

Reactions of tetrahalogeno-*o*-benzoquinones—Part VII*. Reaction of alkyl-2-naphthols with tetrachloro-*o*-benzoquinone

T R KASTURI and R SIVARAMAKRISHNAN
Department of Organic Chemistry, Indian Institute of Science,
Bangalore 560 012

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Abstract. Reaction of 8-methyl-2-naphthol (4a) with the quinone 3 gave a mixture of 8-methyl-2,2-(tetrachloro-*o*-phenylenedioxy)naphthalen-1(2H)-one (1b) and 8-methyl-1,1-(tetrachloro-*o*-phenylenedioxy)naphthalen-2(1H)-one (2b) in almost equal amounts. Similarly, reaction of the naphthols (4b), (4d) and (4e) with 3 gave the corresponding dienones (1c & 2c), (1e & 2e) and (1f & 2f) in almost equal amounts. Reaction of 8-*t*-butyl-2-naphthol (4c) with 3 gave exclusively 8-*t*-butyl-2,2-(tetrachloro-*o*-phenylenedioxy)-naphthalen-1(2H)-one (1d). Oxidation of 3-*t*-butyl-2-naphthol (4f) with 3 gave a mixture of 3-*t*-butyl-2,2-(tetrachloro-*o*-phenylenedioxy)naphthalene-1(2H)-one (1g) and 3-*t*-butyl-1,1-(tetrachloro-*o*-phenylenedioxy)naphthalen-2(1H)-one (2g) in the ratio 1 : 6. Thus, only *t*-butyl group exerts pronounced steric influence on the rearrangement observed in the reaction of β -naphthol with the quinone 3. Structures of all the compounds have been established by spectral data.

Keywords. Oxidation; *o*-chloranil; alkyl naphthols; NMR spectra and dienones.

1. Introduction

We have earlier reported the formation of two isomeric dienones (1a and 2a) during the oxidation of β -naphthol using tetrachloro-*o*-benzoquinone (3) (δ -chloranil), involving an unusual rearrangement (Kasturi *et al* 1970). With a view to studying the generality as well as the effect of substituents on this rearrangement, the synthesis of several substituted α - and β -naphthols (4) & (5) was achieved (Kasturi and Sivaramakrishnan 1975; Kasturi and Sivaramakrishnan 1976). In the present paper, we wish to report the oxidation of some of these substituted naphthols with *o*-chloranil.

In all the cases studied, the naphthol was allowed to react with 2 mols of the quinone in refluxing dry benzene. After the usual work up, (Kasturi *et al* 1970; Kasturi and Arunachalam 1968) the reaction mixture was chromatographed over neutral alumina. Elution with hexane-benzene mixtures followed by benzene gave mainly the dienone(s). The proportion of the dienones in the mixture was determined either from its NMR spectrum or through separation by preparative TLC. Both methods gave comparable results. In the NMR spectrum of the dienone 1a, the

*For Part VI see Kasturi and Sivaramakrishnan (1977).

c-3 and c-4 protons appear as two doublets ($J=10$ Hz) at 6.3 and 6.92** respectively. In the case of the dienone 2a the C-3 proton appears as a doublet at 6.19 ($J=10$ Hz) while the C-4 proton is considerably deshielded and appears as a doublet at 7.44 ($J=10$ Hz) along with the aromatic protons. Hence the proportion of the two isomers in a mixture of the two can be determined from the relative intensities of the signals between 6.1-6.35 and 6.8-6.95 in its NMR spectrum.

2. Results and discussion

2.1. Reaction of 8-alkyl-2-naphthols

(i) 8-Methyl-2-naphthol (4a)

Reaction of this naphthol with the quinone (3) gave a yellow solid which was separated into two compounds in the ratio 3 : 2. The NMR spectrum of the major compound exhibited signals at 2.62 (s, 3H, ar-CH₃), 6.27 (d, $J=10$ Hz, 1H, C-3H), 6.87 (d, $J=10$ Hz, 1H, C-4H) and 7.0-7.60 (m, 3H, Ar-H). The presence of two doublets at 6.27 and 6.87 confirmed the α -dienone structure 1b. The other compound exhibited two mutually coupled doublets ($J=10$ Hz) at 6.17 and 7.43 and hence, was assigned the β -dienone structure 2b. The NMR spectrum of the mixture also indicated that 1b and 2b are formed in the ratio 3 : 2.

