drobromic acid. The excess acid was removed by evaporation under reduced pressure followed by heating for 12 hr under vacuum at 100°. The product consisted of light yellow, hygroscopic crystals (13.5 g, 100%): NMR [$(CD_3)_2SO$] δ 3.37 (t, 2, $J = 7$ Hz, SCH_2), 3.97 (s, 1, SH), 5.01 (t, 2, $J = 7$ Hz, CCH_2), 8.57 (m, 6, aromatic), 10.53 ppm (s, 1, aromatic).

Anal. Calcd for $C_{11}H_{12}BrNS$: C, 48.90; H, 4.48; N, 5.18. Found: C, 48.68; H, 4.36; N, 4.99.

2,3,6,10b-Tetrahydro-5*H*-thiazolo[2,3-*a*]isoquinoline (14). The cyclization of 2-(2-mercaptoethyl)isoquinolinium bromide (10 g, 37 mmol) was carried out under a nitrogen atmosphere essentially as in the cyclization of 10 (X = Cl). Worked up as usual, the residue remaining after removal of the chloroform solvent and excess triethylamine consisted of oily crystals (4.9 g, 70%), which decomposed on standing at room temperature. This substance was not analyzed, but, on spectroscopic evidence, appeared to be largely **13**: uv max ($CHCl_3$) 314, 248 nm; NMR ($CDCl_3$) δ 2.66 (t, 2, J = 6 Hz, SCH_2), 3.33 (t, 2, $J = 6$ Hz, CH_2), 5.55 (d, 1, $J = 7$ Hz, C-6 H), 5.80 (d, 1, $J = 7$ Hz, C-5 H), 6.00 (s, 1, C-10b H), 7.20 ppm (m, 4, aromatic).

The entire crude product (4.9 g) was placed in 50 ml of absolute ethanol, in which it rapidly dissolved, but after 1 min a crystalline substance began to precipitate from solution. The flask was warmed for 10 min and cooled and the product was collected, yielding 1.91 g (27% overall from mercaptan), mp 178–179°. The analytical sample was crystallized from chloroform–hexane: mp 179–180°; NMR ($CDCl_3$) δ 2.90 (br m, 8, aliphatic), 5.07 (s, 1, C-10b H), 7.20 ppm (m, 4, aromatic).

Anal. Calcd for $C_{11}H_{13}NS$: C, 69.06; H, 6.85; N, 7.32. Found: C, 69.26; H, 6.65; N, 7.33.

2-(β-Hydroxyethyl)isoquinolinium Bromide (17, X = Br). A solution containing 20 g of isoquinoline, 20 g of 2-bromoethanol, and 200 ml of acetonitrile was refluxed for 24 hr. On cooling, 26.8 g (68%) of colorless, hygroscopic plates was collected. Recrystallization from methanol–acetonitrile yielded the analytical sample, mp 154–155.5°.

Anal. Calcd for $C_{11}H_{12}BrNO$: C, 51.99; H, 4.74; N, 5.51. Found: C, 51.82; H, 4.81; N, 5.44.

The hexafluorophosphate (17, X = PF_6), mp 154–155.5°, prepared by addition of hexafluorophosphoric acid to an aqueous solution of the bromide salt (17, X = Br) was crystallized from methanol–ethyl acetate.[14]

***syn*-2,3,10,10a,12,13-Hexahydro-11*H*,5,10-[1′,2′]cyclopenta-5*H*-oxazolo[3,2-*b*]isoquinoline (21a).** To a solution of 5 g of 2-(β-hydroxyethyl)isoquinolinium hexafluorophosphate (17, X = PF_6) in 25 ml of acetonitrile, 25 ml of freshly cracked cyclopentadiene was added and the mixture was allowed to stand for 24 days. The solution was then concentrated under reduced pressure. The addition of cyclohexane caused the precipitation of 6 g of oil. To 2 g of the oil, a solution of 6 g of potassium carbonate in 20 ml of deionized water was added, and the mixture was stirred for a few hours at room temperature. The suspension was extracted with ether and the dried (potassium carbonate) solution was concentrated. The residue (1 g) was recrystallized from ethyl ether, affording 0.75 g (60%) of light pink prisms: mp 109–110°; NMR ($CDCl_3$) δ 7.14 (m, 4, aromatic H), 5.23 (s, 2, vinyl H), 4.96 (d, 1, J = 2.5 Hz, H-10a), 3.77 (d, 1, $J = 3$ Hz, H-5), 3.64–1.0 ppm (overlapping m, 9, aliphatic).

