The species responsible for the spectrum exhibits remarkable stability. Experiments carried out using a xenon matrix have shown that the spectrum persists up to at least 73 K, the softening point of the xenon matrix. This is a manifestation of the stabilizing effect of the electron-withdrawing substituents on the thiirene molecule which parallels the behavior of cyclobutadiene; similarly substituted cyclobutadiene has been reported[19] to be stable at room temperature.

In conclusion it may be stated that the IR spectrum consisting of seven bands that has been obtained in the argon matrix isolated photolyzate of **1** is consistent with the carrier being the thiirene molecule. The tentative assignment of the bands is based on analogous data reported for cyclopropene and thiirane.

The IR spectra of the matrix-isolated photolyzate of **4** and **5** are identical and bear close resemblance to the spectrum of the parent thiirene. The shifts in the C=C stretching frequencies of the photolyzates of **4** and **5** with respect to the parent thiirene are similar to those observed for cyclopropene and similarly substituted cyclopropenes. The spectrum is undoubtedly due to methylcarboethoxythiirene. The parallelism in the behavior of thiirene and cyclopropene also extends to their ring-opening reaction, leading respectively to methylacetylene[20] and ethynylthiol. The presence of alkyl substituents apparently hinders the rearrangement of thiirene. Substituents in general, and electron-withdrawing substituents in particular, endow the thiirene ring with an increased stability which manifests itself in an enhanced yield and persistence to higher temperatures on warming of the matrix.

Additional work in the area of thiirene formation and chemistry is presented in the accompanying paper.

Acknowledgments. The authors thank the National Research Council of Canada for financial aid and Drs. E. M. Lown and I. Safarik for helpful discussions.

Registry No.—**1**, 288-48-2; **2**, 273-77-8; **3**, 65702-19-4; **4**, 18212-20-9; **5**, 29682-53-9; **6**, 54191-78-5; thiirene, 157-20-0; benzothiirene, 65330-66-7; trifluoromethylthiirene, 65702-20-7; carboethoxymethylthiirene, 65702-21-8.

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Intra- and Intermolecular Photocycloadditions of Acetylenic Esters to Benzo[*b*]thiophenes

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Direct and sensitized irradiation of 2-(3-benzo[*b*]thienyl)ethyl but-2-ynoate (**1**) leads to an unrearranged intramolecular cycloaddition product, **2**, as primary photoproduct, which can rearrange to **3** on extended photolysis. An intramolecular cycloaddition product, **6**, has been obtained on sensitized irradiation of 2-(2-benzo[*b*]thienyl)ethyl but-2-ynoate (**5**), although a desulfurized naphthopyranone has been isolated as a major product. Reinvestigation of the photochemical cycloaddition of methyl phenylpropiolate to 2-methylbenzo[*b*]thiophene also shows the presence of small quantities of unrearranged photoproducts **14** and **15**. On sensitized and direct irradiation of (2-benzo[*b*]thienyl)alkyl phenylpropiolates **18** and **19**, only cycloadducts of the solvent benzene with the triple bond are observed. In the latter case, an intramolecular cycloaddition product, **23**, has been shown to be present. The mechanism of formation of the unrearranged products is discussed.

The photochemical addition of acetylenic esters to fused heteroaromatic compounds like benzo[*b*]thiophene,[1,2] benzo[*b*]furan,[3] and *N*-methylindole[4] has been investigated extensively in our laboratories. In general, these compounds give cyclobutenes, formed via $[_{\pi}2_s + _{\pi}2_s]$ addition of the acetylene to the 2,3 position of the heteroaromatic compound.[1-5] These cyclobutenes, however, are often not stable and undergo further photochemical[1-6] and/or thermal changes.[4,7] Thus, only rearranged cyclobutenes are found in the photoaddition of dimethyl acetylenedicarboxylate, methyl propiolate, and methyl phenylpropiolate to benzo[*b*]thiophene.[2]

Several important mechanistic questions present themselves in the relatively simple photoaddition of an alkyne ester to benzo[*b*]thiophene. Among these are which excited state

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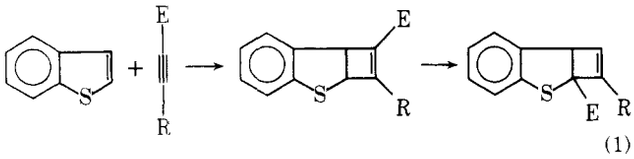
reacts and what intermediates are involved along the reaction coordinate (eq 1). In fact, in our first publications[1,2] on the



(1)

subject, none of the unrearranged adducts expected from [$_{\pi}2_s$ + $_{\pi}2_s$] addition was isolated or even observed. Thus, mechanisms involving either a concerted 1,2 addition or a concerted 1,3 addition could not be excluded.

Subsequent to our report[1] Sasse and co-workers[5] reported isolating an unrearranged adduct as a minor product from the addition of diphenylacetylene to benzo[*b*]thiophene. We subsequently argued[2] that this result was not germane since diphenylacetylene was likely the excited state in this addition.

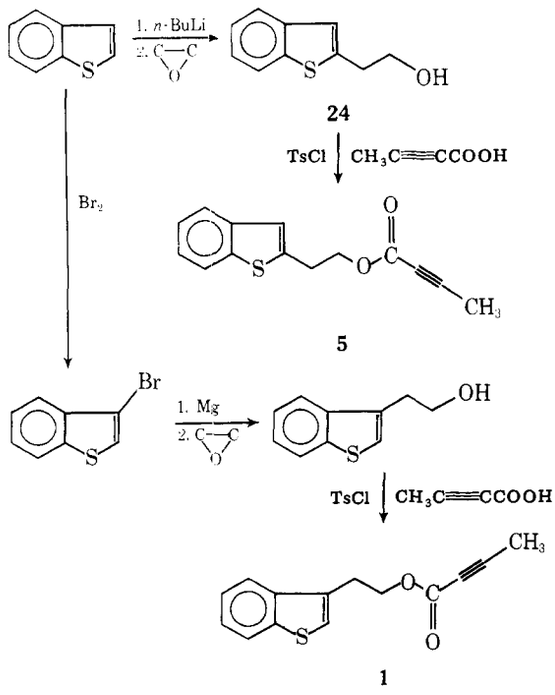
In order to gain more insight in the mechanistic aspects of these processes we have studied the photochemistry of several nonconjugated benzo[*b*]thienyl acetylenic esters. The results of these studies are described herein.

Results

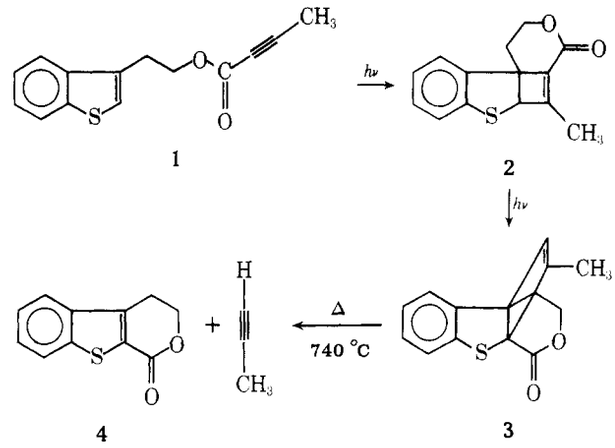
The most efficient, intramolecular cycloadditions are expected to occur on irradiation of benzo[*b*]thienyl acetylenic esters, which may form a six-membered ring fused to the cyclobutene moiety. 2-(3-Benzo[*b*]thienyl)ethyl but-2-ynoate (**1**) and 2-(2-benzo[*b*]thienyl)ethyl but-2-ynoate (**5**) were prepared from the appropriate benzo[*b*]thienylethanols and 2-butynoic acid according to the method of Brewster and Ciotti[8] (Scheme I).

