extracted three times with chloroform. The extract was combined with the original organic phase and concentrated in vacuo. The solid residue was sublimed (40 °C (0.5 Torr)) to give (−)-trishomocubanone, **1a** (98 mg, 81%), of good purity: mp 162–163 °C; α^{20}_D −1.211 ± 0.002°; $[\alpha]^{20}_D$ −98.8°; CD (*c* 0.0355, cyclohexane) [θ] 0 (340), +6.58 × 10^3 (293), 0 (240 nm); lit.[4] mp 159 °C, $[\alpha]^{20}_D$ −99.1°.

A similar procedure produced the enantiomeric ketone **1b**: mp 162–163 °C; α^{20}_D +0.355 ± 0.002°; $[\alpha]^{20}_D$ +98.8°; CD (C 0.0298, cyclohexane) [θ] 0 (330), −6.48 × 10^3 (293), 0 (240 nm).

(−)- and (+)-(D_3)-Trishomocubane. A mixture of resolved ketone **1a** (60 mg), hydrazine hydrate (85%, 1 mL), and triethylene glycol (2.5 mL) was refluxed for 10 min and then cooled. Potassium hydroxide pellets (200 mg) were added, and the mixture was heated vigorously. The clear distillate was collected until the pot residue charred. The distillate was extracted thoroughly with pentane. The extract was washed with dilute hydrochloric acid, followed by water, and then dried. The solvent was blown off in a slow stream of nitrogen. The white residue was sublimed (25 °C (80 Torr)) to give (−)-(D_3)-trishomocubane (**3a**, 48 mg, 88%): mp 148–149 °C; α^{20}_D −0.694 ± 0.002°; $[\alpha]^{20}_D$ −162°; lit.[4] mp 149 °C, $[\alpha]^{20}_D$ −164°.

Similarly, (+)-(D_3)-trishomocubane (**3b**) was obtained: mp 148–149 °C; α^{20}_D +0.571 ± 0.002°; $[\alpha]^{20}_D$ +162°.

Acknowledgments. The research programs of the principal investigator are supported financially by the National Science Foundation (MPS-75-04123) and the National Cancer Institute (PHS-CA-12961). Funds for the purchase of the NMR instruments essential to our work were provided, in part, by the National Cancer Institute (PHS-CA-14599) via The University of Chicago Cancer Research Center and by the National Science Foundation. We are grateful for this support.

Registry No.—**1a**, 61473-76-5; **1b**, 61473-82-3; **2a**, 65957-38-2; **2b**, 66007-13-4; **3a**, 61473-77-6; **3b**, 61473-83-4; (±)-trishomocubanone, 66007-14-5; *l*-ephedrine, 299-42-3.

References and Notes

(1) (a) G. R. Underwood and B. Ramamoorthy, *Tetrahedron Lett.*, 4125 (1970); (b) S. A. Godleski, P. v. R. Schleyer, E. Osawa, and G. J. Kent, *Chem. Commun.*, 976 (1974); (c) P. E. Eaton, R. A. Hudson, and C. Giordano, *Ibid.*, 978 (1974).
(2) G. J. Kent, S. A. Godleski, E. Ōsawa, and P. v. R. Schleyer, *J. Org. Chem.*, **42**, 3852 (1977).
(3) To our knowledge, only two examples of rigid organic systems of this symmetry are known besides (D_3)-trishomocubane: M. Farina and C. Morandi, *Tetrahedron*, **30**, 1819 (1974); R. K. Hill and D. W. Ladner, *Tetrahedron Lett.*, 989 (1975).
(4) G. Helmchen and G. Staiger, *Angew. Chem., Int. Ed. Engl.*, **16**, 116 (1977); M. Nakazaki, K. Naemura, and N. Arashiba, *J. Org. Chem.*, **43**, 689 (1978). Note that the latter has a misprint in the text which reverses the assignment given in the Experimental Section and in Table I.
(5) For example, M. Nakazaki, K. Naemura, and Y. Kondo, *J. Org. Chem.*, **41**, 1229 (1976); M. Nakazaki, K. Naemura, and H. Kadowaki, *Ibid.*, **41**, 3725 (1976).
(6) G. Snatzke and F. Werner-Zamojska, *Tetrahedron Lett.*, 4275 (1972).
(7) C. Djerassi and W. Klyne, *Proc. Natl. Acad. Sci. U.S.A.*, **48**, 1093 (1962).

