 288.1366, found 288.1372. Compound **24**: ^1H NMR δ 0.08 (s, 9 H, vinyl Me_3Si), 0.30 (s, 9 H, bridgehead Me_3Si), 5.76 (s, 1 H, bridgehead), 6.89 (m, 2 H, Ar) 7.06 (s, 1 H, vinyl), 7.2 (m, 2 H, Ar). Difference NOE spectra were obtained, which established the 1,3 relationship of the Me_3Si groups as described in the text.

Evidence for the Formation of 1,4-Dihydro-1,4-epoxy-2-(trimethylsilyl)naphthalene (25). A −78 °C reaction in THF solvent (15 mL) of **22** (177 mg, 1.22 mmol), 2 equiv of Me_3SiCl, and 1.5 equiv of LTMP still exhibited a major TLC spot for **22** (along with one other corresponding to **23**) after 26 h. The mixture was quenched at this point by pouring the −78 °C solution into a large volume of pentane/buffer (to avoid freezing.) The residue after normal workup was chromatographed on silica gel (Skelly-solv), giving only two fractions, the first being the monosilylated material and the second starting material **22**. The former (72 mg, 27%) was analyzed by MS, which showed (confirming TLC evidence) that it contained no bis(silylated) material; along with a significant parent ion, small peaks at m/z 190 and 118, attributed 1-(trimethylsilyl)isobenzofuran and isobenzofuran ions, respectively, were observed. The latter indicates the presence of bridgehead unsilylated material; since no **22** was present, this supports structure **25**. The ^1H NMR of this mixture showed that the major component was **23** (ca. 84%); the minor component (**25**) exhibited two discernible absorptions, at δ 0.01 (vinyl Me_3Si) and at 5.70 (bridgehead proton proximal to the vinyl Me_3Si). The other bridgehead proton was partially obscured by the analogous absorption of **23**. Integration of the bridgehead and Me_3Si region was consistent with this interpretation.

Subsequent treatment of this product mixture with 10 equiv of LTMP/Me_3SiCl (THF, ice bath, 1 h), gave after chromatography a mixture of **24** and **26**; discernible ^1H NMR signals attributed to **26** appear at δ 0.25 (Me_3Si) and 6.91 (vinyl), with the aromatic region for both isomers giving rise to multiplets at δ 6.8–6.9 and 7.1–7.17: MS, m/z (relative intensity) 288 (P, 3), 262 (P − C_2H_2, 2), 190 (P − $C_5H_{10}Si$, 13.)

Reaction of 27 with LTMP/Me_3SiCl. The starting material **27**[20] was prepared[21] by generation of benzyne in the presence of

(20) Wolthuis, E. *J. Org. Chem.* **1961**, *26*, 2215.

2-methylfuran. A sample, 233 mg in 10 mL of THF at 0 °C, was treated with 6 equiv of Me_3SiCl followed by 4 equiv of LTMP in 10 mL of THF. After 0.5 h, the mixture was quenched by adding it to Skelly-solv and washing with buffer (3 × 20 mL). Evaporation and chromatography (30 g of neutral alumina, 10% ether/Skelly-solv with 1% triethylamine) gave two products, **28** (oil, 177 mg, 54%) and **29** (oil, 68 mg, 24%.)

28: ^1H NMR δ 0.30 (s, 9 H), 1.91 (s, 3 H), 6.75 (d, 1 H, J = 5.5 Hz, vinyl), 6.93 (m, 3 H, 2 Ar and 1 vinyl), 7.14 (m, 2 H); MS/Cl calcd for $C_{14}H_{18}OSi$ 230.1126, found 230.1129.

29: ^1H NMR δ 0.09 (s, 9 H), 1.92 (s, 3 H), 5.70 (s, 1 H, bridgehead), 6.89 (s, 1 H, vinyl), 6.95 (m, 2 H), 7.16 (m, 2 H); MS/Cl found 230.1130.

