

Photocyclization Reactions of Aryl Polyenes. VII.¹ The Photocyclization of 1-Phenyl-4-thienyl- and 1,4-Dithienyl-1,3-butadienes²

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The photocyclization-oxidation reaction of 1-phenyl-4-(2'-thienyl)-1,3-butadiene gave 4-phenylbenzo[*b*]thiophene. Similarly, irradiation of 1-phenyl-4-(3'-thienyl)-1,3-butadiene gave 7-phenylbenzo[*b*]thiophene. Thus, photocyclization occurs exclusively to the thiophene ring. Irradiation of 1,4-di(2'-thienyl)-1,3-butadiene and 1,4-di(3'-thienyl)-1,3-butadiene yielded 4-(2'-thienyl)benzo[*b*]thiophene and 7-(3'-thienyl)benzo[*b*]thiophene, respectively. Photocyclization of 1-(2'-thienyl)-4-(3''-thienyl)-1,3-butadiene gave an inseparable mixture of 4-(3'-thienyl)benzo[*b*]thiophene and 7-(2'-thienyl)benzo[*b*]thiophene.

La réaction de photocyclisation-oxydation du phényl-1 (thiényl-2')-4 butadiène-1,3 conduit au phényl-4 benzo[*b*]thiophène. De façon similaire, l'irradiation du phényl-1 (thiényl-3')-4 butadiène-1,3 conduit au phényl-7 benzo[*b*]thiophène. Par suite, la photocyclisation se produit exclusivement à l'anneau du thiophène. L'irradiation du di(thiényl-2')-1,4 butadiène-1,3 et du di(thiényl-3')-1,4 butadiène-1,3 a conduit au (thiényl-2')-4 benzo[*b*]thiophène et au (thiényl-3')-7 benzo[*b*]thiophène, respectivement. La photocyclisation du (thiényl-2')-1, (thiényl-3'')-4 butadiène-1,3 conduit à un mélange inséparable de (thiényl-3')-4 benzo[*b*]thiophène et de (thiényl-2')-7 benzo[*b*]thiophène.

[Traduit par le journal]

The photocyclization-oxidation reaction of stilbene-like molecules has received much attention in recent years from both preparative (1) and mechanistic (2) points of view. The photocyclization-oxidation of 1,2-diarylethylenes, where one or both of the aryl groups represents heteronuclear aromatic groups has led to the synthesis of some interesting heterocyclic aromatic compounds (3, 4).

The related photocyclization-oxidation of 1,4-diphenyl-1,3-butadiene gave 1-phenylnaphthalene (5). This photoreaction has been extended to a wide variety of 1,4-diaryl-1,3-butadienes where the aryl groups are phenyl, substituted phenyl (6), and polynuclear aromatic groups (7, 8) and it was shown that photocyclization always occurred to the polynuclear aromatic substituent (7, 8).

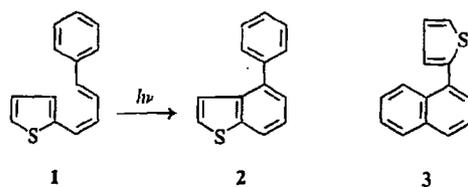
It was of some interest to determine the feasibility of using 1,4-diaryl-1,3-butadienes, where the aryl groups are heteronuclear aromatic groups, as a means of synthesizing polynuclear heteroaromatic systems by photocyclization. Although we had shown that the direction of photocyclization

in 1,4-diaryl-1,3-butadienes can be predicted by molecular orbital calculations (8), when the aryl groups are aromatic hydrocarbons, Laarhoven *et al.* (9) had previously shown in the stilbene series that simple m.o. calculations were unreliable when applied to five-membered ring heteroaromatic groups such as thiophene. Furthermore, Kellogg *et al.* (4) had shown that although 1,2-di(2'-thienyl)ethene and 1-(2'-thienyl)-2-(3''-thienyl)ethene photocyclize to give dithiaphenanthrenes, the 1,2-di(3'-thienyl)ethene failed to give a dithiaphenanthrene. Thus the lack of a suitable means of prediction of the photocyclization reaction and the failure of one dithienylethene to give tractable products made a detailed investigation of 1-phenyl-4-thienyl-1,3-butadienes and 1,4-dithienyl-1,3-butadienes very desirable.

