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# THE SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF SOME HALOGENO-1,2-NAPHTHOQUINONES

R. W. A. OLIVER, R. M. RASHMAN and A. W. SOMERVILLE
University of Salford

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**Abstract**—The synthesis and spectroscopic properties of a number of chloro- and bromo-1,2-naphthoquinones are reported and discussed.

IN CONNECTION with a study of the properties of n→π*, singlet–singlet, and singlet–triplet, electronic transitions occurring in 1,2-naphthoquinones, a number of chloro- and bromo-1,2-naphthoquinones of high purity were required. This paper reports the preparation and purification of these compounds and the spectroscopic properties used to elucidate their molecular structure.

Most previous syntheses of halogeno naphthoquinones involved the oxidation of halogen substituted amino naphthols or dihydroxy naphthalenes using a variety of oxidizing agents. Cassebaum[1] and Teuber *et al.*[2] have reported that Fremy's salt [$NO(SO_3K)_2$] will oxidize naphthols directly to naphthoquinones. If a 1-naphthol is used a 1,4-naphthoquinone is formed, unless the 4-position is blocked by another substituent when a 1,2-naphthoquinone results. If a 2-naphthol is the starting compound 1,2-naphthoquinones result, In the present investigation similar experiments have been performed starting with both halogeno 1-, and 2-naphthols and the results are summarized in Table 1.

Examination of the table shows that crystallizable products are not always formed directly from the reaction mixture and that chromatographic techniques have sometimes to be used.

The UV and visible absorption spectra of the various halogeno quinones were measured at room temperature, in chloroform solution, and the results are summarized in Table 2.

Band assignments are based on the Platt system and are due to Sidman.[8] A comparison of the absorption spectra of the synthetic halogeno-quinones with the spectra of both 1,2-naphthoquinone and 1,4-naphthoquinone provides confirmatory evidence that these compounds are substituted 1,2-naphthoquinones.

It is predicted[9] that the effect of a halogen substituent in close proximity (viz. 3- or possibly 8-position) to a CO group in 1,2-naphthoquinone will increase the intensity of the n → π*, ($^1A \rightarrow {}^1U$) transition. Reference to Table 2 shows that this is the case. It is also found that a halogen atom in the 3-position shifts the π → π*, ($^1A \rightarrow {}^1L_b$) transition to the red.

Substitution in the 6-position of 1,2-naphthoquinone affects two of the π → π* transitions. The longest wavelength band, ($^1A \rightarrow {}^1L_b$) is altered both in shape and intensity, while the intensity of the ($^1A \rightarrow {}^1L_a$) transition is more than doubled. These observations indicate that the electronic absorption spectra of substituted

TABLE 1. PREPARATION OF HALOGENO-1,2-NAPHTHOQUINONES USING FREMY'S SALT

| Starting material | Isolated 1,2-naphthoquinone | M.p. °C | Yield % | Isolation procedure | Found C; H | Analysis % empirical formula | Requires C; H |
|---|---|---|---|---|---|---|---|
| 4-Chloro-1-naphthol (I) | 4-Chloro (VIII) | 135–136 | 39 | Chromatography (silica gel) | 62·3; 2·5 | $C_{10}H_5O_2Cl$ | 62·3; 2·6 |
| 4-Bromo-1-naphthol[3] (II) | 4-Bromo (IX) | 154 | trace | Chromatography (silica gel) | 50·7; 2·2 | $C_{10}H_5O_2Br$ | 50·7; 2·1 |
| 6-Bromo-2-naphthol (III) | 6-Bromo (X) | 167 | 71 | Recrystallization (ethanol) | 50·6; 2·2 | $C_{10}H_5O_2Br$ | 50·7; 2·1 |
| 6-Chloro-2-naphthol[4] (IV) | 6-Chloro (XI) | 161 | 35 | Recrystallization (ethanol) | 62·4; 2·6 | $C_{10}H_5O_2Cl$ | 62·3; 2·6 |
| 3-Chloro-2-naphthol (V) | 3-Chloro (XII) | 172 | 68 | Recrystallization (ethanol) | 62·4; 2·5 | $C_{10}H_5O_2Cl$ | 62·3; 2·6 |
| 8-Chloro-2-naphthol[5] (VI) | None | — | 0 | The starting materials in these two oxidations were recovered quantitatively. | | | |
| 8-Bromo-2-naphthol[5] (VII) | None | — | 0 | | | | |

