Autoxidation of Solid Guaiazulene and of the Solution in DMF in the Presence of Base or Acid: A Comparative Study of the Product Distribution[1]

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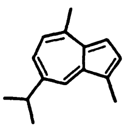
Autoxidation of guaiazulene was examined in detail under the following conditions: in a highly diluted DMF solution, in DMF in the presence of acid or base (at 80—100 °C), and as solid state under sunlight or in the dark (at 25—50 °C). In all cases a wide variety of products were obtained (33 separable compounds altogether), and a comparable study on the distribution of the products under the various reaction conditions was made to establish more precise reaction pathways for the formation of these interesting compounds.

In the past few years we have undertaken a detailed study on various azulenes in *N*,*N*-dimethylformamide (DMF) or hexamethylphosphoric triamide: e.g., guaiazulene (**1**),[2] 4,6,8-trimethylazulene (**2**),[2b,3] 3,3′-methylenebisguaiazulene (**3**),[4] 1-methyl- and 1,3-dimethylazulene (**4**,**5**)[5] as well as azulene itself.[6] As a result, these azulenes gave a wide variety of products possessing interesting structures through such several types of reactions as oxidative dimerization, oxidation of side chains, azulenequinone formation, intermolecular one-carbon transfer reactions, and rearrangements to naphthalenoid, benzenoid, and 1*H*-inden-1-one derivatives. The product distribution of these oxidation and coupling reactions was found to heavily depend upon the type of the starting azulenes employed, although the facility of the radical attack of oxygen (or various other free radical species) on the C-1 and C-3 position of the azulene nucleus mostly exceeded that on various positions of the seven-membered ring, as in the cases of many other electrophilic reactions of azulenes.[7]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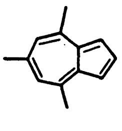
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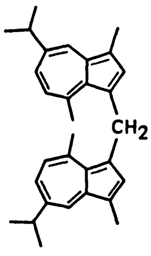
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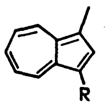

4 R = H
5 R = Me

We now wish to report in this paper the detailed study on autoxidation of guaiazulene (**1**) as a solid (at 25—50 °C) and in a DMF solution in the presence of base or acid (at 80—100 °C). This study was conducted to compare the mode of the oxidation under different reaction conditions to establish a further general aspect of the reaction mechanism of oxidation of azulenes by taking **1** as a representative, model compound.

Results and Discussion

Autoxidation of Guaiazulene (1). The oxidation was conducted under the conditions summarized in Table 1: namely, *A* (expt ii), in a much more dilute DMF solution than the previous experiment;[2] *B* (expt iii), in a DMF solution in the presence of 1,4-diazabicyclo[2.2.2]octane (Dabco/DMF); *C* (expt iv), in a DMF solution in the presence of dilute sulfuric acid (H_2SO_4/DMF); *D* (expt v), as a solid under sunlight; *E* (expt vi) as a solid in a laboratory; *F* (expt vii), as a solid protected from light. The experiments in DMF solutions were carried out in a manner similar to that described previously[2] by allowing finely bubbling oxygen to pass into a solution of the substrate **1** in DMF at 100 °C and the reaction was monitored by the use of the reversed phase high-pressured liquid chromatography (HPLC) or silica-gel TLC. The solid oxidation was conducted by impregnating **1** on a filter paper and allowing it to stand under the conditions shown in Table 1. The time-dependent HPLC diagrams of the expts ii—vii are shown in Fig. 1. Then, the reaction products were separated into each component by using chromatography, when about a half of the starting material was consumed. The products thus obtained as pure components [33 altogether besides the recovered starting material **1** (**1A**$_1$)] are referred to as Compounds **1A**—**S** according to the same

Table 1. Reaction Conditions of Autoxidation of **1**

Expt	Temp/°C	Time/d	Other condition	Recovered **1**/%
i[a]	100	1	In 20 parts of DMF	41
ii	100	1	In 1000 parts of DMF	66
iii	85	6	In 20 parts of DMF +0.5 mol equiv of Dabco	70
iv	85	1	In 20 parts of DMF +0.5 M H_2SO_4	40
v	40—50	8.5	Solid, under sunlight	20
vi	25—35	134	Solid, in a laboratory	40
vii	25—35	127	Solid, protected from light	47

a) From Ref. 2.

