Photochemistry of Benzo[b]thiophenes Addition of Acetylenes

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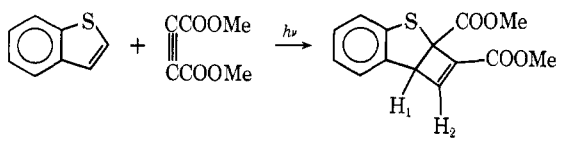
The photochemical addition of dimethyl acetylenedicarboxylate, methyl propiolate, and methyl phenylpropiolate to benzo[b]thiophene leads to cyclobutene derivatives of unexpected structure. Methyl propiolate adds in a direction opposite to the direction of methyl phenylpropiolate suggesting that the excited state of benzo[b]thiophene is highly polarized. The cyclobutenes formed are thermally unstable and rearrange, with loss of sulfur, to naphthalenes.

Photochemical addition reactions of acetylenes to aromatic compounds have been studied as possible routes to cyclobutadienes.[2-12] Addition reactions involving heteroaromatic compounds and acetylenes, though reported less frequently, are similarly attractive as routes to substituted cyclobutadienes. We have studied the addition of acetylene derivatives to the naphthalene-like heterocycle benzo[b]thiophene[13] and report the addition of several acetylenes to this heterocycle and some of its alkylated derivatives.

Results

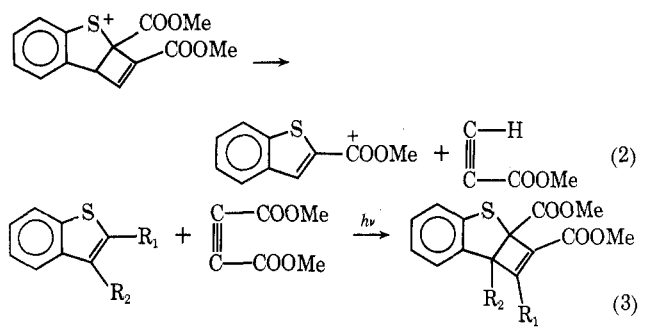
Direct and photosensitized addition of dimethyl acetylenedicarboxylate to benzo[b]thiophene leads to the formation of a cyclobutene derivative in 51% yield (eq 1). The nmr spectrum of the adduct (Table I) confirms that the structure of the product is I,



(1)

I

in that protons 1 and 2 are weakly coupled doublets ($J_{1,2} < 1$ Hz), an observation characteristic of vinyl and allylic protons in cyclobutenes.[14,15] The mass spectra of similar compounds allow us to predict retrocleavage in a direction such that the benzo[b]-thiophene nucleus would remain as a major peak (Table II).[16] Thus, the peak height of fragment II (*m/e* 192) represents 90% of the parent peak (eq 2). Similar additions (eq 3) are observed with 2-methylbenzo[b]-thiophene, 2,3-dimethylbenzo[b]thiophene, and 3-methylbenzo[b]thiophene. The nmr spectra of these



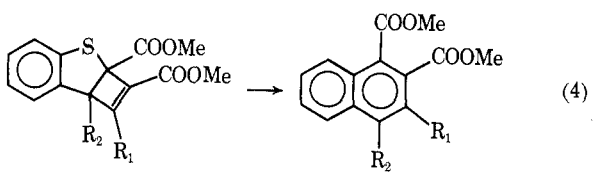
(2)

(3)

III, R_1 = Me; R_2 = H
IV, R_1 = H; R_2 = Me
V, R_1 = Me; R_2 = Me

adducts (Table I) and mass spectra (Table II) are consistent with the assigned structures.

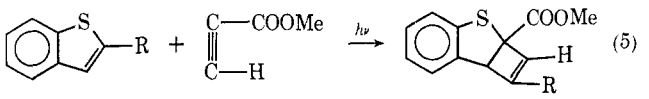
Cyclobutene adducts prepared from dimethyl acetylenedicarboxylate and alkyl benzo[b]thiophenes are thermally unstable. These adducts rearrange to naphthalene derivatives (eq 4) *via* a sulfur extrusion process.[17]



(4)

XX, $R_1 = R_2$ = H
XXI, R_1 = H; R_2 = Me
XXII, R_1 = Me; R_2 = Me

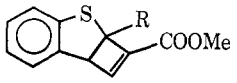
Sensitized addition of methyl propiolate (eq 5) to benzo[b]thiophene derivatives proceeds similarly.



(5)

VI, R = H
VII, R = Me

Yields are as high as 33% when benzo[b]thiophene is used. In all cases additions of methyl propiolate appeared slower than similar additions of dimethyl acetylenedicarboxylate. The addition of methyl propiolate is highly selective and the vapor phase chromatogram of the crude reaction mixture shows only a few per cent of stereoisomers of VI and VII which are VIII



VIII, R = H
IX, R = Me

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(2) D. Bryce-Smith, A. Gilbert, and J. Grzonka, *Chem. Commun.*, 498 (1970).

(3) D. Bryce-Smith, A. Gilbert, and B. H. Orger, *ibid.*, 512 (1966).

(4) D. Bryce-Smith and J. E. Lodge, *Proc. Chem. Soc.*, 333 (1961).

(5) D. Bryce-Smith and J. E. Lodge, *J. Chem. Soc.*, 695 (1963).

(6) J. C. Atkinson, D. E. Ayer, G. Büchi, and E. W. Robb, *J. Amer. Chem. Soc.*, **85**, 2257 (1963).

(7) W. H. F. Sasse, P. J. Collin, and G. Sugowdz, *Tetrahedron. Lett.*, 3373 (1965).

(8) P. J. Collin and W. H. F. Sasse, *ibid.*, 1689 (1968).

(9) W. H. Sasse, *Aust. J. Chem.*, **6**, 1257 (1969).

(10) R. J. McDonald and B. K. Selinger, *Tetrahedron Lett.*, 4791 (1968).

(11) E. H. White and R. L. Stern, *ibid.*, 193 (1964).

(12) R. M. Bowman and J. J. McCullough, *Can. J. Chem.*, **47**, 4503 (1969).

(13) D. C. Neckers, J. H. Dopper, and H. Wynberg, *Tetrahedron Lett.*, 2913 (1969).

(14) E. A. Hill and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 2047 (1967).

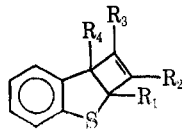
(15) L. Paquette, and W. C. Farley, *J. Org. Chem.*, **32**, 2725 (1967).

(16) D. C. Neckers, J. H. Dopper, and H. Wynberg, *ibid.*, **35**, 1582 (1970).

(17) H. Hofmann, H. Westernacher, and H. J. Haberstroh, *Chem. Ber.*, **102**, 2592 (1969).

