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Dipolar Cycloadditions of Mesoionic Compounds with 2-*tert*-Butylfulvenes. A New Route to Pseudo-heteroazulenes *via* Sterically Assisted [4π + 6π] Cycloadditions, and Isomerization of Adducts [1,2]

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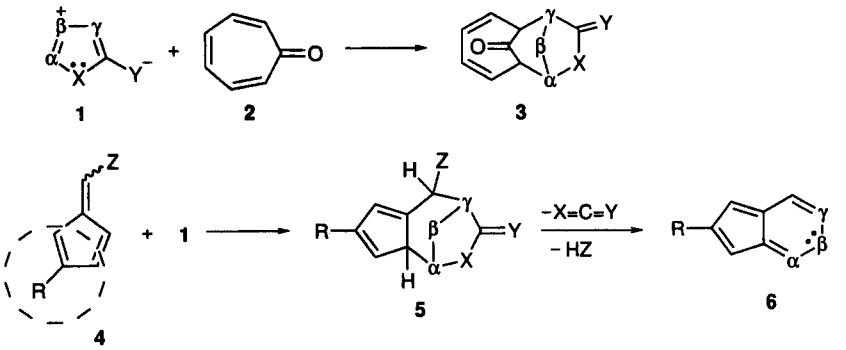
Abstract: Several mesoionic compounds react with 2-*tert*-butylfulvene derivatives to form [4π + 6π] and/or [4π + 2π] cycloadducts. They undergo further fragmentation, elimination, or isomerization under the reaction conditions to give a variety of products including several condensed heterocycles which are isoelectronic with azulene. An oxazolium-4-olate, on contact with a small amount of air, was found to form a tricyclic oxygenated dimer. © 1997 Elsevier Science Ltd.

INTRODUCTION

The dipolar cycloaddition reactions of mesoionic compounds have been extensively investigated, and they are now regarded as an important synthetic route to the construction of many five-membered heterocycles.[3,4] Through a series of studies, we have shown that the cycloaddition–extrusion reactions of mesoionic compounds can be extended to the syntheses of six-,[5] seven-, eight-,[6] nine-, and ten-membered[7,8] fully conjugated heterocyclic systems. It is rather surprising to find that, until very recently, all the known cycloaddition reactions of mesoionic compounds belonged to [4π + 2π] mode. We have recently found for the first time that a few mesoionic compounds **1** react with tropone **2** in a [4π + 6π] mode to give cycloadducts **3**.[9] At the same time, it was found that the cycloadducts **3** are stable, and do not serve the purpose for further manipulation. Our earlier attempts to obtain [4π + 6π] cycloadducts of mesoionic compounds with fulvenes instead gave [4π + 2π] cycloadducts, although coloration of the reaction mixture suggestive of the formation of pseudoazulenes was observed with many of these reactions.[10] It occurred to us that such [4π + 2π] cycloadditions with fulvenes may be hindered by introduction of a bulky substituent on the 2-position of the fulvene ring and, as a consequence, another theoretically possible [4π + 6π] cycloaddition of mesoionic compounds with

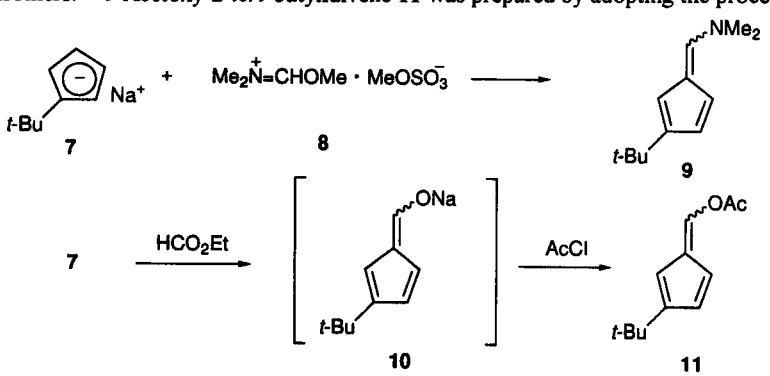
fulvenes may be realized. We also imagined that by the use of suitably 6-substituted fulvenes **4**, extrusion and elimination reactions from such [4π + 6π] cycloadducts **5** should afford a new short route to a variety of conjugated cyclopentaheterocycles **6** which are isoelectronic with azulene (pseudoazulenes).[11]



In this paper, reactions of several mesoionic compounds with 6-(dimethylamino)- and 6-acetoxy-2-*tert*-butylfulvene **9** and **11** are described. These two fulvenes were selected with the expectation that 2-*tert*-butyl group should be bulky enough to block the 3-position of fulvenes to interact with mesoionic compounds, and a molecule of dimethylamine and acetic acid will be readily eliminated from the desired [4π + 6π] cycloadducts or their extrusion products. For the purpose of comparison, the cycloaddition reactions of a few mesoionic compounds with 2-*tert*-butyl-6,6-dimethylfulvene **27** were also investigated with the hope to elucidate the reaction routes with fulvenes devoid of good leaving group. The realization of [4π + 6π] cycloaddition and successful formation of several pseudoazulenes are described below. The formation of conventional [4π + 2π] cycloaddition–extrusion products and isomerizations of primary [4π + 6π] cycloadducts with two mesoionic compounds are also described.

RESULTS AND DISCUSSION

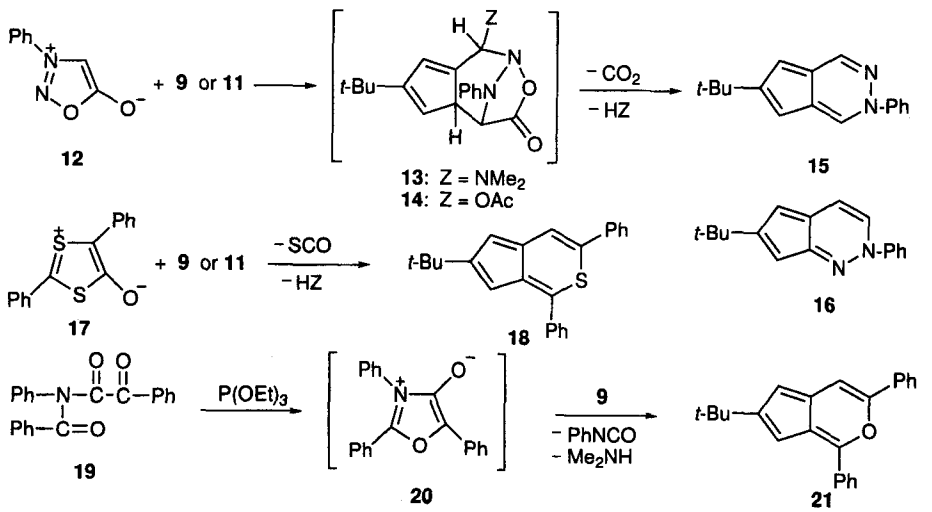
2-*tert*-Butyl-6-(dimethylamino)fulvene **9** has been prepared by the reaction of sodium cyclopentadienide **7** and dimethylformamide diethyl acetal.[12] We prepared this compound by treatment of sodium *tert*-butylcyclopentadienide with the *O*-methyl salt of dimethylformamide **8**. This procedure is essentially the same as that for the preparation of 6-(dimethylamino)fulvene.[13] The product obtained in this way was a *ca.* 1 : 1 mixture of *Z*- and *E*-isomers. 6-Acetoxy-2-*tert*-butylfulvene **11** was prepared by adopting the procedure for the prep-



aration of 6-acetoxyfulvene.[14] Sodium *tert*-butylcyclopentadienide was treated with ethyl formate and the sodium salt of the formyl derivative **10** thus formed was directly treated with acetyl chloride. In this case, only one stereoisomer was isolated, but it was not possible to establish its geometry by NOE or NOESY measurement.

