(11) H. Beierbeck and J. K. Saunders, *Can. J. Chem.*, **53**, 1307 (1975).
(12) R. Hollenstein and W. von Philipsborn, *Helv. Chim. Acta*, **56**, 320 (1973).
(13) A. Rieker and S. Berger, *Org. Magn. Reson.*, **4**, 857 (1972).
(14) K. Jankowski, *J. Org. Chem.*, submitted.
(15) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds", Holden-Day, San Francisco, Calif., 1967, p 118.

Novel Formation of Anti-Bredt Olefins from 2,3,4,5,6,7-Hexahydro-1,6-methano-1*H*-4-benzazonin-7-ols

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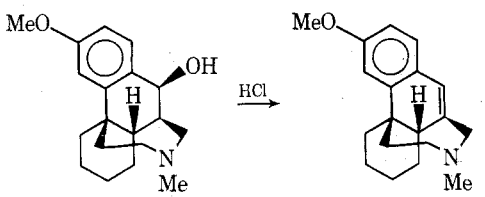
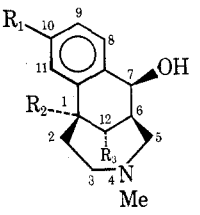
While there are many examples of formation of anti-Bredt olefins[1] by Hofmann elimination[2] or dehydrohalogenation[3] of the corresponding bridgehead substituted compounds or by dehalogenation[4] of 1,2-dihalo compounds, formation by elimination of compounds substituted adjacent to the bridgehead carbon is less common.[5] Recently, we reported that *B/C-cis*-6-methoxy-12-methyl-1,3,4,9,10,10a-hexahydro-2*H*-10,4a-methanoiminoethano-9β-phenanthrol (1), when treated with HCl, gave an olefinic compound **2** in violation of Bredt's rule.[6] This interesting result, which may be not only a new example of formation of anti-Bredt olefin but the first instance of the formation of anti-Bredt olefin under acidic condition, prompted us to examine reaction of the closely related 2,3,4,5,6,7-hexahydro-1,6-methano-1*H*-4-benzazonin-7β-ol[7] derivatives **3a–d** with HCl which might be expected to give similar results.

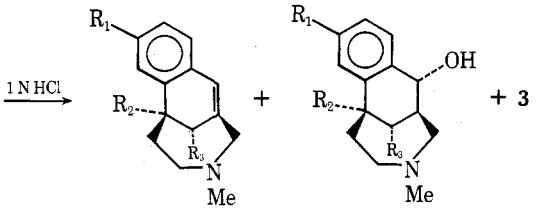


1 2

When 1,4,12α-trimethyl-10-methoxy-2,3,4,5,6,7-hexahydro-1,6-methano-1*H*-4-benzazonin-7β-ol (**3d**)[8] was refluxed with 1 N HCl for 1.5 h, anti-Bredt olefin **4d** was afforded in high yield. The structure of **4d** was confirmed from its NMR and mass spectra. In the NMR spectrum **4d** exhibited an olefinic proton signal at δ 6.16 (singlet). The mass spectrum showed a M^+ peak at *m/e* 257.1778 ($C_{17}H_{23}NO$). Treatment of 4-methyl- (**3a**),[9] 1,4-dimethyl- (**3b**), and 1,4-dimethyl-10-methoxy-2,3,4,5,6,7-hexahydro-1,6-methano-1*H*-4-benzazonin-7β-ol (**3c**)[8] with 1 N HCl gave the corresponding olefins **4a–c**, 7α-hydroxy[4] **5a–c**, and 7β-hydroxy compounds **3a–c** (product ratios are summarized in Table I), respectively. Each of the products was isolated by column chromatography and identified by NMR and/or mass spectrometry. The olefins **4a–c** exhibited, in the NMR, olefinic proton signals as singlets at δ 6.24 for **4a**, 6.25 for **4b**, and 6.27 for **4c**, respectively. The mass spectra showed M^+ at *m/e* 199.1370 ($C_{14}H_{17}N$) for **4a**, 213.1525 ($C_{15}H_{19}N$) for **4b**, and 243.1631 ($C_{16}H_{21}NO$) for **4c**,



