ISSN 1070-4280, Russian Journal of Organic Chemistry, 2011, Vol. 47, No. 7, pp. 1015–1017. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © T.I. Prokof'eva, V.B. Vol'eva, I.S. Belostotskaya, N.L. Komissarova, A.V. Malkova, 2011, published in Zhurnal Organicheskoi Khimii, 2011, Vol. 47, No. 7, pp. 1001–1003.

# Chlorination of 3,6-Di-*tert*-butyl-1,2-benzoquinone in Two-Phase Catalytic System

**T. I. Prokof'eva, V. B. Vol'eva, I. S. Belostotskaya, N. L. Komissarova, and A. V. Malkova**

*Emanuel' Institute of Biochemical Physics, Russian Academy of Sciences, ul. Kosygina 4, Moscow, 119334 Russia*
*e-mail: komissarova@polymer.chph.ras.ru*

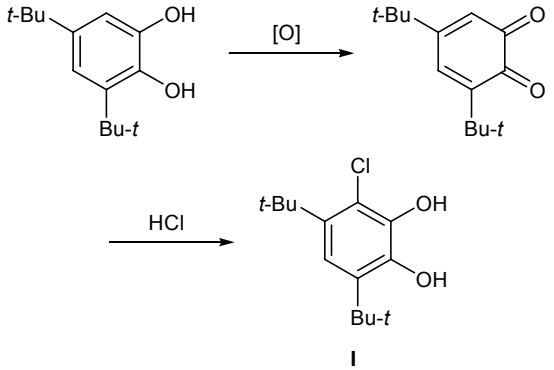
Received October 12, 2010

**Abstract**—Chlorination of 3,6-di-*tert*-butyl-1,2-benzoquinone in a two-phase catalytic system ($CH_2Cl_2$, HCl–$H_2O$, $H_2O_2$, $Bu_4NCl$) led to halogen addition at the C=C bond, and subsequent dehydrochlorination of the adduct gave 3,6-di-*tert*-butyl-4-chloro-1,2-benzoquinone. Chlorination of the latter afforded 3,6-di-*tert*-butyl-4,5-dichloro-1,2-benzoquinone.

**DOI:** 10.1134/S1070428011070086

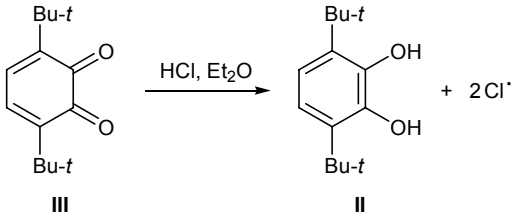
As a rule, direct chlorination of alkyl-substituted pyrocatechols is not used for selective synthesis of monochloro derivatives because of side oxidation, dealkylation, and polyhalogenation processes. Monosubstituted derivatives are obtained most frequently via dipolar 1,4-addition of hydrogen chloride to redox-conjugated quinone. For example, 3,5-di-*tert*-butyl-6-chlorobenzene-1,2-diol (**I**) is synthesized from 3,5-di-*tert*-butylbenzene-1,2-diol through the corresponding quinone (Scheme 1).

**Scheme 1.**




**I**

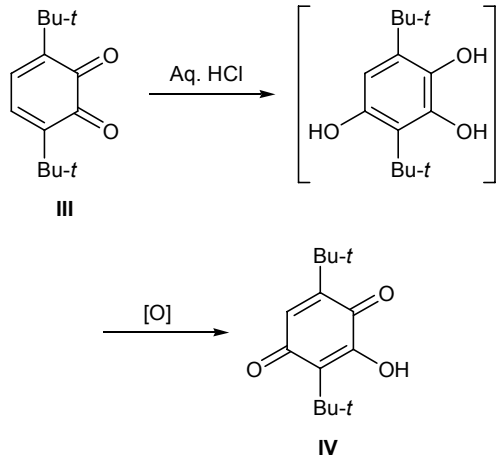
**Scheme 2.**




**III** **II**

However, analogous scheme cannot be applied to the isomeric 3,6-di-*tert*-butylbenzene-1,2-diol (**II**)–3,6-di-*tert*-butyl-1,2-benzoquinone (**III**) couple. Quinone **III** reacts with dry hydrogen chloride according to redox pattern with formation of initial pyrocatechol **II** [1] (Scheme 2). The reaction of **III** with aqueous HCl gives 3,6-di-*tert*-butyl-2-hydroxy-1,4-benzoquinone (**IV**) as a result of hydration [2] (Scheme 3).

