Autoxidation of 1-Methyl- and 1,3-Dimethylazulenes in Polar Aprotic Solvents: Structural Proof for Products and Reaction Pathways[1)]

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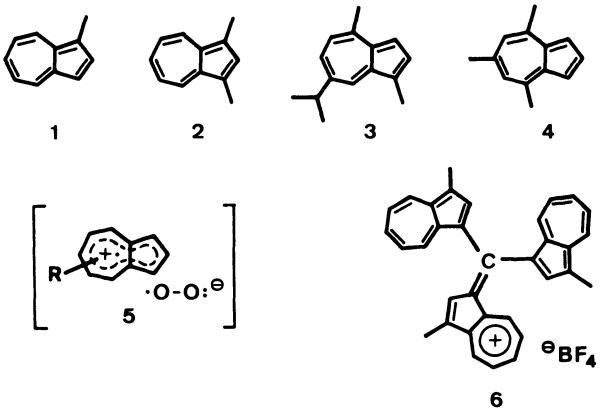
Autoxidation of the title azulenes at 100 °C in HMPA or DMF afforded a wide variety of products: Namely, the oxidation products of the side-chains, 1-substituted azulenes, 1*H*-inden-1-ols, naphthoquinones, benzenoids, and dimeric and trimeric compounds, with or without rearrangements. ^{1}H NMR (200-MHz) parameters of various azulene derivatives are given for comparative study. Possible reaction pathways for the formation of these products are discussed in comparison with the results of the previous studies on guaiazulene and 4,6,8-trimethylazulene.

We reported recently[2-4)] that autoxidation of naturally occurring guaiazulene (**3**) and synthetic 4,6,8-trimethylazulene (**4**) in *N*,*N*-dimethylformamide (DMF) or hexamethylphosphoric triamide (HMPA) gave a wide variety of products possessing interesting structures of azulenequinone, naphthoquinone, 1-indenone, and dimeric forms. It has been presumed[4)] that the oxidation is initiated by the formation of an electron-transferred complex **5**, which would then lead to a covalent linkage between the azulene nucleus and active radical species (produced during the oxidation) at various positions according to the ease of their affinity and steric requirement. Consequently, the autoxidation of **3** and **4** can be classified into such several types of reactions as oxidative dimerization, oxidation of side chains, azulenequinone formation, intermolecular one-carbon transfer reactions, and rearrangements to naphthalenoids, benzenoid, and 1*H*-inden-1-one derivatives. In these oxidation and coupling reactions, the facility of the radical attack on the C-1 and C-3 position of the azulene nucleus appeared to exceed usually that on various positions of the seven-membered ring,[5)] as in the case of many other electrophilic reactions of azulenes.[6)]



We now wish to report in this paper the detailed study on autoxidation of two other alkylazulenes **1** and **2** having methyl substituent(s) on the C-1 and C-3 position(s). This study was conducted to compare the mode of the oxidation with that of the trialkylazulenes **3** and **4** and to establish a further general aspect of the reaction mechanism of oxidation of azulenes. This information would in turn become important in view of an increasing interest in the potential utility of the physicochemical properties as well as biological activity of some synthetic azulene derivatives, exemplified by polyazulenes[7)] and azulenequinones.[8)]

Results and Discussion

Autoxidation of 1-Methylazulene (1). The oxidation was conducted in a manner similar to that described for the trialkylazulenes **3** and **4**.[2-4)] Thus, finely bubbling oxygen was passed into a soln of the substrate **1** in HMPA (or DMF) at 100 °C, while the reaction was monitored by the use of the reversed phase high-pressured liquid chromatography (HPLC) or silica-gel TLC. As in the case of the previous study, the reaction products were separated into each compo-

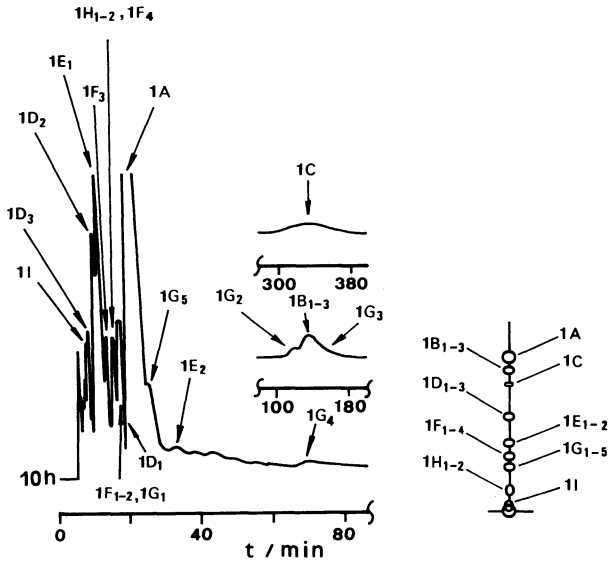


Fig. 1. HPLC and TLC diagrams of the autoxidation products from **1**.

nent by using chromatography, when about a half of the starting material was consumed (10 h); see HPLC and TLC diagrams in Fig. 1. The products thus obtained as pure components [19 altogether besides the recovered starting material **1** (**1A**)] are referred to as Compounds **1A—I** according to the same definition employed in the previous study.[2-4]

In Chart 1 are summarized structures of these products which were established by spectroscopy and chromatography as will be explained below; for the purpose of comparison in determining the structures of the oxidation products, the 200-MHz ^{1}H NMR parameters[9] for azulene derivatives obtained in the present study are summarized in Table 1. Amont these products, the followings were identified as all known compounds: **1B**$_1$,[10] **1D**$_1$,[11] **1D**$_2$, **1D**$_3$,[12] **1E**$_1$,[13] **1F**$_1$,[14] **1F**$_2$,[15] **1G**$_1$,[14] **1H**$_1$,[16] **1H**$_2$,[17] and **1I**[18] (for their spectral and other data, see Table 1 and the Experimental Section). The theoretical yields of these isolated products totaled to 25.2%; besides these, ca. 60% (w/w) yield of unidentified resinous polar products of rather high molecular weights were obtained.

Both Compounds **1B**$_2$ and **1B**$_3$ were shown to have a composition of $C_{22}H_{18}$ by MS and structures of 1′,3-dimethyl-1,2′-biazulene and 3,3′-dimethyl-1,1′-biazulene were respectively assigned to these minor products by the careful comparison of the ^{1}H NMR spectral data (see Table 1) with those of the starting material **1**.

Compound **1C** ($C_{34}H_{28}$ by MS), a major product, was found by spectroscopy to be 1,1′,1″-methylidynetris[3-methylazulene]; while the chemical shifts of other signals of **1C** in the ^{1}H NMR spectrum (Table 1) closely resembled those of **1**, an appreciable upfield shift (ca. 0.5 ppm) was observed for the H-2 signal presumably due to an electronic as well as an anisotropic effect by a nonplanar conformation of the three azulene nuclei owing to the steric repulsion. Although on allowing to stand at room temperature **1C** was gradually converted into a blue, polar substance (R_f=0.0), it remained stable when kept with a small proportion of an antioxidant (hydroquinone). Treatment of **1C** with triphenylmethylium tetrafluoroborate afforded the tetrafluoroborate **6**.[19]

Compound **1E**$_2$ was an extremely minor product which possessed a dimeric composition ($C_{23}H_{20}O$ by MS) having an extra-carbon atom and a carbonyl group (1690 cm^{-1}). The ^{1}H NMR data indicated the presence of a 3-methyl-1-azulenylmethyl moiety attached to a certain nucleus ($C_{11}H_9O$) that exhibited a methyl group (at δ 1.78, doublet, J=1.0 Hz, coupling with a ring-proton at 6.56, quartet), a methine proton (at 5.38, singlet), and four olefinic ring-protons (6.04—6.56); the methylene proton signals of an AB type (at 3.31 and 3.37, J=14 Hz) should also be noticed. All of

