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Supplementary Material Available: Figure 1, a perspective of the molecular structure of **22** (1 page). Ordering information is given on any current masthead page.

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(22) Because of the strain associated with the trans ring fusion in **21**, it was not surprising to find that in contrast to the photostability of *trans*-dihydrothiophene **14**, **21** underwent photopolymerization when exposed to Pyrex-filtered light.
(23) The term "tetravalent sulfur" has been used to denote two trivalent carbon atoms bonded to a central sulfur atom; see ref 18.
(24) Dreiding stereomodels indicate that there is considerably more ring strain in a trans C(4–5) ring junction (fusion of five- and six-member rings) relative to a cis in adducts **23**, **16a**, and **16b**. A trans C(1–6) ring junction (fusion of two five-member rings) in **23** would be exceedingly strained.
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Thione Photochemistry. Mechanism of the Short-Wavelength Cycloaddition of Adamantanethione: Evidence for an Excimer Derived from S_2[1,2]

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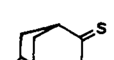
Contribution from the Photochemistry Unit, Department of Chemistry, University of Western Ontario, London, Ontario, Canada. *Received October 30, 1975*

Abstract: Excitation of adamantanethione into the S_2 state leads to reaction from that state. Both dimerization to the 1,3-dithietane and insertion into the solvent (cyclohexane) occur. Neither process appears to involve long-lived radical intermediates. In the presence of ethyl vinyl ether, acrylonitrile, and fumaronitrile, cycloaddition to give the thietane occurs. Unlike the reaction occurring via the $^3(n,\pi^*)$ state, the reaction via S_2, $^1(\pi,\pi^*)$, is stereospecific and nonregiospecific. The dimerization, insertion, and the addition to the first two olefins have been studied kinetically. Differential quenching experiments with olefins have shown that dimerization proceeds via an excimer derived from S_2: its collapse to dimer is quantitative. The lifetime of the thione in the S_2 state, obtained on the basis that concentration quenching or quenching by 1,1′-azoisobutane is diffusion controlled, is ~0.13 ns.

In a previous publication we presented the first report of the photochemical reactions of an alicyclic thione; specifically, adamantanethione (**1**).[3] These reactions, induced by excitation in the $S_1(n,\pi^*)$ band, were dimerization to **2**, and cycloaddition to a number of olefins to give thietanes of type **3**. Briefly, the conclusions reached were the following. The reactions with olefins were, at 500 nm, regiospecific and nonstereospecific, the regiospecificity being that expected assuming the formation of the more stable biradical intermediate. In one instance, that of the addition to α-methylstyrene, support for the intermediacy of the biradical came from the isolation of an "ene" product and proof that the latter was formed by intramolecular hydrogen transfer.



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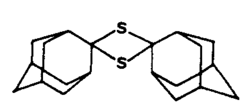

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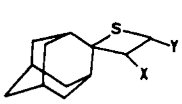

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It was shown that the reactive state involved following excitation into $S_1(n,\pi^*)$ was the triplet, and that Φ_{isc} was of the order of unity. The quantum yields of both dimer and adduct formation were very low ($\Phi \sim 10^{-4}$). Part of the reason for low efficiency in adduct formation was shown to be the diffusion-controlled quenching of the thione triplet by ground-state thione, an observation confirmed by flash photolysis.[4] In addition, it was shown that both in the cycloaddition and in the

Table I. Quantum Yields and Solvent Dependence.[a]

Solvent	Dielectric constant	Φ^b (dimer)	Φ^c (ethyl vinyl ether)	Φ^d (acrylonitrile)
Cyclohexane	2.02	0.083	0.011	0.016
Ethyl ether	4.34	0.078		0.012
Methanol	32.13	0.013	0.0075	0.015[e]
Acetonitrile	38.80	0.0052	0.0052	0.015

[a] Average of three to four determinations. [b] [A] = 0.075 M. [c] [A] = 0.1 M; [O] = 1.0 M. [d] [A] = 0.05 M; [O] = 1.5 M. [e] Error ±20% because of overlapping GLC peaks.

Table II. Excitation of Adamantanethione[a,b]

Mode of excitation	Products	Energy of sensitizer, kcal/mol S_1	T_1
β-Acetonaphthone[c] (λ 306 ± 4 nm)	Dimer ($\Phi = 1.5 \times 10^{-4}$)	77.7	59.4
Michler's ketone[d] (λ 362 ± 4 nm)	Dimer ($\Phi = 1 \times 10^{-4}$)		62.0
Triphenylene[c] (λ 306 ± 4 nm)	Dimer ($\Phi = 1.8 \times 10^{-4}$)	83.4	66.5
p-Methoxyacetophenone[c] (λ 334 ± 4 nm)	Dimer ($\Phi \sim 10^{-4}$)	81.0	71.5
Acetone[e] (λ 306 ± 4 nm)	Dimer and **6**	88.0	79–82
Direct (λ 250 ± 4 nm)	Dimer ($\Phi \sim 1.2 \times 10^{-2}$)		

[a] Cyclohexane solvent. [b] [A] = 0.01 M. [c] [Sens] = 0.01 M. [d] [Sens] = 0.001 M. [e] [Sens] = 1.0 M.

Table III. Sensitized Addition to Acrylonitrile[a]

Sensitizer	Product
β-Acetonaphthone[b] (λ 306 ± 4 nm)	Dimer + **4b**
Michler's ketone[c,e] (λ 362 ± 4 nm)	Dimer + **4b**
Triphenylene[b] (λ 306 ± 4 nm)	Dimer + **4b**
p-Methoxyacetophenone[b,e] (λ 334 ± 4 nm)	Dimer + **4b**
Acetone[d] (λ 306 ± 4 nm)	Dimer, **4b, 6**

[a] Cyclohexane solvent. [b] [A] = 0.01 M; [Sens] = 0.01 M; [O] = 1.5 M. [c] [A] = 0.01 M; [Sens] = 0.001 M; [O] = 1.5 M. [d] [A] = 0.01 M; [Sens] = 1.0 M; [O] = 1.5 M. [e] Prolonged irradiation resulted in the formation of **6.**

dimerization there was an important energy-wasting step: in the dimerization, for instance, only 1 in 7000 of the quenching encounters led to product formation. Arguments were presented favoring the participation both of complexes and biradicals.

