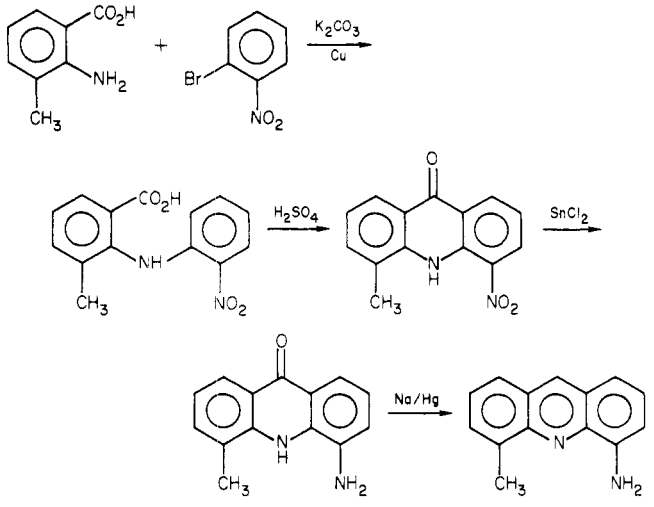
Scheme I



length from 470 to 520 nm. A plot of % R vs. X_{H_2O} is given in Figure 2. Despite the uncertainty in the % R values, Figure 2 depicts clearly the ability of the probe to sort ethanol from water but not water from ethanol.[10]

Since AMA has a large hydrocarbon region, we can reasonably postulate that ethanol molecules preferentially solvate the probe in ethanol–water mixtures. Even the ammonium ion moiety should be specifically solvated by ethanol which, according to Franks and Ives,[11] is more basic (a better electron-pair donor) than water. Consequently, adding 0.1–0.8 mol fraction of water to ethanol hardly affects the solvent shell surrounding the AMA, and the 4-amino group remains the favored protonation site. In 100% water, however, the acridine protonates on the ring nitrogen because steric effects related to the 5-methyl group play no role here. As small amounts of ethanol are added to water, the solvation shell of AMA rapidly becomes rich in ethanol, thereby inducing a proton shift from the ring nitrogen to the 4-amino group nitrogen.

Kinetic studies of many solvolyses in ethanol–water mixtures show distinct minima in ΔH^* at 0.8–0.9 mol fraction of water.[12,13] Partial molal heats of solution for a wide variety of compounds in ethanol–water mixtures give endothermic maxima also in the 0.8–0.9 region.[14] These extrema have been attributed to the fact that 0.1–0.2 mol fraction of ethanol in water actually *increases* solvent structuredness;[11] the trend reverses with additional ethanol. Figure 2 does not manifest these changes in solvent structure, probably because they affect both sides of the prototropic equilibrium equally. If this is true, then AMA offers a useful means for detecting specific solvation without the attendant complexities and uncertainties associated with "structure-making" and "structure-breaking" effects.

Experimental Section

4-Amino-5-methylacridine. This compound was prepared according to Scheme I following known procedures closely. In the first step, 3-methylanthranilic acid (Research Organic/Inorganic Chemical Corp.) and 1-bromo-2-nitrobenzene (Aldrich), active copper powder,[15] potassium carbonate, and cyclohexanol were heated to 175 °C as described by Albert and Goldacre.[8] Cyclization mediated by concentrated sulfuric acid produced 4-nitro-5-methylacridone.[8] Since a direct reduction of the acridone to the final product[8] failed in our hands, we carried out the transformation in two steps. The nitro group was initially reduced to the amino group with stannous chloride dihydrate in concentrated hydrochloric acid.[16] The crude product in 90% ethanol/10% water was then treated with sodium amalgam (City Chemical Corp.) and sodium bicarbonate to give 4-amino-5-methylacridine.[8] After repeated crystallizations from heptane, the compound melted at 110–111 °C (lit.[8] mp 111 °C) and gave a satisfactory elemental analysis. Anal. Calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.56; H, 5.98; N, 13.46.

Procedure. An appropriate volume of 4-amino-5-methylacridine in absolute ethanol (0.001 to 0.10 M) was added with the aid of a micropipet to a volumetric flask partially filled with a particular ethanol–water mixture. The desired acidity was attained by adding a small quantity of 1.0 or 2.0 N aqueous HCl, and the flask was then filled to the mark with the same ethanol–water mixture. Since the acridine appeared sensitive to light, solutions were protected by aluminum foil and used immediately after preparation. Most spectra were traced using 1.10×10^{-3} M 4-amino-5-methylacridine solutions thermostated at 25.0 °C in a Cary 14 spectrophotometer.