Sensitized irradiation of **1** (2.15 × 10^{-3} M in nitrogen-degassed benzene) for 8 h resulted in formation of two monomeric photoproducts, **2** and **3**, in 2 and 42% yield, respectively (Scheme II). The major product, **3**, was found to be isomeric with **1**, and a molecular ion (*m/e* 244) confirmed its molecular weight. The base peak (*m/e* 204) included, as expected,[3] an ion from retrocleavage in a direction such that the benzo[*b*]thiophene nucleus remains intact. The IR spectrum contained an absorption at 1635 cm^{-1} (C=C),[3] and the NMR

Scheme I



Scheme II



spectrum was clearly consistent with structure **3**, including among others an allylic quartet (1 H) at δ 6.10, weakly coupled ($J \sim 1.6$ Hz) with a methyl doublet (3 H) at δ 1.86, and two multiplets centered at δ 2.28 (2 H) and 4.54 (2 H).

Chemical structure proof was derived from pyrolysis of **3** in the vapor phase at 740 °C (7 × 10^{-5} Torr). Ring opening to a benzo[*b*]thiepine, followed by desulfurization, is prohibited because of Bredt's rule. Cyclobutene cleavage occurred giving propyne and the olefinic fragment **4** instead. No reaction was observed at temperatures below 640 °C.

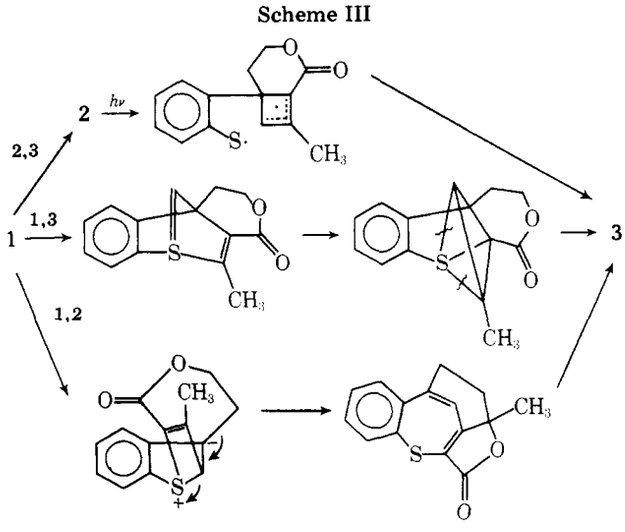
The minor product **2**, shown to be isomeric with **3**, revealed in its NMR spectrum a methyl doublet (3 H) at δ 2.03, weakly coupled ($J \sim 1.2$ Hz) with a methine doublet (1 H) at δ 4.42, proton H_1. Fine structure and chemical shift values are in good agreement with those of 6-methyl-substituted 2-thiabenzo[*b*]bicyclo[3.2.0]hepta-3,6-dienes.[2] Furthermore, compound **2** could be completely converted into **3** when irradiated at 300 nm. Under these conditions **3** appeared to be photostable.

Irradiation of methyl but-2-ynoate gives no cycloaddition product with benzene when irradiated at 350 nm with sensitizers like xanthen-9-one (E_T = 74.2 kcal mol^{-1}) or benzophenone (E_T = 68.5 kcal mol^{-1}), suggesting that the intramolecular cycloaddition of **1** proceeds from the excited state of the benzo[*b*]thiophene moiety.

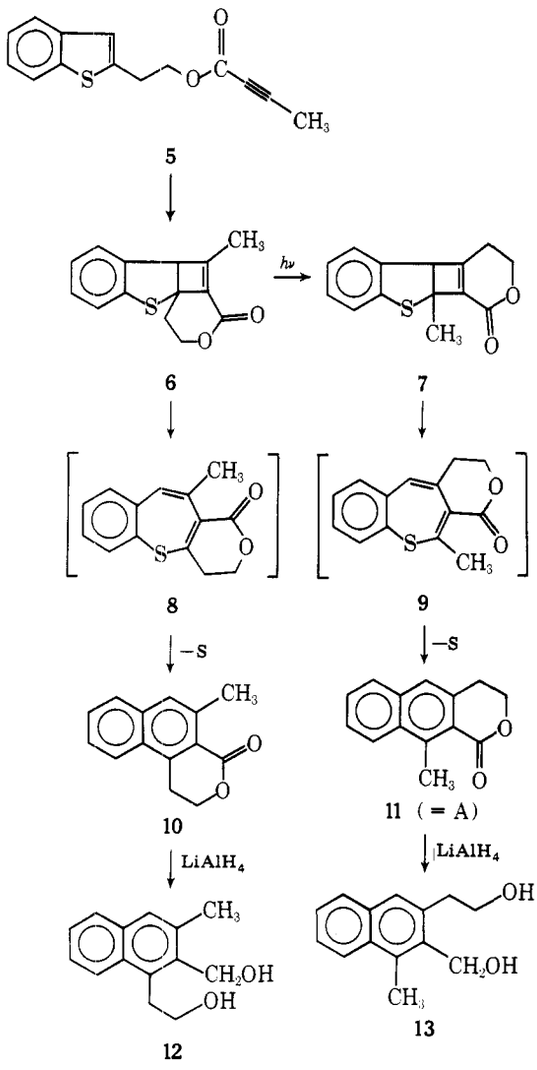
Theoretically the major product **3** can be formed via each of the reaction pathways outlined in Scheme III: a 2,3 addition, a concerted 1,2 addition, and a concerted 1,3 addition. For steric reasons the latter two pathways are unlikely. Formation of **3** via these pathways is also prohibited because it would proceed through highly strained intermediates.

We conclude that a 2,3 addition is operating, leading to the

Scheme III



Scheme IV



photolabile cyclobutene **2**, which is further converted, by a second light quantum, into **3**. In fact, compound **2** is the most likely precursor to **3**, since on irradiation of **1** under the same conditions as above but in the absence of sensitizer, at less than 10% conversion, the relative amount of **2** was substantially increased. As in similar systems,[2] the excited state of the benzo[b]thiophene seems highly polarized. This polarization would result in bond formation involving the acetylene carbon adjacent to the carboxy group rather than the carbon adjacent to the methyl group. This preferred mode of addition in 1* leads to **2**.

2-(2-Benzo[b]thienyl)ethyl but-2-ynoate (**5**; 2.5×10^{-3} M), irradiated in benzene in the presence of acetophenone for 23 h, gave only one photoproduct, A, in 18% yield (Scheme IV). Compound A had a molecular ion peak at *m/e* 212, indicating the loss of sulfur during its formation. Peak matching confirmed the molecular formula $C_{14}H_{12}O_2$. Its IR spectrum contained a strong absorption at 1725 cm^{-1} (C=O). In the NMR spectrum compound A showed two two-proton triplets at δ 3.16 and 4.49, a deshielded methyl singlet at δ 3.07, and a one-proton low field multiplet, centered at δ 8.23. The latter two large downfield shifts are associated with the presence of a peri carbonyl group and alkyl group,[9a] respectively. The spectroscopic data are clearly consistent with either the naphthopyranone **10** or **11**.

More evidence for the presence of **10** or **11** was obtained by reduction of compound A with lithium aluminum hydride, leading to the diol **12** or **13**, with an NMR absorption of an upfield methyl group at δ 2.74 and with an aromatic fine structure pattern in good agreement with 1,2,3-trisubstituted naphthalene. From the relatively low chemical shift value at δ 2.74 it is most likely that **13** is the isolated naphthalene rather than **12**, since β-methylnaphthalenes ($\delta_{CH_3} \sim 2.3$–2.5) absorb about 0.2–0.3 ppm at higher field than α-methylnaphthalenes.[9b] Therefore, 9-methyl-3,4-dihydro-1*H*-naphtho[2,3-*c*]pyran-1-one (**11**) is the most likely structure for the isolated photoproduct A.

