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THE THIENO[3,4-c]-1,2,5-OXADIAZOLE SYSTEM, A NONCLASSICAL 10π-ELECTRON HETEROCYCLE

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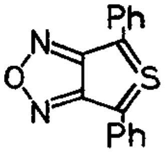
Diphenylthieno[3,4-c]-1,2,5-oxadiazole, a new nonclassical 10π-electron heterocycle, was prepared by two routes starting from dibenzoylfurazane. Cycloadditions of maleimides, dimethyl fumarate and maleate occurred across the thiocarbonyl ylide dipole, giving the corresponding adducts.

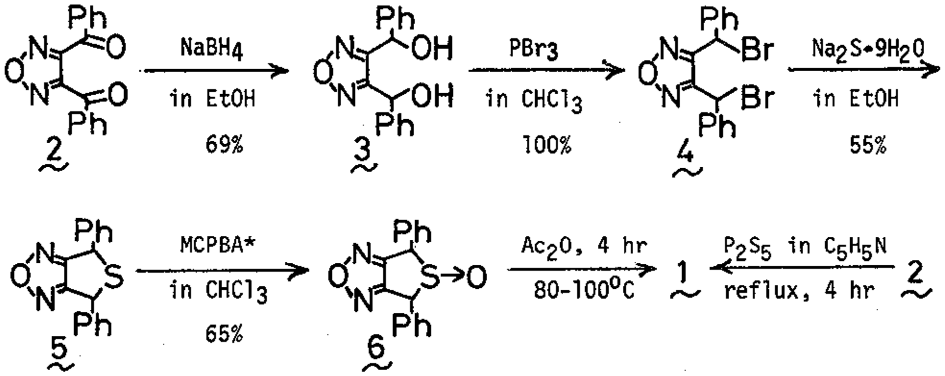
Tetraphenylthieno[3,4-c]thiophene, prepared in 1969, was the first example of an isolable nonclassical condensed thiophene.[1] Syntheses of several stable, nonclassical 10π-electron condensed thiophenes have since been reported in the literature. These compounds containing tetravalent sulfur are of considerable practical and theoretical interest.[2] In this regard, we wish to report the preparation of diphenylthieno[3,4-c]-1,2,5-oxadiazole (1), a new nonclassical 10π-electron heterocycle, and its cycloaddition reactions.



1

Preparation of 1. The heterocycle 1 was prepared by two routes starting from the readily available dibenzoylfurazane (2)[3] (Scheme 1). Borohydride reduction of 2 afforded an epimeric mixture of the corresponding diols 3, mp

94.5-96.5°C, which in turn was converted with phosphorus tribromide into the dibromides 4, pale yellow oil. Conversion of 4 with sodium sulfide into the cis sulfide 5, mp 122.5-123.5°C, followed by oxidation of 5 with m-chloroperbenzoic acid gave the corresponding sulfoxide 6, mp 178.5-179.5°C (ca. 24% overall yield from 2).[4]