Cyclophanes. 9. Dibenzo[*def,pqr*]tetraphenylene: A Benzoannulated Cyclooctatetraene Composed of Orthogonal Aromatic Systems[1]

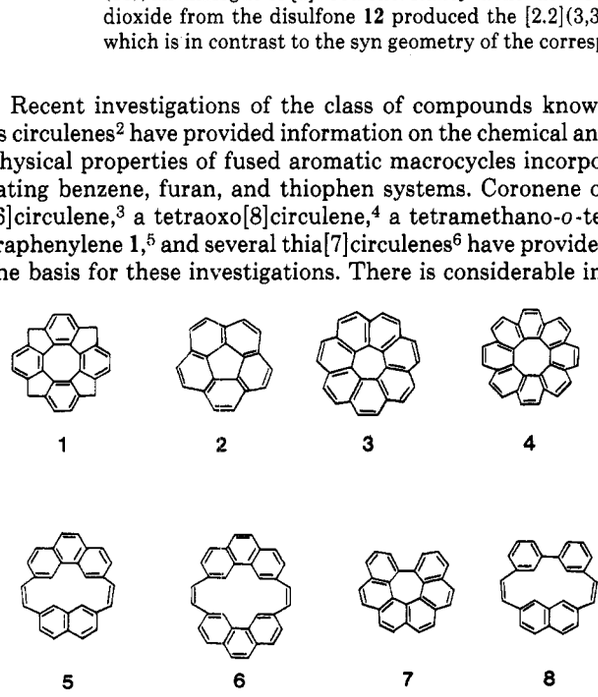
David N. Leach and James A. Reiss*

Department of Organic Chemistry, La Trobe University, Bundoora, Victoria 3083, Australia

Received October 6, 1977

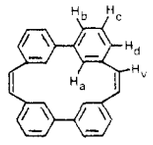
2,17-Dithia[3.3](3,3′)biphenylophane (**10**) was prepared from the coupling of 3,3′-bis(bromomethyl)biphenyl and 3,3′-bis(mercaptomethyl)biphenyl. Bridge contraction to generate the bis(methylthio) ether **14** and subsequent oxidation gave the disulfoxide **15** which undergoes thermal elimination of methylsulfenic acid to yield [2.2](3,3′)-biphenylophane-1,15-diene (**9**). Oxidative photocyclization of the diene **9** gave dibenzo[*def,pqr*]tetraphenylene (**13**), an analogue of [8]circulene. Raney nickel desulfurization of the disulfoxide **15** or thermal elimination of sulfur dioxide from the disulfone **12** produced the [2.2](3,3′)biphenylophane (**16**), which has a preferred anti geometry which is in contrast to the syn geometry of the corresponding diene **9**.

Recent investigations of the class of compounds known as circulenes[2] have provided information on the chemical and physical properties of fused aromatic macrocycles incorporating benzene, furan, and thiophen systems. Coronene or [6]circulene,[3] a tetraoxo[8]circulene,[4] a tetramethano-*o*-tetraphenylene **1**,[5] and several thia[7]circulenes[6] have provided the basis for these investigations. There is considerable interest in the fully carbocyclic aromatic molecules which are expected to be considerably more distorted from planarity than the abovementioned examples. Compounds in this category include corannulene or [5]circulene (**2**),[7] which has been shown by x-ray structure determination[8] to be bowl shaped, and the unreported higher homologs, [7]circulene (**3**) and [8]circulene (**4**). Unsuccessful attempts to synthesize these latter two compounds by the oxidative photochemical cyclization of the cyclophane dienes **5** and **6** have been recorded by ourselves[1] and others.[9] Unlike the bowl-shaped [5]circulene, [7]- and [8]circulene are expected, on the basis of molecular models, to have saddle-shaped geometries similar to that predicted for the hexa[7]circulene (**7**), which has been prepared from the corresponding cyclophane diene **8**.[10]

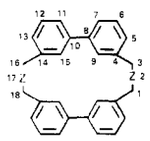


We wish to report the synthesis of [2.2](3,3′)biphenylophane-1,15-diene (**9**) from its corresponding dithiacyclophane **10** and the successful photochemical cyclization to give dibenzo[*def,pqr*]tetraphenylene (**13**), which may be regarded as a cyclooctatetraene composed of two orthogonal phenanthrylene moieties. Thulin and Wennerstrom[11] have recently reported the synthesis of the title compound **13** by an alternative, shorter, albeit lower yielding route.

