Reactions of 7*H*-naphth[3,2,1-*cd*]azulen-7-ones

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6-Chloro-7*H*-naphth[3,2,1-*cd*]azulen-7-ones **9a** and **10a** easily react with some nucleophiles (sodium methoxide, potassium hydrosulfide, and amines) to give the corresponding 6-substituted products. Halogenation of 7*H*-naphth[3,2,1-*cd*]azulen-7-ones with *N*-halosuccinimides occurs at the C-5 position. Grignard reagents add to 7*H*-naphth[3,2,1-*cd*]azulen-7-ones at the seven-membered ring and a subsequent dehydrogenation gives 2-, 3- and 4-substituted products; reactive tendency of the positions of 7*H*-naphth[3,2,1-*cd*]azulen-7-one toward the reagents was 6 ⩾ 3 > 4 > 2, whereas the steric hindrance was (6 >) 4 > 3 > 2. Condensation of 7*H*-naphth[3,2,1-*cd*]azulen-7-ones with active methylene compounds in boiling acetic anhydride occurs at the carbonyl group and gives the corresponding 7-methylene-7*H*-naphth[3,2,1-*cd*]azulene derivatives. 6-Hydroxy-7*H*-naphth[3,2,1-*cd*]azulen-7-one **7** is obtained by the hydrolysis of 6-methoxy-7*H*-naphth[3,2,1-*cd*]azulen-7-one **9b** with hydrobromic acid, in almost quantitative yield. Compound **7** exists in a tautomeric mixture with 7-hydroxy-6*H*-naphth[3,2,1-*cd*]azulen-6-one **8**. Methylation of **7** with diazomethane gives **9b** and 7-methoxy-6*H*-naphth[3,2,1-*cd*]azulen-6-one **18a** in 75% and 25% yield, respectively. Chlorination of **7** with thionyl dichloride also gives a pair of isomers, 5,6-dichloro-7*H*-naphth[3,2,1-*cd*]azulen-7-one **11b** and 5,7-dichloro-6*H*-naphth[3,2,1-*cd*]azulen-6-one **18b**. A tautomerism between 6-(substituted methyl)-7*H*-naphth[3,2,1-*cd*]azulen-7-ones and 7-hydroxy-6*H*-naphth[3,2,1-*cd*]azulen-6-ylidene-methylene derivative is also studied.

7*H*-Naphth[3,2,1-*cd*]azulen-7-one **1** has a highly polarized ketone,[1] resembling phenalenone[2] **2** (Chart 1). The abnormal polarization of 7*H*-naphth[3,2,1-*cd*]azulen-7-ones would modify the ketonic properties as well as aromatic characters, where the seven-membered ring has some tropylium character. In the reactions of phenalenones, characteristic reactions, such as a 1,4-addition with organometallic reagents,[3] the replacement of bromine from 2-bromophenalenone with an amine, in some cases with rearrangement[4] and so on, were observed. Therefore, expecting that the reactions of 7*H*-naphth[3,2,1-*cd*]-azulen-7-ones could give interesting results, we investigated some of their reactions.

Tautomerism of the hydroxyphenalenones, involving prototropic shifts from hydroxy group to carbonyl oxygen,[1,5] is of interest, especially for 9-hydroxyphenalenone, which involves strongly hydrogen-bonded hydroxy ketones (**3A**, **3B**). The resonance energy in a non-alternant conjugation is smaller than that in alternant conjugation, so that the non-alternant conjugated system shows some variety of properties. In studies of the tautomerism of keto–enol equilibration, it is known that acetylcyclopenta[*a*]phenalenone **4A** exists in its isomeric form **4B** predominantly, because of enol-fixation.[6] It is also known that azulenols, such as **5A**, show keto–enol equilibration between 1,2-dihydroazulen-2-one **5B**; the equilibrium is influenced by the nature of the solvent.[7] As a homologous isomer of hydroxyphenalenone, the 4-hydroxy-3*H*-benz[*cd*]-azulen-3-one **6** was synthesized.[8] The ring carbonyl group of 7*H*-naphth[3,2,1-*cd*]azulen-7-one **1** has been found to be highly polarized, so that it is expected that the hydroxy derivative of **1**, such as 6-hydroxy-7*H*-naphth[3,2,1-*cd*]azulen-7-one **7**, has a tautomeric isomer, 7-hydroxy-6*H*-naphth[3,2,1-*cd*]azulen-6-one **8**. In this paper, we report the existence of the tautomerism of 6-hydroxy-7*H*-naphth[3,2,1-*cd*]azulen-7-one and related compounds by chemical and spectroscopic methods.

Results and discussion

It is known that halogenoazulenes react with some nucleophilic reagents to give corresponding substituted azulenes by replacement of the halogeno substituents with the reagents,[9–11] whereas an addition reaction occurred at C-3 in the reaction of 2-bromophenalenone with amines.[4] Because 6-chloro-7*H*-naphth[3,2,1-*cd*]azulen-7-one **9a** has a formal 1-acyl-2-chloroazulene moiety, either substitution or addition could take place. When **9a** was treated with nucleophiles, such as methoxide, sulfide and amines, the chloro substituent was displaced by the nucleophiles and gave the corresponding 6-substituted-7*H*-naphth[3,2,1-*cd*]azulen-7-ones **9b**–**e**. Similar treatment of ethyl 6-chloro-7-oxo-7*H*-naphth[3,2,1-*cd*]azulene-5-carboxylate **10a** gave methyl 6-methoxy-7-oxo-7*H*-naphth[3,2,1-*cd*]azulene-5-carboxylate **10b**.

The calculated total atomic charge of 7*H*-naphth[3,2,1-*cd*]-azulen-7-one suggests that the C-5 position is the most electronegative and would be reactive to electrophiles.[1,12] Therefore it is expected that halogenation would occur at C-5 of 7*H*-naphth[3,2,1-*cd*]azulen-7-ones. Thus, treatment of **9a** with *N*-chlorosuccinimide (NCS) gave 5,6-dichloro-7*H*-naphth-[3,2,1-*cd*]azulen-7-one **11b** quantitatively. Similar treatment of **9a** with *N*-bromosuccinimide (NBS) and **9b** with NBS and *N*-iodosuccinimide (NIS) gave corresponding 5-halogeno-7*H*-naphth[3,2,1-*cd*]azulen-7-ones **11a**, **11c** and **11d**, quantitatively.

It is reported that the reaction of phenalenone with phenylmagnesium bromide, followed by dehydrogenation, gave 9-phenylphenalenone.[3] On the other hand, it is known that the reaction of diethyl azulene-1,3-dicarboxylate with Grignard reagents gave addition products and the reaction of a diethyl 2-alkoxyazulene-1,3-dicarboxylate with phenylmagnesium bromide gave the 2-phenylazulene derivative.[13] Therefore we examined the reaction of 7*H*-naphth[3,2,1-*cd*]azulen-7-ones

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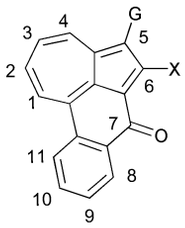
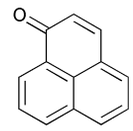


1 : G = X = H
7 : G = H; X = OH
9a : G = H; X = Cl
9b : G = H; X = OMe
9c : G = H; X = SH
9d : G = H; X = NHEt
9e : G = H; X = piperidino
9f : G = H; X = OEt
9g : G = H; X = OAc
10a : G = CO_2Et; X = Cl
10b : G = CO_2Me; X = OMe
10c : G = CO_2Et; X = H
10d : G = CO_2Et; X = Ph
11a : G = Br; X = Cl
11b : G = Cl; X = Cl
11c : G = Br; X = OMe
11d : G = I; X = OMe