One of the most striking general observations that has emerged from a study of thione photochemistry is that, in aromatic,[5-10] aralkyl,[11] and saturated[12,13] thiones, reaction following excitation into S_2 is different from that observed at longer wavelength. This may be a consequence of the long lifetime of S_2 which is itself partly a consequence of the large S_1–S_2 energy separation.[10,14] We wish to present, in the following observations, results which indicate that the pathway followed by adamantanethione after excitation into S_2[3,15] is different from that, characteristic of the $^3(n,\pi^*)$ state, which has been summarized above. We believe that the S_2 behavior of **1,** which we regard as a model for alicyclic thiones, exhibits photochemical behavior which shows no ketonic parallel and has, at present, a number of unique aspects.

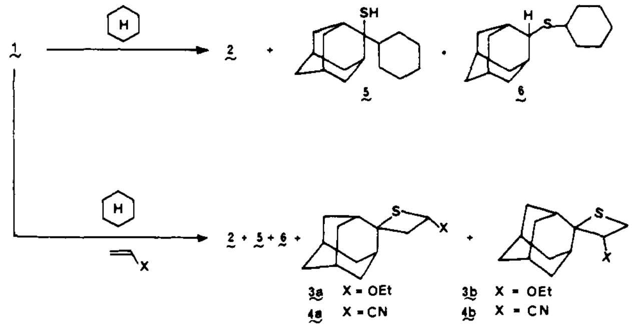
Results

Reactions and Products. (a) Additions. Irradiation of **1** in cyclohexane (254 nm) gave the previously described[3,16] dimer. Irradiation of **1** in cyclohexane containing ethyl vinyl ether or acrylonitrile (254 nm) gave, in both cases, a mixture of isomeric thietanes.[17] Their structures were deduced from analytical and spectroscopic data; in particular, the disposition of the substituents followed from the mass spectra (see Experimental Section). The ratios of the isomeric thietanes were ~1:2 (**3a:3b**) and ~1.3:1 (**4a:4b**) for the ether and nitrile, respectively.

Irradiation of **1** near 278 nm in the presence of fumaronitrile resulted in the formation of a single adduct together with solvent-derived products **5** and **6** (Scheme I). The adduct was found to be identical with one of those, that with mp 103–104 °C, previously described as being obtained at long wavelength.[3] During its formation no olefin isomerization was observed.

(b) Insertion. Irradiation of **1** in cyclohexane gave, together with **2,** two products derived from the solvent. These were shown to be **5** and **6,** and were formed in a ratio of ca. 1:1.5. No bicyclohexyl could be detected (<1% of the amount of **6** formed).

Scheme I



Quantum Yields. The reactions chosen for detailed study were the formation of **2–6.** The results of a general survey of solvent effects on **2–4** are contained in Table I. The dimerization is the most solvent dependent, the addition to acrylonitrile (already a polar substrate) the least. In all cases new products derived from the solvent were formed (but not identified), that with acetonitrile probably including a nitrile addition compound.[12]

Sensitization. The consequences of inducing reaction by energy transfer from a variety of triplet sensitizers (up to E_T ~ 82 kcal/mol) with **1,** alone or in the presence of acrylonitrile, were investigated. The results are contained in Tables II and III. The quantum yields of sensitized dimerization ($\Phi \sim 10^{-4}$) were in all cases that expected of reaction from the lowest triplet,[3] whereas the direct excitation gave a value two orders of magnitude greater. In the cycloaddition, only one of the two possible regioisomeric thietanes was formed, again that expected[3] of the reaction of the lowest triplet. These results indicated that reaction by excitation into S_2, if passing through a triplet, required such to be above ~82 kcal/mol.

Dimerization. The variation of the quantum yield of dimerization with concentration was studied both alone and in the presence, separately, of acrylonitrile and ethyl vinyl ether. The results appear in Figure 1. The dimerization was dependent on thione concentration and a plot of reciprocal quantum yield of dimer against reciprocal thione concentration was linear in all three cases, but the slopes were different. The intercept, the reciprocal quantum yield at infinite thione concentration, was near unity in the absence of olefin, but higher in the presence of 1.5 M olefin.

The variations in quantum yields of dimerization and cyclohexane insertion products in the presence of varying

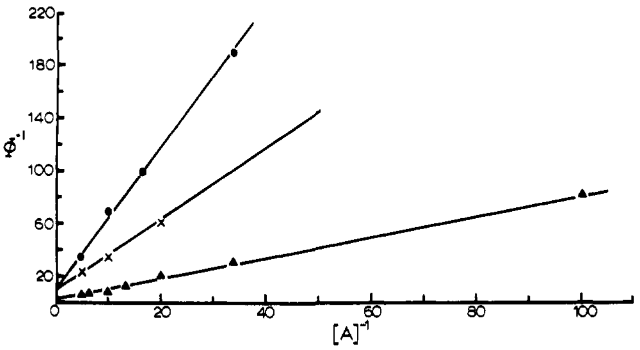


Figure 1. Plot of reciprocal quantum yield of dimerization against reciprocal thione, alone (▲, intercept 1.1 ± 0.33; slope 0.87 ± 0.04), with 1.5 M ether (×, intercept 9.99 ± 1.34; slope 2.44 ± 0.15), and with 1.5 M nitrile (●, intercept, 9.9; slope 5.5 ± 0.25).

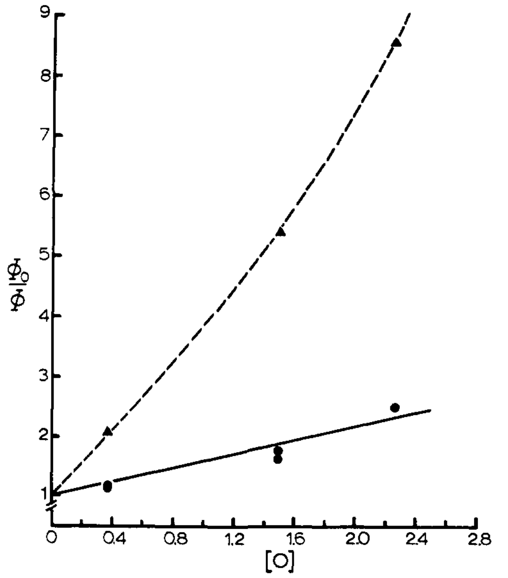


Figure 2. Stern-Volmer: quenching of thione (0.05 M) insertion (●, slope 0.63 ± 0.08) and dimerization (▲) by acrylonitrile.

amounts of olefin acting as quencher were determined; the Stern-Volmer plots are shown in Figures 2 and 3. The dimerization and insertion were quenched at different rates.

Insertion. The variation of the quantum yield of insertion products **5** and **6** with thione concentration is shown in Figure 4. The ratio of **5**:**6** remained unchanged over the range studied.