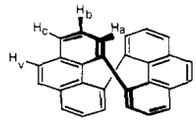
0022-3263/78/1943-2484$01.00/0



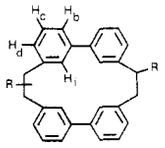
9



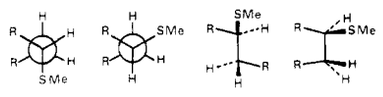
10 Z = S
11 Z = $S^{+}MeBF_4^{-}$
12 Z = SO_2



13



14 R = SMe
15 R = SOMe
16 R = H



14a 14b 14c 14d

R = Biphenylyl

Results and Discussion

2,17-Dithia[3.3](3,3′)biphenylophane (**10**),[12] a compound having poor solubility properties, was prepared under high-dilution conditions by the addition with a mechanical syringe drive[13] of a solution of 3,3′-bis(bromomethyl)biphenyl[14] and 3,3′-bis(mercaptomethyl)biphenyl to a large volume of refluxing basic ethanol. Methylation of compound **10** with dimethoxycarbonium tetrafluoroborate[15] in dichloromethane gave a quantitative yield of the salt **11**, and on treatment with sodium hydride in tetrahydrofuran (Stevens rearrangement conditions), the salt **11** gave rise to the bridge contracted bis(methylthio) ether **14** in high yield, as a mixture of structural isomers and stereoisomers. The ^{13}C-NMR spectrum of **14** showed a singlet at δ 15.2 (SMe), lines at 44.4 and 44.7 (β-benzylic C), resonances at 54.0 and 54.6 (α-benzylic C), as well as aromatic resonance peaks at 125.1–140.8. These data are consistent with the presence of axial and equatorial isomers of the type **14a** and **14b** (showing only one bridge) in approximately equal distribution. This would imply a statistical distribution of the six possible structural isomers.

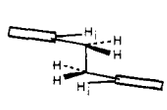
The ^{1}H-NMR spectrum of **14** showed four singlets at δ 2.04–2.08 (SMe), multiplets at 2.55–4.18 (benzylic H), broad singlets at 5.79–6.10 (internal aromatic protons H_i, 2 H) and a multiplet at 6.10–7.68 (aromatic H, 14 H). The presence of four separate methyl resonances, internal shielded protons, and the integral ratio of the aromatic protons suggests that compound **14** consists of approximately equal quantities of the syn and anti isomers **14c** and **14d**. The ^{1}H-NMR spectra of **14** remained unchanged up to a temperature of 178 °C indicating a conformational energy barrier ($\Delta G^{\ddagger}$) of at least 100 kJ between the syn and anti forms.

Although there are several established methods for the ring contraction of dithia[3.3]cyclophanes, it has been our experience that the success of a particular method is dependent on the nature of the cyclophane being investigated. An attempt to ring contract the cyclophane **10** under Wittig rearrangement conditions after the method of Boekelheide[16] (treatment with *n*-butyllithium followed by methyl iodide) was only partially successful and gave low yields of the desired product.

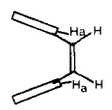
Oxidation of the cyclophane **14** with *m*-chloroperbenzoic acid at 0 °C gave the disulfoxide **15** in high yield, again as a mixture of structural isomers and stereoisomers which was confirmed by the ^{13}C-NMR and ^{1}H-NMR spectra of the product. The mass spectrum (30–70 eV) of the disulfoxide **15** showed no molecular ion. The ion of highest mass was observed at *m/e* 356 indicating a facile thermal loss of two sulfoxide functions.

Pyrolysis of the disulfoxide **15** at 300 °C (8×10^{-4} mm) gave a good yield of [2.2](3,3′)biphenylophane-1,15-diene (**9**). The ^{1}H-NMR spectrum of **9** showed the vinylic protons H_v as a singlet at δ 6.60 and the aromatic protons H_a–H_d as the expected group of multiplets at δ 6.6–7.6, and its ^{13}C-NMR spectrum showed the expected five singlets for the tertiary C's and two singlets for the quaternary C's. A mass spectrum of compound **9** exhibited a stepwise and facile loss of four mass units from the molecular ion to give presumably the radical cation of the dibenzotetraphenylene **13**.

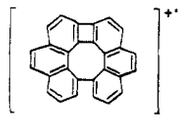
[2.2](3,3′)Biphenylophane (**16**), a related compound with saturated C_2 bridging functions, was prepared in high yield by hydrogenolysis of the disulfoxide **15** with Raney nickel in refluxing ethanol. The cyclophane **16** was also prepared in low yield (<10%) by the pyrolysis (600 °C (8×10^{-4} mm)) of the disulfone **12**, in turn obtained from the oxidation of compound **10** with excess hydrogen peroxide. The yield of product from the pyrolysis reactions could be increased to 70% by effecting the reaction at 500 °C (100 mm), conditions which ensured that the thermal elimination reaction preceded sublimation of the disulfone. The ^{1}H NMR, ^{13}C NMR, and mass spectra confirmed the structure of the cyclophane **16**. In particular,



16a



9a



a

its ^{1}H NMR spectrum showed resonances at δ 2.86 (methylene CH_2) and 5.96 (dt, J = 1.7 and 0.7 Hz; internal aromatic H_i) and a multiplet at 6.97–7.25 (aromatic H). This observed upfield shift of the internal protons indicated that the cyclophane **16** assumes a preferred anti geometry **16a**. In contrast, the ^{1}H-NMR spectrum of the diene **9** showed the equivalent "internal" protons, H_a, at δ 7.62 implying a syn geometry **9a**. Comparison of the UV absorption spectrum of the diene **9** (λ_{max} 213, 243, and 282 nm) with those of *cis*- and *trans*-stilbene also supports a cis configuration about the carbon–carbon double bonds and hence a syn geometry. Molecular models suggest that the syn geometry of the diene **9a** would be much less strained than the alternative anti form.