TABLE I

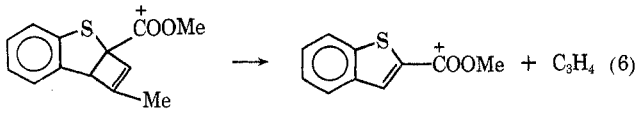
NMR SPECTRA OF SUBSTITUTED CYCLOBUTENE SYSTEMS[a]



Compd	H_5–H_8	R_1	R_2	R_3	R_4
I		COOMe	COOMe	H	H
	7.05 s	3.72 s	3.76 s	6.78 d	4.69 d
	4 H	3 H	3 H	1 H	1 H.
				$J_{3,4}$ <1.0 Hz	
IV		COOMe	COOMe	H	CH_3
	7.11 s	3.76 s	3.80 s	6.76 s	1.58 s
	4 H	3 H	3 H	1 H	3 H
III		COOMe	COOMe	CH_3	H
	7.06 s	3.76 s	3.80 s	1.95 s	4.68 s
	4 H	3 H	3 H	3 H	1 H
V		COOMe	COOMe	CH_3	CH_3
	7.12 s	3.76 s	3.80 s	1.95 s	1.58 s
		3 H	3 H	3 H	3 H
VI		COOMe	H	H	H
	7.09 s	3.76 s	6.24 d	6.19 d	4.87 s
			$H_{2,3}$ AB system	$J_{2,3}$ = 1.8 Hz	
	4 H	3 H	1 H	1 H	1 H
VII		COOMe	H	CH_3	H
	7.14 s	3.76 s	5.92 q	1.75 d	4.74 br s
			$J_{2,3}$ <1 Hz		
	4 H	3 H	1 H	3 H	1 H
XI		Phenyl	COOMe	CH_3	H
	7.0–7.1	7.0–7.6 m	3.78 s	2.07 d	4.19 q
					$J_{3,4}$ = 1.4 Hz
	(9 H)		3 H	3 H	1 H
XIII		COOMe	Phenyl	CH_3	H
	7.0–7.1	3.76 s	7.0–7.6 m	1.87 d	4.52 q
					$J_{3,4}$ <1 Hz
	4 H	3 H	5 H	3 H	1 H
X		Phenyl	COOMe	H	H
	7.07 s	7.1–7.6 m	3.69 s	6.66 d	4.28 d
					$J_{3,4}$ = 1 Hz
	(9 H)		3 H	1 H	1 H
XV		H	H	Cl	H
	7.04 s	4.81 d	6.00 s		4.59 d
		H_1 and H_4	AB doublet		$J_{1,4}$ = 4 Hz
	4 H	1 H	1 H		1 H
XVI		CH_3	H	Cl	H
	7.07 s	1.78 s	5.89 s		4.09 s
	4 H	3 H	1 H		1 H
XVII		CH_3	Cl	H	H
	7.06 s	1.78 s		6.01 d	4.22 d
					$J_{3,4}$ = 1.5 Hz
	4 H	3 H		1 H	1 H
XVIII		H	H	Cl	CH_3
	7.03 s	4.36 s	6.00 s		1.68 s
	4 H	1 H	1 H		3 H

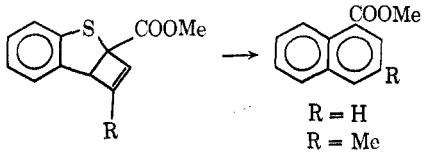
[a] All data in ppm, δ scale, s = singlet, d = doublet, m = multiplet, q = quartet, br = broad.

and IX. The nmr spectrum of VI (Table I) shows an AB quartet between the vinyl protons and a very weak coupling between vinyl and allylic protons. The predominant mass spectral fragment, *m/e* 192, is proof of the derived structure (eq 6).



(6)

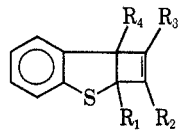
Chemical proof for the structure of the products VI and VII again derives from the thermal rearrangement of the products. Thus, at 240° (2 min), rearrangement takes place (eq 7) to the corresponding naphthalene



(7)

ester. The derived product from VI has an identical infrared spectrum with that of α-naphthoic acid methyl ester.

TABLE II
MASS SPECTRAL DATA



I, $R_1 = R_2 = CO_2CH_3$; $R_3 = R_4 = H$

$M^+ = 276$		90%
M − 31 = 245	$-OCH_3$	65%
M − 32 = 244	−S	100%
M − 59 = 217	$-CO_2CH_3$	40%
M − 84 = 192	$-HC{\equiv}CCO_2Me$	90%
M − 142 = 134	$-H_3CO_2C{\equiv}CCO_2CH_3$	25%

IV, $R_1 = R_2 = CO_2CH_3$; $R_3 = H$; $R_4 = CH_3$

$M^+ = 290$		95%
M − 31 = 259	$-OCH_3$	30%
M − 32 = 258	−S	100%
M − 59 = 231	$-CO_2CH_3$	25%
M − 84 = 206	$-HC{\equiv}CCO_2Me$	85%
M − 142 = 148	$-CH_3O_2CC{\equiv}CCO_2CH_3$	14%

V, $R_1 = R_2 = CO_2Me$; $R_3 = R_4 = CH_3$

$M^+ = 304$		100%
M − 31 = 273	$-OCH_3$	50%
M − 32 = 272	−S	60%
M − 59 = 245	$-CO_2CH_3$	85%
M − 98 = 206	$-CH_3C{\equiv}CCO_2Me$	65%
M − 142 = 162	$-CH_3O_2CC{\equiv}CCO_2Me$	50%

VII, R_1 = COOMe; $R_3 = CH_3$; $R_2 = R_4 = H$

$M^+ = 232$		100%
M − 31 = 201	$-OCH_3$	40%
M − 32 = 200	−S	60%
M − 40 = 192	$-C_3H_4$	50%
M − 59 = 173	$-CO_2CH_3$	45%
M − 71 = 161	$-C_3H_4$–OCH_3	50%
M − 84 = 148	$-HC{\equiv}CCO_2CH_3$	15%

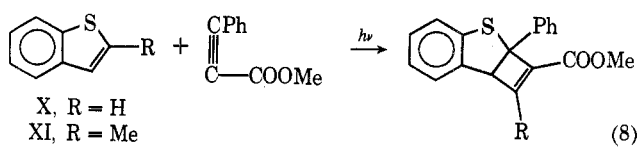
XI, R_1 = Ph; R_2 = CO_2Me; $R_3 = CH_3$; $R_4 = H$

$M^+ = 308$		45%
M − 31 = 277	$-OCH_3$	13%
M − 32 = 278	−S	16%
M − 59 = 249	$-CO_2CH_3$	21%
M − 63 = 245		8%
M − 74 = 234		20%
M − 98 = 210		25%
M − 116 = 192		60%

XIV, $R_1 = R_4 = H$; $R_2 = R_3$ = Ph

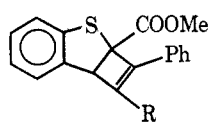
$M^+ = 312$		45%
M − 32 = 280	−S	60%
M − 102 = 210	$-HC{\equiv}CPh$	10%
M − 134 = 178		100%
M − 178 = 134	$-PhC{\equiv}CPh$	50%