Anal. Calcd for $C_{16}H_{16}NO$: C, 80.64; H, 6.77; N, 5.88. Found: C, 80.84; H, 6.95; N, 5.75.

Registry No.—**4** (X = Br), 54423-78-8; **4** (X = BF_4), 54424-04-3; **4** (X = picrate), 54423-80-2; **5**, 54423-85-7; **6**, 54423-86-8; **7**, 54423-87-9; **8**, 54423-88-0; **9**, 54423-89-1; **10** (X = Cl), 54423-81-3; **10** (X = PF_6), 54424-06-5; **11** (X = Br), 54423-82-4; **11** (X = perchlorate), 54423-84-6; **12**, 54424-03-2; **13**, 52131-57-4; **14**, 14692-38-7; **17** (X = Br), 54423-94-8; **17** (X = PF_6), 54423-96-0; **21a**, 54460-93-4; phenanthridine, 229-87-8; ethyl 3-bromopropylmalonate, 10149-21-0; 2-(4,4-dicarboxybutyl)isoquinolinium bromide diethyl ester, 54423-97-1; 2-(4,4-dicarboxybutyl)isoquinolinium perchlorate diethyl ester, 54423-99-3; 2-(4,4-dicarboxybutyl)-3-methylisoquinolinium bromide diethyl ester, 54424-00-9; 2-(4,4-dicarboxybutyl)-3-methylisoquinolinium perchlorate diethyl ester, 54424-02-1; *S*-(2-bromoethyl)thiolacetate, 927-70-8; isoquinoline, 119-65-3; 2-(2-mercaptoethyl)isoquinolinium bromide acetate, 54423-90-4; 2-(2-mercaptoethyl)isoquinolinium perchlorate acetate, 54423-92-6; 2-(2-mercaptoethyl)isoquinolinium bromide, 54423-93-7; 2-bromoethanol, 540-51-2; cyclopentadiene, 542-92-7.

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Periselectivity of Reactions of Fulvenes with Heterodienes and Heterodienophiles[1]

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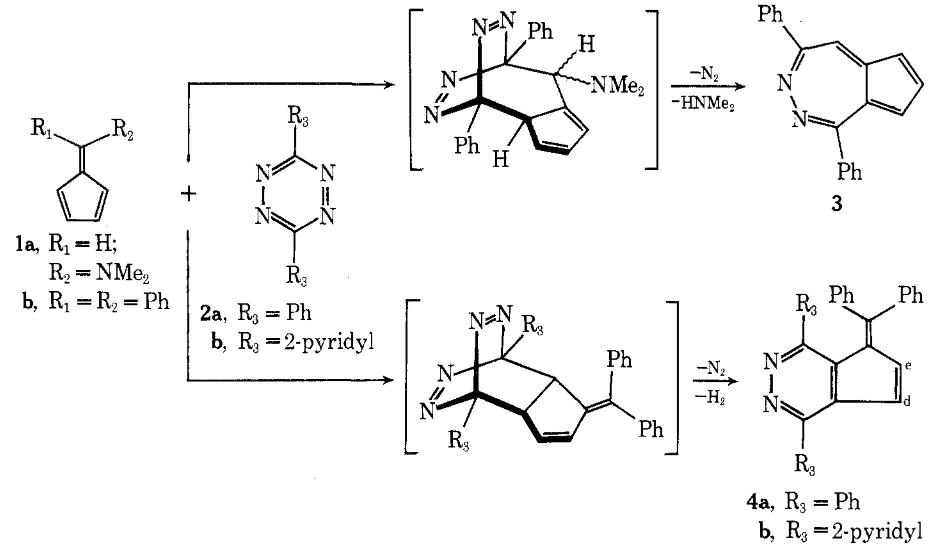
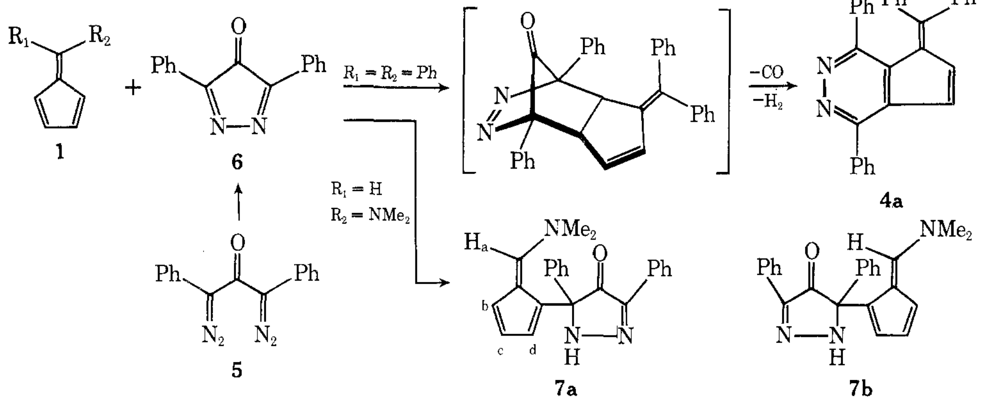
The cycloaddition reactions of 6,6-dimethylfulvene, 6,6-diphenylfulvene, and 6-dimethylaminofulvene with tetrazine, diazacyclopentadienone, and azodicarboxylate are investigated. The periselectivity observed with the tetrazine is explained using the frontier orbital model where the fulvene HOMO–olefin LUMO interaction predominates. Thus, a novel 5,6-diazaazulene was prepared by the reaction of 6-dimethylaminofulvene with the tetrazine.