3a, 3b, 3c, 3d



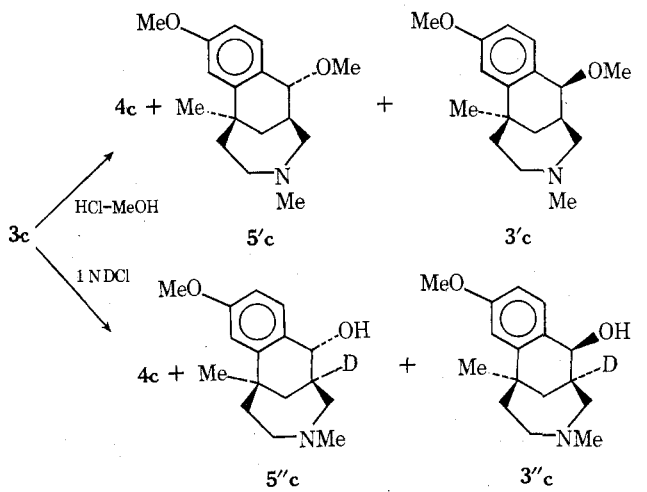
4a, 4b, 4c, 4d **5a, 5b, 5c,**

a, $R_1 = R_2 = R_3 = H$
b, $R_1 = R_3 = H$; $R_2 = Me$
c, $R_1 = OMe$; $R_2 = Me$; $R_3 = H$
d, $R_1 = OMe$; $R_2 = R_3 = Me$

respectively. The 7α-hydroxy isomers **5a–c** and the 7β-hydroxy isomers **3a–c** were easily distinguishable by NMR spectrometry, since the coupling constants of the C-7 proton with the C-6 proton of the former should be smaller than those of the latter (**5a**, 2.2 Hz at δ 4.26, vs. **3a**, 4.0 Hz at δ 4.88; **5b**, 2.8 Hz at δ 4.28, vs. **3b**, 5.5 Hz at δ 4.87; **5c**, 3.5 Hz at δ 4.26, vs. **3c**, 5.0 Hz at δ 4.83).

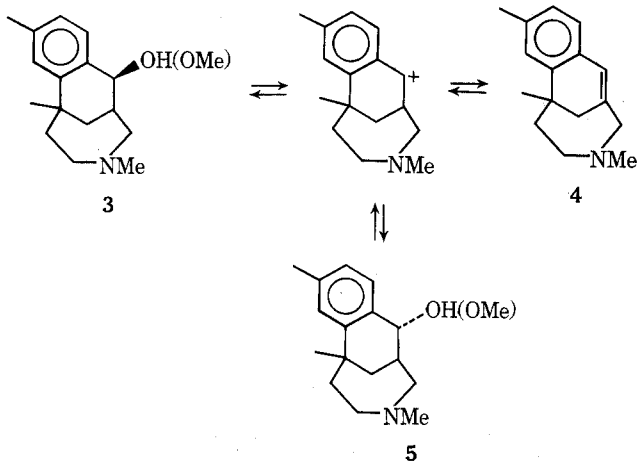
Reaction of 7α-hydroxy compound **5a** with 1 N HCl for 1.5 h gave a mixture of **3a, 4a,** and **5a.** Similarly, **5b** gave **3b, 4b,** and **5b.** Olefin **4a,** when refluxed with 1 N HCl, gave a mixture of **3a, 4a,** and **5a.** Similarly, **4b** gave **3b, 4b,** and **5b.** Under these conditions **4d,** however, was recovered unchanged.

When the reaction of compound **3c** with HCl was carried out in methanol a mixture of **4c,** 7β-methoxy **3'c,** and 7α-methoxy derivative **5'c** was afforded in the ratio 1:3:3 (by GLC). The structures of **3'c** and **5'c** were established by the NMR spectra and elemental analysis. We observed further that reaction of **3c** in 1 N DCl gave a mixture of olefin **4c,** 6-deuterio-7β-hydroxy **3''c,** and 6-deuterio-7α-hydroxy derivative **5''c** in the ratio 1:2:4 (by NMR). The incorporation of deuterium at the C-6 position was confirmed by the change of C-7 proton signals of **3c** and **5c** from doublet to singlet.



