#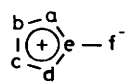 Synthesis of Mesoionic Analogues of Heptafulvene *via* Dicationic Ether Salts Derived from Mesoionic Olates and Trifluoromethanesulphonic Anhydride

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Three kinds of mesoionic analogues of heptafulvene have been synthesized by the base-induced reaction of active methylene compounds with the dicationic ether salts derived from mesoionic olates and trifluoromethanesulphonic anhydride. Based on their spectroscopic properties, it is shown that dipolar structures make an important contribution to the ground state of the synthesized fulvenes.

Mesoionic compounds of the general formula (1) are an interesting family of heterocycles because of their unique structure, reaction behaviour, and pharmaceutical activity.[1] Mesoionic compounds possessing 6 π-electrons in a heterocyclic five-membered ring and with the negative charge associated with carbanionoid (f = CH₂) and cyclopentadienide groups (f = C_5H_4) are isoelectronic with heptafulvene (2) and sesquifulvalene (3), respectively. As part of our study of the
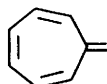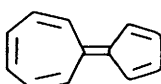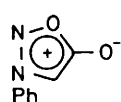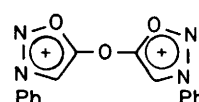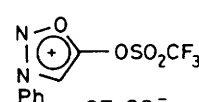

chemistry of these mesoionic analogues of heptafulvene and sesquifulvalene,[2] we describe here the synthesis of mesoionic heptafulvenes by the reaction of the conjugate anion of active methylene compounds with dicationic ether salts derived from mesoionic olates and trifluoromethanesulphonic anhydride (triflic anhydride). A preliminary communication of this work has been published.[3]
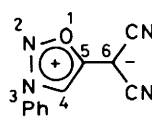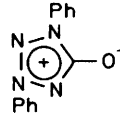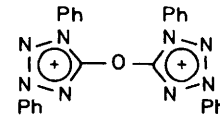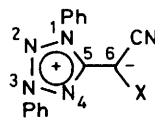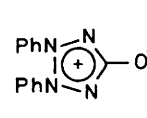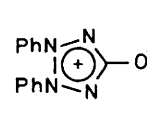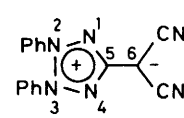
Results and Discussion

Synthesis.—Activated ketones such as annulenones and substituted ureas react with triflic anhydride to produce the corresponding dicationic ether salts.[4] This reaction has been found to be applicable to mesoionic olates. When triflic anhydride was added to a solution of 3-phenylsydnone (4) in dichloromethane, a white precipitate was deposited within a few minutes. Owing to the moisture-sensitivity of this compound, satisfactory analytical data were not obtained. However, the structure was deduced to be 5,5'-oxybis(3-phenyl-1,2,3-oxadiazolium) ditriflate (5) from the spectroscopic evidence. In particular, the ¹⁹F n.m.r. spectrum showed only one singlet at 87.0 p.p.m. downfield from hexafluorobenzene, excluding the possibility of the monocationic structure (6). To a suspension of the dicationic ether (5) thus obtained, malononitrile and then triethylamine were added at −78 °C. An intense yellow colour immediately developed and the mixture was stirred for 30 min. Work-up and purification by column chromatography on silica gel gave orange cubes of the dicyanomethylide (7) in 22% yield. Attempts to obtain compound (7), the first example of an *exo*-methylene analogue of sydnone, by the reaction of 5-ethoxy-3-phenyl-1,2,3-oxadiazolium tetrafluoroborate[5] with malononitrile failed.

1,3-Diphenyltetrazolium-5-olate (8) also gave the corresponding dicationic ether salt (9) on treatment with triflic anhydride. Nucleophilic substitution of the ether (9) by the

conjugate anions of malononitrile and ethyl cyanoacetate led to the formation of the respective mesoionic analogues (10) and (11) of heptafulvene in 75 and 41% yields. Compound (10) has been synthesized by Ollis and co-workers[6] from 5-ethoxy-1,3-diphenyltetrazolium tetrafluoroborate, whereas compound (11) is new.