Additions of methyl phenylpropiolate to benzo[b]-thiophene (eq 8) give a 52% yield of an adduct to which



X, R = H
XI, R = Me (8)

we assign the structure shown. The reaction is directionally selective and only a few per cent of the other possible isomers, XII and XIII, can be detected. The

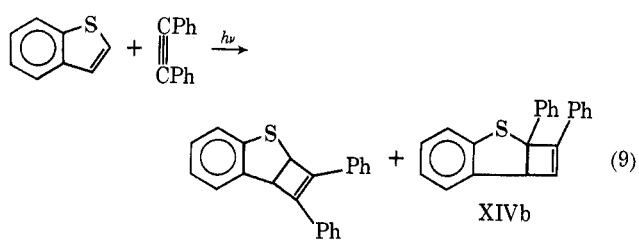


XII, R = H
XIII, R = Me

selectivity is greater in additions to benzo[b]thiophene than it is to 2-methylbenzo[b]thiophene. As before, all adducts rearrange to the corresponding naphthalenes.

Addition of diphenylacetylene to benzo[b]thiophene is a very slow reaction unless special precautions are taken to remove last traces of oxygen. Dimers of diphenylacetylene are detected among the products of the addition reaction (eq 9).

Removal of last traces of oxygen affords ~30% yield of the rearranged adduct XIVb as reported by Sasse.[18] The efficiency of the photochemical addition of benzo[b]thiophene to diphenylacetylene is dependent on the concentration ratio of benzo[b]thiophene to diphenylacetylene as well. In order to obtain maximum yield of 1:1 adducts, several molar excesses of benzo[b]-thiophene must be used.



XIVa

Although it appeared initially that the ring-opening reaction of fused benzo[b]thiophene cyclobutenes might provide facile entry into the relatively inaccessible benzo[b]thiepin system,[18] we have not succeeded in trapping thiepins in thermal rearrangements of our products. Either the temperature required for ring opening is too high for the thiepin to survive, or the mechanism for the ring opening is nonconcentrated and the thiepins have no existence in our system.

Nevertheless the thermal rearrangement provides a very easy way to prepare highly substituted naphthalenes, some of which are not easily obtained by conventional procedures. The reaction is general, as our earlier work with halocyclobutenes fused to benzo-[b]thiophenes has shown.[16] Overall yields of these reactions approach 75% (see Table III).

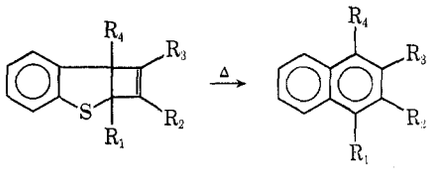
Discussion

The scope of addition reactions to benzo[b]thiophenes is shown by the data in Table IV. This data assumes

(18) W. H. F. Sasse, P. J. Collin, and D. B. Roberts, *Tetrahedron Lett.*, 4791 (1969).

TABLE III

REARRANGEMENT TO NAPHTHALENES



R_1	R_2	R_3	R_4	
CO_2Me	COOMe	H	H	I → XX
COOMe	COOMe	H	CH_3	IV → XXI
COOMe	COOMe	CH_3	CH_3	V → XXII
COOMe	H	H	H	VI → XXIII
COOMe	H	CH_3	H	VII → XXIV
Ph	COOMe	CH_3	H	XI → XXV
Ph	COOMe	H	H	X → XXVI
H	H	Cl	H	XV → XXVII
CH_3	H	Cl	H	XVI → XXVIII

TABLE IV

RATES OF ADDITIONS OF ACETYLENES TO BENZO[b]THIOPHENES

Acetylene AC≡CB	Ease of adduct formation
A = B = COOMe	++++
A = H; B = COOMe	+++
A = Ph; B = COOMe	++++
A = Ph; B = acetyl	+
A = B = Ph	+[a]
A = Ph; B = Me	±
A = B = CH_2Cl	−
A = B = CH_2OMe	−

[a] The addition of diphenylacetylene to benzo[b]thiophene is concentration and oxygen dependent.

that the energy is eventually accepted by the benzo[b]-thiophene so that it is the heteroaromatic compound that is absorbing the light, either directly or by energy transfer.

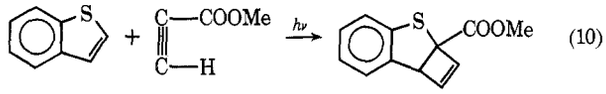
In order for acetylene additions to benzo[b]thiophenes to be efficient, the acetylene must be substituted with strong electron-attracting groups. Further, sensitizers with triplet energies higher than 68.5 kcal/mol increase the efficiency of the additions though sensitizers have no effect on the products.

The ultraviolet spectra of several fused heterocyclic compounds, including benzo[b]thiophene and its 2-methyl derivative, show sharp absorption maxima at wavelengths in the 287–300-nm region. In the case of benzo[b]thiophene the maximum absorption is at 296.5 nm (hexane) (ϵ 4600) while for the 2-methyl derivative the maximum in hexane is at 297.0 nm (ϵ 5400). These maxima shift very slightly to the blue in methanol and have been attributed to n–π^* excitations requiring the nonbonded electrons of the sulfur atom, a result corroborated by the disappearance of these bands in the corresponding benzo[b]thiophene 1,1-dioxide, though there is certainly no consensus that these long wavelength bands derive from n–π^* absorptions.[19]

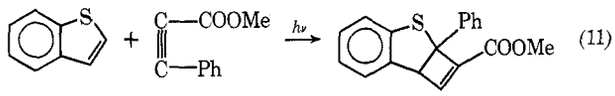
Absorption maxima of dimethyl acetylenedicarboxylate, methyl propiolate, and methyl phenylpropiolate lie below the position of the absorption maxima of the benzo[b]thiophenes and are weaker. In the direct radiation reaction involving these acetylenes most of the light must initially be absorbed by the benzo[b]-thiophene or alkyl derivative. In the sensitized reaction employing benzophenone or acetophenone as the sensitizer, most of the reaction derives from energy transfer from the carbonyl compound to the heteroaromatic compound. Triplet energy levels of the acetylene esters are too high to be competitive in the transfer process, since the triplet-state energy of benzo[b]thiophene is 68.9 kcal/mol.[20] Though benzo[b]thiophene fluoresces efficiently, this fluorescence is only weakly quenched by additives which react with the heterocyclic compound.[21]

Charge distribution in the excited benzo[b]thiophene triplet derives from the direction of addition of unsymmetrical acetylenes, methyl propiolate, and methyl phenylpropiolate to benzo[b]thiophene and its 2-methyl derivative.