Acknowledgment. This work was supported by grants from the National Science Foundation and the National Institutes of Health.

Registry No. 4-Amino-5-methylacridine, 3408-00-2; 3-methylanthranilic acid, 4389-45-1; 1-bromo-2-nitrobenzene, 577-19-5.

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Ring Expansion of 3-Methoxy-6-vinyl-7,8,9,10-tetrahydro-6(5*H*)-benzocyclooctenol

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Received June 22, 1979

Relatively few effective routes[1] to benzo-substituted medium-sized rings are available and fewer still have been applied to systems with substituents on the benzo group. In an earlier paper,[2] we described a reaction sequence which resulted in ring expansion of benzosuberone (**1a**) to a ten-membered ring system **4a**. We were particularly interested in oxygen functionality at the 3-position of benzosuberone because it relates to our synthetic work and because it could provide some mechanistic information.

By use of earlier procedures,[3] benzosuberone (**1a**) was nitrated[4] and converted to the 3-hydroxy derivative **1c** which was methylated with dimethyl sulfate to give **1b**. Trimethylsilyl cyanide (Me_3SiCN) was added to **1b** by using the 18-crown-6 complex of potassium cyanide as a catalyst.[5] This step sometimes gave low conversion to product but normally gave good yields if freshly distilled Me_3SiCN and freshly prepared catalyst were used. The reduction to the amino alcohol followed by treatment with nitrous acid proceeded smoothly to **2b**. The addition of

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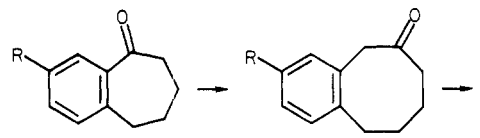
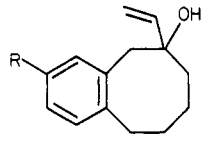


1a, R = H
b, R = OMe
c, R = OH

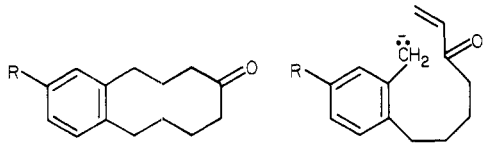
2a-c



3a-c

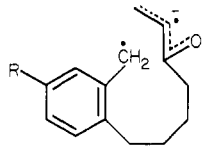
vinylmagnesium bromide utilized a technique wherein the enolate side product is reconverted to ketone, which is reacted again with the Grignard reagent to give complete reaction[6] to **3b**. Demethylation of **3b** to **3c** was carried out with sodium thiobutoxide.[7]

Treatment of **3b** with potassium hydride in hexamethylphosphoric triamide (HMPT)[8] gave the ring-expanded ketone **4b** as the only volatile product. Contrariwise, similar treatment of the hydroxy analogue, **3c**, gave no evidence of rearrangement. Measurement of the rearrangement kinetics of **3a** and **3b** revealed that the methoxy group caused a threefold enhancement (at 30.0 °C, $k_{3a} = 0.025 \pm 0.003$ and $k_{3b} = 0.076 \pm 0.006$ min^{-1}).



4a-c

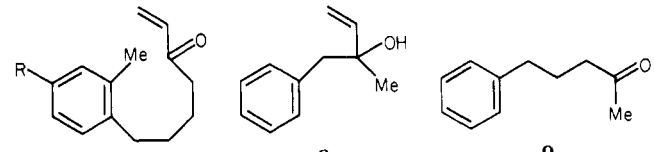
5



6

We have postulated[2] that this type of [1,3] sigmatropic rearrangement could be concerted, as the [3,3] analogues appear to be,[9] or they could involve cleavage to a benzylic anion, **5**, which then undergoes intramolecular Michael addition. A radical, radical anion **6**, is also a conceivable intermediate.[9b] The enhanced rate of the methoxy case, **3b** (for[10] meta OCH_3, $\sigma = +0.12$), and the lack of reactivity of the hydroxy case, **3c**, which would be a meta O^- under the reaction conditions, suggests that substantial negative charge builds up at the benzylic position. Thus a rate-determining formation of **6** seems unlikely, although it could still be an intermediate involved in the Michael addition[11] of **5**. The data seem most consistent with formation of intermediate **5** in the rate-determining step or with a concerted process where the transition state is highly polarized in the same sense as **5**.