Irradiation of $1 \times 10^{-3} M$ solutions of 1-phenyl-4-(2'-thienyl)-1,3-butadiene (1) in dry benzene containing $2 \times 10^{-3} M$ iodine gave, after 3 days, 4-phenylbenzo[*b*]thiophene (2), in 15% yield, identical to the known compound (10). As shown in Scheme 1, photocyclization of 1 can occur to the thiophene ring to give 2, as observed, or photocyclization can occur to the phenyl group to give the known 1-(2'-thienyl)naphthalene (3) (11).

¹For Part VI see ref. 8.

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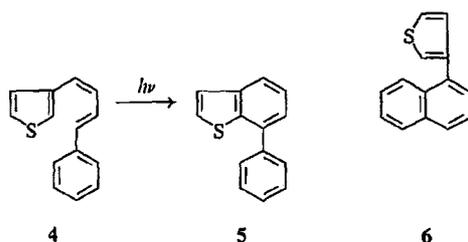


SCHEME 1

The spectral properties of the photoproduct were identical to 2, synthesized previously (10), and comparison of the n.m.r. spectra of the photoproduct and 3, previously synthesized (11), showed that less than 5%, if any, of 3 existed in the photoproduct. Vapor phase chromatography was not useful, as a mixture of synthesized 2 and 3 could not be separated on a variety of columns.

Similarly, irradiation of 1-phenyl-4-(3'-thienyl)-1,3-butadiene (4) gave exclusive formation of 7-phenylbenzo[b]thiophene (5), in 39% yield, identical to the known compound (12).

As shown in Scheme 2, photocyclization can occur to the thiophene ring to give 5 or to the phenyl ring to give the known 1-(3'-thienyl)naphthalene (6) (13). Comparison of the n.m.r. spectra of the photoproduct and the known product 6, however, showed that less than 5%, if any, of 6 was formed.



SCHEME 2

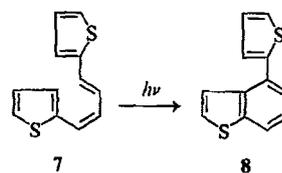
It was possible that 3 and 6 were formed in the photocyclization of 1 and 4, respectively, but that 3 and 6 underwent further photocyclization reactions or suffered decomposition. Irradiation of 3 and 6, however, led to complete recovery of the starting materials.

It has thus been shown that 1-phenyl-4-thienyl-1,3-butadienes undergo photocyclization exclusively to the thiophene nucleus. This selective mode of cyclization enables the synthesis of 4- and 7-arylbenzo[b]thiophenes to be simply accomplished.

The photocyclization of 1 and 4 to give 2 and 5, respectively, showed that the photocycliza-

tion-oxidation reaction to the thiophene ring occurs in high yield to both the 2 and 3 positions of the thiophene nucleus. Due to the unreliability of simple m.o. calculations involving the thiophene nucleus (9), we were unable to predict in advance whether cyclization would occur to the 2 or 3 positions in competitive cyclizations. To elucidate this point a series of 1,4-dithienyl-1,3-butadienes were irradiated.

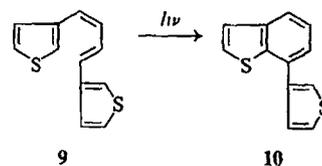
Thus, photocyclization of 1,4-di(2'-thienyl)-1,3-butadiene (7) was irradiated as before to give 4-(2'-thienyl)benzo[b]thiophene (8) as shown in Scheme 3.