Sensitized addition of methyl propiolate to benzo[b]-thiophene produces exclusively the adduct with the carboxymethyl group attached to the 2 position of the benzo[b]thiophene nucleus (eq 10). Addition of methyl phenylpropiolate places the phenyl group at the 2 position of the benzo[b]thiophene and the COOMe group ends up on the cyclobutene ring (eq 11).



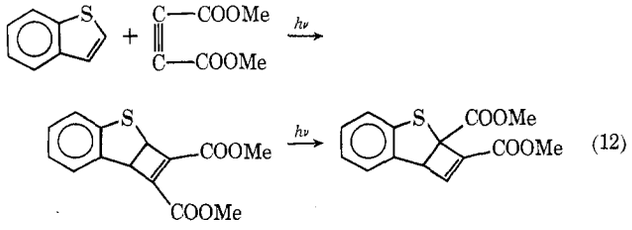
(10)



(11)

From the studies of Huisgen and coworkers[22] it is known that methyl propiolate and methyl phenylpropiolate add dipolar species in opposite directions. A charged excited state of the benzo[b]thiophene might select the carbon of the carbomethoxy group in methyl propiolate while selecting the carbon of the phenyl group in methyl phenylpropiolate, thereby accounting for the observed directional difference in methyl propiolate and methyl phenylpropiolate.

In our first publication describing studies of photochemical addition by dimethyl acetylenedicarboxylate to benzo[b]thiophenes, we suggested that the rearranged product we observed might derive from a 2-quantum process. The initial addition of 1 mol of the acetylene to the benzo[b]thiophene would thereby have to produce a photolabile cyclobutene (eq 12).



(12)

XXIX

There are at least two other mechanisms that could just as well account for the observed rearrangement. Both of these mechanisms involve additions to the sulfur

(19) H. H. Jaffé, and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, p 240.

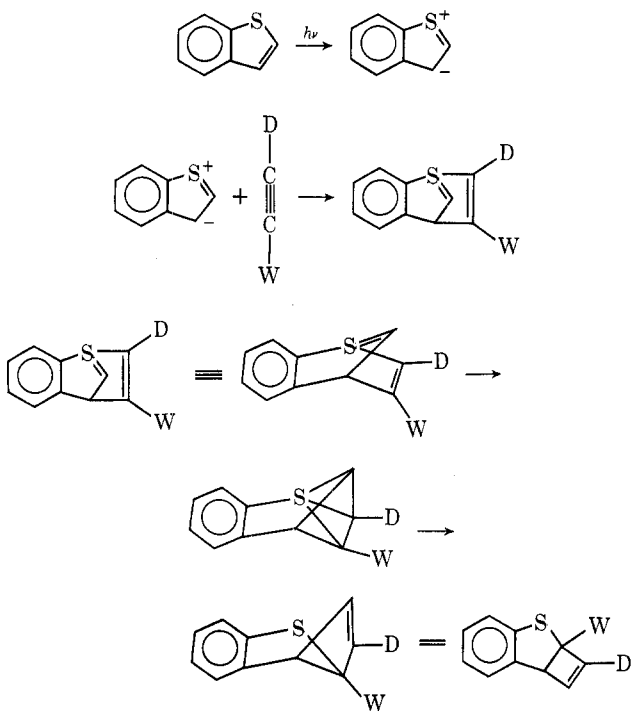
(20) R. C. Heckman, *J. Mol. Spectrosc.*, **2**, 27 (1958).

(21) The peak in the fluorescence spectrum of benzo[b]thiophene at 285 nm appears to be selectively quenched at higher concentrations of benzo[b]-thiophene.

(22) R. Huisgen, H. Golhard, and R. Grashey, *Chem. Ber.*, **101**, 536 (1968).

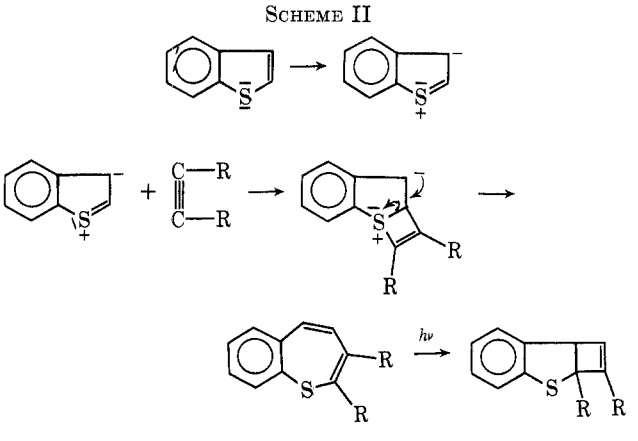
atom. In one mechanism, a 1,3 addition to the sulfur atom and the 3 carbon of the benzo[b]thiophene is the first step followed by bond rearrangement. This mechanism is shown in Scheme I.

SCHEME I



The second possible mechanism involving the sulfur atom requires a 1,2 addition to the sulfur and the 2 carbon of the benzo[b]thiophene. This 1,2-addition mechanism is shown in Scheme II.

SCHEME II



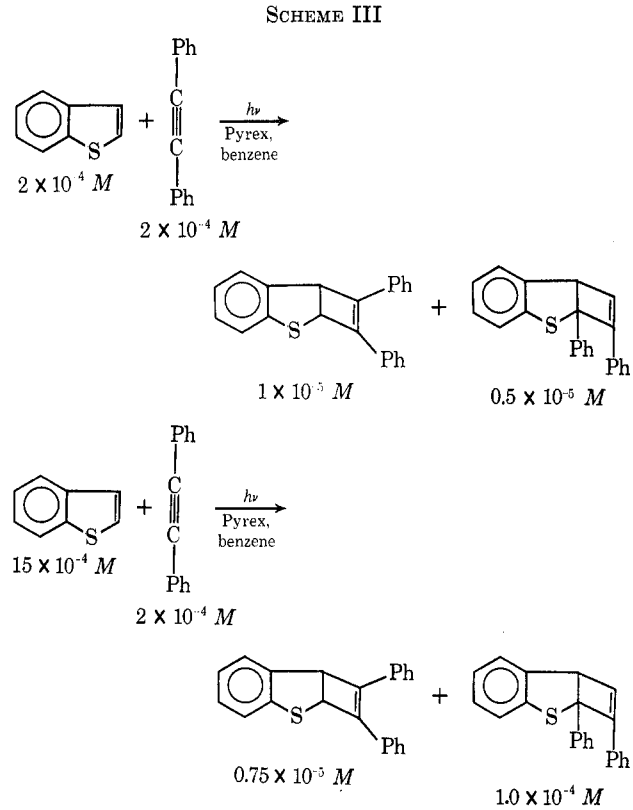
XXX

There are several pieces of information which bear on the question of mechanism, none of which seems all-conclusive, but all of which we list below.