Cycloaddition. The plots of reciprocal quantum yields of thietane formation against reciprocal olefin concentration are shown in Figure 5.

All processes studied were quenched by 1,1′-azoisobutane. Stern-Volmer plots for dimerization, insertion, and addition to ethyl vinyl ether are represented in Figures 6 and 7. With the insertion study only the sulfide **6** was determined because of difficulties of analysis. All processes were quenched at the same rate, strongly indicating one common intermediate.

Discussion

The Products. There are three significant differences in the nature of the products formed at short wavelength from those formed at long wavelength. First, the addition via $^3(n,\pi^*)$ was regiospecific. Such is not the case following excitation into S_2. On the other hand, as becomes a biradical process, the $^3(n,\pi^*)$ reaction was not stereospecific. A direct comparison in the case of fumaronitrile was made. Only the trans product was obtained at S_2 with, at 10% conversion, no detectable olefin isomerization. A long-lived biradical intermediate is, therefore, not involved in the present reaction.

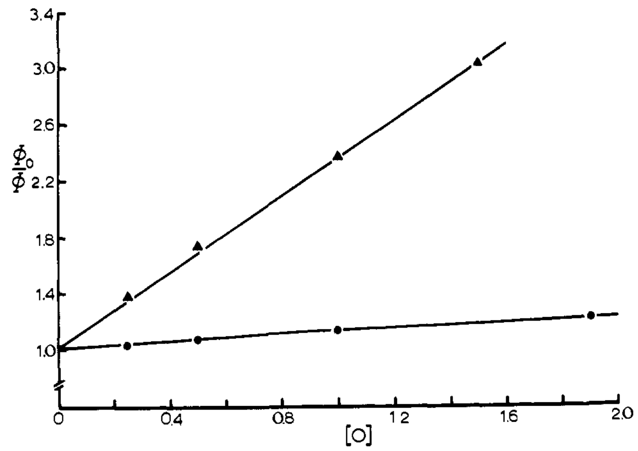


Figure 3. Stern-Volmer: quenching of thione (0.05 M) insertion (●, slope 0.12 ± 0.03) and dimerization (▲) by ethyl vinyl ether.

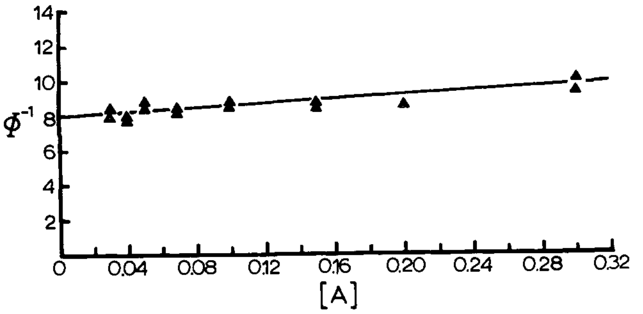


Figure 4. Plot of [insertion products]$^{-1}$ against thione concentration (intercept, 7.9 ± 0.2, slope 5.34 ± 1.06).

Finally, excitation into S_2 leads to reaction with the solvent, a process which does not occur detectably from the lower state. Only in the case of cyclohexane were the products identified since the situation appeared here the least complex. The products, **5** and **6**, could, in principle, have been formed by a hydrogen abstraction process, but there are a number of indications that such is not the case.

In the presence of a good hydrogen donor, adamantanethiol, it has been shown that triplet thione is, indeed, photoreduced, the sole product being the disulfide **7**,[18] and there is no product derived from the thioketyl radical. The disulfide is absent from the S_2 irradiation, although a thiol is being generated. Further, in hydrogen abstractions involving hydrocarbons and alcohols, such as those which occur with excited carbonyl compounds, an inevitable product is that derived by the usual radical termination step: the combination of two radicals derived from the reducing agent. The latter is, in this case, the solvent. The relevant compound, bicyclohexyl, was undetectable, being present, if at all, to the extent of less than 1% of the amount of the insertion product **6**.

Further, when the cyclohexyl radical was generated indirectly (Tables II and III), utilizing hydrogen abstraction by excited acetone, *p*-methoxyacetophenone, or Michler's ketone, only the sulfide **6** was formed. This is a consequence of the known radical trapping ability of ground-state thiones.[19] A hydrogen-abstracting process of this type, since it does not lead to the formation of **5** or **7**, cannot, therefore, be the only route for the formation of **6**.

If it were a contributing process, the quantum yield of **6** would increase with increasing thione concentration, since increased trapping would result. In fact, the reverse is observed (Figure 4). Finally, if two processes for the generation of **5** and **6** were operative, one of which involved a different function of thione concentration than the other, then the ratio of **5**:**6** would

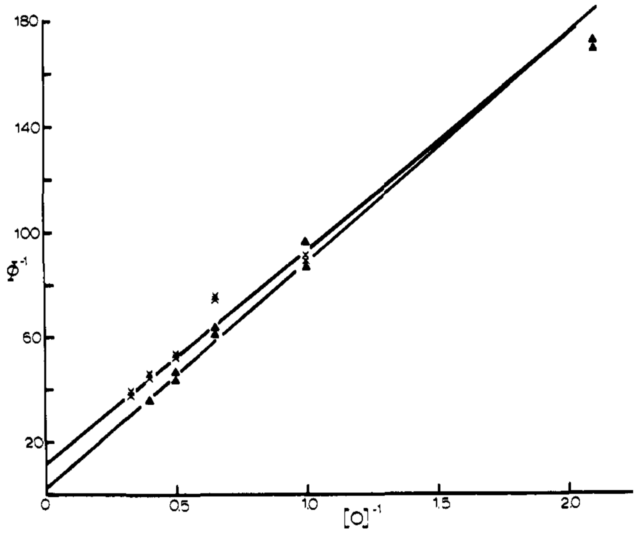


Figure 5. Plot of reciprocal quantum yield of cycloaddition to ethyl vinyl ether (×, 0.1 M thione, slope 91 ± 4) and acrylonitrile (▲, 0.05 M thione, intercept 86.5 ± 3.1) against reciprocal olefin concentration.