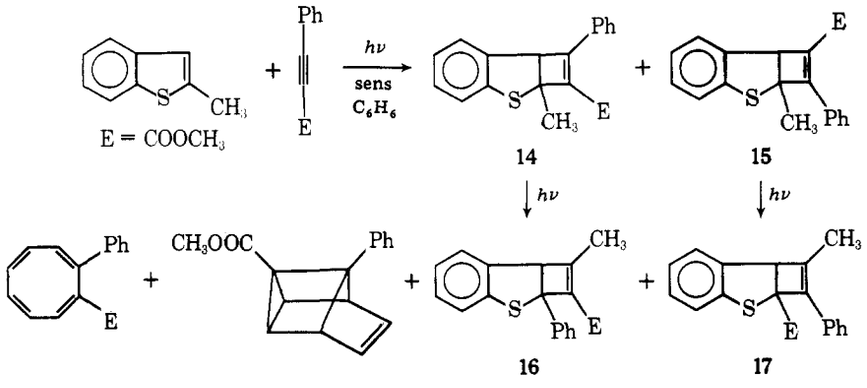
In one experiment at shorter irradiation time a fraction was also isolated which contains a second photoproduct B. Though compound B could not be separated from A, its most likely structure is the primary intramolecular cyclization product **6**. The NMR spectrum showed distinct signals at δ 2.05 (methyl doublet, $J \sim 1.5$ Hz) and a two-proton multiplet at δ 2.35 in agreement with that of **2** and **3**.

Based on the arguments as above, **6** is likely the initially formed photoproduct, and it rearranges to **7**. This rearrangement not only releases the strain at the quaternary carbon C_1, but also leads to an endocyclic conjugated double bond in **7**, which is expected to be thermodynamically more stable than the exocyclic one in **6**.[10] Compound **7** undergoes ring opening to the benzo[b]thiepine **9**. It is not surprising that **9** could not be detected, since it is known that benzo[b]thiepines easily lose sulfur and convert into the corresponding naphthalenes.[7] However, formation of **9** via a 1,2 addition cannot be completely ruled out.

In contrast to our earlier report,[2] sensitized irradiation of 2-methylbenzo[b]thiophene (8.3×10^{-3} M) and methyl phenylpropiolate in benzene for about 20 h at 350 nm resulted in the isolation of the unrearranged cyclobutenes **14** and **15** in 1 and 3% yields (Scheme V). Though these products are obviously minor, their presence is significant in that they represent the first such unrearranged adducts isolated from an intermolecular $[{}_{\pi}2_s + {}_{\pi}2_s]$ addition of an alkyne ester to benzo[b]thiophene.

1-Carbomethoxy-8-phenylcyclooctatetra-1,3,5,7-ene and 4-carbomethoxy-5-phenyltetracyclo[3.3.0.$0^{2,4}$.$0^{3,6}$]oct-7-ene

Scheme V



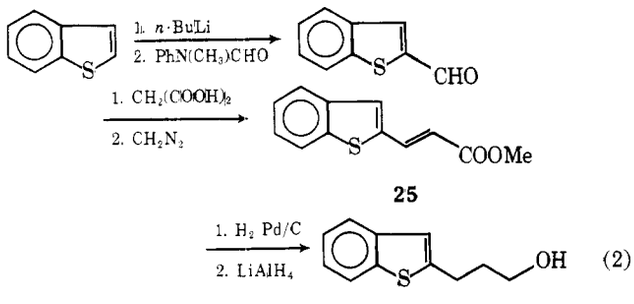
(mp 74–75 °C) were obtained as major products[12] in ~50% yield; the rearranged cyclobutenes **16** and **17** were isolated in 20 and 10% yields, respectively.

The predominant mass spectral fragmentation, *m/e* 210, is proof of the derived structure of the major cycloadduct **16**.[13] The NMR spectrum showed a methyl doublet at δ 2.10, weakly coupled ($J \sim 1.6$ Hz) with a methine quartet at δ 4.32. Compound **16** appeared to be photostable, and was shown to be formed from **14** upon irradiation at 300 nm. Chemical proof for the structure of **16** was derived from the thermal rearrangement at 240 °C. The corresponding 2-carbomethoxy-3-methyl-1-phenylnaphthalene, formed via a sulfur extrusion process,[2,6,14] did not show any absorption in its NMR spectrum below 8.0 ppm, which would be the case if the ester group would be in the 1 position of the formed naphthalene.

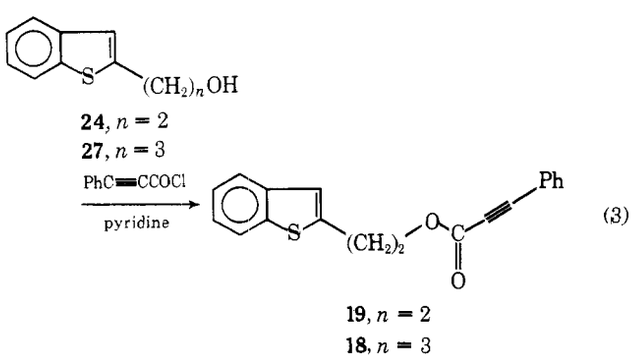
Though isomer **17** could only be obtained mixed with some **16**, there was spectroscopic evidence for its presence. The predominant peak at *m/e* 192 in its mass spectrum, completely absent in **16**, points to the loss of a $PhC{\equiv}CCH_3$ fragment. The NMR spectrum showed a weakly coupled doublet, δ 2.07, and quartet, δ 4.78, consistent with the methyl group and H_5, respectively. Compound **17** also appeared to be photostable, and was exclusively formed from **15** upon irradiation at 300 nm. Spectroscopic data of **14** and **15** are consistent with the assigned structures.

It cannot be excluded that the process producing the unrearranged product involves triplet state methyl phenylpropiolate, as has been shown to occur in the addition to benzene.[15] The huge difference in concentration of benzene vs. benzo[*b*]thiophene, however, would suggest a greater benzene adduct/benzo[*b*]thiophene adduct ratio than is found experimentally (1:1). Therefore, the process producing the cyclobutenes likely derives from an excited state of benzo[*b*]-thiophene.

In view of these results it became interesting to examine the photochemistry of (2-benzo[*b*]thienyl)alkyl phenylpropiolates, **18** and **19**. These compounds were prepared in good yield from the appropriate 2-benzo[*b*]thienyl alcohols and phenylpropiolyl chloride (eq 2 and 3).



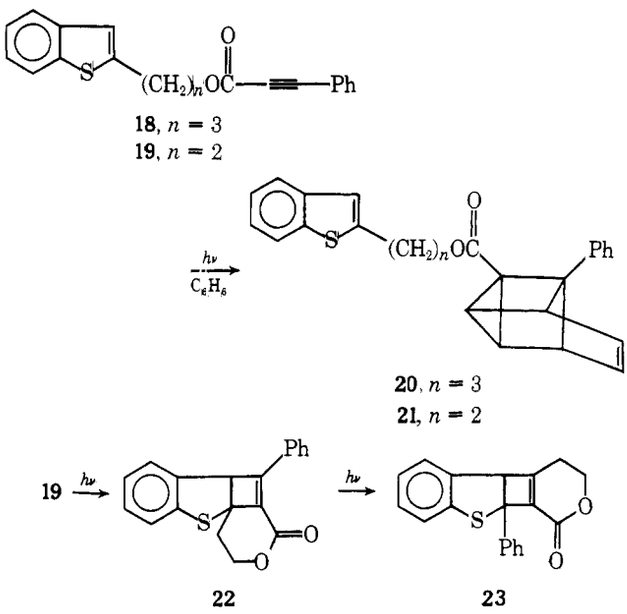
(2)



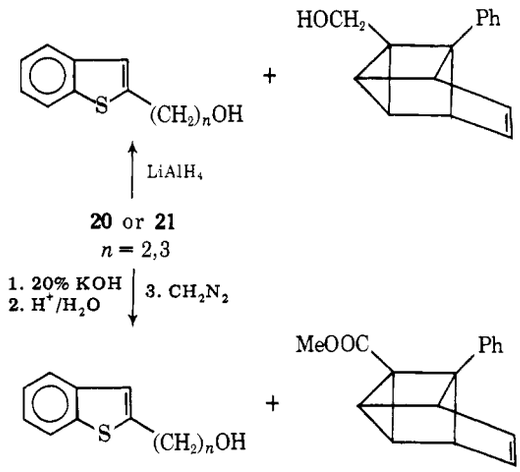
(3)

On sensitized and direct irradiation of 2×10^{-3} M benzene solutions of the esters **18** and **19**, the tetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct-7-enes **20** and **21** could be isolated in 48 and 19% yield, respectively (Scheme VI). Structure proof was

Scheme VI



Scheme VII



based on reduction with lithium aluminum hydride to the known alcohols and by base-catalyzed hydrolysis followed by diazomethane esterification (Scheme VII). Apparently, the intermolecular addition of the triple bond to benzene[12] becomes more important than intramolecular cycloaddition. However, a monomeric compound was formed from **19** in a competitive side reaction. Its NMR spectrum revealed a broad singlet at δ 4.88 (1 H) and two two-proton triplets at δ 4.54 and 2.48. Though the spectral data do not clearly differentiate between **22** and **23**, we have assigned the structure **23** based on the efficient rearrangements which occur in analogous systems (e.g., **14** → **16**).

