1-Methoxy-1,2-dichloro-2,3,3-trifluorocyclopropane (2). A solution of 24.8 g (0.2 mol) of **1a** in 100 ml of methylene dichloride was protected from the light and treated slowly with 14.2 g (0.2 mol) of precondensed chlorine while keeping the reaction temperature below 0 °C. After stirring in the dark at room temperature overnight, the reaction mixture was distilled at atmospheric pressure to remove the solvent, and the residual oil was fractionated in vacuo to give 18.2 g (47%) of **2:** bp 60–63 °C (190 mm); NMR (CCl_4) ^1H δ 3.66 (s), ^{19}F ϕ −142.0, −147.2 (AB m of m, 2, $J_{AB} \simeq 166$ Hz: A, d, $J \simeq 2.8$ Hz; B, d, $J \simeq 2.2$ Hz), −152.0 (d of d, 1, J = 2.8, 2.2 Hz).

Anal. Calcd for $C_4H_3Cl_2F_3O$: C, 24.64; H, 1.55; F, 29.23. Found: C, 24.68; H, 1.53; F, 29.07.

Methanolysis of 1a. A mixture of 2 ml of methanol in 10 ml of carbon tetrachloride was treated dropwise at room temperature with 1.24 g (10 mmol) of **1a**. After stirring overnight, the reaction mixture was concentrated, and the product was taken up in methylene dichloride, filtered, and concentrated to give 1.37 g (94%) of methyl *cis*-2,3-dimethoxyacrylate: bp 61–62 °C (1.2 mm); ir (neat) 1711 (C=O), 1645 cm^{-1} (C=C); NMR (CCl_4) δ 3.58 (s, 3), 3.66 (s, 3), 3.82 (s, 3), 6.90 (s, 1).

Ion Preparations. Under anhydrous conditions a solution of freshly distilled antimony pentafluoride in sulfur dioxide (ca. 2 M) was treated dropwise with 1 equiv of the respective cyclopropene (**1**) while keeping the reaction temperature below −65 °C. After the cyclopropene was added, the solutions were slowly warmed to room temperature while the sulfur dioxide was removed in a slow stream of nitrogen. The hexafluoroantimonate salts (**3**) were deposited as colorless, crystalline solids and were bottled under argon. The solutions for NMR study can be prepared by directly withdrawing samples from the reaction mixture or by redissolving the stock salts in sulfur dioxide.

Registry No.—**1a,** 59034-32-1; **1b,** 59034-33-2; **1c,** 59034-34-3; **2,** 59034-35-4; **3a,** 59015-63-3; **3b,** 59015-65-5; **3c,** 59015-67-7; cyclopropene, 2781-85-3; tetrafluorocyclopropene, 19721-29-0; 1,2-dichlorodifluorocyclopropene, 6262-45-9; methyl *cis*-2,3-dimethoxyacrylate, 59034-36-5.

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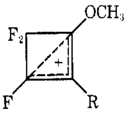

(R = F, Cl, OCH$_3$)

6

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Stabilization of Cyclopropenium Ion and Cyclopropenone by Guaiazulene[1]

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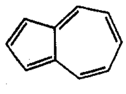
$C_3Cl_3^+AlCl_4^-$ (from tetrachlorocyclopropene and aluminum chloride) reacts with 2 molar equiv of guaiazulene (**8**) in dichloromethane solution to give, after aqueous workup, di-3-guaiazulenylcyclopropenone (**7**). An analogous reaction of $C_3Cl_3^+AlCl_4^-$ with 3 molar equiv of **8** followed by treatment of perchloric acid (70%) afforded tri-3-guaiazulenylcyclopropenium perchlorate (**6**). The dipole moment of **7**, 5.13 D, is analyzed in terms of the dipole moment orientations of the azulenyl groups relative to the cyclopropenone moiety. The ^1H NMR spectra of **6** and **7** are analyzed in comparison with the corresponding spectra of **8** and various of its 3-acyl derivatives. The interactions of the guaiazulenyl groups with the cyclopropenone (in **7**) and the cyclopropenium ion (in **6**) are discussed. The high pK_{R^+} of **6**, >10, indicates the remarkable effect of the three guaiazulenyl groups in delocalizing the positive charge of the three-membered ring.