Irradiation of a solution of the diene **9** in cyclohexane with a mercury–quartz lamp in the presence of iodine as an oxidant afforded dibenzo[*def,pqr*]tetraphenylene (**13**) in an overall yield of 15% from the bis(mercaptomethyl)biphenyl precursor. The structure of **13** was confirmed by the usual spectral methods. In particular, the ^{1}H-NMR spectrum of **13**, a typical AMX spectrum, showed a doublet of doublets at δ 6.63 (J = 7.3 and 1.2 Hz) which were assigned to the H_a proton. We attribute this upfield shift of the H_a proton to the shielding of the opposite aromatic ring system, which has also been noted.[11] The two phenanthrene moieties in compound **13** are most probably orthogonal and such a structure is supported by simple molecular models. The UV absorption spectrum of **13** is similar to that of phenanthrene (Figure 1) but the spectrum shows a bathochromic shift of both the p band (295 to 317 nm) and the α band (345 to 361 nm), which is in accord with the proposed structure having a limited amount of interaction between the two constituent aromatic systems. The ^{13}C-NMR spectrum of **13** was consistent for an aromatic structure containing four tertiary and three quarternary C's. The mass spectrum of **13** showed a facile loss of two hydrogens from the molecular ion which we did not anticipate ($M^+ - 1$, 95%; $M^+ - 2$, 100% of the intensity of M^+). This may indicate the formation of a new C–C bond between two of the phenanthrene moieties to generate the radical cation a. The apparent stability of such a species in the gas phase is intriguing and we are pursuing the parent structure.

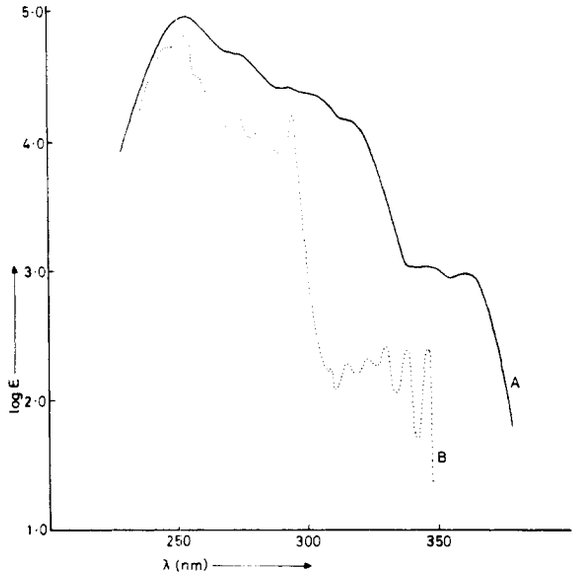


Figure 1. UV absorption spectra (C_6H_{12}) of: (A) dibenzo[*def,pqr*]-tetraphenylene (**13**) and (B) phenanthrene.

The successful photochemical closure of cyclophane dienes containing biphenyl moieties (e.g., **8** → **7**[10] and **9** → **13**) is in direct contrast to the lack of reactivity of cyclophanes **5** and **6** which contain phenanthrene units. This is probably due to the increased flexibility in the biphenyl which allows the cyclophane diene to attain the required transition state geometry for the photochemical ring closure and also decreases the strain due to nonplanarity in the final cyclized product. Although a considerable number of polycyclic aromatic compounds have been synthesized from the appropriate cyclophane dienes, it now appears that a synthetic pathway to [7]- and [8]circulene (**3** and **4**) employing the dienes of the type **5** and **6** as intermediates is unlikely to be successful.

Experimental Section

Melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer. Mass spectra were determined with a JEOL JMS D-100 double-focusing spectrometer. Proton and carbon magnetic resonance spectra were obtained with a JEOL PS-100 PFT spectrometer operating at 100 and 25 MHz, respectively. Both proton and carbon chemical shifts (δ) are recorded in ppm from $SiMe_4$. Ultraviolet absorption spectra were recorded with a Varian Techtron 635 spectrometer. Microanalyses were carried out by the Australian Microanalytical Service, Melbourne.