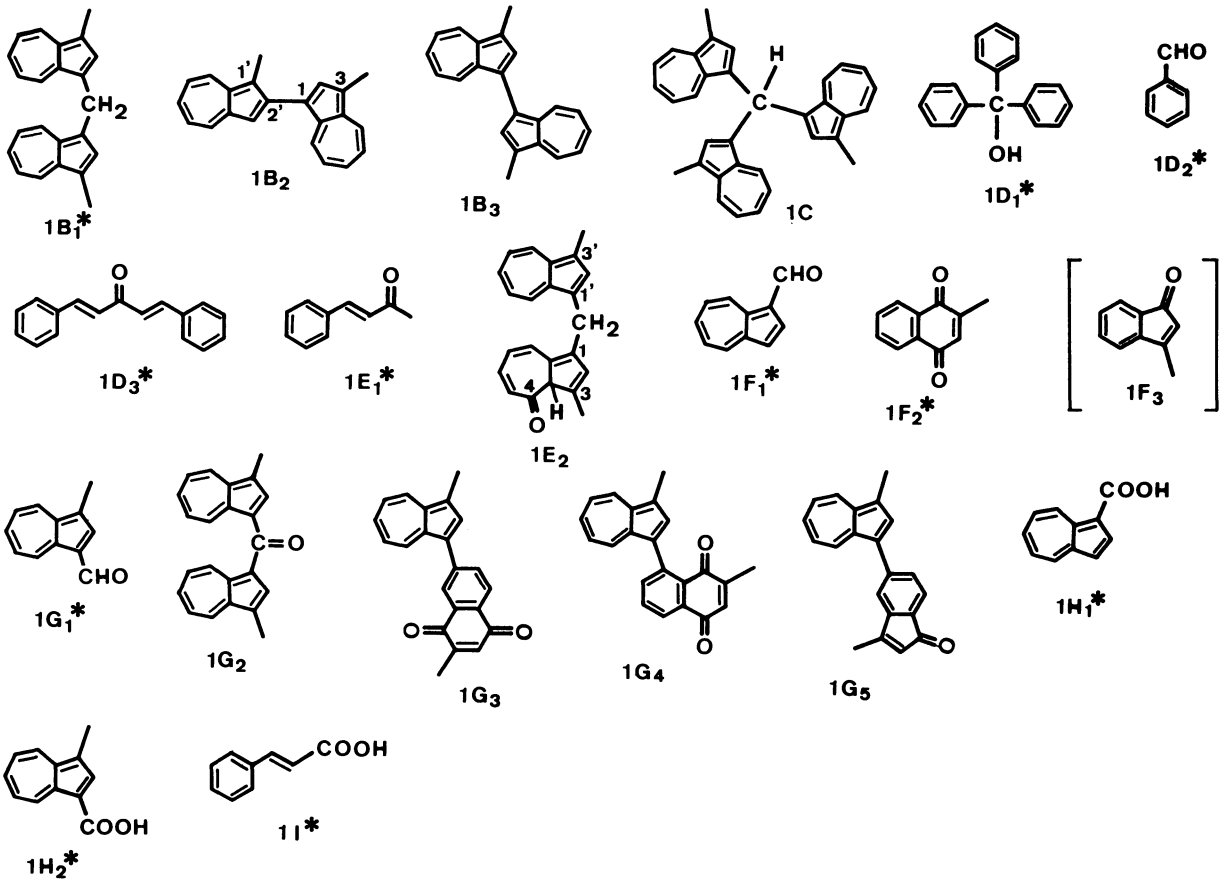


Chart 1. Structures of the autoxidation products from **1**; *previously known compounds.

Table 1. ^{1}H NMR (200 MHz) Parameters for Azulene Derivatives[a)]

Compound	H-1 (H-1′)	H-2 (H-2′)	H-3 (H-3′)	H-4 (H-4′)	H-5 (H-5′)	H-6 (H-6′)	H-7 (H-7′)	H-8 (H-8′)	*J* *J*
1	2.59[b)]	7.68	7.24	8.09	6.92	7.36	6.88	8.09	c, d)
1B$_1$	4.75[c)]	7.37	2.54[b)]	8.05	6.87	7.38	6.89	8.20	d)
1B$_2$	—	7.94	2.50[b)]	7.82	6.98	7.34	7.08	8.20	d)
	(2.76)[b)]	—	(7.34)	(8.25)	(7.03)	(7.49)	(7.03)	(8.24)	d)
1B$_3$	—	7.94	2.76[b)]	8.25	6.93	7.50	7.03	8.25	d)
1C	7.20[f)]	7.20	2.52[b)]	8.09	6.77	7.36	6.91	8.11	g)
1E$_2$	3.31[h)]	6.56	1.78[b)]	5.37[i)]	6.31	6.56	6.25	6.04	j)
	3.37[h)]	(7.30)	(2.52)[b)]	(7.99)	(6.88)	(7.37)	(6.88)	(8.04)	d)
1F$_1$	10.34[k)]	8.27	7.33	8.50	7.53	7.86	7.63	9.59	c, d)
1G$_1$	10.22[k)]	8.02	2.59[b)]	8.30	7.40	7.72	7.45	9.35	d)
1G$_2$	—	8.02	2.67[b)]	8.38	7.37	7.74	7.42	9.51	d)
1G$_3$	2.72[b)]	7.98	—	8.50	7.19	7.63	7.17	8.26	d)
	—	(6.88)	(2.24)[b)]	—	(8.32)	—	(7.96)	(8.21)	l, m)
1G$_4$	2.75[b)]	7.71	—	8.26	7.09	7.50	6.91	7.85	d)
	—	(6.84)	(2.03)[b)]	—	—	(7.65)	(7.73)	(8.18)	l, n)
1G$_5$	2.72[b)]	7.90	—	8.45	7.13	7.58	7.10	8.27	d)
	—	(5.78)	(2.29)[b)]	(7.34)	—	(7.46)	(7.53)	—	l, o)
1H$_1$	1.58[p)]	8.46	7.32	8.50	7.50	7.85	7.62	9.70	c, d)
1H$_2$	1.70[p)]	8.20	2.62[b)]	8.31	7.38	7.72	7.44	9.51	d)
2	2.59[b)]	7.49	2.59[b)]	8.00	6.84	7.34	6.84	8.00	g)
2B$_1$	—	7.74	2.74[b)]	8.20	6.90	7.46	7.04	7.73	d)
	(2.46)[b)]	—	(2.46)[b)]	(8.10)	(6.95)	(7.38)	(6.95)	(8.10)	d)
2D	2.62[b)]	7.54	2.69[b)]	8.51	9.86[k)]	7.85	6.96	8.05	q)

a) Chemical shifts (δ) are parts per million from Me_4Si measured in $CDCl_3$ (concn <ca. 0.5% v/v). Coupling constants (*J*, Hz) were confirmed by double resonance. b) Me. c) $J_{2,3}$=4.0 Hz. d) $J_{4,5}$, $J_{5,6}$, $J_{6,7}$, and $J_{7,8}$: 10.0 Hz. $J_{4,6}$, $J_{5,7}$, and $J_{6,8}$: 1 Hz. e) CH_2-1. f) CH-1. g) $J_{4,5}$, $J_{5,6}$, $J_{6,7}$, and $J_{7,8}$: 9.5 Hz. h) CH_2-1, J=14 Hz. i) H-3a, singlet. j) $J_{2,Me(3)}$=1.0 Hz, $J_{5,6}$=$J_{6,7}$=6.0 Hz, $J_{7,8}$=10 Hz. k) CHO. l) $J_{2,Me(3)}$=1.5 Hz. m) $J_{5,7}$=2.0 Hz, $J_{7,8}$=8.0 Hz. n) $J_{6,7}$=7.5 Hz, $J_{6,8}$=2.0 Hz, $J_{7,8}$=8.0 Hz. o) $J_{4,6}$=1.5 Hz, $J_{6,7}$=7.5 Hz. p) COOH. q) $J_{4,5}$=1.5 Hz, $J_{6,7}$=10.0 Hz, $J_{6,8}$=1.0 Hz, $J_{7,8}$=9.5 Hz.

these signals appeared at slightly up-field compared with the corresponding proton signals of other azulene derivatives described in this paper. Based on these spectral data, 3-methyl-1-[(3-methyl-1-azulenyl)methyl]-4(3aH)-azulenone was tentatively assigned to **1E$_2$** as the most likely structure;[20)] see Table 1 for the assignments of the ^{1}H NMR signals of **1E$_2$**.