Azulene (**1**)[2,3] and cyclopropenium ion (**2**)[3–7] are considered two independent milestones in the chemistry of nonbenzenoid aromatics. The interest in azulene, the "aromatic" nonalternant polycyclic prototype, had somewhat declined during the past decade. The origin of this decline may be traced to the dominant role played by the Hückel $4n + 2$ rule and its experimental "verifications" for $n \neq 1$.[8] Recent cyclopropenium ion (**2**) and cyclopropenone (**3**)[9,10] studies have focused on the stabilization of the "aromatic" but highly strained $2\pi3C$ ring system by appropriate electron-donating substituents, particularly heteroatoms.[11–14] In a search for alternative substituents which are capable of delocalizing the positive charge of the three-membered ring, we have considered the azulenyl group. The rationale underlying this approach is based on the extra "aromatic" stabilization of 1-azulenylcarbenium ion (**4**), a variation of the tropylium ion theme.[9,15] 1-Azulenylcyclopropenium ion (**5**) may formally be considered as a triapentafulvalene system condensed to tropylium ion (**5a**). We report straightforward syntheses and various properties of cyclopropenium ion and cyclopropenone *totally* substituted by guaiazulenyl groups: tri-3-guaiazulenylcyclopropenium perchlorate (**6**) and di-3-guaiazulenylcyclopropenone (**7**). Few examples of azulenyl- (and pseudoazulenyl-) *diphenyl*cyclopropenium salts have previously been described.[16–18] Azulene derivatives of cyclopropenone are unknown.[10]

The synthetic route of choice was the electrophilic substitution of aromatic substrates by trichlorocyclopropenium salts via a Friedel–Crafts pathway (method of West and Tobey),[10,19–22] applied in dichloromethane. In principle, this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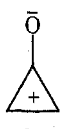
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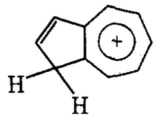

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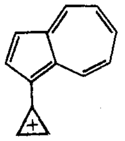
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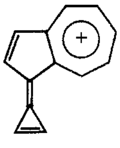
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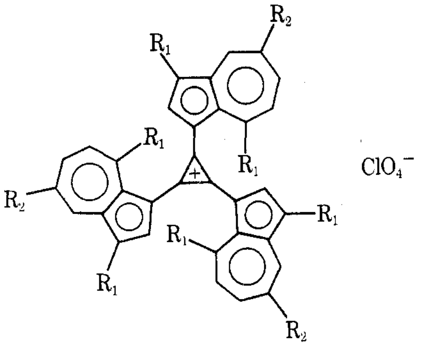
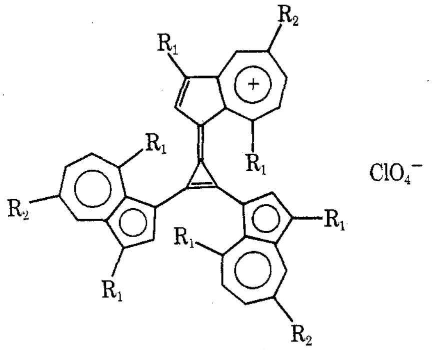


6, $R_1 = CH_3$; $R_2 = CH(CH_3)_2$



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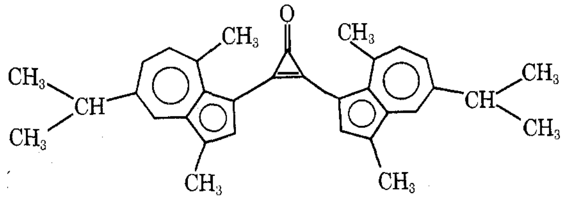