Treatment of 2,3-diphenyltetrazolium-5-olate (12) with triflic anhydride followed by reaction with malononitrile–triethylamine gave dicyano-α-(2,3-diphenyltetrazol-5-ylio)methylide (13) in 23% yield. This compound, an isomer of the 1,3-diphenyl derivative (10), was obtained as orange plates from acetonitrile. The analytical and spectral data revealed that the crystals included a molecule of acetonitrile as the solvent of crystallization. An unsuccessful attempt to synthesize the methylide (13) from 5-ethoxy-2,3-diphenyltetrazolium tetrafluoroborate has been reported.[6]

Mass spectra.—The electron impact (e.i.) mass spectra of mesoionic heptafulvenes (7), (10), (11), and (13) are summarized in Table 1. The mass spectrum of compound (7) reveals an intense molecular ion peak, which loses a nitroxyl radical (˙NO) to give the daughter ion [PhN⁺CH=C=C(CN)₂; *m/z* 180]. This ion further eliminates hydrogen cyanide forming the fragment ion (PhN=C=C=C⁺CN; *m/z* 153). Further fragmentation gives the ions at *m/z* 91 and 77 corresponding to PhN⁺˙ and Ph⁺,

respectively. The interpretation of the mass spectrum of the compound (10) has been reported.[7] The mass spectrum of compound (11) shows a strong molecular ion peak and the peaks arising from the fragmentation of the ethoxycarbonyl

group. The base peak of the mass spectrum of the 2,3-diphenyltetrazolium derivative (13) is phenyl cation (m/z 77). The fragment ion (m/z 260) corresponding to loss of nitrile radical ($^{.}CN$) from the molecular ion and the peaks of PhN_2^+ and $PhN^{+.}$ are also observed.

I.r. spectra.—The i.r. spectra (Table 2) of the three dicyano-methylides (7), (10), and (13) show two intense absorptions resulting from the symmetrical and asymmetrical stretching vibrations of nitrile groups in the region of 2 210—2 170 cm^{-1}. The mononitrile compound (11) shows one peak at 2 190 cm^{-1} in this region. The carbonyl stretching band of this compound appears at 1 674 cm^{-1}, a considerable shift to lower wave-number compared with the normal value for an ethoxycarbonyl group; this suggests the contribution of a dipolar mesoionic structure. Strong absorption due to the stretching vibration of the exocyclic carbon–carbon bond, which is characteristic of fulvenes and fulvalenes,[8] appears at 1 594—1 538 cm^{-1}.

Electronic Spectra.—The long wavelength maxima of the mesoionic compounds (7), (10), (11), and (13) lie in the range 396 and 468 nm (Table 3), and exhibit distinctive bathochromic shifts with a change from a polar to a nonpolar solvent (Table 4). This property indicates that the mesoionic fulvenes are polar compounds, the dipolar structures contributing significantly to the resonance hybrid,[9] as is demonstrated by the dipole moment measurement.[6]

1H and 13C N.m.r. Spectra.—The ^1H n.m.r. spectrum of the fulvene (7) exhibits a phenyl multiplet at δ 7.88—7.74 and a singlet due to the oxadiazolium ring proton at δ 7.69. The latter signal is deshielded by more than 1 p.p.m. compared with that for the corresponding proton of 3-phenylsydnone (4) (δ 6.78);[10] this suggests that the electron density on the oxadiazolium ring of (7) is less than that of (4). This is consistent with the large lowfield shift (109.8 p.p.m.) of the ring carbon (C-4) of (7) compared with that of 3-phenylsydnone (4) (94.9 p.p.m.) (Table 5). On the other hand, the *exo*-methylene carbon (C-6) of the methylide (7) resonates at very high field (33.9 p.p.m.), indicating the high electron density on this carbon. These spectral properties are again in accord with a large contribution of the dipolar structure to the ground state. Analogously, the highfield chemical shift (22.4 p.p.m.) of the *exo*-methylene carbon (C-6) of the fulvene (13) indicates that the equilibrium between the mesoionic form (13A) and the covalent form (13B) lies far over towards (13A). It is interesting to compare the ^{13}C n.m.r. chemical shifts of the 1,3-diphenyltetrazolium compound (10) with those of the 2,3-diphenyl compound (13). The tetrazolium ring carbon (C-5) of (13) resonates at lower field

Table 1. Mass spectra of the fulvenes (7), (10), (11), and (13)