(a) 3,3′-Bis(mercaptomethyl)biphenyl. 3,3′-Bis(bromomethyl)biphenyl[14] (10.0 g; 29.4 mmol) and thiourea (4.47 g; 58.8 mmol) were heated under reflux in water (50 mL) for 2 h. To the clear solution was added sodium hydroxide (2.35 g; 58.8 mmol) in water (10 mL) and heating was continued for another 2 h. The solution was cooled, acidified with concentrated hydrochloric acid, and extracted with ether. The ether extracts yielded 3,3′-bis(mercaptomethyl)-biphenyl (6.0 g, 81%) as white plates (EtOH): mp 54–55 °C; ^1H NMR ($CDCl_3$) δ 1.78 (t, J = 7.6 Hz, 2 H, exchanged with D_2O), 3.74 (d, J = 7.6 Hz, 4 H), and 7.23–7.50 (m, 6 H, aromatic H); ^{13}C NMR ($CDCl_3$) δ 29.0 (CH_2), 125.9, 126.9, 127.1, 129.1 (tertiary C), 141.3, 141.6 (lower intensity, quaternary C); mass spectrum (75 eV) M^+ + 2 at m/e 248 (7% rel intensity), M^+ + 1 247 (10), M^+ 246.0537 (54) [$C_{14}H_{14}S_2$ requires 246.0537], and fragmentation ions at 215 (22), 214 (100), 180 (27), and 165 (22). Anal. Calcd for $C_{14}H_{14}S_2$: C, 68.24; H, 5.69; S, 26.05. Found: C, 67.94; H, 5.75; S, 25.7.

(b) 2,17-Dithia[3.3](3,3′)biphenylophane (10). 3,3′-Bis(bromomethyl)biphenyl (3.4 g; 10 mmol) and 3,3′-bis(mercaptomethyl)-biphenyl (2.46 g; 10 mmol) were dissolved in benzene (200 mL) and added dropwise to refluxing basic ethanol (NaOH, 0.88 g; 20 mmol dissolved in 2 L) with syringe drives over 7 h. After refluxing for a further 18 h, the solvents were evaporated and the residue was extracted with toluene. Chromatography on alumina with toluene at 100 °C (using a jacketed glass column) gave, as the single major product, 2,17-dithia[3.3](3,3′)biphenylophane (**10**) (3.4 g; 74%) as white prisms (toluene): mp 266–268 °C; mass spectrum (75 eV) M^+ + 2 at m/e 426 (14% rel intensity), M^+ + 1 425 (24), M^+ 424.1318 (69%) [$C_{28}H_{24}S_2$ requires 424.1319], and fragmentation peaks at 243 (16), 212 (41), 211 (33), 183 (22), 182 (100), 181 (53), 180 (22), and 165 (43); ^1H NMR ($AsCl_3$) δ 3.7 (bs, 2 H), and 7.2–7.5 (m, 4 H); ^{13}C NMR ($AsCl_3$) δ 33.7 (benzylic C), 124.9, 126.0, 127.4, 128.6 (tertiary C), 136.6, 138.7 (quaternary C). Anal. Calcd for $C_{28}H_{24}S_2$: C, 79.26; H, 5.66; S, 15.09. Found: C, 79.32; H, 5.92; S, 14.8.

(c) Bis(methyl tetrafluoroborate) Salt (11) of Cyclophane (10). Cyclophane **10** (1.0 g, 2.36 mmol) in dry dichloromethane (100 mL) was treated with dimethoxycarbonium tetrafluoroborate[15] (1.0 g, excess) at room temperature with stirring for 18 h. Ethanol was added and the precipitated product was filtered, washed with dichloromethane, and dried to yield 2,17-bis(methylsulfonium)[3.3](3,3′)-biphenylophane (**11**) in quantitative yield as a white powder, mp > 300 °C (a phase change occurred at 185 °C). The product was used without further purification.

(d) Stevens Rearrangement of the Salt 11. The bis(methylsulfonium) salt **11** (1.3 g; 2.0 mmol) was suspended in dry THF (100 mL) with excess sodium hydride and the mixture was stirred under nitrogen at room temperature for 4 days. Water (100 mL) was carefully added and the mixture was extracted with chloroform. The combined extracts were washed, dried, and evaporated to yield a mixture of the structural isomers and stereoisomers of bis(methylthio)[2.2](3,3′)-biphenylophane (**14**) (630 mg, 67%) as a pale yellow glass: mp 82–92 °C; mass spectrum M^+ + 2 at m/e 454 (4% rel intensity) M^+ + 1 453 (10), M^+ 452.1632 (27) [$C_{30}H_{28}S_2$ requires 452.1632], and major fragmentation peaks at 423 (9), 422 (20), 322 (29), 210 (38), 182 (62), 181 (62), 179 (43), 178 (62), 166 (43), and 165 (100); ^1H NMR ($CDCl_3$) δ 2.04–2.08 (four singlets, 3 H, Me), 2.55–4.18 (m, 3 H, benzylic H), 5.79–7.68 (m, 8 H, aromatic); ^{13}C NMR ($CDCl_3$) δ 15.2 (SMe), 44.4, 44.7 (β-benzylic C), 54.0, 54.6 (α-benzylic C), 124.7–140.9 (aromatic C). Anal. Calcd for $C_{30}H_{28}S_2$: C, 79.58; H, 6.25; S, 14.17. Found: C, 79.34; H, 6.19; S, 13.8.