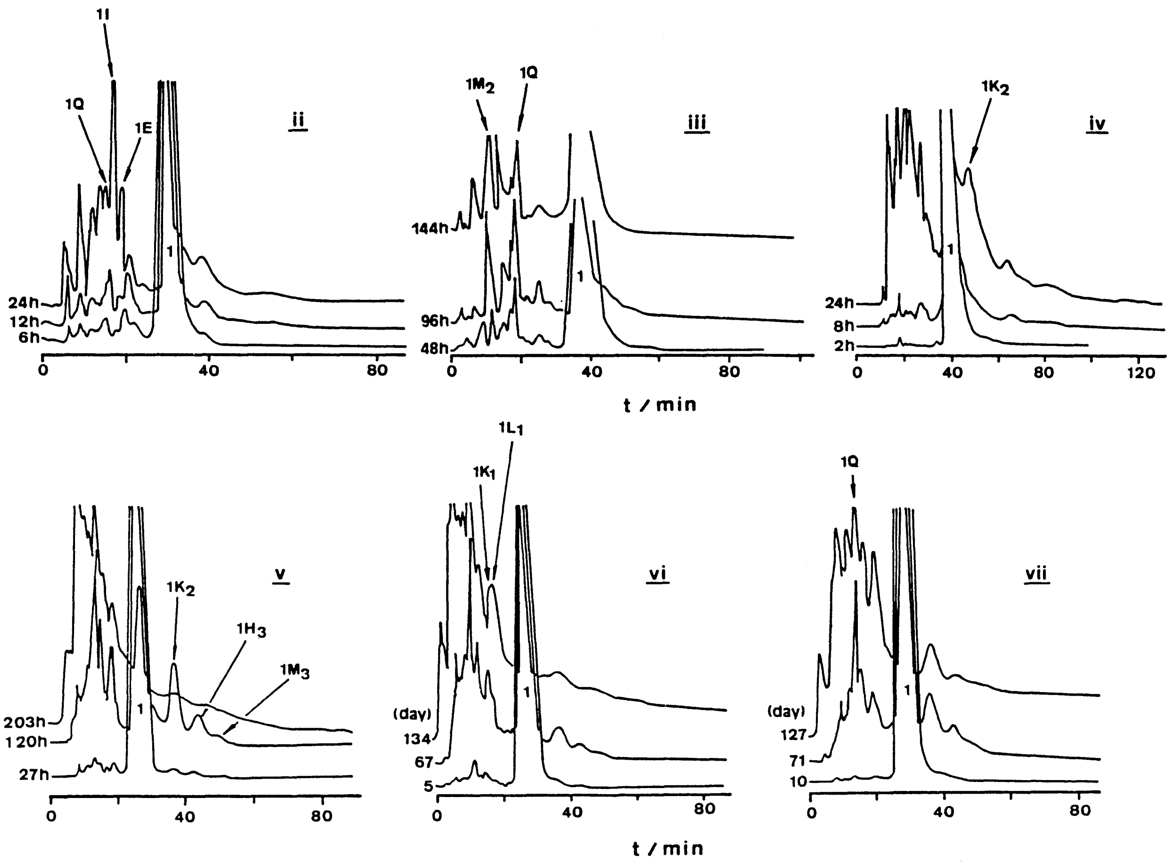


Fig. 1. The time-dependent HPLC diagrams of the autoxidation of **1** (expts ii—vii).

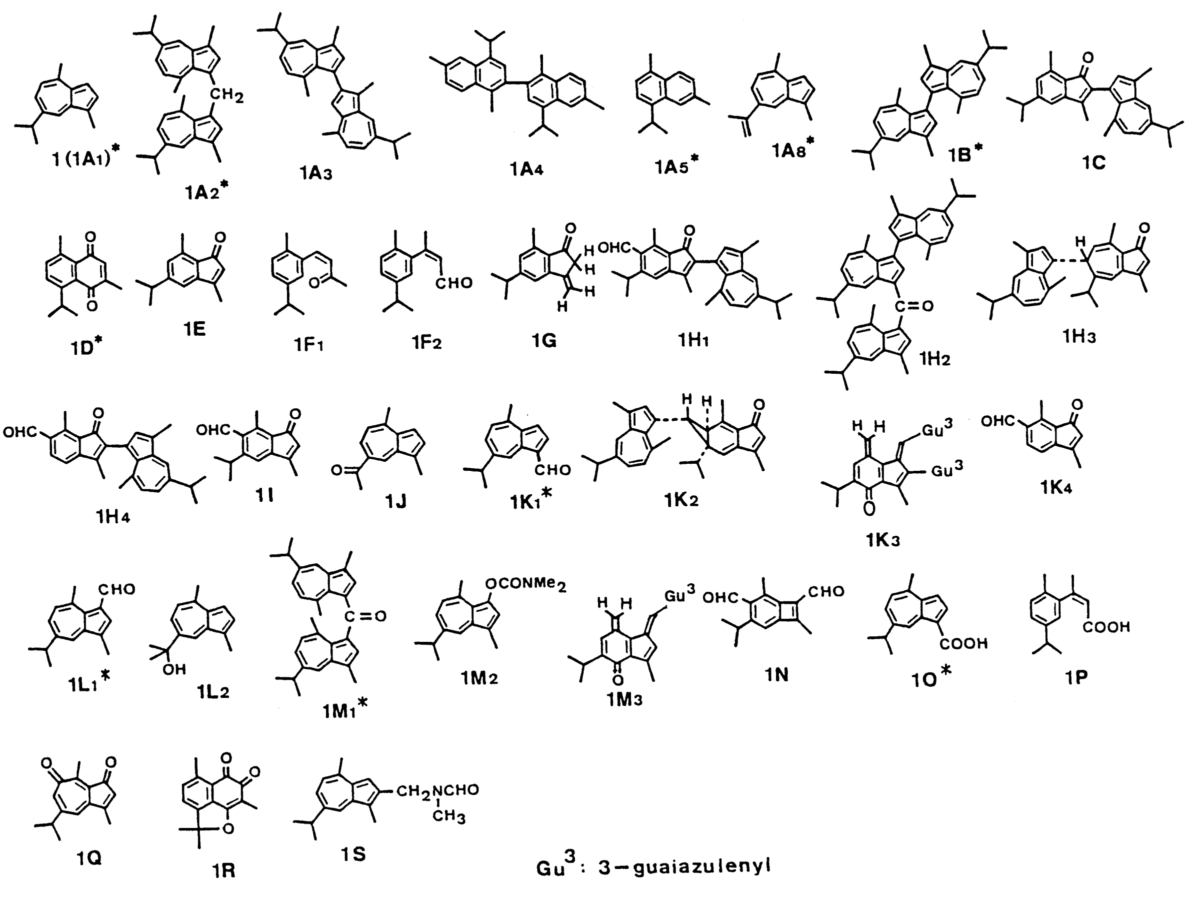


Chart 1. Structures of the autoxidation products from **1**; *previously known compounds.

definition employed in the previous study.[2—6]

In Chart 1 are summarized structures of these products which were established by spectroscopy and chromatography by taking into account the parameters established earlier[2—6] for similar compounds as will be explained below. Among these products, the followings were isolated for the first time in the present study: **1A**$_8$,[8] **1H**$_3$, **1H**$_4$, **1K**$_2$, **1K**$_3$, **1K**$_4$, **1L**$_2$, and **1M**$_3$; other products were identified as all known compounds.[9] The theoretical yields of these isolated products and of an unidentified resinous polar product of rather high molecular weights are summarized in Table 2.