*Cycloadditions with 6-(dimethylamino)- and 6-acetoxy-2-*tert*-butylfulvene*

The reaction of 3-phenylsydnone **12** with 6-(dimethylamino)- and 6-acetoxy-2-*tert*-butylfulvene **9** and **11** regioselectively gave the cyclopenta[*d*]pyridazine **15** in 31 and 47% yield respectively by spontaneous extrusion of carbon dioxide and elimination of a molecule of dimethylamine or acetic acid from the [4π + 6π] adducts **13** and **14**. The product is not the [*c*]-condensed isomer **16** because it does not show any ^{1}H NMR signals assignable to two adjacent hydrogen atoms on the condensed ring.

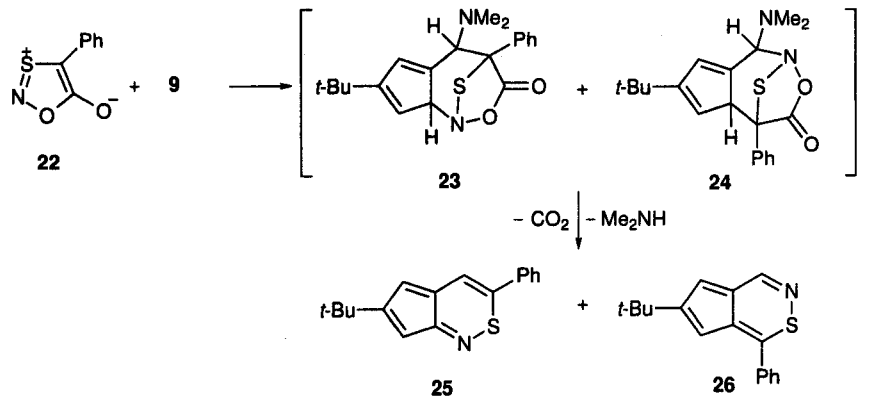


The mesoionic 2,5-diphenyl-1,3-dithiolium-4-olate **17** reacted similarly with the dimethylamino- and the acetoxy-fulvenes **9** and **11** to give the cyclopenta[*c*]thiopyrane **18** in 52 and 29% yield respectively *via* [4π + 6π] cycloadducts. The reaction of the mesoionic triphenyloxazolium-4-olate **20** with the dimethylaminofulvene **9** gave only a trace amount of the expected cyclopentapyrane **21** probably due to the instability of the oxazolium-4-olate. However, when it was generated *in situ* by treatment of *N*-benzoylphenylglyoxyanilide **19** with triethyl phosphite in the presence of the aminofulvene **9**, the diphenylcyclopenta[*c*]pyrane **21** could be isolated (18%).

The mesoionic 4-phenyl-1,3,2-oxathiazolium-5-olate **22** reacted with the dimethylaminofulvene **9** to give two products, to which cyclopenta[*c*][1,2]thiazine **25** (32%) and cyclopenta[*d*][1,2]thiazine **26** (3.5%) structures were assigned on the basis of NMR spectra. The C-4 and C-7a signals of the major [*c*]-isomer **25** appear at δ 119.1 and 170.1 while those of the minor [*d*]-isomer **26** appear at δ 135.8 and 118.5 respectively. Moreover, the signal of the H-7 of the [*d*]-isomer **26** is shifted downfield to δ 7.44 by the deshielding effect of the nearby 1-phenyl substituent. Therefore, the cycloaddition in this case proceeded less regioselectively than other reactions described above, and gave two [4π + 6π] cycloadducts **23** and **24**, from which extrusion of

carbon dioxide and elimination of dimethylamine took place to give the two final products.

All the pseudoazulenes described above are deeply colored, and their UV-VIS spectral profiles (See Experimental) are similar to that of azulene, showing the presence of some degree of intramolecular charge transfer in these molecules.



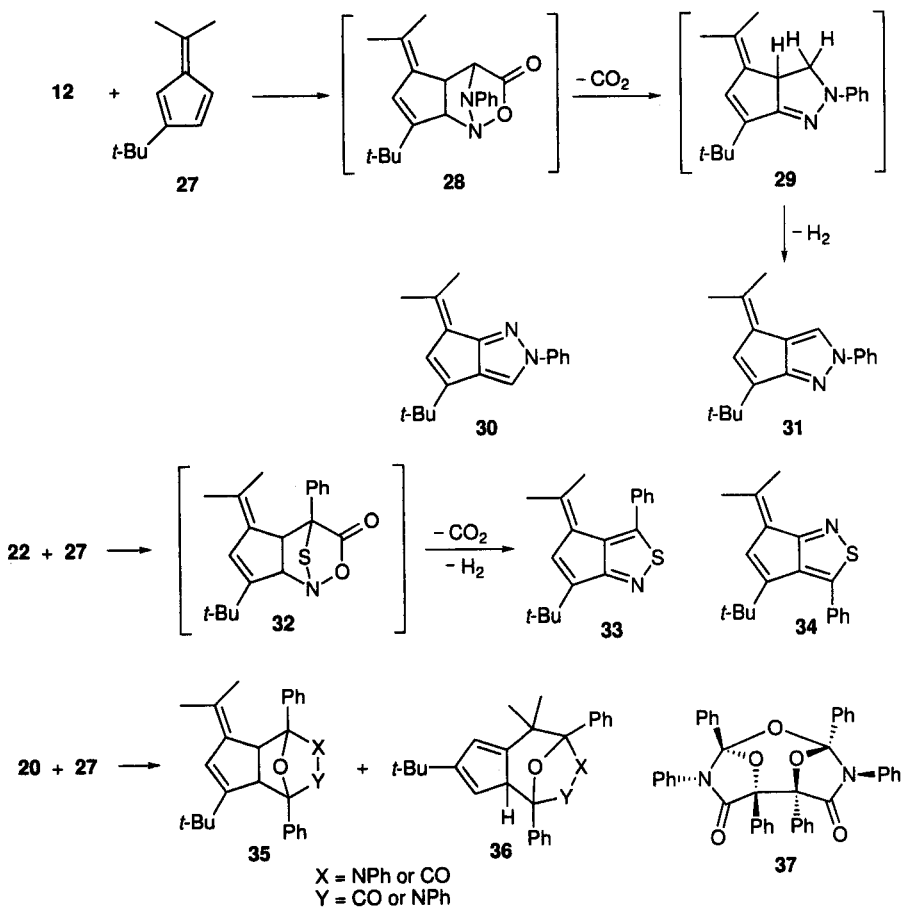
Cycloadditions with 2-tert-*butyl-6,6-dimethylfulvene*