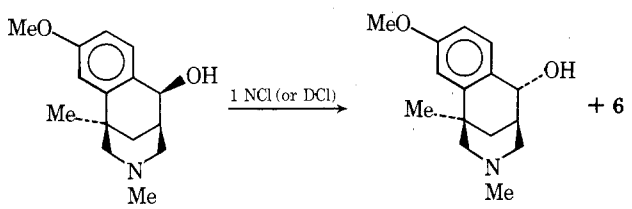
These experimental results made it evident that anti-Bredt olefins **4** are easily formed from the corresponding 7-hydroxy- (or methoxy-) 2,3,4,5,6,7-hexahydro-1,6-methano-1*H*-4-benzazonine derivatives **3** and **5** by treatment with acid, and that 7-hydroxy (or methoxy) derivatives **3** and **5** are formed, under these conditions, not by a simple substitution of the

Scheme I



corresponding isomers but by hydration (or addition of methanol) of the anti-Bredt olefins. Thus, it may be suggested that these three compounds, **3, 4,** and **5,** are in equilibrium as shown in Scheme I. In the case of **4d,** attack of hydronium ion at C-6 (the first step of the hydration) is greatly hindered by 12α-methyl, so that no C-7 hydroxy compound is formed.

For comparison, 1,3-dimethyl-9-methoxy-1,2,3,4,5,6-hexahydro-1,5-methano-3-benzazocin-6β-ol (**6**) was refluxed with



6 7

1 N HCl. From the reaction mixture no olefinic compound was detected but only 6β-hydroxy **6** and 6α-hydroxy derivative **7** (ratio 1:4) were obtained. The reaction of **6** in 1 N DCl gave no C-5 deuterio compound, which suggested that no anti-Bredt olefin is formed, even as an intermediate, from compound **6** (or **7**) under these conditions. The failure of **6** to form the corresponding olefin may be caused by the great strain to form an eight-membered trans cyclic olefin.

Experimental Section

General Comments. The following compounds were prepared by known procedure: **3a,**[9] **3c,** and **3d.**[8]

The melting points were determined on a micro melting point apparatus (Yanagimoto) and are uncorrected. The NMR ($CDCl_3$, δ, Me_4Si as internal standard) were recorded, at 60 MHz, on a JEOL PMX-60 spectrometer or at 100 MHz on a JEOL PS-100 spectrometer. Ir spectra were taken on a Hitachi 215 grating infrared spectrometer. Mass spectra were recorded on a JEOL JMS-01SG mass spectrometer. GLC analyses were performed on a Shimadzu GC-4B PTF flame-ionization chromatograph using an internal standard method (**4a, 4b,** and **4c** previously isolated were used as standard). The column contained SE-30 (20% on Shimalite, 1 m × 3 mm), and the column temperature was 250 °C. Nitrogen was used as carrier.

Preparation of 3b. A solution of $ClCO_2Et$ (43.2 g) in benzene (200 ml) was added to a refluxing solution of 4-methyl-4-(2-dimethylaminoethyl)-3,4-dihydronaphthalen-1(2*H*)-one[10] (60 g) in benzene (800 ml) over 45 min. The mixture was refluxed for 2 h. The cooled mixture was washed with 5% HCl and H_2O and dried ($MgSO_4$). After evaporation of the benzene, the residue (pale yellow syrup, 61 g) was refluxed with 12 M HCl (900 ml) for 18 h. Evaporation of the solvent gave 37 g of a crystalline mass, which was recrystallized from MeOH to give a pure sample of 4-methyl-4-(2-methylaminoethyl)-3,4-dihydronaphthalen-1(2*H*)-one hydrochloride, mp 206–208 °C. Anal. Calcd for $C_{14}H_{19}NO$·HCl: C, 66.25; H, 7.95; N, 5.52. Found: C, 66.23; H, 8.11; N, 5.68.

The above amino ketone HCl (35 g) was dissolved in MeOH (780 ml) and Formalin (74 ml). The mixture was kept at 40 °C for 3 days.