Compounds **1A**$_8$ and **1M**$_3$ were shown to have compositions of $C_{15}H_{16}$ and $C_{15}H_{18}O$ by MS. Thus structures of 7-isopropenyl-[8] and 7-(1-hydroxy-1-methylethyl)-1,4-dimethylazulene were respectively assigned to these minor products by the careful comparison of the ^{1}H NMR spectral data (see the Experimental section) with those of the starting material **1**.

Compounds **1K**$_4$ and **1H**$_4$ showed similar UV and IR spectra to those[2] of **1I** and **1H**$_1$, respectively. The ^{1}H NMR spectra of **1K**$_4$ and **1H**$_4$ also closely resembled those[2] of **1I** and **1H**$_1$, respectively, except for the absence of 5-isopropyl group in **1K**$_4$ and **1H**$_4$. Therefore, the structures without the 5-isopropyl group were assigned to these newly isolated products and were confirmed by MS. Compound **1K**$_4$ appears to gradually dimerize on setting aside at 25 °C (after ca. 7 d).[10]

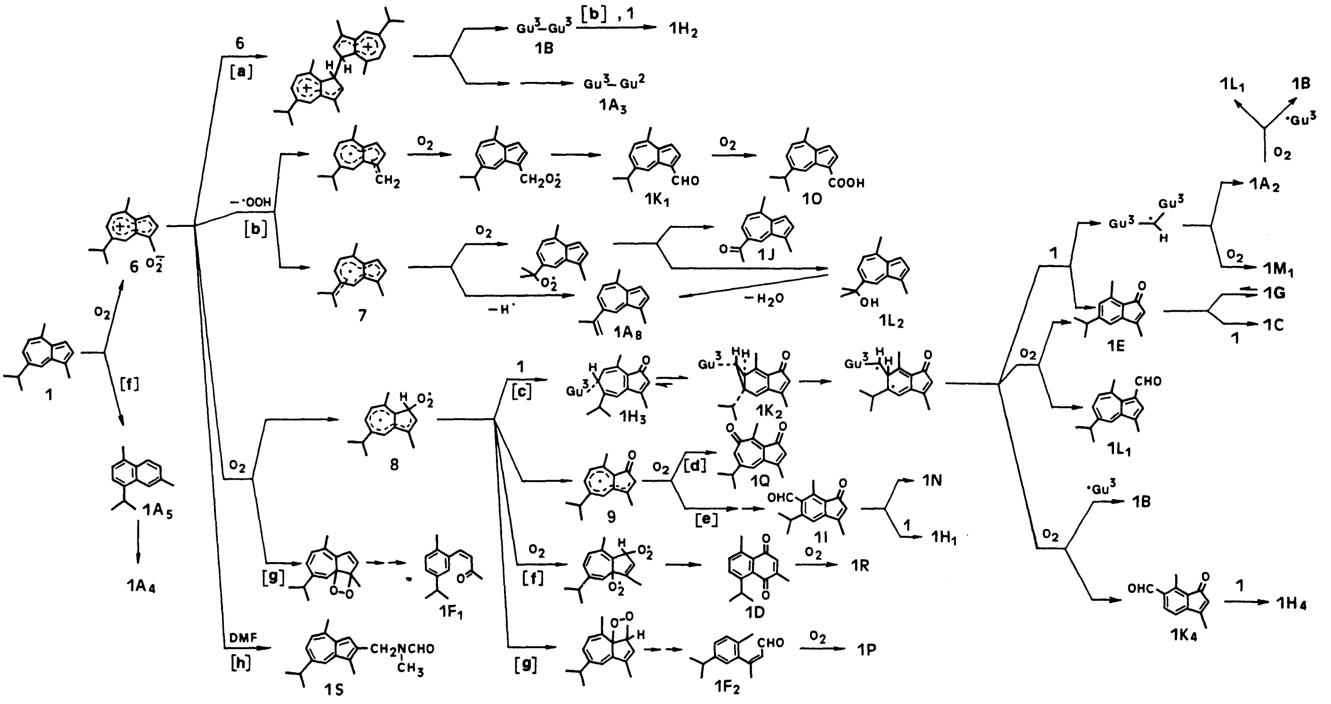
Compounds **1H**$_3$ and **1K**$_2$ (both $C_{30}H_{34}O$ by MS) were shown by ^{1}H NMR to be dimeric guaiazulenes having a 3-guaiazulenyl moiety ($C_{15}H_{17}$) attached to different nuclei that both consisted of $C_{15}H_{17}O$ containing a carbonyl group (1685—1680 cm^{-1}). By the careful analysis of the parameters of the ^{1}H NMR of these compounds as well as their reactivities (see below), structures of 6-(3-guaiazulenyl)-1(6*H*)-guaiazulenone (**1H**$_3$) and its norcaradiene isomer **1K**$_2$ were assigned to these products. When either of these compounds was kept in oxygen-free cyclohexane, a noticeable equilibrium was observed between them; the equilibrium ratio was 20/80 for **1H**$_3$/**1K**$_2$ at 25 °C. The reasons for the equilibrium in favor of **1K**$_2$ are assumed to be not only electronic and steric effects of the substituents on the cyclopropane ring but also the noncyclopentadienone structure of the fused five-membered ring.[11] It is the first example, to the best of our knowledge, among carbocyclic compounds that both norcaradiene and cycloheptatriene forms have been separated as pure compounds and an equilibrium has been confirmed between them.[12]