The dimethylfulvene **27** reacted sluggishly with 3-phenylsydnone **12**. After heating a toluene solution of the two components for ten days in the air, 11% of the sydnone **12** was still recovered and 21% of the dihydrocyclopenta[*c*]pyrazole **31** was formed. The possibility of the formation of other regioisomer **30** could be eliminated by NOE measurement: signal enhancements between the isopropylidene methyl protons and H-3, H-5 and between the *tert*-butyl protons and H-5 were observed but no response between the *tert*-butyl protons and H-3. Apparently, the reaction in this case proceeded in a [4π + 2π] manner, and the cycloadduct **28** underwent extrusion of carbon dioxide and spontaneous dehydrogenation to the aromatic ring. It is interesting to note that the sydnone **12** also undergoes cycloaddition with tropone in a [4π + 2π] manner.[9] When the reaction was performed under an inert gas blanket and especially after a shorter reaction time (a few days), variable amounts of another product, assumed as the 2,3,3a,4-tetrahydro derivative **29** was formed in admixture with the dihydro derivative **31**. However, attempted isolation of the tetrahydro derivative **29** was not successful due to its ready dehydrogenation to the aromatic **31**.

The mesoionic oxathiazoliumolate **22** also reacted with the dimethylfulvene **27** in a [4π + 2π] manner and gave the condensed isothiazole **33** (19%) by extrusion of carbon dioxide from the cycloadduct **32** and spontaneous dehydrogenation. The appearance of one methyl ^{1}H NMR signal at a relatively high magnetic field (δ 1.53) indicates a shielding effect from the 3-phenyl group and supports the assigned structure **33** rather than its regioisomer **34**. Indeed, MNDO calculation[15] performed on this molecule showed that the phenyl substituent is perpendicular (89°; PM3 and AM1) to the isothiazole ring, and the *syn*-methyl group lies just above the plane of the phenyl ring.

The reaction of the oxazolium-4-olate **20** with the dimethylfulvene **27** did not proceed periselectively, and gave both the [4π + 2π] and the [4π + 6π] adducts (**35**; 11% and **36**; 15%). It was not possible to spectroscopically differentiate between the two possible regioisomers and we have not been able to prepare crystals of the two cycloadducts suitable for X-ray analysis. During attempts of preparing single crystals of the ad-

ducts, a very small amount of crystals of another product separated out. X-Ray analysis showed this product to have an interesting tricyclic oxygenated dimer structure **37** (See Fig. 1 for an ORTEP representation).[16] This oxygenated dimer was not formed by passing oxygen to a solution of the oxazoliumolate **20**, but it was formed in 10% yield by intermittently introducing a small amount of air to a refluxing toluene solution of the oxazoliumolate **20**. This shows that it is formed only when a small amount of oxygen interact with a large excess of the oxazoliumolate though the mechanism of its formation has not been elucidated. ^{13}C NMR of this oxygenated dimer **37** shows 16 signals assignable to phenyl substituents while it shows six quaternary carbon signals. This shows that free rotation of two phenyl groups in this symmetrical molecule is restricted.



When the dithioliumolate **17** and the dimethylfulvene **27** was heated under reflux in toluene, an adduct (68%) was isolated, but its spectra were not compatible with a simple cycloadduct, and suggested a deep-seated rearrangement. It shows, among others, the presence of geminal hydrogen atoms on the allylic position of the molecule, and the two methyl groups are on a sp^3 carbon atom. The structure of this product was established as the bridged dithiepinone **40** by single crystal X-ray analysis (See Fig. 2 for an ORTEP representation).[17] The formation of **40** is best rationalized by assuming rearrangement of the primary [4π + 6π] cy-

cloadduct **38**. Owing to the absence of a good leaving substituent, **38** would undergo C-S bond cleavage to form a resonance-stabilized betaine intermediate **39**, whose recyclization at the 4a-position should give the final product **40**.

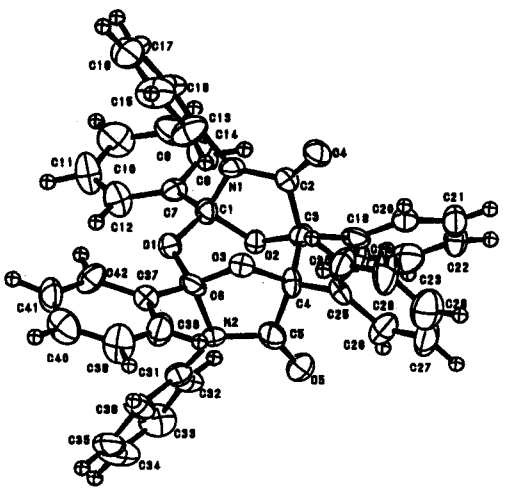


Fig. 1. ORTEP view of the oxygenated dimer **37**

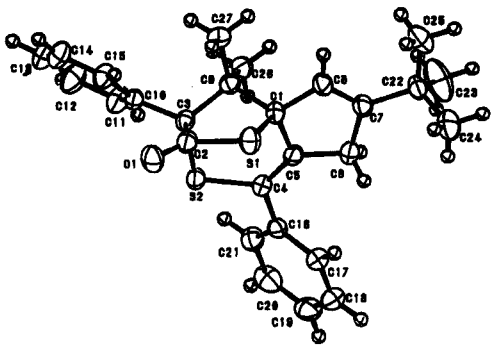
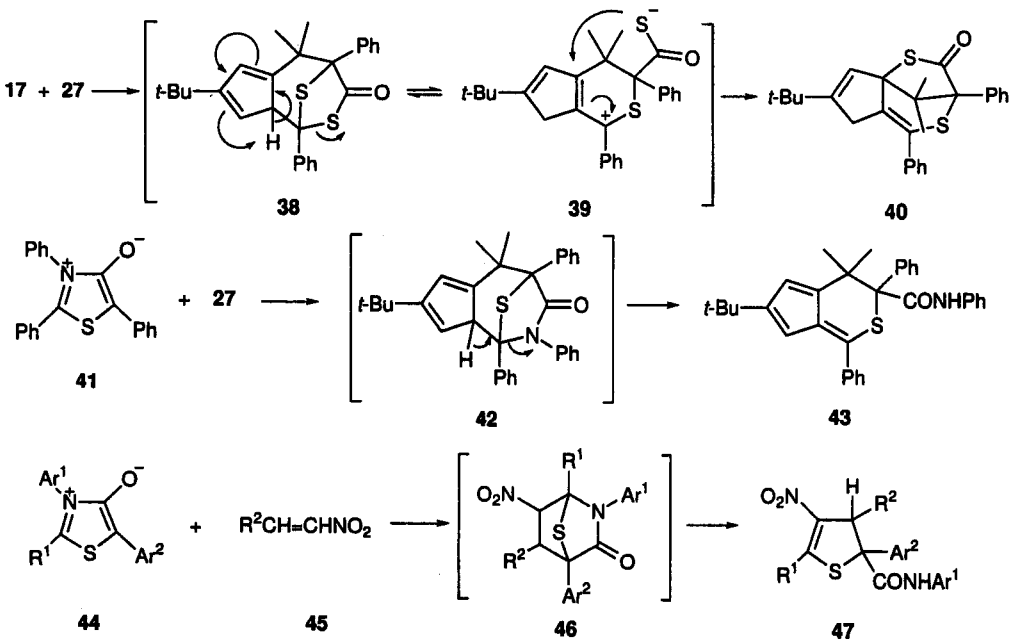