(ii) 8-Isopropyl-2-naphthol (4b)

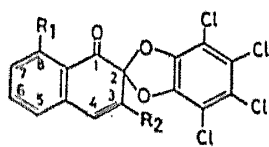
Reaction of 4b with the quinone 3 also resulted in the formation of a mixture of the two dienones 1c and 2c. A study of its NMR spectrum as well as separation by preparative TLC showed that 1c and 2c are formed approximately in the ratio 3 : 2. The structures of these two compounds followed from their NMR spectra.

(iii) 8-*t*-Butyl-2-naphthol (4c)

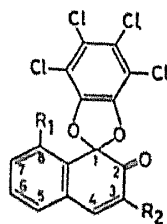
8-*t*-Butyl-2-naphthol (4c) on reaction with the quinone 3 afforded a yellow solid in 25% yield, which was found to be a mixture of compounds (TLC). Purification of this solid by preparative TLC furnished a yellow solid (70% of the mixture). In the NMR spectrum, two one proton doublets ($J=10$ Hz) appeared at 6.25 (C-3H) and 6.84 (C-4H) suggesting that this compound is the α -dienone (1d). Further, the signals at 1.38 [s, 9H, -C(CH₃)₃], 7.05 (d, $J_0 = 7$ Hz, $J_m = 2$ Hz, 1H, ar-H) and 7.3-7.65 (m, 2H, ar-H) confirmed this structure.

Since the isomeric spirodienone 2d could not be isolated from the reaction product, the NMR spectrum of the crude mixture was examined. It exhibited the two doublets at 6.25 and 6.84 due to the C-3 and C-4 protons of the α -dienone (1d). The intensity

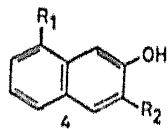
**Chemical shifts reported here and elsewhere in the paper are in δ values (ppm) relative to TMS as internal standard.

1

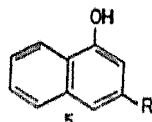
- a : $R_1 = R_2 = H$
 b : $R_1 = CH_3$; $R_2 = H$
 c : $R_1 = -CH(CH_3)_2$; $R_2 = H$
 d : $R_1 = -C(CH_3)_3$; $R_2 = H$
 e : $R_1 = H$; $R_2 = CH_3$
 f : $R_1 = H$; $R_2 = -CH(CH_3)_2$
 g : $R_1 = H$; $R_2 = -C(CH_3)_3$

2

- a : $R_1 = R_2 = H$
 b : $R_1 = CH_3$; $R_2 = H$
 c : $R_1 = -CH(CH_3)_2$; $R_2 = H$
 d : $R_1 = -C(CH_3)_3$; $R_2 = H$
 e : $R_1 = H$; $R_2 = CH_3$
 f : $R_1 = H$; $R_2 = -CH(CH_3)_2$
 g : $R_1 = H$; $R_2 = -C(CH_3)_3$

4

- a : $R_1 = CH_3$; $R_2 = H$
 b : $R_1 = -CH(CH_3)_2$; $R_2 = H$
 c : $R_1 = -C(CH_3)_3$; $R_2 = H$
 d : $R_1 = H$; $R_2 = CH_3$
 e : $R_1 = H$; $R_2 = -CH(CH_3)_2$
 f : $R_1 = H$; $R_2 = -C(CH_3)_3$

5

- $R = CH_3; -CH(CH_3)_2; -C(CH_3)_3$

of these two signals were almost equal, indicating that the β -dienone 2d was not present to any significant extent in the reaction product.

2.2. Reaction of 3-alkyl-2-naphthols

(i) 3-Methyl-2-naphthol (4d)

Reaction of this naphthol with the quinone afforded a yellow solid in 62% yield. Separation by preparative TLC followed by identification based on their NMR spectra showed the two compounds to be the dienones 1e and 2e formed in almost equal amounts. In the NMR spectrum, the methyl protons of the dienones 1e and 2e appeared as doublets ($J=1$ Hz) at 2.02 and 2.0 respectively due to the allylic coupling of the methyl protons with the vinylic C-4 proton (Jackman and Sternhell 1969). The signal due to the C-4 proton of the α -dienone 1e appeared as a broad singlet at 6.64 while that of the β -dienone 2e merged with the aromatic proton signals.

The NMR spectrum of the mixture showed a triplet ($J=1$ Hz) centred at 2.01 and a singlet at 6.64 their intensities having a 6 : 1 relationship. This is in agreement with the above observation that the two compounds 1e and 2e are formed in almost equal amounts.