Discussion

Though the experiments do not completely rule out concerted 1,2 or 1,3 additions, which produce the rearranged adducts directly, the preponderance of evidence is not in their favor and these pathways are not necessary.

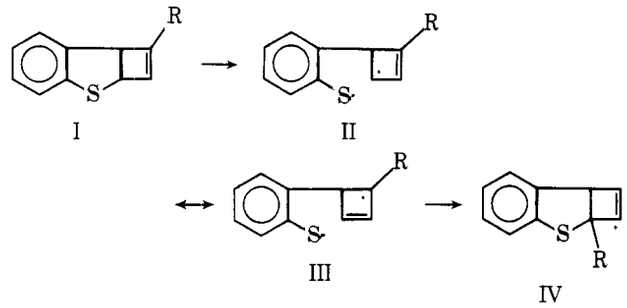
The results above, coupled with those published by us earlier, definitively prove that (i) the photocycloaddition of benzo[*b*]thiophene to acetylenic esters occurs from a triplet state of the heteroaromatic compound, (ii) unrearranged adducts form from this addition, though they are minor products, and (iii) these unrearranged adducts irreversibly and with great efficiency rearrange to the observed major products.

Consider the results: xanthone (E_T = 74.2 kcal mol^{-1}, λ_{max} 366 nm) sensitizes the intramolecular photoaddition of 1 forming 2. Though there is a sensitized addition of the separated reagents, benzo[b]thiophene and the alkyne ester, to one another under similar conditions, there is no addition of alkyne ester to benzene sensitized by xanthone under conditions where xanthone alone is absorbing the light. Since benzene is more reactive than benzo[b]thiophene toward the excited triplet state of another alkyne ester, methyl phenylpropiolate (E_T < 68 kcal mol^{-1}), one would expect the butynoate ester triplet to add to benzene if it was formed.

The photoaddition of diphenylacetylene (E_T = 62.5 kcal mol^{-1}) to benzo[b]thiophene likely occurs from the excited state of the diphenylacetylene, as has been argued by us earlier[2] and corroborated by Kuhn and Gollnick.[11] Benzophenone sensitizes the intermolecular addition of methyl phenylpropiolate to benzo[b]thiophene as well as to benzene. The triplet energy of methyl phenylpropiolate should therefore be lower than 68 kcal mol^{-1}, and the addition products to benzo[b]thiophene likely were derived from the triplet state of the alkyne ester.

Unrearranged adducts formed from the addition of excited benzo[b]thiophene to acetylenic ester have been isolated in every case reported in this paper, though they are minor products. These unrearranged adducts are all shown to rearrange with great efficiency to the observed major products. The reverse reaction, from major to minor product, does not occur under the same experimental conditions.

It remains to argue why the photorearrangement of I → IV is so facile. In essence the question is: why do compounds of the general structure I undergo facile (sensitized) rearrangement to IV?



R = Ph or COOMe

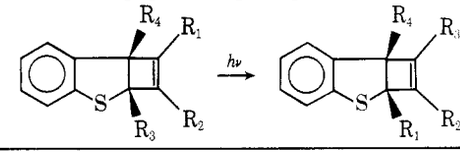
We would suggest that rearrangement of I → IV likely proceeds via rupture of the C_1–S bond to give a stabilized diradical (II ↔ III). The answer may lie in the higher electron density at the R-substituted carbon or the rapid ring closure of one or the other to cyclic products. Since the contribution of the resonance structure III when R = Ph is greater than that of II, and since polar contribution when R = COOMe would favor ring closure from III, the theory supports the experimental result.

Still another possible explanation can be seen by considering the photoadducts which exclusively rearrange (Table I).

In every case the double bond of the cyclobutene which eventually forms is less highly substituted with conjugated functional groups than the original photoproduct. The original adduct, in every case, likely has a lower triplet energy than the final product and the unrearranged product is a more efficient energy-transfer acceptor than the rearranged adduct. These results suggest therefore that the rearranged adduct is the energy sink in the system and that once it is formed there is no convenient photochemical pathway whereby it can be converted to other isomers.

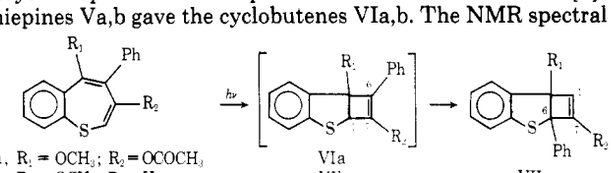
The cases of 6 and 7 present another interesting comparison: in this case alone are naphthalenes isolated from photo-

Table I. Photorearrangements of 2-Thiabenzo[b]bicyclo[3.2.0]hepta-3,6-dienes[a]



R_1	R_2	R_3	Ref
$COOCH_3$	$COOCH_3$	H or CH_3	1, 2, 6
$COOCH_3$	$COOCH_3$	$C(CH_3)_3$	*b*
$COOCH_3$	H	H or CH_3	2
$COOCH_3$	Ph	H or CH_3	2, *c*
e	CH_3	H	*c*
Ph	$COOCH_3$	H or CH_3	2, *c*
Ph	Ph	H	2, 5
Ph	$-C(=O)OCH_2CH_2-$		*c*
CH_3	$-C(=O)OCH_2CH_2-$		*c*
Ph	H	H	*d*

[a] R_4 = H unless otherwise indicated. [b] A. H. A. Tinnemans and D. C. Neckers, unpublished results. [c] This work. [d] Hofman and Meyer[16] reported that the photoisomerization of the benzo[b]thiepines Va,b gave the cyclobutenes VIa,b. The NMR spectral



Va, R_1 = OCH_3; R_2 = $OCOCH_3$
Vb, R_1 = OCH_3; R_2 = H

VIa
VIb

VIIa
VIIb

data reported showed, among other peaks, a singlet at δ 5.7 for VIa and two "singlets" at δ 6.10 and 6.12 for VIb. However, since all known 2-thiabenzo[b]bicyclo[3.2.0]hepta-3,6-dienes[2,5,6] reveal in their NMR spectra vinylic absorptions at 5.9–6.8 and methine absorptions (H_1) at δ 4.05–4.75, it is more likely the isolated compounds were VIIa,b, in agreement with the expected rearrangement of VIa,b → VIIa,b under the reaction conditions used. [e] R_1R_4 = $-CH_2CH_2OC(=O)-$.

rearrangement. It is possible that these products ring open to benzo[b]thiepines rather than rearrange by biradical intermediates, thereby losing sulfur.