Compound **1F$_3$** was a pale yellow oil which appeared to be hitherto unknown 3-methyl-1*H*-inden-1-one by judging from the R_f values (on HPLC and TLC) in comparison with those of 5-isopropyl-3,8-dimethyl-1*H*-inden-1-one.[2,4)] However, on allowing to stand at room temp **1F$_3$** gradually changed into a rather unstable dimer (**1F$_4$**, $C_{20}H_{16}O_2$ by MS).[21)]

Compound **1G$_2$** ($C_{23}H_{18}O$ by MS) was a minor product which showed a similar ^{1}H NMR spectrum to that of **1G$_1$** (except for the aldehyde signal of the latter). Therefore, structure of bis(3-methyl-1-azulenyl) ketone was assigned for **1G$_2$**. Both Compounds **1G$_3$** and **1G$_4$** ($C_{22}H_{16}O_2$) were found spectroscopically to possess a 3-methyl-1-azulenyl group attached to a 2-methyl-1,4-naphthoquinone moiety; a careful analysis of the ^{1}H NMR data (Table 1) led to the most likely coupling positions of **1G$_3$** and **1G$_4$** at C-6 and C-5 of the naphthoquinone nucleus, respectively. Compound **1G$_5$** ($C_{21}H_{16}O$ by MS), on the other hand, was found to possess a 3-methyl-1-azulenyl group attached to a 3-methyl-1*H*-inden-1-one moiety at C-5 on the evidence of ^{1}H NMR spectral data (Table 1).

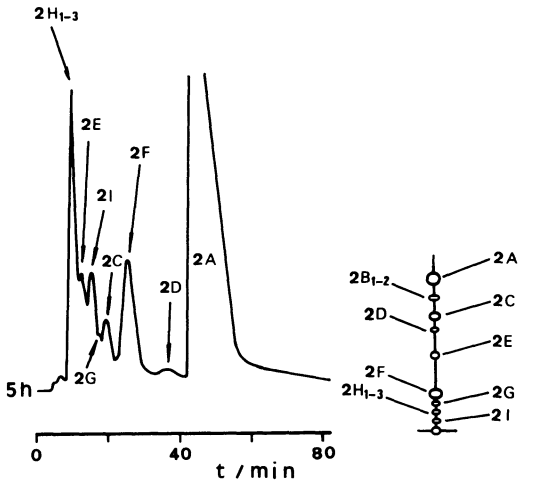


Fig. 2. HPLC and TLC diagrams of the autoxidation products from **2**.

Autoxidation of 1,3-Dimethylazulene (2). The oxidation was carried out in HMPA or DMF at 100 °C for 5 h in a manner similar to that described for **1**; compared with that of **1**, the oxidation of **2** was observed to take place slightly faster at 100 °C (HPLC). The resulting mixture (see HPLC and TLC in Fig. 2)

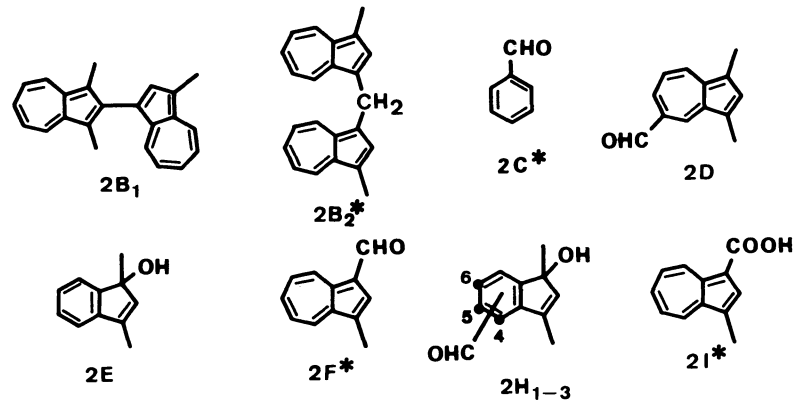


Chart 2. Structures of the autoxidation products of **2**; *previously known compounds.

was carefully separated by using chromatography, and 11 products (**2A—I**) were obtained besides the recovered starting material **2** (**2A**). Structures of these products which have been similarly established are shown in Chart 2; among these, Compounds **2B**$_2$,[10] **2C**, **2F**,[14] and **2I**[17] were identified to be already known. The total theoretical yields of these isolated products were 35.4%. Besides these, a large amount (ca. 60%, w/w) of unidentified polar products of relatively high molecular weights were obtained.

Compound **2B**$_1$ ($C_{23}H_{20}$ by MS) was readily found to possess an asymmetric structure, 1′,3,3′-trimethyl-1,2′-biazulene, on the basis of the ^{1}H NMR data (Table 1) which closely resembled those of **1B**$_2$ except for the presence of a Me-3′ signal of **2B**$_1$.

Compound **2D** ($C_{13}H_{12}O$), a minor product, was proved to be 1,3-dimethyl-5-azulenecarbaldehyde on the evidence of spectral data (UV, ^{1}H NMR, and MS).

Compound **2E** ($C_{11}H_{12}O$ by MS) possessed the structure of 1,3-dimethyl-1*H*-inden-1-ol on the evidence of UV, IR, and ^{1}H NMR data, whereas Compounds **2H**$_{1\text{-}3}$ which remained inseparable by chromatography were found spectroscopically to be a mixture of 1-hydroxy-1,3-dimethyl-1*H*-indene-4-, 5-, and 6-carbaldehydes in an approximate ratio of 1 : 2 : 1, respectively.

Compound **2G** was an extremely minor product but its structure has remained to be clarified owing to the limited amount for sufficient spectroscopic data.

Possible Reaction Pathways for the Formation of Autoxidation Products of 1 and 2. As was observed for the trialkylazulenes **3** and **4**, the autoxidation of **1** and **2** has resulted in the simultaneous formation of many kinds of products by competitive processes. An attempt will now be made here to suggest the most probable reaction pathways for the formation of the major products (and in some cases minor products as well) after having been divided into four groups according to the type of reactions involved: (a) Side chain oxidation, (b) one-carbon transfer reactions, (c) rearrangement reactions to naphthoquinonoids, benzenoids, and indenols, and (d) oxidative dimerization, as illustrated in Schemes 1 and 2. Although the yield of each product may not necessarily reflect the ease of the corresponding reaction pathway, the combined yields of the products formed by the above reactions from alkylazulenes **1**—**4** are summarized in Table 2 for comparison.