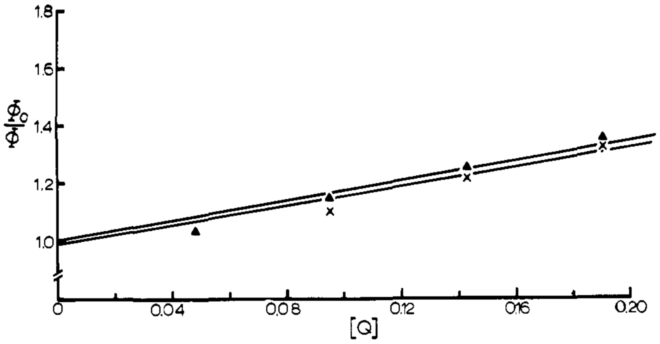


Figure 6. Stern-Volmer: quenching of insertion (▲, slope 1.74 ± 0.11) into cyclohexane and cycloaddition to ethyl vinyl ether (×, 1.0 M, slope 1.73 ± 0.07). Quencher is 1,1′-azoisobutane.

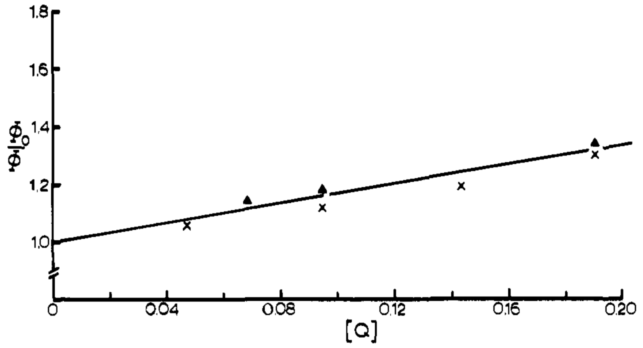
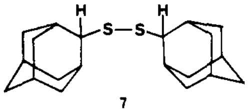


Figure 7. Stern-Volmer: quenching of dimerization in the presence of ethyl vinyl ether (×, 1.0 M) or acrylonitrile (▲, 1.5 M). Quencher is 1,1′-azoisobutane (slope 1.65 ± 0.06).

Table IV. Comparison of Φ^a at 500 and 250 nm

Reaction	$\Phi_{500}{}^b$	$\Phi_{250}{}^c$
Dimerization [A] = 0.2 M	1.5×10^{-4}	0.22
Cycloaddition to Acrylonitrile [A] = 0.2 M [O] = 1.5 M	2.3×10^{-4}	0.017
Cycloaddition to ethyl vinyl ether [A] = 0.1 M [O] = 2.0 M	9.0×10^{-4}	0.019

[a] Error ±10%. [b] Solvent: benzene. [c] Solvent: cyclohexane.



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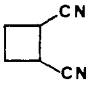

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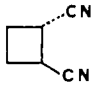

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change with thione concentration. Over the range studied, it did not. We conclude that a hydrogen atom abstracting process, unless in a cage, is not concerned in the formation of **5** or **6**. An alternative is that they are both the consequence of a nonregiospecific $(2_\pi + 2_\sigma)$ addition of the excited thione to the C–H bond, although charge transfer ($S_2 \rightarrow S_0$) followed by proton transfer has not been rigorously excluded.

The Reactive State. Evidence has been provided that the products of the reaction from excitation into S_2 are, in part, different from those obtained from the lowest triplet. There is a quantitative difference also, and it may be seen that both for dimerization and cycloaddition the S_2 reaction under similar concentration conditions has a quantum yield two orders of magnitude higher than that from the triplet (Table IV), despite the fact that $\Phi_{isc} \sim 1$. The lowest triplet and singlet are excluded, and S_2 itself, or higher states in the triplet manifold must now be considered as the chemically active state. Since the energy of S_2 is ca. 95 kcal/mol and that of S_1 is ca. 55 kcal/mol the energy of any chemically active higher triplet must be between these limits. Because of absorption and other difficulties, an unambiguous triplet quencher for this range was unavailable. However, the following arguments lead us to exclude this possibility.

Acrylonitrile itself has a triplet energy in the region of 60–70 kcal/mol[20] based on sensitization data, and the singlet is higher than S_2 of **1**. Since we have used it as a substrate the presence of a triplet donor above 70 kcal/mol should lead, at least in part, to the products of acrylonitrile triplet: the dimers **8** and **9**.[21] Such were not formed. Hence either acrylonitrile triplet was not formed or, being formed, it was intercepted by some other species. The only probable species available is the ground-state thione, and interaction with this would result in formation of the thietane **4b** via the more stable biradical.[22] Thietanes would then be formed by two routes, and the ratio of isomers should vary with thione concentration. This is contrary to observation, since the ratio has been found to be independent of both thione and acrylonitrile concentration. With a triplet above $\sim$70 kcal/mol excluded, there remain species between 55 and 70 kcal/mol. Adamantanethione was irradiated in the presence of a wide variety of sensitizers with cyclohexane as solvent. The product obtained was indeed the dimer, but in quantum yields indicative of triplet reaction (Tables II and III). The additional formation of the sulfide **6** by a hydrogen-abstraction process has already been mentioned. Sensitization of cycloaddition to acrylonitrile (1.5 M), again with various sensitizers, produced only one thietane (**4b**), again indicative of reaction via the $^3(n,\pi)$ state. Hence the participation of a higher triplet in cycloaddition appears excluded. Since the same species is involved in dimerization, the triplet would be excluded here also. It may also be excluded by another argument. At infinite thione concentration (Figure 1) the quantum yield of dimerization is unity. The excited species from which it is formed must therefore be formed in unit yield. If this species is a higher triplet, then there is the improbable requirement that intersystem crossing from S_2 to this triplet also is unity.

Taken together these experiments indicate that no species in the triplet manifold is responsible for the chemical processes initiated by excitation into S_2. We are left with S_2 as the remaining candidate, or some species derived from it other than a triplet.

If thione cycloadditions are stereospecific, then the simplest rationalization is that these are $2\pi + 2\pi$ transformations. Such has already been proposed for xanthione and *p*-methoxythiobenzophenone cycloaddition[6,9] where stereospecificity has also been observed. It is not certain that S_2, which overlaps with S_3, is a $\pi^* \leftarrow \pi$ transition, but this is not unreasonable.

Because of absorption and other problems it was difficult to find a suitable singlet quencher for the S_2 state. We were, faute de mieux, led to the use of 1,1′-azoisobutane, despite its undesirable properties.[23] As can be seen from Figures 6 and 7, Stern–Volmer plots for the quenching of dimerization, insertion into cyclohexane, and cycloaddition to ethyl vinyl ether were obtained over the possible concentration range. The lifetimes derived from the slopes will be discussed later since, being the consequence of several competing processes, their values might not be expected to be identical. The fact that they are very close and of the order of 1.3×10^{-10} s [k_{diff} (cyclohexane) = 10^{10} M^{-1} s^{-1}][25] indicated that radiationless unimolecular decay was probably the most important contributor. Such a lifetime is of the same order as that determined for other thiones: thiobenzophenone (0.5×10^{-10} s[10]), aralkylthiones ($\sim 4 \times 10^{-10}$ s[14b]), xanthione ($< 0.8 \times 10^{-9}$ s[14c]).