*MCPBA: m-chloroperbenzoic acid

Scheme 1

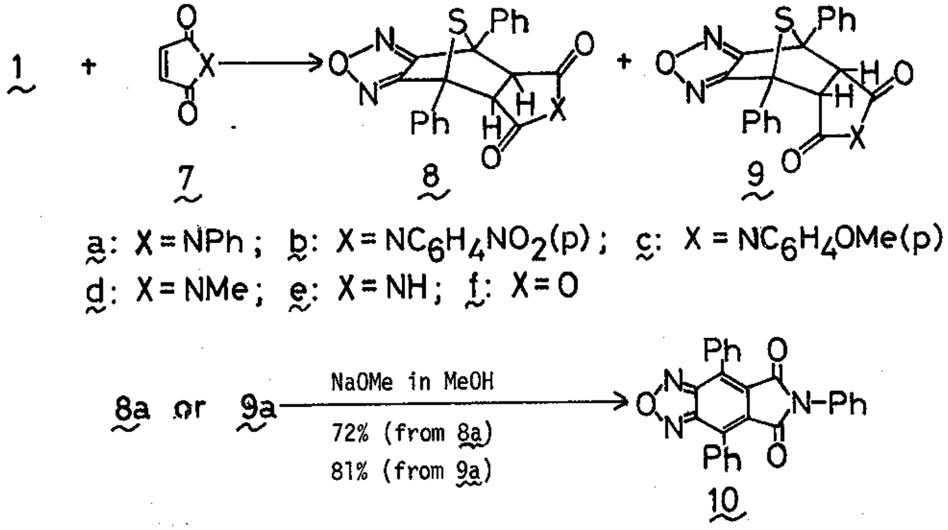
Dehydration of 6 in acetic anhydride afforded a 40% yield of 1, mp 161-165°C dec, as blue crystals. The heterocycle 1 (30% yield) could also be obtained in a single operation by the direct reaction of 2 with phosphorus pentasulfide in refluxing pyridine. Though nmr and uv spectra of 1 could not be measured due to its insolubility in ordinary solvents, its mass spectrum showed major peaks at m/e 278 (M^+, 87%), 139 (M^{2+}, 9%), and 121 ($PhCS^+$, 100%), reflecting the stability of 1 as was observed with other tetravalent sulfur compounds. Additional evidence in support of structure 1 comes from the formation of cycloadducts described below.

Cycloaddition Reactions. When a mixture of equimolar amounts of 1 and N-phenylmaleimide (7a) in benzene was refluxed under nitrogen for 12 hr, two 1:1 adducts, 8a and 9a, were obtained in 40 and 34% yields respectively.[5] On treatment with sodium methoxide in methanol, both 8a and 9a were readily converted into the same benzo[c]oxadiazole derivative 10 by loss of hydrogen sulfide. It is thus evident that 7a adds across the thiocarbonyl ylide dipole of 1. Such an addition is consistent with that observed previously in other tetravalent sulfur systems.[2]

8a: mp 214-216.5°C dec, colorless prisms; ir (KBr) 1720 cm^{-1} (C=O); nmr (DMSO-d_6) δ 4.68 (2H, s, $\geqslant$C$\underline{H}$), 7.25-8.0 (15H, m); mass spectrum m/e (rel. intensity %) 451 (M$^+$, 44), 417 (M$^+$ - H_2S, 37), 278 (100), 121 (79).

9a: mp 184-185.5°C, colorless needles; ir (KBr) 1720 cm^{-1} (C=O); nmr (DMSO-d_6) δ 5.41 (2H, s, $\geqslant$C$\underline{H}$), 6.8-7.1 (2H, m), 7.4-7.95 (9H, m), 7.95-8.3 (4H, m); mass spectrum m/e (rel. intensity %) 451 (M$^+$, 13), 417 (M$^+$ - H_2S, 1), 278 (100), 121 (59).

10: mp 244-245°C, yellow needles; ir (KBr) 1720 cm^{-1} (C=O); nmr (CDCl$_3$) δ 7.35-7.95 (m, Ar$\underline{H}$); mass spectrum m/e 417 (M$^+$, base peak).



a: X = NPh; b: X = $NC_6H_4NO_2$(p); c: X = NC_6H_4OMe(p)
d: X = NMe; e: X = NH; f: X = O

Scheme 2

The major isomer 8a was assigned the exo structure and the minor isomer 9a was assigned the endo structure on the basis of nmr data. Thus, the protons α to the imide carbonyls of 8a appear at higher field (δ 4.68) than the corresponding protons of 9a (δ 5.41), because of the deshielding effect of the sulfur bridge. Analogous effects have been noted for other related exo-endo adducts pairs containing a sulfur bridge.[6]

Similarly, 1 afforded the corresponding exo adducts, 8b-8e, and endo adducts, 9b-9e, in the reaction with maleimides 7b-7e under the same conditions. The results are summarized in Table 1. The ratio of exo adduct 8 to endo adduct 9 in each crude product was estimated by nmr spectroscopy, and the value was also given in Table 1. Though the exo adduct 8f was only iso-