**Scheme 3.**

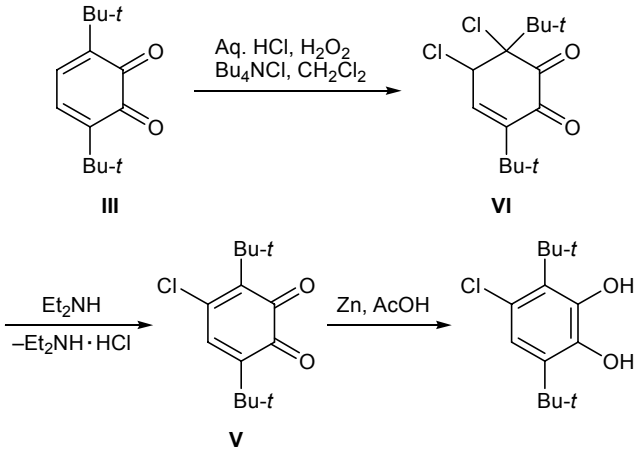



**III** **IV**

We succeeded in synthesizing 3,6-di-*tert*-butyl-4-chloro-1,2-benzoquinone (**V**) through intermediate adduct of quinone **III** with chlorine, which was generated *in situ* with the aid of hydrogen peroxide in a two-phase catalytic system containing quinone **III** in methylene chloride or carbon tetrachloride and aqueous HCl and $Bu_4NCl$. Compound **III** failed to react with

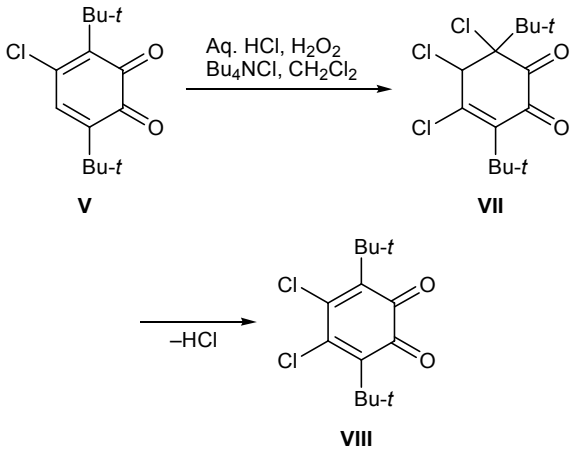
HCl or $H_2O$ in a nonpolar solvent. Chlorine liberated in the reaction of HCl with $H_2O_2$ is transferred by $Bu_4NCl$ (phase-transfer catalysis) to the organic phase where it reacts with quinone **III** to produce the corresponding adduct at the double bond, 3,6-di-*tert*-butyl-5,6-dichlorocyclohex-3-ene-1,2-dione (**VI**). Dehydrochlorination of **VI** by the action of triethylamine affords chloro-substituted quinone **V** which can be reduced to the corresponding pyrocatechol with zinc in acetic acid (Scheme 4).

**Scheme 4.**



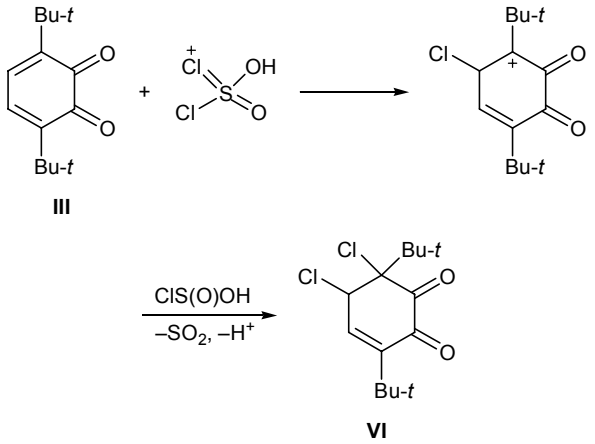

Analogous reaction sequence with quinone **V** as starting compound involves intermediate formation of 3,6-di-*tert*-butyl-4,5,6-trichlorocyclohex-3-ene-1,2-dione (**VII**) and yields 3,6-di-*tert*-butyl-4,5-dichloro-1,2-benzoquinone (**VIII**) (Scheme 5).

**Scheme 5.**



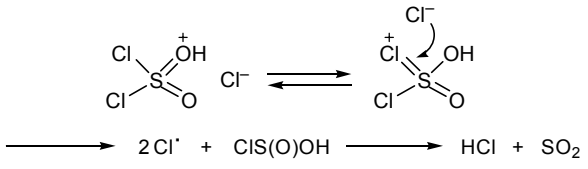

Analogous syntheses of quinones **V** and **VIII** were reported in [3] where intermediate adducts **VI** and **VII** were obtained by reaction of quinone **III** or **V** with $SO_2Cl_2$. Here, the presence of a proton donor in the reaction system was necessary, otherwise $SO_2Cl_2$ was inactive. The proposed reaction scheme implied protonation of $SO_2Cl_2$ to generate cationoid species responsible for electrophilic attack on the quinone (Scheme 6).

**Scheme 6.**




With account taken of the data obtained in the present work, a more probable reaction scheme is that implying radical rather than ionic mechanism of formation of adducts **VI** and **VII**, according to which protonation of $SO_2Cl_2$ promotes its redox dehalogenation (Scheme 7). The process may be both intra- and intermolecular with participation of acid catalyst.