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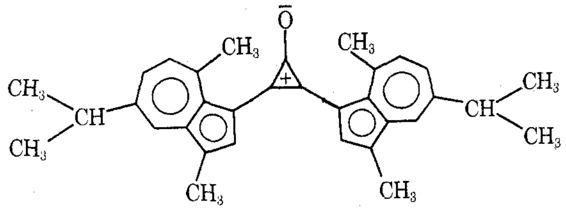
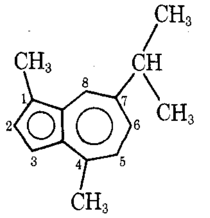


7a



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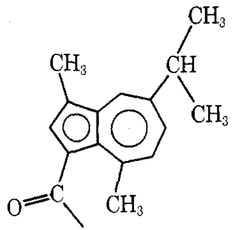
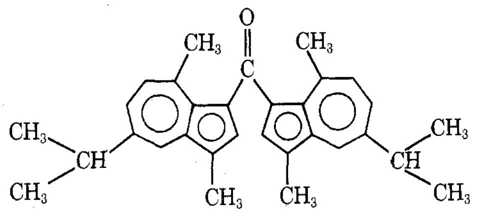


9, R = CH_3
10, R = C_6H_5
11, R = H



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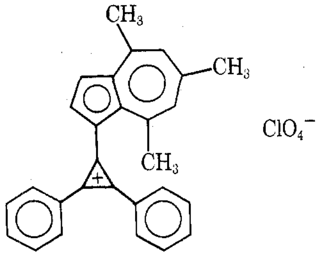

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method may result in mono-, di-, and trisubstitution products, providing (after working up the reaction mixture) aryltrichlorocyclopropene, diarylcyclopropenone, and triarylcyclopropenium cation. Guaiazulene (8) was preferred over azulene (1) as the aromatic substrate on the following grounds: (1) in azulene, double consecutive electrophilic substitution may occur (at positions 1 and 3), while in guaiazulene only single electrophilic substitution is expected (as position 1 is blocked);[2b,23] (2) the NMR spectra of the derivatives of 8 are expected to be simpler than those of 1; (3) 8 is more readily available than azulene. Treatment of $C_3Cl_3^+AlCl_4^-$ (prepared from tetrachlorocyclopropene and aluminum chloride) with 2 molar equiv of guaiazulene in dichloromethane at −90 to −80 °C gave a dark red complex which was decomposed with aqueous acetone (20%) at −60 °C. Purification by dry column chromatography on silica gel afforded **7**. Analogous reaction with 3 molar equiv of guaiazulene at −70 °C gave a dark red complex which was decomposed with aqueous acetone followed by treatment with perchloric acid (70%) leading to **6**. Purification was effected by column chromatography on microcrystalline cellulose. Elemental analyses and spectral properties were all consistent with the formulation of **6** and **7**.

The mass spectrum of **7** revealed an initial elimination of CO from the molecular ion to give the parent di-3-guaiazulenylacetylene radical cation: $M\cdot^+$ (*m/e* 446, 2%) → $[M - CO]\cdot^+$ (*m/e* 418, 100%). This most facile fragmentation was substantiated by appropriate metastable transitions. The following prominent signals indicated fragmentations of the alkyl substituents from the parent ion: $[M - CO - CH_3]\cdot^+$ (*m/e* 403, 32%), $[M - CO - i\text{-Pr}]\cdot^+$ (*m/e* 375, 24%), $[M - CO - CH_3 - i\text{-Pr}]^+$ (*m/e* 360, 18%), $[M - CO - CH_3 - i\text{-Pr} - i\text{-Pr}]\cdot^+$ (*m/e* 317, 24%).