(21) The benzyne was generated by slow concurrent addition (two separatory funnels) of anthranilic acid (13.7 g in DME solvent) and ethyl nitrile (20 mL) to a refluxing solution of 2-methylfuran (70 mL) in DME (70 mL.) Distillation gave 9.3 g (59%) of **27**: bp 59 °C (0.4 torr); ^1H NMR δ 1.91 (s, 3 H), 5.61 (d, 1 H, J = 2 Hz, bridgehead), 6.75 (d, 1 H, J = 5.5 Hz, vinyl proximal to methyl), 6.95 (m, 3 H, 2 Ar and 1 vinyl), 7.15 (m, 2 H).

Acknowledgment. Financial support of this work by the University of California Cancer Research Coordinating Committee is gratefully acknowledged. We thank Randy Jackson for carrying out the preparation of **27**, Dr. Ata Shirazi for obtaining the difference NOE spectra of **24**, and Dr. Hugh Webb for obtaining MS spectra.

Dynamic Stereochemistry of Imines and Derivatives. 19. Mutarotation and *E*–*Z* Isomerization of Chiral Imines in [$^2H_4$]Methanol Solution[1]

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Received May 28, 1985

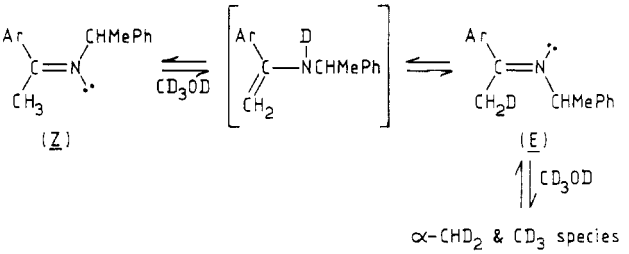
NMR studies indicate that the origin of the mutarotation of optically active *N*-[1-phenylethylidene]-1-phenylethylamine (**1**) and *N*-[1-(1′-naphthyl)ethylidene]-1-phenylethylamine (**2**) in CD_3OD solution is *E*–*Z* isomerization and not tautomerization to the enamine as proposed previously for imine **1**. An equilibrium overshoot effect was observed during the isomerization of imine **2**. It is concluded that the *E*–*Z* isomerization probably proceeds via a thermodynamically unstable enamine which is not observable by NMR. A second dynamic process occuring in **2** is assigned to atropisomerism about the naphthyl–imino bond in the hindered (*Z*)-imine.

The mutarotation of chiral imines derived from optically pure 1-phenylethylamine has been extensively studied over the past 15 years by Perez-Ossorio and co-workers.[2-6] The origin of the mutarotation was rationalized either in terms of *E*–*Z* isomerization or a restricted rotation around bonds between the imino group and substituents.[2-5] Recently an alternative explanation involving imine → enamine tautomerization alone has been advanced in this journal[6] to account for the observed mutarotation of imine **1** in methanol solvent. In support of this hypothesis it was reported[6] that the ^{13}C NMR spectrum of imine **1** on standing in CD_3OD solution was essentially that expected for the enamine tautomer.

Previous work in these laboratories has shown that in CD_3OD solution, imines closely related to **1** undergo *E*–*Z* isomerization with concomitant deuteration of the vinylic methyl group.[7] It was suggested[7] that the isomerization proceeded via a transient enamine intermediate which was less energetically stable than the imine and was not observed in the NMR spectra. Accordingly the proposal[6] that the enamine tautomer of imine **1** was more stable than the imine in CD_3OD solution was of considerable interest and merited further investigation in the light of related studies reported here.

Imine **2**, which is structurally related to **1**, exhibited mutarotation following dissolution of the crystals in CH_3OH at ambient temperature; $[\alpha]_D$ decreased exponentially from ca. +277° to +133°. The mutarotation was much slower in CD_3OD and gave a markedly nonexponential plot of optical rotation vs. time (Figure 1). A parallel ^1H NMR study of the imine in CD_3OD showed a change in the *E*:*Z* the distribution with time which closely followed the profile of the mutarotation curve (Figure 1). Spectra recorded a few minutes after dissolution indicated that the crystalline form of imine **2** consisted exclusively of the *Z* isomer. On standing in CD_3OD the compound slowly equilibrated to a final isomer distribution *Z*:*E* = 78:22, and the close correspondence of the curves in Figure

Scheme I



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