Fig. 2. ORTEP view of the methanodithiepinone **40**



A similar rearrangement of the plausible [4π + 6π] cycloadduct intermediate was observed with the reaction of the generally unreactive mesoionic triphenylthiazolium-4-olate **41** with the dimethylfulvene **27**. This

compound did not react with the aminofulvene **9**. The reaction with the dimethylfulvene **27** occurred sluggishly and required refluxing for nine days in toluene. The only product which was isolated was the dihydrothiopyranecarbanilide **43** (17%). The structural assignment is based mainly on spectral data which show the presence of an amide group, the presence of two methyl groups on a sp^3 carbon atom, and the absence of hydrogen atoms on the thiopyrane ring The product **43** should be formed by the C-N bond cleavage of the [4π + 6π] cycloadduct **42** and proton migration. Shortly after our preliminary report,[2] a report by Avalos *et al.* on similar isomerization appeared.[18] They independently found that several mesoionic thiazolium-4-olates **44** react with nitroalkenes **45** to give dihydrothiophene-2-carbanilides **47** *via* the [4π + 2π] cycloadduct **46**.

Molecular Orbital Considerations

As shown in the Table, with the exception of 6-HOMO coefficients of the fulvenes **11** and **27** and 4-HOMO coefficient of the aminofulvene **9**, PM3-MNDO calculations[15] show that the reaction centers of both the mesoionic compounds and fulvenes have sufficiently large LUMO and HOMO coefficients. In contrast, the NLUMO and NHOMO coefficients of 2- and 4(5)-positions of mesoionic compounds are very small (0.00–0.05 and 0.01–0.18 respectively). In the most stable conformer of the thiazolium-4-olate **41**, the plane of the 2-phenyl substituent is severely twisted from the plane of the mesoionic ring (PM3: 83°; AM1: 58°), and prohibits approach of fulvenes to the reaction centers. However, fixing of the twist angle to 30° had only a small effect on the coefficient values: the 2-LUMO coefficient is reduced from 0.63 to 0.56, but the changes on other positions were less than 0.02.

Table. MO Energies and Coefficients of Fulvenes and Mesoionic Compounds (PM3-MNDO)[a]

compound No.	9 (anti)			11 (anti)			27		
LUMO energy	−0.03			−0.68			−0.58		
HOMO energy	−8.36			−8.92			−8.90		
position	3	4	6	3	4	6	3	4	6
LUMO coefficient	0.33	−0.36	0.59	−0.33	0.35	−0.58	0.35	−0.36	0.59
HOMO coefficient	−0.28	0.04	0.30	0.28	0.50	0.13	0.24	0.48	0.18

compound No.	12		17		20		22		41	
LUMO energy	−1.52		−2.26		−1.31		−2.71		−1.54	
HOMO energy	−9.32		−8.45		−7.51		−9.11		−7.74	
position	2	4	2	5	2	5	2	4	2	5
LUMO coefficient	0.37	0.33	−0.58	−0.40	−0.48	−0.28	0.53	0.51	−0.63	−0.34
HOMO coefficient	0.60	−0.65	0.43	−0.58	−0.34	0.59	0.54	−0.46	−0.33	0.58

[a] Data for the most stable conformers are given. Other conformers and geometrical isomers gave similar values.

With the exception of the aminofulvene **9**, the signs of coefficients at the reaction centers are such that both [4π + 2π] and [4π + 6π] cycloadditions can proceed in a concerted way irrespective of whether the reactions are HOMO(mesoion)–LUMO(fulvene) or HOMO(fulvene)–LUMO(mesoion) controlled. With the aminofulvene **9**, both types of cycloadditions can proceed concertedly if the reaction is HOMO(mesoion)–LUMO(fulvene) controlled, but only [4π + 6π] cycloaddition can take place concertedly if the reaction is HOMO(fulvene)–LUMO(mesoion) controlled. These considerations would suggest that these cycloadditions generally occur in a HOMO(mesoion)–LUMO(fulvene) controlled mode. However, with a few exceptions,

the LUMO–HOMO energy gaps of these reactions generally show somewhat smaller values for HOMO-(fulvene)–LUMO(mesoion) controlled reactions. Adequate explanation could not be provided from orbital symmetry consideration why the amino- and acetoxy-fulvenes **9** and **11** invariably gave pseudoazulenes arising from [4π + 6π] cycloadducts while dimethylfulvene **27** gave both [4π + 2π] and [4π + 6π] cycloadducts.

The results presented above show that, depending on the structures of mesoionic compounds and fulvenes, quite versatile reactions showed up with regard to cycloaddition periselectivity, regioselectivity, and ensuing reactions. These studies also show that, with suitably substituted fulvenes, reactions of this type will provide a new general short route to many deeply colored condensed heterocycles which are isoelectronic with azulene. If bulky and readily removable or replaceable substituents can be introduced on the 2-position of the fulvene ring, these reactions should afford a variety of pseudoazulene derivatives. The construction of six-membered heterocycles presented above have an added novelty in that these reactions are 3 + 3 → 6 type without cleavage of dipolarophile rings. Heretofore, heterocycles with ring sizes larger than five have been generally formed from mesoionic compounds either by cleavage of dipolarophile rings or by extrusion of unit β in structure **1** from cycloadducts.

EXPERIMENTAL SECTION

Melting points were determined on a Yanagimoto hot stage and are not corrected. IR (KBr disk) spectra were measured on a Hitachi 345 or a JEOL Diamond-20 and UV-VIS on a Shimadzu UV-260 spectrophotometer. NMR Spectra were recorded mainly with a JEOL JNM-FX-90Q (90 MHz) spectrometer on solutions in deuteriochloroform (tetramethylsilane internal standard). NOE, 2D-NMR, and a few 1D-NMR spectra were measured on a JEOL LA-400 (400 MHz) spectrometer. Mass spectra (EI) were measured with a Shimadzu GCMS-QP1000EX spectrometer. X-Ray single crystal analyses were performed on a Rigaku AFCS5S diffractometer with graphite monochromated Mo Kα radiation and a 12KW rotating anode generator. Elemental analyses were performed with a Perkin-Elmer Model 240. Chromatographic separations were performed on Merck Kieselgel 60 (column) or Merck Kieselgel 60 PF_{254} (TLC). Yamazen preparative medium pressure liquid chromatography was used for preparative liquid chromatography. All solvents were purified and dried by usual methods, and the reactions with mesoionic compounds were performed under an inert atmosphere. Yields are based on isolated products with sufficient purity.