(e) Bis(methylthio)[2.2](3,3′)biphenylophane *S,S′*-Dioxide (15). The cyclophane **14** (200 mg; 0.44 mmol) and *m*-chloroperbenzoic acid (153 mg; 0.88 mmol) were dissolved in chloroform (50 mL) at 0 °C and the solution was stirred for 18 h at room temperature. The solution was extracted with a phosphate/citric acid buffered solution (pH 7.6) and water, dried over anhydrous $MgSO_4$, and concentrated. Bis(methylthio)[2.2](3,3′)biphenylophane *S,S′*-dioxide (**15**) (190 mg, 89%) was obtained as a yellow glass: mp 173–175 °C; IR ($CHCl_3$) ν_{max} 1050 cm^{-1} (strong, sharp, S=O); ^1H NMR ($CDCl_3$) δ 2.43–2.83 (m, Me), 3.37–3.91 (m, benzylic H), 5.90–7.30 (m, aromatic); ^{13}C NMR ($CDCl_3$) 37.5 (m, Me and β-benzylic C), 72.9 (m, α-benzylic C), 125.0–142.4 (aromatic C); mass spectrum (10–75 eV) showed only fragmentation peaks at m/e 358 (11% rel intensity), 357 (42), 356 (100), 206 (33), 192 (83), 179 (24), 178 (65), 165 (38), and 152 (32). A satisfactory elemental analysis could not be obtained.

(f) [2.2](3,3′)Biphenylophane-1,15-diene (9). The disulfoxide **15** (170 mg; 0.35 mmol) was heated in a silica tube at 320 °C (8×10^{-4} mm). The product which sublimed to the cold portion of the tube was collected. Chromatography on alumina with cyclohexane gave a single major band which yielded [2.2](3,3′)biphenylophane-1,15-diene (**9**) (70 mg, 56%) as white needles (EtOH): mp 124–125 °C [lit.[11] mp 113–115 °C]; mass spectrum M^+ + 2 at m/e 358 (17% rel intensity), M^+ + 1 357 (35), M^+ 356.1565 (91) [$C_{28}H_{20}$ requires 356.1565], and fragmentation ions at 355 (10), 354 (10), 353 (10), 352 (10), 351 (10), 350 (10), 208 (59), 193 (67), 182 (80), 179 (48), 178 (67), 168 (48), and 166 (100); ^1H NMR ($CDCl_3$) δ 6.6–7.6 (m); ^{13}C NMR ($CDCl_3$) δ 127.1, 127.9, 128.5, 128.9, 130.1 (tertiary C), 136.4, and 142.5 (lower intensity, quaternary C); UV (C_6H_{12}) λ_{max} 213 nm (log ϵ 4.74), 243 sh (4.51), and 282 sh (4.28). Anal. Calcd for $C_{28}H_{20}$: C, 94.34; H, 5.66. Found: C, 94.25; H, 5.87.

(g) Dibenzo[*def,pqr*]tetraphenylene (13). The cyclophane diene **9** (80 mg; 0.22 mmol) dissolved in spectroscopic grade cyclohexane (85 mL) with a small quantity of iodine was irradiated for 3.5 h with a Philips 125-W high-pressure mercury-quartz lamp in a water-cooled photochemical reactor. The solution was stirred during the irradiation and the course of the reaction was monitored by determining the UV–visible absorption spectra. The solvent was evaporated and the product was chromatographed on alumina with cyclohexane as eluent to yield dibenzo[*def,pqr*]tetraphenylene (**13**) (50 mg, 63%) as white prisms (EtOH): mp 258–260 °C [lit.[11] mp 262–263 °C]; mass spectrum (75 eV) M^+ + 2 at m/e 354 (5% rel intensity), M^+ + 1 353 (36), M^+ 352.1258 (100) [$C_{28}H_{16}$ requires 352.1252] and fragmentation peaks at 351 (91), 350 (100), 175 (68), 173 (45); ^1H NMR ($CDCl_3$) δ 6.62 (dd, J = 7.3 and 1.2 Hz, H_a), 7.39 (t, overlapping doublets, J = 7.3 and 7.8 Hz, H_b), 7.66 (s, H_v), 7.79 (dd, J = 7.7 and 1.3 Hz, H_c); ^{13}C NMR

($CDCl_3$) δ 126.0, 126.2 (2 C), 130.9 (tertiary C), 131.2, 132.0, 142.2 (lower intensity, quaternary C); UV (C_6H_{12}) λ_{max} 254 nm (log ε 4.94), 273 sh (4.66), 294 sh (4.40), 304 sh (4.32), 317 sh (4.14), 346 sh (3.02), and 361 sh (2.96). Anal. Calcd for $C_{28}H_{16}$: C, 95.42, H, 4.58. Found: C, 94.84, H, 4.74.