Table I. Products and Ratios in Reaction of 2,3,4,5,6,7-Hexahydro-1,6-methano-1*H*-4-benzazonine Derivatives

Registry no.	Compd	Reflux in 1 N HCl, h	Product ratio[a] 3	4	5
60384-67-0	**3a**	1.5	2.5	1	2.5
60384-68-1	**3b**	1.5	2.5	1	2.5
59122-63-3	**3c**	1.5	2.0	1	2.6
59122-62-2	**3d**	1.5	0	1	0
60363-75-9	**4a**	3.5	0.63	1	0.63
60363-76-0	**4b**	3.0	2.5	1	2.5
60363-77-1	**4d**	2.0	0	1	0
60384-69-2	**5a**	3.5	1.7	1	1.7
60384-70-2	**5b**	3.0	2.5	1	2.5

[a] Obtained by gas chromatography.

After evaporation to dryness, the residue was dissolved in H_2O, washed with benzene, basified with 10% NaOH, extracted with Et_2O, and dried (K_2CO_3). The residue (16.3 g) from the ethereal solution was dissolved in MeOH and added to a solution of picric acid (16 g) in MeOH to give 21.5 g of 1,4-dimethyl-2,3,4,5-tetrahydro-1,6-methano-1*H*-4-benzazonin-7(6*H*)-one picrate, mp 188–195 °C. From the pricrate 9.7 g of the free base was obtained: bp 140–150 °C (1 mmHg); ir (neat) 1675 cm^{-1} (C=O). Hydrochloride: mp 174–180 °C (from MeOH); NMR (CD_3OD) δ 1.60 (3 H, s, C-1 Me), 2.95 (3 H, s, N-Me), 7.30–7.90 (3 H, m, C-9, 10, 11 H), 8.04 (1 H, double d, J = 7.5, J' = 1.5 Hz, C-8 H). Anal. Calcd for $C_{15}H_{19}NO$·HCl: C, 67.79; H, 7.58; N, 5.27. Found: C, 67.90; H, 7.50; N, 5.48.

To a solution of the free base of the above ketone (8.7 g) in MeOH (200 ml) was added $NaBH_4$ (5 g) over 30 min under ice cooling. After stirring for 3 h at room temperature, the mixture was acidified with AcOH, evaporated to dryness, dissolved in H_2O, made alkaline with 20% NaOH, extracted with $CHCl_3$, and dried (K_2CO_3). Evaporation of the solvent gave 8 g of crude **3b** as a solid mass, which was recrystallized from Et_2O to give 5.5 g of pure sample: mp 102–105 °C; ir (Nujol) 3300 cm^{-1} (OH); NMR δ 1.27 (3 H, s, C-1 Me), 2.23 (3 H, s, N-Me), 2.70 (1 H, s, exchangeable with D_2O, OH), 4.87 (1 H, d, J = 5.5 Hz, C-7 H), 7.10–7.25 (3 H, m, C-9, 10, 11 H), 7.45–7.75 (1 H, m, C-8 H). Anal. Calcd for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.05. Found: C, 78.03; H, 8.86; N, 5.86.

Preparation of 6. To a stirred mixture of 1,3-dimethyl-9-methoxy-1,2,3,4,5,6-hexahydro-1,5-methano-3-benzazocine[11] (1.6 g) and $Na_2Cr_2O_7$ (3.1 g) in 100 ml of 1 N H_2SO_4 was added 10 N H_2SO_4 (215 ml) with ice cooling during 2 h. After stirring for 15 h at room temperature, the mixture was cooled (ice bath), basified with 12 M NH_4OH, extracted with Et_2O, and dried (K_2CO_3). Evaporation of the ether gave 1 g of 1,3-dimethyl-9-methoxy-1,2,3,4-tetrahydro-1,5-methano-3-benzazocin-6(5*H*)-one as a viscous syrup: ir (neat) 1690 cm^{-1} (C=O); NMR δ 1.36 (3 H, s, C-1 Me), 2.05 (3 H, s, N-Me), 3.82 (3 H, s, O-Me), 6.75 (1 H, double d, J = 9.0, J' = 2.0 Hz, C-8 H), 6.77 (1 H, d, J = 2.0 Hz, C-10 H), 7.96 (1 H, d, J = 9.0 Hz, C-7 H), 1.50–3.27 (7 H, m). Picrate: mp 140–144° (from MeOH). Anal. Calcd for $C_{15}H_{19}NO_2$·$C_6H_3N_3O_7$: C, 53.17; H, 4.67; N, 11.81. Found: C 53.07; H, 4.65; N, 11.61.