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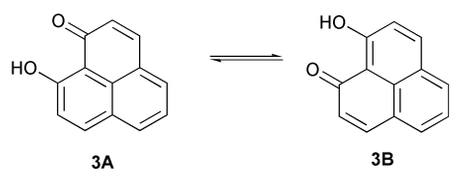
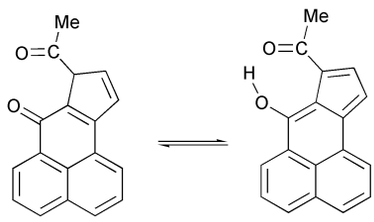
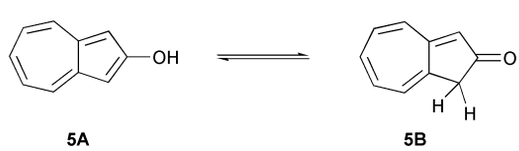


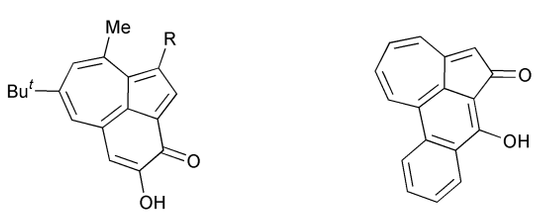
3A **3B**



4A **4B**



5A **5B**



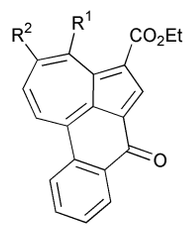
6 **8**

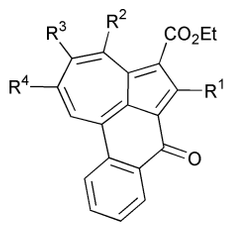
Chart 1

with Grignard reagents. When ethyl 7-oxo-7*H*-naphth[3,2,1-*cd*]azulene-5-carboxylate **10c** was treated with phenylmagnesium bromide followed by dehydrogenation with tetrachloro-*o*-benzoquinone (TCQ), three phenyl-substituted 7*H*-naphth-[3,2,1-*cd*]azulen-7-ones (**10d**, **12** and **13**) were obtained (see Chart 2). On the other hand, the reactions of ethyl 6-chloro-7-oxo-7*H*-naphth[3,2,1-*cd*]azulene-5-carboxylate **10a** with phenylmagnesium bromide followed by dehydrogenation with TCQ gave diphenyl-substituted 7*H*-naphth[3,2,1-*cd*]azulen-7-ones (**14a**–**16a**). The result shows that the reagent displaced the chloro substituent at the 6-position to form the substitution product **10d** first, and then the excess of reagent added to **10d** at the 4-, 3- or 2-position. It is known that the methoxy group is displaced in the reaction of 2-methoxyazulene, but the chloro group was not displaced and an addition reaction occurred in the reaction of diethyl 2-chloroazulene-1,3-dicarboxylate with Grignard reagent.[13] Therefore it is suggested that the halogen of **10a** is more reactive than that of halogenoazulenes. Similar treatment of **10a** with α-naphthylmagnesium bromide and

Table 1 Reactions of ethyl 7-oxo-7*H*-naphth[3,2,1-*cd*]-azulene-5-carboxylates with Grignard reagents

Run	Compounds	Reagents	Products (yield/%)		
1	**10c**	PhMgBr	**10d**(80)	**12**(2)	**13**(2)
2	**10a**	PhMgBr	**14a**(14)	**15a**(32)	**16a**(5)
3	**10a**	α-NaphMgBr	**14b**(9)	**15b**(27)	**16b**(5)
4	**10a**	MeMgI	**14c**(21)	**15c**(9)	**16c**(—)





12 : R^1 = Ph, R^2 = H
13 : R^1 = H, R^2 = Ph

14a : $R^1 = R^2$ = Ph, $R^3 = R^4$ = H
14b : $R^1 = R^2$ = α-Nap, $R^3 = R^4$ = H
14c : $R^1 = R^2$ = Me, $R^3 = R^4$ = H
15a : $R^1 = R^3$ = Ph, $R^2 = R^4$ = H
15b : $R^1 = R^3$ = α-Nap, $R^2 = R^4$ = H
15c : $R^1 = R^3$ = Me, $R^2 = R^4$ = H
16a : $R^1 = R^4$ = Ph, $R^2 = R^3$ = H
16b : $R^1 = R^4$ = α-Nap, $R^2 = R^3$ = H
16c : $R^1 = R^4$ = Me, $R^2 = R^3$ = H

Chart 2

methylmagnesium iodide gave results which are listed in Table 1. These results show that a reaction tendency of the positions of 7*H*-naphth[3,2,1-*cd*]azulen-7-one toward the reagents was 6 ⩾ 3 > 4 > 2, whereas the steric hindrance was (6 >) 4 > 3 > 2. The structures of the obtained compounds were deduced from their spectroscopic data, mainly by ^{1}H NMR spectroscopy, as well as elemental analyses. It is shown that the ester group of compounds **14a**, **14b**, **15a** and **15b** is highly hindered by phenyl and naphthyl groups as seen by spectroscopic results.

Next, we investigated the reaction of the carbonyl group of 7*H*-naphth[3,2,1-*cd*]azulen-7-ones. 2,4-Dinitrophenylhydrazine did not react with **9a** in the presence of hydrochloric acid in boiling ethanol. Hydroxylamine also did not react with **9a** in the presence of sodium acetate in boiling ethanol.

It is known that an activated carbonyl group can condense with active methylene compounds. Therefore we treated **10a** with malononitrile in refluxing acetic anhydride; the reaction gave a complex mixture, from which ethyl 6-chloro-7-dicyanomethylene-7*H*-naphth[3,2,1-*cd*]azulene-5-carboxylate **17d**, where condensation of the methylene moiety with the carbonyl had occurred, was isolated in 15% yield. Similarly, 7*H*-naphth[3,2,1-*cd*]azulen-7-ones (**9a**, **9b**, **10c**) reacted with malononitrile in boiling acetic anhydride to give corresponding condensed products (see Chart 3), and the results are listed in Table 2. In the reaction of **9b** with malononitrile, compound **17c**, an acetylated product at C-5, was obtained together with **17b**. In comparison of the electronic spectra of **17a** and **9a**, the maxima of the absorption bands in **17a** are shifted to longer wavelengths and are strengthened compared with those of **9a** (Fig. 1); this suggested that the large contribution of an extended heptafulvene moiety exists in the ground state of **17a**.

When 6-methoxy-7*H*-naphth[3,2,1-*cd*]azulen-7-one **9b** was heated at 100 °C with 48% hydrobromic acid for 1 h, 6-hydroxy-7*H*-naphth[3,2,1-*cd*]azulen-7-one **7** was obtained as an acidic compound in almost quantitative yield. Treatment of 6-chloro-7*H*-naphth[3,2,1-*cd*]azulen-7-one **9a** with potassium hydroxide in ethanol gave **7** in only poor yield along with 6-ethoxy-7*H*-naphth[3,2,1-*cd*]azulen-7-one **9f**. Compound **7** was quantitatively obtained by the hydrolysis of ethyl 6-chloro-

Table 2 Condensation reactions of 7*H*-naphth[3,2,1-*cd*]azulen-7-ones with active methylene compounds

Run	Reactants G	Reactants X	Products (formula) G	Products (formula) X	Yield (%) (recovery)	Mp (°C)	M^+ (*m*/*z*)	Found (%) (required) C	Found (%) (required) H	Found (%) (required) N	IR (ν/cm^{-1})
1	**9a**		**17a** ($C_{20}H_9ClN_2$)		5	299.5–301	312	76.9	2.8	8.7	2200, 2195
	H	Cl	H	Cl				(76.8	2.9	9.0)	
2	**9b**		**17b** ($C_{21}H_{12}N_2O$)		5	263–265	308	81.9	4.1	9.0	2205, 2195
	H	OMe	H	OMe				(81.8	3.9	9.1)	
			17c ($C_{23}H_{14}N_2O_2$)		50	244.5–245.5	350	79.3	3.8	7.9	2200, 2195
			MeCO	OMe				(78.8	4.0	8.0)	1644
3	**10a**		**17d** ($C_{23}H_{13}ClN_2O_2$)		15	294.5–295.5	384	71.8	3.5	7.2	2210, 1685
	CO_2Et	Cl	CO_2Et	Cl				(71.8	3.4	7.3)	
4	**10c**		**17e** ($C_{23}H_{14}N_2O_2$)		15	>300	350	78.0	3.8	7.6	2205, 1710
	CO_2Et	H	CO_2Et	H	(60)			(78.8	4.0	8.0)	

