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QUINONE DEHYDROGENATION - A GENERAL METHOD OF PREPARATION OF ORGANIC CATIONS

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EVIDENCE has been presented[1] that the dehydrogenation of hydroaromatic compounds by quinones proceeds as a two-stage ionic process. In the first and the rate-determining step abstraction of hydrogen occurs as hydride ion, and is followed by the rapid transfer of a proton from the resulting conjugate acid of the substrate to the quinol anion:

$$RH_2 + Q \rightarrow RH^+ + QH^- \qquad (1)$$

$$RH^+ + QH^- \rightarrow R + QH_2 \qquad (2)$$

However, step (1) may itself represent a summary of two successive reactions:

$$RH_2 + Q \rightarrow RH^\bullet + QH^\bullet \qquad (1a)$$

$$RH^\bullet + QH^\bullet \rightarrow RH^+ + QH^- \qquad (1b)$$

In the case where $RH^\bullet$ is a stable, long-lived radical, it is likely that reaction (1a) would be followed by

$$RH_2 + QH^\bullet \rightarrow RH^\bullet + QH_2 \qquad (3)$$

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[1] E.A. Braude, L.M. Jackman and R.P. Linstead, J.Chem.Soc. 3548, 3564 (1954); J.R. Barnard and L.M. Jackman, J.Chem.Soc. 3110 (1960); E.A. Braude, L.M. Jackman, R.P. Linstead and J.S. Shannon, J.Chem.Soc. 3116 (1960).

Alternatively, steps (1a) and (3) might merge into a single process:

$$2RH_2 + Q \rightarrow 2RH^{\bullet} + QH_2 \qquad (4)$$

It seemed that by the use of structurally suitable substrates it might be possible to isolate stable cations (RH^+) or radicals ($RH^{\bullet}$) in quinone dehydrogenations. Isolated instances[2] appear in the literature of the formation of heterocyclic quaternary ammonium salts by the action of quinones on heterocyclic hydroaromatic compounds. Overall loss of hydrogen as hydride ion must occur in these cases. We now describe the use of quinones in a novel general method of preparation of stable hydrocarbon cations, in a systematic application to the preparation of heterocyclic salts, and, in specific instances, for the preparation of stable radicals.

In reactions involving hydride abstraction the dehydrogenative efficiency of quinones was found to increase with increasing redox potential. The following quinones proved to be the most useful (abbreviated names henceforth used are in brackets): tetrachloro-1,2-benzoquinone (T.B.Q.), $E^o = 0.87v$; 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (D.D.Q.), $E^o \simeq 1.0v$; and chloranil, $E^o = 0.71v$. The first of these possesses distinct practical advantages over the other two, chiefly owing to its ready solubility in acetic acid, the preferred reaction solvent, and to the high solubility of the corresponding quinol in ether. Using these quinones, members of the following classes of organic salts were readily prepared.

Tropylium salts

Cycloheptatriene reacted instantly with D.D.Q., best in methylene chloride, to give a complex* (91%),** black needles from crimson solutions in acetonitrile, m.p. 177-178° (decomp.), which is provisionally formulated

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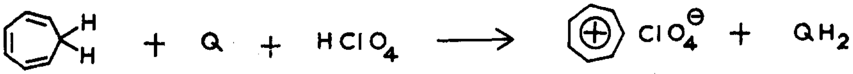
* Compounds whose names are underlined are new.

** Yields in brackets.

[2] D. Buckley, S. Dunstan and H.B. Henbest, J.Chem.Soc. 4883 (1957).

as tropylium 2,3-dichloro-5,6-dicyano-1,4-quinolate. The fine structure of this complex, and that from 1,2,3-triphenylcyclopropene with D.D.Q. (see below), is under investigation. In contrast, cycloheptatriene reacted immediately with D.D.Q. and 70% (w/w) perchloric acid in cold acetic acid to give tropylium perchlorate (92%), colourless fern-shaped crystals which become translucent > 275° and decompose with bubbling > 285°, also produced (90%) by the action of perchloric acid in acetic acid on the complex. Replacement of D.D.Q. by the following quinones also gave tropylium perchlorate: T.B.Q. (97%); chloranil (70%); and 1,4-benzoquinone (30%).



The following salts were similarly prepared from cycloheptatriene or the cycloheptatriene - D.D.Q. complex in acetic acid, using the reagents indicated: tropylium picrate, D.D.Q. and picric acid (51%), yellow needles, m.p. 120-125° (decomp.);[3] tropylium tetroxalate, T.B.Q. and oxalic acid dihydrate (83%), colourless spears, m.p. 140-145° (decomp.) with darkening > 130°; ditropylium iodide-triiodide, complex and sodium iodide (79%), dark brown needles, m.p. 128.5-129.5°; tropylium iodide,[4,5] T.B.Q. and sodium iodide (75%), or by the action of acetone on tropylium iodide-triiodide (54%), scarlet needles, m.p. 132-133°;[6] tropylium triiodide, (along with tropylium iodide) by the action of acetone on tropylium iodide-

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[3] M.J.S. Dewar and R. Pettit, J.Chem.Soc. 2026 (1956), give m.p. 114-115°.

[4] H.J. Dauben, F.A. Gadecki, K.M. Harmon and D.L. Pearson, J.Amer. Chem.Soc. 79, 4557 (1957).

[5] M.J.S. Dewar and R. Pettit, J.Chem.Soc. 2021 (1956).