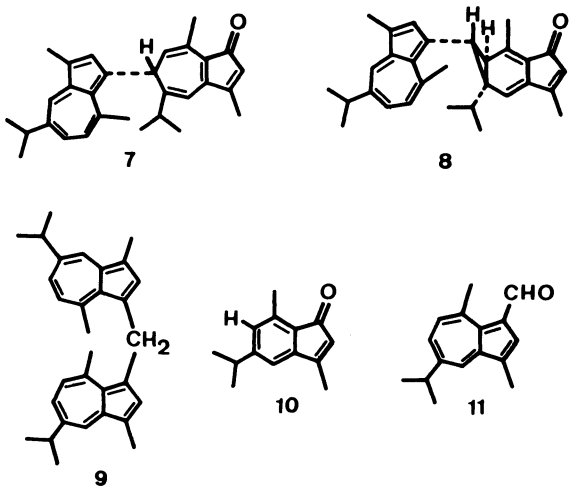
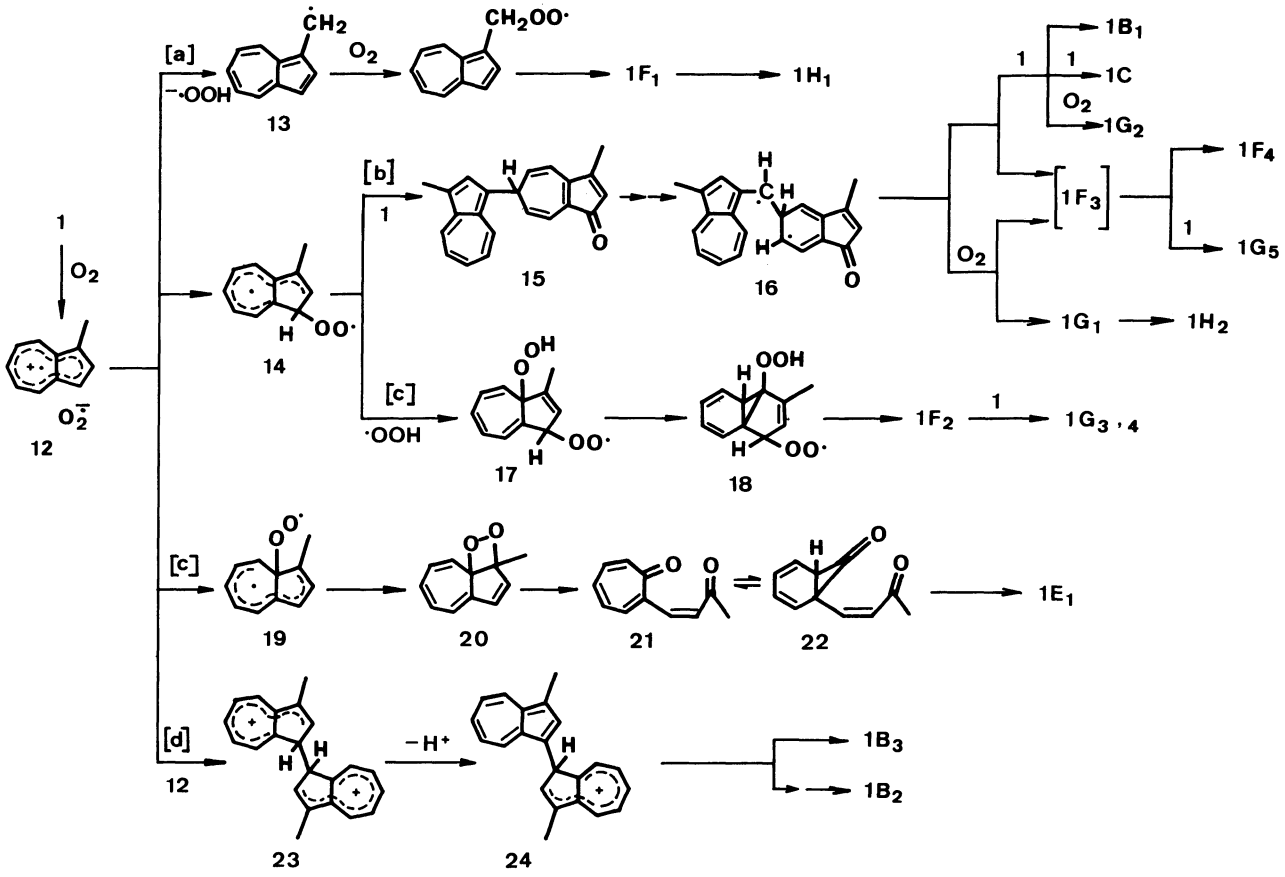


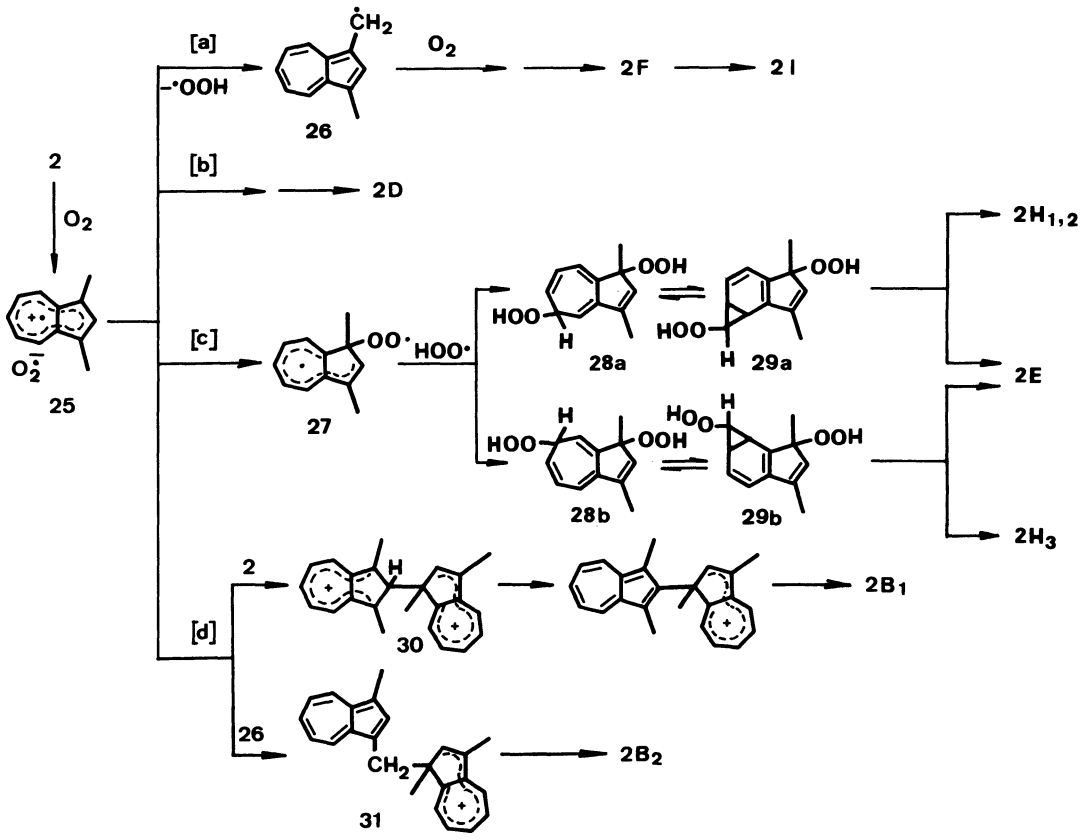
Table 2. Combined Yields (%, Isolated) of the Autoxidation[a] Products Classified into the Reaction Pathways

Reaction pathways	Starting alkylazulene			
	1	**2**	**3**[b]	**4**[c]
[a]	4	20.7	9.7	0.5
[b]	14.8	0.7	21.3	17.5
[c]	5.6	6.7	12.8	1.3
[d]	0.6	6.6	7.7	0
[e]	0	0	1.5	4.6
[f]	60	60	34	59

Reaction pathways: [a], side-chain oxidation; [b], one-carbon transfer reactions; [c], rearrangement reactions to naphthalenoids, benzenoids, and indene derivatives; [d], oxidative dimerization; [e], 1,5- and 1,7-azulenequinone formation; [f] polar resinous substance formation. a) Oxygenation in DMF or HMPA at 100 °C. b) From Refs. 2 and 4. c) From Refs. 3 and 4 (oxygenation at 120 °C).



Scheme 1. Possible reaction pathways for the autoxidation products from **1**.



Scheme 2. Possible reaction pathways for the autoxidation products from **2**.

a) As was postulated in the case[4] of **3** and **4**, the facile oxidation of **1** and **2** with molecular oxygen is likely to form the radical cation complexes **12** and **25**, respectively, from which various products are derived (see Schemes 1 and 2). Then the transformation of these complexes into the radical intermediates **13** and **26** (path [a]) would result in the oxidation of the side chain, thus yielding 1-azulenecarbaldehydes $\mathbf{1F}_1$ and **2F**, respectively, by the consecutive oxidation with another molecule of oxygen in a manner similar to the well-accepted mechanism for the autoxidation of side chains of alkylbenzenes and naphthalene.[22] Further autoxidation of these aldehydes in the usual way gives the 1-azulenecarboxylic acids $\mathbf{1H}_1$ and **2I**. It is particularly a characteristic feature, in comparison with the case[4] of **3** and **4**, that oxidation of a side chain on the C-1 and 3 positions of azulene nucleus constitutes an exclusive process in the autoxidation of **2**, while it takes place only moderately in **1** under the present conditions (see Table 2).

b) It is significant in the present autoxidation that compounds having extra-carbon(s) such as 1,1′-methylenebis[3-methylazulene] ($\mathbf{1B}_1$), and related compounds **1C**, $\mathbf{1G}_1$, $\mathbf{1G}_2$, and $\mathbf{1H}_2$ have been obtained in relatively high yields from **1**, whereas **2** has afforded 1,3-dimethyl-5-azulenecarbaldehyde (**2D**) as the only compound of this type in an extremely low yield.