Mechanism

Dimerization and insertion will first be considered since they occur concurrently. The simplest general scheme that can be written is contained in the following set of equations (1–6)

$$A \xrightarrow{h\nu} {}^2A \qquad (1)$$

$${}^2A \xrightarrow{k_1} A \qquad (2)$$

$${}^2A + A \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A_2^* \qquad (3)$$

$$A_2^* \xrightarrow{k_3} A_2 \qquad (4)$$

$$A_2^* \xrightarrow{k_4} 2A \qquad (5)$$

$${}^2A + RH \xrightarrow{k_5} \text{products} \qquad (6)$$

where ${}^2A$ is adamantanethione in the S_2 state, A_2 is the dimer, and A_2^* is, for the moment, unspecified as to whether it is an encounter complex or an excimer. Based on these equations the following expressions for the reciprocal quantum yields of dimerization and insertion are obtained:

$$\Phi_D^{-1} = \frac{(k_3 + k_4 + k_{-2})(k_1 + k_2[A] + k_5[RH]) - k_2k_{-2}[A]}{k_2k_3[A]} \qquad (7)$$

$$\Phi_{\text{sol}}^{-1} = \frac{(k_3 + k_4 + k_{-2})(k_1 + k_2[A] + k_5[RH]) - k_2k_{-2}[A]}{k_5[RH](k_3 + k_4 + k_{-2})} \qquad (8)$$

As can be seen from Figure 1 the plot of Φ_D^{-1} against $[A]^{-1}$ is linear and the former has the value of unity (1.1 ± 0.33) at infinite thione concentration; the plot of Φ_{sol}^{-1} against $[A]^{-1}$ is also linear. These conditions may be satisfied if $k_3 \gg k_4, k_{-2}$, when the equations simplify to (9) and (10).

$$\Phi_D^{-1} = 1 + \frac{k_1 + k_5[RH]}{k_2[A]} \qquad (9)$$

$$\Phi_{\text{sol}}^{-1} = 1 + \frac{k_1}{k_5[RH]} + \frac{k_2[A]}{k_5[RH]} \qquad (10)$$

We now make the assumption that k_2 has the value of diffusion control. It appears a reasonable assumption since it is otherwise in competition with the diffusion-controlled quenching of an excited molecule by another of the same multiplicity having a lower excited level available (eq 11): a molecule which is, in this instance, chemically identical.

$$A_{S_2} + A \rightarrow A + A_{S_1} \qquad (11)$$

From the slope of Figure 4 k_5 can be evaluated ([RH] = 10.3 M) and is 2.0×10^8 M^{-1} s^{-1}. This is much faster than the intermolecular hydrogen abstraction rate constants for aliphatic carbonyl (n,π^*) functions.[26]

From the intercept (Figure 4) we obtain k_1 giving $\tau_{S_2} \approx 0.8 \times 10^{-10}$ s. A value may also be obtained independently from eq 10 and is found to be $\sim 1.5 \times 10^{-10}$ s, and we shall take $\tau_{S_2} \sim 1.3 \times 10^{-10}$ s in further discussion.

In the presence of olefin a third process, formation of thietane (AO), competes with those already considered. We shall add eq 12–14 without comment as to whether AO*, the association of excited thione and olefin, has any intrinsic stability. Expression 9 is now replaced by (15) and at infinite thione concentration the reciprocal quantum yield of dimer should be unchanged by the presence of (1.5 M) olefin. This is not the case. It is, in fact, significantly larger both with ethyl vinyl ether and acrylonitrile, and the plots are linear in both cases. We interpret this as indicating that under circumstances when all excited thione molecules could be expected to be trapped by thione and would normally give dimer, the olefin molecule may yet intervene. One rationalization of this observation is that the complex A_2^*, quantitatively formed, is an excimer, and is quenched by olefin. Such quenching of complexes has analogy in other cycloadditive processes.[27,28] Equation 16 is thus required:

$${}^2A + O \xrightarrow{k_6} AO^* \qquad (12)$$

$$AO^* \xrightarrow{k_7} AO \qquad (13)$$

$$AO^* \xrightarrow{k_8} A + O \qquad (14)$$

$$\Phi_D^{-1} = 1 + \frac{k_1 + k_5[RH] + k_6[O]}{k_2[A]} \qquad (15)$$

$$A_2^* + O \xrightarrow{k_9} ? \qquad (16)$$

At this point, the fate of the triple association implied in eq 16, be it collision complex or "exterplex",[27,29] cannot be defined beyond the fact that its formation reduces dimer formation.[30] The insertion products do not derive from the excimer. If this were so the quantum yield for insertion would increase with thione concentration, whereas it is found to decrease (Figure 4).

We have postulated (eq 16) that the excimer is quenched by olefin, but there is no reason to presume that k_6, the rate constant for quenching of S_2 by olefin, will be the same as k_9. In fact, inspection of Figures 2 and 3 shows that it is not: the quenching of dimerization by both acrylonitrile and ethyl vinyl ether is considerably more efficient than that of insertion and substantiates the view that *different reacting species are involved.*

In the presence of olefin as quencher the Stern–Volmer expression for quenching of insertion is given by the equation

$$\frac{\Phi_0}{\Phi} = 1 + \frac{k_6[O]}{k_1 + k_2[A]} \qquad (17)$$

Taking $\tau_{S_2} = 1.3 \times 10^{-10}$ s from the slopes in Figures 2 and 3, we have k_6 as 5.2×10^9 and 3.8×10^8 M^{-1} s^{-1} for acrylonitrile and ethyl vinyl ether, respectively. Such very high rates are commonly found in photocycloaddition processes[31] and have been interpreted as indirect evidence for exciplex formation.

It is possible that AO* (eq 10) has, thus, some stabilization energy (see further, below).

With the quenching parameters for the excited thione in the S_2 state evaluated, it can be seen that unimolecular decay is most important. The lifetime to be obtained by the quenching of cycloaddition by azoisobutane (conditions delineated in Figures 6 and 7) can be estimated. In ethyl vinyl ether a value of $1.2 \times 10^{-10}\ s^{-1}$ is calculated, the value from quenching (Figure 6) being 1.5×10^{-10} s. In acrylonitrile the values are 0.8×10^{-10} and 1.5×10^{-10} s (Figure 7). These differences are of the same order as the experimental deviation in k_1 estimation and the coincidence of the estimates reinforces our interpretation, but points out the probable order of magnitude of error in these determinations.