(ii) 3-Isopropyl-2-naphthol (4e)

Reaction of the quinone 3 with this naphthol 4e afforded a yellow solid in 65% yield which showed a single spot in TLC in different solvent systems. The NMR spectrum of this solid exhibited two overlapping doublets at 1.19, 1.25 [$J=7$ Hz in both cases] 12 units], a broad multiplet between 2.4–3.4 (2u) singlet at 6.70 (1u) and a multiplet between 7.1–8.14 (9u). The occurrence of two overlapping doublets indicated the presence of two isopropyl groups. This suggested that the solid obtained is a mixture of the two dienones 1f and 2f. The singlet at 6.7 can be assigned to the C-4 proton of the α -dienone (1f). From the ratio of the intensities of the signals due to the isopropyl methyl protons and the vinyl proton of 1f, it can be concluded that the two dienones 1f and 2f are formed in nearly equal amounts. Attempts to separate these compounds by either preparative TLC or fractional crystallization proved to be unsuccessful.

(iii) 3-t-Butyl-2-naphthol (4f)

Oxidation of this compound using the quinone 3 afforded a yellow compound in 70% yield. Fractional crystallization of this solid from benzene-hexane afforded a yellow solid (70% of the mixture) which exhibited in the NMR spectrum a singlet at 1.28 (9H) and a multiplet between 7.23–7.25 (5H) suggesting the compound to be the β -dienone (2g). Preparative TLC of the mother liquor obtained after removing 2g afforded two yellow solids. One of them was found to be identical with the aforementioned β -dienone 2g obtained by fractional crystallization. The NMR spectrum of the other compound exhibited signals at 1.3 [s, 9H, $-\text{C}(\text{CH}_3)_3$], 6.87 (s, 1H, C-4H) and 7.1–8.2 (m, 4H or H) in agreement with the α -dienone structure 1g. The two compounds (1g) and (2g) were thus obtained approximately in the ratio 1 : 6.

2.3. Conclusions

Thus, it is seen that oxidation of β -naphthols with *o*-chloranil is a general reaction and it leads to the formation of the isomeric dienones invariably. The steric effect of the substituents at 8 and 3 positions on the rearrangement reaction is not obvious, except when a very bulky group like *t*-butyl group is present at 8 and 3 position. Further work to elicit electronic effects, if any, on this rearrangement reaction is in progress.

3. Experimental*

3.1. Reaction of naphthols with the quinone

General procedure: To a solution of the naphthol (1 mole) in dry benzene (10 ml for 0.001 mole of naphthol) the quinone 3 (2 moles) was added and the solution was

*For details see Kasturi and Sivaramakrishnan 1977.

refluxed for 6 hr. Solvent was removed *in vacuo* and the residue chromatographed over neutral alumina (1 : 40 ratio). The product was further purified by TLC and/or crystallization.

3.2. Reaction of 8-methyl-2-naphthol (4a) with the quinone 3

The naphthol 4a (0.63 g) and the quinone 3 (2g) in benzene (40 ml) furnished a yellow solid (0.7g). Preparative TLC (benzene) gave 8-methyl-2,2-(tetrachloro-*o*-phenylenedioxy)-naphthalene-1-(2H)-one 1b (0.39g), m.p. 180–181° (benzene-hexane); IR (nujol); ν_{\max} 1682 (conjugated C=O) and 1500 cm^{-1} (C=C); UV (EtOH); λ_{\max} 220 (ϵ , 50,910), 242 (54,260), 307 (6095) and 364 nm (2800); [Found: C, 51.05; H, 2.33; Cl, 35.30. $\text{C}_{17}\text{H}_8\text{Cl}_4\text{O}_3$ requires: C, 50.79; H, 2.01; Cl, 35.27%] and 8-methyl-1,1-(tetrachloro-*o*-phenylenedioxy)-naphthalen-2(1H)-one (2b) (0.25 g), m.p. 187° (benzene-hexane); IR (nujol): ν_{\max} 1680, 1620 and 1580 cm^{-1} ; UV (EtOH): λ_{\max} 223 (ϵ , 48, 230), 237 (36,980), 310 (4180) and 364 nm (5630); NMR (CDCl_3): 2.33 (s, 3H, ar- CH_3), 6.17 (d, $J=10\text{Hz}$, 1H, C-3H) and 7.2–7.5 (m, 4H, -C-4H and ar-H) [Found: C, 51.27; H, 2.42; Cl, 35.05. $\text{C}_{17}\text{H}_8\text{Cl}_4\text{O}_3$ requires: C, 50.79; H, 2.01; Cl, 35.27%].