Table 1

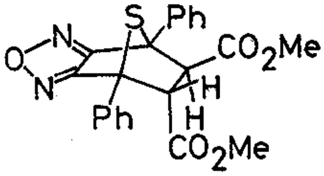
Adduct	Yield %	Mp., °C	Nmr,a) δ ppm >C$\underline{H}$	exo/endob)
8a(exo)	40	214-216.5 dec.	4.68	8/5
9a(endo)	34	184-185.5	5.41	
8b(exo)	31	207-208 dec.	4.61	1/1
9b(endo)	32	218-219.5	5.38	
8c(exo)	43	218-219.5 dec.	4.53	8/5
9c(endo)	26	158-159	5.30	
8d(exo)	37	210-211 dec.	4.43	2/3
9d(endo)	38	195.5-196	5.20	
8e(exo)	38	204-205.5 dec.	4.35	2/1
9e(endo)	25	206-208.5 dec.	5.17	
8f(exo)	51	193-194 dec.	4.88	11/1
9f	—	———	5.56	

a) Measured in DMSO-d_6.

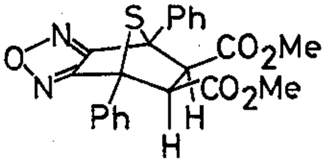
b) Estimated by nmr spectroscopy using the methine protons signals.

lated from the reaction of **1** with maleic anhydride (**7f**), an estimation of nmr spectroscopy showed the formation of endo adduct **9f**.

Next, we investigated the reaction of **1** with dimethyl fumarate and maleate. When a mixture of equimolar amounts of **1** and fumarate in benzene was refluxed under nitrogen for 8 hr, the corresponding 1:1 cycloadduct **11**, mp 125-126°C, as colorless prisms was obtained in 15% yield, with 29% recovery of **1**. A similar reaction of **1** with maleate afforded a 4% yield of exo cycloadduct **12**, mp 198.5-199°C, as colorless needles; 84% of **1** was recovered. Thus it may be concluded that the cycloaddition reaction proceeds stereospecifically. Structural elucidation of **11** and **12** was accomplished on the basis of spectral data.



11



12

11: ir (KBr) 1740 cm^{-1} (C=O); nmr ($CDCl_3$) δ 3.32, 3.49 (each 3H, s, $OC\underline{H}_3$), 3.77, 4.82 (each 1H, s, $\geqslant C\underline{H}$), 7.3-8.15 (10H, m); mass spectrum m/e (rel. intensity %) 422 (M^+, 49), 278 (100), 121 (93).

12: ir (KBr) 1740 cm^{-1}; nmr (DMSO-d_6) δ 3.30 (6H, s, $OC\underline{H}_3$), 4.55 (2H, s, $\geqslant C\underline{H}$), 7.35-7.55 (10H, m); mass spectrum m/e (rel. intensity %) 422 (M^+, 46), 278 (96), 121 (100).

However, the reaction of **1** with fumarate or maleate for a long time gave a mixture of several products whose structures are not yet established.

Study on cycloaddition reactions using other olefins and acetylenes is now in progress.

REFERENCES AND NOTES

1. M. P. Cava and G. E. M. Husbands, *J. Amer. Chem. Soc.*, 1969, **91**, 3952.
2. For a recent summary of work in this area see M. P. Cava and M. V. Lakshmikantham, *Acc. Chem. Res.*, 1975, **8**, 139.
3. A. Angeli, *Ber.*, 1893, **26**, 528.
4. The structures of **3**-**6** were confirmed by elemental analyses and spectral data.
5. No interconversion between **8a** and **9a** was observed in boiling xylene. However, **8a** or **9a** reacted with **7a** in refluxing xylene, giving the corresponding 1:1 adduct **A** (mp 277-279°C dec) or **B** (mp 185-187°C) respectively. The reaction of **1** with **7a** in refluxing xylene afforded a mixture of **8a**, **9a**, **A**, and **B**, but the structures of **A** and **B** are not yet established.
6. M. P. Cava, N. M. Pollack, O. A. Mamer, and M. J. Mitchell, *J. Org. Chem.*, 1971, **36**, 3932; M. P. Cava, N. M. Pollack, and G. A. Dieterle, *J. Amer. Chem. Soc.*, 1973, **95**, 2558; M. P. Cava, M. Behforonz, G. E. M. Husbands, and M. Srinivasan, *ibid.*, 1973, **95**, 2561.

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