Meanwhile, we have recently isolated[23] both the dimeric cycloheptatriene form **7** and its norcaradiene isomer **8** on autoxidation of guaiazulene (**3**) either at 85 °C in DMF–0.5 M sulfuric acid (1 M=1 mol dm^{-3}) or at 25—35 °C on the surface of a filter paper. These compounds were shown to exist in an equilibrium and to constitute important intermediates for the intermolecular one-carbon transfer reactions. For examples, treatment of **8** with one equivalent of **3** under nitrogen exclusively yields 3,3′-methylenebis[guaiazulene] (**9**) and 5-isopropyl-3,7-dimethyl-1*H*-inden-1-one (**10**), whereas **8** is transformed into 3-guaiazulenecarbaldehyde (**11**) and indenone **10** on exposure to air.

From these facts, similar dimeric cycloheptatriene **15** (formed by the coupling of the 3-methyl-1-azulenylperoxyl diradical **14** with **1**) and its equilibrated norcaradiene isomer (similar to the structural formula **8**) are also considered to be the most likely key intermediates for the one-carbon transfer reactions (path [b] in Scheme 1). The fragmentation of the latter intermediate through a dimeric diradical **16** in the presence of **1** would give 1,1′-methylenebis(3-methylazulene) ($\mathbf{1B}_1$) and 3-methyl-1*H*-inden-1-one ($\mathbf{1F}_3$); the latter is unstable and gradually changes to its dimer $\mathbf{1F}_4$. Further oxidative coupling of $\mathbf{1B}_1$ (or of its precursor) with another molecule of **1** would form the trimer **1C**. Concomitantly, oxidative cleavage of **16** would give 3-methyl-1-azulenecarbaldehyde $\mathbf{1G}_1$ (and its carboxylic acid derivative $\mathbf{1H}_2$) and $\mathbf{1F}_3$, whereas bis(3-methyl-1-azulenyl) ketone ($\mathbf{1G}_2$) appears to be derived from **16** through oxidation of a subsequent, yet unclarified intermediate (Scheme 1). It should be noticed that this type of reaction involving one-carbon transfer constitutes the major pathway in the oxidation of **1** (see Table 2).

In contrast, **2D** apparently formed as the result of the intermolecular one-carbon transfer reaction (path [b] in Scheme 2) was isolated in an extremely small amount (Table 2). Although this pathway seems to be of interest in view of the reactivity of the azulene nucleus, the exact mechanism has remained to be clarified.

c) As in the case[4] of the oxidative rearrangement of guaiazulene **3** to naphthoquinonoids, addition of another molecule of oxygen (or ·OOH) to C-3a of **14** (Scheme 1) is expected to give the intermediate **17** (path [c]) that can be converted into 2-methyl-1,4-naphthoquinone ($\mathbf{1F}_2$) through the equilibrated norcaradiene form **18**. It is more likely that (*Z*)-4-phenyl-3-buten-2-one ($\mathbf{1E}_1$) obtained from **1** in the highest yield among the benzenoid compounds is derived by transformation of **12** into the diradical **19** (path [c]) and then into the dioxetane intermediate **20**, followed by the ring opening, the tropone-norcaradiene dicarbonyl equilibrium between **21** and **22**, and then by facile decarbonylation of **22** accompanied by isomerization of the olefinic side chain.

On the other hand, possible reaction pathways for the formation of the rearrangement products (1-indenols **2E** and $\mathbf{2H}_{1\text{-}3}$) from **2** are shown as path [c] in Scheme 2: transformation of **25** into 1,3-dimethyl-1-azulenylperoxyl diradical **27**, followed by addition of peroxyl radical to the C-5 (or C-7) position, would give an intermediate such as hydroperoxide **28a** (or **28b**) that rearranges into 1,3-dimethyl-1*H*-inden-1-ols **2E** and $\mathbf{2H}_{1\text{-}3}$ presumably through the equilibrated norcaradiene form **29a**/**29b**.

d) Dimerization of the radical cation **12** is expected to give **23**, from which the proton loss would lead to the intermediate **24** (path [d] in Scheme 1). This yields then 3,3′-dimethyl-1,1′-biazulene ($\mathbf{1B}_3$) and a smaller proportion of the 1,2′-isomer $\mathbf{1B}_2$ through a 1,2-rearranged intermediate as in the case of guaiazulene **3**.[4] It is another significant feature that these dimers from **1** were isolated in extremely small proportions in comparison with the case of the oxidation of **3**. On the other hand, the radical coupling of **25** with **2** and **26** is likely to afford dimeric intermediates **30** and **31**, respectively, and then loss of the methyl group on C-1 from these dimeric intermediates would result in the formation of the oxidative dimers $\mathbf{2B}_1$ and $\mathbf{2B}_2$ as illustrated in Scheme 2 (path [d]). The dimers $\mathbf{1G}_{3\text{-}5}$ are apparently derived as the result of oxidative couplings of **1** with the rearranged monomers $\mathbf{1F}_2$ and $\mathbf{1F}_3$, as illustrated in Scheme 1.

It is noteworthy that neither 3-methyl-1,5- nor 1,7-azulenequinone was isolated in the present autoxidation of **1** or **2** (Table 2). This is most likely due to lability of these unknown azulenequinones under the

reaction conditions presently employed (at 100 °C),[24] taking into account the melting points of e.g. parent 1,5- and 1,7-azulenequinones: both mp 100 °C decomp.[8d]

The detailed mechanistic consideration for the formation of other minor compounds is not made here because of the limited evidences at this stage with regard to the reaction pathways. Besides these isolated compounds described so far, considerable amounts (ca. 60%) of intractable resinous substances are accompanied also by the present autoxidation of **1** and **2** as was observed particularly in the case[3,4] of **4** (Table 2).

Nevertheless, it has now become apparent that the autoxidation of the alkylazulenes **1** and **2** is highly competitive involving oxidation of the nucleus and side chains (exclusively at C-1 position), substitutions, ring contraction, and other reactions such as rearrangement to naphthoquinones in a similar manner to the oxidation of the previously studied trialkylazulenes in many respects. However, depending upon the kinds and positions of alkyl substituents on the azulene nucleus, some significant differences in the reactivities between them were also observed as described above. Thus, although the exact mechanism is under further investigation in detail by employing azulene itself and other alkylazulenes under various reaction conditions, the present findings are believed to provide valuable information on autoxidation of azulenoid compounds.[24]

Experimental

Melting points were determined with a Yanagimoto MP-S3 instrument and are uncorrected. Column chromatography was performed with Wako C-300 silica-gel. TLC was conducted on plates precoated with silica-gel 60F-254 (0.25 mm, Merck) by using 15:85 AcOEt–hexane as eluant. HPLC was carried out with Hitachi gel #3011 packed in a Pyrex column (ϕ 5 mm, 500 mm length) with 1:9 hexane–MeOH as solvent.

UV and IR (both in $CHCl_3$ unless otherwise stated) spectra were taken on a Hitachi 323 spectrophotometer and a Nihonbunko IR-A-202 Grating spectrometer, respectively. NMR spectra were recorded in $CDCl_3$ (unless otherwise stated) with a JEOL-FX200 cryospectrometer (200-MHz for ^1H and 50-MHz for ^{13}C) at 27 °C. Chemical shifts are reported as δ values in parts per million rel to tetramethylsilane (δ 0.0) as the internal standard. The assignments of all signals were made by employing a first-order analysis with the aid of decoupling technique and the parameters were confirmed by a computer-assisted simulation analysis; those values for azulene derivatives are summarized in Table 1. Mass spectra were taken on a JEOL JMS-HX100 (with a JEOL JMA-DA5000 mass data system) high-resolution instrument and are given in terms of m/z (rel intensity) compared with the base peak.

Oxidation of 1-Methylazulene (1) in HMPA. A soln of **1**[25] (1.00 g) in freshly distilled HMPA (20 g) was placed in a Pyrex flask (ϕ 1.8 cm, 60 cm height) and subjected to autoxidation by allowing finely bubbling oxygen to pass through the soln (from the bottom of the flask) for 10 h at 100±5 °C. After cooling, the mitxture was diluted with water (200 cm^3) and extracted with ether (4×50 cm^3). The combined organic layers were washed with water, dried (Na_2SO_4), and evaporated in vacuo, giving a brown oil (0.96 g); the HPLC and TLC diagrams of this crude mixture are given in Fig. 1. This oil was preliminarily separated into five fractions by means of preparative HPLC with Hitachi gel #3019 (100 g) using methanol as eluant. Then each fraction was carefully separated by silica-gel column or thin layer with AcOEt–hexane; when necessary, this chromatographic procedure was repeated. Thus, the following 19 products were obtained as pure substances (**1A—I**), besides the reccovered starting material **1** (**1A**: 0.50 g; R_f=0.83; ^1H NMR, see Table 1) and polar resinous substances [0.30 g, 60% (w/w); R_f=0.0]. The yield of each product is based on the consumed starting material (0.50 g).

