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PHOTOCHEMISTRY OF BENZO(b)THIOPHENES. ADDITION OF ACETYLENES.

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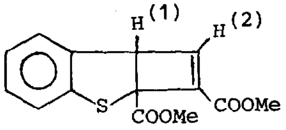
Photochemical additions of alkynes to olefins, carbonyl compounds and other unsaturated molecules lead to four-membered ring products[2] that are, themselves prone to photochemical rearrangement[3]. Because of our interest in the photochemistry of benzo(b)thiophene and its derivatives[4], we have studied the addition of dimethyl acetylene dicarboxylate to several benzo(b)thiophenes.

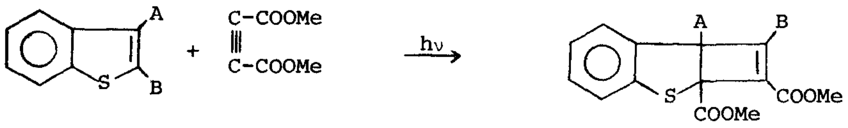
Dimethyl acetylene dicarboxylate (3.5 mmole) and benzo(b)thiophene (3.7 mmole) were irradiated for 12-24 hours in 650 ml. of benzene[5]. The initially formed product (an orange oil) was separated from residual starting materials by chromatography on silica gel (1.5 g. ≈ 16%)[6].

On the basis of its n.m.r. spectrum (1 H, 4.69 ppm δ doublet, J < 1.0 cps, 1 H, 6.78 ppm δ, doublet, J < 1.0 cps, 3 H, 3.72 ppm δ, singlet, 3 H, 3.76 ppm δ, singlet and 4 H, 7.05 ppm δ, singlet), and its mass spectrum[7] structure I was assigned to the adduct. Thus weakly coupled doublets represent hydrogens 1 and 2 in the n.m.r. spectrum while the retro cleavage in the mass spectrometer produces 2-carbomethoxybenzo(b)thiophene rather than the parent benzo(b)thiophene as the major cracking[4b].



I

Similar additions are observed with 2-methylbenzo(b)thiophene, 3-methylbenzo(b)thiophene and 2,3-dimethylbenzo(b)thiophene. The n.m.r. spectra of these adducts (Table I), isolated by chromatography on silica gel as well as the mass spectra[7] are consistent with the assigned structures (1)

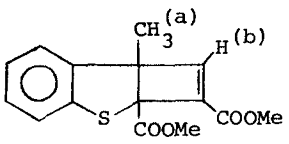
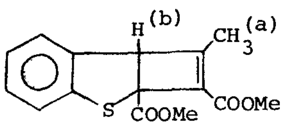
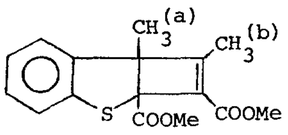


(1)

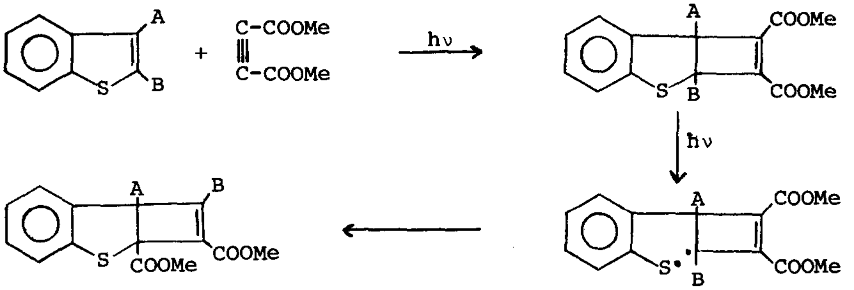
A = Me, B = H
A = H, B = Me
A = B = Me

TABLE I

N.M.R. Spectra of Alkylated Benzo(b)thiophene Adducts.