If both S_2 and excimer were quenched by the azoisobutane, then the Stern-Volmer should have the form in the equation:

$$\frac{\Phi_0}{\Phi} = (1 + k_{q_1}\tau_{S_2}[Q])(1 + k_{q_2}\tau_{ex}[Q]) \qquad (18)$$

With the parameters evaluated this can only be (Figure 7) quasi linear (over the limited concentration range investigated) if $k_{q_2}\tau_{ex} < k_q\tau_{S_2}$. Some measure of τ_{ex} is given in Figures 2 and 3, where the excimer quenching is compared with that of the excited singlet. Even allowing that the excimer quenching by olefin be diffusion controlled, τ_{ex} cannot have a lifetime comparable with S_2. This would then require k_{q_2}, the quenching rate constant of the excimer by the azoisobutane, to be significantly less than diffusion controlled. This is possible, but an alternative interpretation is available. The consequences of energy transfer quenching is not known. If the overall process generates dimer (eq 19), then the quenching process will not be detectable since we have shown that, in the absence of quencher, all excimer molecules give dimer.

$$A_2^* + Q \rightarrow {}^1Q(?) + A_2 \qquad (19)$$

If eq 16 is replaced by the equations:

$$A_2^* + O \xrightarrow{k_{9'}} A_2 + O \qquad (16')$$

$$\xrightarrow{k_{9''}} 2A + O \qquad (16'')$$

then the Stern-Volmer quenching of dimer by olefin is given by

$$\frac{\Phi_0}{\Phi} = \left(1 + \frac{k_9''[O]}{k_3 + k_9'[O]}\right)\left(1 + \frac{k_6[O]}{k_1 + k_2[A] + k_5[RH]}\right) \qquad (20)$$

In the case of ethyl vinyl ether the plot (Figure 3) appears linear. Linearity will be observed if two requirements are met. The first is that the second parenthetical term in eq 20 has a value near unity. This can hold since $k_6[O]$ is small with respect to $k_2[A] + k_1$ over the concentration range used. The second is that $k_9'[O] < k_3$, i.e., 16′, is unimportant. The Stern-Volmer plot is approximated, then, by

$$\frac{\Phi_0}{\Phi} = 1 + \frac{k_9''[O]}{k_3} \qquad (21)$$

With the same approximations, the reciprocal quantum yield of dimerization in the presence of olefin is given by

$$\Phi_D^{-1} = \left(1 + \frac{k_9''[O]}{k_3}\right)\left(1 + \frac{k_1 + k_5[RH]}{k_2[A]}\right) \qquad (22)$$

The second term in eq 22 is the slope of a plot of Φ_D^{-1} vs. $[A]^{-1}$ (Figure 1) in the absence of olefin, and the slope in the presence of olefin for the same plot can be calculated using (21). The ratio of the slopes, with and without olefin $(1 + k_9''[O]/k_3)$, is 2.8. The experimental value from Figure 1 is 2.3. This suggests that in the case of ethyl vinyl ether, at least, the quenching of the excimer by olefin does not produce dimer.

With acrylonitrile the lack of linearity (Figure 2) indicates that the approximations do not hold, and k_6 is indeed found to be larger than for ethyl vinyl ether.

Cycloaddition. The interaction of the singlet thione is required (eq 12) because of the quenching of the insertion products formation. If the thietanes derive entirely from the consequences of this interaction (eq 13), the following relationship is indicated

$$\Phi_T^{-1} = \left\{1 + \frac{k_8}{k_7}\right\}\left\{1 + \frac{k_1 + k_2[A] + k_5[RH]}{k_6[O]}\right\} \qquad (23)$$

Thus the reciprocal quantum yield of thietane, Φ_T^{-1}, should decrease linearly with olefin concentration. This appears to be the case (Figure 6). Incorporation of steps having importance involving formation of thietane from the excimer or from AO* by collision with thione would result in nonlinearity, and appears not to be required.

From the plot of Figure 6 other estimates of k_6 can be, in principle, obtained. However, the derivation necessitates the use of intercepts and the direct plot of the data indicates that the projection of the curve must be unreliable.

The linearity of the plots in Figure 6, if real and not apparent, and the identical slopes suggest that AO* is unaffected by the azoisobutane over the concentration range studied, perhaps because of decreased lifetime, or that collapse on quenching generates adduct with the same efficiency as decay. That the intermediate be a singlet biradical seems, in view of the stereoselectivity,[32] improbable, and the lack of regiospecificity tends to confirm this. Whether one exciplex may give both regioisomers, or whether two similar, and possibly interconvertible, exciplexes are required may not be deduced from the present data.

Experimental Section

Materials. Adamantanethione was prepared according to the method of Greidanus[16] and was chromatographed over silica gel (BDH, 60–200 mesh) using light petroleum (bp 30–60 °C) and was sublimed (100 °C (0.05 mm)) before use. Ethyl vinyl ether (Aldrich) was refluxed over sodium and distilled under nitrogen. Acrylonitrile (BDH) was purified by the method of Bevington and Eaves[33] and was dried over molecular sieves before the final distillation. 1,1′-Azoisobutane was prepared by the method of Blackham and Eatough[34] and was distilled (50 °C (20 mmHg)). Fumaronitrile (Aldrich) was once sublimed (100 °C (0.05 mm)) before use. 2-Acetonaphthone (Aldrich) was recrystallized twice from petroleum ether (60–80 °C), Michler's ketone four times from methanol, triphenylene chromatographed over alumina and recrystallized from petroleum ether (60–80 °C), and *p*-methoxyacetophenone recrystallized twice from methanol and sublimed once before use.

Irradiation Techniques. The preparative irradiations were carried out using either a Hanovia 450-W medium-pressure mercury arc lamp or Rayonet reactor (λ 254 nm). Quantum yield measurements (λ 250 ± 4 nm) were carried out on a JASCO CRM-FA spectroirradiator calibrated at 250 nm using ferrioxalate actinometry.[35] All samples were degassed (residual pressure 3×10^{-5} mm) using freeze-pump-thaw cycles. The dimer (**2**) was analyzed using 2.5 ft × 0.125 in. 3% Poly A (230°) 9,10-diphenylanthracene as internal standard. The products derived from the solvent, cyclohexane (**5** and **6**), were analyzed using 6 ft × 0.125 in. 5% SE-30 (165°) using *n*-docosane as internal standard. Thietanes **3b** and **4b**, derived from acrylonitrile, were analyzed using 6 ft × 0.125 in. 10% SE-30 (215°) using *n*-docosane as internal standard, and **3a** and **4a** derived from ethyl vinyl ether using either 6 ft × 0.125 in. 5% SE-30 (165°) or 6 ft × 0.25 in., 10% Carbowax (185°) using *n*-docosane as internal standard.