1,1′-Methylenebis[3-methylazulene][10] ($1B_1$): Dark blue prisms; 30 mg (6.0% yield); mp 79 °C (Ref. 10, 79—80 °C); R_f=0.76; UV 245 (log ε 4.65), 288 (4.83), 345 (sh, 4.23), 355 (4.29), 410 (sh, 2.80), 430 (sh, 2.70), 590 (sh, 2.70), 640 (sh, 2.80), and 652 nm (2.81); MS m/z 296 (M^+; 100), 281 (65), 265 (55), 252 (11), 239 (6), and 155 (24); ^1H NMR, see Table 1. (Found: m/z.296.1549).

1′,3-Dimethyl-1,2′-biazulene ($1B_2$): A yellow-green oil; 1 mg (0.2%); R_f=0.76; UV 245 (log ε 4.69), 251 (4.72), 257 (4.74), 263 (4.76), 272 (4.76), 301 (4.70), 315 (4.68), 350 (sh, 4.35), 410 (3.91), 580 (sh, 2.94), 634 (3.04), and 676 nm (sh, 3.02); MS m/z 282 (M^+; 100), 265 (26), and 252 (11); ^1H NMR, see Table 1.

Found: m/z 282.1446. Calcd for $C_{22}H_{18}$: M, 282.1409.

3,3′-Dimethyl-1,1′-biazulene ($1B_3$): Dark green paste; 2 mg (0.4%); R_f=0.76; MS m/z 282 (M^+; 100), 276 (5), 265 (31), 252 (20), 239 (7), 141 (13), 132 (9), 126 (8), and 119 (4); ^1H NMR, see Table 1.

Found: m/z 282.1421. Calcd for $C_{22}H_{18}$: M, 282.1409.

1,1′,1″-Methylidynetris[3-methylazulene] (1C): Dark blue prisms; mp 138 °C; 20 mg (4.0%); R_f=0.68; UV 245 (log ε 4.50), 280 (sh, 4.54), 290 (4.55), 349 (sh, 4.26), 358 (4.29), 370 (4.29), 596 (sh, 2.76), and 636 nm (2.80); MS m/z 436 (M^+; 100), 421 (41), 405 (13), 391 (12), 377 (5), 294 (25), 279 (80), 265 (23), 252 (10), 239 (5), 218 (8), 195 (7), 155 (13), 141 (10), 115 (7), 83 (4), 71 (6), 57 (9), and 43 (6); ^1H NMR, see Table 1; ^{13}C NMR 139.45, 137.06, 134.78, 133.44, 132.97, 132.74, 124.56, 120.88, 120.53, 35.21, and 12.73.

Found: m/z 436.2262. Calcd for $C_{34}H_{28}$: M, 436.2191.

Treatment of **1C** with an equivalent of triphenylmethylium tetrafluoroborate in dry acetonitril at 20 °C for 1 h gave the tetrafluoroborate (**6**) as dark blue-green crystals: mp>300 °C; UV 643 nm.

Triphenylcarbinol[11] ($1D_1$): Colorless prisms; 5 mg (1.0%); mp 163 °C (Ref. 11, 161—162 °C); R_f=0.49; MS m/z 260 (M^+; 100); ^1H NMR, identical with the spectrum of the authentic sample.

Benzaldehyde ($1D_2$): Colorless oil; 1 mg (0.2%); R_f= 0.49; MS m/z 106 (M^+; 100); ^1H NMR, identical with the spectrum of the authentic sample.

(1Z),(4Z)-1,5-Diphenyl-1,4-pentadien-3-one[12] ($1D_3$): Colorless prisms; 1 mg (0.2%); mp 103 °C (Ref. 12, 104—107 °C); R_f=0.49; MS m/z 234 (M^+; 100); ^1H NMR, identical with that of the authentic sample.

(Z)-1-Phenyl-1-buten-3-one[13] ($1E_1$): Colorless prisms; 5 mg (1.0%); mp 41 °C (Ref. 13, 39—41 °C); R_f=0.36; MS m/z 146 (M^+; 100); ^1H NMR, identical with that of the authentic sample.

3-Methyl-1-[(3-methyl-1-azulenyl)methyl]-4(3a*H*)-azulenone[20] (1E$_2$): Green prisms; 2 mg (0.4%); mp 143 °C; R_f= 0.36; UV (MeOH) 243 (log ε 4.55), 285 (4.57), 340 (sh, 4.17), 351 (4.22), 380 (sh, 3.37), 430 (sh, 3.20), 580 (sh, 2.80), 600 (sh, 2.84), 626 (2.87), 650 (sh, 2.81), and 684 nm (sh, 2.80); MS m/z 312 (M^+; 4%), 297 (1), 279 (1), 265 (1), 252 (1), 170 (1), 155 (100), 141 (4), 128 (3), and 115 (3); IR (KBr) 1690 cm^{-1} (C=O); ^{1}H NMR, see Table 1.

Found: m/z 312.1575. Calcd for $C_{23}H_{20}O$: M, 312.1635.

1-Azulenecarbaldehyde[14] (1F$_1$): Red oil; 15 mg (3.0%); R_f=0.28; MS m/z 156 (M^+; 100); ^{1}H NMR, identical with the reported spectrum.[14]

2-Methyl-1,4-naphthoquinone[15] (1F$_2$): Pale yellow needles; 5 mg (1.0%); mp 105 °C (Ref. 15, 105—107 °C; R_f=0.28; MS m/z 172 (M^+; 100); ^{1}H NMR, identical with that of the authentic sample.

Compound 1F$_3$: Pale yellow oil; 1 mg (0.2%); R_f=0.28. This product, which was presumed to be hitherto unknown 3-methyl-1*H*-inden-1-one, gradually changed to Compound **1F$_4$**:[21] colorless oil; R_f=0.28; UV 242 (log ε 3.17), 255 (sh, 3.13), and 285 nm (sh, 2.82); IR 1730—1680 cm^{-1} (C=O); MS m/z 288 (M^+; 24%), 144 (100), and 116 (8).

Found: m/z 288.1169. Calcd for $C_{20}H_{16}O_2$: M, 288.1150.

3-Methyl-1-azulenecarbaldehyde[14] (1G$_1$): Dark violet needles; 10 mg (2.0%); mp 73 °C (Ref. 14, 73 °C); R_f=0.23; MS m/z 170 (M^+; 100); ^{1}H NMR, identical with the reported spectrum.[14]

Bis(3-methyl-1-azulenyl) Ketone (1G$_2$): Dark green prisms; 3 mg (0.6%); mp 163 °C; R_f=0.23; UV 242 (log ε 4.48), 280 (sh, 4.51), 295 (4.60), 315 (4.54), 327 (sh, 4.46), 422 (4.39), 566 (2.71), and 596 nm (sh, 2.65); MS m/z 310 (M^+; 100), 295 (63), 281 (12), 267 (27), 252 (27), 239 (6), 215 (2), 189 (2), 169 (13), 153 (11), 141 (34), 126 (11), 115 (40), 97 (9), 85 (11), 71 (18), 57 (30), and 43 (28); IR 1720 cm^{-1} (C=O); ^{1}H NMR, see Table 1.

Found: m/z 310.1354. Calcd for $C_{23}H_{18}O$: M, 310.1357.

2-Methyl-7-(3-methyl-1-azulenyl)-1,4-naphthoquinone (1G$_3$): Dark violet prisms; 5 mg (1.0%); mp 122 °C; R_f=0.23; UV (MeOH) 250 (log ε 4.37), 294 (4.34), 360 (sh, 3.44), 380 (sh, 3.43), and 500 nm (3.35); MS m/z 312 (M^+; 100), 295 (9), 239 (8), 215 (11), 165 (5), 141 (20), 118 (17), 108 (5), 97 (7), 83 (8), 69 (8), 55 (9), and 44 (16); IR 1655 cm^{-1} (C=O); ^{1}H NMR, see Table 1.

