

## Syntheses and Properties of the Mesoionic Analogues of Sesquifulvalene possessing a 1,3-Diphenyltetrazolium Ring

Shuki Araki and Yasuo Butsugan\*

Department of Synthetic Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466, Japan

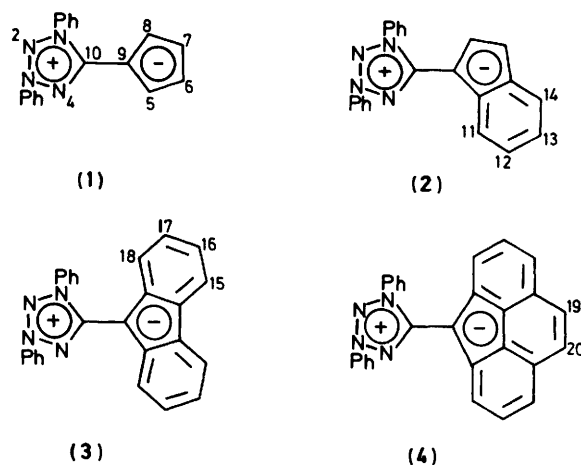
The mesoionic analogue of sesquifulvalene, 1,3-diphenyltetrazol-5-yliocyclopentadienide (1), and the benzannelated indenide (2), fluorene (3), and cyclopenta[*def*]phenanthrenide derivatives (4), have been synthesized from the 5-ethoxy-1,3-diphenyltetrazolium salt and the corresponding carbanion. The electronic structures of the synthesized fulvalenes are discussed on the basis of their spectroscopic evidence and it is shown that the polarized structures make a significant contribution to the ground state of these  $\pi$ -electron systems. The influence of benzannelation on the structure of the mesoionic fulvalene system is also described.

We recently reported the synthesis of 1,3-diphenyltetrazol-5-yliocyclopentadienide (1), a mesoionic analogue of sesquifulvalene, and suggested, on the basis of the spectroscopic evidence, that this dipolar (tetrazol-5-yliocyclopentadienide) canonical structure makes a significant contribution to the ground state.<sup>1</sup> We have also achieved a successful electrophilic substitution of the cyclopentadienide ring, demonstrating the aromatic character of this novel cross-conjugated electronic system.<sup>2</sup> In order to investigate further the nature of the mesoionic sesquifulvalene, we synthesized three benzannelated analogues of (1), namely the indenide (2), fluorene (3), and cyclopenta[*def*]phenanthrenide derivatives (4).† In this paper, their physicochemical properties and the influence of benzannelation upon the mesoionic  $\pi$ -electron system are discussed on the basis of the spectroscopic data. For comparison, full spectral data of the parent fulvalene (1) are also included.

### Results and Discussion

**Synthesis.**—The syntheses of the benzannelated fulvalenes (2)–(4) were performed in an analogous manner to that of the parent fulvalene (1). The reactions of 5-ethoxy-1,3-diphenyltetrazolium tetrafluoroborate<sup>3</sup> with the lithium salts of indene, fluorene, and cyclopenta[*def*]phenanthrene<sup>4</sup> gave moderate yields (57–62%) of the desired mesoionic compounds (2)–(4) as deep coloured crystalline solids. The indenide derivative (2) was isolated as fine purple needles after recrystallization from acetonitrile–diethyl ether. The fluorene (3) and cyclopenta[*def*]phenanthrenide analogues (4) were recrystallized from moist chloroform–hexane. The elemental analyses revealed that compounds (3) and (4) were obtained as the hemihydrates. The fulvalenes (2)–(4) are soluble in polar solvents such as acetonitrile and chloroform, and insoluble in nonpolar solvents such as cyclohexane and light petroleum. They are stable to air in crystalline form, but the solutions gradually decompose on contact with atmospheric oxygen.