The results are, in our judgment, consistent with a mechanism involving two distinct photoprocesses:

benzo[b]thiophene (BT) + sensitizer* → BT*

BT* + alkyne → unrearranged adduct

unrearranged adduct + sens* → [unrearranged adduct]*

[unrearranged adduct]* → rearranged product

Based on the results, it is safe to predict that any benzo[b]thiophene will add to any alkyne, particularly electron-deficient ones, to give fused cyclobutenes which are rearranged and that 2-thiabenzo[b]bicyclo[3.2.0]hepta-3,6-dienes will likely rearrange to the isomer in which the double bond is less highly substituted.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded either in chloroform solution or in KBr disks using a Perkin-Elmer 337 infrared spectrophotometer. NMR spectra were recorded either on a Varian A-60 or CFT-20 spectrometer with deuteriochloroform as the solvent and tetramethylsilane as the internal reference. UV spectra were determined in methanol using a Beckman Acta MIV spectrophotometer. Mass spectra were obtained using a Varian MAT Model CH-7 mass spectrometer. Elemental analyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, Mich.

Photolysis experiments were carried out in a Rayonet RPR-100 reactor fitted with 300- or 350-nm fluorescence lamps. Otherwise, the photolyses were performed in a 400-mL Pyrex immersion well apparatus using a 450-W Hanovia medium-pressure mercury lamp.

Before the irradiation all samples were purged with nitrogen for at least 30 min.

2-(2-Benzo[*b*]thienyl)ethanol (24). Under a slight stream of dry nitrogen 181 mL of a 2.6 M solution of *n*-butyllithium in hexane was slowly added to a solution of 63 g (0.47 mol) of benzo[*b*]thiophene in 300 mL of anhydrous ether at 0–5 °C. The solution was warmed to reflux temperature and stirred for 1 h. The red solution was cooled to 0 °C and 21 g (0.48 mol) of ethylene oxide in 40 mL of cold ether was added to the reaction solution. Stirring was continued for an additional 1 h at 0 °C. The reaction was hydrolyzed with water, and the aqueous phase was extracted with ether. The ethereal extracts were combined, washed with water until neutral, dried, and concentrated. Crystallization from carbon tetrachloride gave 67 g of white plates, mp 68–78 °C. Recrystallization gave 64 g (76%) of analytically pure **24**: mp 77–78.5 °C (lit.[17] 79.5–80.5 °C); NMR δ 2.13 (s, 1 H, OH), 3.08 (asymm t, 2 H, CH_2), 3.89 (asymm t, 2 H, CH_2), 7.08 (br s, 1 H, H_3), 7.2–7.9 (m, 4 H, Ar). Anal. Calcd for $C_{10}H_{10}OS$: C, 67.38; H, 5.65; S, 17.99. Found: C, 67.20; H, 5.56; S, 17.80.

2-(2-Benzo[b]thienyl)ethyl But-2-ynoate (5). A solution of 3.36 g (0.019 mol) of 2-(2-benzo[*b*]thienyl)ethanol (**24**) and 1.68 g (0.020 mol) of 2-butynoic acid[18] in 40 mL of anhydrous pyridine was cooled to 8 °C, and to this was slowly added a solution of 6.60 g (0.032 mol) of *p*-toluenesulfonyl chloride in 10 mL of pyridine. The reaction mixture was stirred at 15 °C for 2.5 h and then poured into water. After extraction with ether the organic layers were subsequently washed with 1 N hydrochloric acid solution, saturated sodium bicarbonate, and brine. After drying over magnesium sulfate, the solvent was removed and the residual oil was chromatographed over Florisil with benzene/petroleum ether (1:5) as eluent, yielding 3.5 g (76%) of **5**. The product was crystallized from methanol to give white needles: mp 41–42 °C; NMR δ 1.83 (s, 3 H, CH_3), 3.17 (t, 2 H, CH_2), 4.43 (t, 2 H, CH_2), 7.05 (br d, 1 H, H_3), 7.1–7.9 (m, 4 H, Ar); IR (KBr) 2235 cm^{-1} (C≡C); UV_{max} 257 nm (log ϵ 3.94), 288 sh (3.25). Anal. Calcd for $C_{14}H_{12}O_2S$: C, 68.82; H, 4.95; S, 13.12. Found: C, 68.88; H, 4.90; S, 13.17.

2-(3-Benzo[*b*]thienyl)ethyl But-2-ynoate (1). This compound was prepared in 83% yield according to the procedure described for **5**, starting with 5.04 g (0.028 mol) of 2-(3-benzo[*b*]thienyl)ethanol, prepared from the Grignard reagent of 3-bromobenzo[*b*]thiophene[19] and ethylene oxide according to Cagniant and Cagniant,[20] 2.52 g (0.030 mol) of 2-butynoic acid,[18] and 9.9 g (0.048 mol) of *p*-toluenesulfonyl chloride. The crude ester was crystallized from methanol to give **1** as very pale yellow needles: mp 53.5–54 °C; NMR δ 1.92 (s 3 H, CH_3), 3.17 (t, 2 H, CH_2), 4.44 (t, 2 H, CH_2), 7.18 (br s, 1 H, H_2), 7.2–8.0 (m, 4 H, Ar); IR (KBr) 2235 cm^{-1} (C≡C); UV_{max} 259 nm (log ϵ 3.68), 284–288 (3.35). Anal. Calcd for $C_{14}H_{12}O_2S$: C, 68.82; H, 4.95; S, 13.12. Found: C, 68.80; H, 4.94; S, 13.05.

Methyl *trans*-β-(2-Benzo[*b*]thienyl)acrylate (25). A solution of β-(2-benzo[*b*]thienyl)acrylic acid[21] in tetrahydrofuran was treated with an ethereal solution of diazomethane at 0 °C. The excess diazomethane was destroyed by carefully adding formic acid and the organic layer was washed with saturated sodium bicarbonate solution and subsequently with water until neutral. After drying ($MgSO_4$) the solvent was removed and the residual crude ester was crystallized from methanol, giving pale yellow needles: mp 122–123 °C; NMR δ 3.85 (s, 3 H, $COOCH_3$), 6.35 and 7.93 (AB, 2 H vinylic, J_{AB} = 15.5 Hz), 7.47 (br s, 1 H, H_3), 7.28–7.52 (m, 2 H, Ar), 7.63–7.95 (m, 2 H, Ar); UV_{max} 256 nm (log ϵ 3.77), 315 (4.50). Anal. Calcd for $C_{12}H_{10}O_2S$: C, 66.03; H, 4.62; S, 14.69. Found: C, 66.45; H, 4.52; S, 14.26.

Methyl β-(2-Benzo[*b*]thienyl)propionate (26). The unsaturated ester **25** (1.0 g) and 5% palladium on charcoal (0.15 g) in ethyl acetate (100 mL) were shaken with hydrogen overnight, at which time another small amount of catalyst (0.15 g) was added and the mixture was shaken with hydrogen until no vinylic hydrogens could be detected by NMR. The catalyst was filtered off and the solvent was removed under reduced pressure. The residue was crystallized from methanol, giving **26** as white plates: 88%; mp 70–71.5 °C; NMR δ 2.51–2.88 (m, 2 H, CH_2), 3.04–3.41 (m, 2 H, CH_2), 3.68 (s, 3 H, $COOCH_3$), 7.04 (br s, 1 H, H_3), 7.11–7.92 (m, 4 H, Ar). Anal. Calcd for $C_{12}H_{12}O_2S$: C, 65.43; H, 5.49; S, 14.55. Found: C, 65.36; H, 5.51; S, 14.33.

3-(2-Benzo[*b*]thienyl)propanol (27). Reduction of the ester **26** with lithium aluminum hydride in anhydrous ether gave the alcohol **27** in almost quantitative yield. The crude product was crystallized from carbon tetrachloride, giving **27** as white plates: mp 50–51.5 °C (lit.[22] 50 °C); NMR δ 1.92 (q, 2 H, CH_2), 2.70 (s, 1 H, OH), 2.96 (t, 2 H, CH_2), 3.66 (t, 2 H, CH_2), 7.01 (br s, 1 H, H_3), 7.06–7.92 (m, 4 H, Ar). Anal. Calcd for $C_{11}H_{12}OS$: C, 68.72; H, 6.29; S, 16.67. Found: C, 69.01; H, 6.25; S, 16.36.