First, in both the 2,3-addition mechanism (eq 12) and the 1,2-addition mechanism (Scheme II), isolable intermediates should be obtained. In the 2,3-addition mechanism, the intermediate should have the structure XXIX (eq 12); *i.e.*, the first formed product should be a cyclobutene with both substituent groups attached to the double bond of the cyclobutene. In the 1,2-cycloaddition process, the product should be a benzo[b]-thiepin, XXX (Scheme II). In no case have we observed either said intermediate even when the additions are carried out to low conversion in a nmr tube, when acetylenes with carbomethoxy groups, -COOMe, are attached. Only in the addition of diphenylacetylene to benzo[b]thiophene[18] have unrearranged adducts been observed.

To our knowledge, diphenylacetylene is the only alkyne from which an unrearranged 1:1 adduct to benzo[b]thiophene can be isolated, (Scheme III). Even

SCHEME III



this adduct accounts, however, for only $^1/_{30}$th of the total adduct yield under the most favorable conditions. Even though this unrearranged adduct can be shown to rearrange to the major isolated adduct, there is compelling evidence which suggests that diphenylacetylene is a special case. This evidence is twofold. First, diphenylacetylene absorbs light in the same region of the spectrum as benzo[b]thiophene and some ten times more strongly.[19] Thus, unless benzo[b]thiophene is in substantial excess, most of the light is absorbed by diphenylacetylene. Second, there is a substantial concentration dependence on the yield of adducts. When solutions which are 1 *M* in benzo[b]-thiophene and 1 *M* in diphenylacetylene are irradiated, both adducts form very slowly and the unrearranged adduct predominates, albeit in very low total yield. As the molar ratio of benzo[b]thiophene is increased, the yield of rearranged adduct grows while the yield of unrearranged adduct decreases slightly for a comparable irradiation time.

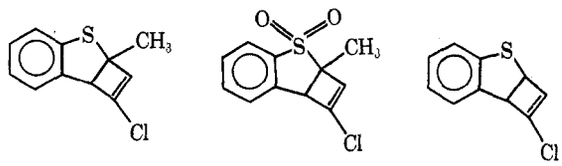
The concentration dependence of benzo[b]thiophene additions to diphenylacetylene suggests that competitive photochemical processes are occurring in this case. One photochemical process, the process producing the unrearranged adduct, involves light absorption and excited-state formation from diphenylacetylene. The other photochemical process, the pro-

cess producing the rearranged adduct, derives from an excited state of the benzo[*b*]thiophene and must be regarded as the normal *modus operandi* in benzo[*b*]-thiophene–alkyne systems.

Second, in both the 2,3-addition mechanism (eq 12) and the 1,2-addition mechanism (Scheme II), a secondary photochemical rearrangement reaction is required to obtain the observed products. We have isolated several related cyclobutenes (Chart I), and,

CHART I

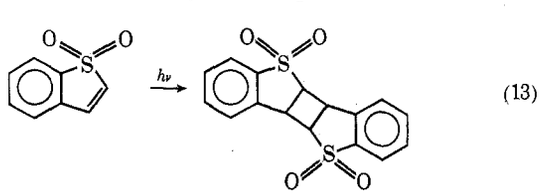
STABLE ADDUCTS OF BENZO[*b*]THIOPHENE



though the models have some significant drawbacks, these compounds are not observed to rearrange under the conditions of our experiments.

The rearrangement of benzo[*b*]thiepins like that proposed in Scheme II has not been observed. Benzo[*b*]-thiepins are rather elusive compounds,[23] and we have not succeeded in isolating them as yet. Nevertheless, their photochemical rearrangement is predicted and has been observed in the corresponding oxepins.[24]

Third, both the 1,3-addition mechanism (Scheme I) and the 1,2-addition mechanism (Scheme II) require the sulfur atom of the benzo[*b*]thiophene to have available unshared electrons. The 2,3-addition mechanism does not. Therefore, it is significant that benzo-[*b*]thiophene 1,1-dioxide fails to add either acetylenes or related derivatives. Instead, benzo[*b*]thiophene 1,1-dioxide undergoes a cinnamic acid type dimerization (eq 13). Other heterocyclic compounds which contain

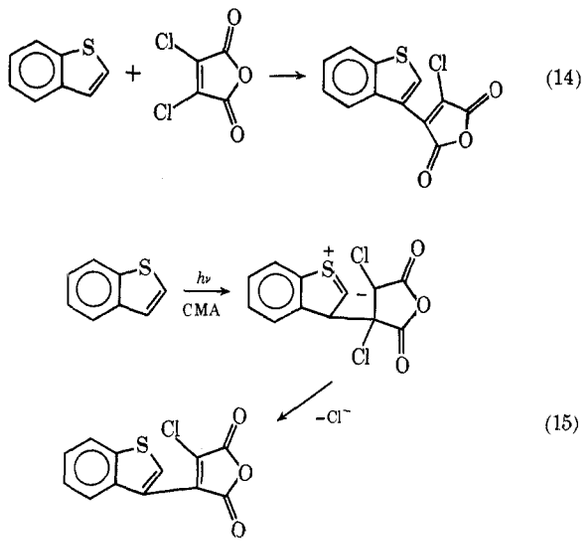


(13)

atoms with a lesser ability to accommodate more than eight electrons than sulfur also undergo just dimerization and do not add acetylenes.[25]

Finally, thermal additions of many acetylene derivatives to a variety of heteroaromatic compounds involve dipolar additions. Thus, dimethyl acetylenedicarboxylate adds to thiazole and benzothiazole *via* a dipolar intermediate.[26]

At this point, we feel that either of the mechanisms involving the sulfur atom, Scheme I or II, probably accounts for the experimental facts better than does the secondary rearrangement mechanism (eq 12). This statement is reinforced by the observation that some reactions of benzo[*b*]thiophene, *e.g.*, the photochemical addition of dichloromaleic anhydride, occur with substitution rather than addition (eq 14). A dipolar mechanism, like that shown (eq 15), accounts for this



(14)

(15)

observation. Experiments are continuing in an effort to isolate the intermediates suggested by the 1,2-dipolar addition mechanism and the 2,3-addition process above.