2-*tert*-Butyl-6-(dimethylamino)fulvene (9). *N,N*-Dimethylaminomethoxymethylium sulfate[13] prepared from dimethylformamide (7.7 ml, 0.1 mol) was added to a stirred and cooled suspension of sodium *tert*-butylcyclopentadienide prepared from 2-*tert*-butylcyclopentadiene[19] (12.2 g, 0.1 mol) in tetrahydrofuran (THF) (70 ml). After 2 h at room temperature, the mixture was filtered, diluted with water, and extracted with dichloromethane. The extract was washed with brine, dried (Na_2SO_4), concentrated, and the residue was triturated with cyclohexane, and the solid which separated out was distilled (b.p. 116–119 °C/1 torr) to give *ca.* 1 : 1 mixture of *Z*- and *E*-isomers of the aminofulvene **9** (6.93g, 39%), m.p. 42–45 °C (lit[12] 44–45 °C). ^{1}H NMR: essentially the same as the reported values.

6-Acetoxy-2-*tert*-butylfulvene (11). Ethyl formate (16.2 ml, 0.2 mol) was added to a cooled and

stirred suspension of sodium *tert*-butylcyclopentadienide prepared from *tert*-butylcyclopentadiene (12.2 g, 0.1 mol) and sodium hydride (*0.21* mol) in THF (120 ml). After heating the mixture under reflux for 1 h, the mixture was cooled to −5 °C, and a solution of acetyl chloride (28.6 ml, 0.4 mol) in THF (70 ml) was added. After 3 h at room temperature, the mixture was somewhat concentrated, diluted with water, and extracted with dichloromethane. The extract was washed successively with aq. sodium hydrogen carbonate and brine, dried, and concentrated. The solid which formed on cooling was recrystallized from hexane to give the acetoxyfulvene **11** (8.56 g, 45%) as yellow needles, m.p. 68 °C. IR 1780, 1770 (C=O), 1660, 1190, 895 cm^{-1}; ^1H NMR δ 1.20 (9H, s, *t*-Bu), 2.28 (3H, s, Me), 6.22 (1H, m, H-1), 6.34 (1H, dd, J = 5.4, 2.0 Hz, H-3), 6.50 (1H, dd, J = 5.4, 1.8 Hz, H-4), 7.75 (1H, br s, H-6); ^{13}C NMR δ 20.6 (q, Me), 29.5 (q, *t*-Bu), 32.4 (s, *t*-Bu), 108.7 (d), 124.7 (d), 130.3 (s, C-5), 131.3 (d), 136.8 (d, C-6), 159.2 (s, C-2), 167.1 (s, C=O); MS *m/z* (rel. int.) 192 (13, M^+), 150 (32, M − CH_2CO), 135 (100, M − *t*-Bu), 107 (30), 91 (28); *Anal.* Calcd. For $C_{12}H_{16}O_2$: C, 74.97; H, 8.39%. Found: C, 74.81; H, 8.50%.

6-*tert*-Butyl-2-phenyl-2*H*-cyclopenta[*d*]pyridazine (15). *From the Aminofulvene 9.* A solution of the sydnone **12**[20] (0.81 g, 5 mmol) and the aminofulvene **9** (0.89 g, 5 mmol) in xylene (25 ml) was heated under reflux for 21 h. The reaction mixture was concentrated, triturated with methanol, and the solid was recrystallized from methanol to give the cyclopentapyridazine **15** as yellow needles (0.39 g, 31%), m.p. 167 °C. UV λ_{max} (EtOH) (log ε) 210 (4.21), 216 (4.22), 222 (4.24), 259 (4.56), 291 (4.53), 320 (4.03), 307 nm (3.62); IR 1585, 1495, 1355, 1210, 765 cm^{-1}; ^1H NMR δ 1.42 (9H, s, *t*-Bu), 6.81 (2H, s, H-5,7), 7.38–7.72 (5H, m, Ph), 8.71 (1H, d, J = 1.8 Hz, H-4), 8.75 (1H, d, J = 1.8Hz, H-1); ^{13}C NMR δ 31.9 (q, *t*-Bu), 33.3 (s, *t*-Bu), 104.5 and 105.6 (d, C-5, 7), 120.9 (s, C-7a), 122.3 (d, C-1), 124.6 (s, C-4a), 127.5 (d, Ph), 129.6 (d, Ph), 130.3 (d, Ph), 140.3 (d, C-4), 145.9 (s, Ph), 161.6 (s, C-6); MS *m/z* (rel. int.) 250, (45, M^+), 235 (100, M − Me), 77 (27, Ph); *Anal.* Calcd. For $C_{17}H_{18}N_2$: C, 81.56; H, 7.25; N, 11.19%. Found: C, 81.87; H, 7.41; N, 11.45%.

From the acetoxyfulvene 11. A solution of the sydnone **12** (1.62 g, 10 mmol) and the acetoxyfulvene **11** (1.92 g, 10 mmol) in toluene (80 ml) was refluxed for 27 h. Similar work-up gave the cyclopentapyridazine **15** (1.17 g, 47%).

6-*tert*-Butyl-1,3-diphenyl-2*H*-cyclopenta[*c*]thiopyrane (18). *From the Aminofulvene 9.* A solution of the dithioliumolate **17**[21] (1.0 g, 3.7 mmol) and the aminofulvene **9** (1.0 g, 5.7 mmol) in toluene (10 ml) was refluxed for 1 h. The mixture was concentrated and the residue was separated on a silica-gel column (benzene) to give the cyclopentathiopyrane **18** (0.66 g, 52%), red plates (from methanol), m.p. 122–123 °C. UV λ_{max} (CH_2Cl_2) (log ε) 225 (4.33), 245 (4.34), 279 (4.57), 305 (4.47), 372 (3.98), 478 nm (3.24); IR 1580, 1515, 1360, 1230, 755 cm^{-1}; ^1H NMR δ 1.36 (9H, s, *t*-Bu), 6.59 (1H, d, J = 1.5 Hz, H-5), 6.99 (1H, d, J = 1,5 Hz, H-7), 7.33–7.82 (10H, m, Ph), 8.02 (1H, br s, H-4); ^{13}C NMR δ 31.3 (q, *t*-Bu), 33.2 (s, *t*-Bu), 104.9 and 115.9 (d, C-5, 7), 120.8 (d, C-4), 128.0, 128.8, 129.1, 129.3, 129.9, 130.2, 131.9, 132.2, 133.1, 137.1, 138.3, 144.5, 162.2 (s, C-6); MS *m/z* (rel. int.) 342 (94, M^+), 327 (100, M − Me), 300 (13, M − C_3H_6), 286 (14, M − C_4H_8), 121 (12, PhCS), 69 (29, *t*-BuC), 57 (15, *t*-Bu); *Anal.* Calcd. For $C_{24}H_{22}S$: C, 84.17; H, 6.47%. Found: C, 84.20; H, 6.36%.

From the acetoxyfulvene 11. A solution of the dithioliumolate **17** (0.54 g, 2 mmol) and the acetoxyfulvene **11** (0.39 g, 2 mmol) in toluene (25 ml) was refluxed for 6 h. Similar work-up gave the cyclopen-

tathiopyrane **18** (0.2 g, 29%).