Found: m/z 312.1057. Calcd for $C_{22}H_{16}O_2$: M, 312.1150.

1-Methyl-3-(3-methyl-1,4-dioxo-5-naphthyl)azulene (1G$_4$): dark blue violet prisms; 5 mg (1.0%); mp 192 °C; R_f=0.23; UV 245 (sh, log ε 4.52), 251 (4.53), 257 (4.52), 263 (4.52), 290 (4.53), 340 (sh, 4.11), 375 (3.40), 590 (3.13), and 670 nm (sh, 3.00); MS m/z 312 (M^+; 100), 297 (61), 286 (11), 269 (4), 260 (1), 243 (2), 228 (2), 215 (4), 141 (2), 71 (1), and 57 (1); IR 1665 and 1660 cm^{-1} (C=O); ^{1}H NMR, see Table 1.

Found: m/z 312.1163. Calcd for $C_{22}H_{16}O_2$: M, 312.1150.

3-Methyl-5-(3-methyl-1-azulenyl)-1*H*-inden-1-one (1G$_5$): Dark brown prisms; 5 mg (1.0%); mp 80 °C; R_f=0.23; UV 246 (log ε 4.11), 299 (4.09), 306 (sh, 4.08), 353 (3.25), 458 (3.24), 620 (2.42), and 670 nm (sh, 2.34); MS m/z 284 (M^+; 100), 253 (5), 239 (18), 215 (7), and 141 (16); IR 1700 cm^{-1} (C=O); ^{1}H NMR, see Table 1.

Found: m/z 284.1208. Calcd for $C_{21}H_{16}O$: M, 284.1201.

1-Azulenecarboxylic Acid[16] (1H$_1$): Red needles; 5 mg (1.0%); mp 182 °C (Ref. 16, 181—182 °C); R_f=0.10; MS m/z 172 (M^+; 100); ^{1}H NMR, identical with the reported spectrum.[16]

3-Methyl-1-azulenecarboxylic Acid[17] (1H$_2$): Dark violet needles; 5 mg (1.0%); mp 196 °C (Ref. 17, 196 °C); R_f=0.10; MS m/z 186 (M^+; 100); ^{1}H NMR, identical with the reported spectrum.[17]

Cinnamic Acid[18] (1I): Colorless prisms; 1 mg (0.2%); mp 130 °C (Ref. 18, 132—133 °C); R_f=0.04; MS and ^{1}H NMR, identical with those of the authentic sample.

Autoxidation of 1 in DMF. The same oxidation procedure was employed, and virtually the same products were obtained as in the case of the oxidation in HMPA described above.

Oxidation of 1,3-Dimethylazulene (2) in HMPA. Autoxidation of **2**[25] (0.40 g) in HMPA (16 g) was carried out for 5 h at 100±5 °C in a manner similar to that described for **1**, thus affording, after the careful chromatographic separation, 11 products (**2A—I**; see Fig. 2 for HPLC and TLC), besides the recovered starting material **2** (**2A**, 0.25 g, R_f 0.83: ^{1}H NMR, see Table 1) and polar resinous substances [0.09 g, 60% (w/w); R_f 0.0]; the yield of each product is based on the consumed starting material (0.15 g).

1′,3,3′-Trimethyl-1,2′-biazulene (2B$_1$): Green prisms; 5 mg (3.3%); mp 78 °C; R_f=0.74; UV 245 (log ε 4.37), 277 (4.52), 300 (4.51), 310 (sh, 4.47), 355 (4.18), 436 (3.25), 572 (sh 2.62), 624 (2.67), and 680 nm (sh, 2.65); MS m/z 296 (M^+; 100), 281 (17), 279 (17), 265 (44), and 252 (8); ^{1}H NMR, see Table 1.

Found: m/z 296.1562. Calcd for $C_{23}H_{20}$: M, 296.1564.

1,1′-Methylenebis[3-methylazulene][10] (2B$_2$): Dark blue prisms; 5 mg (3.3%); mp 79 °C; R_f=0.74; MS and ^{1}H NMR, identical with those of **1B$_1$** obtained by the oxidation of **1** in HMPA or DMF as described above.

Benzaldehyde (2C): Colorless oil; 1 mg (0.7%); R_f=0.64; MS and ^{1}H NMR, identical with those of the authentic sample.

1,3-Dimethyl-5-azulenecarbaldehyde (2D): Yellow green oil; 1 mg (0.7%); R_f=0.56; UV 245 (log ε 4.03), 284 (sh, 4.09), 292 (4.13), 304 (sh, 4.12), 332 (sh, 3.74), 415 (3.42), 620 (2.76), and 672 nm (sh, 2.72); MS m/z 184 (M^+; 100), 169 (41), and 155 (19); IR 1690 cm^{-1} (C=O); ^{1}H NMR, see Table 1.

Found: m/z 184.0881. Calcd for $C_{13}H_{12}O$: M, 184.0888.

1,3-Dimethyl-1-indenol (2E): Colorless oil; 7 mg (4.7%); R_f=0.42; UV 248 (sh, log ε 4.17), 253 (4.18), 265 (sh, 4.12), 271 (sh, 4.08), 276 (sh, 4.06), 282 (sh, 4.04), and 294 nm (sh, 3.86); MS m/z 160 (M^+; 61%), 145 (100), 128 (12), 127 (12), and 115 (32); IR 3750—3100 cm^{-1} (OH); ^{1}H NMR 1.55 (3H, s, Me-1), 1.66 (1H, brs, HO-1), 2.02 (3H, d, $J_{2,Me(3)}$=1.5 Hz, Me-3), 5.92 (1H, q, H-2), 7.06 (1H, ddd, $J_{6,7}$=7.0 Hz, $J_{5,7}$=1.3 Hz, $J_{4,7}$=0.6 Hz, H-7), 7.12 (1H, ddd, $J_{5,6}$=7.2 Hz, $J_{4,5}$=7.0 Hz, H-5), 7.19 (1H, ddd, H-6), and 7.31 (1H, ddd, H-4).

Found: m/z 160.0885. Calcd for $C_{11}H_{12}O$: M, 160.0888.

3-Methyl-1-azulenecarbaldehyde[14] (2F): Dark violet needles; 30 mg (20%); R_f=0.19; MS and ^{1}H NMR, identical with the spectra of **1G$_1$** described above.

Compound 2G: Yellow crystals; R_f=0.14; UV 245 (sh, log ε 3.90), 255 (3.94), 360 (sh, 3.46), 378 (3.49), 398 (sh, 3.45), 430 (sh, 2.97), 460 (sh, 2.76), 496 (sh, 2.48), and 530 nm (sh, 2.13); MS m/z 160 (MS^+; 100), 131 (63), 104 (20), 103 (20), 78 (19), 77 (20), and 51 (20).

1-Hydroxy-1,3-dimethyl-1*H*-indene-4-, 5-, and 6-carbaldehyde (2H$_1$, 2H$_2$, and 2H$_3$): (as a ca. 1:2:1 mixture, respectively): Colorless oil; 3 mg (2.0%); R_f=0.10; MS m/z 188 (M^+; 100), 173 (89), 159 (50), 145 (59), 128 (22), 127 (22), and 115 (59); IR 3750—3150 (OH) and 1690 cm^{-1} (C=O); ^{1}H NMR (DMSO-d_6) **2H$_1$** δ= 1.41 (3H, s, Me-1), 2.27 (3H, d,

$J_{2,Me(3)}$=1.5 Hz, Me-3), 5.10 (1H, brs, HO-1), 6.20 (1H, q, H-2), 7.24 (1H, t, $J_{5,6}=J_{6,7}$=7.5 Hz, H-6), 7.51 (1H, dd, $J_{5,7}$=1.5 Hz, H-7), 7.69 (1H, dd, H-5), and 10.40 (1H, s, CHO-4), **2H**$_2\delta$=1.43 (3H, s, Me-1), 2.02 (3H, d, $J_{2,Me(3)}$=1.5 Hz, Me-3), 5.10 (1H, brs, OH-1), 6.17 (1H, q, H-2), 7.27 (1H, brd, $J_{6,7}$=8.0 Hz, H-7), 7.72 (1H, brd, $J_{4,6}$=1.5 Hz, H-4), 7.74 (1H, dd, H-6), and 9.88 (1H, s, CHO-5), and **2H**$_3\delta$=1.41 (3H, s, Me-1), 2.03 (3H, d, $J_{2,Me(3)}$=2.0 Hz, Me-3), 5.10 (1H, brs, HO-1), 6.04 (1H, q, H-2), 7.46 (1H, brd, $J_{4,5}$=8.0 Hz, H-4), 7.55 (1H, d, $J_{5,7}$=1.5 Hz, H-7), 7.61 (1H, dd, H-5), and 9.88 (1H, s, CHO-6).