3-(2-Benzo[*b*]thienyl)propyl Phenylpropiolate (18). To a stirred solution of freshly distilled phenylpropiolyl chloride[23] (3.62 g, 22 mmol) in 50 mL of benzene at 0 °C was added anhydrous pyridine (2.75 g, 34.8 mmol). Instantaneously a yellow precipitate was obtained which almost completely disappeared upon adding dropwise a solution of the above alcohol **27** (3.84 g, 20 mmol) in 30 mL of benzene. The resulting mixture was stirred for 2 h at 55 °C and kept overnight at room temperature. The reaction was poured into 200 mL of water. After extraction with benzene, the organic layers were respectively washed with a 1 N hydrochloric acid solution, saturated sodium bicarbonate, and water and dried over magnesium sulfate. The solvent was removed and the residual oil was chromatographed over Florisil (100–200 mesh) with carbon tetrachloride/benzene (4:1) as eluent. The white material eluted was crystallized from methanol, giving **18** as white needles in 85% yield: mp 73–75 °C; NMR δ 2.12 (q, 2 H, CH_2), 3.01 (t, 2 H, CH_2), 4.32 (t, 2 H, CH_2), 7.06 (br s, 1 H, H_3), 7.10–7.93 (m, 9 H, Ar); UV_{max} 257 nm (log ϵ 4.39). Anal. Calcd for $C_{20}H_{16}O_2S$: C, 74.97; H, 5.03; S, 10.00. Found: C, 74.63; H, 4.98; S, 9.87.

2-(2-Benzo[*b*]thienyl)ethyl Phenylpropiolate (19). Ester **19** was prepared according to the procedure described for **18**, starting with 3.0 g (0.018 mol) of phenylpropiolyl chloride,[23] 1.98 g (0.025 mol) of pyridine, and 2.70 g (0.015 mol) of 2-(2-benzo[*b*]thienyl)ethanol (**24**). After column chromatography the white material eluted was crystallized from methanol, giving **19** as white needles in 95% yield: mp 90–91.5 °C; NMR δ 3.30 (t, 2 H, CH_2), 4.53 (t, 2 H, CH_2), 7.14 (br s, 1 H, H_3), 7.20–7.95 (m, 9 H, Ar); UV_{max} 258 nm (log ϵ 4.39). Anal. Calcd for $C_{19}H_{14}O_2S$: C, 74.48; H, 4.60; S, 10.46. Found: C, 74.27; H, 4.55; S, 10.31.

Photolysis of 2-(3-Benzo[*b*]thienyl)ethyl But-2-ynoate (1). A solution of 210 mg (0.86 mmol) of **1** and about 24 mg (0.2 mmol) of acetophenone in 400 mL of benzene was irradiated in an immersion well apparatus for 8 h. After evaporation of the solvent the results of six consecutive runs were combined and purified by column chromatography over Florisil. With 250 mL of CCl_4 and 250 mL of CCl_4/CH_2Cl_2 (6:1) as eluent the acetophenone and 90 mg (7%) of the starting material was obtained. Further elution with CCl_4/CH_2Cl_2 mixtures of increasing ratio as eluent gave 470 mg of **3**. Finally, elution with CH_2Cl_2 gave a fraction which contained 52 mg of **3** and 28 mg of **2**. This fraction was further purified by TLC using C_6H_6/CH_2Cl_2 (1:1) as eluent to give 20 mg of almost pure **2**.

4a,9a-(1-Methyletheno)-1*H*-3,4-dihydro[1]benzothieno-[2,3-*c*]pyran-1-one (3): yield, 522 mg (42%); mp 97–98 °C (pale yellow plates from methanol); NMR δ 1.86 (d, 3 H, CH_3, $J \sim 1.6$ Hz), 2.17–2.38 (m, 2 H, CH_2), 4.43–4.64 (m, 2 H, CH_2), 6.10 (q, 1 H, H_{allyl}, $J \sim 1.6$ Hz), 7.19 (br s, 4 H, Ar); UV_{max} 247 nm (log ϵ 3.80), 285–287 (3.17); IR (KBr) 1635 cm^{-1} (C=C), 1720, 1725 (C=O); mass spectrum *m/e* (relative intensity) 244 (84), 204 (100), 184 (18), 174 (58), 146 (35). Anal. Calcd for $C_{14}H_{12}O_2S$: C, 68.82; H, 4.95; S, 13.12. Found: C, 68.79; H, 4.96; S, 13.06.

No reaction of **3** was observed upon irradiation of 175 mg of **3** and about 20 mg of acetophenone in 400 mL of benzene for 21 h in a Rayonet reactor with 300-nm lamps. No rearranged products could be detected by NMR analysis. The same result was obtained if no sensitizer was added.

6-Methyl-9-oxa-4-thia-2,3-benzotricyclo[5.4.0.$0^{1,5}$]undeca-2,6-dien-8-one (2): 28 mg (2%); NMR δ 2.03 (d, 3 H, CH_3, $J \sim 1.2$ Hz), 2.42–2.63 (m, 2 H, CH_2), 4.40–4.88 (m, 2 H, CH_2), 4.42 (d, 1 H, methine, $J \sim 1.2$ Hz), 7.12 (br s, 4 H, Ar); mass spectrum *m/e* 244.

Upon irradiation of a solution of 20 mg of **2** in 15 mL of benzene for 5 h in a Rayonet reactor with 300-nm lamps, compound **2** was completely converted into the lactone **3**, as shown by NMR analysis.

A solution of 230 mg (0.94 mmol) of **1** in 400 mL of benzene was irradiated in an immersion well apparatus for 9 h. After evaporation of the solvent, the residue was passed through a Florisil column with CH_2Cl_2 as eluent in order to remove polymeric materials. NMR analysis of the eluate showed the presence of both **2** and **3** in about a 1:3 ratio at a <10% conversion.

Pyrolysis of 3 into 1*H*-3,4-Dihydro[1]benzothieno[2,3-*c*]-pyran-1-one (4). Pyrolysis of 148 mg of **3**, preheated to 120 °C, was conducted in the gas phase in a flow system by passing the vapor through a quartz tube packed with quartz chips at 720 °C (7×10^{-5} Torr). No reaction occurred below 640 °C. The resultant crude pyrolysate was collected at −195 °C, and almost pure **4** was scraped off the walls of the collector. NMR analysis of the crude pyrolysate revealed the presence of **4** (70%) and **3** (20%). Recrystallization from carbon tetrachloride gave white crystals of **4**: mp 172–173 °C; NMR δ 3.20 (t, 2 H, CH_2), 4.76 (t, 2 H, CH_2), 7.40–8.10 (m, 4 H, Ar); IR 1705 cm^{-1} (C=O), mass spectrum *m/e* (rel intensity) 204 (100), 174 (79), 146 (93). Anal. Calcd for $C_{11}H_8O_2S$: C, 64.68; H, 3.95; S, 15.70. Found: C, 64.40; H, 3.85; S, 15.61.

Photolysis of 2-(2-Benzo[*b*]thienyl)ethyl But-2-ynoate (5).

A solution of 250 mg (1.02 mmol) of **5** and 83 mg (0.69 mmol) of acetophenone in 400 mL of benzene was irradiated in an immersion well apparatus for 23 h. After evaporation of the solvent, the residue of three consecutive runs was passed through a Florisil column. Elution with CCl_4/CH_2Cl_2 (9:1) gave 76 mg (10%) of **5**, followed by the acetophenone. Further elution with CCl_4/CH_2Cl_2 (1:1), and finally with CCl_4/CH_2Cl_2 (1:3), gave 120 mg (15%) of crude **11 (10)**. Compound **11 (10)** was further purified by TLC using ether/petroleum ether (1:4) as eluent. Analytically pure **11 (10)** was obtained by crystallization from hexane: mp 98–101 °C; NMR δ 3.07 (s, 3 H, CH_3), 3.16 (t, 2 H, CH_2), 4.49 (t, 2 H, CH_2), 7.5–7.9 (m, 4 H, Ar), 8.16–8.30 (m, 1 H, Ar); IR (KBr) 1725 cm^{-1} (C=O); mass spectrum *m/e* (rel intensity) 212 (100), 197 (16), 182 (51), 169 (22), 154 (38), 153 (41), 152 (29).