6-*tert*-Butyl-1,3-diphenyl-2*H*-cyclopenta[*c*]pyrane (21). A solution of *N*-benzoylphenylglyoxyanilide **19**[8,22] (2.47 g, 7.5 mmol), the aminofulvene **9** (0.89 g, 5 mmol), and triethyl phosphite (2.49 g, 15 mmol) in toluene (50 ml) was refluxed for 5 h. The products were separated on a silica-gel column (hexane) to give the cyclopentapyrane **21** (0.29 g, 18%), red needles (from methanol), m.p. 100 °C. UV λ_{max} (EtOH) (log ε) 206 (4.46), 228 (4.24), 235 (2.23), 299 (4.45), 361 (4.09), 455 nm (3.13); IR 1610, 1481, 1373, 1248, 854, 790 cm^{-1}; ^1H NMR δ 1.39 (9H, s, *t*-Bu), 6.60 (1H, d, *J* = 1.3, H-7), 6.73 (1H, br s, H-5), 7.50 (1H, br s, H-4), 7.35-7.57 (6H, m, Ph), 7.81-8.15 (4H, m, Ph); ^{13}C NMR δ 31.2 (q, *t*-Bu), 33.3 (s, *t*-Bu), 104.2 and 104.4 (d, C-5, 7), 109.6 (d, C-4), 121.8, 124.6, 128.2, 128.9, 129.8, 130.1, 134.4, 147.5 and 158.0 (s, C-1, 3), 163.7 (s, C-6); MS *m z* (rel. int.) 326 (36, M^+), 311 (32, M – Me), 149 (33), 77 (14, Ph), 73 (47), 57 (66, *t*-Bu), 43 (100, C_3H_7); *Anal.* Calcd. For $C_{24}H_{22}O$: C, 88.31; H, 6.79%. Found: C, 88.41; H, 6.66%.

Reaction of 4-phenyl-1,3,2-oxathiazolium-5-olate 22 with the 6-(dimethylamino)fulvene 9. A solution of the oxathiazoliumolate **22**[23] (3 g, 17 mmol) and the aminofulvene **9** (2.5 g, 14 mmol) in benzene (100 ml) was stirred overnight at room temperature. An evolution of carbon dioxide was observed during the initial 1 h of the reaction. Separation of the mixture by preparative LC (silica gel/hexane–dichloromethane, 7 : 3) and recrystallization from methanol gave 6-*tert*-butyl-3-phenylcyclopenta[*c*][1,2]thiazine (**25**) (1.21 g; 32%) and 6-*tert*-butyl-1-phenylcyclopenta[*d*][1,2]thiazine (**26**) (0.13 g; 3.5%). The [*c*]-isomer **25**: violet needles (from methanol), m.p. 67 °C; UV λ_{max} (CH_2Cl_2) (log ε) 205 (4.15), 216 (4.14), 270 (4.53), 309 (4.45), 382 nm (3.62); IR 1570, 1479, 1365, 1356, 800 cm^{-1}; ^1H NMR δ 1.38 (9H, s, *t*-Bu), 6.61 (1H, d, *J* = 1.5 Hz, H-5), 6.87 (1H, d, *J* = 1.5 Hz, H-7), 7.37–7.54 (5H, m, Ph), 7.93 (1H, s, H-4); ^{13}C NMR δ 30.4 (q, *t*-Bu), 33.6 (s, *t*-Bu), 105.5 and 113.8 (d, C-5, 7), 119.1 (d, C-4), 119.7 (s, C-4a), 126.7 (d, Ph), 128.8 (d, Ph), 129.3 (d, Ph), 135.7 (s, Ph), 141.4 (s, C-3), 163.1 (s, C-6), 170.1 (s, C-7a); MS *m z* (rel. int.) 267 (74, M^+), 253 (32), 252 (100, M – Me), 225 (24, M – Me – CH_2N), 121 (18, PhCS), 112 (24), 77 (13, Ph), 57 (13, *t*-Bu), 51 (16); *Anal.* Calcd. For $C_{17}H_{17}NS$: C, 76.36; H, 6.41; N, 5.24%. Found: C, 76.31; H, 6.58; N, 5.16%. The [*d*]-isomer **26**: bluish violet needles (from methanol), m.p. 65–66 °C; UV λ_{max} (CH_2Cl_2) (log ε) 213 (4.71), 264 (4.36), 304 (4.26), 380 (3.66), 549 nm (3.09); IR 1485, 1460, 1362, 876, 773 cm^{-1}; ^1H NMR δ 1.49 (9H, s, *t*-Bu), 6.70 (1H, d, *J* = 3.0 Hz, H-5), 7.44 (1H, d, *J* = 3.0 Hz, H-7), 7.37–7.54 (5H, m, Ph), 7.91 (1H, s, H-4); ^{13}C NMR δ 30.8 (q, *t*-Bu), 32.9 (s, *t*-Bu), 113.4 (d, C-7), 118.5 (s, C-7a), 120.2 (d, C-5), 126.9 (d, Ph), 128.7 (d, Ph), 129.3 (d, Ph), 134.6 (s, C-4a), 135.8 (d, C-4), 136.2 (s, Ph), 138.6 (s, C-1), 161.5 (s, C-6); MS *m z* (rel. int.) 267 (20, M^+), 253 (18), 252 (100, M – Me), 121 (7, PhCS), 77 (6, Ph); HRMS Calcd. 267.1082. Found 267.1075; *Anal.* Calcd. For $C_{17}H_{17}NS$: C, 76.36; H, 6.41; N, 5.24%. Found: C, 76.37; H, 6.28; N, 4.97%.

6-*tert*-Butyl-4-isopropylidene-2,4-dihydro-2-phenylcyclopenta[*c*]pyrazole (31). A solution of the sydnone **12** (3.2 g, 20 mmol) and the dimethylfulvene **27**[24] (3.2 g, 20 mmol) in toluene (110 ml) was refluxed for 10 d without inert gas blanket. Unreacted sydnone **12** (0.9 g, 11%) was filtered off after addition of hexane, and the filtrate was separated on a silica-gel column (hexane–ethyl acetate, 1 : 1) to give the cyclopenta[*c*]pyrazole **31** (1.16 g, 21%; 29% based on consumed **12**), yellow needles (from hexane), m.p. 113–114 °C. UV λ_{max} (CH_2Cl_2) (log ε) 219 (4.10), 228 (4.14), 276 nm (4.67); IR 1590, 1375, 1220, 950, 745

cm^{-1}; ^1H NMR δ 1.47 (9H, s, *t*-Bu), 2.15 (3H, s, Me), 2.19 (3H, s, Me), 6.52 (1H, s, H-5), 7.25 (1H, t, J = 7.5 Hz, Ph), 7.45 (2H, t, J = 7.5 Hz, Ph), 7.76 (2H, m, Ph), 7.77 (1H, s, H-3); ^{13}C NMR δ 21.3 (q, Me), 23.6 (q, Me), 29.4 (q, *t*-Bu), 32.8 (s, *t*-Bu), 118.5 (d, C-5), 118.9 (d), 123.4 (s), 124.7 (d), 125.3 (d), 128.5 (s), 129.2 (d), 135.5 (s), 142.2 (s), 146.7 (s, C-6), 162.4 (s, C-6a); MS *m/z* (rel. int.) 278 (34, M^+), 263 (100, M – Me), 248 (M – 2Me), 77 (14, Ph); *Anal.* Calcd. For $C_{19}H_{22}N_2$: C, 81.97; H, 7.96; N, 10.06%. Found: C, 81.67; H, 8.01; N, 10.16%. When the reaction was performed under nitrogen, especially when the reaction time was shorter, the presence of variable amounts of the 2,3,3a,4-tetrahydro derivative **29** was suggested by NMR. However, it could not be isolated pure due to dehydrogenation during attempts of purification. ^1H NMR of the tetrahydrocyclopentapyrazole **29**: δ 1.32 (9H, s, *t*-Bu), 1.83 (6H, s, Me), 3.02 (1H, dd J = 7.7, 14.0, 3a-H), 3.83, (1H, br t, J = 14.0, H-3), 4.28 (1H, dd, J = 7.7, 9.0, H-3), 6.65 (1H, s, H-5), 6.80–7.81 (m, Ph).