If **5** is an intermediate, it might be expected to form some **7**, e.g., by transfer of a proton from the methylene α to the ketone. No **7** was detected in the volatile products; however, the terminal α,β-unsaturated ketone moiety of **7** would be prone to polymerization under the basic conditions. The NMR spectrum of the crude product from **3a** showed no detectable singlet for an aryl methyl near δ 2.2; crude products from **3b** showed a small extra peak (<10%) at δ 2.22 which could be such a methyl (3,4-dimethylanisole[12] exhibits methyl singlets at δ 2.21 and 2.17). It appears that formation of **7** is at most a very minor process for **3a,b**; however, cleavage is quite significant for the acyclic analogue, **8**, which gave a 21% yield of [1,3]-shift product **9** and 9% of the cleavage product, toluene.[13] The formation of toluene and the low overall yield from **8** do not prove that an anionic intermediate (e.g., **5**) must be involved in the [1,3]-shift process, but show that this behavior is consistent with such an intermediate since the reactive parts are not tied together in **8** as they are in **3a,b**.



7 8 9

Experimental Section

Spectral measurements were made on Perkin-Elmer 727 B, Varian HA-100, Atlas CH 7, and CDC 110 B instruments.[14] Gas–liquid chromatography was carried out with Varian 1200 or 920 instruments, in most cases by using a 5 ft × $^1/_4$ in. 6.5% OV101 on 8–100-mesh Chromosorb G column.

3-Methoxybenzosuberan-5-one (1b) was prepared by methylation[15] of the hydroxy derivative (**1c**), which was prepared by the published method.[3] Vacuum transfer gave a 63% yield of **1b**: IR (neat) 2930, 2860, 1670, 1600, 1570, 1495, 1460, 1410, 1320, 1280, 1260, 1240, 1205, 1180, 1170, 1150, 1100, 1080, 1040, 970, 860, 840, 740, 700 cm^{-1}; NMR ($CDCl_3$) δ 7.17 (d, J = 2 Hz, 1 H), 7.04 (d, J = 8 Hz, 1 H), 6.85 (dd, J = 2, 8 Hz, 1 H), 3.8 (s, 3 H), 2.85 (t, J = 6 Hz, 2 H), 2.65 (t, J = 6 Hz, 2 H), 1.94–1.7 (m, 4 H).

3-Methoxy-5-(aminomethyl)-6,7,8,9-tetrahydro-5-benzocycloheptenol. A 0.046-g portion of catalyst consisting of a 1:1 complex of 18-crown-6 and KCN was placed in a flask under nitrogen.[5] A 0.73-mL (5.8 mmol) portion of freshly distilled trimethylsilyl cyanide was then injected at room temperature followed by 1.014 g (5.3 mmol) of **1b**. The reaction was stirred for 3 h, and then 0.504 g (12.6 mmol) of $LiAlH_4$ in 20 mL of ethyl ether (distilled from Na/benzophenone) was added dropwise. The reaction was stirred overnight and treated sequentially with 0.5 mL of water, 0.5 mL of 15% NaOH, and 1.5 mL of water. The white precipitate was extracted with ether (10 × 100 mL), and the combined extracts were extracted with 10% H_2SO_4 (4 × 250 mL). The aqueous layer was brought to pH 10 with 15% NaOH and extracted with ether (3 × 300 mL). The ether extracts were dried ($MgSO_4$) and concentrated to give 0.984 g of granular solid: mp 109–112.5 °C; IR (KBr) 3355, 3295 (NH stretch buried in broad OH peak), 2010, 2850, 2755, 1600, 1480, 1445, 1170, 1105, 1095, 1040, 970, 950, 740 cm^{-1}; NMR ($CDCl_3$) δ 7.37 (d, J = 3 Hz, 1 H), 7.02 (d, J = 8 Hz, 1 H), 6.68 (dd, J = 3, 8 Hz, 1 H), 3.82 (s, 3 H), 3.22 (d, J = 12 Hz, 1 H), 2.93 (d, J = 12 Hz, 1 H), 2.93–2.74 (m, 2 H), 2.30–1.74 (br m, 9 H); exact mass m/e 221.143 (calcd for $C_{13}H_{19}O_2N$, 221.143).