A mixture of the ketone (1.0 g) and $LiAlH_4$ (1.0 g) in dioxane (40 ml) was refluxed for 6.5 h. After cooling, the mixture was treated with aqueous Rochelle salt solution, extracted with $CHCl_3$, and dried (K_2CO_3). Evaporation of the solvent gave 1.0 g of crude **6.** Distillation under reduced pressure gave pure sample as a colorless oil: bp 145–165 °C (5 mmHg) (bath temperature); ir (neat) 3420 cm^{-1} (OH); NMR δ 1.23 (3 H, s, C-1 Me), 2.01 (3 H, s, N-Me), 3.73 (3 H, s, O-Me), 2.75 (1 H, broad d, exchangeable with D_2O, OH), 4.79 [1 H, broad t, changed to doublet (J = 7.0 Hz) by treatment with D_2O, C-6 H], 6.65 (1 H, d, J = 2.5 Hz, C-10 H), 6.66 (1 H, double d, J = 9.0, J' = 2.5 Hz, C-8 H), 7.38 (1 H, d, J = 9.0 Hz, C-7 H). Picrate: mp 217–219 °C (from MeOH). Anal. Calcd for $C_{15}H_{21}NO_2$·$C_6H_3N_3O_7$: C, 52.94; H, 5.08; N, 11.76. Found: C, 52.60; H, 5.07; N, 11.69.

Reaction of 3a, 3b, 3c, 3d, 4a, 4b, 4d, 5a, 5b, and 6 with 1 N HCl. As an example, we will describe the reaction of **3c** with 1 N HCl. All other reactions were done following a similar procedure and we will report the experimental and spectroscopic data related to the compounds which were not already published.

I. Reaction of 3c. A solution of **3c** (800 mg) in 1 N HCl (50 ml) was refluxed for 1.5 h. After cooling, the mixture was basified with 10% NaOH, extracted with $CHCl_3$, and dried (Na_2SO_4). Evaporation of

the solvent gave 500 mg of **3c + 4c + 5c** as a yellow, viscous syrup, which was chromatographed on silica gel (Wakogel C-200). Elution with $CHCl_3$–MeOH–12 M NH_4OH (150:10:1) gave pure samples of **3c** (150 mg), **4c** (80 mg), and **5c** (200 mg).

3c: NMR δ 1.28 (3 H, s, C-1 Me), 2.35 (3 H, s, N-Me), 3.83 (3 H, s, O-Me), 4.83 (1 H, d, J = 5.0 Hz, C-7 H), 6.78 (1 H, d, J = 3.0 Hz, C-11 H), 6.88 (1 H, double d, J = 8.0, J' = 3.0 Hz, C-9 H), 7.60 (1 H, d, J = 8.0 Hz, C-8 H), 1.55–3.25 (10 H, m).

4c: bp 110–120 °C (0.01 mmHg) (bath temperature); ir (neat) 1670 cm^{-1} (C=C); NMR δ 1.36 (3 H, s, C-1 Me), 2.36 (3 H, s, N-Me), 3.16 and 3.28 (2 H, AB, J_{AB} = 10.0 Hz, C-5 H_2), 3.84 (3 H, s, O-Me), 6.27 (1 H, s, C-7 H), 6.73 (1 H, double d, J = 8.5, J' = 2.5 Hz, C-9 H), 6.88 (1 H, d, J = 2.5 Hz, C-11 H), 7.17 (1 H, d, J = 8.5 Hz, C-8 H), 1.45–2.70 (6 H, m); mass spectrum m/e 243.1631 (M^+, calcd for $C_{16}H_{21}NO$, 243.1632).

5c: mp 73–75 °C (from hexane); ir (Nujol) 3350 cm^{-1} (broad, OH); NMR δ 1.31 (3 H, s, C-1 Me), 2.21 (3 H, s, N-Me), 2.63 (1 H, s, exchangeable with D_2O, OH), 3.82 (3 H, s, O-Me), 4.26 (1 H, d, J = 3.5 Hz, C-7 H), 6.76 (1 H, double d, J = 8.0, J' = 2.5 Hz, C-9 H), 6.82 (1 H, d, J = 2.5 Hz, C-11 H), 7.24 (1 H, d, J = 8.0 Hz, C-8 H), 1.45–3.20 (9 H, m). Anal. Calcd for $C_{16}H_{23}NO_2$: C, 73.53; H, 8.87; N, 5.36. Found: C, 73.26; H, 8.88; N, 5.30.