TABLE 2. ELECTRONIC ABSORPTION SPECTRUM OF NAPHTHOQUINONES IN CHLOROFORM

| Compound | $\lambda_{max}$ mμ | $\varepsilon_{max}$ | $M^{-1}$ $cm^{-1}$ | |
|---|---|---|---|---|
| | $^1A \rightarrow {}^1B_b$ | $^1A \rightarrow {}^1L_a$ | $^1A \rightarrow {}^1L_b$ | $^1A \rightarrow {}^1U$ |
| XII | 256 (25,120)<br>262 (25,120) | 350 (2454) | 431 (2399) | 525 (148) |
| 3-Bromo-1,2-naphthoquinone[6] (XIII) | 256 (23,440)<br>262 (22,910) | 350 (2512) | 432 (2189) | 527 (162) |
| XI | 259·5 (24,540) | 352·5 (4571) | 405 (1950)<br>(inflexion) | 524 (50) |
| X | 263 (24,540) | 355 (5370) | 407 (1549)<br>(inflexion) | 523 (66) |
| VIII | 250 (26,300)<br>255 (28,840) | 351 (2691) | 400 (2818) | 526 (60) |
| 1,2-Naphthoquinone (XIV) | 250 (31,620) | 350 (1919) | 400 (3162) | 520 (60) |
| 1,4-Naphthoquinone[7] (XV) | 260 (11,220)<br>265 (7943) | | 335 (1995) | 420 (63) |

1,2-naphthoquinones provides information on the position of the substituent groups.

The IR spectra of the naphthoquinones were measured using the KBr disc technique (1% w/w) and the results are listed in Table 3.

In the absence of a complete vibrational analysis of 1,2-naphthoquinone it is not possible to make definite band assignments. However, a study of the absorption bands occurring in the carbonyl region of the spectra and of the very strong and strong absorptions at lower frequencies enabled two absorptions to be tentatively assigned and revealed characteristic substitution patterns.

Since the very strong absorption band found at 1648 $cm^{-1}$ in 1,2-naphthoquinone is practically independent of the substituent it is tentatively assigned to the carbonyl stretching vibration of the quinone carbonyl in the 1- position. The other very strong absorption band found at 1650 $cm^{-1}$ in the 1,2-naphthoquinone is markedly affected by the substituent, especially by the presence of a halogen atom in the 3- position and this is tentatively assigned to the carbonyl stretching vibration of the second carbonyl group of the quinone. The 3-halogeno-1,2-naphthoquinones may be further characterised in the carbonyl region by the absence of absorption at high frequencies.

At lower frequencies all of the 1,2-naphthoquinones absorb strongly in the three regions 1573–1587 $cm^{-1}$, 1278–1288 $cm^{-1}$ (except for the 3-chloro-derivative which has a weak absorption band at 1278 $cm^{-1}$), and 1230–1250 $cm^{-1}$. The absence of a very strong absorption band at 853 $cm^{-1}$ coupled with the presence of a very strong absorption band at 759 $cm^{-1}$ appears to be characteristic of halogeno-1,2-naphthoquinones with the halogen substituent in the quinonoid ring. Further, it is