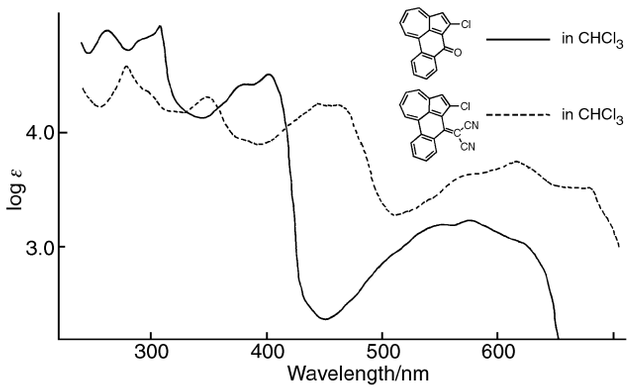


Fig. 1 The electronic spectra of 6-chloro-7*H*-naphth[3,2,1-*cd*]azulen-7-one **9a** (solid line) and 6-chloro-7-dicyanomethylene-7*H*-naphth-[3,2,1-*cd*]azulene **17a** (dashed line) in $CHCl_3$.

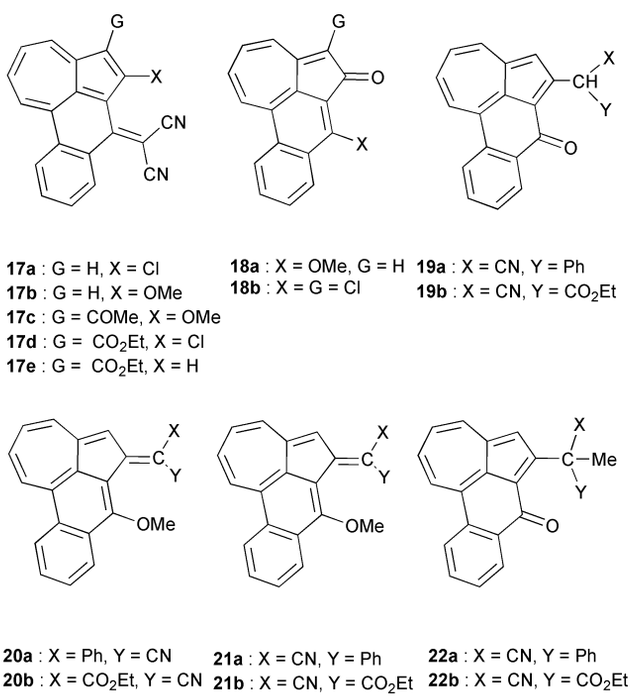


Chart 3

7-oxo-7*H*-naphth[3,2,1-*cd*]azulene-5-carboxylate **10a** with acetic acid under reflux for 48 h. The mass spectrum of **7** showed a molecular peak at *m*/*z* 246 (M^+), and treatment of **7** with iron(III) chloride showed a weak green coloration. The electronic spectrum of **7** resembled that of **9b** and the ^{1}H NMR spectral data were appropriate for the structure. In the ^{13}C NMR spectrum of **7**, seventeen signals were seen; two lower field peaks appeared at δ_C 177.79 and 176.29, which would be assigned to C-7 and C-6, respectively. The IR spectrum

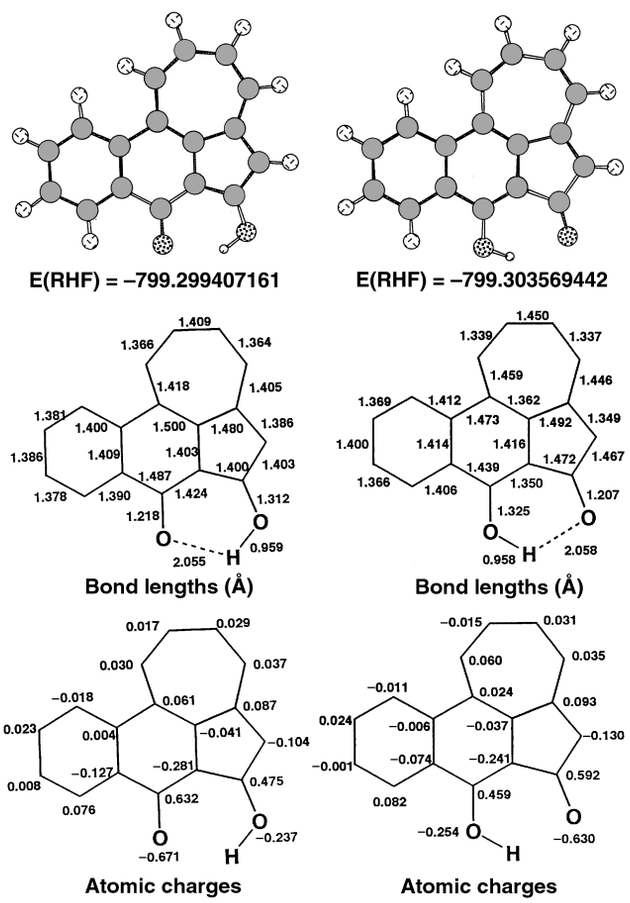


Fig. 2 Calculated bond lengths and total atomic charges for optimized structures of 6-hydroxy-7*H*-naphth[3,2,1-*cd*]azulen-7-one **7** (left) and 7-hydroxy-6*H*-naphth[3,2,1-*cd*]azulen-6-one **8** (right) by Gaussian 98 using RHF/6-31G*.

of **7** showed two carbonyl absorptions, at ν_{max} 1627 (strong) and 1650 (medium) cm^{-1}. The former is assignable to $\nu_{C=O}$ of **7**, while the latter is assignable to that of 7-hydroxy-6*H*-naphth[3,2,1-*cd*]azulen-6-one **8**; this assignment is reasonable since the $\nu_{C=O}$ of the five-membered-ring carbonyl in 1,2-dihydroazulen-2-one **5B** appeared at 1642 cm^{-1}. These facts suggest that **8** exists in a tautomeric mixture between **7** and **8**, where **7** is predominant, and that the hydroxy group would form a strong hydrogen bond with the carbonyl oxygen; there would be much less of the tautomer having two carbonyl groups. For assistance in our comprehension, *ab initio* molecular orbital calculations using RHF/6-31G* of **7** and **8** were made (Fig. 2). From a consultation of the bond lengths of **7**, the strong intramolecular hydrogen bond was observed, and the azulene moiety showed heptafulvene-like character. A larger inclination toward a heptafulvene character was observed in **8**.

The existence of the tautomerism between **7** and **8** could be also supported from chemical evidence. Thus, the methylation of **7** with diazomethane was performed; two isomeric products, **9b** (75%) and 7-methoxy-6*H*-naphth[3,2,1-*cd*]azulen-6-one **18a** (25%), were isolated. The structure of **18a** was established on the basis of its spectral data as well as its mass (M^+, *m*/*z* 260) and elemental analysis. In the IR spectrum of **18a**, an absorption due to the carbonyl group appeared at 1657 cm^{-1}, which is comparable to that of **5B**. In the ^1H NMR spectrum of **18a**, the signals due to the seven-membered ring appeared at higher field (δ 6.30–7.00) than those in **9b**, and this is consistent with **18a** having a heptafulvene-type structure.[14] A similar conclusion was drawn following the reaction of **7** with thionyl dichloride, where two kinds of dichloro derivative, 5,6-dichloro-7*H*-naphth[3,2,1-*cd*]azulen-7-one **11b** (58%) and 5,7-dichloro-6*H*-naphth[3,2,1-*cd*]azulen-6-one **18b** (16%), were obtained. In spite of the above results, the acetylation of **7** gave 6-acetoxy-7*H*-naphth[3,2,1-*cd*]azulen-7-one **9g** only.