**Scheme 7.**




The proposed radical mechanism for the formation of adducts **VI** and **VII** is also consistent with the ability of quinone **III** to form adducts with radical species at the endocyclic double C=C bonds, which was demonstrated in other reactions, for example, in the reaction of **III** with dihalocarbenes and in the dimerization of **III** [4, 5].

Thus selective monohalogenation of the redox couple pyrocatechol (**II**)–quinone (**III**) or substituted analogs can be performed through intermediate quinone adducts with halogen generated *in situ*. These adducts do not undergo uncontrolled transformations, and their dehydrohalogenation selectively yields the corresponding mono- and dihalo-substituted quinones.

## EXPERIMENTAL

The $^1$H NMR spectra were recorded on a WH-250 spectrometer at 250 MHz) from solutions in carbon tetrachloride using TMS as internal reference.

Compounds **V**–**VIII** were isolated in almost quantitative yields (≥95%).

**3,6-Di-*tert*-butyl-5,6-dichlorocyclohex-3-ene-1,2-dione (VI).** Quinone **III** [6], 1.1 g, was dissolved in 20 ml of methylene chloride ($c = 5\times10^{-3}$ M), 20 ml of concentrated hydrochloric acid and 0.55 g ($2\times10^{-3}$ M) of tetrabutylammonium chloride were added, and hydrogen peroxide was then added under vigorous stirring until dark brown color typical of the initial quinone disappeared. The organic phase was separated, washed with water, dried over $Na_2SO_4$, and evaporated, and the residue was recrystallized from heptane. Light yellow crystals, mp 154°C. $^1$H NMR spectrum, δ, ppm: 1.25 s (9H), 1.40 s (9H), 5.10 d (1H, $J$ = 6.4 Hz), 6.83 d (1H, $J$ = 6.4 Hz). Found, %: C 57.70; H 6.91. $C_{14}H_{20}Cl_2O_2$. Calculated, %: C 57.73; H 6.94.

**3,6-Di-*tert*-butyl-4-chlorocyclohexa-3,5-diene-1,2-dione (V).** Diethylamine, 0.44 g ($6\times10^{-3}$ M), was added to a solution of 1.46 g ($5\times10^{-3}$ M) of adduct **VI** in pentane, the precipitate was filtered off, the filtrate was washed with water, dried over $Na_2SO_4$, and evaporated, and the residue was recrystallized from hexane. Dark red crystals, mp 50–51°C [6].

**3,6-Di-*tert*-butyl-4,5,6-trichlorocyclohex-3-ene-1,2-dione (VII)** was synthesized from quinone **V** as described above for compound **VI**. Light yellow crystals, mp 86°C. $^1$H NMR spectrum, δ, ppm: 1.37 s (9H), 1.40 s (9H), 4.83 s (1H). Found, %: C 51.65; H 5.82. $C_{14}H_{19}Cl_3O_2$. Calculated, %: C 51.63; H 5.89.

**3,6-Di-*tert*-butyl-4,5-dichlorocyclohexa-3,5-diene-1,2-dione (VIII)** was synthesized from adduct **VII** as described above for quinone **V**. Dark red crystals, mp 48°C. $^1$H NMR spectrum: δ 1.40 ppm, s. Found, %: C 58.04; H 6.27. $C_{14}H_{18}Cl_2O_2$. Calculated, %: C 58.13; H 6.29.

## REFERENCES

1. Belostotskaya, I.S., Vol'eva, V.B., Komissarova, N.L., and Ershov, V.V., *Izv. Ross. Akad. Nauk, Ser. Khim*., 1976, p. 709.
2. Novikova, I.A., Vol'eva, V.B., Komissarova, N.L., Belostotskaya, I.S., and Ershov, V.V., *Izv. Ross. Akad. Nauk, Ser. Khim*., 1981, p. 2110.
3. Garnov, V.A., Navodchikov, V.I., Abakumov, G.A., Cherkasov, V.K., Abakumova, L.G., and Kurskii, Yu.A., *Izv. Ross. Akad. Nauk, Ser. Khim*., 1985, p. 2793.
4. Vol'eva, V.B., Prokof'eva, T.I., Novikova, I.A., Belostotskaya, I.S., and Ershov, V.V., *Izv. Ross. Akad. Nauk, Ser. Khim*., 1984, p. 1632.
5. Vol'eva, V.B., Prokof'ev, A.I., Zhorin, V.A., Prokof'eva, T.I., Belostotskaya, I.S., Komissarova, N.L., Karmilov, A.Yu., and Ershov, V.V., *Chem. Phys. Rep*., 1996, vol. 15, p. 13.
6. Vol'eva, V.B., Novikova, I.A., Belostotskaya, I.S., Dzhuaryan, E.V., and Ershov, V.V., *Izv. Ross. Akad. Nauk, Ser. Khim*., 1983, p. 1416.