Examination of the mass spectra of the fused cyclobutene adducts point to the observation that one might at least predict the facile loss of sulfur by the adducts, particularly since the parent peak minus sulfur is significant in all the mass spectra. The cyclobutanes show no tendency to lose sulfur in the same sort of process. Thus, as others as well as ourselves have pointed out before, there is a distinct parallel between thermal, photochemical, and mass spectral fragmentation reactions.[27]

Experimental Section

All melting points are uncorrected. Infrared spectra were taken either in carbon tetrachloride solution or in pure form using a Perkin-Elmer 621. Nmr spectra were taken (10% in CCl_4 or $CDCl_3$) using a Varian A-60 spectrometer. Reference is to tetramethylsilane. Mass spectra were recorded on an A.E.I. MS9 equipped with an A-700 F & M vpc with thermalconductivity detectors. Uv spectra were taken on a Cary 14. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Starting Materials.—Benzo[*b*]thiophene, dimethyl acetylenedicarboxylate, methyl propiolate, diphenylacetylene, phenylacetylene, 1,4-dichlorobutyne-2, dichloromaleic anhydride, hexafluorobutyne-2, benzophenone, and acetophenone were commercial materials purified when necessary by conventional methods. 2-Methylbenzo[*b*]thiophene, 3-methylbenzo[*b*]thiophene, and 2,3-dimethylbenzo[*b*]thiophene were prepared as previously described.[16] 1,4-Dimethoxybutyne-2 was prepared from 1,4-dihydroxybutyne-2.[28] Phenylmethylacetylene was prepared from phenylacetone.[29] 2-Phenyl-1-acetoacetylene was prepared from phenylacetylene.[30] Phenyl methylpropiolate was prepared from phenylpropiolic acid (Aldrich) (nmr phenyl δ 7.18–7.68 (m, OCH_3) and 3.77, ir $\nu_{C\equiv C}$ 2220 (s), $\nu_{C=O}$ 1720 cm^{-1}). Benzo[*b*]thiophene 1,1-dioxide was prepared by oxidation of benzo[*b*]thiophene, with *m*-chloroperbenzoic acid in chloroform,[16] mp 140–141° (lit.[31] mp 142°).

General Irradiation Procedures.—Irradiations were carried out using a Hanau S81 or a Hanovia 450-W medium pressure mercury

(23) H. Hofmann and H. Westernacher, *Chem. Ber.*, **102**, 205 (1969).

(24) See, *e.g.*, L. A. Paquette, "Modern Heterocyclic Chemistry," W. A. Benjamin, New York, N. Y., 1968.

(25) T. H. Barton and coworkers, private communication.

(26) See, *e.g.*, O. Diels and K. Alder, *Justus Liebigs Ann. Chem.*, **498**, 16 (1932); E. Winterfeldt, *Chem. Ber.*, **98**, 3537 (1965); D. H. Reid, F. S. Skelton, and W. Bonthrone, *Tetrahedron. Lett.*, 1797 (1964).

(27) N. J. Turro, D. C. Neckers, *et al.*, *J. Amer. Chem. Soc.*, **87**, 4097 (1965).

(28) G. F. Hennion and F. P. Kuiecki, *J. Org. Chem.*, **18**, 1601 (1953).

(29) C. D. Hurd and A. Tochman, *ibid.*, **23**, 1087 (1958).

(30) J. W. Kroeger and J. A. Nieuwland, *J. Amer. Chem. Soc.*, **58**, 1961 (1936).

(31) E. N. Karaalova, O. Sh. Meilanova, and G. D. Ga'pern, *Dokl. Akad. Nauk SSSR*, **123**, 99 (1958).

arc lamp. All irradiations were carried out using Pyrex filters. The temperature was held at 25°.

Addition of Dimethyl Acetylenedicarboxylate to Benzo[b]thiophene.—Benzo[b]thiophene (3.0 g, 0.22 mol), dimethyl acetylenedicarboxylate (3.5 g, 0.024 mol), and benzophenone (0.5 g, 0.0027 mol) were dissolved in 400 ml of pure benzene and the solution was irradiated for 7 days. The benzene was removed *in vacuo* on a rotating evaporator and vpc analysis (column SE-30, oven temperature 250°) of the crude mixture showed formation of one product in 51% yield. The dimethyl acetylenedicarboxylate and part of the benzo[b]thiophene was distilled *in vacuo*. The orange-colored residue was chromatographed over a silica gel column using CCl_4 as elution agent. With CCl_4, unreacted benzo[b]thiophene eluted. Changing solvents carefully from CCl_4 to $CHCl_3$ separated benzophenone and a little dimethyl acetylenedicarboxylate. Changing from $CHCl_3$ as elution agent to $CHCl_3$–CH_2Cl_2 (1:1) and finally to pure CH_2Cl_2 delivered 2.7 g (45%) of pure product (I) as a bright yellow oil; nmr is in Table I, mass spectrum in Table II. For purposes in which very pure material is required, the adduct can be purified further using preparative thin layer chromatography techniques. On a 20 × 100 cm glass plate a 2-mm layer of silica gel (Merck PF-254) was prepared and activated at 110° for 1 hr. One gram of material was dissolved in 25 ml of CH_2Cl_2 and added carefully to the plate with a 50-ml syringe. The elution was carried out using CH_2Cl_2. The products were removed from the silica gel by extracting for 12 hr with methanol. After removing the MeOH *in vacuo*, the dissolved silica gel was separated from the product by stirring the mixture for 2 hr with $CHCl_3$. After filtration, the solution was dried over sodium sulfate and after filtering, the $CHCl_3$ was removed. After 6 months, the adduct crystallized to a white solid, which could be further purified by washing with pentane. The adduct, mp 79–81°, had λ_{max} at 305 nm (ϵ 1350), 293 (1700), 281 (1750), and 235 (16,700); calcd mol wt[32] for $C_{14}H_{12}O_4S$, 276.0456 (found, 276.0458).

Similar methods were used for the addition of 3-methylbenzo[b]thiophene to dimethyl acetylenedicarboxylate (yield ~40%), [calcd mol wt for $C_{15}H_{14}O_4S$, 290.06128 (found, 290.0613)] and for the other alkylbenzo[b]thiophenes. For example, for the adduct of 2,3-dimethylbenzo[b]thiophene and dimethyl acetylenedicarboxylate, the following data were obtained: mp 89–92°; λ_{max} 308 nm (ϵ 1900) and 229 (23,800). *Anal.* Calcd for $C_{16}H_{16}O_4S$: C, 63.14; H, 5.30; S, 10.54; mol wt, 304.07693. Found: C, 62.80; H, 5.19; S, 10.65; mol wt, 304.0766.

Addition of Methyl Propiolate to Benzo[b]thiophene.—Benzo[b]thiophene (3.5 g, 0.026 mol), methyl propiolate (3 g, 0.035 mol), and acetophenone (0.5 g, 0.0025 mol) were dissolved in 400 ml of benzene and irradiated for 7 days. The benzene and methyl propiolate were removed *in vacuo* on a rotating evaporator and vpc analysis (5-ft Carbowax 20-m, 10%, oven temperature 220°) of the crude mixture showed formation of one product in 33% yield. The acetophenone and part of the benzo[b]thiophene was distilled off *in vacuo*. (Note: One should not use a higher pot temperature than 100°, because rearrangements to the corresponding naphthalene of the cyclobutene derivatives will become a serious side reaction). The dark-colored residue was chromatographed over a silica gel column using CCl_4 as the elution agent. With CCl_4 unreacted benzo[b]thiophene could be separated first. After that the product VI and a little acetophenone were separated. The total weight of the almost pure fractions was 1.30 g (23%). In order to purify this mixture further the 1.30 g was chromatographed again over silica gel using cyclohexane as an elution agent. Acetophenone separated first and after that 1.18 g of pure product could be obtained as a light yellow oil: calcd mol wt for $C_{12}H_{10}O_2S$, 218.04015 (found mol wt, 218.0403).