A similar tautomerism between 6-(substituted methyl)-7*H*-naphth[3,2,1-*cd*]azulen-7-ones **19** and 7-hydroxy-6-methylene-6*H*-naphth[3,2,1-*cd*]azulene derivative was considered. Therefore we next examined the synthesis and reactions of compounds **19**. As shown above, the chloro substituent of **9a** was easily replaced with a nucleophile to give the corresponding substitution products. Thus, treatment of **9a** with the carbanion derived from phenylacetonitrile gave 6-(α-cyanophenylmethyl)-7*H*-naphth[3,2,1-*cd*]azulen-7-one **19a**. Its IR spectrum showed absorptions at *v* 2248 (CN, weak) and 1622 cm^{-1} (C=O) and its ^1H NMR spectrum showed signals at δ 6.78 (1H, s), 7.30–8.10 (10H, m) and 8.20–8.80 (4H, m); these are consistent with the structure. Treatment of **19a** with diazomethane gave mainly recovered **19a** (61%) together with a mixture of *O*-methylated compounds **20a** and **21a** (3 : 2 mixture by ^1H NMR). The mixture showed a molecular ion peak at *m*/*z* 359 in the mass spectrum. A signal due to a conjugated cyano group appeared at *v* 2175 cm^{-1} in its IR spectrum, and two singlet signals are seen at δ 3.90 and 3.01 in its ^1H NMR spectrum. These support the structure assigned. In the methylation reaction, *C*-methylated product **22a** was not observed.

To clarify the above results, we next performed the reaction of **9a** with a carbanion derived from ethyl cyanoacetate, followed by treatment of diazomethane; three methylated compounds **22b**, **20b** and **21b** were isolated in 7, 5 and 4% yield respectively. In the IR spectrum of **22b**, signals at *v* 2250 (CN, weak), 1748 (ester carbonyl) and 1628 cm^{-1} (ring carbonyl) were seen. The ^1H NMR spectrum of **22b** showed a methyl signal at δ 2.26 and other signals were consistent with the 7*H*-naphth[3,2,1-*cd*]azulen-7-one system. The results show that compound **22b** is the *C*-methylated derivative. The occurrence of *C*-methylation can be attributed to the high acidity of the active hydrogen of **19b**. In the IR spectrum of **20b**, signals at *v* 2195 (conjugated CN) and 1700 cm^{-1} (conjugated ester carbonyl) were seen and a ring-carbonyl signal was not seen. The ^1H NMR spectrum of **20b** showed an *O*-methyl signal at δ 3.98 and other signals were consistent with a heptafulvene-type system.[14] In addition, a 1H singlet assignable to H-5 resonated at lower field (δ 7.48), which would be deshielded by the ester group. In the IR spectrum of **21b**, signals at *v* 2200 (conjugated CN) and 1713 cm^{-1} (hindered conjugated ester carbonyl) were seen and a ring-carbonyl signal was not seen. The ^1H NMR spectrum of **21b** showed an *O*-methyl signal at δ 4.37, a 1H singlet assignable to H-5, and other signals were also consistent with a heptafulvene-type system.[14] The downfield shift of the methyl signal would be due to deshielding by the ester group. In addition, an NOE was observed between *O*-methyl and ethyl protons. From the results we assigned the structures.

Experimental

Mps are uncorrected. ^1H NMR spectra (60 MHz) were recorded on a Varian A-60D spectrometer (60 MHz) and a Varian HA100 spectrometer (100 MHz), and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400S (100.6 MHz) using deuteriochloroform as solvent with tetramethylsilane as internal standard unless otherwise stated; *J*-values are recorded in Hz. Electronic spectra were taken with an Hitachi EPS-3 spectrophotometer. IR spectra were recorded for KBr pellets on a Shimadzu IR-27 infracord unless otherwise stated. Mass spectra were taken with an Hitachi RMU-6D mass spectrometer at 25 eV. Kieselgel 60 and Wako-gel C-200 were used for column chromatography.

Reaction of 6-chloro-7*H*-naphth[3,2,1-*cd*]azulen-7-one 9a with sodium methoxide

To a solution of sodium methoxide prepared from sodium metal (0.500 g) and absolute methanol (120 ml) was added 6-chloro-7*H*-naphth[3,2,1-*cd*]azulen-7-one **9a** (1.000 g), and the mixture was refluxed for 1 h. Water was added to the mixture and the mixture was neutralized with dil. hydrochloric acid and extracted with chloroform. The extract was washed with water, dried over sodium sulfate, and evaporated. The residue was subjected to silica gel column chromatography. Elution with chloroform gave 6-methoxy-7*H*-naphth[3,2,1-*cd*]azulen-7-one **9b** (0.980 g, 99.5%) as red needles (from ethanol), mp 218–219 °C; δ_H 4.18 (3H, s, OCH_3), 6.55 (1H, s, H-5), 7.40–7.80 (4H, m, H-2, -3, -9 and -10) and 7.90–8.70 (4H, m, H-1, -4, -8 and -11); ν_{max}/cm^{-1} 1624 (C=O); λ_{max} (CHCl3)/nm (log ε) 264 (4.52), 290 (4.43), 297 (4.49), 308 (4.63), 363 (3.97), 382 (4.07), 401 (4.09), 425 (4.19), 510 (3.09), 540 (3.11), 570 (2.88) and 586 (2.78) (Found: C, 82.8; H, 4.5. $C_{18}H_{12}O_2$ requires C, 83.1; H, 4.7%).

Reaction of 9a with potassium hydrosulfide

A mixture of **9a** (0.100 g) and aq. potassium hydrosulfide (2 ml) in ethanol (100 ml) was stirred overnight at room temperature. Water was added to the mixture and the mixture was neutralized with dil. hydrochloric acid and extracted with chloroform. The extract was washed with water, dried over sodium sulfate, and evaporated. The residue was subjected to silica gel column chromatography. Elution with benzene–chloroform (2 : 1) gave 6-mercapto-7*H*-naphth[3,2,1-*cd*]azulen-7-one **9c** (0.035 g, 35%) as dark green prisms (from ethanol), mp 200–202 °C; δ_H 6.66 (1H, s, H-5), 7.10–8.80 (8H, m, H-1, -2, -3, -4, -8, -9, -10 and -11); ν_{max}/cm^{-1} 1622 (C=O); λ_{max} ($CHCl_3$)/nm (log ε) 252 (4.31, sh), 260 (4.33), 289 (4.24), 305 (4.13), 320 (4.19), 337 (4.06, sh), 373 (3.76), 400 (3.74, sh), 447 (3.94), 463 (3.86, sh), 540 (3.54), 580 (3.68), 628 (3.74) and 678 (3.45); *m*/*z* (rel. intensity) 262 (M^+, 100), 261 (6), 234 (13), 230 (4), 202 (17), 201 (3) and 200 (3) (Found: C, 79.1; H, 4.9. $C_{20}H_{14}O_3$ requires C, 79.4; H, 4.7%).