3-Methoxy-7,8,9,10-tetrahydro-6(5*H*)-benzocyclooctenone (2b). Rearrangement of 1.5 g of the above amino alcohol by the earlier procedure[2] produced 1.00 g of ketone **2b**: IR (neat) 2930, 2850, 1700, 1610, 1580, 1500, 1460, 1320, 1250, 1160, 1105, 1040,

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995, 950, 810, 760, 700 cm^{-1}; NMR (CCl_4) δ 7.03 (d, J = 8 Hz, 1 H), 6.80–6.56 (m, 2 H), 3.77 (s, 3 H), 3.66 (s, 2 H), 2.86–2.68 (m, 2 H), 2.36–2.16 (m, 2 H), 2.0–1.6 (m, 4 H); exact mass m/e 204.115 (calcd for $C_{13}H_{16}O_2$, 204.116).

3-Methoxy-7,8,9,10-tetrahydro-6-vinyl-6(5*H*)-benzocyclooctenol (3b). Eight milliliters of 0.96 M vinylmagnesium bromide in THF was added dropwise with stirring to 1.00 g of **2b** in 5 mL of THF while raising the temperature to 65 °C. After 1.25 h, the reaction was cooled and treated with 0.25 mL of methanol. This procedure[6,16] was repeated twice more and gave, after the usual workup,[2] 0.673 g (59% yield) of **3b**: IR (neat) 3300 (br), 2920, 2850, 1600, 1580, 1500, 1460, 1320, 1295, 1260, 1200, 1160, 1040, 1000, 920, 810, 760, 780 cm^{-1}; NMR ($CDCl_3$) δ 7.14–7.04 (m, 1 H), 6.96–6.70 (m, 2 H), 6.14 (dd, J = 10, 17 Hz, 1 H), 5.34 (dd, J = 1, 17 Hz, 1 H), 5.14 (dd, J = 1 Hz, 1 H), 3.8 (s, 3 H), 3.0–2.6 (m, 4 H), 1.9–1.35 (m, 7 H); exact mass m/e 232.146 (calcd for $C_{15}H_{20}O_2$, 232.146).

3-Methoxy-5,6,9,10,11,12-hexahydro-8(7*H*)-benzocyclodecenone (4b) was prepared in 38% yield from **3b** by the earlier procedures[2] using KH and HMPT at room temperature for 40 min: IR (neat) 2920, 2850, 1698, 1605, 1570, 1500, 1480, 1450, 1365, 1295, 1245, 1230, 1212, 1180, 1140, 1100, 1040, 1000, 995, 970, 930, 910, 880, 860, 850, 800, 750, 700 cm^{-1}; NMR (CCl_4) δ 7.02 (d, J = 8 Hz, 1 H), 6.6 (m, 2 H), 3.72 (s, 3 H), 2.7–1.5 (br m, 14 H); exact mass m/e 232.146 (calcd for $C_{15}H_{20}O_2$, 232.146).

Rate Measurements of 3a,b. A constant-temperature bath, maintained at 30.0 °C by a Bailey proportional controller, was equipped with a mechanical stirrer which had a strong magnetic bar in the bath. Three test tubes with magnetic stirrers were equilibrated under nitrogen in the bath with 0.1 g of **3a**, 0.1 g of **3b**, and 0.7 g of hexane-washed potassium hydride (KH) in 8 mL of HMPA, respectively. After 10 and 2 min, respectively, 5–9 aliquots (150 μL each) were taken sequentially to 2 half-lives of reaction. Each aliquot was quenched in ether–water, washed five times with water, dried over $MgSO_4$, and analyzed by GLC. An internal GLC standard indicated a 50–60% material balance. Duplicate, independent rate measurements by use of the logarithm of the peak-area ratio **3a,b**/(**3a,b** + **4a,b**) vs. time and with analysis by least-squares methods gave rate constants for **3a** of 0.0227 and 0.0277 and for **3b** of 0.798 and 0.728 with correlation coefficients of 0.8795, 0.9954, 0.9949, and 0.9968, respectively.

Attempted Rearrangement of 3c. Compound **3b** was demethylated with sodium thiobutoxide by the method described earlier.[7] The resultant diol **3c** (very broad IR band at 3300 cm^{-1} and OH peak at δ 5.6) was treated with KH/HMPA in the usual way for 2.3 h. The NMR spectrum of the recovered material strongly resembled starting **3c**, and the IR spectrum showed no absorption in the carbonyl region.