Compounds **1M**$_3$ and **1K**$_3$ were found by MS to have dimeric ($C_{30}H_{32}O$) and trimeric ($C_{45}H_{48}O$) compositions, respectively. The ^{1}H NMR, UV, and IR spectra of both compounds showed the presence of a 3-guaiazulenyl group and a common non-azulenic nucleus containing a conjugated carbonyl; **1K**$_3$ contained another 3-guaiazulenyl group attached to the above nucleus. Combination of these spectral data led to 1-[(3-guaiazulenyl)methylene]-5-isopropyl-3-methyl-7-methylene-4,7-dihydro-4(1*H*)-indenone and its 2-(3-guaiazulenyl) derivative as the most likely structures

Table 2. Isolated Yield[a)]/% of the Autoxidation Products from **1**

Reaction pathway[b)]	Product	Expt (reaction condition)[c)] i	ii	iii	iv	v	vi	vii
[a]	**1B**	6.8	—	—	7.0	2.5	4.7	9.4
	1A$_3$	0.9	—	—	1.0	1.3	2.0	1.9
	1H$_2$	0.2	—	—	—	—	—	—
	total	7.9	—	—	8.0	3.8	6.7	11.3
[b]	**1K**$_1$	7.9	7.4	20.0	8.0	5.0	13.3	17.0
	1O	1.5	1.6	1.4	1.5	1.3	2.0	0.6
	1M$_3$	—	—	—	2.0	*	0.7	0.6
	1K$_3$	—	—	—	2.0	*	0.7	0.6
	1A$_8$	—	—	—	0.3	—	—	—
	1J	0.3	1.6	1.4	0.3	0.3	0.7	0.6
	1L$_3$	—	1.6	1.4	0.3	*	0.7	0.6
	total	9.7	12.2	24.2	15.3	6.6	18.1	20.0
[c]	**1A**$_2$	8.2	—	—	8.0	*	0.7	0.6
	1M$_1$	1.6	—	—	2.0	*	0.7	0.6
	1H$_3$	—	0.1	—	—	0.4	0.1	0.1
	1K$_2$	—	0.7	—	4.0	1.0	0.7	0.6
	1E	1.7	3.7	2.5	2.0	2.5	3.3	3.8
	1G	0.8	1.6	—	1.0	*	0.7	0.6
	1L$_1$	1.5	1.6	1.4	1.5	1.3	2.0	3.8
	1C	2.2	1.6	—	2.0	1.3	0.7	3.8
	1K$_4$	—	0.4	—	2.0	0.5	0.4	0.4
	1H$_4$	—	1.6	—	2.0	1.3	0.7	0.7
	total	16.0	11.2	3.9	24.5	8.3	10.0	15.0
[d]	**1Q**	1.5	7.4	10.0	1.5	3.8	6.7	18.9
[e]	**1I**	2.9	3.7	5.0	3.0	5.0	6.7	9.4
	1N	0.3	—	—	—	—	—	—
	1H$_1$	2.1	1.6	—	2.0	1.3	0.7	3.8
	total	5.3	5.3	5.0	5.0	6.3	7.4	13.2
[f]	**1D**	5.1	3.7	—	5.0	—	—	—
	1R	0.7	1.6	—	1.0	—	—	—
	1A$_5$	0.9	—	—	—	—	—	—
	1A$_4$	0.4	—	—	—	—	—	—
	total	7.1	5.3	—	6.0	—	—	—
[g]	**1F**$_1$	1.7	1.6	1.4	2.0	*	0.7	0.6
	1F$_2$	1.7	1.6	1.4	2.0	*	0.7	0.6
	1P	2.3	1.6	1.4	2.0	*	0.7	0.6
	total	5.7	4.8	4.2	6.0	*	2.1	1.8
[h]	**1F**$_2$	0.6	14.8	30.0	2.0	—	—	—
	1S	0.6	14.8	2.5	1.0	—	—	—
	total	1.2	29.6	32.5	3.0	—	—	—
	RS[d)]	34.0	22.2	15.0	30.0	67.5	45.0	18.9

a) The yield of each product is based on the consumed **1** (see Table 1); *, Although the compound was detected by the HPLC and TLC checking during the oxidation, it was not isolable after the work-up owing to decomposition; —, the compound was not detected. b) [a]. Oxidative dimerization; [b], side-chain oxidation; [c], one-carbon-transfer reaction; [d], 1,7-azulenequinone formation; [e], rearrangement to indenone derivatives; [f], rearrangement to naphthalenoids; [g], rearrangement to benzenoids; [h], condensation with solvent. c) Expts i—vii correspond those in Table 1. d) Polar resinous substance.



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

for $\mathbf{1M_3}$ and $\mathbf{1K_3}$, respectively;[13] the assignments for the NMR parameters are given in the Experimental section.

Possible Reaction Pathways for the Formation of Autoxidation Products of 1 and a Comparative Study of the Product Distribution. Autoxidation of **1** under various different conditions has resulted in the simultaneous formation of many kinds of complex products by competitive processes as was observed earlier.[2] In order to grasp an overall view of the autoxidation of **1** and other azulenes, an attempt will now be made here to consider the various reaction pathways as a whole and the product distribution under these different conditions. The possible reaction pathways are summarized in Scheme 1, although many of these intermediates in the Scheme have been presented previously.[2]

By attack of oxygen, guaiazulene (**1**) is considered to initially form an electron-transfer complex **6**, which in turn leads to the formation of various products mainly through the following six kinds of reaction pathways [a]—[g] as illustrated in Scheme 1. The yields of the products shown in Table 2 are grouped together by the reaction pathway and the total yield of each pathway is also given in the Table. Although the figures of these yields do not necessarily reflect the ease of the corresponding reaction pathway, they are listed for a comparative study of the product distribution and the reaction pathways under various conditions as will be explained below.