Previously we reported that 6,6-diphenylfulvene reacted with tropone to afford only a [4 + 2] adduct instead of an expected [6 + 4] adduct.[2] By contrast, the reaction of 6,6-dimethylfulvene with tropone resulted in the formation of a 2:1 [6 + 4] adduct.[3] The different behavior of these fulvenes indicates sensitivity to steric and electronic requirements of substitutents at the C-6 position of the fulvene. Recently, reactivity, regioselectivity, and periselectivity in cyloaddition reactions have been explained by employing quantitative perturbation molecular orbital theory.[4] These considerations led us to further investigation of the cycloaddition reaction of substituted fulvenes.

Scheme I



Scheme II



In this paper, we report the reaction of fulvenes with electron-deficient heterodienes such as tetrazine and diazacyclopentadienone, and the heterodienophile azodicarboxylate.

Results

Reaction of 6-dimethylaminofulvene (**1a**) with 3,6-diphenyltetrazine (**2a**) in benzene at room temperature for 5 days gave a fluorescent yellow compound (**3**), $C_{20}H_{14}N_2$, in 40% yield. The uv spectrum showed a conjugated system, and resembled that of 6-dimethylamino-5,7-diazaazulene[5] as shown in Figure 1. These data indicated that the product was 4,7-diphenyl-5,6-diazaazulene, the formation of which can be rationalized via the initial [6 + 4] addition followed by loss of nitrogen and dimethylamine as shown in Scheme I.

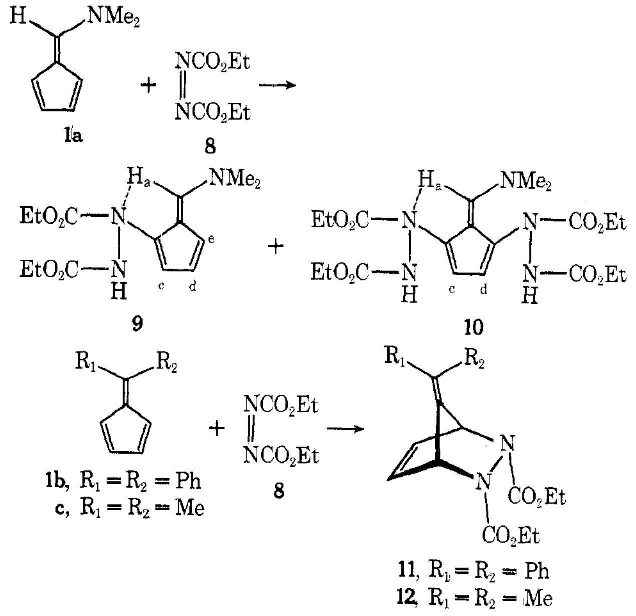
On the other hand, reaction of 6,6-diphenylfulvene (**1b**) with 3,6-diphenyltetrazine (**2a**) in benzene at 80° for 1 day gave compound **4a** in 60% yield. The NMR spectrum of **4a** showed doublets for two olefinic protons at δ 6.62 and 6.65 (J = 8.4 Hz). Presumably the formation of **4a** might proceed via the initially produced [4 + 2] adduct followed by loss of nitrogen and hydrogen as shown in Scheme I. Similar reaction of **1b** and **2b** in chloroform at room temperature for 14 hr gave **4b** in 83% yield. However, 6,6-dimethylfulvene (**1c**) reacted with **2a** or **2b** in chloroform at room temperature with evolution of nitrogen to give a mixture of several products, which decomposed during attempted separation.