(h) 2,17-Dithia[3.3](3,3')biphenylophane *S,S,S',S'*-Tetroxide (12). The dithiacyclophane **10** (100 mg; 0.23 mmol) was dissolved in toluene (100 mL) and acetic acid (20 mL) and brought to reflux. Hydrogen peroxide (30%, 5 mL, excess) was added dropwise and the mixture was heated under reflux for 18 h. The precipitate was filtered, washed with sodium bicarbonate (5% aqueous) and water, and dried to yield 2,17-dithia[3.3](3,3')biphenylophane *S,S,S',S'*-tetroxide (**12**) (90 mg, 84%) as white prisms: mp >300 °C; mass spectrum $M^+ + 2$ at *m/e* 490 (6% rel intensity), $M^+ + 1$ 489 (10), M^+ 488.1116 (24) [$C_{28}H_{24}S_2O_4$ requires 488.1116], and fragmentation ions at 360 (74), 194 (86), 181 (69), 180 (82), 179 (71), 178 (98), 167 (100), and 165 (94); IR (Nujol mull) ν_{max} 1120, 1320 cm^{-1} (strong, sharp, $-SO_2-$). Anal. Calcd for $C_{28}H_{24}S_2O_4$: C, 68.85; H, 4.92; S, 13.12. Found: C, 68.48; H, 4.89; S, 13.0.

(i) [2.2](3,3')Biphenylophane (16). (A) Freshly prepared W-2 Raney Nickel[17] (0.5 g) was added to a solution of the disulfoxide **15** (100 mg; 0.21 mmol) in ethanol (50 mL) and the mixture was heated under reflux for 3 h. The solution was filtered and concentrated; the residue was chromatographed on alumina to yield [2.2](3,3')biphenylophane (**16**) (50 mg, 67%) as white needles (C_6H_{12}): mp 174–176 °C; mass spectrum $M^+ + 2$ at *m/e* 362 (14% rel intensity), $M^+ + 1$ 361 (32), M^+ 360.1878 (100) [$C_{28}H_{24}$ requires 360.1878], and fragmentation peaks at 178 (23), 177 (36), 176 (23), 175 (27), 166 (27), and 164 (32); ^1H NMR ($CDCl_3$) δ 2.86 (s, 2 H), 5.95 (dt, J = 1.7 and 0.7 Hz, H_i), 6.97 (dt, J = 7 and 1.7 Hz, $H_{b/d}$), 7.13 (dt, J = 7 and 1.7 Hz, $H_{d/b}$), 7.15 (t, J = 7 Hz, H_c); ^{13}C NMR ($CDCl_3$) δ 38.6 (benzylic C), 124.6, 127.0, 128.5, 131.2 (tertiary C), 140.4, 141.3 (lower intensity, quaternary C). Anal. Calcd for $C_{28}H_{24}$: C, 93.33; H, 6.66. Found: C, 93.23; H, 6.59.

(B) The disulfone **12** (80 mg; 0.16 mmol) was heated at 500 °C (100 mm) in a silica tube using a tube-furnace and a slow stream of nitrogen. The product which sublimed was collected and chromatographed on alumina with cyclohexane to yield the cyclophane **16** (40 mg, 68%) identical in all respects to the sample described in (A).

Acknowledgments. We thank the Australian Research Grants Committee for financial support and Dr. L. W. Deady for helpful discussions and encouragement. One of us (D.N.L.) wishes to thank La Trobe University for a Research Scholarship.

Registry No.—**9**, 66018-33-5; **10**, 66018-32-4; **11**, 66018-31-3; **12**, 66018-34-6; **13**, 63838-46-0; **14**, 66008-63-7; **15**, 66008-62-6; **16**, 24656-54-0; 3,3'-bis(mercaptamethyl)biphenyl, 66018-35-7; 3,3'-bis(bromomethyl)biphenyl, 24656-53-9; dimethoxycarbonium tetrafluoroborate, 18346-68-4.