[a] Oxidative Dimerization: It is characteristic that this type of reaction does not take place in dilute DMF or Dabco/DMF. Dimerization of **6** thus appears to be retarded by the presence of the base. Under other conditions, the 3,3′-dimer **1B** is always obtained as one of the main products in the oxidation, whereas 2,3′-dimer $\mathbf{1A_3}$ is formed in a much smaller quantity.

[b] Side-Chain Oxidation: Under all conditions employed in the present study, the methyl group at C-1 of the azulene nucleus is preferentially oxidized, giving the aldehyde $\mathbf{1K_1}$ as one of the main products. Of particular, it is noted that the yield of this type of compound considerably increases in the case of the solid oxidation in the dark and in Dabco/DMF, under which conditions other reactions are presumed to be relatively suppressed due to the facile decomposition (by Dabco) of the secondarily formed various peroxide intermediates.

Compared with the oxidation of 1-methyl group, the α-hydrogen of the isopropyl group at C-7 of **1** is not readily oxidized in all cases on the evidence of the extremely low yields of the 7-acetyl derivative **1J**. In the present study minor quantities of compounds $\mathbf{1A_8}$ and $\mathbf{1L_2}$ which are apparently derived through the same reaction pathways as **1J** (via **7**, see Scheme 1) have been obtained as well.

Also newly isolated in the present study are small quantities of compounds $\mathbf{1M_3}$ and $\mathbf{1K_3}$. The former is most likely formed by further oxidation[4] of $\mathbf{1A_2}$ accompanied by rearrangement, and the latter ($\mathbf{1K_3}$) is derived by condendation of $\mathbf{1M_3}$ with another molecule of **1**. This indicates that the side chain at C-4 is also susceptible, to a small extent, to the autoxidation of **1** as solid or in H_2SO_4-DMF. Under all conditions examined in the present study, the side chain oxidation as a whole is apparently one of the main reactions in the autoxidation of **1**, by taking into consideration the total yield of the reaction products of this type.

[c] Intermolecular One-Carbon-Transfer Reaction: This reaction path has been established by the following additional, experimental facts[1] as illustrated in Scheme 1: *1)* 6-(3-guaiazulenyl)-1(6*H*)-guaiazulenone (**1H$_3$**) was isolated and confirmed to become in an equilibrium with the norcaradiene isomer **1K$_2$**; *2)* in the presence of one equivalent of **1**, **1K$_2$** afforded 3,3′-methylenebisguaiazulene (**1A$_2$**) and 5-isopropyl-3,7-dimethyl-1*H*-inden-1-one (**1E**) under nitrogen at 100 °C in DMF; *3)* on exposure to air, however, **1K$_2$** yielded 3-formylguaiazulene (**1L$_1$**) and **1E** at 25 °C. It has become evident presently that in the presence of oxygen **1K$_2$** and **1** afford **1B** as well as **1K$_4$** and **1H$_4$**, an elimination of the 5-isopropyl group being accompanied in the last to compounds. Compound **1A$_2$** has also been confirmed to yield **1B** and **1L** in the presence of air. The most likely intermediates and the reaction pathways of these transformation are shown in Scheme 1.

It is a characteristic feature that only a very small quantity of **1A$_2$** was obtained by the autoxidation of solid **1** and in dilute DMF or Dabco/DMF, whereas **1A$_2$** was isolated as a main product in a concentrated DMF solution and in H_2SO_4/DMF. In particular, the presence of Dabco suppresses the reaction path [c] considerably as a whole. It is also notable in the present study that the presence of dilute sulfuric acid in DMF resulted in the formation of **1K$_2$** in as high as 4% yield, although the role of acid on the reaction mechanism is still under investigation.

[d] 1,7-Guaiazulenequinone (1Q) Formation: As for the reaction path for **1Q**, diradical **8** and then 3-oxoguaiazulenyl radical **9** shown in Scheme 1 were presumed[2] as possible intermediates. It should be noticed that the solid autoxidation at 25—30 °C in the dark and the oxidation in Dabco/DMF produce **1Q** in as high as 19 and 10% yield, respectively (see Table 2). This would be mainly due to the stability of **1Q** under the above reaction conditions compared with others, although the exact role of Dabco in this case has also remained to be clarified. However, the present result is of significance in view of exploitation of a convenient synthetic scheme for azulenequinones, which are currently drawing increasing interest in the potential utility of the physicochemical properties and biological activity.[14]

[e] Rearrangement to 6-formyl-1*H*-inden-1-one (1I) and its Derivatives: This type of reaction takes place under all reaction conditions examined, yielding **1I** and its 2-(3-guaiazulenyl) derivative **1H$_1$** illustrated in Scheme 1. The solid oxidation of **1** in the dark gives the highest total yield of the products via path [e].

[f] Rearrangement to Naphthalenoids: These compounds have been presumed[2] to be derived through the pathways shown as path [f] in Scheme 1. It has become apparent by the present experiment that no skeletal rearrangement of this type takes place in Dabco/DMF and as a solid, the reason for which is not certain at this stage.

[g] Rearrangement to Benzenoids: Although in relatively small quantities, these compounds have been found to be always produced under all conditions. However, this reaction path (Scheme 1) can be regarded as a minor one.

[h] Condensation with Solvent DMF: It has become apparent in the present study that the product **1S** of this type considerably increases in a dilute DMF solution and in the presence of Dabco/DMF.

The polar resinous substances (R_f=0 on TLC) appears to relatively decrease in the autoxidation of **1** in Dabco/DMF and as solid state in the dark, under which conditions various oligomerization and polymerization reactions seem to be suppressed.