Reaction of **1b** with 3,4-diaza-2,5-diphenylcyclopentadienone (**6**),[6] derived from 1,3-bisdiazo-1,3-diphenyl-2-propanone (**5**), in benzene at room temperature for 8 hr gave **4a** in 68% yield. Presumably compound **4a** was formed by initial [4 + 2] addition followed by loss of carbon monoxide and hydrogen.

Similar reaction of **1a** with **6** under the same conditions gave the 1:1 adduct (**7**) as yellow crystals in a quantitative yield. The ir spectrum of **7** showed an amino group at 3250 cm^{-1} and a ketoimino group at 1662 cm^{-1} (broad band). The NMR spectrum of **7** exhibited four olefinic protons at δ 6.85 (s, 1 H, H_a), 6.57 (dd, 1 H, H_b), 6.32 (dd, 1 H, H_c), 6.31 (t, 1 H, H_d) with coupling constants of J_{bc} = 4.4, J_{cd} = 2.5, and J_{bd} = 2.5 Hz, two N-methyl groups at δ 2.97 (s, 6 H), and aromatic and amino protons in the regions of δ 7.17–8.22 (1 H, exchangeable by D_2O). Particularly, the chemical shift of H_a (exocyclic olefin) for **7** was similar to that of **1a** (δ 6.58). These data were in accord with the proposed structure (**7a**) as depicted in Scheme II, and alternative structures such as **7b**, [4 + 2] and [6 + 4] cycloadducts could be ruled out.

Treatment of **1a** and diethyl azodicarboxylate (**8**) in benzene at room temperature for 1 day gave a mixture of **9** and **10** in 14 and 7% yields. The elemental analyses indicated that **9** and **10** consisted of 1:1 and 1:2 adducts of **1a** and **8**, respectively. The NMR spectrum of **9** showed four olefinic protons and one amino proton. Interestingly, the H_a proton suffered a downfield shift (δ 7.78) compared to those of 6-dimethylaminofulvene (δ 6.58) and compound **7** (δ 6.85). This indicated that H_a and the nitrogen of the azodicarboxylate group interacted strongly as depicted in Scheme III. The NMR spectrum of **10** showed one olefinic proton at δ 7.79 as a broad singlet, two olefinic protons at δ 6.05 as a

Scheme III



sharp singlet, and two amino protons at δ 6.80 as a singlet. These data were compatible with structures **9** and **10**, and no [4 + 2] cycloadduct was detected. By contrast, the reaction of diethyl azodicarboxylate (**8**) with 6,6-dimethylfulvene (**1c**) or 6,6-diphenylfulvene (**1b**) gave the corresponding [4 + 2] adduct **11** or **12**.[7]

Discussion

Houk et al. have recently shown that consideration of frontier orbital interactions can provide a good rationalization of reactivity, regioselectivity, and periselectivity in a variety of cycloaddition reactions,[4] and also estimated frontier orbital energies and coefficients of fulvenes[8] as shown in Figure 2.

On the other hand, it is known that ethyl azodicarboxylate (**8**), and the tetrazine **2**[9] were all electron-poor olefins. Generally, the electron-poor olefin has relatively lower LUMO (lowest unoccupied molecular orbital) and HOMO (highest occupied molecular orbital) energy levels.[4] Moreover, it is pointed out that the fulvene HOMO interaction is much more important than the fulvene LUMO interaction in the reaction of the fulvene with cyclopentadienone, cyclopentadiene, α-pyrone, and cycloheptadienone.[10] Therefore, the fulvene HOMO–heterodiene or heterodienophile LUMO interaction is expected to be more predominant than the inverse interaction of the fulvene LUMO–heterodiene or heterodienophile HOMO in the reactions of the fulvenes with the tetrazine **2**, diazacyclopentadienone (**6**), and azodicarboxylate **8**.

Since the HOMOs of 6,6-dimethylfulvene (**1c**) and 6,6-diphenylfulvene (**1b**) and the LUMO of ethyl azodicarboxylate (**8**) are also antisymmetric, the [4 + 2] cycloaddition reaction of the fulvene (4π) with ethyl azodicarboxylate (2π) is favored to give the usual Diels–Alder adduct. However, the LUMOs of the tetrazine and diazacyclopentadienone are symmetric, if considered like butadiene, and the [4 + 2] addition of the fulvene (2π) and the heterodiene (4π) should be favored.