Reaction of 9a with ethylamine

A mixture of **9a** (0.120 g) and 30% ethylamine (1 ml) in ethanol (50 ml) was refluxed for 20 min. The mixture was evaporated and the residue was subjected to silica gel column chromatography. Elution with benzene gave 6-ethylamino-7*H*-naphth[3,2,1-*cd*]azulen-7-one **9d** (0.121 g, 98%) as red needles (from cyclohexane), mp 114–115.5 °C; δ_H 1.43 (3H, t, *J* 7.2, CH_3), 3.58 (2H, q, *J* 7.2, NCH_2), 6.37 (1H, s, H-5), 7.40–7.80 (5H, m, H-2, -3, -4, -9 and -10) and 7.90–8.70 (4H, m, H-1, -8, -11 and NH); ν_{max}/cm^{-1} 3310 (NH) and 1620 (C=O); λ_{max} ($CHCl_3$)/nm (log ε) 264 (4.54), 275 (4.50, sh), 304 (4.41), 316 (4.48), 335 (3.96), 350 (3.99, sh), 363 (4.21), 382 (4.32), 403 (3.99), 429 (4.04), 455 (4.07), 502 (3.87) and 541 (3.94) (Found: C, 83.8; H, 5.6; N, 5.0. $C_{19}H_{15}NO$ requires C, 83.5; H, 5.5; N, 5.1%).

Reaction of 9a with piperidine

A mixture of **9a** (0.120 g) and piperidine (0.300 g) in ethanol

(50 ml) was refluxed for 10 min. The mixture was evaporated and the residue was subjected to silica gel column chromatography. Elution with benzene gave 6-piperidino-7*H*-naphth[3,2,1-*cd*]azulen-7-one **9e** (0.140 g, 98%) as dark green prisms (from ethanol), mp 168–169.5 °C; δ_H 1.60–2.00 (6H, m), 3.60 (4H, m), 6.55 (1H, s, H-5), 7.40–7.80 (5H, m, H-2, -3, -4, -9 and -10) and 7.90–8.70 (3H, m, H-1, -8 and -11); ν_{max}/cm^{-1} 1613 (C=O); λ_{max} ($CHCl_3$)/nm (log ε) 271 (4.54), 308 (4.40), 322 (4.45), 367 (4.15), 384 (4.22), 450 (4.10, sh), 470 (4.13) and 553 (3.95) (Found: C, 83.9; H, 6.2; N, 4.3. $C_{22}H_{19}NO$ requires C, 84.3; H, 6.1; N, 4.5%).

Reaction of ethyl 6-chloro-7-oxo-7*H*-naphth[3,2,1-*cd*]azulene-5-carboxylate (10a) with sodium methoxide

To a solution of sodium methoxide prepared from sodium metal (0.140 g) and absolute methanol (35 ml) was added **10a** (0.250 g), and the mixture was refluxed for 40 min. Water was added to the mixture and the mixture was neutralized with dil. hydrochloric acid and extracted with chloroform. The extract was washed with water, dried over sodium sulfate, and evaporated. The residue was subjected to silica gel column chromatography. Elution with chloroform gave methyl 6-methoxy-7-oxo-7*H*-naphth[3,2,1-*cd*]azulene-5-carboxylate **10b** (0.200 g, 85%) as orange needles (from methanol), mp 177–178 °C; δ_H 3.99 (3H, s, OCH_3), 4.41 (3H, s, CO_2CH_3), 7.50–7.80 (4H, m, H-2, -3, -9 and -10), 7.90–8.70 (3H, m, H-1, -8 and -11) and 9.0–9.2 (1H, m, H-4); ν_{max}/cm^{-1} 1690 and 1630 (C=O); λ_{max} ($CHCl_3$)/nm (log ε) 276 (4.62), 297 (4.71), 307 (4.80), 381 (4.18), 403 (4.26) and 523 (3.04) (Found: C, 75.1; H, 4.6. $C_{20}H_{14}O_4$ requires C, 75.5; H, 4.4%).

Halogenation of 7*H*-naphth[3,2,1-*cd*]azulen-7-ones

(a) Typical procedure. A mixture of **9a** (0.100 g) and NBS (0.070 g) in dichloromethane (10 ml) was stirred for 10 min. The mixture was chromatographed with chloroform to give **11a** (0.105 g, 81%) as green needles (from ethanol), mp 299–300 °C; δ_H 7.40–7.80 (4H, m, H-2, -3, -9 and -10) and 7.90–8.70 (4H, m, H-1, -4, -8 and -11); ν_{max}/cm^{-1} 1630 (C=O); λ_{max} ($CHCl_3$)/nm (log ε) 264 (4.51), 270 (4.50), 294 (4.47), 302 (4.52), 313 (4.50), 368 (3.90), 390 (4.13), 405 (4.26), 425 (3.55), 570 (3.16), 616 (3.20) and 660 (2.70) (Found: C, 59.5; H, 2.4. $C_{17}H_8BrClO$ requires C, 59.4; H, 2.4%).

In a similar manner, **9a** and **9b** were treated with NCS, and NBS and NIS, respectively, and the corresponding compounds **11b**–**11d** were obtained quantitatively.

11b: Violet needles (from ethanol), mp 297.5–298 °C; δ_H 7.40–7.80 (4H, m, H-2, -3, -9 and -10) and 7.90–8.70 (4H, m, H-1, -4, -8 and -11); ν_{max}/cm^{-1} 1630 (C=O); λ_{max} ($CHCl_3$)/nm (log ε) 263 (4.51, sh), 269 (4.53), 292 (4.50), 302 (4.52), 309 (4.55), 365 (3.90), 384 (4.17), 405 (4.26), 425 (3.59, sh), 576 (3.16), 616 (3.20) and 670 (2.94, sh) (Found: C, 68.5; H, 2.5. $C_{17}H_8Cl_2O$ requires C, 68.3; H, 2.7%).

11c: Violet needles (from ethanol), mp 217.5–218 °C; δ_H 4.60 (3H, s, OCH_3), 7.30–7.90 (4H, m, H-2, -3, -9 and -10) and 8.20–8.70 (4H, m, H-1, -4, -8 and -11); ν_{max}/cm^{-1} 1618 (C=O); λ_{max} ($CHCl_3$)/nm (log ε) 255 (4.56, sh), 265 (4.59, sh), 273 (4.62), 294 (4.59, sh), 303 (4.62, sh), 312 (4.67), 367 (4.06, sh), 390 (4.17), 409 (4.18), 555 (3.14, sh) and 577 (3.16) (Found: C, 63.8; H, 3.1. $C_{18}H_{11}BrO_2$ requires C, 63.8; H, 3.3%).

11d: Violet needles (from ethanol), mp 215–216.5 °C; δ_H 4.56 (3H, s, OCH_3), 7.50–8.00 (4H, m, H-2, -3, -9 and -10) and 8.20–8.70 (4H, m, H-1, -4, -8 and -11); ν_{max}/cm^{-1} 1630 (C=O); λ_{max} ($CHCl_3$)/nm (log ε) 274 (4.47), 298 (4.47), 312 (4.50), 390 (4.08), 412 (4.09), 555 (3.05, sh), 577 (3.07) and 625 (2.81, sh) (Found: C, 56.0; H, 2.6. $C_{18}H_{11}IO_2$ requires C, 55.8; H, 2.9%).

Reaction of ethyl 7-oxo-7*H*-naphth[3,2,1-*cd*]azulene-5-carboxylates 10a and 10c with Grignard reagents

Typical procedure. Under nitrogen atmosphere, a solution of ethyl 7-oxo-7*H*-naphth[3,2,1-*cd*]azulene-5-carboxylate (**10c**) (0.500 g) in dry diethyl ether–benzene (1 : 1, 100 ml) was added to an ethereal solution of phenylmagnesium bromide, prepared from bromobenzene (0.650 g) and magnesium metal (0.120 g) in dry diethyl ether (30 ml), and the mixture was stirred for 20 min at room temperature. The reaction mixture was cooled on an ice-bath, and then methanol (8 ml) and 2 M hydrochloric acid (5 ml) were added. The mixture was extracted with benzene, then the extract was washed with 2 M aq. sodium hydroxide. TCQ (1.5 g) was added to the solution, and the mixture was stirred for 2 days at room temperature, then evaporated. The residue was subjected to alumina column chromatography with chloroform as eluant. The eluate was evaporated and the residue was chromatographed on silica gel. Elution with benzene gave ethyl 6-phenyl-7-oxo-7*H*-naphth[3,2,1-*cd*]azulene-5-carboxylate[1] **10d** (0.495 g, 80%) and a mixture (1 : 1) of ethyl 7-oxo-4-phenyl-7*H*-naphth[3,2,1-*cd*]azulene-5-carboxylate **12** and ethyl 7-oxo-3-phenyl-7*H*-naphth[3,2,1-*cd*]azulene-5-carboxylate **13** (0.032 g, 5%).