II. Reaction of 3a. 3a gave an 80% yield of **3a + 4a + 5a. 4a:** bp 105–110 °C (0.02 mmHg) (bath temperature); ir (neat) 1680 cm^{-1} (C=C); NMR δ 2.36 (3 H, s, N-Me), 2.95 and 3.61 (2 H, AB, J_{AB} = 10.0 Hz, C-5 H_2), 6.24 (1 H, s, C-7 H), 1.17–2.95 (7 H, m), 7.13 (4 H, m, aromatic H); mass spectrum m/e 199.1370 (M^+, calcd for $C_{14}H_{17}N$, 199.1361).

5a: mp 108–109 °C (from hexane); ir (Nujol) 3270 cm^{-1} (OH); NMR δ 2.20 (3 H, s, N-Me), 2.47 (1 H, s, exchangeable with D_2O, OH), 4.26 (1 H, d, J = 2.2 Hz, C-7 H), 1.50–3.25 (10 H, m), 7.18 (4 H, m, aromatic H). Anal. Calcd for $C_{14}H_{19}NO$: C, 77.37; H, 8.81; N, 6.45. Found: C, 77.03; H, 8.64; N, 6.50.

III. Reaction of 3b. 3b gave a 70% yield of **3b + 4b + 5b. 4b:** bp 110–115 °C (0.02 mmHg) (bath temperature); ir (neat) 1680 cm^{-1} (C=C); NMR δ 1.37 (3 H, s, C-1 Me), 2.34 (3 H, s, N-Me), 3.13 and 3.50 (2 H, AB, J_{AB} = 10.0 Hz, C-5 H_2), 4.25 (1 H, s, C-7 H), 7.17 (4 H, m, aromatic H), 1.20–2.70 (6 H, m); mass spectrum m/e 213.1525 (M^+, calcd for $C_{15}H_{19}N$, 213.1517).

5b: mp 103–104 °C (from hexane); ir (Nujol) 3250 cm^{-1} (OH); NMR δ 1.34 (3 H, s, C-1 Me), 2.22 (3 H, s, N-Me), 4.28 (1 H, d, J = 2.8 Hz, C-7 H), 7.27 (4 H, m, aromatic H), 1.20–3.30 (10 H, m). Anal. Calcd for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.06. Found: C, 77.68; H, 9.03; N, 6.28.

IV. Reaction of 3d. 3d gave a 75% yield of **4d. 4d:** bp 120–130 °C (0.01 mmHg) (bath temperature); ir (neat) 1670 cm^{-1} (C=C); NMR δ 0.79 (3 H, d, J = 7.0 Hz, C-12 Me), 1.31 (3 H, s, C-1 Me), 2.37 (3 H, s, N-Me), 3.05 and 3.45 (2 H, AB, J_{AB} = 10.0 Hz, C-5 H_2), 3.80 (3 H, s, O-Me,), 6.16 (1 H, s, C-7 H), 6.63 (1 H, double d, J = 8.0, J' = 2.5 Hz, C-9 H), 6.78 (1 H, d, J = 2.5 Hz, C-11 H), 7.06 (1 H, d, J = 8.0 Hz, C-8 H), 1.50–2.73 (5 H, m); mass spectrum m/e 257.1778 (M^+, calcd for $C_{17}H_{23}NO$, 257.1780).

V. Reaction of 4a. Reflux of **4a** with 1 N HCl for 3.5 h gave a 90% yield of **3a + 4a + 5a.**

VI. Reaction of 4b. Reflux of **4b** with 1 N HCl for 3 h gave an 85% yield of **3b + 4b + 5b.**

VII. Reaction of 4d. Reflux of **4d** with 1 N HCl for 3 h gave a 95% yield of recovery of **4d.**

VIII. Reaction of 5a. Reflux of **5a** for 3.5 h gave an 85% yield of **3a + 4a + 5a.**

IX. Reaction of 5b. Reflux of **5b** with 1 N HCl for 3 h gave a 90% yield of **3b + 4b + 5b.**

X. Reaction of 6. Reflux of **6** (211 mg) with 1 N HCl (20 ml) for 1 h gave a mixture of **6** and **7** (185 mg). The mixture was chromatographed on a silica gel column. Elution with $CHCl_3$–MeOH (150:10) gave pure samples of **6** and **7.** Compound **6** was identified by comparison of ir spectrum with that of the authentic sample.

