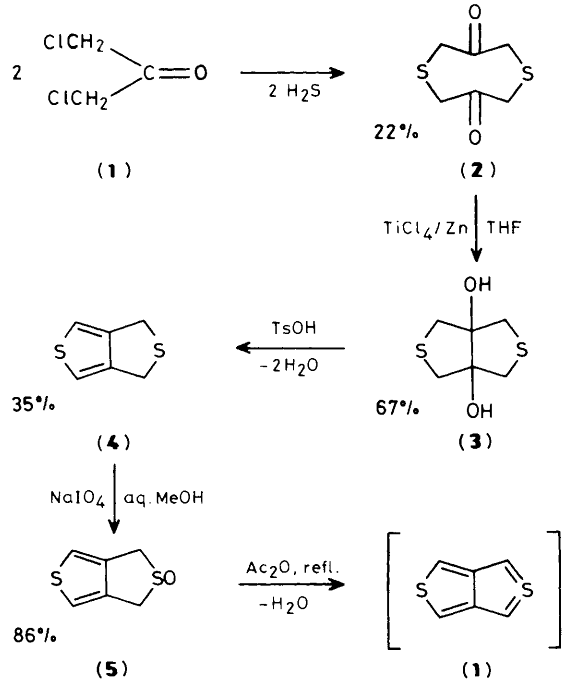
Generation and Characterization of the Parent $2\lambda^4\delta^2$-Thieno[3,4-*c*]thiophene

Juzo Nakayama,* Akihiko Ishii, Yasunobu Kobayashi, and Masamatsu Hoshino

Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338, Japan

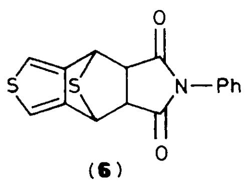
The parent $2\lambda^4\delta^2$-thieno[3,4-*c*]thiophene was generated by Pummerer dehydration of 1*H*,3*H*-thieno[3,4-*c*]thiophene 2-oxide and characterized by chemical trapping experiments.

The chemistry of $2\lambda^4\delta^2$-thieno[3,4-*c*]thiophenes (so-called 'non-classical' thienothiophenes) has been attracting considerable attention.[1—3] Although no report has appeared on the preparation of the parent thieno[3,4-*c*]thiophene (**1**), several derivatives of (**1**) have been prepared and characterized; tetrasubstituted derivatives are obtained as relatively stable, deeply coloured crystals;[4—7] disubstituted derivatives are highly reactive and have eluded isolation.[8,9] Here we report the generation and characterization of the parent species (**1**).

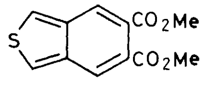


Scheme 1

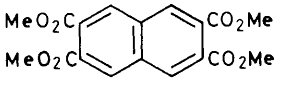
Pummerer dehydration of the sulphoxide (**5**), synthesized as depicted in Scheme 1,[10] was our method of choice for the generation of (**1**). Heating (**5**) with *N*-phenylmaleimide (5 equiv.) in refluxing acetic anhydride for 5 h afforded compound (**6**) in 84% yield. The product (**6**) corresponds to the adduct of (**1**) with the maleimide and was obtained as a mixture of *endo*- and *exo*-isomers in the ratio 1 : 1.8 (determined by ^{1}H n.m.r.). Both isomers were isolated in pure form



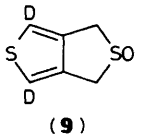
(**6**)



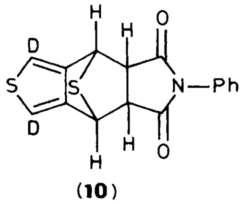
(**7**)



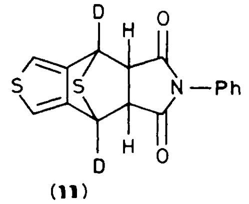
(**8**)



(**9**)



(**10**)



(**11**)

by column chromatography;† neither undergoes isomerisation in refluxing acetic anhydride. Thus the isomer ratio observed is kinetically controlled. A similar *exo* preference was observed in reactions of dimethyl and bis(methoxycarbonyl) derivatives of (**1**) with *N*-phenylmaleimide.[8,9]

Heating the imide (**5**) with an excess of dimethyl acetylenedicarboxylate (DMAD) in refluxing acetic anhydride afforded the naphthalene derivative (**8**)[11] in 73% yield. Elimination of sulphur from the initial adduct of (**1**) and DMAD presumably gave the benzothiophene derivative (**7**), which then underwent further reaction with DMAD followed by loss of sulphur.

