Tetrahedron Letters No. 7, pp 557 - 560, 1976. Pergamon Press. Printed in Great Britain.

ANODIC ELECTROGENERATION OF A STABLE BIRADICAL

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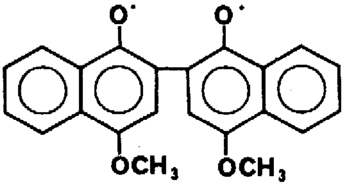
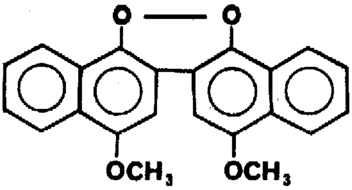
(Received in UK 19 November 1975; accepted for publication 7 January 1976)

In the anodic oxidation of naphthalene at a constant current and in an SSE formed by methanol saturated with calcium oxide, an intense blue colour appears due to the formation of the biradical (I

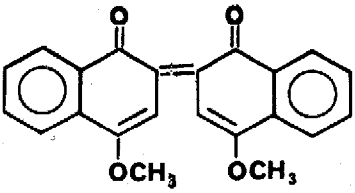


(I)

In 1928 Goldschmidt and Wessbecher[1] stated that some years before Russig had obtained a blue compound by means of the chemical oxidation of 4-methoxy-α-naphthol, and assigned to it, using only the data of molecular weight and elemental analysis, the structure (II). Goldschmidt, using oxidation of 4-methoxy-α-naphthol with PbO_2, obtained the same blue compound, assigning to it the structure (III).



(II)



(III)

The structure (III) has been maintained to the present time.

Inoue et al.[2] observed that 4-methoxy-α-naphthol in an alkaline medium was transformed into a blue compound through exposure to air, and Matsunaga[3] found that the compound had paramagnetic properties, but accepted the structure (III), explaining the paramagnetism as due to occluded radical matter in the crystallization of the compound, since on dissolution no paramagnetism was observed.

Goldschmidt noted that solutions of the blue compound were decolourized by the triphenylmethyl radical[1].

In 1964 Guilbault and Kramer[4] reported the oxidation of 4-methoxy-α-naphthol by enzymatic means and found an application of the blue colourant for biochemical valuations. The authors proposed a mechanism for obtaining the blue colourant, to which they assigned the structure (III) and gave an interpretation of its IR spectrum with which we differ.

Experimental: The electrolysis of naphthalene in methanol saturated with calcium oxide was performed with constant current and potential in both a divided and an undivided cell and employing

SSE´s other than those mentioned of MeOH-CaO (Note: It is necessary to leave the methanol with CaO for some ten days).

The results are summarized in the following table:

Anode	Cathode	SSE	Cell	$I_{const.}$	$V_{const.}$	Observations
Pt	C	MeOH-CaO	Undivided	"		Blue colourant
"	"	"	Divided	"		Blue colourant in the anodic compartment
"	"	"	"		0.8 V	" "
C	"	"	Undivided	"		Greenish colourant
Pt	Pt	"	"	"		Blue colourant
"	C	MeOH-Bu_4NBF_4	"	"		No blue colourant
"	"	MeOH-Bu_4NBF_4 & O_2 in the anode	"	"		Blue colourant.
"	"	MeOH-$Ca(NO_3)_2$	"	"		No blue colourant
"	"	MeOH-Na_2O_2	"	"		"
"	"	MeOH-BaO or MgO	"	"		Weak blue colourant
"	"	MeOH-$Ca(ClO)_2$ & H_2O_2	"	"		No blue colourant
"	"	MeOH-NaOH & O_2 in the anode	"	"		"

All the electrolysis was carried out on naphthalene as the substrate, employing refrigerated cells at temperatures below 5 °C and in darkness.

The isolation of the blue colourant was performed by elimination of the methanol in a "rotavapor", extraction with water and ether, evaporation of the ethereal mantle, separation in an acid alumina column, activity I, eluting with n-hexane until the gas chromatograph showed no presence of naphthalene, desorption of the blue colourant with acetone. By partial evaporation of the acetone, some star-shaped blue fibres separated.

The melting point of the blue colourant was from 255 to 260°C. The IR spectrum showed bands at 2820 and 1258 cm^{-1} corresponding to the methoxyl joined to the aryl group. Bands that appeared at 1577 and 1553 cm^{-1} disappeared when the compound was reduced, for which reason we designated them as responsible for the aryloxyl radical groups. The band at 1598 cm^{-1} was assigned to the condensed aromatic system, as was that appearing at 1480 cm^{-1}.

The UV spectrum showed bands at 280, 225 and 206 $m\mu$ and the visible spectrum showed a strong band at 620 $m\mu$.