The infrared spectrum of **7** contained the two molecular bands at 1552 and 1837 cm^{-1} which are diagnostic for the cyclopropenone nucleus.[10,24–26] Although specific assignments have been controversial,[27] it seems to be established that the two fundamental frequencies are out-of-phase and in-phase mixtures of the C═O and the C═C stretches, with some contribution from the symmetric C–C stretch. If the assignment of the band in the 1600-cm^{-1} region to a molecular vibration that predominantly involves the stretching of the carbonyl band is valid,[28] then the occurrence of this band at such a low wavenumber (1552 cm^{-1}) may indicate a considerable contribution of an "aromatic" dipolar form (e.g., **7a**)

Table I. ^{1}H NMR Spectra of 6, 7, 8, and Related Guaiazulene Derivatives

		δ, ppm[a]							
Compd	Solvent	H-2	H-5	H-6	H-8	CH_3-1	CH_3-4	$(CH_3)_2CH$-7	$(CH_3)_2CH$-7
8	$CDCl_3$	7.59 s	6.92 d (11)	7.32 dd (11, 2)	8.17 d (2)	2.63 s	2.76 s	3.02 h (7)	1.32 d (7)
8[30]	$CDCl_3$	7.59 d (4)	6.94 d (11)	7.37 dd (11, 2)	8.17 d (2)	2.63 s	2.78 s	3.04 h (7)	1.32 d (7)
8	CD_3CN	7.56 d (4)	6.97 d (11)	7.39 dd (11, 2)	8.20 d (2)	2.61 s	2.75 s	3.04 h (7)	1.31 d (7)
6	$CDCl_3$	8.04 s	7.56 d (10)	7.84 dd (10, 1)	8.41 d (1)	2.65 s	2.92 s	3.25 h (7)	1.44 d (7)
7	$CDCl_3$	8.31 s	7.29 d (11)	7.50 dd (11, 2)	8.24 d (2)	2.67 s	3.39 s	3.10 h (7)	1.36 d (7)
9[31]	CCl_4	7.78 s	7.14 d	7.39 dd	8.10 d	2.54 s	2.79 s	3.03 m	1.34 d
10[32]	$CDCl_3$	7.55 s	7.12 d (11)	7.3–8.0 m[b]	8.20 d (1.8)	2.55 s	2.71 s	3.09 m	1.37 d (6)
11[33]	c	8.22 s	7.36 d	7.55 dd	8.27 d	2.57 s	3.08 s	c	1.38 d (6.5–7.0)
12[33]	c	7.53 s	7.05 d	7.32 dd	8.10 d	2.52 s	2.86 s	c	1.33 d (6.5–7.0)

[a] Chemical shifts are followed by multiplicity and coupling constants (J) in hertz: s, singlet; d, doublet; dd, doublet of doublets; h, heptet; m, multiplet. [b] Including phenyl [c] Not given.

Table II. Electronic Absorption Spectra of 6, 7, and 13

Compd	Solvent	λ, nm (ε)								
6	CH_3CN	240s (32 300)	290 (25 900)		335 (20 300)		483 (26 200)			
7	CH_3CN	242 (39 000)	289 (26 000)		335 (30 000)	455 (47 000)	478 (53 000)	520s (1500)		
7	EtOH	244 (40 000)	290 (27 000)	326 (24 000)	336 (28 000)	456s (46 000)	479 (53 000)		590s (3100)	650 (1600)
7	Dioxane		291 (25 000)		336 (27 000)	459 (42 000)	482 (46 000)	556s (2600)	600s (25 500)	660s (1500)
7	C_6H_6		293 (28 000)		338 (30 000)	460 (45 000)	484 (50 000)	560s (2700)	600s (2700)	650s (1500)
7	C_6H_{12}	242 (36 000)	290 (25 000)	325s (24 000)	336 (30 000)	456 (41 500)	480 (46 000)	564 (2300)	610s (2300)	660s (1500)
13[16]	CH_3CN	249 (36 300)	272 (31 600)		341 (26 900)	416 (33 900)				

to the ground state of **7**. (On the other hand, the 1552-cm^{-1} vibration may still be mainly a C=C stretch.[27]) The infrared spectrum of **6** shows strong absorptions at 1468 and 1448 cm^{-1} which are indicative of cyclopropenium ion.[11,25,29] The cyclopropenium structure of **6** was verified by the characteristic Raman line at 1815 cm^{-1} due to the totally symmetric stretching vibration (A_1') of the "aromatic" C_3^+ ring.[11,25,29] In comparison, the corresponding absorptions of trimethyl-, triphenyl-, tris(dimethylamino)-, and trichlorocyclopropenium ion appear at 1880, 1845, 1985, and 1791 cm^{-1}, respectively.[11,29] It should be noted that no infrared band appears at the 1820-cm^{-1} region either in solution or in the solid. Such a band was reported in the spectrum of 1-azulenyldiphenylcyclopropenium perchlorate and was ascribed to the corresponding triapentafulvalenic structure of this salt.[17]