7: colorless, viscous oil; ir (neat) 3340 cm^{-1} (OH); NMR δ 1.27 (3 H, s, C-1 Me), 2.00 (3 H, s, N-Me), 3.75 (3 H, s, O-Me), 4.47 (1 H, s, C-6 H), 6.67 (1 H, double d, J = 9.0, J' = 2.5 Hz, C-8 H), 6.70 (1 H, d, J = 2.5 Hz, C-10 H), 7.15 (1 H, d, J = 9.0 Hz, C-7 H). Picrate: mp 197–203 °C (from MeOH). Anal. Calcd for $C_{15}H_{21}NO_2 \cdot C_6H_3N_3O_7$: C, 52.94; H, 5.08; N, 11.76. Found: C, 53.14; H, 5.06; N, 11.57.

Reaction of 3c with HCl in MeOH. A solution of **3c** (500 mg) and 12 M HCl (1 ml) in MeOH (10 ml) was refluxed for 2 h, the solvent, evaporated, diluted with H_2O, basified with 10% NaOH, and extracted with $CHCl_3$. After drying (Na_2SO_4), the solvent was evaporated to give 300 mg of **3'c + 4c + 5'c** (3:1:3). The mixture was chromatographed on silica gel (Wakogel C-200). Elution with $CHCl_3$–MeOH–12 M NH_4OH (150:10:1) gave pure samples of **3'c** (110 mg), **4c** (30 mg, identified by comparison of ir spectrum with that of the authentic sample) and **5'c** (100 mg).

3'c: bp 150–160 °C (1.5 mmHg) (bath temperature); NMR δ 1.22 (3 H, s, C-1 Me), 2.24 (3 H, s, N-Me), 3.48 (3 H, s, C-7 O-Me), 3.76 (3 H, s, C-10 O-Me), 4.28 (1 H, d, J = 4.0 Hz, C-7 H), 6.69 (1 H, double d, J = 8.0, J' = 2.8 Hz, C-9 H), 6.62 (1 H, d, J = 2.8 Hz, C-11 H), 7.43 (1 H, d, J = 8.0 Hz, C-8 H), 1.56–2.88 (9 H, m). Anal. Calcd for $C_{17}H_{25}NO_2$: C, 74.14; H, 9.15; N, 5.09. Found: C, 73.88; H, 8.91; N, 4.70.

5'c: bp 150–160 °C (1.5 mmHg) (bath temperature); NMR 1.28 (3 H, s, C-1 Me), 2.22 (3 H, s, N-Me), 3.33 (3 H, s, C-7 O-Me), 3.76 (3 H, s, C-10 O-Me), 3.68 (1 H, d, J = 2.5 Hz, C-7 H), 6.64 (1 H, double d, J = 8.0, J' = 2.5 Hz, C-9 H), 6.72 (1 H, d, J = 2.5 Hz, C-11 H), 7.07 (1 H, d, J = 8.0 Hz, C-8 H). Anal. Calcd for $C_{17}H_{25}NO_2$: C, 74.14; H, 9.15; N, 5.09. Found: C, 74.29; H, 9.15; N, 5.09.

Reaction of 3c with 1 N DCl. A solution of **3c** (101 mg) in 1 N DCl (6 ml) was refluxed for 1 h. After cooling, the mixture was basified with 10% NaOH, extracted with $CHCl_3$, and dried (K_2CO_3). Evaporation of the solvent gave 99 mg of a yellow oil. The NMR showed that it was a mixture of olefin **4c,** 6-deuterio-7β-hydroxy **3''c,** and 6-deuterio-7α-hydroxy compound **5''c** in the ratio 1:2:4 [C-7 proton signal of **4c,** δ 6.20 (singlet); C-7 proton signal of **3''c,** δ 4.78 (singlet); C-7 proton signal of **5''c,** δ 4.25 (singlet)].