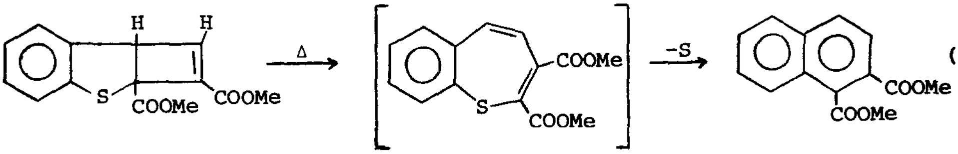
Compound	Spectrum
	(a) 3 H at 1.58 ppm δ (singlet) (b) 1 H at 6.76 ppm δ (singlet) phenyl 4 H at 7.16 ppm δ (singlet) carbomethoxy groups 3 H at 3.76 ppm δ (singlet) 3 H at 3.80 ppm δ (singlet)
	(a) 3 H at 1.95 ppm δ (singlet) (b) 1 H at 4.68 ppm δ (singlet) phenyl 4 H at 7.10 ppm δ (singlet) carbomethoxy groups 3 H at 3.76 ppm δ (singlet) 3 H at 3.80 ppm δ (singlet)
	(a) 3 H at 1.58 ppm δ (singlet) (b) 3 H at 1.95 ppm δ (singlet) phenyl 4 H at 7.08 ppm δ (singlet) carbomethoxy groups 3 H at 3.76 ppm δ (singlet) 3 H at 3.80 ppm δ (singlet)

Genesis of the rearranged adduct probably derives from initial addition to the benzo(b)thiophene by the acetylene decarboxylate followed by photorearrangement of the adduct (2).[4a]



(2)

Most significantly, adducts (II) were not stable thermally. When collected from the v.p.c., (GE-SE-30 column, 220°, detector temperature 300°) or when heated in tetraethylene glycol dimethylether[8] the adducts from benzo(b)-thiophene and acetylene dimethyl carboxylate lost sulfur to give naphthalene 1,2-dimethyl carboxylate, m.p. 84°, literature m.p. 85°.[9] This naphthalene ester presumably arises from ring opening to benzo(b)thiepin 2,3-dimethylcarboxylate from which sulfur is readily lost (3).



(3)

Thus, the photochemical addition of acetylenes to benzo(b)thiophene and its derivatives should provide a route to the elusive benzo(b)thiepin system[10], a project we are actively investigating[11].

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1. Author to whom inquiries concerning this work should be addressed; Department of Chemistry, Hope College, Holland, Michigan 49423.
2. For reviews see:
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5. A Hanau S-81 medium pressure mercury arc lamp was used for all irradiations. Pyrex filters were generally employed and the temperature maintained near 30°.
6. Carbon tetrachloride and a mixture (1:1) of carbon tetrachloride, methylene chloride eluted the starting materials. Pure methylene chloride was used to remove the product.
7. The mass spectral cracking patterns of the adducts from alkyl benzo(b)thiophenes and dimethylacetylene dicarboxylate:

	$\%(M^+)$	$\%(M-S)$	$\%[M-(\overset{R}{C}CCOOMe)]$	$\%[M-(CCOOMe)_2]$
Adduct from benzo(b)thiophene R = H	90	100	90	25
Adduct from 3-Methylbenzo(b)thiophene R = H	95	100	85	14
Adduct from 2,3-Dimethylbenzo(b)-thiophene R = Me	100	60	65	50

8. Best results were obtained when the adducts, in tetraethyleneglycol dimethylether were dipped (10-15 sec.) in a Woods metal bath thermostatted at 240°.
9. Authentic naphthalene 1,2-dimethylcarboxylate prepared by the method of K. von Auwers and K. Möller, *J. Prakt. Chemie*, **109**, 124 (1924), had a superimposable i.r. spectrum with our material.
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    b) H. Hofman and H. Westernacker, *Angew. Chem*., Int. Ed., **6**, 255 (1967).
    c) W.E. Parham and D.G. Weetman, J. Org. Chem., **34**, 56 (1969) and references cited therein.
11. One of the authors (DCN) thanks the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. He also thanks the administrations of Hope College and the University of Groningen, The Netherlands for making his year as a Netherlands exchange professor possible. The mass spectra reported were obtained with the able assistance of Dr. W.D. Weringa.