3.3. Reaction of 8-isopropyl-2-naphthol (4b) with the quinone (3)

Reaction of 4b (0.55g) with the quinone 3 (1.5g) in benzene (30 ml) afforded a yellow solid (0.48g). Preparative TLC [benzene-hexane (1 : 1)] of the solid gave 8-isopropyl-2,2-(tetrachloro-*o*-phenylenedioxy)-naphthalen-1-(2H)-one (1c) (0.27g), m.p. 167° (benzene-hexane); IR (nujol): ν_{\max} 1690, 1590 and 1588 cm^{-1} ; UV (EtOH); λ_{\max} 223 (ϵ , 43,000), 243 (45,870), 307(6165) and 362 nm (2880); NMR (CDCl_3): 1.23 [d, $J=7\text{ Hz}$, 6H, -CH (CH_3)₂], 4.0 (m, $J=7\text{ Hz}$, 1H, -CH (CH_3)₂), 6.28 (d, $J=10\text{ Hz}$, 1H, C-3H), 6.88 (d, $J=10\text{Hz}$, 1H, C-4H), 7.09 (d of d, $J_0=7\text{ Hz}$, $J_m=2\text{ Hz}$, ar-H) and 7.4–7.65 (m, 2H, ar-H) [Found: C, 53.51; H, 3.14; Cl, 32.72. $\text{C}_{19}\text{H}_{12}\text{Cl}_4\text{O}_2$ requires: C, 53.06; H, 2.81; Cl, 32.96%] and 8-isopropyl-1,1-(tetrachloro-*o*-phenylenedioxy)-naphthalen-2-(1H)-one (2c) (0.17g), m.p. 283° (benzene-hexane); IR (nujol): ν_{\max} 1682, 1620 and 1580 cm^{-1} ; UV (EtOH); λ_{\max} 221 (ϵ , 46, 440), 240 (37,840), 310 (5330) and 354 nm (8000); NMR (CDCl_3): 1.21 [d, $J=7\text{ Hz}$, 6H, -CH (CH_3)₂], 2.92 [m, 1H, CH (CH_3)₂], 6.19 (d, $J=10\text{ Hz}$, 1H, C-3H) and 7.15–7.62 (m, 4H, C-4H and ar-H) [Found: C, 53.44; H, 2.91; Cl, 33.18. $\text{C}_{19}\text{H}_{12}\text{Cl}_4\text{O}_3$ requires: C, 53.06; H, 2.81 and Cl, 32.96%].

3.4. Reaction of 8-*t*-butyl-2-naphthol (4c) with the quinone (3)

The naphthol 4c (0.4g) and the quinone 3 (1g) in benzene (20 ml) gave a yellow solid (0.3g), preparative TLC [benzene-hexane (2 : 1)] of which afforded 8-*t*-butyl-2,2-(tetrachloro-*o*-phenylenedioxy)-naphthalen-1-(2H)-one (1d) (0.22 g), m.p. 192–193° (benzene-hexane); IR (nujol); ν_{\max} 1685, 1610 and 1580 cm^{-1} ; UV (EtOH): λ_{\max} 219 (ϵ , 44,400), 242 (33,900), 206 sh (3990), 306(4400) and 350 nm (1780); [Found: C, 54.62; H, 3.43; Cl, 31.65. $\text{C}_{20}\text{H}_{14}\text{Cl}_4\text{O}_3$ requires: C, 54.09; H, 3.17; Cl, 31.93%].