12: δ_H 1.05 (3H, t, *J* 7.3, CH_3), 3.62 (2H, q, *J* 7.3, OCH_2) and 7.20–8.60 (13H, m, H-1, -2, -3, -6, -8, -9, -10, -11 and phenyl).

13: δ_H 1.45 (3H, t, *J* 7.3, CH_3), 4.45 (2H, q, *J* 7.3, OCH_2), 7.20–8.50 (12H, m, H-1, -2, -6, -8, -9, -10, -11 and phenyl) and 10.09 (1H, d, *J* 1.5, H-4).

In a similar manner, **10a** was treated with Grignard reagents and the results are listed in Table 1.

14a: Green needles (from ethanol), mp 210–212 °C; δ_H 0.77 (3H, t, *J* 7.0, CH_3), 3.33 (2H, q, *J* 7.0, OCH_2), 7.30–7.80 (13H, m, H-3, -8, -9, -10, -11, *m*-, *p*-phenyl and phenyl), 7.93 (1H, t, *J* 10.2, H-2), 8.30–8.50 (2H, m, *o*-phenyl) and 8.59 (1H, br d, *J* 11.0, H-1); ν_{max}/cm^{-1} 1690 and 1637 (C=O); λ_{max} ($CHCl_3$)/nm (log ε) 255 (4.56, sh), 265 (4.59, sh), 273 (4.62), 294 (4.59, sh), 303 (4.62, sh), 312 (4.67), 367 (4.06, sh), 390 (4.17), 409 (4.18), 555 (3.14, sh) and 577 (3.16) (Found: C, 84.3; H, 4.9. $C_{32}H_{22}O_3$ requires C, 84.6; H, 4.9%).

15a: Green needles (from ethanol), mp 230–231 °C; δ_H 0.92 (3H, t, *J* 7.0, CH_3), 4.07 (2H, q, *J* 7.0, OCH_2), 7.30–7.70 (12H, m, H-8, -9, -10, -11, *m*-, *p*-phenyl and phenyl), 8.12 (1H, dd, *J* 10.2 and 2.0, H-2), 8.20–8.40 (2H, m, *o*-phenyl), 8.56 (1H, br d, *J* 11.0, H-1) and 9.79 (1H, d, *J* 2.0, H-4); ν_{max}/cm^{-1} 1712 and 1628 (C=O); λ_{max} ($CHCl_3$)/nm (log ε) 264 (4.51), 291 (4.52), 313 (4.48), 327 (4.48, sh), 386 (4.14), 567 (3.30, sh), 596 (3.33) and 629 (3.06, sh) (Found: C, 84.9; H, 4.5. $C_{32}H_{22}O_3$ requires C, 84.6; H, 4.9%).

16a: Green needles (from ethanol), mp 255–257.5 °C; δ_H 0.93 (3H, t, *J* 7.0, CH_3), 4.08 (2H, q, *J* 7.0, OCH_2), 7.30–7.70 (12H, m, H-8, -9, -10, -11, *m*-, *p*-phenyl and phenyl), 7.96 (1H, dd, *J* 10.2 and 1.7, H-3), 8.20–8.40 (2H, m, H-*o*-phenyl), 8.84 (1H, d, *J* 1.7, H-1) and 9.79 (1H, d, *J* 10.2, H-4); ν_{max}/cm^{-1} 1690 and 1637 (C=O) (Found: C, 84.3; H, 4.9. $C_{32}H_{22}O_3$ requires C, 84.6; H, 4.9%).

14b: Green needles (from ethanol), mp 143.5–145 °C; δ_H −0.97 (3H, t, *J* 7.3, CH_3), 0.20–1.10 (1H, m, OCH_2), 2.10–3.00 (1H, m, OCH_2) and 7.30–9.20 (21H, m, H-1, -2, -3, -8, -9, -10, -11, and naphthyl); ν_{max}/cm^{-1} 1724 and 1629 (C=O); λ_{max} ($CHCl_3$)/nm (log ε) 272 (4.59), 304 (4.64), 382 (4.17), 402 (4.18), 560 (3.31) and 595 (3.17, sh) (Found: C, 86.5; H, 4.9. $C_{40}H_{26}O_3$ requires C, 86.6; H, 4.7%).

15b: Green needles (from ethanol), mp 187–188 °C; δ_H 0.35 (3H, t, *J* 7.3, CH_3), 3.74 (2H, q, *J* 7.3, OCH_2), 7.30–8.10 (16H, m, H-8, -9, -10, -11, naphthyl), 8.30 (1H, dd, *J* 11.0 and 2.0, H-2), 8.30–8.60 (2H, m, β-naphthyl), 8.85 (1H, br d, *J* 11.0, H-1) and 10.02 (1H, d, *J* 2.0, H-4); ν_{max}/cm^{-1} 1692 and 1637 (C=O); λ_{max} ($CHCl_3$)/nm (log ε) 271 (4.62), 303 (4.42), 403 (4.33), 555 (3.38, sh), 580 (3.42) and 622 (3.21, sh) (Found: C, 86.5; H, 4.6. $C_{40}H_{26}O_3$ requires C, 86.6; H, 4.7%).

16b: Green needles (from ethanol), mp 203–205 °C; δ_H 0.42 (3H, t, *J* 7.0, CH_3), 3.90 (2H, q, *J* 7.0, OCH_2), 7.10–9.10 (20H, m, H-1, -3, -8, -9, -10, -11, naphthyl) and 8.59 (1H, d, *J* 10.5,

H-4); ν_{max}/cm^{-1} 1695 and 1632 (C=O) (Found: C, 86.7; H, 4.8. $C_{40}H_{26}O_3$ requires C, 86.6; H, 4.7%).

14c: Green needles (from ethanol), mp 123–125 °C; δ_H 1.50 (3H, t, *J* 7.0, CH_3), 2.78 (3H, s, CH_3), 3.13 (3H, s, CH_3), 4.48 (2H, q, *J* 7.0, OCH_2), 7.30–8.80 (7H, m, H-1, -2, -3, -8, -9, -10 and -11); ν_{max}/cm^{-1} 1695 and 1620 (C=O) (Found: C, 79.8; H, 5.6. $C_{22}H_{18}O_3$ requires C, 80.0; H, 5.5%).

15c: Green needles (from ethanol), 147–149 °C; δ_H 1.53 (3H, t, *J* 7.0, CH_3), 2.73 (3H, s, CH_3), 3.10 (3H, s, CH_3), 4.07 (2H, q, *J* 7.0, OCH_2), 7.30–7.70 (6H, m, H-1, -2, -4, -8, -9, -10 and -11) and 8.59 (1H, d, *J* 1.5, H-4); ν_{max}/cm^{-1} 1692 and 1625 (C=O) (Found: C, 79.9; H, 5.3. Calc. for $C_{22}H_{18}O_3$: C, 80.0; H, 5.5%).

Condensation of 9 and 10 with active methylene compounds

Typical procedure. A mixture of **9a** (0.200 g) and malononitrile (0.140 g) in acetic anhydride (10 ml) was refluxed for 14 h, then poured into water. The mixture was extracted with chloroform, and the extract was dried over sodium sulfate and evaporated. The residue was chromatographed with chloroform to give **17a** (0.010 g).

In a similar manner, **9b**, **10a** and **10c** were treated and the corresponding compounds **17b**–**17e** were obtained. Results are listed in Table 2.