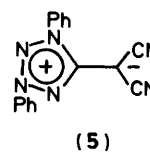
**Mass Spectra.**—The electron-impact mass spectra of compounds (1)–(4) exhibit the corresponding molecular ion peaks with strong intensities (Table 1), indicating the high stability of these fulvalene systems. The molecular ion peaks are the most abundant species in the mass spectra of compounds (1)



N.m.r. numbering scheme shown (see footnote †)

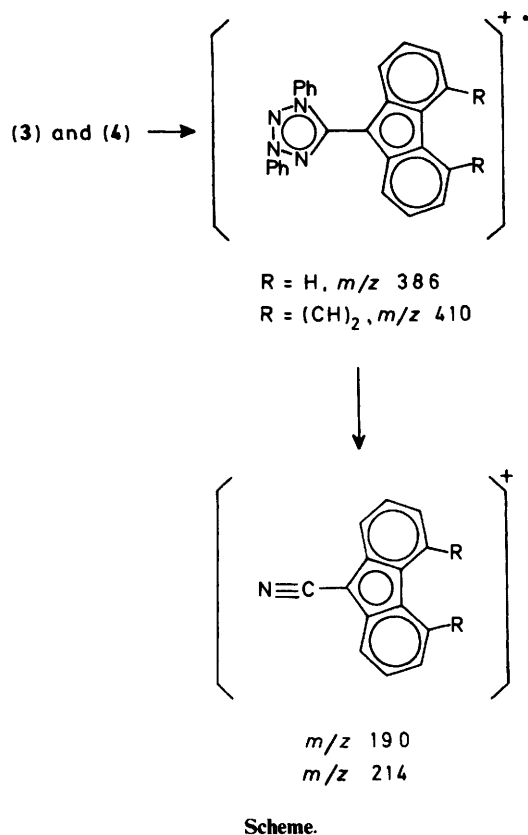
and (2), whereas the base peaks of compounds (3) and (4) are at  $m/z$  190 and 214 ( $M - 196$ ), respectively, a possible fragmentation being the loss of  $\text{PhN}=\text{NNPh}$  ( $m/z$  196) as shown in the Scheme. This type of fragmentation is often observed in mesoionic heterocycles.<sup>5</sup> Interestingly, the corresponding fragment ions were not observed in the mass spectra of compounds (1) and (2).

**I.R. Spectra.**—The i.r. spectra of compounds (1)–(4) showed intense and characteristic absorptions in the region of 1563–1544  $\text{cm}^{-1}$  (Table 2). The related cross-conjugated  $\pi$ -electron systems, fulvenes, fulvalenes, and their heteroatom-containing analogues, all show strong absorptions around 1550  $\text{cm}^{-1}$ .<sup>6</sup> Although these absorptions have not been completely analysed,<sup>7</sup> they are generally considered to result from the stretching vibrations of the exocyclic or pivotal carbon–carbon double bond. The corresponding band of the fulvene analogue of compound (1), dicyano- $\alpha$ -(1,3-diphenyltetrazol-5-yl)-methylide (5), appears at 1545  $\text{cm}^{-1}$ .<sup>8</sup>



(5)

† The numbering system for the n.m.r. assignments of the fulvalenes (1)–(4) in this paper is analogous to that for sesquifulvalene and its benzannelated derivatives, for ease of comparison with the literature.



**Table 1.** Mass spectra of the fulvalenes (1)–(4) [ $m/z$  (relative intensity/%)]

(1)	286 ( $M^+$ ; 100%), 257 (10), 167, (10), 91 (19), 77 (24)
(2)	336 ( $M^+$ ; 100%), 203 (9), 202 (12), 77 (14)
(3)	386 ( $M^+$ ; 85%), 253 (15), 190 (100), 77 (25)
(4)	410 ( $M^+$ ; 72%), 276 (9), 214 (100), 77 (15)