References and Notes

(1) Part VIII: P. J. Jessup and J. A. Reiss, *Aust. J. Chem.*, **30**, 851 (1977). This work was presented in part at an Organic Synthesis Symposium of the Royal Australian Chemical Institute, Melbourne, in December 1976.
(2) J. H. Dopper and H. Wynberg, *Tetrahedron Lett.*, 763 (1972).
(3) (a) E. Clar and M. Zander, *J. Chem. Soc.*, 4616 (1957); (b) W. Baker, F. Glocking, and J. F. W. McOmie, *ibid.*, 118 (1951); (c) J. T. Craig, B. Halton, and S. F. Lo, *Aust. J. Chem.*, **28**, 913, (1975); (d) J. R. Davy and J. A. Reiss, *J. Chem. Soc., Chem. Commun.*, 806 (1973).
(4) H. Erdtmann and H. E. Hogberg, *Tetrahedron Lett.*, 3389 (1970).
(5) D. Hellwinkel and G. Reiff, *Angew. Chem., Int. Ed. Engl.*, **9**, 527 (1970).
(6) J. H. Dopper and H. Wynberg, *J. Org. Chem.*, **40**, 1957 (1975).
(7) W. E. Barth and R. G. Lawton, *J. Am. Chem. Soc.*, **93**, 1730 (1971).
(8) J. C. Hanson and C. E. Nordman, Abstracts of the American Crystallography Association, August 1967, p 69 (N8). See also ref 7.
(9) B. Thulin and O. Wennerstrom, *Acta Chem. Scand., Ser. B*, **30**, 369 (1976).
(10) P. J. Jessup and J. A. Reiss, *Aust. J. Chem.*, **29**, 173 (1976).
(11) B. Thulin and O. Wennerstrom, *Tetrahedron Lett.*, 929 (1977).
(12) (a) The nomenclature that we have used for the biphenylcyclophanes is based on that of Staab[12b] for a related series of (4,4')biphenylophanes; (b) H. A. Staab and M. Haenel, *Chem. Ber.*, **106**, 2190 (1973).
(13) D. F. Balaam, J. Chippindall, J. R. Davy, and J. A. Reiss, *Chem. Ind. (London)*, 354 (1975).
(14) W. Wenner, *J. Org. Chem.*, **17**, 523 (1952).
(15) R. F. Borch, *J. Org. Chem.*, **34**, 627 (1969).
(16) R. H. Mitchell, T. Otsubo, and V. Boekelheide, *Tetrahedron Lett.*, 219 (1975).
(17) R. Mozingo, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 181.

Gas-Phase Photolysis of 1,2,3-Thiadiazoles: Evidence for Thiirene Intermediates

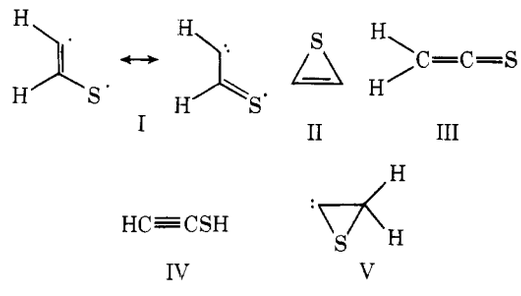
J. Font, M. Torres, H. E. Gunning, and O. P. Strausz*

Department of Chemistry, The University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Received August 16, 1977

The gas-phase photolyses of 1,2,3-thiadiazole (VIa), 4-methyl-1,2,3-thiadiazole (VIb), and 5-methyl-1,2,3-thiadiazole (VIc) have been studied. Evidence for the formation of thiirene intermediates has been obtained by trapping experiments with hexafluoro-2-butyne. While VIa yields 2,3-bis(trifluoromethyl)thiophene, both isomers VIb and VIc yield only one and the same product, 5-methyl-2,3-bis(trifluoromethyl)thiophene, suggesting a common precursor, namely, methylthiirene.

The question of the existence of thiirenes, the family of unsaturated thiiranes, has only recently been considered. Thiirenes were first postulated as short-lived transients in the addition of $^1D_2$ sulfur atoms to alkynes[1] and in the case of acetylene the following isomeric C_2H_2S structures can be considered:



I II III

HC≡CSH

IV V

Flash photolysis experiments with kinetic mass spectrometry[2] have shown the presence of adducts having lifetimes from a tenth to several seconds, depending on the nature of the alkyne. Conventional photolysis of COS, a source of $S(^1D_2)$ atoms, in the presence of alkynes has been shown to yield thiophene, carbon disulfide, benzene, and a solid polymer as end products. The thiophene yield is highest from the $S(^1D_2) + CF_3C{\equiv}CCF_3$ reaction, which makes III, IV, and V unlikely precursors since forth and back migration of CF_3 would be required here and the migrational aptitude of CF_3 is lower than that of H or CH_3 in C_2H_2, $CH{\equiv}CCH_3$, or $CH_3C{\equiv}CCH_3$. Preference for thiirene II as the precursor, compared with thioformyl methylene I, was stated on the basis of preliminary semiempirical MO computations which indicated that the least motion reaction path

$$S(^1D_2) + C_2H_2 \longrightarrow$$

0022-3263/78/1943-2487$01.00/0