Autoxidation of guaiazulene and the product distributions under various conditions have been closely examined. As a result, complex reaction pathways of the autoxidation of a representative, naturally occurring azulene **1** have been made clarified to a considerable extent. Such information in turn gives important suggestion for the elucidation of exact mechanism of the oxidation of azulenes using various other oxidizing reagents.[15]

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 (in MeOH and $CHCl_3$, respectively, unless otherwise specified) 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. 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 Guaiazulene (1) in DMF. A. In Dilute DMF Solution (expt ii): A soln of **1**[16] (0.020 g) in freshly distilled HMPA (20 g) was placed in a Pyrex flask (ϕ 18 mm, 600 mm height) and subjected to autoxidation by allowing finely bubbling oxygen to pass through the soln (from the bottom of the flask) for 24h at 100 ±5 °C. Time-dependent HPLC diagrams of this reaction are given in Fig. 1. After cooling, the mixture 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. This oil was preliminarily separated into five fractions by means of preparetive 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 22 products were obtained as pure substances (**1A—S**), besides the recovered starting material **1** (**1A$_1$**: 13.2 mg (66%); R_f=0.95) and polar resinous substances [1.5 mg, 22.2% (w/w), R_f=0.0]. The yield of each product based on the consumed starting material (6.8 mg) is summarized in Table 2.

B. In the Presence of Dabco (expt iii): The same oxidation procedures as those shown above (expt ii) were employed. Thus, a solution of **1** (1.00 g) dissolved in DMF (20 g) containing Dabco (0.28 g, 0.5 mole equiv.) was oxidized at 85±5 °C for 6 d, and the yield of each product is summarized in Table 2; 70% of the starting material **1** was recovered.

C. In the Presence of Sulfuric Acid (expt iv): Similarly, a solution of **1** (1.00 g) in DMF (20 g) containing 0.5 M sulfuric acid (5 cm^3) was oxidized, and the yield of each product is summarized in Table 2.

Oxidation of Solid Guaiazulene (1). A. Under Sunlight (expt v): Solid **1** (0.10 g) dissolved in hexane (0.5 cm^3) was homogeneously impregnated into a filter paper (70×50 mm, 0.27 mm thickness), which was hanged on a wire in a Pyrex beaker (500 cm^3) covered with a thin layer of cotton and allowed to stand at 40—50 °C for 8.5 d under the sunlight. After the same work-up, the yield of each product isolated is summarized in Table 2.

B. In a Laboratory (expt vi): **1** (0.10 g) was similarly oxidized on exposure to air in an ordinary laboratory room (without protection from light) at 25—35 °C for 134 d, and the yield of each product is summarized in Table 2.

C. Under the Protection from Light (expt vii): **1** (0.10 g) was similarly oxidized in a dark room at 25—35 °C for 127 d; the time-dependent HPLC diagrams are shown in Fig. 1. The yield of each product is summarized in Table 2.

7-Isopropenyl-1,4-dimethylazulene (Lactarazulene,[8] 1A$_8$). Blue prisms: mp 22 °C (Ref. 8, 20—22 °C); R_f 0.95; UV λ_{max} nm (log ε) 243 (4.53), 290 (4.58), 354sh (4.08), 368 (4.11), 374sh (4.10), 604 (2.94), 630sh (2.93), and 650sh (2.92); MS m/z 196 (M$^+$; 100), 181 (49), 165 (56), and 28 (54); ^{1}H NMR δ=2.27 (3H, brs, CH$_3$–C-7), 2.66 (3H, s, Me-1), 2.83 (3H, s, Me-4), 5.15 (1H, dq, J=1.0 Hz, (E)-HC=C-7), 5.27 (1H, brs, (Z)-HC=-C-7), 6.97 (1H, d, $J_{5,6}$=11.0 Hz, H-5), 7.23 (1H, d, $J_{2,3}$=4.0 Hz, H-3), 7.57 (1H, dd, $J_{6,8}$=2.0 Hz, H-6), 7.59 (1H, d, H-2), and 8.36 (1H, d, H-8); (Found: m/z 196.1281).

6-(3-Guaiazulenyl)-1(6*H*)-guaiazulenone (1H$_3$). Dark blue prisms: mp 137 °C (from hexane); R_f 0.64; UV λ_{max} (hexane) nm (log ε) 225sh (4.19), 249 (4.29), 290 (4.31), 307sh (4.20), 340sh (3.94), 355 (3.98), 373 (3.96), 624 (3.03), and 650sh (2.99); MS m/z 410 (M$^+$; 100), 395 (28), 367 (45), and 198 (66); IR 1685 cm^{-1} (C=O); ^{1}H NMR δ=1.08, 1.12 (3H each, d, J=7.0 Hz, i-Pr-5), 1.34 (6H, d, J=7.0 Hz, i-Pr-7′), 2.02 (3H, s, Me-4′), 2.26 (3H, d, $J_{2,Me}$=1.5 Hz, Me-3), 2.54 (1H, sept, HC-5), 2.67 (3H, s, Me-1′), 2.68 (3H, brs, Me-8), 3.01 (1H, sept, HC-7′), 4.66 (1H, d, $J_{6,7}$=6.0 Hz,H-6), 5.86 (1H, brd, H-7), 5.92 (1H, brq, H-2), 6.45 (1H, s, H-4), 6.79 (1H, d, $J_{5',6'}$=11.0 Hz, H-5′), 7.23 (1H, dd, $J_{6',8'}$=2.0 Hz, H-6′), 7.76 (1H, s, H-2′), and 8.09 (1H, d, H-8′), (DMSO-d_6) 1.07, 1.09 (3H each, d, J=7.0 Hz, i-Pr-5), 1.29 (6H, d, J=7.0 Hz, i-Pr-7′), 1.90 (3H, s, Me-4′), 2.26 (3H, d, $J_{2,Me}$=1.5 Hz, Me-3), 2.36 (3H, d, $J_{7,Me}$=1.5 Hz, Me-8), 2.63 (3H, s, Me-1′), 3.00 (1H, sept, HC-7′), 4.57 (1H, d, $J_{6,7}$=6.0 Hz, H-6), 5.89 (1H, dq, H-7), 5.95 (1H, qd, $J_{2,4}$≃0.3 Hz, H-2), 6.56 (1H, d, H-4), 6.83 (1H, d, $J_{5',6'}$=11.0 Hz, H-5′), 7.30 (1H, dd, $J_{6',8'}$=2.0 Hz, H-6′), 7.81 (1H, s, H-2′), and 8.05 (1H, d, H-8′).