The NMR data of **6** and **7** are given in Table I along with the relevant data of guaiazulene (**8**),[30] 3-acetylguaiazulene (**9**),[31] 3-benzoylguaiazulene (**10**),[32] 3-formylguaiazulene (**11**),[33] and 3,3′-diguaiazulene ketone (**12**).[33] A number of conclusions may be drawn. (1) In each of the guaiazulenyl derivatives under study, the seven-membered ring protons (H-5, H-6, H-8) give rise to an ABX system. (2) The guaiazulenyl substituents in **6** and **7** are magnetically equivalent. (3) The seven-membered ring protons of **6** are significantly shifted to lower field relative to the parent guaiazulene (**8**): $\delta(6) - \delta(8) = 0.64$ (H-5), 0.52 (H-6), and 0.24 ppm (H-8). This effect probably reflects partial delocalization of the positive charge from the three-membered ring into the seven-membered ring indicating a contribution of the tropylium structure (**6a**) to the ground state of **6**. An analogous trend but much smaller in extent is seen in **7**: $\delta(7) - \delta(8) = 0.37$ (H-5), 0.17 (H-6), and 0.07 ppm (H-8). It is noteworthy that even with respect to the corresponding absorption of 3,3-diguaiazulenyl ketone (**12**) the seven-membered ring protons of **7** are shifted to lower field indicating, in this particular case, greater fractional charge separation than in the ordinary ketones: (4) The five-membered ring methyl protons in CH_3-1 in **6** as well as in **7** are hardly shifted relative to **8**. (5) The five-membered ring proton (H-2) in **6** and **7** is substantially shifted to lower field relative to **8**; $\Delta\delta$ (H-2) = 0.45 for **6** and 0.72 ppm for **7**. The considerable shift in **7** is mainly due to the carbonyl anisotropy, while the effect of the partial positive charge in the three-membered ring is only marginal. On the other hand, the shift in **6** is mainly due to the anisotropy of the C_3^+ system. (6) The CH_3-4 protons in **7** are affected in the same way as H-2, $\Delta\delta$ (CH_3-4) = 0.63 ppm. In **6** the corresponding shift is only 0.16 ppm and corresponds to the change of the electron density at the seven-membered ring.

The electronic absorption spectra of **6** and **7** are summarized in Table II. The disappearance of the low-intensity but significant absorption at the 600-nm region of the azulene moiety in **6** indicates change in the character of the substituent moiety to resemble tropylium cation. Noteworthy also is the substantial red shift of the high intensity longest wavelength absorption band from 416 nm in 4,6,8-trimethylazulenyldiphenylcyclopropenium perchlorate (**13**)[16] to 484 nm in **6**.

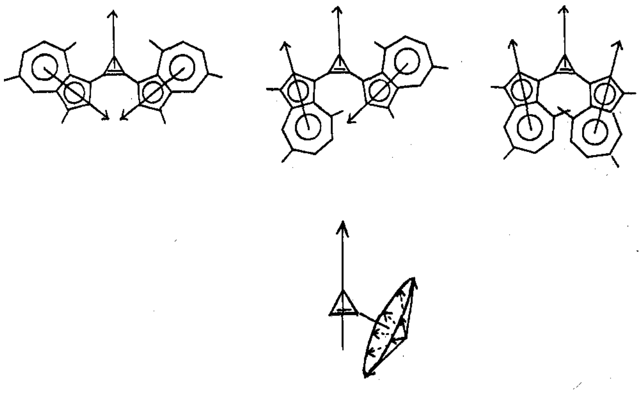

Figure 1. Dipole moment orientations of the azulenyl groups relative to the cyclopropenone moiety in **7**.