SCHEME 3

Compound 8 was readily synthesized by a route similar to that described for 1-arylnaphthalenes (6).

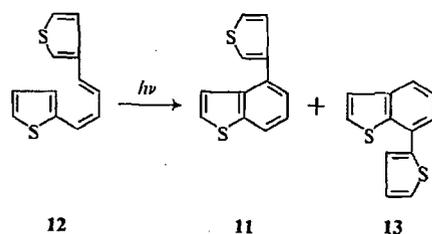
Similarly, irradiation of 1,4-di(3'-thienyl)-1,3-butadiene (9) gave 7-(3'-thienyl)benzothiophene (10), as shown in Scheme 4. Compound 10 exhibited a strong parent ion in the mass spectrum. The u.v. spectrum of 10 was very similar to that of 4-(3'-thienyl)benzothiophene (11) described below and is consistent with the assigned structure. The n.m.r. spectrum of 10 shows complex absorption between 7 and 8 p.p.m. The spectral data and the mode of synthesis are consistent with structure assigned to 10.



SCHEME 4

Irradiation of 1-(2'-thienyl)-4-(3''-thienyl)-1,3-butadiene (12) as before gave a mixture of products, inseparable even by vapor phase chromatography. As shown in Scheme 5, photocyclization-oxidation of 12 can occur to the 3' position of the 1-thienyl group to give 11 and to the 2'' position of the 4-thienyl group to give 7-(2'-thienyl)benzo[b]thiophene (13).

Compound 11 was synthesized in the same



SCHEME 5

way as described above for the synthesis of **8**, except that 3-thienyllithium was used instead of 2-thienylmagnesium bromide. Comparison of the photoproduct from **12**, isolated as a single fraction by t.l.c., indicated the presence of **11**, but also showed that the photoproduct was not solely **11**. Although the mass spectrum of the photoproducts gave a parent ion identical to that of **11**, the cleavage pattern was slightly different. The i.r. and the n.m.r. spectra of the photoproducts were similar but not identical to **11**. The u.v. spectra of **11** and the photoproducts were informative and indicated that the composition of the photoproducts could be explained by a mixture of **11** and **13**.

The u.v. spectra of thienyl compounds are quite informative. Conjugation of the thienyl group with other chromophores is more readily achieved through attachment to the 2 position. This extended conjugation in 2-substituted thiophenes is reflected in a bathochromic shift when compared to 3-substituted thiophenes. For example, 1,2-di(2'-thienyl)ethene, 1-(2'-thienyl)-2-(3'-thienyl)ethene, and 1,2-di(3'-thienyl)ethene exhibit λ_{\max} values at 338, 316, and 291 nm, respectively (4); the phenylthienyl butadienes **1** and **4** at 360 and 340 nm, respectively (14); and the dithienylbutadienes **7**, **12**, and **9** at 375, 352, and 332 nm, respectively (14, 15). Thus, it is not surprising that the λ_{\max} value for **8** at 300 nm exhibits a bathochromic shift when compared to **11** at 282 nm. Also the λ_{\max} value for **10** is 280 nm and hence one should expect a λ_{\max} value for **13** of ~ 300 nm. The u.v. spectrum of the photoproducts from **12** shows λ_{\max} at 282 nm corresponding to **11** and a shoulder at ~ 300 nm corresponding to **13** and is consistent with the u.v. predicted for a mixture of **11** and **13**.

Some time ago Wynberg and van Driel reported the photoisomerization of 2-phenylthiophene to 3-phenylthiophene (**16**) as well as related photoisomerizations. Thus it is possible that photoproduct **8** could isomerize to **11** and

photoproduct **13** could isomerize to **10** under the irradiation conditions. We feel this is highly unlikely as our irradiation conditions (low pressure mercury lamp, room temperature, and Pyrex vessels) are quite different from those of Wynberg and van Driel. Thus the properties of compound **8**, synthesized by both classical and photochemical means, were identical and hence photoisomerization of **8** to **11** had not occurred.