Reduction of **11 (10)** with $LiAlH_4$ gave **13 (12)**: mp 103–105 °C; NMR δ 2.74 (s, 3 H, CH_3), 3.07 (t, 2 H, CH_2), 3.88 (t, 2 H, CH_2), 4.84 (s, 2 H, CH_2), two low-field one-proton multiplets in the aromatic region are present, centered at δ 8.01 and 7.74.

Photoaddition of Methyl Phenylpropiolate to 2-Methylbenzo[*b*]thiophene. Consecutively, six solutions of 512 mg (3.2 mmol) of methyl phenylpropiolate, 474 mg (3.21 mmol) of 2-methylbenzo[*b*]thiophene, and 105 mg (0.58 mmol) of benzophenone in 400 mL of benzene were irradiated in a Rayonet RPR-100 reactor fitted with 350-nm fluorescence lamps for 17–21 h. NMR analysis of the crude reaction mixtures revealed a conversion of 30–40% of the 2-methylbenzo[*b*]thiophene. After evaporation of the solvent the residues were combined and purified by column chromatography over Al_2O_3. With CCl_4 as eluent 1.65 g (58%) of 2-methylbenzo[*b*]thiophene was recovered. Further elution with CCl_4/CH_2Cl_2 mixtures of increasing ratio gave fractions of the photocycloaddition products. Each fraction was purified by TLC using ether/petroleum ether (1:19) as eluent. Thus, all four possible photocycloadducts of methyl phenylpropiolate to 2-methylbenzo[*b*]thiophene could be isolated. Unfortunately, the compounds **14, 15,** and **17** could only be obtained mixed with some 1-carbomethoxy-8-phenylcyclooctatetraene.

7-Carbomethoxy-1-methyl-6-phenyl-2-thiabenzo[*b*]bicyclo[3.2.0]hepta-3,6-diene (14): yield ~1%; NMR δ 1.90 (s, 3 H, CH_3), 3.87 (s, 3 H, $COOCH_3$), 4.65 (s, 1 H, H_5, methine); mass spectrum *m/e* 308, 148 (100).

Upon irradiation of a solution of ~25 mg of **14** in 50 mL of benzene at 300 nm for 21 h, compound **16** was obtained, determined by NMR analysis.

6-Carbomethoxy-1-methyl-7-phenyl-2-thiabenzo[*b*]bicyclo[3.2.0]hepta-3,6-diene (15): yield ~3%; mixed with some **14;** NMR δ 1.94 (s, 3 H, CH_3), 3.84 (s, 3 H, $COOCH_3$), 4.42 (s, 1 H, H_5 methine); mass spectrum *m/e* 308, 148 (100).

Upon irradiation of a solution of ~25 mg of **15** in 50 mL of benzene at 300 nm for 22 h, compound **17** was obtained, determined by NMR analysis.

7-Carbomethoxy-6-methyl-1-phenyl-2-thiabenzo[*b*]bicyclo[3.2.0]hepta-3,6-diene (16): yield ~20%; mp 108–109 °C (from methanol); NMR δ 2.10 (d, 3 H, CH_3, $J \sim 1.4$ Hz), 3.80 (s, 3 H, $COOCH_3$), 4.32 (q, 1 H, H_5 methine, $J \sim 1.2$ Hz), 7.10–7.75 (m, 9 H, Ar); mass spectrum *m/e* (rel intensity) 308 (100), 276 (59, $M^+ - S$), 249 (73, $M^+ - COOCH_3$), 248 (70), 234 (64), 215 (57), 210 (61). Anal. Calcd for $C_{19}H_{16}O_2S$: C, 74.00; H, 5.23; S, 10.40. Found: C, 74.01; H, 5.23; S, 10.44.

Compound **16** appeared to be photostable on irradiation of a solution of 50 mg of **16** in 50 mL of benzene for 24 h at 300 nm. Also, no traces of the isomers **14, 15,** or **17** could be detected when a solution of 50 mg of **16** in 50 mL of benzene was irradiated at 350 nm for 22 h in the presence of 50 mg of benzophenone.

1-Carbomethoxy-6-methyl-7-phenyl-2-thiabenzo[*b*]bicyclo[3.2.0]hepta-3,6-diene (17): yield ~10%; NMR δ 2.07 (d, 3 H, CH_3, $J = 1.4$ Hz), 3.78 (s, 3 H, $COOCH_3$), 4.78 (q, 1 H, H_5 methine, $J \sim 1.2$ Hz); mass spectrum showed major fragmentation peak at *m/e* 192.

Compound **17** appeared to be photostable on irradiation of a solution of **17** in benzene for 24 h at 300 nm. No isomers could be detected by TLC or NMR analysis.

Photolysis of 3-(2-Benzo[*b*]thienyl)propyl Phenylpropiolate (18). A solution of 250 mg (0.78 mmol) of **18** in 400 mL of benzene was irradiated in an immersion well apparatus for 20 h. After evaporation of the solvent the results of two consecutive runs were combined and purified by column chromatography over Florisil. With $CCl_4/CHCl_3$ (9:1) as eluent, 60 mg (14%) of **18** was obtained. Further elution with $CCl_4/CHCl_3$ (1:1) gave 298 mg (48%) of **3-(2-benzo[*b*]thienyl)propyl 5-phenyltetracyclo[3.3.0.$0^{2,4}$.$0^{3,6}$]oct-7-ene-4-carboxylate (20).** Further purification of **20** was done by TLC using benzene/$CHCl_3$ (1:1) as eluent: NMR δ 1.90 (m, 2 H, CH_2), 2.75 (t, 2 H, CH_2), 2.98 (t, 2 H, H′$_2$ and H′$_3$), 3.92 (m, 2 H, H′$_1$ and H′$_6$), 4.12 (t, 2 H, CH_2), 6.12 (t, 2 H, H′$_7$ and H′$_8$), 6.93 (br s, 1 H, H_3), 7.29–7.95 (m, 9 H, Ar) with a singlet (5 H, Ph) centered at δ 7.28. Anal. Calcd for $C_{26}H_{22}O_2S$: C, 78.36; H, 5.56; S, 8.04. Found: C, 78.40; H, 5.68; S, 7.85.

Chemical structure proof was obtained by reducing the ester **20** with lithium aluminum hydride, giving the alcohols **27** and 4-hydroxymethyl-5-phenyltetracyclo[3.3.0.$0^{2,4}$.$0^{3,6}$]oct-7-ene[12] with the same spectroscopic properties. The ester **20** (460 mg) was also saponified in a solution of 10 mL of 20% KOH solution and 50 mL of dioxane at 85 °C for 14 h. The reaction mixture was poured into water, neutralized, and extracted with ether. The combined ether extracts were dried and treated with an ethereal diazomethane solution. After workup as described for **25,** the residual oil was separated by TLC, using benzene/CH_2Cl_2 (1:1) as eluent. The top band showed the presence of methyl 5-phenyltetracyclo[3.3.0.$0^{2,4}$.$0^{3,6}$]oct-7-ene-4-carboxylate, contaminated with some 1-phenyl-8-carboxymethylcyclooctatetraene, which thermally arose during the saponification.[12]

Actually, the yield of **20** during the photolysis is much higher because addition products of **18** to **20** were also obtained. However, neither an intramolecular cycloadduct nor a cyclooctatetraene adduct could be detected.

The same result was observed when **18,** under the same conditions, was irradiated in the presence of 50 mg (0.41 mmol) of acetophenone.