Hydrolysis of 6-methoxy-7*H*-naphth[3,2,1-*cd*]azulen-7-one 9b with hydrobromic acid

A mixture of **9b** (0.400 g) and 48% hydrobromic acid (20 ml) was heated at 100 °C on a water-bath for 1 h. Water was added to the mixture which was then neutralized with dil. hydrochloric acid and extracted with chloroform. The extract was washed with water, dried over sodium sulfate, and evaporated. 6-Hydroxy-7*H*-naphth[3,2,1-*cd*]azulen-7-one **7** was obtained as red crystals (0.360 g, 95%) (from ethanol), mp 198–199 °C; δ_H 5.82 (1H, s, OH, disappeared with D_2O), 6.43 (1H, s, H-5), 7.30–8.00 (4H, m, H-2, -3, -9 and -10) and 8.10–8.70 (4H, m, H-1, -4, -8 and -11); ν_{max}/cm^{-1} 1650 (medium) and 1627 (strong) (C=O); δ_C 106.98, 111.55, 125.67, 126.47, 128.21, 129.61, 130.47, 131.73, 132.02, 132.82, 133.46, 133.86, 135.19, 137.45, 150.91, 176.29 and 177.79; ν_{max}/cm^{-1} 1650 (medium) and 1627 (strong) (C=O); λ_{max} ($CHCl_3$)/nm (log ε) 268 (4.50), 287 (4.37), 298 (4.36), 309 (4.44), 364 (3.93, sh), 379 (4.00), 402 (4.05), 424 (4.10), 455 (3.19, sh), 566 (3.23, sh), 590 (2.94, sh) and 612 (2.58, sh); λ_{max} (MeOH)/nm (log ε) 228 (4.46), 263 (4.54), 285 (4.39), 295 (4.38), 306 (4.42), 356 (4.00), 373 (4.07), 399 (4.03), 421 (4.06), 515 (3.55) and 548 (3.54); λ_{max} (MeOH–NaOH)/nm (log ε) 225 (4.56), 238 (4.53), 261 (4.69), 298 (4.46), 309 (4.43), 338 (4.08), 356 (4.25), 373 (4.37), 413 (4.07), 437 (4.05), 510 (3.90) and 543 (3.83); *m*/*z* 246 (M^+) (Found: C, 82.8; H, 4.0. $C_{17}H_{10}O_2$ requires C, 82.9; H, 4.1%).

Reaction of 6-chloro-7*H*-naphth[3,2,1-*cd*]azulen-7-one 9a with potassium hydroxide

A mixture of **9a** (0.050 g) and 40% aq. potassium hydroxide (0.5 ml) in ethanol (50 ml) was refluxed for 20 min, then the solvent was evaporated off. Water (20 ml) was added to the residue and the mixture was extracted with chloroform. The extract was washed with 1 M aq. potassium hydroxide. The organic layer was dried over sodium sulfate, and evaporated. Chromatography of the residue with chloroform gave 6-ethoxy-7*H*-naphth[3,2,1-*cd*]azulen-7-one **9f** (0.012 g, 23%) as red microneedles (from cyclohexane), mp 190–192 °C; δ_H 1.66 (3H, t, *J* 7.2, CH_3), 4.48 (2H, q, *J* 7.2, OCH_2), 6.68 (1H, s, H-5), 7.50–8.00 (4H, m, H-2, -3, -9 and -10) and 8.10–8.80 (4H, m, H-1, -4, -8 and -11); ν_{max}/cm^{-1} 1625 (C=O) (Found: C, 83.1; H, 5.0. $C_{19}H_{14}O_2$ requires C, 83.2; H, 5.1%).

The combined aqueous solution was neutralized with dil. hydrochloric acid and extracted with chloroform. The extract was washed with water, dried over sodium sulfate, and evaporated, and 6-hydroxy-7*H*-naphth[3,2,1-*cd*]azulen-7-one **7** (0.003 g, 6%) was obtained.

Hydrolysis of ethyl 6-chloro-7-oxo-7*H*-naphth[3,2,1-*cd*]azulene-5-carboxylate 10a with acetic acid

A solution of **10a** (0.500 g) in acetic acid (50 ml) was refluxed for 48 h, and poured into water. The mixture was extracted with chloroform. The extract was washed with water, dried over sodium sulfate, and evaporated, and **7** (0.360 g, 98%) was obtained.

Reaction of 6-hydroxy-7*H*-naphth[3,2,1-*cd*]azulen-7-one 7 with diazomethane

Under ice-cooling an ethereal solution of diazomethane (≈ 0.6 M; 10 ml) was added to a solution of **7** (0.100 g) in chloroform (20 ml), and the mixture was set aside for 15 h at 0 °C. The solvent was evaporated off and the residue was subjected to silica gel column chromatography. Elution with benzene–chloroform (1 : 1) gave 7-methoxy-6*H*-naphth[3,2,1-*cd*]azulen-6-one **18a** (0.026 g, 25%) and 6-methoxy-7*H*-naphth[3,2,1-*cd*]azulen-7-one **9b** (0.079 g, 75%), successively.

18a: Dark green prisms (from ethanol), mp 164–165 °C; δ_H 4.43 (3H, s, OCH_3), 5.77 (1H, s, H-5), 6.30–7.00 (5H, m, H-3, -9 and -10), 7.30–7.80 (3H, m, H-2, -4 and -11) and 8.00–8.50 (2H, m, H-1 and -8); ν_{max}/cm^{-1} 1657 (C=O); λ_{max} ($CHCl_3$)/nm (log ε) 257 (4.44), 275 (4.27, sh), 288 (4.27), 306 (4.12), 335 (3.86, sh), 355 (3.93), 380 (3.87), 430 (3.52, sh), 458 (3.38, sh), 502 (3.30), 536 (3.29), 572 (3.14) and 625 (2.76, sh); *m*/*z* (rel intensity) 260 (M^+, 86), 259 (29), 231 (100), 230 (14), 202 (47), 201 (14) and 200 (10) (Found: C, 83.3; H, 4.7. $C_{18}H_{12}O_2$ requires C, 83.1; H, 4.7%).

Reaction of 7 with thionyl dichloride

A solution of **7** (0.200 g) and thionyl dichloride (1.00 ml) in dry benzene (100 ml) was refluxed for 4 h. The mixture was poured into water, and extracted with chloroform. The extract was washed with water, dried over sodium sulfate, and evaporated. The residue was chromatographed with benzene–chloroform (1 : 1) to give 5,7-dichloro-6*H*-naphth[3,2,1-*cd*]azulen-6-one **18b** (0.040 g, 16%) and 5,6-dichloro-7*H*-naphth[3,2,1-*cd*]-azulen-7-one **11b** (0.140 g, 58%), successively.

18b: Green scales (from ethanol), mp 290–292 °C; δ_H (CF_3CO_2H) 7.9–9.5 (m); ν_{max}/cm^{-1} 1686 (C=O); λ_{max} ($CHCl_3$)/nm (log ε) 245 (4.62), 258 (4.60), 269 (4.54, sh), 277 (4.46, sh), 287 (4.35, sh), 307 (4.23), 329 (4.12), 343 (4.14), 357 (4.12), 383 (4.06), 423 (3.82), 442 (3.82), 475 (3.33, sh), 522 (3.14), 559 (3.28), 607 (3.28) and 663 (3.07); λ_{max} (CF_3CO_2H)/nm 293 (4.61), 325 (4.20, sh), 339 (3.94), 427 (4.07), 450 (4.15), 598 (3.36, sh), 635 (3.42) and 685 (3.24, sh); *m*/*z* 302, 300 and 298 (M^+) (Found: C, 68.3; H, 2.6. $C_{17}H_8Cl_2O$ requires C, 68.3; H, 2.7%).