**Table 2.** I.r. spectra of the fulvalenes (1)–(4) ( $\nu_{\max}$ (KBr)/cm<sup>-1</sup>)

(1)	1 561, 1 354, 1 056, 984, 880, 762, 735, 714
(2)	1 563, 1 374, 1 212, 1 147, 1 114, 1 066, 994, 936, 752, 698
(3)	1 562, 1 544, 1 321, 1 288, 1 152, 1 119, 990, 759, 726, 692
(4)	1 570, 1 554, 1 488, 1 434, 1 330, 1 202, 1 152, 820, 763, 759, 698

**Table 3.** Electronic spectra of the fulvalenes (1)–(4) in acetonitrile [ $\lambda_{\max}$ /nm (log  $\epsilon$ )]

(1)	258 (4.26), 335 (4.49), 475 (3.08)
(2)	213 (s, 4.44), 242 (s, 4.24), 277 (4.47), 363 (s, 4.36), 376 (4.49), 530 (3.08)
(3)	246 (4.57), 257 (4.55), 276 (4.60), 300 (s, 4.33), 372 (s, 4.14), 393 (s, 4.28), 412 (4.35), 589 (3.17)
(4)	227 (4.74), 245 (4.67), 266 (s, 4.39), 313 (4.20), 335 (4.20), 386 (s, 4.32), 406 (4.57), 568 (3.18)

**Electronic Spectra.**—Table 3 shows the electronic spectral results of compounds (1)–(4) in acetonitrile. Each fulvalene shows a strong absorption (log  $\epsilon$  ca. 4) near 400 nm (band A) and a weak one (log  $\epsilon$  ca. 3) in the visible region (band B). On benzannulation, both absorption maxima shift to longer wavelength, demonstrating the extended conjugation of the  $\pi$ -electron system. Thus, on mono- and di-benzannulation, band A

**Table 4.** Solvent effect on the first-excitation band of the fulvalenes (1)–(4) ( $\lambda_{\max}$ /nm)

	CCl <sub>4</sub>	Et <sub>2</sub> O	CH <sub>2</sub> Cl <sub>2</sub>	EtOH	Me <sub>2</sub> CO	MeOH	MeCN
(1)	565	548	485	476	493	464	475
(2)	640	614	575	565	555	530	530
(3)	682	647	622	619	600	605	589
(4)	679	628	590	587	574	567	568

**Table 5.** <sup>1</sup>H N.m.r. parameters of the fulvalenes (1)–(4) in CDCl<sub>3</sub> ( $\delta$ /p.p.m.)

(1)	8.23 (2 H, m, Ph), 7.71 (8 H, m, Ph), 6.20 (4 H, m, 5–8-H)
(2)	8.28 (2 H, m, Ph), 7.67 (10 H, m, Ph, 11- and 14-H), 7.12 (2 H, m, 12- and 13-H), 6.35 (1 H, d, $J$ 4.6 Hz, 7-H), 6.11 (1 H, d, $J$ 4.6 Hz, 8-H)
(3)	8.28 (2 H, m, Ph), 8.02 (2 H, m, 14- and 15-H), 7.75–7.40 (8 H, m, Ph), 7.30–7.00 (6 H, m, 11–13-H and 16–18-H)
(4)	8.30 (2 H, m, Ph), 7.91 (2 H, s, 19- and 20-H), 7.80–7.50 (14 H, m, Ph, 11–13-H, and 16–18-H)