3.5. Reaction of 3-methyl-2-naphthol (4d) with the quinone 3

Reaction of 4d (0.63g) with the quinone 3 (0.2g) in benzene (40ml) gave a solid. Preparative TLC [benzene-hexane (4 : 1)] of this solid gave 3-methyl-2, 2-(tetrachloro-*o*-phenylenedioxy)-naphthalen-1-(2H)-one (1c) (0.5g), m.p. 218–219° (benzene-hexane); IR (nujol): ν_{\max} 1690 and 1600 cm^{-1} ; UV(EtOH): λ_{\max} 220 (ϵ , 46,380), 244 (68,000) 304 (7730) and 375 nm (3030); NMR (CDCl_3): 2.03 (d, $J=1\text{Hz}$, 3H, $-\text{CH}=\text{C}-\text{CH}_3$) 6.64 (br.s., 1H, C–4H), 7.1–7.5 (m, 3H, ar–H) and 8.0 (*d* of *d*, $J_0=7\text{Hz}$, $J_m=2\text{Hz}$, 1H, C–8H) [Found: C, 50.64; H, 2.01; $\text{C}_{17}\text{H}_8\text{Cl}_4\text{O}_3$ requires: C, 50.79; H, 1.99%] and 3-methyl-1,1-(tetrachloro-*o*-phenylenedioxy)-naphthalen-2(1H)-one (2e) (0.51g), m.p. 209–210° (benzene-hexane); IR (nujol): ν_{\max} 1695 cm^{-1} ; UV (EtOH): λ_{\max} 220 (ϵ , 47,300), 240 (41,260), 244 (40,580), 307 (5150) and 355 nm (6080); NMR (CDCl_3): 2.0 (d, $J=1\text{Hz}$, 1H, $-\text{CH}=\text{C}-\text{CH}_3$) and 7.2–7.8 (m, 5H, C–4H and ar–H) [Found: C, 50.48; H, 2.17, $\text{C}_{17}\text{H}_8\text{Cl}_4\text{O}_3$ requires: C, 50.79; H, 1.99%].

3.6. Reaction of 3-isopropyl-2-naphthol (4e) with the quinone (3)

Reaction of the naphthol (4e) (0.37g) and the quinone 3 (1g) in benzene (20ml) gave a red solid. Crystallization of this from benzene-hexane gave a mixture ($\sim 1:1$) (0.56g) of isomeric 3-isopropyl-2, 2-(tetrachloro-*o*-phenylenedioxy)-naphthalen-1 (2H)-one (1f) and 3-isopropyl-1,1-(tetrachloro-*o*-phenylenedioxy)-naphthalen-2(1H)-one (2f). It showed a single spot in TLC (different solvent systems like benzene-hexane ethylacetate-hexane, chloroform-hexane, etc.); NMR (CDCl_3): 1.19 and 1.25 [d, $J=7\text{Hz}$, 12H, $2 \times \text{CH}(\text{CH}_3)_2$], 2.4–3.4 [m, 2H, $2 \times -\text{CH}(\text{CH}_3)_2$], 6.7 (*s*, $\sim 1\text{H}$, C–4H of 1f) and 7.1–8.14 (m, 9H, C–4H and ar–H) [Found: C, 53.33; H, 3.10; Cl, 33.45. $\text{C}_{19}\text{H}_{12}\text{Cl}_4\text{O}_3$ requires: C, 53.06; H, 2.81; Cl, 32.96%].

3.7. Reaction of 3-*t*-butyl-2-naphthol (4f) with the quinone 3

3-*t*-Butyl-2-naphthol (4f) (1g) and the quinone 3 (2.5g) in benzene (50ml) gave a yellow solid (1.7g). Crystallization of this solid from benzene-hexane mixture afforded 3-*t*-butyl-1,1-(tetrachloro-*o*-phenylenedioxy)-naphthalen-2-(1H)-one (1g) (1.1g), m.p. 242°; IR (nujol): ν_{\max} 1695, 1605 and 1590 cm^{-1} ; UV (EtOH): λ_{\max} 220 (ϵ , 49,500), 240 (37,100), 245 sh (36,980), 308 (5480) and 350 nm (5830); [Found: C, 54.15; H, 3.60; Cl, 31.96. $\text{C}_{20}\text{H}_{14}\text{Cl}_4\text{O}_3$ requires: C, 54.09; H, 3.17; Cl, 31.93%]. Preparative TLC [benzene-hexane (3 : 7)] of the mother liquor gave 1g (0.22g), identical with the sample obtained above, and 3-*t*-butyl-2,2-(tetrachloro-*o*-phenylenedioxy)-naphthalen-1(2H)-one (2g) (0.23g), m.p. 148–149° (benzene-hexane); IR (nujol): ν_{\max} 1700 and 1600 cm^{-1} ; UV(EtOH): λ_{\max} 221 (ϵ , 46,960), 241 sh (51,390), 246 (54,140), 301 sh (6020), 305 (6130) and 380 nm (2045); [Found: C, 54.56; H, 3.58, Cl, 31.78. $\text{C}_{20}\text{H}_{14}\text{Cl}_4\text{O}_3$ requires: C, 54.09; H, 3.17; Cl, 31.93%].

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