Addition of Methyl Propiolate to 2-Methylbenzo[b]thiophene.—Additions were carried out in exactly the same way as described for benzo[b]thiophene. Yields of VI were as high as 35%: calcd mol wt for $C_{13}H_{12}O_2S$, 232.0559 (found, 232.0560).

Addition of Phenylpropiolic Acid Methyl Ester to Benzo[b]thiophene.—Benzo[b]thiophene (3 g, 0.22 mol), methyl phenylpropiolate (3.5 g, 0.022 mol), and acetophenone (0.5 g, 0.0038 mol) were dissolved in 400 ml of benzene and the solution was irradiated for 7 days. The benzene was removed *in vacuo* on a rotating evaporator and vpc analysis (column SE-30, oven temperature 250°) of the crude mixture showed formation of one product (52%). The acetophenone and part of the other starting material were distilled *in vacuo*. The dark-colored residue was chromatographed over a Florisil column (Fisher F-100) with cyclohexane as the eluting agent. With cyclohexane, benzo[b]thiophene and methyl phenylpropiolate eluted. Changing solvents from cyclohexane to $CHCl_3$ separated (45%) 2.9 g of X.

Addition of Methyl Phenylpropiolate to 2-Methylbenzo[b]thiophene.—Additions were carried out in exactly the same way as described for benzo[b]thiophene. The total (XI + XIII) was 50%.

Preparative Addition of Diphenylacetylene to Benzo[b]thiophene.—Benzo[b]thiophene (2 g, 0.015 mol) and diphenylacetylene (2.8 g, 0.016 mol) were dissolved in 400 ml of benzene and irradiated for 10 days. The benzene was removed *in vacuo* on a rotating evaporator and vpc analysis of the crude mixture (column SE-30, oven temperature 285°) showed formation of two products. The yields were very low and certainly not more than 1% where the solutions were not degassed. Taking mass spectra of the two major products from a vpc column GE-SE-30 showed the product with the lowest retention time to be a 1:1 adduct, mass 312. On the basis of the cracking pattern (Table II) the structure XIV was assigned. The product with the highest retention time on the vpc showed a mass of 356 and is probably derived from a dimer or tetramer of diphenylacetylene.

Nmr Studies of Diphenylacetylene and Benzo[b]thiophene Photoadditions.—Five samples of diphenylacetylenes (35.6 mg, 2×10^{-4} mol) were added to five separate clear Pyrex nmr tubes and 1 ml of benzene was added to each tube. A constant quantity of *tert*-butylbenzene was added to each tube as an nmr integration standard. To each successive tube sufficient benzo[b]thiophene was added so that the molar ratio of benzo[b]thiophene to diphenylacetylene in tube 1 was 1:1, in tube 2, 2.5:1, in tube 3, 5.0:1, in tube 4, 7.5:1, and in tube 5, 10.0:1. Each tube was outgassed three times and sealed, after which the tubes were strapped around a Hanovia lamp and irradiated. The molar concentration of product was calculated from integration of the *tert*-butylbenzene singlet at 1.20 ppm and the two vinyl region protons of the adducts at 5.00 and 6.45 ppm. Spectra were taken at various time intervals and the buildup in product was recorded as a function of time.

Additions of Other Acetylenes to Benzo[b]thiophenes.—A solution of 1 g (0.008 mol) of benzo[b]thiophene, 1.3 g (0.011 mol) of 1,4-dimethoxybutyne-2, and 0.2 g (0.001 mol) of benzophenone in 100 ml of benzene irradiated for 7 days showed, after removal of the benzene, by vpc analysis (GE-SE-30 column, oven temperature 230°) no products. Even after prolonged radiation no products could be detected. 1,4-Dichlorobutyne-2 behaved similarly. When the same experiments were carried out using phenylacetylene and methylphenylacetylene, vpc analysis showed the formation of two products, but the yield was too small to identify these products even after prolonged radiation.

Addition of 2-Phenylacetylacetylene to Benzo[b]thiophene.—Benzo[b]thiophene (2 g, 0.015 mol), 2-phenyl-1-acetylacetylene (2.5 g, 0.017 mol), and acetophenone (0.5 g, 0.03 mol) were dissolved in 400 ml of benzene and irradiated for 20 hr. The benzene was removed on a rotating evaporator and vpc analysis (5-ft Carbowax, 10%, oven temperature 210°) showed the formation of two products in 4% yield.

Addition of Dichloromaleic Anhydride to Benzo[b]thiophene.—Benzo[b]thiophene (3 g, 0.022 mol), dichloromaleic anhydride (3 g, 0.017 mol), and benzophenone (0.25 g, 0.001 mol) were dissolved in 400 ml of benzene and irradiated for 16 hr. The benzene was removed on a rotating evaporator and vpc analysis (column GE-SE-30, oven temperature 240°) of the crude residue showed the formation of two products in 4 and 2% yield. The acetophenone and part of the benzo[b]thiophene were distilled *in vacuo*, and the dark residue was separated by preparative vpc (column GE-SE-30, oven temperature 225°). Isolated was 60 mg of XXIX which had the lowest retention time as very fine yellow needles: mp 149–150°; nmr δ 6.82 (s, 1 H) and 6.9–7.75 (phenyl H); ir 1245 (CO), 1622 (C=C), and 1784 and 1838 cm^{-1} (C=O); mass spectrum *m/e* (rel intensity, fragment) 266 (32, M + 2), 264 (84, M^+), 192 (100, M − 72, C_2O_3), 157 (10.6, M − 107, C_2O_3Cl), and 132 (3, M − 132, C_4O_3ClH).

Thermal Rearrangement of 1,2-Dicarboxymethyl-5,6-benzo[3.0.2]bicyclo-7-thiaheptane-2,3 (I → XX) to Naphthalene-1,2-dicarboxylic Acid Dimethyl Ester.—I (3.56 g, 0.0128 mol) was dissolved in 5 ml of tetraethylene glycol dimethyl ether and heated for 15 min in a Woods metal bath thermostated at 240°.

(32) Samples for which high-resolution mass spectral molecular weights are reported were determined pure by vapor phase chromatography.

The dark-colored mixture was, after cooling, chromatographed over silica gel using CH_2Cl_2 as an eluting agent. By this procedure 2.6 g (0.016 mol, 82%) of XX was obtained, mp 77–79°. After five recrystallizations from CCl_4-hexane (3:5), we obtained 1.8 g of white crystals, mp 84° (lit.[32] mp 85°).