The electric dipole moment of **7** (in benzene) is 5.13 D and closely resembles that of diphenylcyclopropenone (5.08 D).[10] The relatively high dipole moment of cyclopropenones was originally attributed to high contribution of the cyclopropenium oxide structure (**3a**) to the ground state of **3**. However, Tobey had effectively shown that this is not a necessary rationale.[34] The fractional charge separation is comparable with that in ordinary ketones but the effective conjugation in the three-membered ring causes shifting of the center of the positive charge into the three-membered ring and increasing the charge separation distance. Ammon's recent x-ray crystallographic investigation of diphenylcyclopropenone, in conjunction with CNDO/2 calculations, led to the conclusion that the three-membered ring of the ketone has some cyclopropenium ion character.[35-37] The overall moment of **7** is a combination of two contributions: the cyclopropenone moiety and the azulenyl groups (ca. 1.1 D oriented from the seven-membered ring to the five-membered ring). Figure 1 shows various dipole moment orientations of the azulenyl groups relative to the cyclopropenone moiety. Models show steric hindrance of the type 2–2′, 2–4′, and for much greater extent of the type 4–4′. Relief of this strain can be achieved in two ways: (a) by *correlation of the groups free rotation maintaining* phase difference between the two substituents, and (b) by widening the angle between the substituents. Both effects tend to decrease the overall contribution of the azulenyl moiety to the electrical moment dipole. The wider angle between the two substituents forces H-2 and CH_3-4 into the diamagnetic anisotropic field of the carbonyl. A rapid equilibrium between such conformations as the central one in Figure 1 may also be favored on the basis of the ^1H NMR deshielding effect noted for H-2 and CH_3-4. The similarity in the dipole moment of **7** and diphenylcyclopropenone could be rationalized in terms of this conformer, in view of the partial cancellation of the azulenyl contributions. In **6** the introduction of the third substituent does not permit wider angle between the substituents. The steric strain may be relieved only by mechanism a. This imposes twisting of the substituents in a propeller-like arrangement with respect to the cyclopropenium ion ring. The twist angles are probably larger than in the case of the triphenylcyclopropenium ion. (This can explain the lack of absorption at 1820 cm^{-1} found in the infrared of 1-azulenyldiphenylcyclopropenium perchlorate.)

The "aromatic" stabilization of **6** may be inferred from its high pK_{R^+}, >10, determined by the equilibrium between the cyclopropenium ion and the cyclopropenol as measured by potentiometric titration method, in 50% aqueous acetonitrile. The corresponding values of triphenyl-, tris(*p*-anisyl)-, and tris(diphenylamine)cyclopropenium ion are 3.1, 6.75, and >10, respectively.[11,29,38] The result indicates the remarkable effect of the three guaiazulenyl groups in delocalizing the positive charge of the three-membered ring of **6**.

Finally, the interaction of the guaiazulenyl groups with the cyclopropenium ion **6** closely resembles the recently observed "aromatic" stabilization in the highly delocalized triferrocenylcyclopropenium ion.[39] The interaction with the cyclopropenone imposes higher charge separation than in known cyclopropenones. A more general picture will emerge from the study of the unsubstituted 1-azulenyl substituents, tri-1-azulenylcyclopropenium ion, and di-1-azulenylcyclopropenone.