TABLE 3. IR ABSORPTION SPECTRA OF 1,2-NAPHTHOQUINONES

| Compound | $\nu$ (cm$^{-1}$) of absorption bands in the carbonyl region | | | | $\nu$ (cm$^{-1}$) of the very strong and strong (s) absorption bands | | | | | | | | | | $\nu$ (cm$^{-1}$) of characteristic absorption bands | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| XIV | 1685 (m) | 1650 (vs) | 1648 (vs)<br>sh | 1630 (vs)<br>sh | 1586 | — | 1288 | 1249 | — | — | 850 | 796 (s) | 761 | — | 1610 (vs) | 1400 (vs) | — |
| XII | — | 1675 (vs) | 1655 (vs)<br>sh | 1640 (s)<br>sh | 1587 | 1345 (s) | 1278 (w) | 1230<br>(broad) | — | — | — | — | 759 | 550 (s) | 838 (s) | — | — |
| XIII | — | 1673 (vs) | 1654 (s)<br>sh | 1636 (m)<br>sh | 1586 | 1342 (s) | 1280 (s) | 1240<br>(broad) | — | — | — | 795 (s) | 757 | 542 (s) | 1145 (s) | 765 (vs) | — |
| VIII | 1702 (s) | 1664 (vs) | 1652 (vs)<br>sh | 1636 (m)<br>sh | 1584 | — | 1282 (s) | 1240 | — | — | — | — | 760 | — | 1322 (vs) | — | — |
| XI | 1688 (m)<br>sh | 1664 (vs) | 1647 (vs)<br>sh | 1634 (s)<br>sh | 1573 | — | 1279 | 1243 (s) | 956 (s) | 904 (s) | 855 | 790 | — | — | 1196 (s) | 112 (s) | 673 (s) |
| X | 1691 (s) | 1667 (vs) | 1648 (s)<br>sh | 1620 (w)<br>sh | 1582 | — | 1278 | 1250 (m) | 955 (s) | 905 (s) | 855 | 789 (s) | — | — | 1105 (vw) | — | — |

Abbreviations: vs: very strong, s: strong, m: medium, w: weak, vw: very weak, sh: shoulder.

possible to distinguish between halogeno-1,2-naphthoquinones with the substituent in the 3- or 4- position since the former have strong absorption bands at 1343 $cm^{-1}$ and 546 $cm^{-1}$. The Table shows that the 6-halogeno-1,2-naphthoquinones absorb strongly at 956 $cm^{-1}$ and 904 $cm^{-1}$ and it is possible that these absorptions are characteristic of substitution in the benzenoid ring of the quinone.

The PMR spectra of the naphthoquinones were measured and although no detailed analysis of the spin–spin multiplets was attempted the spectra were interpreted, with the aid of integrated intensity measurements and known chemical shift values for aromatic and olefinic protons, and confirmed the expected structures. Table 4 summarizes the analysis.

TABLE 4. CHEMICAL SHIFTS OF 1,2-NAPHTHOQUINONES IN $\tau$ UNITS USING TMS AS INTERNAL STANDARD

| Compound | Ring proton number | | | | | |
|---|---|---|---|---|---|---|
| | 3 | 4 | 5 | 6 | 7 | 8 |
| XII | — | 2·46 (singlet) | 2·67–2·73 (quartet) | 2·36–2·56 (complex multiplet) | 2·36–2·56 (complex multiplet) | 1·95–2·02 (quartet) |
| XIII | — | 2·19 (singlet) | 2·67–2·77 (quartet) | 2·29–2·54 (complex multiplet) | 2·29–2·54 (complex multiplet) | 1·90–2·02 (quartet) |
| XI | 2·61, 2·71 (doublet) | 3·53, 3·63 (doublet) | 2·34–2·52 (complex multiplet) | — | 2·34–2·52 (complex multiplet) | 2·05, 2·13 (doublet) |
| X | 2·63, 2·72 (doublet) | 3·52, 3·62 (doublet) | 2·34–2·52 (complex multiplet) | — | 2·34–2·52 (complex multiplet) | 2·04, 2·12 (doublet) |
| VIII | 3·21 (singlet) | — | 2·26–2·36 (quartet) | 1·98–2·24 (complex multiplet) | 1·98–2·24 (complex multiplet) | 1·74–1·87 (quartet) |

Finally the mass spectra of the 1,2-naphthoquinones were measured and whilst they all yielded the expected molecular ion (M), this was found to be very weak and a much stronger ion of mass M + 2 predominated. The loss of carbon monoxide to give M − CO, and M − 2CO fragments was observed which parallels the behaviour of the 1,4-naphthoquinones.[10] These interesting preliminary observations are being further investigated and whilst this paper was in the course of preparation another report of an M + 2 ion from a 1,2-quinone was published[11] which was pressure dependant. Experiments to date on the 1,2-naphthoquinones have shown that the M + 2 ion intensity does not vary with pressure.