6-*tert*-Butyl-4-isopropylidene-3-phenyl-4*H*-cyclopenta[*c*]isothiazole (33). A solution of the mesoionic oxathiazoliumolate **22** (2.68 g, 15 mmol) and the dimethylfulvene **27** (1.62 g, 10 mmol) in toluene (70 ml) was stirred for 3 d at room temperature. The mixture was chromatographed over a silica-gel column to give the product **33** (0.55 g, 19%), needles (from ethanol), m.p. 145–146 °C. UV λ_{max} (CH_2Cl_2) (log ε) 222 (4.27), 242 (4.37), 266 nm (4.47); IR 1450, 1440, 1360, 1095, 760 cm^{-1}; ^1H NMR δ 1.42 (9H, s, *t*-Bu), 1.53 (3H, s, Me), 2.05 (3H, s, Me), 6.98 (1H, s, H-5), 7.38 (5H, s, Ph); ^{13}C NMR δ 22.5 (q, Me), 25.6 (q, Me), 29.1 (q, *t*-Bu), 32.8 (s, *t*-Bu), 127.9 (s), 128.0 (d), 128.7 (d), 129.7 (d), 132.8 (d), 133.1 (d), 133.9 (s), 138.1 (s) 146.9 (s), 153.6 (s, C-6), 176.9 (s, C-6a); MS *m/z* (rel. int.) 295 (36, M^+), 280 (100, M – Me), 265 (11, M – 2Me), 250 (13, M – 3Me); *Anal.* Calcd. For $C_{19}H_{21}NS$: C, 77.24; H, 7.16; N, 4.74%. Found: C, 77.39; H, 7.27; N, 4.45%.

Reaction between the Mesoionic Oxazolium-4-olate 20 and the Dimethylfulvene 27. A solution of the mesoionic oxazolium-4-olate **20**[8,22] (0.88 g, 2.6 mmol) and the dimethylfulvene **27** (0.35 g, 2.2 mmol) in toluene (25 ml) was refluxed for 5 h. Separation of the products on a silica-gel column (benzene–dichloromethane, 1 : 1) gave the [4π + 2π] cycloadduct **35** (114 mg, 11%) and the [4π + 6π] adduct **36** (0.15 g, 15%). When the product was recrystallized very slowly from a large amount of ethyl acetate, a very small amount of the oxygenated dimer **37** separated out. 5-*tert*-Butyl-7-isopropylidene-1,2,4-triphenyl-1,4,4a,7a-tetrahydro-1,4-epoxycyclopenta[*c*]pyridin-3(1*H*)-one or the corresponding 7-*tert*-butyl-5-isopropylidene derivative (**35**): needles (from ethyl acetate), m.p. 239–242 °C. IR 1738 (C=O), 1720, 1495, 1450, 1383 cm^{-1}; ^1H NMR δ 0.94 (9H, s, *t*-Bu), 1.45 (3H, s, Me), 1.75 (3H, s, Me), 4.25 and 4.43 (each 1H, d, J = 8.1 Hz, H-4a, 7a), 6.37 (1H, s, H-6), 6.97–7.49 (13H, m, Ph), 8.05–8.19 (2H, m, Ph); ^{13}C NMR δ 21.2, (q, Me), 23.7 (q, Me), 30.7 (q, *t*-Bu), 33.9 (s, *t*-Bu), 58.4 and 60.2 (d, C-4a, 7a), 88.2 and 98.3 (s, C-1, 4), 125.8, 126.7, 127.9, 128.3, 128.9, 130.4, 133.7, 134.6, 135.1, 136.4, 154.2 (s, C-5), 170.9 (s, C=O); MS *m/z* (rel. int.) 475 (2, M^+), 313 (100, **20**), 180 (59 PhCNPh), 105 (12, PhCO), 77 (28, Ph); *Anal.* Calcd. For $C_{33}H_{33}NO_2$: C, 83.33; H, 6.99; N, 2.94%. Found: C, 83.37; H, 6.68; N, 3.22%. 7-*tert*-Butyl-5,5-dimethyl-1,3,4-triphenyl-1,4,5,8a-tetrahydro-1,4-epoxycyclopenta[*d*]azepine-2(3*H*)-one or the corresponding [*c*]azepin-3(2*H*)-one isomer (**36**): needles (from methanol), m.p. 169 °C. IR 1712 (C=O), 1596, 1353, 797 cm^{-1}; ^1H NMR δ 1.09 (9H, s, *t*-Bu), 1.16 (3H, s, Me), 1.50 (3H, s, Me), 4.02 (1H, t, J = 1,5 Hz, H-8a), 5.96 and 6.44 (each 1H, t, J = 1.5 Hz, H-6, 8), 6.68–6.80 (2H, m, N-Ph), 6.94–7.06 (3H, m, Ph), 7.34–7.48 (6H, m, Ph), 7.70–7.81 (2H, m, Ph), 7.95–8.06 (2H, m, Ph); ^{13}C NMR δ 20.9 (q, Me), 25.3 (q, Me), 29.2 (q, *t*-Bu), 32.4 (s, *t*-Bu), 43.5 (s, C-5), 57.1 (d, C-

8a), 85.6 and 97.8 (s, C-1, 4), 120.9 and 126.3 (d, C-6, 8), 127.0, 127.2, 127.3, 127.6, 127.9, 128.2, 128.4, 128.9, 129.7, 134.7, 135.8, 138.4, 154.7, 158.5 (s, C-7), 171.9 (s, C=O); MS *m/z* (rel. int.) 475 (7, M^+), 341 (12, M – Ph – Me), 313 (100, **20**), 180 (66, PhCNPh), 105 (15, PhCO), 77 (34, Ph); *Anal.* Calcd. For $C_{33}H_{33}NO_2$: C, 83.33; H, 6.99; N, 2.94%. Found: C, 83.38; H, 6.71; N, 3.11%.