2-Methyl-1-phenylbut-3-en-2-ol (8) was prepared in 86% yield from phenyl-2-propanone by reaction with vinylmagnesium bromide:[2] IR (neat) 3550, 3440, 3090, 3060, 3030, 2980, 2930, 1500, 1460, 1420, 1380, 1290, 1240, 1160, 1100, 1060, 1040, 1020, 1000, 920, 880, 770, 720, 700 cm^{-1}; NMR (CCl_4) δ 7.14 (s, 5 H), 5.90 (d of d, J = 18, 11 Hz, 1 H), 5.08 (dd, J = 2, 18 Hz, 1 H), 4.94 (dd, J = 2, 11 Hz, 1 H), 2.72 (s, 2 H), 2.18 (OH), 1.18 (s, 3 H); exact mass m/e 162.104 (calcd for $C_{11}H_{14}O$, 162.104).

Rearrangement of 8. Treatment of **8** with KH and HMPT as before[2] for 4 h at room temperature gave 2% recovered **8**, 9% of toluene, and 21% of 5-phenyl-2-pentanone: IR (neat) 3090, 3060, 3030, 3000, 2940, 2860, 1710, 1670, 1600, 1500, 1460, 1370, 1360, 1250, 1220, 1180, 1160, 1080, 1030, 750, 700 cm^{-1}; NMR (CCl_4) δ 6.95–7.35 (m, 5 H), 2.55 (t, J = 7 Hz, 2 H), 2.31 (t, J = 7 Hz, 2 H), 1.98 (s, 3 H), 1.82 (pentet, J = 7 Hz, 2 H); the mass spectrum matched the published spectrum.[17]

Acknowledgment. This investigation was supported by NIH Research Grant No. R01 HD08550 from the National Institute of Child Health and Human Development. The research was also assisted by Institution Research Grants from the National Science Foundation for the purchase of NMR spectrometers. We thank Mrs. Susan Randall for capable NMR assistance and Richard Weilesec for mass spectra on the CDC 110B instrument at the University of Oregon.

Registry No. 1b, 6500-62-5; **1c**, 5454-03-5; **2b**, 71885-72-8; **3a**, 64871-09-6; **3b**, 71885-73-9; **3c**, 71885-74-0; **4b**, 71885-75-1; **8**, 42548-91-4; **9**, 2235-83-8; 3-methoxy-5-(aminomethyl)-6,7,8,9-tetrahydro-5-benzocycloheptenol, 71885-76-2; phenyl-2-propanone, 103-79-7; toluene, 108-88-3; vinyl bromide, 593-60-2.

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Mechanism of Hydrolysis of Aryl Vinyl Selenides. Selenium-Stabilized Carbonium Ions

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Received May 9, 1979

Recently there have been reported[1-8] several comparisons of the relative effect that oxygen and sulfur heteroatoms have on stabilizing an adjacent carbonium ion center. One such investigation[4] focused on a comparison of rate constants for the hydrolysis of vinyl ethers and vinyl sulfides, which are reactions with a rate-determining proton transfer to the olefinic bond, generating the α-heteroatom stabilized cation.

$$RYCH{=}CH_2 + H^+ \xrightarrow{\text{slow}} RY\overset{+}{C}HCH_3 \xrightarrow{\text{fast}} RYH + CH_3CHO$$

Organoselenium compounds have recently received considerable attention as reagents for organic syntheses,[9] and it is well established that, like sulfur, selenium has a pronounced effect of stabilizing an adjacent carbanion center. We felt it of interest to determine the extent to which selenium is also capable of stabilizing an adjacent carbonium ion center. Accordingly, we have prepared a series of aryl vinyl selenides and report here a study of their acid-catalyzed hydrolysis.

Experimental Section

Aryl vinyl ethers and aryl vinyl sulfides were the same as those used previously.[4] Benzene selenol was the gift of Dr. D. G. Garratt and was distilled immediately before use. Aryl vinyl selenides ($XC_6H_4SeCH{=}CH_2$) were prepared as follows. Ethylene was bubbled through a solution in methylene chloride of the aryl selenenyl chloride (ArSeCl) to produce a β-(arylseleno)ethyl chloride[10] ($ArSeCH_2CH_2Cl$). The solvent was removed, the adduct taken up in dimethyl sulfoxide, and potassium *tert*-butoxide added. After being stirred for 3 h, the solution was poured into an excess of water and extracted with ether. The ether was dried

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