Experimental Section

Melting points were taken on a Unimelt Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer in Nujol and in KBr disks. Ultraviolet spectra were recorded on a Unicam Model SP800A spectrophotometer. The ^1H NMR spectra were taken on a Varian HA-100 spectrometer at 100 MHz. ^1H chemical shifts are reported in parts per million downfield from Me_4Si (internal standard). Mass spectra were measured on a Varian MAT-311 double focusing instrument operating at 70 eV, employing the direct insertion technique. Metastable transitions were detected by the defocusing method (alteration of accelerating voltage mode). Analytical TLC separations were carried out at 24 °C on precoated plastic sheets (layer thickness 0.2 mm), Polygam Sil N-HR/UV_{254} and Polygam Cel 400/UV_{254} (Machery-Nagel and Co.). Materials were detected with uv light. Column chromatography separations were performed on silica gel 60 (Kieselgel 60 Merck) and on microcrystalline cellulose (Merck). For dry column chromatography, silica was deactivated with ethyl acetate. Dipole moment was determined in benzene solution at 30 °C. The dielectric constants of the solutions were measured in a heterodyne beat apparatus (500 kHz), the specific volumes, with a Sprengel-Oswald type pycnometer. The molar refraction was calculated according to LeFevre and Steel.[40] The polarization $P_{2\infty}$ and the dipole moment were calculated according to Halverstadt and Kumler.[41] The pK_{R^+} values of the cyclopropenium ions were determined by the potentiometric titration method in 50% aqueous acetonitrile.[6,34] The pH measurements were made in a Radiometer Type TTT IC pH meter equipped with glass–calomel electrodes. The pH meter was standardized with an appropriate buffer before each measurement.[38] Raman spectra were obtained on a rotating KBr pellet. Instrumentation consists of a Spex 1401 monochromator, a Spex 1419A sample illuminator, and a Spectra Physics Model 164 Kr^+ laser supplying about 50 mW power at the sample. Tetrachlorocyclopropene was obtained from Aldrich Chemical Co., Inc., Milwaukee, Wis. Guaiazulene (puriss), mp 30–31.5 °C, was obtained from Fluka AG (Buchs, Switzerland). Petroleum ether (bp 40–60 °C) and dry dichloromethane were used.

Di-3-guaiazulenylcyclopropenone (7). A solution of tetrachlorocyclopropene (1.78 g, 10 mmol) in dry dichloromethane (5 ml) was added dropwise, under inert anhydrous atmosphere, to a magnetically stirred suspension of anhydrous aluminum chloride (1.47 g, 11 mmol) in dry dichloromethane (100 ml). The mixture was gradually heated to 20 °C, and left at this temperature for 15 min, to give trichlorocyclopropenium tetrachloroaluminate. More dichloromethane (50 ml) was added and the resulting suspension was cooled to −85 °C and treated dropwise, during 105 min, below −80 °C, with a solution of guaiazulene (**8**, 3.72 g, 19 mmol) in dry dichloromethane (100 ml). The dark complex was stirred at −90° for an additional 75 min and treated below −60 °C with aqueous acetone (20%, 50 ml). After gradual heating to room temperature, the organic layer was washed with water to neutrality, dried over magnesium sulfate, and evaporated to dryness under vacuum. The resulting crude oily product was purified by dry column chromatography over deactivated silica, using a mixture (1:1) of ethyl acetate and petroleum ether as developers. Three main spots were obtained. The middle, green-colored spot (R_f 0.16) was extracted with methanol, the solvent was evaporated under vacuum, and the remaining product dissolved in dichloromethane, dried over magnesium sulfate, and the solvent evaporated to dryness to give crude **7** as a dark green solid (14% yield). Further purification was effected by column chromatography on silica, using 5% of ethyl acetate in dichloromethane as developer. The remaining solid, after evaporation of the solvent from the main dark green fraction, was triturated with petroleum ether to give pure **7**, mp 176–177 °C (0.27 g, 6%), R_f [silica, petroleum ether–ethyl acetate (5:1)] 0.24. Anal. Calcd for $C_{33}H_{34}O$: C, 88.74; H, 7.07. Found: C, 88.55; H, 7.49. Ir ν_{max} (KBr) 2960 (m), 2920 (m), 2860 (m), 1850 (s), 1837 (s), 1820 (s), 1552 (s), 1433 (vs), 1393 (s), 1368 (s), 1242 (s), and 1010 cm^{-1} (s); μ (C_6H_6, 30 °C) 5.13 ± 0.03 D ($\alpha' = 33.93$, $\beta' = -1.40$, $P_{2\infty} = 628.1$ cm, MR_{calcd} 97.9 cm^{-1}).