The photocyclization-oxidation reactions of **1**, **4**, **7**, **9**, and **12** described in this paper occur with equal facility to both the 2 and 3 positions of the thienyl moiety. Kellogg *et al.* (4) showed that the 1,2-di(3'-thienyl)ethene failed to cyclize and demonstrated that the failure to isolate a phenanthrene was due to complications in the oxidation of the dihydro intermediate and not in the photocyclization step (4). The facile photocyclizations of **1**, **4**, **7**, **9**, and **12** to both the 2 and 3 positions of the thiophene nucleus support their results.

The fact that photocyclization of **1** and **4** occurs exclusively to the thiophene nucleus is not too surprising as formation of the dihydro intermediates leading to **2** and **5** results in the destruction of the aromaticity of the thiophene nucleus, but photocyclization to **3** and **6** would give dihydro intermediates resulting from destruction of the much more resonance stabilized aromatic phenyl group.

Thus, the photocyclization-oxidation reaction of thienylbutadienes provides a facile route to the synthesis of 4- and 7-arylbenzo[*b*]thiophenes and could be readily adapted to more complex heterocyclic aromatic compounds.

Experimental

All m.p.'s were determined on a Kofler hot stage and are uncorrected. The i.r. spectra were recorded on a Unicam SP1000 spectrometer as neat liquids. The u.v. spectra were measured using a Unicam SP800A spectrometer and cyclohexane as solvent. The n.m.r. spectra were measured on a Varian A60 spectrometer using tetramethylsilane as an internal standard ($\delta = 0$ p.p.m.) and deuteriochloroform as solvent. Mass spectra were recorded on a Hitachi-Perkin-Elmer RMU-6 mass spectrometer. The number in brackets after the mass peak represents the percentage of base peak. Silica gel was used for thin- and thick-layer chromatography. All photochemical reactions were carried out in a Rayonet photochemical reactor using RPR 3500 Å lamps. Microanalyses were performed by Dr. C. Daesslé of Montreal.

Irradiation of the Butadienes

The irradiations of **1** (14), **4** (14), **7** (15), **9** (14), and **12** (14) were carried out in a manner previously des

TABLE 1. Thienylbenzo[*b*]thiophenes

Compound	Substituent	Method of synthesis	Yield (%)	Molecular formula	Analysis (%)			
					Found		Calculated	
					C	H	C	H
8	4-(2'-Thienyl)	Photochemical	49	C ₁₂ H ₈ S	66.55	4.06	66.66	3.74
10	7-(3'-Thienyl)	Grignard	10	C ₁₂ H ₈ S	66.41	3.54	66.66	3.74
11	4-(3'-Thienyl)	Photochemical	62	C ₁₂ H ₈ S	66.44	3.86	66.66	3.74
		Grignard	22*					
			15					

*This yield represents a mixture of 11 and 13.

TABLE 2. Spectral characteristics of thienylbenzo[*b*]thiophenes

Compound	Substituent	Ultraviolet spectra $\lambda_{max}(nm)$ (ϵ)	Infrared spectra $\nu(cm^{-1})$	Mass spectra*
				<i>m/e</i> M ⁺ , other peaks
8	4-(2'-Thienyl)	300 (10 000)	1575(m), 801(m), 758(s)	216(100), 171(23)
10	7-(3'-Thienyl)	281 (7320)	1460(s), 860(m), 775(s)	216(100), 171(30)
11	4-(3'-Thienyl)	282 (7050)	1580(m), 798(m), 775(s)	216(100), 171(30)

*Number in parentheses represents % of base peak.

cribed. The analytical and spectral data of the unknown photoproducts are given in Tables 1 and 2, respectively. The n.m.r. spectra of the photoproducts, although generally uninformative, showed complex absorption between 7 and 7.7 p.p.m. The lack of absorption at 8.2 p.p.m. in the photoproducts eliminated the possible formation of 3 and 6 in the irradiation of 1 and 4, respectively.