Mass spectrometry yielded a molecular weight of 344 units of mass, however the product reduced with $SnCl_2$ yielded a molecular weight of 346. The electronic spin resonance, executed by dissolving the colourant in CCl_4 , showed a wide singlet in which no appreciable coupling could be observed even using a scan time of 60 minutes and a scan range of 40 G and a receiver gain of 2.10^4, yielding a value of g=2.0032. In the case we use a scan range of 1000 G, we could appreciate only the wide singlet. The line-width was of 6.8 ± 0.4 G.

The paramagnetic suseptibility, using the Faraday method, was of the order of $7.65 . 10^{-6}$.Applying the Curie-Weiss Law for this value, a value of 6.53 was obtained for μ^2, which led to a concentration of the biradical of 108 %.

The solutions of the blue compound were decolourized by I_2 and the trityl radical.

The attempts to obtain a NMR spectrum failed owing to the paramagnetic properties of the compound and to the low solubility of the compound in CCl_4 and deuterated acetone. Through the CAT technique a broad band was obtained in the aromatic zone, in which the couplings could not be distinguished.

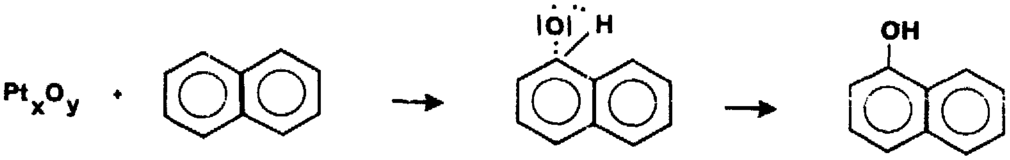
The oxidation of the blue radical with concentrated nitric acid yielded a yellow compound, which by mass spectrometry gave a molecular weight of 314 and which was identified by its physical constants with the quinone Meldola and Hughes[5].

Discussion: In view of the reaction which occurs at a potential of 0.8 V and even below 0.6 V at the calomel electrode, it would appear that the naphthalene does not undergo anodic oxidation, since it has an oxidation potential of about 1.4 V.

The active electrogenerated matter we believe, arises from a complex of oxygen with the platinum electrode, since the reaction takes place either by bubbling O_2 on the anode or by means of the presence of calcium oxide, and observing in the latter case the electrodeposition of a film of metallic calcium on the cathode.

If in the electrolysis with MeOH-CaO, bubbling O_2 is added on the anode, the reaction is enhanced considerably.

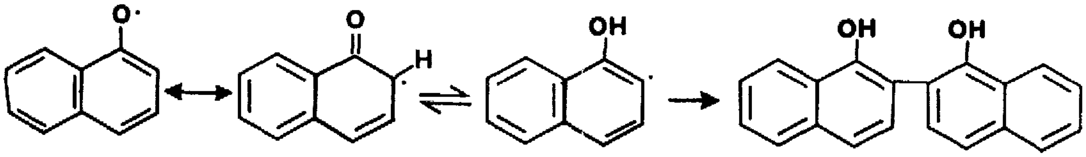
The effect of the electrogenerated matter on the naphthalene can be considered as a concerted reaction:



The obtention of α-naphthol as a possible intermediary in the reaction has been confirmed by conducting the electrolysis with α-naphthol in methanol saturated with CaO, resulting in a reaction which is simpler and gives a greater yield. Starting with β-naphthol as the substrate no blue colourant is obtained.

The next step would be the formation of the aryloxy radical, a reaction that as indicated in the bibliography[2,4,6], is carried out at quite low potentials and even by enzymatic means.

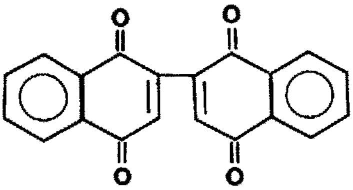
The tautomerization of one of the canonical forms of the hybrid leads to the dimerization:



The aryloxy radicals would again reproduce themselves since the electrode in kept at the same potential.

If one keeps in mind that the reaction medium is also generating $CH_3O^\cdot$ radicals[7] arising from the oxidation of the solvent, the action of these in the ring by way of radical substitution is not surprising.

The structure (I) which we proposed is based on the following: a) By oxidation this quinone is obtained:



b) The oxygen radical has to be in position α, since the compound is obtained from α -naphthol and not from β-naphthol and c) the methoxyls have to be in position 4, since the same compound is obtained as with the oxidation of 4-methoxy-α-naphthol and also as in a).

The behaviour of the biradical is quite surprising, since it is stable in the solid state at temperatures above 100°C, in contrast with the behaviour of other naphthalenic biradicals described in the bibliography[8].

In dissolution it is decolourized by sunlight in a few minutes.

In the proposed structure, all the conditions for stability of a radical as established by Cook[9] have been summarized, such as:1) Substitution in position 2 and 4 to prevent nuclear dimerization
2) The substituents have no hydrogen in position α.

Acknowlegements: To Drs. Parraga and Ruano of the Central Laboratory of "Aduanas"; to Dr. Aldaz of t Autonomous University of Madrid; and to Drs. Castañer and Riera of the "Patronato Juan de la Cierva" of Barcelona, for their aid and advice.

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