Dimerization of Adamantanethione. An *n*-pentane solution (degassed) of adamantanethione (0.114 M, 50 ml) was irradiated (250 nm) using a Rayonet reactor until all the thione had completely disappeared. The solid material formed was filtered, washed with pentane, and sublimed (190 °C (0.005 mm)) to give the dimer **2** (650 mg, 1.8 mmol), which was identical in all respects with the dimer obtained from long-wavelength irradiation, and the authentic dimer was prepared by the method of Greidanus.[16]

Irradiation of Adamantanethione and Cyclohexane. A cyclohexane solution (50 ml, degassed) of adamantanethione (166 mg, 1 mmol) was irradiated to 70% conversion using a Rayonet reactor (λ 254 nm). The residue after evaporation of the solvent showed the presence, aside from that of the dimer, of two major compounds, in the ratio of ~3:2. Two components were separated by preparative VPC and further purified by TLC (Keisselgel DF-5, petroleum ether) and distillation (70 °C (0.04 mm)). The major component, cyclohexyl 2-adamantyl sulfide (**6**), had ir (CCl_4) 2660, 1465, 1445, 1095, and 670 cm^{-1}; NMR (CCl_4) δ 2.98 (1 H br s), 1.1–2.6 (25 H); mass spectrum *m/e* 250 (M^+), 166, and 135. Anal. Calcd for $C_{16}H_{26}S$: 250.1754. Found: 250.1744.

This substance was also found to be identical with the 2-adamantyl cyclohexyl sulfide prepared by irradiating an acetone solution of 2-adamantanethiol and cyclohexene.[36] The minor component, thiol **5**, exhibited the following spectral properties: ir (CCl_4) 2660, 2590, 1450, 1100, and 680 cm^{-1}; NMR (CCl_4) δ 1.2 (1 H, s), 1.0–2.7 (25 H); mass spectrum *m/e* 250 (M^+), 216 (parent peak), 167, 166, and 135. Anal. Calcd for $C_{16}H_{26}S$: C, 76.75; H, 10.47; S, 12.78. Found: C, 76.69; H, 10.61; S, 12.66.

Solutions of adamantanethione (0.01 M) in cyclohexane were irradiated (λ 250 ± 4 nm) to 2, 5, and 10% conversions and the mixtures analyzed (15% FFAP, 6 ft × 0.25 in. at 130°, and 10% SE-30, 6 ft × 0.25 in. at 130°). The product mixture did not show the presence of any peak corresponding to bicyclohexyl. This indicated the formation of bicyclohexyl, if at all, in less than 1% of the amount of insertion products.

Irradiation of Adamantanethione and Ethyl Vinyl Ether. An *n*-hexane solution (10 ml) of adamantanethione (166 mg, 1 mmol) and ethyl vinyl ether (1.9 g, 25.4 mmol) was degassed in a quartz irradiation tube which was then sealed. The solution was irradiated at 254 nm using a Rayonet reactor for 40 min (50% conversion of the thio ketone by uv analysis) and the solvent removed. GLC analysis (6 ft × 0.25 in., 10% Carbowax on Chromosorb W column at 185°) of the residue showed that it contained at least ten peaks. Chromatography on preparative TLC plates (Keisselgel DF-5; petroleum ether 30–60°–methylene chloride 1:1 eluent) gave three broad zones. The upper zone was not investigated, the middle zone contained the thio ketone, and the lower zone was extracted with chloroform and the fraction obtained was further separated into two components (ratio 2:1) using GLC (6 ft × 0.25 in., 10% Carbowax on Chromosorb W, column at 185°). The minor component was shown to be identical with an authentic sample of the thietane **4a** prepared by Liao[3] by GLC retention time and by ir and NMR spectroscopy. The major component (thietane **3a**) was further purified by TLC (Keisselgel DF-5; petroleum ether 30–60°–methylene chloride 1:1 eluent) followed by distillation (90 °C (0.03 mmHg)): *m/e* 238 (M^+), 166, and 148: NMR δ 1.20 (3 H, X_3 part of ABX_3, $J_{AX} = J_{BX} = 7$ Hz, OCH_2CH_3), 2.59, 2.97 (2 H, A and B of ABX, $J_{AX} = 7.3$, $J_{BX} = 3.5$, $J_{AB} = 13$ Hz, $-SCH_2CH$), 3.10, 3.45 (2 H, AB of ABX_3, $J_{AB} = 9$ Hz, OCH_2CH_3), 4.92 (1 H, X of ABX). Anal. Calcd for $C_{14}H_{22}OS$: mol wt, 238.1386. Found: mol wt, 238.1356.

Irradiation of Adamantanethione and Acrylonitrile. A solution (degassed) of adamantanethione (500 mg ~3 mmol) and acrylonitrile (6 g, 100 mmol) in cyclohexane (15 ml) was irradiated at 254 nm using a Rayonet reactor to 70% conversion. At the end of the irradiation a white polymer derived from acrylonitrile separated from the reaction mixture, and this was removed by filtration, washing the residue several times with *n*-pentane. After removal of the solvent, the filtrate showed by VPC (6 ft × 0.125 in., 5% SE-30 140°, or 6 ft × 0.25 in. 5% Carbowax 170°) the presence of two major components (3:2) apart from solvent-derived products **5** and **6**. The material was chromatographed over silica gel (BDH, 60–200 mesh) using benzene–light petroleum (1:9). The first fraction contained adamantanethione and was followed by solvent-derived products **5** and **6**. The last fraction to be eluted contained thietanes **3b** and **4b**. After bulb-to-bulb distillation, the mixture was separated by preparative GLC (6 ft × 0.25 in. 5% Carbowax 170°). The major component was identical in all respects with the thietane **4b** obtained by long-wavelength irradiation.[3] The minor component had ir (CCl_4) 2250, 1420, 1090, 1050, and 950 cm^{-1}; NMR (CCl_4) δ 3.35 (1 H, X part of ABX pattern, $J_{AX} = 6.5$, $J_{BX} = 8$ Hz), 2.60 (1 H, A part of ABX pattern, $J_{AB} = 12$ Hz), 2.40 (1 H, B part of ABX pattern), 1.50–2.50 (14 H); mass spectrum (*m/e*) 219 (M^+), 166, and 148. Anal. Calcd for $C_{13}H_{17}NS$: mol wt, 219.1081. Found: mol wt, 219.0917.