Acetylation of 7

A mixture of **7** (0.050 g) and one drop of pyridine in acetic anhydride (2 ml) was stirred for 2 days at room temperature. Water was added to the mixture and the mixture was extracted with chloroform. The extract was washed with water, and dried over sodium sulfate. Evaporation of the mixture gave 6-acetoxy-7*H*-naphth[3,2,1-*cd*]azulen-7-one **9g** (0.055 g, 94%) as violet needles (from cyclohexane), mp 220–222 °C; δ_H 2.58 (3H, s, CH_3), 6.96 (1H, s, H-5), 7.30–7.90 (4H, m, H-3, -4, -9 and -10) and 7.90–8.70 (4H, m, H-1, -2, -8 and -11); ν_{max}/cm^{-1} 1769 and 1628 (C=O) (Found: C, 79.4; H, 4.1. $C_{19}H_{12}O_2$ requires C, 79.2; H, 4.2%).

Reaction of 9a with phenylacetonitrile

To a solution of the sodium salt prepared from 50% sodium

hydride (0.250 g) and phenylacetonitrile (0.400 g) in dry 1,6-dioxane (50 ml) was added a solution of **9a** (0.300 g) in dry 1,4-dioxane (150 ml), and the mixture was stirred for 24 h, then evaporated. To the suspension of the residue in chloroform (100 ml) was added acetic acid (10 ml). After stirring of the mixture for 5 min, water was added and the mixture was extracted with chloroform. The extract was dried over sodium sulfate, and evaporated. The residue was chromatographed with benzene to give **19a** (0.139 g, 35%) as violet needles (from ethanol), mp 257.5–258.5 °C; δ_H 6.78 (1H, s, H-5), 7.30–8.10 (10H, m, H-3, -4, -9, -10, methine and phenyl), 8.20–8.80 (4H, m, H-1, -2, -8 and -11) ν_{max}/cm^{-1} 2248 (CN) and 1622 (C=O); λ_{max} ($CHCl_3$)/nm (log ε) 262 (4.62), 290 (4.55), 309 (4.56), 362 (4.05, sh), 380 (4.25), 401 (4.29), 415 (4.00, sh), 562 (3.26), 597 (3.29) and 644 (3.06, sh); λ_{max} (CH_3CN)/nm (log ε) 228 (4.49), 259 (4.63), 288 (4.57), 298 (4.55), 306 (4.52), 360 (3.99, sh), 376 (4.20), 395 (4.25), 410 (3.96, sh), 550 (3.24, sh), 587 (3.27) and 631 (3.03, sh); λ_{max} (CH_3CN–NaOH)/nm (log ε) 227 (4.74), 256 (4.80), 289 (4.75), 295 (4.74, sh), 305 (4.70, sh), 378 (4.63), 555 (4.67, sh) and 620 (4.61, sh) (Found: C, 86.5; H, 4.4; N, 3.6. $C_{25}H_{15}NO$ requires C, 86.9; H, 4.4; N, 4.1%).

Reaction of 19a with diazomethane

Under ice-cooling an ethereal solution of diazomethane (≈0.6 M, 20 ml) was added to a solution of **19a** (0.100 g) in chloroform (20 ml), and the mixture was set aside for 3 days at 0 °C. The solvent was evaporated off and the residue was subjected to silica gel column chromatography. Elution with benzene gave a 3 : 2 mixture of **20a** and **21a** (0.020 g, 18%) and recovered **19a** (0.061 g, 61%).

The mixture of **20a** and **21a** was obtained as reddish violet prisms (from ethanol); δ_H 3.01 (s, OCH_3), 3.90 (s, OCH_3), 6.35 (s, H-5), 6.75 (s, H-5), 6.20–7.00 (m, H-9 and -10), 7.30–8.00 (m, H-2, -3, -4, -8 and phenyl) and 8.10–8.40 (2H, m, H-1 and -11); ν_{max}/cm^{-1} 2175 (CN); *m*/*z* 359 (M^+) (Found: C, 86.8; H, 4.8; N, 3.7. $C_{26}H_{17}NO$ requires C, 86.9; H, 4.8; N, 3.9%).

Reaction of 9a with ethyl cyanoacetate

To a solution of the sodium salt prepared from 50% sodium hydride (0.250 g) and ethyl cyanoacetate (0.400 g) in dry 1,4-dioxane (30 ml) was added a solution of **9a** (0.300 g) in dry 1,4-dioxane (170 ml), and the mixture was stirred for 24 h, then evaporated. To a suspension of the residue in chloroform (100 ml) was added acetic acid (10 ml). After stirring of the mixture for 5 min, water was added and the mixture was extracted with chloroform, and the extract evaporated. The residue was suspended in chloroform (30 ml). Under ice-cooling an ethereal solution of diazomethane (≈0.6 M; 20 ml) was added to the solution, and the mixture was set aside for 1 day at 0 °C. The solvent was evaporated off and the residue was subjected to silica gel column chromatography. Elution with benzene gave **20b** (0.025 g, 5%), **21b** (0.022 g, 4%) and **22b** (0.030 g, 7%), successively.

20b: Dark blue prisms (from ethanol), mp 165.5–166 °C; δ_H 1.43 (3H, t, *J* 7.2, CH_3), 3.98 (3H, s, OCH_3), 4.39 (2H, q, *J* 7.2, OCH_2), 6.40–7.00 (3H, m, H-2, -9 and -10), 7.3–7.7 (3H, m, H-3, -4 and -11), 7.48 (1H, s, H-5) and 8.00–8.40 (2H, m, H-1 and -8); ν_{max}/cm^{-1} 2195 (CN) and 1700 (C=O); λ_{max} ($CHCl_3$)/nm (log ε) 248 (4.51), 262 (4.48, sh), 270 (4.42, sh), 275 (4.39, sh), 294 (4.34), 309 (4.29, sh), 320 (4.19, sh), 347 (3.99), 365 (3.94), 389 (3.95), 417 (4.00), 501 (3.88), 536 (3.89), 577 (3.87) and 678 (3.70, sh); *m*/*z* 355 (M^+) (Found: C, 77.6; H, 4.6; N, 3.6. $C_{23}H_{17}NO_3$ requires C, 77.7; H, 4.8; N, 3.9%).

21b: Brown prisms (from ethanol), mp 148–151 °C; δ_H 1.60 (3H, t, *J* 7.2, CH_3), 4.37 (3H, s, OCH_3), 4.72 (2H, q, *J* 7.2, OCH_2), 6.55 (1H, s, H-5), 6.40–7.00 (3H, m, H-2, -9 and -10) and 7.3–8.5 (5H, m, H-1, -3, -4, -8 and -11); ν_{max}/cm^{-1} 2200 (CN) and 1713 (C=O); λ_{max} ($CHCl_3$)/nm (log ε) 280 (4.54), 302 (4.53), 335 (4.21, sh), 360 (4.06, sh), 376 (3.89), 398 (3.90), 461 (3.80, sh), 484 (3.83), 533 (3.43, sh), 577 (3.21) and 630 (2.97, sh); *m*/*z* 355 (M^+) (Found: C, 77.8; H, 4.6; N, 3.7. $C_{23}H_{17}NO_3$ requires C, 77.7; H, 4.8; N, 3.9%).

22b: Violet needles (from ethanol), mp 230–231.5 °C; δ_H 1.32 (3H, t, *J* 7.3, CH_3), 2.26 (3H, s, CH_3), 4.72 (2H, q, *J* 7.2, OCH_2), 7.50 (1H, s, H-5), 7.50–8.10 (4H, m, H-2, -3, -9 and -10) and 7.3–8.5 (4H, m, H-1, -4, -8 and -11); ν_{max}/cm^{-1} 2250 (CN), 1748 and 1628 (C=O); λ_{max} ($CHCl_3$)/nm (log ε) 262 (4.45), 287 (4.42), 298 (4.40), 307 (4.40), 358 (3.89), 376 (4.10), 395 (4.17), 415 (3.84, sh), 558 (3.15), 593 (3.15) and 648 (2.87, sh); *m*/*z* 355 (M^+) (Found: C, 77.8; H, 4.7; N, 3.7. $C_{23}H_{17}NO_3$ requires C, 77.7; H, 4.8; N, 3.9%).

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