Synthesis of 7-Halo-6*H*-benz[*cd*]azulen-6-ones

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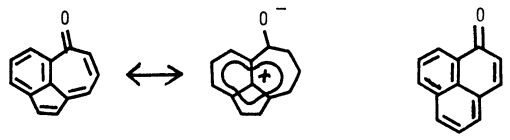
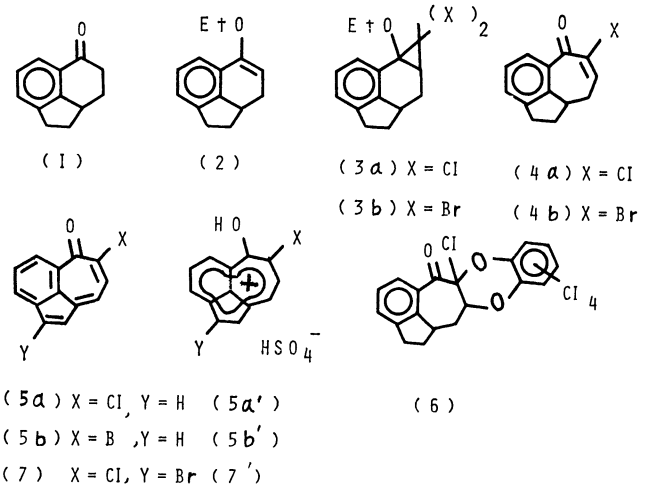
Synopsis. 7-Bromo-6*H*-benz[*cd*]azulen-6-one, 7-Chloro-6*H*-benz[*cd*]azulen-6-one and its derivative were prepared in four steps starting from tetrahydroacenaphthene. Formation of the corresponding cations in strong acid is suggested on the basis of ^{1}H NMR and UV spectra.

6*H*-Benz[*cd*]azulen-6-one (**A**), one of the isomers of phenalenone (**B**),[1] was synthesized from acenaphthene,[2] but although its physical properties were reported no ^{1}H NMR spectral data were given on its cation. Because of the poor yield, chemical and biological properties have not been examined. We wish to report an alternative preparation of the title compounds in good yields, together with the ^{1}H NMR and UV spectra of their cations in strong acid.



(A) (B)

The reaction of 2*a*,3,4,5-tetrahydroacenaphthen-5-one (**1**)[3] with triethyl orthoformate in the presence of a catalytic amount of *p*-toluenesulfonic acid gave enol ether (**2**) as colorless crystals. Dihalocyclopropanation[4] of **2** proceeded smoothly by using chloroform and bromoform in the presence of potassium *t*-butoxide in cyclohexane to give dihalocyclopropyl ethers (**3a**) and (**3b**) as colorless needles in 73% and 25% yields, respectively. Treatment of **3a** and **3b** with silver nitrate in aqueous methanol[5] afforded ring expanded halo enones (**4a**) and (**4b**) as colorless needles in 64% and 66% yields, respectively. Treatment of **4a** with *o*-chloranil in refluxing benzene gave a trace amount of the desired fully conjugated compound (**5a**) together with colorless crystals (**6**), presumably formed by cyclo-addition of the ene moiety of **4a** with *o*-chloranil.[6] Dehydrogenation of **4a** was achieved by using 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in refluxing dioxane to give **5a** as reddish needles in 75% yield. Bromo compound **4b** also gave (**5b**) under the same reaction conditions. Dehydrogenation of **4a** with *N*-bromosuccinimide (NBS) afforded 2-bromo-7-chloro compound (**7**) as deep red needles in 58% yield. Its structure was assigned by comparison of ^{1}H NMR spectra with those of **5a**. The fact that the treatment of **5a** with NBS resulted only in the recovery of the starting material is significant as regards the mechanism of formation of **7**. The ^{1}H NMR and UV spectra of **5a**, **5b**, and **7** in strong acid such as concd sulfuric acid suggest the formation of cations **5a**′, **5b**′, and **7**′, respectively. The chemical shifts of **5a**, **5b**, and **7** in concd H_2SO_4 are about 0.6—1.6 ppm lower than those in $CDCl_3$ (Table 1). The UV spectra of these compounds in the acid show absorption maxima at around 550—600 nm, in a greater wavelength by *ca.* 200 nm than those in EtOH. These cations regenerated the original ketones quantitatively when diluted with a large amount of water.