**Table 6.** <sup>1</sup>H N.m.r. parameters of cations (1')–(4') in CF<sub>3</sub>CO<sub>2</sub>H ( $\delta$ /p.p.m.)

(1')	8.38 (2 H, m, Ph), 7.85 (8 H, m, Ph), 7.30 (1 H, m, 8-H), 7.05 (1 H, m, 7-H), 6.75 (1 H, m, 6-H), 3.65 (2 H, br s, 5-H)
(2')	8.42 (2 H, m, Ph), 8.10–7.20 (12 H, m, Ph and 11–14-H), 7.05 (1 H, br s, 8-H), 3.75 (2 H, br s, 7-H)
(3')	8.38 (2 H, m, Ph), 7.85 (2 H, m, 14- and 15-H), 7.65–6.90 (12 H, m, Ph, 12-, 13-, 16-, and 17-H), 6.53 (2 H, d, $J$ 8 Hz, 11- and 18-H), 6.02 (1 H, s, 9-H)
(4')	8.42 (2 H, m, Ph), 8.10–7.50 (8 H, m, Ph), 7.75 (2 H, s, 19- and 20-H), 7.10–6.20 (6 H, m, 11–13-H and 16- and 18-H), 6.48 (1 H, s, 9-H)

is bathochromically shifted by 41 and 77 nm, respectively, relative to (1), and by 55 and 114 nm for band B. It is important to note that band B shows an extremely large solvent effect, the absorption maxima shifting to longer wavelength as the solvent polarity decreases (Table 4). Therefore, these absorptions can be considered to be due to the intramolecular charge transfer from the cyclopentadienide ring to the tetrazolium ring.<sup>9</sup> The unusually large shifts [ $\Delta\lambda = \lambda_{\max}(\text{CCl}_4) - \lambda_{\max}(\text{MeCN}) = 93$ –111 nm] indicate the significant contribution made by the polar structures to the ground states of these  $\pi$ -electron systems. The magnitudes of  $\Delta\lambda$  of compounds (2)–(4) are close to that of (1) (90 nm), suggesting that the benzannulation does not affect the contribution of the dipolar canonical structure to the resonance hybrid.

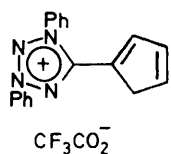
**<sup>1</sup>H N.M.R. Spectra.**\*—The <sup>1</sup>H chemical shifts of the fulvalenes (2)–(4) are listed in Table 5 together with those of the parent compound (1). The cyclopentadienyl protons (7-H and 8-H) of the indenide derivative (2) appear at  $\delta$  6.35 and 6.11, respectively, as an AB-type quartet with  $J$  4.6 Hz. The chemical shift of 7-H ( $\delta$  6.35) is between the values of the corresponding protons of indene ( $\delta$  6.82) and the indenide anion ( $\delta$  5.93).<sup>10</sup> Moreover, the coupling constant  $J_{7,8}$  of compound (2) (4.6 Hz) is the average of those of indene (5.8 Hz) and the indenide anion (3.3 Hz).<sup>10</sup> These data show the contribution of the polar structure to the ground state of (2). The 19-H and 20-H protons of the cyclopentaphenanthrenide (4) appear as a sharp singlet at  $\delta$  7.91, almost coincident with the corresponding protons of cyclopenta[*def*]phenanthrene ( $\delta$  7.86) and its anion ( $\delta$  7.73).<sup>4</sup>

\* See footnote on p. 2545.

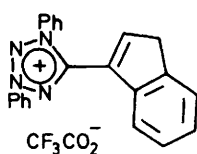
Table 7.  $^{13}\text{C}$  N.m.r. chemical shifts of the fulvalenes (1)–(4) in  $\text{CDCl}_3$  ( $\delta/\text{p.p.m.}$ )<sup>a</sup>

	(1)	(2)	(3)	(4)
C-5	[113.1] <sup>b</sup>	133.7	132.8	c
C-6	[116.5] <sup>b</sup>	136.8	135.9	c
C-7		112.3		
C-8		121.0		
C-9	96.9	88.1	83.3	83.1
C-10	158.3	155.3	153.6	155.2
C-11		[119.6] <sup>b</sup>	[119.3] <sup>b</sup>	[115.7] <sup>b</sup>
C-12		[119.7] <sup>b</sup>	[119.3] <sup>b</sup>	[116.0] <sup>b</sup>
C-13		[120.2] <sup>b</sup>	[124.2] <sup>b</sup>	[127.4] <sup>b</sup>
C-14		[120.5] <sup>b</sup>	119.1	c
C-19				125.1
Phenyl	<i>ipso</i>	134.5	135.1	135.8
		135.7	135.7	135.9
	<i>ortho</i>	130.1	129.9	129.4
		130.4	130.3	129.8
	<i>meta</i>	120.7	120.5	120.6
		126.9	126.6	122.5
	131.9	131.3	129.0	129.7
	132.5	132.1	132.0	132.0