Tri-(3-guaiazulenyl)cyclopropenium Perchlorate (6). A magnetically stirred suspension of trichlorocyclopropenium tetrachloroaluminate prepared as described above from tetrachlorocyclopropene (1.78 g, 10 mmol) and anhydrous aluminum chloride (1.47 g, 11 mmol) in dry dichloromethane (85 ml) was cooled to −70 °C and treated dropwise, below −70 °C, under anhydrous inert atmosphere, during 50 min, with a solution of guaiazulene (**8**, 5.58 g, 28.2 mmol) in dry dichloromethane (50 ml). The resulting red complex, which darkened during the addition, was kept at −70 °C for 40 min, heated gradually to room temperature, and kept at room temperature overnight. The complex was decomposed below −60 °C by the addition of aqueous acetone (20%, 50 ml). The mixture was heated to room temperature, water and dichloromethane were added, and the organic fraction was washed with water and dried over magnesium sulfate. The solution was concentrated under vacuum to a volume of 100 ml and treated with perchloric acid (70%, 15 ml), and stirred magnetically for 150 min. The layers were separated, the organic layer was washed with water and dried over magnesium sulfate, and the solvent evaporated under vacuum. Treatment of the remaining oil with petroleum ether gave crude **6** as a dark solid (4.48 g, 69%). Purification was effected by column chromatography on microcrystalline cellulose, using 15% dichloromethane in petroleum ether. The resulting oily product was dissolved in dichloromethane and precipitated with petroleum ether (four times) to give **6** as a dark solid, mp 171–173 °C dec (23% yield), R_f [microcrystalline cellulose, petroleum ether–dichloromethane (1:1)] 0.66. Anal. Calcd for $C_{48}H_{51}ClO_4$: C, 79.25; H, 7.07. Found: C, 79.52; H, 7.15%. Ir ν_{max} (KBr) 2955 (m), 2920 (m), 2860 (m), 1760 (w), 1705 (w), 1524 (m), 1468 (vs), 1448 (vs), 1392 (vs), 1368 (vs), 1335 (s), 1270 (vs), 1215 (s), 1120 (m), 1090 (s), 1010 (s), 891 (m), 649 (m), 618 (m), and 592 cm^{-1} (m).

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Registry No.—**6**, 58815-85-3; **7**, 58815-87-5; **8**, 489-84-9; trichlorocyclopropenium tetrachloroaluminate, 10438-65-0.

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Organometallic Chemistry. 10.[1] Carbon-13 Nuclear Magnetic Resonance Study of *cis*-π-Pentadienyliron Tricarbonyl Cations and Protonated Norbornadieneiron Tricarbonyl

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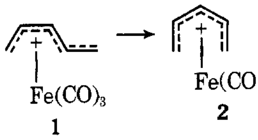
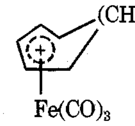
Acyclic and cyclic cisoid π-pentadienyliron tricarbonyl cations were studied by ^{13}C NMR spectroscopy in strong acids. The origin of the unusual stability of these ions and their fluxional behavior are discussed. The nature of bonding and the structure of the protonated norbornadieneiron tricarbonyl were also studied and are discussed.

The preparation of the tropyliummolybdenum tricarbonyl cation via hydride abstraction from tropylidenemolybdenum tricarbonyl by Dauben and Honnen[3] and that of cyclohexadienyliron tricarbonyl cation by Fischer and Fischer[4] have drawn considerable interest from both organic and inorganic chemists, and particularly theoretical chemists, in recent years. A large variety of organometallic cations has since been prepared and their chemistry reviewed.[5] All these cationic species exhibit remarkable stability due to the complexation of the unsaturated organic moiety with the metal atom (i.e., transition metals).

Acyclic *trans*-pentadienyliron tricarbonyl cations **1** have



1 **2**



3, $n = 1$; **4**, $n = 2$