Reaction of 6 with 1 N DCl. Reflux of **6** (90 mg) in 1 N DCl (6 ml) gave a mixture of **6** and **7** (70 mg). The NMR showed that substitution of C-5 hydrogen of **6** and **7** with deuterium did not occur at all.

Registry No.—3'c, 60363-78-2; **3''c,** 60363-79-3; **4c,** 60363-80-6; **5c,** 60409-21-4; **5'c,** 60409-20-3; **5''c,** 60384-71-6; **6,** 60363-81-7; **7,** 60384-72-7; **7** picrate, 60409-18-9; 4-methyl-4-(2-dimethylaminoethyl)-3,4-dihydronaphthalen-1(2*H*)-one, 60363-82-8; 4-methyl-4-(2-methylaminoethyl)-3,4-dihydronaphhalen-1(2*H*)-one HCl, 54782-00-2; 1,4-dimethyl-2,3,4,5-tetrahydro-1,6-methano-1*H*-4-benzazonin-7(6*H*)-one picrate, 60384-73-8; 1,4-dimethyl-2,3,4,5-tetrahydro-1,6-methano-1*H*-4-benzazonin-7(6*H*)-one, 54782-07-9; 1,4-dimethyl-2,3,4,5-tetrahydro-1,6-methano-1*H*-4-benzazonin-7(6*H*)-one HCl, 60384-74-9; 1,3-dimethyl-9-methoxy-1,2,3,4,5,6-hexahydro-1,5-methano-3-benzazocine, 37639-69-3; 1,3-dimethyl-9-methoxy-1,2,3,4-tetrahydro-1,5-methano-3-benzazocin-6(5*H*)-one, 60363-83-9.

References and Notes

(1) (a) G. L. Buchanan, *Chem. Soc. Rev.*, **3,** 41 (1974); (b) R. Keese, *Angew. Chem., Int. Ed. Engl.*, **14,** 528 (1975).
(2) (a) J. R. Wiseman, H.-K. Foon, and C. J. Ahola, *J. Am. Chem. Soc.*, **91,** 2812 (1969); (b) J. R. Wiseman and J. A. Chong, *ibid.*, **91,** 7775 (1969); (c) M. Kim and J. D. White, *ibid.*, **97,** 451 (1975).
(3) (a) N. Takanishi, Y. Fujikura, Y. Inamoto, H. Ikeda, and K. Aigami, *J. Chem. Soc., Chem. Commun.*, 372 (1975); (b) C. B. Quinn and J. R. Wiseman, *J. Am. Chem. Soc.*, **95,** 1342, 6120 (1973); (c) H. O. Krabbenfoft, J. R. Wiseman, and C. B. Quinn, *ibid.*, **96,** 258 (1974).
(4) J. R. Wiseman and W. A. Pletcher, *J. Am. Chem. Soc.*, **92,** 956 (1970).
(5) W. Carruthers and M. I. Qureshi, *J. Chem. Soc. C*, 2238 (1970).
(6) S. Shiotani, *J. Org. Chem.*, **40,** 2033 (1975).
(7) The α and β designations used in this paper are with respect to the hydroaromatic ring. The compounds **3a–d** and **6** were prepared from the corresponding C-7 (C-6 for **6**) keto compounds by reduction with $LiAlH_4$ or $NaBH_4$. These reactions should give the 7β-hydroxy (6β- for **6**) derivatives, since the reagents attack from the less hindered side of the molecule.
(8) S. Shiotani, T. Kometani, K. Mitsuhashi, T. Nozawa, A. Kurobe, and O. Futsukaichi, *J. Med. Chem.*, **19,** 803 (1976).
(9) S. Shiotani and T. Kometani, *Chem. Pharm. Bull.*, **21,** 1053 (1973).
(10) E. L. May and J. G. Murphy, *J. Org. Chem.*, **20,** 257 (1955).
(11) S. Shiotani, T. Kometani, and K. Mitsuhashi, *J. Med. Chem.*, accepted.

(*E*)- and (*Z*)-4-Methyl-5-[5-(2,6,6-trimethylcyclohexen-1-yl)-3-methyl-2(*E*),4(*E*)-pentadienylidene]-2(5*H*)-furanone. Synthesis and Spectral Properties

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In the course of some other research on vitamin A and its derivatives, we became interested in the preparation of the