Heating (**5**) alone in refluxing acetic anhydride gave a complex mixture, from which the thiophene (**4**) was isolated in 27% yield.‡

The labelled sulphoxide (**9**) (deuterium content, 95%) was synthesized§ and heated with *N*-phenylmaleimide in boiling acetic anhydride. ^{1}H N.m.r. analysis of the products revealed that the both *endo*- and *exo*-isomers produced were 1 : 1 mixtures of compounds (**10**) and (**11**); relative intensities of signals due to maleimide protons bridgehead protons, and thiophene ring protons were about 2.0 : 1.05 : 1.05 in both cases.¶ These findings confirm that the species generated was truly the parent thieno[3,4-*c*]thiophene (**1**), in which the two five-membered rings are chemically equivalent.

Received, 10th March 1988; Com. 8/00979A

References

1 M. P. Cava and M. V. Lakshmikantham, *Acc. Chem. Res.*, 1975, **8**, 139.

2 V. P. Litvinov and Ya. L. Gol'dfarb, *Adv. Heterocycl. Chem.*, 1976, **19**, 123.

3 M. P. Cava and M. V. Lakshmikantham, 'Comprehensive Heterocyclic Chemistry,' vol. 4, eds. C. W. Bird and G. W. H. Cheeseman, Pergamon, Oxford, 1984, 1037.

4 M. P. Cava and G. E. M. Husbands, *J. Am. Chem. Soc.*, 1969, **91**, 3952; M. P. Cava, M. Behforouz, G. E. M. Husbands, and M. Srinivasan, *ibid.*, 1973, **95**, 2561.

5 M. D. Glick and R. E. Cook, *Acta Crystallogr., Sect. B*, 1972, **28**, 1336.

6 S. Yoneda, K. Ozaki, T. Inoue, A. Sugimoto, K. Yanagi, and M. Minobe, *J. Am. Chem. Soc.*, 1985, **107**, 5801.

7 S. Yoneda, A. Tsubouchi, and K. Ozaki, *Nippon Kagaku Kaishi*, 1987, 1328.

8 M. P. Cava and N. M. Pollack, *J. Am. Chem. Soc.*, 1967, **89**, 3639.

9 M. P. Cava, N. M. Pollack, and G. A. Dieterle, *J. Am. Chem. Soc.*, 1973, **95**, 2558.

10 For the preparation of (**2**), the literature method was slightly modified: C. Rappe and R. Gustafsson, *Acta Chem. Scand.*, 1967, **21**, 705. For the conversion of (**2**) into (**4**), see J. Nakayama, M. Machida, R. Saito, and M. Hoshino, *Tetrahedron Lett.*, 1985, **26**, 1983.

11 O. W. Webster and W. H. Sharkey, *J. Org. Chem.*, 1962, **27**, 3354.

12 P. C. Myhre, M. Beug, and L. L. James, *J. Am. Chem. Soc.*, 1968, **90**, 2105.

---

† *endo*-Isomer: m.p. 220 °C (decomp.); ^{1}H n.m.r. δ (CDCl$_3$) 4.16—4.21 (m, 2H, *exo*-protons), 4.91—4.96 (m, 2H, bridgehead protons), 6.64—6.75 (m, 2H, Ph), 6.90 (s, 2H, thiophene ring protons), and 7.2—7.4 (m, 3H, Ph); *exo*-isomer: m.p. 220 °C (decomp.); ^{1}H n.m.r. δ (CDCl$_3$) 3.52 (s, 2H, *endo*-protons), 4.96 (s, 2H, bridgehead protons), 6.86 (s, 2H, thiophene ring protons), and 7.2—7.6 (m, 5H, Ph).

‡ Although the formation of (**4**) may be explained by assuming a biradical nature for (**1**), a detailed mechanism is not apparent.

§ The thiophene (**4**) was treated twice with a mixture of D$_2$O and trifluoroacetic anhydride in carbon tetrachloride[12] and then oxidised by sodium periodate.

¶ These results imply that the secondary isotope effect is too small to be observed under present conditions.