Compound	m/z (relative intensity/%)
(7)	210 ($M^{+.}$; 100), 180 [PhN$^+$CH=C=C(CN)$_2$; 35], 153 (PhN=C=C$^+$CN; 27), 91 (PhN$^{+.}$; 19), 77 (Ph$^+$; 32)
(10)	286 ($M^{+.}$; 100), 260 ($M^{+.}$ − $^{.}CN$; 2), 167 [PhN$^+$ $^{.}$=C=C(CN)$_2$; 2], 91 (PhN$^{+.}$; 14), 77 (Ph$^+$; 29)
(11)	333 ($M^{+.}$; 100), 288 ($M^{+.}$ − $^{.}OEt$; 28), 261 ($M^{+.}$ − C$_2$H$_4$ − CO$_2$; 74), 236 (37), 91 (PhN$^{+.}$; 17), 77 (Ph$^+$; 39)
(13)	286 ($M^{+.}$; 19), 260 ($M^{+.}$ − $^{.}CN$; 9), 105 (PhN$^+$≡N; 52), 91 (PhN$^{+.}$; 13), 77 (Ph$^+$; 100)

Table 2. I.r. spectra of the fulvenes (7), (10), (11), and (13)

Compound	$v_{max.}$(KBr)/cm^{-1}
(7)	3 100, 2 201, 2 175, 1 606, 1 594, 1 588, 1 472, 1 378, 1 281, 996, 914, 756
(10)	3 060, 2 210, 2 180, 1 552, 1 470, 1 370, 1 278, 1 194, 984, 772, 695
(11)	3 050, 2 190, 1 674, 1 538, 1 306, 1 236, 1 204, 1 062, 764, 696
(13)	3 080, 2 200, 2 170, 1 540, 1 488, 1 149, 998, 770, 690

Table 3. Electronic spectra of the fulvenes (7), (10), (11), and (13) in acetonitrile

Compound	$\lambda_{max.}$/nm (log ε)
(7)	220 (3.78), 268 (4.49), 417 (3.99)
(10)	223 (s, 3.90), 272 (4.48), 396 (3.12)
(11)	283 (4.45), 397 (3.16)
(13)	266 (4.50), 468 (2.97)

Table 4. Solvent effect on the first-excitation band of the fulvenes (7), (10), (11), and (13) ($\lambda_{max.}$/nm)

Compound	Solvent					
	DMSO	MeCN	EtOH	CH$_2$Cl$_2$	Et$_2$O	CCl$_4$
(7)	417	417	421	432	442	452
(10)	392	396	391	413	440	450
(11)	395	397	389	413	438	447
(13)	450	468	*a*	504	*a*	*a*

a Not soluble.

Table 5. ^{13}C N.m.r. chemical shifts of the fulvenes (7), (10), (11), and (13) and the olates (4), (8), and (12) in (CD$_3$)$_2$SO (δ/p.p.m.)

Compound	C-4	C-5	C-6	Phenyl				CN	Others
				ipso	*ortho*	*meta*	*para*		
(7)	109.8	174.2	33.9	132.5	130.3	122.4	133.3	115.6	
(4)	94.9	168.5		134.5	130.1	121.5	132.4		
(10)		160.9	25.0	131.7	129.4	120.8	132.2	117.2	
				134.7	130.4	127.3	132.7		
(11)		159.9	47.5	133.8	129.2	120.9	131.2	119.0	165.0 (CO)
				135.0	130.3	126.0	132.5		58.2 (CH$_2$)
									14.6 (Me)
(8) *a*		159.3		134.2	129.4	119.8	128.6		
				136.4	129.7	120.3	131.4		
(13)		169.2	22.4	133.2	129.9	126.2	133.1	119.6	
(12)		169.6		134.2	129.5	126.1	131.8		

a In CDCl$_3$.
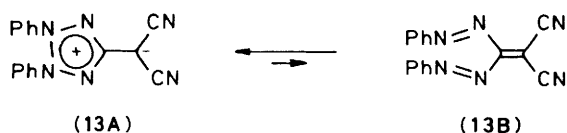
(169.2 p.p.m.) than that of (10) (160.9 p.p.m.), whereas the *exo*-methylene carbon (C-6) resonates at higher field (22.4 p.p.m.) than that of (10) (25.0 p.p.m.). These facts suggest that the extent of the contribution of the dipolar structure in (13) is larger than in (10).

Experimental

M.p.s were determined with a hot-stage apparatus and are uncorrected. I.r. spectra were taken for KBr discs with a JASCO A-102 instrument. Electronic spectra were measured on a Hitachi 124 spectrophotometer. Mass spectra were recorded with a Hitachi M-52 instrument at 20 eV using a direct inlet system. ^{1}H, ^{13}C, and ^{19}F N.m.r. spectra were run with Hitachi R-24A (60 MHz), Varian XL-200 (50.3 MHz), and Hitachi R-20B (56.5 MHz) spectrometers, respectively. Elemental analyses were performed at the Elemental Analysis Centre of Kyoto University.