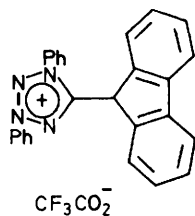
<sup>a</sup> See structures (1)–(4) for numbering scheme. <sup>b</sup> Values in parentheses are interchangeable. <sup>c</sup> Not observed owing to the poor solubility of (4) in  $\text{CDCl}_3$ .



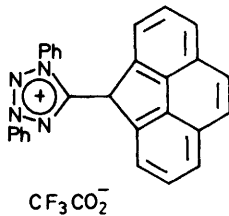
(1)



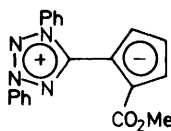
(2)



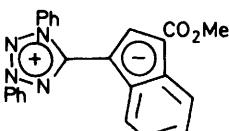
(3')



(4')



(6)



(7)

The  $^1\text{H}$  n.m.r. data of compounds (1)–(4) in trifluoroacetic acid are summarized in Table 6, and indicate the existence of the protonated species (1')–(4'). The cations (1')–(4') reversible regenerate the free bases (1)–(4) by the treatment with aqueous sodium hydrogen carbonate. This easy protonation is consistent with the highly polarized nature of these fulvalenes. It should be noted that the position of protonation of compounds (2) (at C-7 to avoid the formation of the unstable *o*-quinonoid cation) differs from that of the non-annelated compound (1) [protonated at C-5 to produce (1')]. The highly annelated fulvalenes (3) and (4) are protonated at the pivotal carbon (C-9) to give the cations (3') and (4'). The

position of electrophilic substitution is in marked contrast in compounds (1) and (2). Methoxycarbonylation of compound (1) with methyl chloroformate gave the 2-substituted cyclopentadienide (6) as the main product,<sup>2</sup> while (2) exclusively gave the 3-methoxycarbonylindenide (7). The position of the methoxycarbonyl group of compound (6) was deduced from the  $^1\text{H}$  n.m.r. parameters of the cyclopentadienyl ring protons,<sup>2</sup> while the structure of (7) was unambiguously confirmed by comparison with an authentic sample prepared from lithium 1-methoxycarbonylindenide and 5-ethoxy-1,3-diphenyltetrazolium tetrafluoroborate.

<sup>13</sup>C N.M.R. Spectra.—Table 7 lists the  $^{13}\text{C}$  n.m.r. data of compounds (1)–(4) in  $\text{CDCl}_3$ . Individual assignments, some of which are tentative, were made with the aid of off-resonance and selective decoupling spectra. The  $^{13}\text{C}$  chemical shifts of the tetrazolium ring carbon (C-10) for compounds (1)–(4) are almost coincident (158.3–153.6 p.p.m.); however, the pivotal carbon (C-9) of the cyclopentadienyl ring is shifted to higher magnetic field on successive benzannelation: e.g. 96.9 p.p.m. for (1), 88.1 for (2), 83.3 for (3), and 83.1 for (4). This indicates that the  $\pi$ -electron density on this carbon increases in the order (1) < (2) < (3) < (4). It should be noted that the chemical shifts of the corresponding pivotal carbons of sesquifulvalene and 7,8,9,10-dibenzosquifulvalene, which are known to have little aromaticity, are 138.6<sup>11</sup> and 129.6 p.p.m.,<sup>12</sup> respectively, more than 40 p.p.m. downfield of the mesoionic analogues (1) and (3).