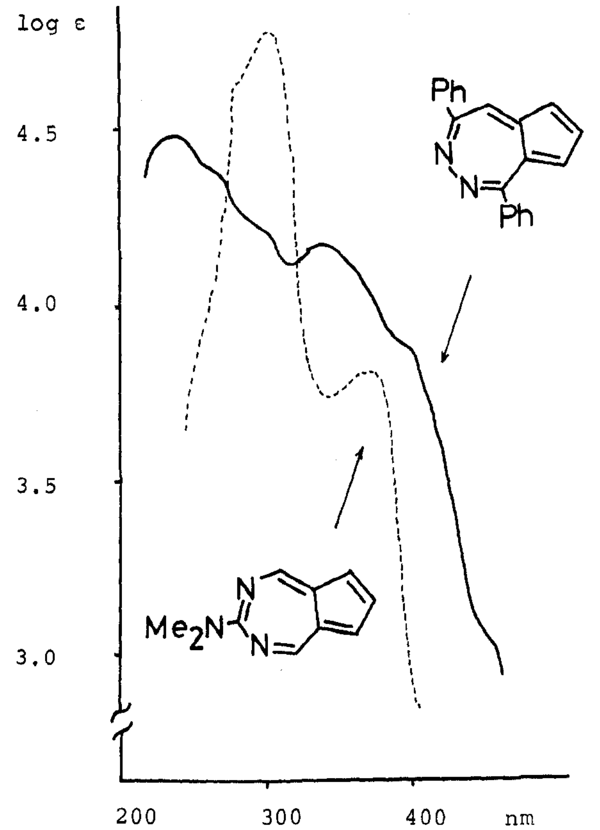


Figure 1. Uv spectra of **3** (EtOH) and 6-dimethylamino-5,7-diazaazulene (*n*-hexane).

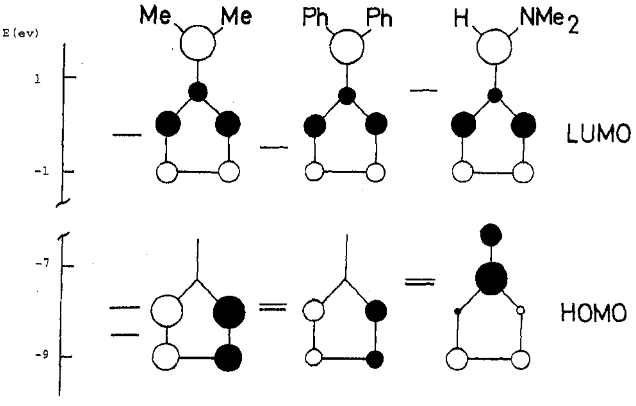
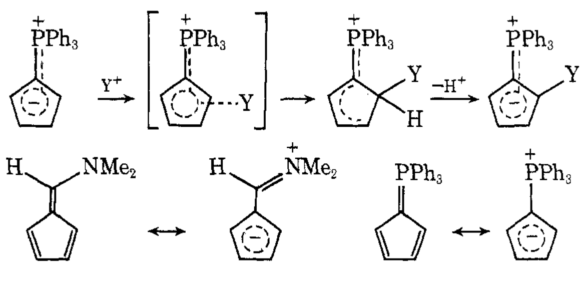


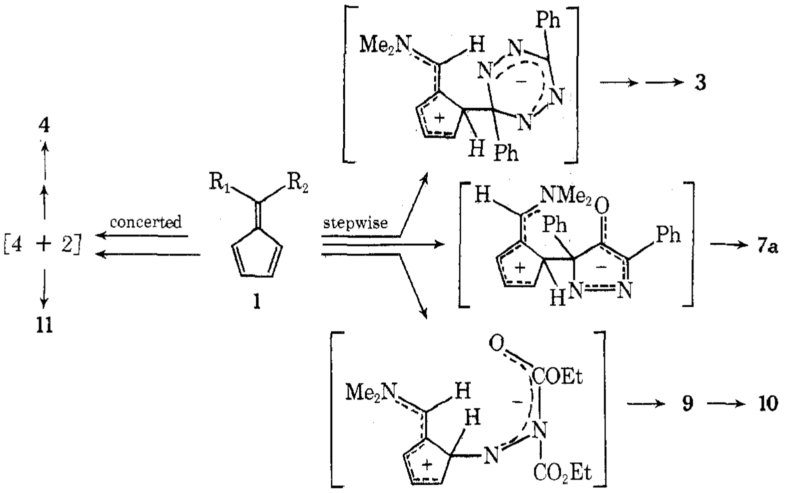
Figure 2.