1,3,4,6,7,9-Hexaphenyl-2,10,11-trioxa-4,9-diazatricyclo[5.2.1.1^{3,6}]undecane-5,8-dione (37). A solution of the oxazoliumolate **20** (0.5 g) in deaerated toluene (25 ml) was heated under reflux for 5 h under argon. During the reflux, ten batches of air (4 ml each) was intermittently introduced to the argon atmosphere through a syringe. The solution was concentrated and the residue was recrystallized from ethyl acetate to give the oxygenated dimer **37** (50 mg, 9.8%), prisms (from ethyl acetate), m.p. 245–246 °C. IR 1737 (C=O), 1496, 1450, 1382, 950 cm^{-1}; ^1H NMR δ 7.05–7.75 (m, Ph); ^{13}C NMR δ 88.7 (s, C-6, C-7), 111.4 (s, $C-1_{,}$, C-3), 127.0, 127.2, 127.4_7, 127.5_3, 127.8, 127.9, 128.3, 128.5, 128.8, 129.3, 129.5, 130.1, 131.0, 132.3, 133.8, 136.5, 167.9 (s, C=O); quaternary ^{13}C NMR (by QUAT pulse mode) δ 88.6, 111.4, 130.9, 133.8, 136.4, 167.9; EI-MS (20 eV): *m/z* (rel. int.) 313 (51, **20**), 301 (17, **20** + O – CO), 180 (35, PhCNPh), 105 (100, PhCO), 77 (36); CI-MS *m/z* (rel. int.) 521 (46, M + H - $PhCO_2H$), 330 (38, **20** + O + H), 314 (31, **20** + H), 198 (89, PhCONHPh + H), 123 (24, $PhCO_2H$ + H), 105 (100, PhCO); FAB-MS *m/z* 643 (M + H); *Anal.* Calcd. For $C_{42}H_{30}N_2O_5$: C, 78.49; H, 4.70; N, 4.36%. Found: C, 78.17; H, 4.74; N, 4.22%. See note 16 for a summary of X-Ray analysis data.

6-*tert*-Butyl-11,11-dimethyl-1,3-diphenyl-2,9-dithiatricyclo[6.2.1.0^{4,8}]undeca-3,6-dien-10-one (40). A solution of the mesoionic diphenyldithioliumolate **17** (0.54 g, 2 mmol) and the dimethylfulvene **27** (0.33 g, 2 mmol) in toluene (25 ml) was refluxed for 5 d. The mixture was concentrated, the residue was triturated with benzene, and the solid was collected to give the product **40** (0.59 g, 68%), prisms (from ethyl acetate), m.p. 253 °C. IR 1680 (C=O), 1440, 1360, 1040, 695 cm^{-1}; ^1H NMR δ 1.02 (3H, s, Me), 1.07 (9H, s, *t*-Bu), 1.14 (3H, s, Me), 3.06 and 3.58 (each 1H, dd, J = 21.2, 1.7 Hz, H-5), 5.42 (1H, t, J = 1.7 Hz, H-7), 7.31–7.54 (8H, m, Ph), 7.73–7.84 (2H, m, Ph); ^{13}C NMR δ 18.6 (q, Me), 21.4 (q, Me), 29.1 (q, *t*-Bu), 33.4 (s, *t*-Bu), 37.5 (t, C-5), 43.6 (s, C-11), 71.7 (s, C-8), 73.4 (s, C-1), 117.7 (d, C-7), 127.4, 127.8, 128.5, 128.7, 130.3, 132.5, 133.6, 137.2, 159.5 (s, C-6), 198.5 (s, C=O); MS *m/z* (rel. int.) 432 (M^+), 372 (8, M – SCO), 357 (100, M – SCO – Me), 301 (24, M – SCO – Me – *t*-Bu); *Anal.* Calcd. For $C_{27}H_{28}OS_2$: C, 74.96; H, 6.52%. Found: C, 74.76; H, 6.56%. See note 17 for a summary of X-Ray analysis data.

(6-*tert*-Butyl-4,4-dimethyl-1,3-diphenyl-3,4-dihydrocyclopenta[*c*]thiopyran-3-yl)carbanilide (43). A solution of the thiazolium-4-olate **41**[25] (2 g, 6 mmol) and the dimethylfulvene **27** (1.96 g, 12 mmol) in toluene (60 ml) was refluxed for 9 d. The mixture was separated on a silica-gel column (benzene) to give the product **43** (0.49 g, 17%), reddish orange prisms (from methanol), m.p. 153–154 °C. UV λ_{max} (CH_2Cl_2) (log ε) 223, (4.39), 247 (4.45), 348 nm (4.21); IR 3340 (NH), 1675 (C=O), 1515, 1440, 760, 690 cm^{-1}; ^1H NMR δ 1.18 (9H, s, *t*-Bu), 1.32 (3H, s, Me), 1.55 (3H, s, Me), 5.70 and 6.45 (each 1H, d, J = 1.8 Hz, H-5, 7), 7.06–7.72 (m, 15H, Ph), 8.57 (1H, br s, NH); ^{13}C NMR δ 22.6 (q, Me), 28.6 (q, Me), 29.8 (q, *t*-Bu), 32.3 (s, *t*-Bu), 39.5 (s, C-4), 72.2 (s, C-3), 118.8 and 119.9 (d, C-5, 7), 124.2, 125.0, 127.7, 128.4, 128.9, 129.7, 130.0, 135.6, 136.5, 136.9, 138.2, 140.8, 142.7, 156.1 (s, C-6), 169.5 (s, C=O); MS *m/z* (rel. int.) 491 (43, M^+), 458 (100, M – S), 434 (40, M – *t*-Bu), 371 (36, M – Ph – PhNHCO), 357 (28, M – 2Ph), 315 (M– PhNHCO – *t*-Bu), 121 (27, PhCS); *Anal.* Calcd. For $C_{33}H_{33}NOS$: C, 80.61; H, 6.76; N, 2.85%. Found: C, 80.72; H, 6.68;

N, 2.62%.

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15. These results were calculated with precise option by "Pasocon MOPAC/386" which is based on the MOPAC (Ver. 6.0, QCPE No. 455), of Toray System Center.
16. *Crystal data* for the oxygenated dimer **37**: $C_{42}H_{30}N_2O_5$, M_w = 432.6, Monoclinic, P_{bca}, a = 120.384(4), b = 18.084(5), c = 17.642(8) Å, V = 6503(6) Å^3, T = 293 K, D_c = 1.313 g cm^{-3}, $F(000)$ = 2688, R = 0.060, R_w = 0.067, GOOF = 1.76 for 1707 data [$F > 3.00\ \sigma(F)$]. Atomic coordinates, bond lengths and angles, and thermal parameters will be deposited at the Cambridge Crystallographic Data Centre.
17. *Crystal data* for the dithiepinone **40**: $C_{27}H_{28}OS_2$, M_w = 432.6, Monoclinic, $P2_1/c$, a = 15.260(3), b = 9.051(3), c = 16.718(2) Å, β = 95.92(1)°, V = 2296.8(8) Å^3, T = 295 K, D_c = 1.251 g cm^{-3}, $F(000)$ = 920, R = 0.050, R_w = 0.083, GOOF = 2.54 for 3270 data [$F > 3.00\ \sigma(F)$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. Any request to the CCDC for this material should quote the full literature citation (Ref. 1) and the reference number 182/18.
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