## EXPERIMENTAL

IR spectra were obtained for all compounds using a Perkin–Elmer 337 grating spectrometer and the electronic absorption spectra were measured on a Perkin-Elmer 137 UV and visible spectrometer; NMR spectra were measured on a Varian HR100 instrument, using an internal standard of TMS, and $CDCl_3$ as solvent. The mass spectra were measured on an A.E.I. M.S.9 double focusing spectrometer.

*Preparation of 3-chloro-2-naphthol.* This was prepared by a Sandmeyer reaction on 3-amino-2-naphthol.[12] 3-amino-2-naphthol (5 g) was suspended in conc HCl (60 ml) and the suspension cooled to 0° using an ice–salt mixture. It was diazotized for 15 min with a soln of $NaNO_2$ (2·1 g) in $H_2O$ (20 ml). This diazo soln was mixed with a soln of $Cu_2Cl_2$ made from $CuSO_4 \cdot 5H_2O$ (3·9 g), NaCl (1·2 g) and $H_2O$ (5 ml) and the mixture was slowly stirred. The mixture tended to blacken and froth. After the evolution of $N_2$ had ceased the mixture was warmed on a water bath at 60° for ½ hr, and it was then steam distilled to give white crystals of 3-chloro-2-naphthol, (1·8 g) m.p. 90° after recrystallization from petroleum ether (b.p. 60–80°).

*General method for the preparation of the naphthoquinones.* The halogeno naphthol (2 mmoles) was dissolved in MeOH (20 ml) and added to a soln of $NO(SO_3K)_2$[13] (1·23 g) dissolved in water (70 ml) and M/6 $KH_2PO_4$ solution (20 ml). The soln became brown or orange and after a few min a solid precipitated. This soln was cooled to 0° for ½ hr, the solid filtered, washed with water, and dried under vacuum.

4-Chloro- and 4-bromo-1,2-naphthoquinones were isolated from the solid product by TLC using silica gel G, or by using columns of silica gel (0·05–0·02 mm), and benzene as the eluent. In all the other preparations, except when the starting materials 8-chloro- and 8-bromo-2-naphthol were recovered quantitatively from their attempted oxidations, the naphthoquinones were obtained by recrystallization of the crude product from EtOH.

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## REFERENCES

[1] H. Cassebaum, *Chem. Ber.* **90**, 2876–2888 (1957).
[2] H. J. Teuber and N. Gotz, *Ibid.* **87**, 1236 (1954).
[3] W. Militzer, *J. Am. Chem. Soc.* **6L**, 257 (1938).
[4] P. Ruggli, F. Knapp, E. Merz and A. Zimmermann, *Helv. Chim. Acta* **12**, 1048 (1929).
[5] W. Dilthey, F. Quint and J. Heinen, *J. Prakt. Chem.* **152**, 73 (1939).
[6] T. Zincke, *Ber. Dtsch. Chem. Ges.* **27**, 738 (1894).
[7] S. Nagakura, A. Kuboyama, *J. Am. Chem. Soc.* **76**, 1004 (1954).
[8] J. W. Sidman, *J. Am. Chem. Soc.* **78**, 4567 (1956).
[9] A. Kuboyama, *Bull. Chem. Soc. Japan* **35**, 295 (1962).
[10] J. M. Bowie, D. W. Cameron and D. H. Williams, *J. Am. Chem. Soc.* **87**, 5094 (1965).
[11] T. C. McMorris and M. Anchel, *Tetrahedron* **23**, 3986 (1967).
[12] K. Fries, *Chem. Ber.* **58**, 2845 (1925).
[13] G. Harvey and R. G. W. Hollingshead, *Chem. & Ind.* 245 (1953).