On the other hand, the HOMO energy and coefficients of **1a** are very different from those of **1c** or **1b** (see Figure 2). Large coefficients at the C-6 position of the HOMO of 6-dimethylaminofulvene (**1a**) suggest that **1a** can act as a 6π component. Thus, the [6 + 4] cycloaddition of **1a** to **2a** should be favored and resulted in the formation of the 5,6-diazaazulene (**3**). Furthermore, the relatively higher HOMO energy of 6-dimethylaminofulvene than that of 6,6-dimethyl- and 6,6-diphenylfulvene indicates it to be a strong electron donor, while electron-poor olefins can become a strong electron acceptor. In this connection, Yoshida et al. reported the reaction of 6-phosphafulvene with a dienophile such as tetracyanoethylene to be a Michael-type

Scheme IV



Scheme V



substitution at the C-2 position as outlined in Scheme IV.[11] Dipole moments of 6-phosphafulvene, 6-dimethylaminofulvene (**1a**), 6,6-diphenylfulvene (**1b**), and 6,6-dimethylfulvene (**1c**) are 7.0, 4.48, 1.40, and 1.44 D, respectively.[12]

From these data, 6-dimethylaminofulvene (**1a**) might be predominant in the resonance contribution (dipolar structure) at the ground state as shown in Scheme IV. Accordingly, the reactions of 6-dimethylaminofulvene (**1a**) with electron-deficient diazacyclopentadienone (**6**), tetrazine **2**, and azodicarboxylate **8** might proceed via the dipolar intermediates by either the stepwise [6 + 4] cycloaddition or the electronphilic substitution as indicated in Scheme V.

From these results, it is concluded that the interactions between the fulvene HOMO and the heterodiene or heterodienophile LUMO are stronger than the inverse interactions between the fulvene LUMO and the olefin HOMO, and the reaction of the diene or dienophile with 6,6-dimethyl- or 6,6-diphenylfulvene might proceed in a concerted fashion. By contrast, the reaction with the strongly electron-rich 6-dimethylaminofulvene gives way to a stepwise fashion involving the zwitterionic intermediates as shown in Scheme V. However, the HOMO of dimethylaminofulvene shown in Figure 2 does not rationalize the site of reaction with electrophiles. The N HOMO is also important, and the fulvenes invariably undergo attack by electrophiles at the C-1 position. Probably charge and frontier orbital interactions are important.[8]

Experimental Section

Melting points are uncorrected. Microanalyses were performed with a Perkin-Elmer 240 elemental analyzer. Uv spectra were determined with a Jasco ORD/UV-5 spectrometer. NMR spectra were taken with a Jeol C-60-XL spectrometer and with a Varian A-60 recording spectrometer, with tetramethylsilane as internal standard. Ir spectra were taken with a Jasco Ir-S spectrophotometer. Mass spectra were obtained with a Hitachi RMU-D double-focusing spectrometer operating at an ionization potential of 70 eV. The solid samples were ionized by electron bombardment after sublimation directly into the electron beam at 100–150°.

Reaction of 6-Dimethylaminofulvene (1a) with 3,6-Diphenyltetrazine (2a). A solution of **1a** (0.15 g) and **2a** (0.29 g) in benzene (20 ml) was stirred at room temperature under argon in the dark for 5 days. Then the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using chloroform to give **3** (0.14 g, 40%): mp 289–292° (from chloroform); uv (EtOH) λ_{max} 235 nm (log ϵ 4.49), 256 (4.39), 292 (4.27), 340 (4.14), 395 (3.88), and 450 (3.06); mass spectrum *m/e* 282 (M^+); the NMR spectrum could not be obtained because of low solubility.

Anal. Calcd for $C_{20}H_{14}N_2$: C, 85.08; H, 5.00; N, 9.92. Found: C, 84.96; H, 5.16; N, 9.87.

Reaction of 6,6-Diphenylfulvene (1b) with 3,6-Diphenyltetrazine (2a). A solution of **1b** (0.62 g) and **2a** (0.75 g) in benzene (30 ml) was heated in a sealed tube at 80° for 1 day. Then the solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel) using chloroform as an eluent to give **4a** (0.7 g, 60%): mp 174–176° (from MeOH); NMR ($CDCl_3$) δ 6.62 (d, J = 8.4 Hz, 1 H, H_d or H_e), 6.65 (d, J = 8.4 Hz, H_d or H_e), 6.38–8.10 (complex m, 20 H, aromatic H); mass spectrum *m/e* 434 (M^+).

Anal. Calcd for $C_{32}H_{22}N_2$: C, 88.45; H, 5.10; N, 6.45. Found: C, 88.23; H, 5.35; N, 6.41.