In conclusion, these results demonstrate that the benzannelated mesoionic sesquifulvalenes (2)–(4) are highly polarized compounds, as is the parent fulvalene (1), and although benzannelation does not influence the polarity of the mesoionic sesquifulvalene system, the negative charge on the cyclopentadienyl ring increasingly tends to localize on the pivotal carbon as the number of fused benzene rings increases.

### 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 IRA-1 instrument, and electronic spectra were measured on a Hitachi 200-20 spectrophotometer. Mass spectra were recorded

with a Hitachi M-52 instrument at 20 eV using a direct-inlet system.  $^1\text{H}$  and  $^{13}\text{C}$  N.m.r. spectra\* were run with Hitachi R-24A (60 MHz) and Varian XL-200 (50 MHz) spectrophotometers, respectively. Elemental analyses were performed at the Elemental Analysis Centre of Kyoto University.

**1-(1,3-Diphenyltetrazol-5-yl)indenide (2).**—To a solution of lithium indenide, prepared by the addition of butyl-lithium (1.6M; 1.9 ml, 3 mmol) in hexane to a solution of indene (348 mg, 3 mmol) in tetrahydrofuran (THF) (10 ml), was added 5-ethoxy-1,3-diphenyltetrazolium tetrafluoroborate (352 mg, 1 mmol) as a powder in one portion and the mixture was stirred at 0 °C for 5 min under nitrogen. The reaction mixture was poured into water and the product was extracted with dichloromethane. The extracts were dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated. The residue was recrystallized from acetonitrile–diethyl ether to give fine purple needles of *compound (2)* (243 mg, 72%), m.p. 209 °C (decomp.) (Found: C, 78.25; H, 4.8.  $\text{C}_{22}\text{H}_{16}\text{N}_4$  requires C, 78.55; H, 4.79%). The spectral data are listed in the Tables.

**9-(1,3-Diphenyltetrazol-5-yl)fluorene (3) and 4-(1,3-Diphenyltetrazol-5-yl)cyclopenta[def]phenanthrene (4).**—These fulvalenes were synthesized in the same manner as (2). *Compound (3)* (76%) was obtained as dark green crystals (recrystallized from chloroform–hexane), m.p. 229 °C (decomp.) (Found: C, 78.8; H, 4.5; N, 14.0.  $\text{C}_{26}\text{H}_{18}\text{N}_4 \cdot 0.5\text{H}_2\text{O}$  requires C, 78.97; H, 4.84; N, 14.7%). *Compound (4)* (52%) was obtained as dark green crystals (recrystallized from chloroform–hexane), m.p. 245 °C (decomp.) (Found: C, 80.3; H, 4.3; N, 13.1.  $\text{C}_{28}\text{H}_{18}\text{N}_4 \cdot 0.5\text{H}_2\text{O}$  requires C, 80.17; H, 4.56; N, 13.36%).