Found (for the mixture of **2H**$_{1\text{-}3}$): *m/z* 188.0839. Calcd for $C_{12}H_{12}O_2$: M, 188.0837.

3-Methyl-1-azulenecarboxylic Acid[17] **(2I):** Dark violet needles; mp 196 °C (Ref. 17, 196 °C); 1 mg (0.7%); R_f=0.06; MS and ^{1}H NMR, identical with the spectra of **1H**$_2$ described above.

Autoxidation of 2 in DMF. The same procedures as those for **2** in HMPA were employed, and virtually the same products were obtained.

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References

1) A part of the results have been preliminarily presented: S. Takekuma, O. Okabe, Y. Matsubara, H. Yamamoto, and T. Nozoe, 50th National Meeting of the Chemical Society of Japan, Tokyo, April 1985, Abstr. No. 1T11; Y. Matsubara, S. Takekuma, K. Kitajima, H. Yamamoto, and T. Nozoe, 52nd National Meeting of the Chemical Society of Japan, Kyoto, April 1986, Abstr. No. 2V28.

2) T. Nozoe, S. Takekuma, M. Doi, Y. Matsubara, and H. Yamamoto, *Chem. Lett.*, **1984**, 627

3) Y. Matsubara, S. Takekuma, K. Yokoi, H. Yamamoto, and T. Nozoe, *Chem. Lett.*, **1984**, 631

4) Y. Matsubara, S. Takekuma, K. Yokoi, H. Yamamoto, and T. Nozoe, *Bull. Chem. Soc. Jpn.*, **60**, 1415 (1987).

5) These experimental results are also in agreement with a preliminary theoretical calculation: T. Kurihara, S. Ishikawa, and T. Nozoe, 52nd National Meeting of the Chemical Society of Japan, Kyoto, April 1986, Abstr. No. 2V26.

6) For reviews and monographs, see K. Hafner, *Angew. Chem.*, **70**, 419 (1958); *Angew. Chem., Int. Ed. Engl.*, **3**, 167 (1964); T. Nozoe and S. Ito, *Fortschr. Chem. Org. Naturst.*, **19**, 33 (1961); A. G. Anderson and R. G. Anderson, *J. Org. Chem.*, **27**, 3578 (1962), and references cited therein; K. Takase and M. Yasunami, *Yuki Gosei Kagaku Kyokai Shi*, **39**, 1172 (1981); D. Lloyd, "Non-Benzenoid Conjugated Carbocyclic Compounds," Elsevier, Amsterdam (1984), pp. 351—377.

7) R. J. Waltman and J. Bargon, *Can. J. Chem.*, **64**, 76 (1986) and references cited therein.

8) a) L. T. Scott, M. D. Rozeboom, K. N. Houk, T. Fukunaga, H. J. Lindner, and K. Hafner, *J. Am. Chem. Soc.*, **102**, 5169 (1980), and references cited therein; b) L. T. Scott, *Pure Appl. Chem.*, **1983**, 363; c) L. T. Scott, P. Grutter, and R. Chamberlain, III, *J. Am. Chem. Soc.*, **106**, 4852 (1984); d) L. T. Scott and C. M. Adams, *ibid.*, **106**, 4857 (1984); e) T. Morita, M. Karasawa, and K. Takase, *Chem. Lett.*, **1980**, 197; f) T. Morita, F. Ise, and K. Takase, *ibid.*, **1982**, 1303.

9) Slightly different, unresolved values have been reported for a few of these azulenes (mostly measured at 60-MHz in much concentrated CCl_4 or $CDCl_3$ soln); see the Exptl section.

10) K. Hafner and W. Senf, *Justus Liebigs Ann. Chem.*, **656**, 34 (1962).

11) W. E. Bachmann and H. P. Hetzner, *Org. Synth.*, Coll. Vol. III, 839 (1955).

12) C. R. Conard and M. A. Dolliver, *Org. Synth.*, Coll. Vol. II, 167 (1943).

13) N. L. Drake and P. Allen, Jr., *Org. Synth.*, Coll. Vol. I, 77 (1932).

14) K. Hafner and C. Bernhard, *Angew. Chem.*, **69**, 533 (1957); *Justus Liebigs Ann. Chem.*, **625**, 108 (1959); W. Treibs, J. Hiebsch, and H.-J. Neupert, *Naturwiss.*, **44**, 352 (1957); W. Treibs, H.-J. Neupert, and J. Hiebsch, *Chem. Ber.*, **92**, 141 (1959).

15) L. F. Fieser, M. Tishler, and W. L. Sampson, *J. Am. Chem. Soc.*, **62**, 996 (1940).

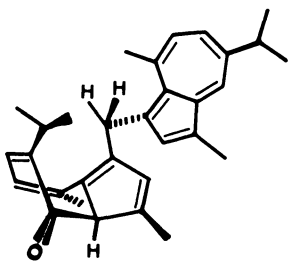
16) W. Treibs, H.-J. Neupert, and J. Hiebsch, *Chem. Ber.*, **92**, 1216 (1959); A. G. Anderson, Jr., R. G. Anderson, and L. L. Roplogle, *Proc. Chem. Soc.*, **1960**, 72.

17) R. N. McDonald, R. R. Reitz, and J. M. Richmond, *J. Org. Chem.*, **41**, 1822 (1976).

18) J. R. Johnson, *Organic Reactions*, **1**, 210 (1942).

19) The chloride of this cation has been reported: K. Hafner, H. Pelster, and J. Schneider, *Justus Liebigs Ann. Chem.*, **650**, 62 (1961).

20) Autoxidation of 1,1′-methylenebis[3-methylazulene] (**1B**$_1$) under similar conditions has been found to produce **1E**$_2$ besides other products. Moreover, on oxidation of 3,3′-methylenebisguaiazulene with peracetic acid in hexane at 25 °C, we have recently isolated a structurally similar compound 5-isopropyl-3,8-dimethyl-1-[(3-guaiazulenyl)methyl]-4(3a*H*)-azulenone (dark green prisms, mp 117 °C, 61% yield), which is presumed on the molecular model inspection to exist in a favorable conformation **32** in $CDCl_3$. ^{1}H NMR parameters of **1E**$_2$ closely resemble those of the corresponding positions of **32**. Problems of keto-enol equilibria of these compounds and related other azulene analogues will be reported elsewhere together with their preparation and detailed structural determination.



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21) Although composition of the dimer **1F**$_4$ was confirmed by MS, its purification and structural determination are currently under investigation.

22) E.g. See J. Santamaria, *Tetrahedron Lett.*, **22**, 4511 (1981); H. Iwamoto, M. Kanehiro, and Y. Matsubara, *Yukagaku*, **31**, 222 (1982); S. Takekuma, Y. Matsubara, H. Yamamoto, and T. Nozoe, *ibid.*, **34**, 1026 (1985).

23) Y. Matsubara, S. Takekuma, K. Ueno, H. Yamamoto, and T. Nozoe, 52nd National Meeting of the Chemical Society of Japan, Kyoto, April 1986, Abstr. No. 2V27; Y. Matsubara, S. Takekuma, K. Kitajima, H. Yamamoto, and T. Nozoe, 53rd National Meeting of the Chemical Society of Japan, Nagoya, October 1986, Abstr. No. 3D07; Y. Matsubara, S. Takekuma, H. Yamamoto, and T. Nozoe, *Chem. Lett.*, **1987**, 455.

24) Studies on more selective, aerobic, as well as anodic, oxidation of azulenes at lower temps or under more dilute conditions are in progress.

25) We are grateful to Professor Masafumi Yasunami (Tohoku University) for a generous gift of 1-methyl- and 1,3-dimethylazulene.