[6] Reported m.p.s. 127° [4] and 117°.[5]

triiodide (58%), garnet-red needles, m.p. 132-133°;[7] tropylium bromide,[4,5,8] complex and lithium bromide (12%), yellow crystals, m.p. 198-204° (decomp.);[9] *tropylium hydrogen sulphate*, complex and sulphuric acid (low yield), colourless needles, decomp. > 175°; *tropylium toluene*-p-*sulphonate*, complex and toluene-p-sulphonic acid (55%), pale buff plates, m.p. 125-130° (decomp.); tropylium pyrophosphate (?), D.D.Q. and 90% orthophosphoric acid (55%), colourless plates, m.p. 125-129° (decomp.).

Cyclopropenylium salts

1,2,3-Triphenylcyclopropene with D.D.Q. in methylene chloride gave a *complex* (79%), purple needles from crimson solutions, m.p. 179-181° (decomp.). However, addition of perchloric acid to a hot solution of 1,2,3-triphenylcyclopropene and D.D.Q. in acetic acid gave *triphenylcyclopropenylium perchlorate* (95%), colourless needles, m.p. 229-231° (decomp.), also prepared by the action of perchloric acid on the complex. Similar conditions were employed for the preparation of the following salts from 1,2,3-triphenylcyclopropene, using the reagents specified: triphenylcyclopropenylium picrate, D.D.Q. and picric acid (88%), yellow needles, m.p. 193-197°;[10] *triphenylcyclopropenylium iodide complex* and sodium iodide (80%), yellow needles, m.p. 221-224°.

Perinaphthenylium salts

The product obtained by the action of quinones on perinaphthene depends on the presence or absence of a strong acid (see also below). Perinaphthene, chloranil, and perchloric acid in cold acetic acid gave perinaphthenylium perchlorate (75%),[11,12] yellow needles which decompose slowly on being heated,

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[7] Reported m.p. 127°.[4]

[8] W.E. Doering and L.H. Knox, *J.Amer.Chem.Soc.* **76**, 3203 (1954).

[9] Reported m.p. 203°.[4,5,8]

[10] R. Breslow and C. Yuan, *J.Amer.Chem.Soc.* **80**, 5991 (1958), give m.p. 194-197° (decomp.).

[11] W. Bonthrone and D.H. Reid, *J.Chem.Soc.* 2773, (1959).

[12] R. Pettit, *J.Amer.Chem.Soc.* **82**, 1972 (1960); *Chem. & Ind.* 1306 (1956).

also produced (81%) using 1,4-benzoquinone in place of chloranil. Addition of 3,6,9-trimethylperinaphthan-1-ol to a boiling solution of T.B.Q. and perchloric acid in acetic acid gave directly 1,4,7-trimethylperinaphthenylium perchlorate[11] (89%), dehydration to 3,6,9-trimethylperinaphthene occurring in situ, copper coloured needles which decompose > 240°.

Heterocyclic salts

The wide preparative possibilities in heterocyclic chemistry are illustrated by the preparation of the following salts in acetic acid containing perchloric acid: thiaxanthylium perchlorate,[13] chloranil and thiaxanthene (87%), scarlet prisms, m.p. 216-218°; 5-*methylphenanthridinium perchlorate*, chloranil and 5-methyl-5,6-dihydrophenanthridine (94%), colourless needles, m.p. 192-195°; 3-(1,2-*dimethylindolizin*-3-*yl*)*methylene*-1,2-*dimethylindolizinium perchlorate*, chloranil and di-(1,2-dimethylindolizin-3-yl)methane (10%), greenish-black rosettes of needles, decomp. > 261°; 1-thioxonianaphthalene perchlorate,[13,14] T.B.Q. and 1-thiachroman-4-ol (92%), greenish-yellow needles which melt (decomp.) on a block preheated to 221°. With D.D.Q. alone in acetic acid 9,10-dihydroacridine gave *acridinium* 2,3-*dichloro*-5,6-*dicyano*-1,4-*quinolate* (93%), orange needles from acetonitrile, m.p. 220.5-222.5° with resolidification to yellow crystals which decompose slowly with partial melting on being further heated.

Radicals

In contrast to its behaviour in the presence of strong acids, perinaphthene reacted at room temperature with many quinones (D.D.Q., chloranil, T.B.Q., 1,4-benzoquinone, 1,2- and 1,4-naphthaquinone) in both polar and non-polar solvents (benzene, methylene chloride, carbon tetrachloride, acetonitrile, nitromethane) to give the perinaphthyl radical.[15]

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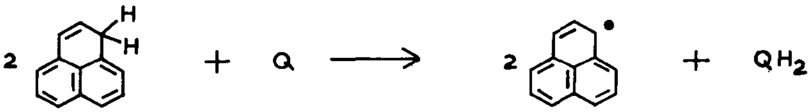
[13] W.Bonthrone and D.H. Reid, *Chem. & Ind.* 1192 (1960).

[14] A. Lüttringhaus and N. Engelbert, *Chem.Ber.* *93*, 1525 (1960).

[15] D.H. Reid, *Chem. & Ind.* 1504 (1956); *Tetrahedron* *3*, 339 (1958).



The results reported demonstrate that quinones can dehydrogenate both by a hydrogen atom and by an overall hydride-transfer mechanism.

We hope to study the reactions of quinones, along these lines, with hydrocarbon complexes of the transition metals and related compounds, e.g. the cycloheptatriene-metal carbonyls.

Full details of these and related experiments will be published later.

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