Brief Communications

p-(Chloro-*tert*-butyl)cumene hydroperoxide

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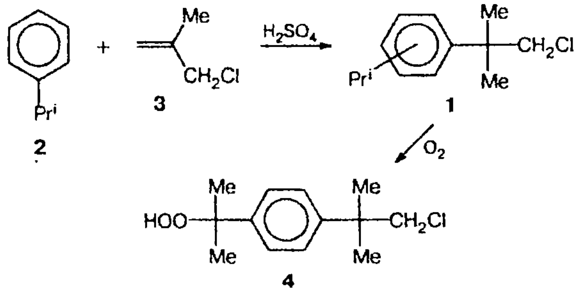
Oxidation of a mixture of *m*- and *p*-(chloro-*tert*-butyl)cumenes (12 : 88) by molecular oxygen gives only *p*-(chloro-*tert*-butyl)cumene hydroperoxide in a high yield; this product can be used for the synthesis of the pyrethroid ethofenprox.

Key words: *p*-(chloro-*tert*-butyl)cumene, oxidation by molecular O_2, hydroperoxide, pyrethroids

Ethofenprox occupies a special place in the series of synthetic pyrethroids; its structure, unlike those of the majority of pyrethroids, contains no cyclopropane fragment or ester group. Methods for the preparation of *p*-(chloro-*tert*-butyl)phenol, which is an intermediate in the synthesis of ethofenprox, have been described in the literature;[1] however, even the most efficient procedure based on the alkylation of phenol with methallyl chloride affords a mixture of *o*- and *p*-isomers, which is difficult to separate. We propose a new scheme for the synthesis of this compound based on the liquid-phase oxidation of *m*- and *p*-(chloro-*tert*-butyl)cumenes by oxygen followed by transformation of the resulting hydroperoxide into *p*-(chloro-*tert*-butyl)phenol.

The mixture of isomeric (chloro-*tert*-butyl)cumenes (**1**)* (with a *m*- to *p*-isomer ratio of 12 : 88) was prepared by alkylating[2] cumene (**2**) with methallyl chloride (**3**) in the presence of H_2SO_4. We were able to increase the yield of cumenes **1** from 80 to 90% by decreasing the reaction temperature from 10 to 0 °C and decreasing the velocity of the delivery of **3** from 1.0 to 0.33 mol h^{-1} with the same ratio of the reactants (**2** : **3** : H_2SO_4 = 3 : 1 : 0.3).



Cumenes **1** were oxidized by molecular oxygen at 80—90 °C in the presence of an initiator, azo-*bis*-isobutyronitrile (AIBN) used to shorten the induction period. The oxidation process was stopped when the

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* The systematic name of the *para*-isomer of **1** is 1-isopropyl-4-(1-chloro-2-methylprop-2-yl)benzene.

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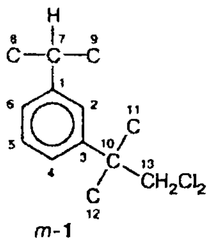
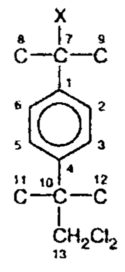
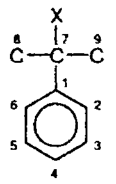


m-**1**



p-**1**: X = H
4: X = OOH



2: X = H
6: X = OOH

Table 1. ^{13}C NMR spectra ($CDCl_3$), δ of cumene and *tert*-butylcumene derivatives

Atom	*m*-**1**	*p*-**1**	**2**	**4**	**6**
C(1)	148.2	146.2	148.8	145.2	145.5
C(2, 6)	123.1, 123.8	125.9	126.8	126.1	125.9
C(3, 5)	145.7, 127.9	125.6	128.8	125.5	128.3
C(4)	123.9	143.2	126.3	142.6	127.2
C(7)	33.9	33.2	34.6	83.8	84.0
C(8, 9)	25.7	25.7	24.3	26.4	26.6
C(10)	39.0	38.9		39.6	
C(11, 12)	23.4	23.3		26.0	
C(13)	55.8	55.8		56.2	