Photolysis of 2-(2-Benzo[*b*]thienyl)ethyl Phenylpropiolate (19). A solution of 250 mg (0.82 mmol) of **19** in 400 mL of benzene was irradiated in an immersion well apparatus for 20 h. After evaporation of the solvent the results of two consecutive runs were combined and purified by column chromatography over Florisil. With CCl_4/CH_2Cl_2 mixtures of increasing ratio were eluted 105 mg (21%) of **19** and 120 mg (19%) of **21.** Further purification by TLC using benzene/$CHCl_3$ (1:1) as eluent gave pure **2-(2-benzo[*b*]thienyl)ethyl 5-phenyltetracyclo[3.3.0.$0^{2,4}$.$0^{3,6}$]oct-7-ene-4-carboxylate (21):** NMR δ 3.03 (t, 2 H, H′$_2$ and H$_3$′), 3.11 (m, 2 H, H′$_1$ and H′$_6$), 4.46 (t, 2 H, CH_2), 6.11 (t, 2 H, H′$_7$ and H′$_8$), 6.93 (br s, 1 H, H_3), 7.15–7.91 (m, 9 H, Ar) with a sharp singlet (5 H, pH) centered at δ 7.25. Anal. Calcd for $C_{25}H_{20}O_2S$: C, 78.10; H, 5.24; S, 8.34. Found: C, 78.11; H, 5.17; S, 8.17. Chemical degradation as described for **20** proved the assigned structure of **21.**

Further elution gave 76 mg (15%) of a monomeric compound [NMR δ 2.48 (t, 2 H, CH_2), 4.54 (t, 2 H, CH_2), 4.88 (br s, 1 H); mass spectrum *m/e* 306, 274] to which we assigned the structure of **23** (vide supra). A pure sample could not be obtained. In the fractions eluted with CH_2Cl_2 addition products of **19** to **21** were shown to be present.

Upon irradiation of **19** under the same conditions in the presence of 50 mg (0.41 mmol) of acetophenone, 250 mg (40%) of **21** was isolated in addition to 65 mg (13%) of starting material **19.** Furthermore, a trace of **23** could be detected besides dimeric compounds. No cyclooctatetraene adducts could be observed on irradiation with or without sensitizer.

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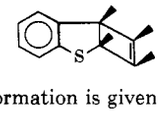
Registry No.—**1,** 65942-59-8; **2,** 65942-60-1; **3,** 65942-61-2; **4,** 65942-62-3; **5,** 65942-63-4; **6,** 65942-64-5; **7,** 65942-65-6; **11,** 65942-66-7; **13,** 65942-67-8; **14,** 65942-68-9; **15,** 65942-69-0; **16,** 31739-35-2; **17,** 31739-36-3; **18,** 56942-70-3; **19,** 65942-71-4; **20,** 65942-72-5; **21,** 65942-73-6; **23,** 65942-74-7; **24,** 30962-69-7; **25,** 65942-75-8; **26,** 65942-76-9; **27,** 31909-05-4; benzo[*b*]thiophene, 95-15-8; 2-butynoic acid, 590-93-2; 2-(3-benzo[*b*]thienyl)ethanol, 3133-87-7; β-(2-benzo[*b*]thienyl)acrylic acid, 25050-08-2; phenylpropiolyl chloride, 7299-58-3; methyl phenylpropiolate, 4891-38-7; 2-methylbenzo[*b*]thiophene, 1195-14-8.

Supplementary Material Available: Full NMR data for all known compounds of the general structure



(2 pages). Ordering information is given on any current masthead page.

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Bis(trifluoromethyl)thioketene. 3. Further Cycloadditions

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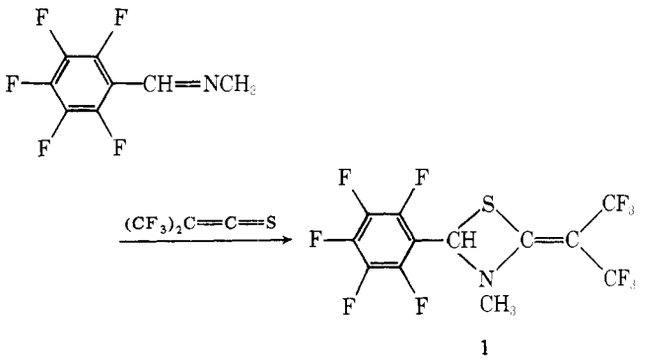
Bis(trifluoromethyl)thioketene cycloadds to Schiff bases to form thiazetidines and 1,3,5-dithiazines. Three moles of the thioketene adds to methyl isothiocyanate in a similar reaction. The thioketene adds to aryl azides to yield Δ^3-1,2,3,4-thiatriazolines which can be pyrolyzed to 2,1-benzisothiazoles. With phosphite esters, the thioketene forms phosphoranylidene-1,3-dithiolanes which hydrolyze to phosphonates. From certain methylbenzenes, substituted 1-phenethyl-3-hexafluoroisopropylidene-1,3-dithietanes are obtained. Novel heterocycles have been made by Diels–Alder reactions. Thiothiophthene forms adducts with 2 and 4 mol of the thioketene.

Previous articles have described the synthesis,[2a] cycloadditions,[2a] and acyclic derivatives[2b] of bis(trifluoromethyl)thioketene. The versatility of the thioketene as a reactant in a variety of cycloadditions is now further illustrated by its reaction with Schiff bases, aryl azides, phosphite esters, methylbenzenes, dienes, and thiothiophthene.

Cycloaddition to Schiff Bases. Both mono- and diadducts of bis(trifluoromethyl)thioketene with Schiff bases have been obtained. With *N*-(pentafluorobenzylidene)methylamine a 1,3-thiazetidine **1** is formed by a cycloaddition involving the thiocarbonyl group.

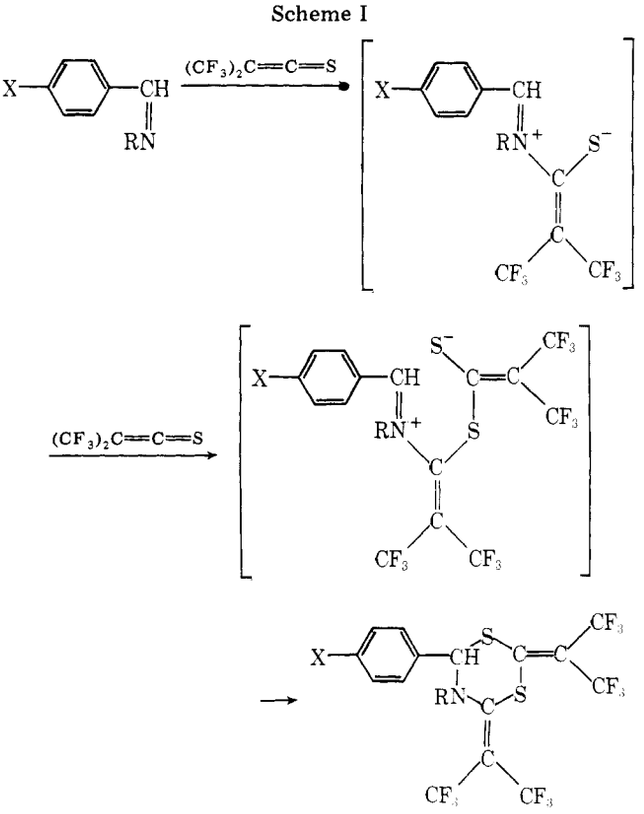


1

The structure was derived from IR and NMR data, with H–F and F–F couplings, as given in the Experimental Section. The mode of addition is analogous to the 1:1 reaction of the thioketene with carbodiimides to form 1,3-thiazetidines.[2a]

With ordinary arylideneamines, the reaction takes a different course and does not stop at the 1:1 stage even in the presence of excess Schiff base. Two molecules of the thioketene participate to form the 1,3,5-dithiazines **2** (Scheme I).

Scheme I



2a, X = H; R = CH_3
b, X = H; R = *i*-Pr
c, X = Cl; R = CH_3
d, X = O_2N; R = CH_3
e, X = CH_3O; R = *p*-$CH_3OC_6H_4$

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