(1) (2) (3a) X = Cl (4a) X = Cl
(3b) X = Br (4b) X = Br
(5a) X = Cl, Y = H (5a′)
(5b) X = B, Y = H (5b′)
(7) X = Cl, Y = Br (7′)
(6)

Experimental

Melting points and boiling points are uncorrected. Mass spectra were measured on a JEOL JMS-OISG-2 mass

TABLE 1. ^{1}H NMR DATA OF **5a**, **5a**′, **5b**, **5b**′, **7** AND **7**′

	δ/ppm (Multiplicity, *J*/Hz)							
	H_1	H_2	H_3	H_4	H_5	H_8	H_9	Δ_{ppm}
5a	6.40 (d, 5.6)	6.77 (d, 5.6)	7.37 (m)		8.05 (m)	7.59 (d, 8.8)	6.64 (d,8.8)	0.67—1.61
5a′	7.07 (d, 5.6)	7.50 (d, 5.6)	8.10 (m)		8.78 (m)	9.10 (d, 10.2)	8.25 (d, 10.2)	
5b	6.55 (d, 6.0)	6.97 (d, 6.0)	7.50 (m)		8.20 (m)	8.07 (d, 8.0)	6.70 (d, 8.0)	0.50—1.40
5b′	7.05 (d, 6.0)	7.55 (d, 6.0)	8.10 (m)		8.75 (d, 7.2)	9.35 (d, 9.6)	8.10 (m)	
7	6.82 (s)	—	7.28 (m)		8.00 (m)	7.66 (d, 10.0)	6.80 (d, 10.0)	0.78—1.64
7′	7.60 (s)	—	8.12 (m)		8.80 (d, 8.0)	9.30 (d, 10.0)	8.44 (d, 10.0)	

spectrometer, IR spectra on a JASCO IRA-1, UV spectra on a Hitachi EPS-3T spectrometer, and ^{1}H NMR on a JEOL JNM-MH-100 (100 MHz) and Hitachi R-24B (60 MHz) spectrometer in deuteriochloroform and concd sulfuric acid containing tetramethylsilane and dichloromethane as an internal standard, respectively.

2a,3-Dihydro-5-ethoxyacenaphthene (2). Triethyl orthoformate (72 ml, 0.44 mol) and *p*-toluenesulfonic acid (0.72 g) were added at 25 °C to a solution of ketone (**2**)[3] (28 g, 0.16 mol) in dry ethanol (540 ml). The mixture was stirred at room temperature for 12 h and then distilled under reduced pressure to give 33 g (98%) of enol ether (**2**); bp 110—112 °C/5 Torr, (1 Torr=133.322 Pa), which crystallized on standing. Recrystallization from ethanol gave colorless needles; mp 79—81 °C. IR (neat) 2950, 1630 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.85—7.20 (m, 4H), 4.70 (q, 2H, J=7.2 Hz), 3.52 (m, 4H), 2.40 (m, 1H), 1.45 (t, 3H, J=7.2 Hz), 1.52 (m, 1H); MS *m/e* 200 (M$^+$). Found: C, 83.93; H, 7.79%. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05%.

Dichlorocyclopropanation of 2. Potassium *t*-butoxide (20 g, 18 mmol) was added to a solution of 3.7 g (19 mmol) of **2** in 90 ml of dry cyclohexane, and the solution was cooled to 10 °C in an ice bath. Freshly distilled chloroform (50 g, 42 mmol) was then added to the solution over a period of 12 h. After addition of 100 ml of water, the mixture was extracted with chloroform and worked up in the usual way. The crude product was chromatographed on silica gel (hexane and benzene, 1 : 1) to give 4.8 g (73%) of **3a**, which was recrystallized from hexane to give colorless needles; mp 98—100 °C; IR (KBr) 3020, 2950, 1540 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.42 (m, 3H), 3.52 (q, 2H, J=7.2 Hz), 3.12 (m, 1H), 2.86 (m, 3H), 2.32 (m, 1H), 2.04 (m, 1H), 1.52 (m, 1H), 1.16 (t, 3H, J=7.2 Hz); MS *m/e* 284 (M$^+$). Found: C, 63.70; H, 5.79%. Calcd for $C_{15}H_{16}Cl_2O$: C, 63.62; H, 5.70%.

Dibromocyclopropanation of 2. The dibromo compound (**3b**) was prepared from **2** (6.0 g 30 mmol) by the same method as described above in 25% (2.6 g) yield. It was then recrystallized from hexane to give colorless needles; mp 101—102 °C; IR (KBr) 2960, 1460 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.08 (m, 3H), 3.40 (q, 2H, J=8 Hz), 3.04 (m, 1H), 2.76 (m, 3H), 2.24 (m, 1H), 1.44 (m, 1H), 1.14 (t, 3H, J=8 Hz); MS *m/e* 372 (M$^+$). Found: C, 48.13; H, 4.31%. Calcd for $C_{15}H_{16}Br_2O$: C, 48.42; H, 4.33%.

7-Chloro-1,2,6,9,9a-pentahydrobenz[cd]*azulen-6-one (4a).* A solution of silver nitrate (18 g, 116 mmol) in 530 ml of water was added to a solution of **3a** (7.3 g, 26 mmol) in 1.5 l of ethanol, and then the resulting solution was refluxed for 24 h. After being worked up in the usual way, the crude product was chromatographed on silica gel (benzene) to give 3.6 g (64%) of **4a** and 2.4 g (33%) of **3a**. A pure sample of **4a** was obtained by recrystallization from hexane as colorless needles; mp 66.2—68 °C; IR (KBr) 1640, 1610 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.78 (d, 1H, J=8 Hz), 7.14 (m, 3H), 3.52 (m, 1H), 2.29 (m, 2H), 2.44 (m, 3H), 1.72 (m, 1H); MS *m/e* 220, 218 (M$^+$). Found: C, 71.13; H, 5.15%. Calcd for $C_{13}H_{11}ClO$: C, 71.40; H, 5.07%.