Reaction of 6,6-Diphenylfulvene (1b) with 3,6-Di(2-pyridyl)tetrazine (2b). A solution of **1b** (0.3 g) and **2b** (0.3 g) in chloroform (20 ml) was stirred at room temperature for 14 hr. Then the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using chloroform to give **4b** (0.47 g, 83%): mp 198–200° (from MeOH); NMR ($CDCl_3$) δ 6.61 (d, J = 8.0 Hz, 1 H, H_d or H_e), 6.65 (d, J = 8.0 Hz, 1 H, H_d or H_e), 6.80–8.82 (complex m, 18 H, aromatic H).

Anal. Calcd for $C_{30}H_{20}N_4$: C, 82.54; H, 4.62; N, 12.84. Found: C, 82.45; H, 4.86; N, 12.68.

Reaction of 6,6-Diphenylfulvene (1b) with 3,4-Bisdiazo-2,5-diphenylcyclopentadienone (6). To a solution of **1b** (0.2 g) in benzene (15 ml) was added powdered 1,3-bisdiazo-1,3-diphenyl-2-propanone (**5**, 0.5 g), and the mixture was stirred at room temperature for 10 hr. Then the solvent was evaporated under reduced pressure and the residue was purified by silica gel chromatography using chlroform to give **4a** (0.21 g, 68%).

Reaction of 6-Dimethylaminofulvene (1a) with 3,4-Bisdiazo-2,5-diphenylcyclopentadienone (6). To a solution of **1a** (0.4 g) in benzene (30 ml) was added powdered compound **5** (0.5 g). The mixture was stirred at room temperature under argon in the dark for 8 hr. Then the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using benzene to give yellow crystals of **7** (0.58 g): mp 186–188° (from benzene); ir (KBr) 3250 (NH), 1662 cm^{-1} (N=C–C=O); NMR ($CDCl_3$) δ 2.97 (s, 6 H, NCH_3), 6.31 (t, 1 H, H_d), 6.32 (dd, 1 H, H_c), 6.57 (dd, 1 H, H_b), 6.85 (s, 1 H, H_a), 7.17–8.22 (complex m, 10 H, aromatic H); J_{bc} = 4.4, J_{cd} = 2.5, J_{bd} = 2.5 Hz.

Anal. Calcd for $C_{23}H_{21}N_3O$: C, 77.72; H, 5.96; N, 11.82. Found: C, 77.81; H, 5.85; N, 11.87.

Reaction of 6-Dimethylaminofulvene (1a) with Diethyl Azodicarboxylate (8). A solution of 6-dimethylaminofulvene (**1a**, 0.7 g) and **8** (1.0 g) in benzene (50 ml) was stirred at room temperature under argon in the dark for 1 day. Then the mixture was filtered to give **10** (0.12 g). The filtrate was evaporated under reduced pressure and the residue was purified by silica gel chromatography using benzene as an eluent to give **9** (0.24 g).

9: mp 172–173° (from EtOH); ir (KBr) 3276 (NH), 1745, 1680 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.20 (t, J = 8.0 Hz, 3 H, CH_3), 1.23 (t, J = 8.0 Hz, 3 H, CH_3), 3.21 (s, 6 H, NCH_3), 4.13 (q, J = 8.0 Hz, 2 H, CH_2), 4.17 (q, J = 8.0 Hz, 2 H, CH_2), 6.16 (dd, 1 H, H_d), 6.36 (t, 1 H, H_c), 6.45 (dd, 1 H, H_e), 7.03 (s, 1 H, NH), 7.78 (broad s, 1 H, H_a); J_{cd} = 2.6, J_{de} = 4.5, J_{ce} = 2.6 Hz.

Anal. Calcd for $C_{14}H_{21}N_3O_4$: C, 56.93; H, 7.17; N, 14.23. Found: C, 56.91; H, 6.99; N, 14.12.

10: mp 193–195° (from MeOH); ir (KBr) 3272 (NH), 1740, 1682 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.21 (t, J = 8.0 Hz, 3 H, CH_3), 1.24

(t, J = 8.0 Hz, 3 H, CH_3), 3.15 (s, 6 H, NCH_3), 4.09 (q, J = 8.0 Hz, 2 H, CH_2), 4.13 (q, J = 8.0 Hz, 2 H, CH_2), 6.05 (s, 2 H, H_c and H_d), 6.80 (s, 2 H, NH), 7.79 (broad s, 1 H, H_a).

Anal. Calcd for $C_{20}H_{31}N_5O_8$: C, 51.16; H, 6.66; N, 14.92. Found: C, 51.30; H, 6.57; N, 14.88.