**Reaction of Compound (1) with Methyl Chloroformate.**—Methyl chloroformate (1 ml) was added to a mixture of compound (1) (286 mg, 1 mmol) and anhydrous potassium carbonate (138 mg, 1 mmol) in dichloromethane (4 ml). The reaction mixture was stirred overnight at room temperature. The reaction was quenched by the addition of water and the products were extracted with dichloromethane. After being dried ( $\text{Na}_2\text{SO}_4$ ), the solvent was removed and the residue was chromatographed on silica gel (chloroform as eluant) to give a dark red solid (140 mg, 41%), shown by  $^1\text{H}$  n.m.r. analysis to be a 3:1 mixture of 2-methoxycarbonyl-1-(1,3-diphenyltetrazol-5-yl)cyclopentadienide (6) and 3-methoxycarbonyl-1-(1,3-diphenyltetrazol-5-yl)cyclopentadienide. These isomers were separated by fractional recrystallization from acetone–hexane. *Compound (6)* was obtained as a deep red solid, m.p. 85 °C (Found: C, 69.2; H, 4.8.  $\text{C}_{20}\text{H}_{16}\text{N}_4\text{O}_2$  requires C, 69.76; H, 4.68%;  $m/z$  344 ( $M^+$ , 100%);  $v_{\text{max}}$ . 1 668, 1 548, 1 361, 1 064, and 756  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ ( $\text{CDCl}_3$ ) 8.20 (2 H, m, Ph), 7.8–7.4 (8 H, m, Ph), 6.87 (1 H, dd,  $J$  3.4, 2.2 Hz, 6-H), 6.45 (1 H, dd,  $J$  3.7, 2.2 Hz, 8-H), 6.10 (1 H, br t,  $J$  3.7, 3.4 Hz, 7-H), and 3.40 (3 H, s,  $\text{CO}_2\text{Me}$ ). The 3-methoxycarbonyl isomer was obtained as deep red needles, m.p. 206 °C (Found: C, 69.7; H, 4.55.  $\text{C}_{20}\text{H}_{16}\text{N}_4\text{O}_2$  requires C, 69.76; H, 4.68%;  $m/z$  ( $M^+$ , 100%);  $v_{\text{max}}$ . 1 668, 1 552, 1 328, 1 298, 1 178, 1 136, and 895  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ ( $\text{CDCl}_3$ ) 8.20 (2 H, m, Ph), 7.65 (8 H, m, Ph), 6.92 (1 H, br t,  $J$  2.4, 2.0 Hz, 5-H), 6.49 (1 H, dd,  $J$  4.4, 2.0 Hz, 7-H), 6.03 (1 H, dd,  $J$  4.4, 2.4 Hz, 8-H), and 3.69 (3 H, s,  $\text{CO}_2\text{Me}$ ).

**Reaction of Compound (2) with Methyl Chloroformate.**—Methyl chloroformate (0.3 ml) was added to a mixture of compound (2) (50 mg, 0.15 mmol) and anhydrous potassium carbonate (25 mg, 0.19 mmol) in dichloromethane (1 ml). The reaction mixture was stirred overnight at room temperature and then treated as above. Column chromatography on silica gel (dichloromethane–methanol, 9:1, as eluant) gave the cyclopentadiene (7) (25 mg, 42%) as a solid. Recrystallization from ethanol–acetonitrile afforded deep purple needles, m.p. 273 °C (decomp.) (Found: C, 73.2; H, 4.7.  $\text{C}_{24}\text{H}_{18}\text{N}_4\text{O}_2$  requires C, 73.08; H, 4.60%;  $m/z$  394 ( $M^+$ , 100%);  $v_{\text{max}}$ . 1 668, 1 552, 1 478, 1 170, and 753  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ [ $(\text{CD}_3)_2\text{SO}$ ] 8.6–7.6 (12 H, m, aromatic), 7.05 (2 H, m, aromatic), 6.68 (1 H, s, 8-H), and 3.69 (3 H, s,  $\text{CO}_2\text{Me}$ ).

**Reaction of Lithium 1-Methoxycarbonylindenide and 5-Ethoxy-1,3-diphenyltetrazolium Tetrafluoroborate.**—To a solution of methyl indene-3-carboxylate  $^{13}$  (174 mg, 1 mmol) in dry THF (3 ml) was added a hexane solution of butyl-lithium (1.6M; 0.62 ml, 1 mmol) and the mixture stirred at 0 °C for 5 min. 5-Ethoxy-1,3-diphenyltetrazolium tetrafluoroborate (100 mg, 0.28 mmol) as a powder was then added and the mixture was stirred at 0 °C for 10 min, then poured into water and the product extracted with dichloromethane. The extracts were dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated. The residue was recrystallized from ethanol–acetonitrile to give deep purple needles (90 mg, 80%). The m.p. and the spectra data (i.r. and  $^1\text{H}$  n.m.r.) of this product were in agreement with those of compound (7) obtained above.

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\* See footnote on p. 2545.