Found: m/z 410.2620. Calcd for $C_{30}H_{34}O$: M, 410.2609.

2-(3-Guaiazulenyl)-3,7-dimethyl-1-oxo-1*H*-indene-6-carbaldehyde (1H$_4$). Dark red-violet prisms: mp 145 °C (from hexane); R_f 0.64; UV λ_{max} nm (log ε) 248 (4.15), 291 (4.15), 305sh (4.10), 351 (3.81), 368 (3.79), 384sh (3.73), and 526 (3.53); MS m/z 382 (M$^+$; 100) and 367 (23); IR 1700 and 1680 cm^{-1} (C=O); ^{1}H NMR δ=1.38 (6H, d, J=7.0Hz, i-Pr-7′), 2.38 (3H, s, Me-3), 2.64 (3H, s, Me-1′), 2.65 (6H, s, Me-7.4′), 3.08 (1H, sept, HC-7′), 6.96 (1H, d, $J_{5',6'}$=11.0 Hz, H-5′), 7.10 (1H, d, $J_{4,5}$=8.0 Hz, H-4), 7.38 (1H, dd, $J_{6',8'}$=2.0 Hz, H-6′), 7.39 (1H, s, H-2′), 7.82 (1H, d, H-5), 8.16 (1H, d, H-8′), and 10.63 (1H, s, OHC-6); ^{13}C NMR δ=197.27, 189.50, 151.43, 148.68, 145.70, 142.49, 141.15, 140.21, 139.63, 138.93, 135.78, 135.31, 133.79, 132.21, 131.16, 129.47, 128.07, 127.72, 125.03, 115.63, 37.96, 25.81, 24.70, 18.45, 17.81, and 12.96.

Found: m/z 382.1897. Calcd for $C_{27}H_{26}O_2$: M, 382.1933.

The Norcaradiene Isomer of 1H$_3$: 1-(3-Guaiazulenyl)-6a-isopropyl-2,5-dimethyl-1,1a,3,6a-tetrahydrocyclopropa[*f*]-inden-3-one (1K$_2$). Dark green prisms: mp 155 °C (from hexane); R_f 0.49; UV λ_{max} (hexane) nm (log ε) 228sh (4.18), 247 (4.27), 251 (4.28), 289 (4.25), 305sh (4.17), 364 (400), 385 (4.02), 638 (2.81), and 670sh (2.77); MS m/z 410 (M$^+$; 100), 395 (27), 367 (53), and 198 (78); IR 1680 cm^{-1} (C=O); ^{1}H NMR* δ=0.79, 0.87 (3H each, d, J=7.0 Hz, i-Pr-5), 1.11 (1H, sept, HC-5), 1.34 (6H, d, J=7.0 Hz, i-Pr-7′), 2.22 (3H, d, $J_{2,Me}$=1.5 Hz, Me-3), 2.46 (1H, d, $J_{6,7}$=5.5 Hz, H-7), 2.55 (1H, d, H-6), 2.58 (3H, s, Me-8), 2.63 (3H, s, Me-1′), 2.90 (3H, s, Me-4′), 3.01 (1H, sept, HC-7′), 6.08 (1H, q, H-2), 6.36 (1H, s, H-4), 6.84 (1H, d, $J_{5',6'}$=11.0 Hz, H-5′), 7.26 (1H, dd, $J_{6',8'}$=2.0 Hz, H-6′), 7.48 (1H, s, H-2′), and 8.05 (1H, d, H-8′), * the numbering of **1K$_2$** for the assignment of the NMR spectrum corresponds to that of **1H$_3$** for the purpose of comparison.

Found: m/z 410.2607. Calcd for $C_{30}H_{34}O$: M, 410.2609.

2-(3-Guaiazulenyl)-1-[(3-Guaiazulenyl)methylene]-5-isopropyl-3-methyl-7-methylene-4,7-dihydro-4(1*H*)-indenone (1K$_3$). A dark red-violet paste: R_f 0.49; UV λ_{max} nm (log ε) 246 (4.41), 288 (4.41), 305sh (4.34), 325sh (4.28), 392 (4.03), and 546 (4.10); MS m/z 604 (M$^+$; 62), 410 (100), and 44 (97); IR 1720, 1680, and 1620 cm^{-1} (C=O); ^{1}H NMR δ=1.14 (6H, d, J=7.0 Hz, i-Pr-5), 1.34 (6H, d, J=7.0 Hz, i-Pr-7′), 1.36 (6H, d, J=7.0 Hz, i-Pr-7″), 2.14 (3H, s, Me-3), 2.47 (1H, sept, HC-5), 2.57 (3H, s, Me-4″), 2.59 (3H, s, Me-1′), 2.64 (3H, s, Me-1″), 2.96 (3H, s, Me-4′), 3.00 (1H, sept, HC-7′), 3.06 (1H, sept, HC-7″), 6.12 [1H, d, $^2J_{H,H}$=1.0 Hz, (E)-HC=C-7], 6.79 [1H, dd, $^4J_{6,H}$≃0.5 Hz, (Z)-HC=C-7], 6.89 (1H, d, $J_{5'',6''}$=11.0 Hz, H-5″), 6.93 (1H, d, $J_{5',6'}$=11.0 Hz, H-5′), 7.23 (1H, d, H-6), 7.26 (1H, dd, $J_{6','8}$=2.0 Hz, H-6′), 7.34 (1H, s, HC=C-1), 7.34 (1H, dd, $J_{6'',8''}$=2.0 Hz, H-6″), 7.38 (1H, s, H-2″), 7.76 (1H, s, H-2′), 7.99 (1H, d, H-8′), and 8.14 (1H, d, H-8″).