7-Bromo-1,2,6,9,9a-pentahydrobenz[cd]*azulen-6-one (4b).* The bromo compound (**4b**) was obtained from **3b** (2.6 g) by the same method as described above in 66% (1.2 g) yield. It was then recrystallized from ethanol to give colorless needles; mp 87.5—89.5 °C; IR (KBr) 1640, 1610 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.80 (d, 1H, J=8 Hz), 7.32 (m, 3H), 3.52 (m, 1H), 2.88 (m, 2H), 2.40 (m, 3H), 1.66 (m, 1H); MS *m/e* 264, 262 (M$^+$). Found: C, 59.18; H, 3.94%. Calcd for $C_{13}H_{11}BrO$: C, 59.34; H, 4.21%.

7-Chloro-6H-benz[cd]*azulen-6-one (5a)* A solution of **4a** (1.5 g, 6.7 mmol) and DDQ (3.7 g, 16 mmol) in 50 ml of dry dioxane was refluxed for 30 h. The resulting solution was chromatographed on silica gel (benzene) to give 0.39 g (30%) of **5a** and 0.98 g (66%) of **4a**. The yield of **5a** was 75% accumulatively after repetation of the reaction three times with recovered **4a**. Recrystallization from ethanol gave red needles; mp 109—111 °C; IR (KBr) 1620, 1600, 745 cm^{-1}; UV (EtOH) nm (log ε) 240 (4.55), 283 (4.08), 335 (3.43), 385 (4.01); MS *m/e* 216, 214 (M$^+$). Found: C, 72.48; H, 3.18%. Calcd for $C_{13}H_7ClO$; C, 72.74; H, 3.29%.

5a′: UV (concd H_2SO_4) nm (log ε) 251 (4.45), 284 (4.17), 292 (4.19), 332 (3.43), 348 (3.48), 402 (3.08), 422 (3.95), 590 (2.59).

7-Bromo-6H-benz[cd]*azulen-6-one (5b).* A solution of **4b** (0.81 g, 3.1 mmol) and DDQ (1.9 g, 8.2 mmol) in 28 ml of dry dioxane was refluxed for 12 h. The resulting solution was worked up by the same method as described above to give **5b** in 11% (0.09 g) yield and 0.02 g (3%) of recovered **4b**. Recrystallization from ethanol gave deep red needles; mp 123—124.5 °C; IR (KBr) 1610, 1600, 1590 cm^{-1}; UV (EtOH) nm (log ε) 236 (4.60), 275 (4.09), 280 (4.11), 337 (3.83), 385 (4.07); MS *m/e* 260, 258 (M$^+$). Found: C, 59.98; H, 3.00%. Calcd for $C_{13}H_7BrO$: C, 60.26; H, 2.72%.

5b′: UV (concd H_2SO_4) nm (log ε) 245 (4.60), 270 (4.36), 291 (4.75), 330 (3.55), 364 (3.31), 408 (3.81), 418 (3.90), 427 (3.96), 450 (3.43), 470 (2.95), 560 (2.59).

2-Bromo-7-chloro-6H-benz[cd]*azulen-6-one (7).* A solution of 3.1 g (1.4 mmol) of **5a** and 5.0 g (2.8 mmol) of NBS in 45 ml of CCl_4 was refluxed for 3.5 h under irradiation with a 100-W tungsten lamp. The reaction mixture was cooled, filtered and chromatographed on silica gel (benzene) to afford 2.4 g (58%) of **7**, which was recrystallized from ethanol to give deep red needles; mp 171—174 °C; IR (KBr) 1610, 1590, 755 cm^{-1}; UV (EtOH) nm (log ε) 280 (4.19), 336 (3.90), 384 (4.12); MS *m/e* 294 (M$^+$). Found: C, 52.93; H, 1.81%. Calcd for $C_{13}H_6BrClO$: C, 53.19; H, 2.06%.

7′: UV (concd H_2SO_4) nm (log ε) 244 (4.49), 269 (4.45), 287 (4.61), 327 (3.70), 360 (3.52), 540 (2.94).

Cycloadduct of 4a with o-Chloranil. A solution of 1.0 g (4.5 mmol) of **4a** and 2.7 g (11 mmol) of *o*-chloranil in 35 ml of dry dioxane was refluxed for 30 h. The solution was cooled, filtered and chromatographed on silica gel (benzene) to give 0.61 g (29%) of **6** and a trace amount of **5a**. Recrystallization from acetone gave colorless needles; mp 250 °C; IR (KBr) 1700 cm^{-1}; ^{1}H NMR (DMSO-d_6–TMS) δ 7.50—6.90 (m, 4H), 2.30—1.70 (m, 7H); MS *m/e* 468 (M$^+$). Found: C, 49.08; H, 2.45; Cl, 38.20%. Calcd for $C_{19}H_{11}Cl_5O$: C, 49.12; H, 2.45; Cl, 38.16%.

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