reaction mixture contained 17—20% hydroperoxide **4***. When the content of **4** increased above 20%, noticeable formation of by-products started, due to decomposition of the hydroperoxide. To isolate and purify the hydroperoxide thus obtained, the reaction mixture was treated with a solution of NaOH to give the sodium salt **5**; the crystalline salt was separated from the liquid oxidate by filtration and washed with anhydrous benzene. The purity of the salt, checked by iodometric titration, amounted to ~100%, and its yield was ~90%. The treatment could be accomplished over the shortest period when a 30% solution of NaOH was used. Then the sodium salt **5** was treated with CO_2, and this gave pure hydroperoxide **4**.

The absence of *m*-isomer or other impurities in peroxide **4** was confirmed by ^{1}H and ^{13}C NMR spectra. The ^{1}H NMR spectrum exhibits a signal at 7.56 ppm, due to the hydroperoxide group, and two doublets for the four protons of the aromatic ring, typical of *para*-substituted benzenes. When the sample contains water, the signal for the hydroperoxide proton shifts to 7.35 ppm. The ^{13}C NMR spectrum of hydroperoxide **4** (Table 1) contains a signal at δ 83.8 ppm, typical of the benzyl carbon atom (C-7) attached to a hydroperoxide group (the corresponding signal in the spectrum of nonsubstituted cumene hydroperoxide (**6**) occurs at 84.0 ppm).[3] The ^{13}C NMR spectrum of hydroperoxide **4** contains no signals for the C atom in the *m*-isomer, whereas the ^{13}C NMR spectrum of the initial mixture of substituted cumenes **1** exhibits all the signals due to both *p*- and *m*-isomers (see Table 1). The spectrum of the *m*-isomer contains four signals for the CH atoms of the benzene ring. The three nonsubstituted C atoms of the aromatic ring in the *m*-isomer are responsible for signals at 123.1 (C-2), 123.8 (C-6), and 123.9 ppm (C-4). One lower-field signal (127.9 ppm) corresponds to the nonsubstituted C-5 atom; in the spectrum of the *p*-isomer, the signals of nonsubstituted C atoms in positions 2, 6 and 3, 5 are identical in pairs (125.9 and 125.6, respectively). The C atoms were assigned based on the additive scheme proposed in a previous study.[4] Thus, the spectral data confirm that the hydroperoxide **4** obtained is the *p*-isomer with a high degree of purity. The *p*-isomer results from the selective oxidation of the mixture of *m*- and *p*-cumenes **1**; this is apparently due to the fact that the *p*-isomer, which predominates in the initial mixture (88 : 12), is more readily oxidized at a low degree of conversion (~20%).

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 300 spectrometer (300 and 75 MHz, respectively) in CD_2Cl_2 or $CDCl_3$. GLC analysis was carried out on a Shimadzu GC-9A chromatograph (25×0.0002 m capillary column, PEG-20M as the stationary phase, flame ionization detector, temperature programming from 80 to 180 °C at a rate of 12 deg. min^{-1}, temperature of the detector and vaporizer 250 °C, He as the carrier gas).

Oxidation of (chloro-*tert*-butyl)cumene (1). Oxygen (~20 L h^{-1}) was bubbled through a mixture of AIBN (0.07 g, 0.5 mmol) and isomeric cumenes **1** (29.5 g, 0.14 mol) (ratio of the *m*- to *p*-isomers 12 : 88 according to GLC) at 80—90 °C (the temperature inside the reaction flask) for 13—17 h. When the concentration of hydroperoxide became ~20 % (determined by iodometric titration), the oxidation was terminated. The resulting oxidate was cooled to 0 °C and washed twice with a 1—2% solution of NaOH in order to remove the acids formed during the oxidation. After that, 2.5 mL of 30% NaOH was added with stirring at ~0 °C to the organic solution containing ~25 mmol of hydroperoxide **4**. The thick reaction mixture thus formed was kept for 10 h at −5 °C, the precipitate of the crystalline salt **5** was filtered off, washed 3 times with dry benzene (3—4 mL), and dried *in vacuo* at 10 Torr to give 8.38 g (22.5 mmol based on hexahydrate) of salt **5**, whose purity was checked by iodometry. On treatment of the salt with 60 mL of water, the crystals were rapidly converted into an oil, which solidified within 0.5—1 min and, upon trituration in water, it turned again into a powder. Carbon dioxide was passed through the resulting suspension of the salt for 10 min, and hydroperoxide **4** was filtered off and dried at 10 Torr for 10—15 h. The yield of **4** from the Na-salt was 5.19 g (95%); according to the results of iodometric titration, the content of hydroperoxide was ~100%.