Found: m/z 604.3721. Calcd for $C_{45}H_{48}O$: M, 604.3705.

3,7-Dimethyl-1-oxo-1*H*-indene-6-carbaldehyde (1K$_4$). Pale yellow prisms: mp 125 °C (from hexane); R_f 0.49; UV λ_{max} (CHCl$_3$) nm (log ε) 242 (3.97), 273 (3.96), 280sh (3.93), 315 (3.30), 342 (3.01), 355sh (2.97), and 370sh (2.86); MS m/z 186 (M$^+$; 100), 171 (2), 157 (25), 143 (3), 129 (34), and 115 (35); IR (KBr) 1700 and 1680 cm^{-1} (C=O); ^{1}H NMR δ=2.51 (3H, d, $J_{2,Me}$=1.5 Hz, Me-3), 2.59 (3H, s, Me-7), 5.88 (1H, brq, H-2), 7.13 (1H, brd, $J_{4,5}$=8.0 Hz, H-4), 7.77 (1H, d, H-5), and

10.53 (1H, s, OHC-6).

Found: m/z 186.0613. Calcd for $C_{12}H_{10}O_2$: M, 186.0681.

7-(1-Hydroxy-1-methylethyl)-1,4-dimethylazulene (1L$_2$). A blue paste: R_f 0.38; MS m/z 214 (M^+; 84), 199 (100), 196 (6), 181 (6), 171 (8), 165 (9), 157 (26), 155 (22), 152 (12), 141 (18), 128 (11), 115 (14), 92 (6), 77 (5), 43 (35), and 40 (20); ^{1}H NMR* δ=1.56 (1H, HO-C-7), 1.73 (6H, s, *i*-Pr-7), 2.69 (3H, s, Me-1), and 2.85 (3H, s, Me-4), * other signals were not observed due to a small quantity of the sample.

Found: m/z 214.1348. Calcd for $C_{15}H_{18}O$: M, 214.1357.

1-[(3-Guaiazulenyl)methylene]-5-isopropyl-3-methyl-7-methylene-4,7-dihydro-4(1*H*)-indenone (1M$_3$). A dark red-violet paste: R_f 0.35; UV λ_{max} nm (log ε) 243 (4.18), 282 (4.07), 329 (3.90), 386 (3.62), and 532 (3.94); MS m/z 408 (M^+; 100) and 44 (74); IR 1720, 1675, and 1615 cm^{-1} (C=O); ^{1}H NMR δ=1.10 (6H, d, J=7.0 Hz, *i*-Pr-5), 1.34 (6H, d, J=7.0 Hz, *i*-Pr-7′), 2.26 (3H, d, $J_{2,Me}$=1.0 Hz, Me-3), 2.40 (1H, sept, HC-5), 2.59 (3H, s, Me-1′), 2.95 (3H, s, Me-4′), 3.01 (1H, sept, HC-7′), 6.09 [1H, d, $^2J_{H,H}$=1.0 Hz, (*E*)-HC=C-7], 6.34 (1H, qd, $^4J_{2,H}\approx$0.3 Hz, H-2), 6.80 [1H, dd, $^4J_{6,H}\approx$0.5 Hz, (*Z*)-HC=C-7), 6.94 (1H, d, $J_{5',6'}$=11.0 Hz, H-5′), 7.13 (1H, d, H-6), 7.30 (1H, dd, $J_{6',8'}$=2.0 Hz, H-6′), 7.35 (1H, d, HC=C-1), 7.76 (1H, s, H-2′), and 8.03 (1H, d, H-8′).

Found: m/z 408.2502. Calcd for $C_{30}H_{32}O$: M, 408.2453.

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8) F. Sorm, V. Benesova, and V. Herout, *Chem. Listy*, **47**, 1856 (1953); *Collect. Czech. Chem. Commun.*, **19**, 357 (1954).

9) See Ref. 2 and references cited therein for the corresponding compounds.

10) A dimer: white prisms, mp >300 °C; UV λ_{max} (MeOH) nm (log ε) 229 (3.73), 255sh (3.60), 304sh (3.14), and 313 (3.16); MS m/z 372 (M^+; 24), 186 (100), 158 (14), 128 (14), and 115 (16); IR 1740—1690 cm^{-1} (C=O); Found: m/z 372.1367; Calcd for $C_{24}H_{20}O_4$: M, 372.1361. The structures of the dimers are under investigation.

11) More precise kinetic study for this equilibrium and investigation of reactivities of these two compounds are in progress. A temperature-dependent conformational analysis of **1H$_3$** is also under investigation to eliminate any unambiguousness of the NMR assignments. The results will be reported elsewhere.

12) For the norcaradiene-cycloheptatriene equilibrium systems confirmed in solution at low temperatures, see e.g., K. Takeuchi, Y. Senzaki, and K. Okamoto, *J. Chem. Soc., Chem. Commun.*, **1984**, 111; M. Balci, H. Fischer, and H. Günther, *Angew. Chem., Int. Ed. Engl.*, **19**, 301 (1980) and references, cited therein.

13) Related compounds, 8-(3-guaiazulenyl)-5-isopropyl-3,7-dimethyl-benzofulvenes, have been isolated by autoxidation of **1A$_2$** in DMF (Ref. 4).

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15) Studies on more selective, aerobic, as well as anodic, oxidation of azulenes at lower temperatures are in progress.

16) **1** is commercially available from Konan Kako, Co. (Osaka): blue-violet prisms, mp 31 °C.