Registry No.—**1a**, 696-68-4; **1b**, 2175-90-8; **2a**, 6830-78-0; **2b**, 1671-87-0; **3**, 54384-98-4; **4a**, 54384-99-5; **4b**, 54385-00-1; **6**, 32683-51-5; **7a**, 54385-01-2; **8**, 1972-28-7; **9**, 54385-02-3; **10**, 54385-03-4.

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The Oxetane Function Spiro to Polyoxaaza Macroheterocycles

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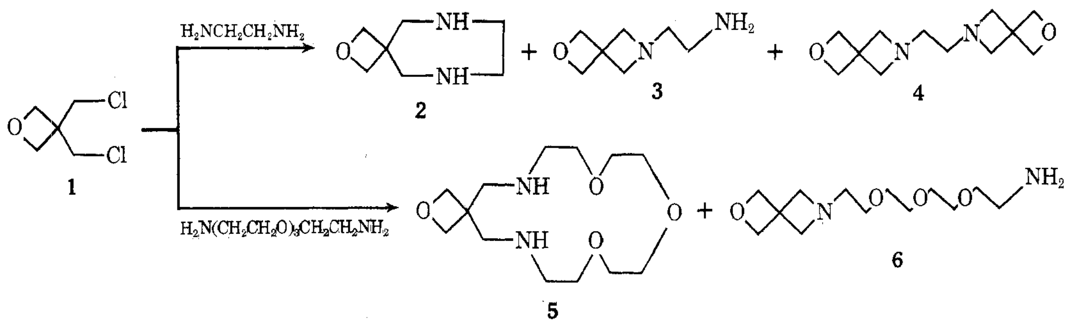
Base-induced condensation of oxaazadiols with 3,3-bis(chloromethyl)oxetane gives macrocyclic aza polyethers bearing one or two spirooxetane rings. Thermolysis of appropriately constituted oxaaza macrocycles is shown to give novel polycyclic structures, as does condensation with bis(acid chloride). Ring closure of α,ω-diamines with 3,3-bis(chloromethyl)oxetane leads to polyoxaaza macrocycles in low yield.

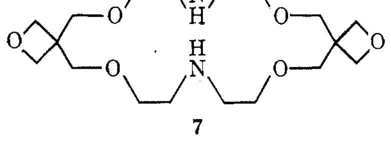
The previous paper[1] in this series described the one-step synthesis of macrocyclic polyethers and polysulfides bearing one or two spirooxetane substituents. This paper presents syntheses of a number of related polyoxaaza macrocycles and some chemistry of the imine group in such rings.

Synthesis from α,ω-Diamines. Alkylation of α,ω-diamines with dihalides does not usually lead to good yields of diaza macrocycles,[2] and reaction of 3,3-bis(chloromethyl)oxetane (**1**) with primary α,ω-diamines has been found to give several types of products. Ethylenediamine with **1** gave volatile products resulting from monoalkylation of both nitrogen atoms (i.e., **2**) and from dialkylation (i.e., **3** and **4**) along with low polymers. A similar result was observed starting from **1** and 3,6,9-trioxaundecane-1,11-diamine, since both macrocycle **5** and azetidine **6** were formed. The distillation cut which contained **5** and **6** in roughly equal amounts was separated by taking advantage of the superior ability of **5** to form complexes. The crystalline complex, **5** · NaSCN, was precipitated while **6** remained in solution.



Synthesis from α,ω-Diols. Three α,ω-diols having aza nitrogen were condensed with **1** or with 3,3-bis(bromomethyl)oxetane. Attempts to selectively benzoylate the amine function in these diols under mild conditions gave little derivatization, a result indicative of rather low nucleophilicity of the amine centers. The condensations were therefore carried out with the dipotassium salts of the diols containing unmasked imine groups. Alkylation on nitrogen appeared to be a minor side reaction, and the results are roughly comparable to those obtained with the polyethylene glycols.[1]

In the presence of 2 equiv of potassium *tert*-butoxide and in *tert*-butyl alcohol as solvent, diethanolamine condensed with **1** to give dispiro macrocycle **7** in 17% yield along with 1% of N-alkylated product (**8**). The effect of nitrogen in the macrocyclic polyether on complex formation is indicated by the fact that **7** readily displaced water from cupric acetate hydrate to form **7** · $Cu(OAc)_2$.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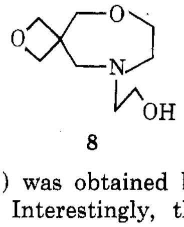
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3,9-Dioxa-6-azaundecane-1,11-diol (**9**) was obtained by the following sequence of reactions. Interestingly, the three-stranded compound **10** was the only acyclic polyether encountered in this study which gave a crystalline complex, namely **10** · NaSCN.