

## Intermediate formation of a thio-1,4-benzoquinoid structure in the reactions of 2,5-di-*tert*-butyl-4-chlorosulfanylphenol

Egor E. Novikov,\* Nataliya V. Chumachenko and Yurii A. Kopel'tsiv

*L'vivs'ka Politekhnika* State University, 290013 L'viv, Ukraine. Fax: +7 0322 27 1501; e-mail: yugin@avicena.med.lviv.ua

Some chemical properties of a noncondensed thio-1,4-benzoquinoid structure were experimentally studied for the first time.

The purpose of this work is to study the chemical properties of some noncondensed thio-1,4-benzoquinones. Compounds of this series are poorly understood because they are extremely unstable, and the data on them are restricted to that on nonsubstituted thio-1,4-benzoquinone isolated in an argon matrix at 10 K.<sup>1</sup>

It is known<sup>2</sup> that the introduction of *tert*-butyl groups at positions adjacent to the carbonyl group enhances the stability of quinoid compounds. Therefore, we attempted to obtain 2,6-di-*tert*-butyl-4-thioxocyclohexa-2,5-dien-1-one **2**.

1,6-Elimination of hydrogen chloride from 2,6-di-*tert*-butyl-4-chlorosulfanylphenol **1** under the action of a base seems to be the mildest method for preparation of **2** (Scheme 1).

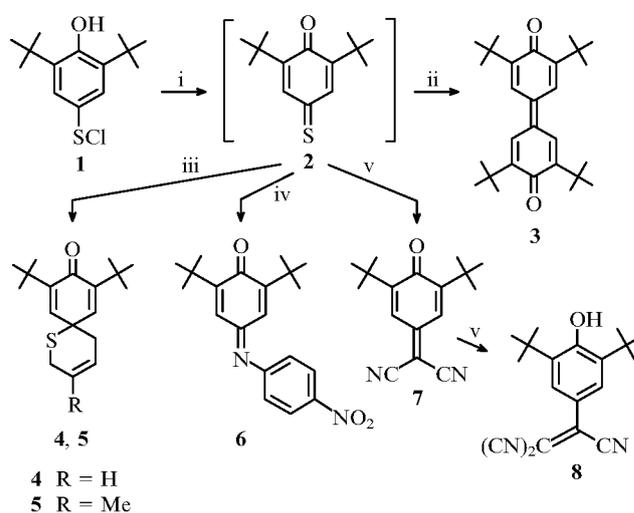
Compound **1** was obtained by chlorination of 3,5,3',5'-tetra-*tert*-butyl-4,4'-dihydroxydiphenyl disulfide by a known procedure.<sup>3</sup> P. D. Stephen<sup>3</sup> treated compound **1** with triethylamine and, after 72 h, isolated 1,1'-bis(3,5-di-*tert*-butylcyclohexa-2,5-dien-4-one-1-ylidene) **3** in 86% yield.

We have investigated time changes in the concentration of **3** ( $\lambda = 420.6$  nm) in this reaction by UV spectroscopy. It has been established that at 20 °C the reaction has ceased after less than 5 min. We suppose that the dehydrohalogenation of **1** results in the formation of **2**, which then self-condenses. Similar reactions are known for thioketones.<sup>4</sup> The intermediate formation of **2** was established on the basis of analysis of the products obtained by the 1,6-elimination of hydrogen chloride from **1** in the presence of intercepting agents such as butadiene, isoprene, 4-nitroaniline and malonodinitrile (Scheme 1).

In Diels–Alder reactions, thioketones are considerably more active as dienophiles than the corresponding carbonyl compounds.<sup>5</sup> The treatment of **1** with triethylamine in the presence of butadiene at –10 °C results in the formation of 8,10-di-*tert*-butyl-1-thiaspiro[5.5]undeca-3,7,10-trien-9-one **4**. A similar reaction in the presence of isoprene results in the

formation of one isomer, 8,10-di-*tert*-butyl-3-methyl-1-thiaspiro[5.5]undeca-3,7,10-trien-9-one **5**. The physicochemical constants of the colourless crystalline products **4** and **5** (recrystallized from methanol) were obtained.<sup>†</sup> The position of the methyl group in **5** was determined on the basis of its <sup>1</sup>H NMR spectrum.

Thioketones condense with amines more easily than the corresponding ketones to give similar products.<sup>6</sup> When 4-nitroaniline was used for the dehydrochlorination of **1** (DMF, –10 °C, 5 min, 85% yield), *N*-(4-nitrophenyl)-3,5-di-



**Scheme 1** Reagents and conditions: i base; ii, Et<sub>3</sub>N, 20 °C; iii, Et<sub>3</sub>N, butadiene or isoprene, –10 °C; iv, nitroaniline, DMF, –10 °C; v, malonodinitrile, NaOPr, Pr<sup>3</sup>OH, 0 °C.

*tert*-butyl-4-oxocyclohexa-2,5-dien-1-imine **6** described previously<sup>2</sup> was obtained. The high selectivity of the reaction makes it possible to assume that the intermediate formation of **2** is almost quantitative.

Knoevenagel condensation of thioketones usually occurs readily.<sup>7</sup> The addition of **1** to an excess of malonodinitrile in propan-2-ol in the presence of sodium isopropylate (0 °C, 5 min, 78% yield) results in the formation of 2,6-di-*tert*-butyl-4-(tricyanovinyl)phenol **8**. It is evident that the intermediate product is 4-(dicyanomethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **7** which, according to the literature,<sup>2</sup> condenses with malonodinitrile to form **8**.

---

<sup>†</sup> 8,10-di-*tert*-butyl-1-thiaspiro[5.5]undeca-3,7,10-trien-9-one **4**. (Yield 80%); mp 115–117 °C;  $\nu/\text{cm}^{-1}$  2960 (C–H), 1656 (C=O); <sup>1</sup>H NMR  $\delta$  (ppm) 1.237 s (18 H), 2.380 m (2 H), 3.333 m (2 H), 5.890 m (1 H), 5.990 m (1 H), 6.589 s (1 H), 6.594 s (1 H).

8,10-di-*tert*-3-methyl-1-thiaspiro[5.5]undeca-3,7,10-trien-9-one **5**. (Yield 75%); mp 120 °C;  $\nu/\text{cm}^{-1}$  2960 (C–H), 1653 (C=O); <sup>1</sup>H NMR  $\delta$  (ppm) 1.233 s (18 H), 1.881 s (3 H), 2.360 m (2 H), 3.195 s (2 H), 5.578 m (1 H), 6.570 s (1 H), 6.578 s (1 H).

## References

- 1 H. Bock, S. Mohmand, T. Hirabayashi, G. Maier and H. P. Reisenauer, *Chem. Ber.*, 1983, **116**, 273.
- 2 Houben-Weyl, *Methoden der organischen Chemie*, Georg Thieme Verlag, Stuttgart, 1977, Bd. VII/3a, Teil 1, S. 832.
- 3 P. D. Stephen, *J. Org. Chem.*, 1984, **49**, 5260.
- 4 E. Campaigne, in *The Chemistry of the Carbonyl Group*, ed. S. Patai, Wiley-Interscience, New York, 1966, ch. 17.
- 5 W. J. Middleton, *J. Org. Chem.*, 1965, **30**, 1390.
- 6 R. Mayer, J. Morgenstern and J. Fabian, *Angew. Chem.*, 1964, **76**, 157.
- 7 R. Couturier, D. Paquer and A. Vibet, *Bull. Soc. Chim. Fr.*, 1975, 1670.

Received: Moscow, 27th November 1995  
Cambridge, 6th February 1996; Com. 5/07959D