The ^{1}H NMR spectrum of hydroperoxide **4** (CD_2Cl_2), δ: 1.3 and 1.45 (both s, 2×6 H, 4 Me); 3.57 (s, 2 H, CH_2Cl); 7.25 and 7.32 (both d, 4 H, C_6H_4, J = 7.0 Hz); 7.56 (s, 1 H, OOH). The ^{13}C NMR spectrum is presented in Table 1.

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* The systematic name of hydroperoxide **4** is 2-[4-(1-chloro-2-methylprop-2-yl)phenyl]prop-2-yl hydroperoxide.

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Unusual nucleophilic substitution in the nitrophthalimide series

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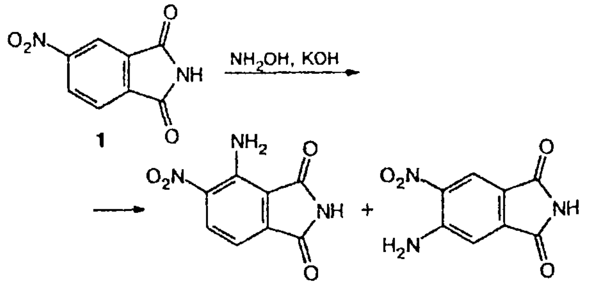
The reactions of 3- and 4-nitrophthalimides with hydroxylamine in aqueous alcohol media were studied. A mixture of 3-amino-4-nitro- and 4-amino-5-nitrophthalimides is formed in the case of 4-nitrosubstituted derivative, whereas 3,6-dihydroxyphthalimide is unexpectedly found to be the main product of the reaction of 4-nitrosubstituted derivative. A possible mechanism of the transformation was suggested.

Key words: phthalimide, hydroxylamine, nucleophilic substitution, 3,6-dihydroxyphthalimide.

Many works, summarized in the monograph,[1] are devoted to the chemistry of hydroxylamine. These studies showed that hydroxylamine is a convenient aminating reagent, which allows amino groups to be inserted in electron-deficient heterocycles, for example, in nitrosubstituted derivatives of quinoline.[2] Aromatic compounds activated by electron-withdrawing substituents also react sufficiently readily, for example, *m*-dinitrobenzene affords 2,4-dinitroaniline in high yield.[2]

Substituted phthalimides are the starting compounds in the synthesis of the corresponding phthalonitriles,[3] phthalocyanines, and tetrabenzoporphines, which are of unambiguous practical interest as mesomorphic[4] and nonlinear-optic[5] materials, dyes and pigments, whose properties are mainly dependent on the number and nature of substituents in the macrocycle periphery.[4]

In order to obtain isomeric nitroaminophthalimides, we studied the reactions of hydroxylamine with 4- and 3-nitrophthalimide (**1** and **2**) in aqueous-alcohol media in the presence of KOH.



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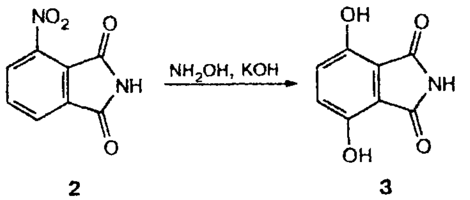

2 **3**

In the presence of 4-nitrophthalimide, as should be expected, we obtained a mixture of 3-amino-4-nitro- and 5-amino-4-nitrophthalimides with a ~60 : 40 isomer ratio (according to the ^{1}H NMR spectroscopic data). The presence of the nitro and amino groups in the

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