Dicyano-α-(3-phenyl-1,2,3-oxadiazol-5-ylio)methylide (7).—To a stirred solution of 3-phenylsydnone (162 mg, 1 mmol) in dichloromethane (3 ml) was added dropwise triflic anhydride (0.17 ml, 1 mmol). After a few minutes, a white precipitate was deposited. The solvent and excess of triflic anhydride were evaporated under reduced pressure to give a white solid of the dicationic ether (5) in quantitative yield. The ^{19}F n.m.r. spectrum (in CH_2Cl_2, hexafluorobenzene as an external standard) of the compound (5) showed a singlet at 87.0 p.p.m. To a suspension of the salt (5) (303 mg, 0.5 mmol) in dichloromethane (3 ml) were added a solution of malononitrile (66 mg, 1 mmol) in dichloromethane (2 ml) and then triethyl-amine (0.28 ml, 2 mmol) at −78 °C. The mixture was stirred at −78 °C for 30 min. The reaction was quenched by the addition of water and the product was extracted with dichloromethane. The extracts were dried (Na_2SO_4) and concentrated. The residue was chromatographed on silica gel (dichloromethane–diethyl ether 1:1 as eluant) and a yellow band was collected. Recrystallization from acetonitrile–diethyl ether gave orange cubes of fulvene (7) (23 mg, 22%), m.p. 219 °C (decomp.) (Found: C, 63.15; H, 2.65; N, 26.6. $C_{11}H_6N_4O$ requires C, 62.85; H, 2.88; N, 26.66%); δ_H(CDCl$_3$) 7.88—7.74 (5 H, m, Ph), and 7.69 (1 H, s, ring-H).

Dicyano-α-(1,3-diphenyltetrazol-5-yliomethylide (10).—The dicationic ether salt (9) was obtained quantitatively in the same manner as (5). The salt (9) showed a signal at 86.7 p.p.m. in the ^{19}F n.m.r. spectrum (in CH_2Cl_2, hexafluorobenzene). To a suspension of the salt (9) (379 mg, 0.5 mmol) in dichloromethane (3 ml) was added a solution of malononitrile (66 mg, 1 mmol) in dichloromethane (1 ml) and then triethylamine (0.28 ml, 2 mmol) at −78 °C. The mixture was stirred at −78 °C for 1 h. The reaction was quenched by the addition of water and the product was extracted with dichloromethane. The extracts were dried (Na_2SO_4) and concentrated. The residue was chromatographed on silica gel (diethyl ether as eluant) and a yellow band was collected. Recrystallization from acetone–diethyl ether gave yellow crystals of fulvene (10) (108 mg, 75%), m.p. 227 °C (lit.,[6] 234 °C); δ_H(CDCl$_3$) 8.15 (2 H, m, Ph) and 7.65 (8 H, m, Ph).

Cyanoethoxycarbonyl-α-(1,3-diphenyltetrazol-5-ylio)-methylide (11).—This compound was prepared in the same manner as (10) in 41% yield, m.p. 207 °C (Found: C, 65.05; H, 4.4; N, 20.95. $C_{18}H_{15}N_5O_2$ requires C, 64.86; H, 4.54; N, 21.01%); δ_H(CDCl$_3$) 8.20 (2 H, m, Ph), 7.57 (8 H, m, Ph), 4.11 (2 H, q, *J* 7 Hz, C*H*$_2$Me), and 1.22 (3 H, t, *J* 7 Hz, CH$_2$*Me*).

Dicyano-α-(2,3-diphenyltetrazol-5-ylio)methylide (13).—Triflic anhydride (0.085 ml, 0.5 mmol) was added dropwise to a suspension of 2,3-diphenyltetrazolium-5-olate (12) (238 mg, 1 mmol) in dichloromethane (10 ml) and the mixture was stirred for 5 min. A solution of malononitrile (33 mg, 0.5 mmol) in dichloromethane (1 ml) and then triethylamine (0.1 ml) were added at room temperature and the mixture was kept for 2 h. The red crystals which were deposited were filtered off and washed with dichloromethane. Recrystallization from aceto-nitrile gave red plates of the fulvene (13) (33 mg, 23%), m.p. >300 °C (Found: C, 65.95; H, 3.85; N, 30.35. $C_{16}H_{10}N_6$·MeCN requires C, 66.05; H, 4.00; N, 29.95%); δ_H[(CD$_3$)$_2$SO] 7.67 (10 H, m, Ph) and 2.09 (3 H, s, MeCN).

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