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

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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.[1]

It is known[2] 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**.

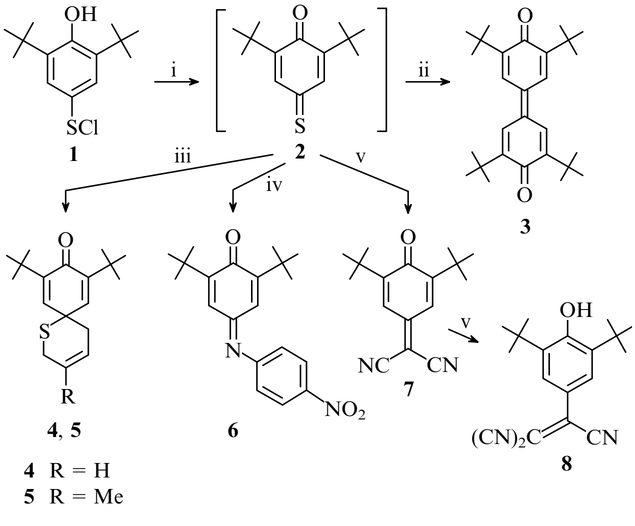
1,6-Elimination of hydrogen chloride from 2,6-di-*tert*-butyl-4-chlorosulfanylphenol **1** under the action of a base seems to be the mildest method for preparation of **2** (Scheme 1).

Compound **1** was obtained by chlorination of 3,5,3′,5′-tetra-*tert*-butyl-4,4′-dihydroxydiphenyl disulfide by a known procedure.[3] P. D. Stephen[3] 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** (λ = 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.[4] 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.[5] 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.† The position of the methyl group in **5** was determined on the basis of its ^{1}H NMR spectrum.

Thioketones condense with amines more easily than the corresponding ketones to give similar products.[6] 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_3N, 20 °C; iii, Et_3N, butadiene or isoprene, –10 °C; iv, nitroaniline, DMF, –10 °C; v, malonodinitrile, $NaOPr^i$, Pr^iOH, 0 °C.

tert-butyl-4-oxocyclohexa-2,5-dien-1-imine **6** described previously[2] 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.[7] 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,[2] condenses with malonodinitrile to form **8**.

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[†] 8,10-di-*tert*-butyl-1-thiaspiro[5.5]undeca-3,7,10-trien-9-one **4**. (Yield 80%); mp 115–117 °C; ν/cm^{-1} 2960 (C–H), 1656 (C=O); ^{1}H NMR δ (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; ν/cm^{-1} 2960 (C–H), 1653 (C=O); ^{1}H NMR δ (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).