Synthesis of 4-(2'-Thienyl)benzo[*b*]thiophene (8) and 4-(3'-Thienyl)benzo[*b*]thiophene (11)

Compound 8 was synthesized according to the previously described method for the synthesis of 1-aryl-naphthalenes (6, 17) except that 4-oxo-4,5,6,7-tetrahydrothionaphthene (purchased from Aldrich Chemical Co.) and 2-thienylmagnesium bromide were used as reactants.

The synthesis of 11 was the same as that described for the known 6 (13), except that 3-thienyllithium was used as a reactant. The analytical and spectral data of 8 and 11 are given in Tables 1 and 2, respectively.

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- C. S. WOOD and F. B. MALLORY. *J. Org. Chem.* **29**, 3373 (1964); E. V. BLACKBURN and C. J. TIMMONS. *Q. Rev.* **23**, 482 (1969).
- H. GÜSTEN and L. KLASINC. *Tetrahedron*, **24**, 5499 (1968); K. A. MUSZKAT and E. FISCHER. *J. Chem. Soc. (B)* 662 (1967); F. B. MALLORY, C. S. WOOD, and J. T. GORDON. *J. Am. Chem. Soc.* **86**, 3094 (1964); W. M. MOORE, D. D. MORGAN, and F. R. STEIMETZ. *J. Am. Chem. Soc.* **85**, 829 (1963); M. V. SARGENT and C. J. TIMMONS. *J. Am. Chem. Soc.* **85**, 829 (1963); M. V. SARGENT and C. J. TIMMONS. *J. Am. Chem. Soc.* **85**, 2186 (1963).
- W. CARRUTHERS and H. N. M. STEWART. *J. Chem. Soc.* 6221 (1965).
- R. M. KELLOGG, M. B. GROEN, and H. WYNBERG. *J. Org. Chem.* **32**, 3093 (1967).
- G. J. FONKEN. *Chem. Ind.* 1327 (1962).
- C. C. LEZNOFF and R. J. HAYWARD. *Can. J. Chem.* **48**, 1842 (1970).
- R. J. HAYWARD and C. C. LEZNOFF. *Tetrahedron*, **27**, 2085 (1971).
- R. J. HAYWARD, A. C. HOPKINSON, and C. C. LEZNOFF. *Tetrahedron*, **28**, 439 (1972).
- W. H. LAARHOVEN, TH. J. H. M. CUPPEN, and R. J. F. NIVARD. *Rec. Trav. Chim.* **87**, 687 (1968).
- M. C. KLOETZEL, J. E. LITTLE, JR., and D. M. FRISCH. *J. Org. Chem.* **18**, 1511 (1953).
- N. V. STULIN and N. I. PUTOKHIN. *Khim. Geterosikl. Soedin. Akad. Nauk. Latv. SSR*, 512 (1965).
- D. W. H. MACDOWELL and THOMAS D. GREENWOOD. *J. Heterocycl. Chem.* **2**, 44 (1965).
- D. W. H. MACDOWELL, R. A. JOURDENAIS, R. NAYLOR, and G. E. PAULOVICKS. *J. Org. Chem.* **36**, 2683 (1971).
- P. RIBEREAU, G. QUEGUINER, and P. PASTOUR. *Bull. Soc. Chim. Fr.* 1581 (1972).
- P. RIBEREAU and P. PASTOUR. *Bull. Soc. Chim. Fr.* 2076 (1969).
- H. WYNBERG and H. VAN DRIEL. *J. Am. Chem. Soc.* **87**, 3998 (1965).
- F. G. BADDAR, L. S. EL-ASSAL, and M. GINDY. *J. Chem. Soc.* 1270 (1948); F. G. BADDAR, L. S. EL-ASSAL, and N. A. DOSS. *J. Chem. Soc.* 1027 (1959).