The thermal rearrangements of 1,2-dicarboxymethyl-4-methyl-5,6-benzo[3.0.2]bicyclo-7-thiaheptene-2,3 to 4-methylnaphthyl-1,2-dicarboxylic acid dimethyl ester (IV → XXI) and 1,2-dicarboxymethyl-3,4-dimethyl-5,6-benzo[3.0.2]bicyclo-7-thiaheptene-2,3 to 3,4-dimethylnaphthyl-1,2-dicarboxylic acid dimethyl ester (V → XXII) were carried out by the same procedure, yields 75%.

Thermal Rearrangement of 1-Carboxymethyl-5,6-benzo[3.0.2]-bicyclo-7-thiaheptene-2,3 (VI → XXIII) to α-Naphthylcarboxylic Acid Methyl Ester.—VI (1 g, 0.0045 mol) was in its pure form heated up in a Woods metal bath thermostated at 240° for 20 min. After 5–10 sec the mixture started to change color and the smell of sulfur was observable. The dark mixture was chromatographed over silica gel using CCl_4 as an eluting agent, yielding 0.65 g (77%) of pure methyl α-naphthoate: ir 1131 and 1276 (CO) and 1720 cm^{-1} (C=O); nmr δ 3.99 (s, OCH_3) and 7.3–8.1 (m, aromatic H).

The thermal rearrangement of 3-methyl-1-carboxymethyl-5,6-benzo[3.0.2]bicyclo-7-thiaheptene-2,3 (VII → XXIV) to 3-methylnaphthyl-1-carboxylic acid methyl ester was carried out in the same way: yields 70%; nmr δ 2.44 (s, CH_3), 3.93 (s, OCH_3), and 7.1–8.0 (m, aromatic H).

Thermal Rearrangement of 1-Phenyl-2-carboxymethyl-5,6-benzo[3.0.2]bicyclo-7-thiaheptene-2,3 (X → XXVI) to 1-Phenyl-2-naphthoic Acid Methyl Ester.—X (1 g, 0.0032 mol) was heated in a Woods metal bath thermostated at 240° for 10 min. After 5–10 sec the mixture became dark. The reaction was cooled and the mixture was chromatographed over silica gel using $HCCl_3$ as eluting agent to 0.72 g (81%) of pure 1-phenyl-2-naphthoic acid methyl ester. If very pure substance is required, one may purify this further by preparative vpc (column SE-30, oven temperature 260°), nmr δ 3.50 (s, OCH_3) and 7.0–7.9 (m, aromatic H).

The thermal rearrangement of 1-phenyl-2-carboxymethyl-3-methyl-5,6-benzo[3.0.2]bicyclo-7-thiaheptene-2-3 (XI → XXV) to 1-phenyl-3-methyl-2-naphthoic acid methyl ester was carried out in the same way: yields 80%; nmr δ 2.50 (s, CH_3), 3.5 (s, OCH_3), and 7.0–7.9 (aromatic H).

Registry No.—I, 31739-28-3; III, 24014-47-9; IV, 24014-46-8; V, 24014-48-0; VI, 31739-32-9; VII, 31739-33-0; X, 31739-34-1; XI, 31739-35-2; XIII, 31739-36-3; XV, 31739-37-4; XVI, 31739-38-5; XVII, 31739-39-6; XVIII, 31739-40-9; XXIX, 31739-41-0; XX, 10060-32-9; XXIII, 2459-24-7; XXIV, 31739-44-3; XXV, 31739-45-4; XXVI, 31790-95-1; dimethyl acetylenedicarboxylate, 762-42-5; benzo[*b*]thiophene, 95-15-8; methyl propiolate, 922-67-8; 2-methylbenzo[*b*]thiophene, 1195-14-8; phenylpropiolic acid methyl ester, 4891-38-7; diphenylacetylene, 501-65-5; 2-phenylacetylene, 31739-46-5; dichloromaleic anhydride, 1122-17-4.

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Effects of Micelles on the Efficiency of Photoinduced Substitution Reactions and Fluorescence Quenching[1,2]

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The reactions of cyanide ion with photoexcited aromatic nitro compounds (4-nitrophenyl alkyl ethers, 1-nitronaphthalene, and 4-methoxy-1-nitronaphthalene) were examined in aqueous solutions containing micelles derived from hexadecyltrimethylammonium halide, sodium dodecyl sulfate, and mixtures of hexadecyltrimethylammonium halide and quaternary nitrogen detergents of the type $(CH_3)_3N^+(CH_2)_mOC_6H_4O(CH_2)_nCH_3$ (m = 4, 10; n = 0, 3, 7, 9). It was found that hexadecyltrimethylammonium chloride enhances the quantum yield of the reaction of 4-methoxy-1-nitronaphthalene by a factor of about 6800 and has little effect on the reaction of the 4-nitrophenyl alkyl ethers and that sodium dodecyl sulfate strongly inhibits the reactions of cyanide with nitroaromatics solubilized by the detergent. The results are rationalized on the basis of the effect of the micelles on both the local concentration of reactants and the character of the excited state of the nitroaromatic. Studies with the mixed micelles revealed that the efficiency of interaction of two organic groups (4-methoxy-1-nitronaphthalene and ROC_6H_4OR') can be altered by changing the relative position of these groups in the micelles. Thus, both the effectiveness of ROC_6H_4OR' as a quencher of the photoinduced reaction of the nitroaromatic with cyanide and the extent of quenching of fluorescence from ROC_6H_4OR' by the nitroaromatic were found to depend upon the position of the aromatic ring in the detergent (*i.e.*, on m and n) when the conditions favored micelle formation.

This paper reports results of a study of the effect of detergents on the course of some photochemical reactions of aromatic nitro compounds. The experiments were designed to test the extent to which rates of photoinduced bimolecular reactions might be influenced and controlled by exploiting local organizing and environmental effects of micelles.

That ionic detergents may appreciably alter rates of reaction of nucleophiles with organic substances in the ground state is well known.[3] For example, the rate of alkaline hydrolysis of 4-nitrophenyl esters of long-chain aliphatic acids is increased 8–18-fold by quaternary am-

(1) This research was supported by a grant from the National Science Foundation (GP-5 715).

(2) Part IX in the series on photoinduced substitution reactions. For part VIII, see K. E. Steller and R. L. Letsinger, *J. Org. Chem.*, **35**, 308 (1970).

(3) J. Baumrucker, M. Calzadilla, M. Centeno, G. Lehrmann, P. Lindquist, D. Dunham, M. Price, B. Sears, and E. H. Cordes, *J. Phys. Chem.*, **74**, 1152 (1970); C. A. Bunton and L. Robinson, *J. Org. Chem.*, **34**, 773, 780 (1969); **35**, 733 (1970); *J. Amer. Chem. Soc.*, **91**, 6072 (1969); **92**, 356 (1970); *J. Phys. Chem.*, **74**, 1062 (1970). For a review of the earlier literature, see E. H. Cordes, *Accounts Chem. Res.*, **2**, 329 (1969).