Irradiation of Adamantanethione and Fumaronitrile. Several solutions (degassed) of adamantanethione (83 mg, 0.1 M) and fumaronitrile (200 mg, 0.5 M) in cyclohexane (5 ml) were irradiated (278 ± 4 nm) in a JASCO CRM-FA spectroirradiator for 6, 12, 18, and 24 h. The concentrated reaction mixtures were analyzed by GLC (6 ft × 0.125 in., 10% SE 30, 215 °C for thietanes and 6 ft × 0.25 in., 15% FFAP, 180 °C for isomerized olefin). Only one of the two isomeric thietanes was present, that, obtained by long wavelength irradiation, of mp 103–104°. Less than 1% of the amount of this isomer was produced of the other isomer (mp 132–134°[3]). No maleonitrile could be detected in the solvent.

Sensitized Irradiation of Adamantanethione. A degassed solution (0.01 M) of adamantanethione in cyclohexane was irradiated in presence of a variety of sensitizers (1×10^{-2}–1×10^{-3} M) using a JASCO CRM-FA spectroirradiator in the region where only the sensitizer absorbed the light. The irradiated mixtures (less than 2% thione consumption) were analyzed for dimer (2.5 ft × 0.125 in. 3% poly-A 230°) and for cyclohexyl products (6 ft × 0.125 in. 5% SE-30, 160 °C). A similar series was irradiated in the presence of added acrylonitrile (1.5 M). The thietanes were analyzed (6 ft × 0.125 in., 10% SE-30 at 215°). The results are summarized in Tables II and III.

References and Notes

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(2) Publication No. 155 from the Photochemistry Unit, University of Western Ontario.

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Cyclobuta[1,2-*d*]benzyne. Generation, Trapping, and Dimerization to 2,3:6,7-Dicyclobutabiphenylene

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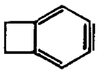
Abstract: Cyclobuta[1,2-*d*]benzyne has been generated from 4,5-bromoiodobenzocyclobutene and magnesium or butyllithium. The transient reactive species can be trapped with furan as the Diels–Alder adduct. In the absence of trapping agents dimerization occurs to 2,3:6,7-dicyclobutabiphenylene, a novel strained benzenoid hydrocarbon with distinctly olefinic properties.

Among the more interesting C_8H_6 isomers, *cis,cis*-octa-3,5-diene-1,7-diyne,[1] 1,2-dehydrocyclooctatetraene,[2] triapentafulvalene,[3,4] pentalene,[4,5] and benzocyclobutadiene[6] have received considerable attention. We now wish to add another unusual member to this illustrious family by the synthesis of cyclobuta[1,2-*d*]benzyne (**1**), the reactivity of which is of interest in comparison with *o*-benzyne. Dimerization provides access to a hitherto unknown[7] hydrocarbon system, 2,3:6,7-dicyclobutabiphenylene (**10**), formed by linear fusion of three alternating four-membered rings and two benzene rings.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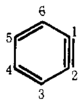

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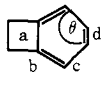
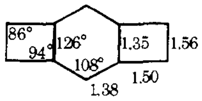


3

Numerous theoretical investigations[8] of *o*-benzyne (**2**) have indicated a distorted geometry of the six-carbon framework characterized by a short 1,2 bond, a relatively long 4,5 bond, and bond angle increases at $\angle C_{123}$ and $\angle C_{345}$. It seems reasonable to assume that a chemical modification of the *o*-benzyne nucleus which leads to augmentation of this structural distortion will result in increased stability of the strained triple bond.[9] One such modification could be fusion to strained rings, for instance, as in benzocyclobutenes. Benzocyclobutenes have also been the subject of theoretical calculations,[10] and the fused ring leads to changes in the benzene nucleus best described by (accentuated) structure **3** in which bond a is elongated, bond d shortened when compared with benzene, and angle θ is increased. The notion thus seemed attractive, that stabilization of the *o*-benzyne nucleus might be achieved by fusion to a four-membered ring at the 4,5 positions leading to cyclobutabenzyne **1**. The added stability of this species might then manifest itself in its relatively greater ease of formation when compared with model compounds. In addition, we hoped that **1** would provide synthetic entry into the unknown ring system **10**, which could then be subjected to physical and chemical investigation. Our interest in dimer **10** stemmed from its anticipated strain-related and potentially antiaromatic properties. Thus, 1,2:4,5-dicyclobutabenzene (**4**), the closest known analogue of **5** reveals its increased strain in the electronic spectrum with bathochromic shifts of ca. 10 nm in comparison with durene.[11]

Examination of x-ray crystallographic data on **4**[12] and biphenylene **5**[13] (bond angles and bond lengths (Å) as shown) indicate that **10** should be much more strained than either model. For instance, fusing a benzene ring to **4** might be expected to cause an unfavorable shortening of the cyclobutane bond to which the benzene ring is being fused by ca. 0.14 Å. Alternatively, fusing four-membered rings to biphenylene as in **10** should cause a contraction of its cyclobutene bonds by ca. 0.08 Å, increasing unfavorable cyclobutadienoid[14] overlap. We therefore expected dimer **10** to be a molecule with unusual chemical and physical properties, possibly too unstable to be formed and/or too reactive to be isolable. It became an even greater synthetic challenge after publication of a report[7] that described the generation and trapping of 2,3-dehydrobiphenylene (**6**), a benzo derivative of **1**, and the unsuccessful attempts to obtain dimers from this species.



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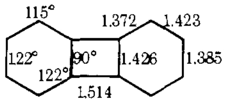

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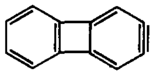
6

Generation, Trapping, and Dimerization of Cyclobuta[1,2-*d*]benzyne (1). 4,5-Bromoiodobenzocyclobutene (**7**)[15] was chosen as a suitable precursor to **1**.

Compound **1** can be efficiently generated by the action[2,16] of ca. 2 M *n*-butyllithium in hexane on **7** and trapped as the furan adduct **8**[17] (70%; mp 83–84 °C; *m/e* 170.0759; calcd 170.0756). The NMR spectrum (CCl_4) of **8** shows signals at τ 3.12 (t, $J \approx 0.5$ Hz, 2 H, vinyls), 3.15 (s, 2 H, benzenic), 4.52 (bs, 2 H, bridgehead), and 7.02 (s, 4 H, cyclobutene). The vinylic and bridgehead protons absorb at unusually low field as observed in related compounds.[18] Alternatively, treatment of **7** with 1 equiv of magnesium in the presence of furan leads to