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# Generation of Radicals from Sulphoxides with Fenton's Reagent

## A New Radical Alkylation Method

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Decomposition of hydrogen peroxide by ferrous sulphate in sulphoxides produces alkyl radicals which can be trapped by suitable substrates. The reaction has synthetic potentialities. The mechanism of the reaction has been elucidated and is described by eqns. (6), (4), and (10a).

It was discovered by ESR technique that alkyl radicals were formed by decomposition of hydrogen peroxide in sulphoxides,[1-3] eqn. (1). The reaction failed for R = aryl and allyl.[1]

$$HO\cdot + R_2SO \rightarrow R\cdot + RSO_2H \qquad (1)$$

The production of radicals was high enough to warrant an investigation of the possible synthetic applications.** We found that various substrates in fact could be alkylated in reasonable yields under mild conditions. Different ways of decomposing hydrogen peroxide were tested: UV irradiation, treatment with peroxidase, catalase, $Fe^{2+}$, $Cu^{+}$, and $Cr^{2+}$ salts, and Pt. The iron salt (the Fenton reagent) gave the best yields, UV irradiation somewhat less, but the other salts afforded no or only traces of alkylated products. The enzymes were quite active in the nearly waterfree solvent but no methylated products were produced.

The sulphoxides served both as solvent and reagent. Dilution by other organic solvents (acetone, methanol, *t*-butanol, dimethylformamide, benzene, acetic acid) always decreased the yield; water could be used as co-solvent but decreased on the other hand the solubility of many organic compounds.

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## GENERATION OF METHYL RADICALS. METHYLATION

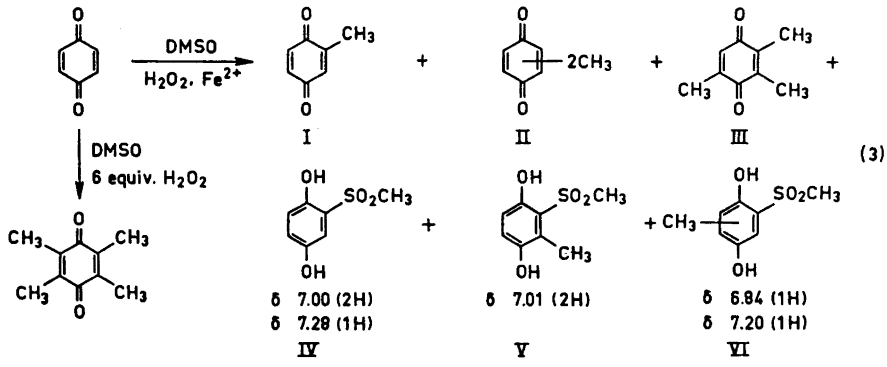
The methyl radicals were conveniently generated by the reaction of Fenton's reagent with DMSO. The reaction (2) was controlled by the rate of addition of hydrogen peroxide to the solution of ferrous sulphate in DMSO.

$$H_2O_2 + (CH_3)_2SO \xrightarrow{Fe^{2+}} CH_3\cdot + CH_3SO_2H \qquad (2)$$

Reactive substrates, such as 1,3,5-trinitrobenzene or quinones, were readily alkylated at room temperature, but other substrates, *e.g.* pyridine, thiophene, naphthalene, *etc.*, needed a reaction temperature of 60 – 80°C before reasonable yields of alkylated products were obtained. The nitrobenzenes were alkylated in the *ortho* position, *e.g.*, *m*-dinitrobenzene gave two products: 2,6-dinitrotoluene (10 %) and 2,4-dinitrotoluene (40 %). Trinitrotoluene was obtained in a yield of 67 % from 1,3,5-trinitrobenzene. Under more drastic conditions, methylation with lead tetraacetate gave 33 % of trinitrotoluene.[4] Nitrobenzene gave about 10 % of *o*-nitrotoluene, and *m*-nitrobenzoic acid gave about 20 % of two isomeric methyl derivatives. Benzene, toluene, benzoic acid, and other simple aromatics tested, such as phenol, 1,2-, 1,3-, and 1,4-dihydroxybenzene, *p*-nitrophenol, benzonitrile, *m*-nitroacetophenone, pyrrole, 2-acetylpyrrole, indole, and phenanthrene, gave no or only traces of methylated products under our reaction conditions (80°C, excess of hydrogen peroxide). We were not successful in methylating olefins. Acrylonitrile, styrene, and phenylacetylene underwent polymerisation. 1,1-Diphenylethylene, β-nitrostyrene, and cyclohexene gave only traces of methylated products. β,β-Dicyanostyrene gave 10 – 20 % of 1,1-dicyano-2-phenylpropane.

Benzoquinone with an equimolecular amount of hydrogen peroxide gave a mixture of mono-, di-, and trimethylated quinones (16 %) together with minor amounts of sulphones. The structures of the products were determined by chemical and spectroscopic methods, eqn. (3).

With excess of hydrogen peroxide (6 equiv.) duroquinone could be obtained in a yield of 8 % as the only isolable product. 1,4-Naphthoquinone gave rise to two products: 2,3-dimethyl-1,4-naphthoquinone, VII (15 %) and 2-(1,4-

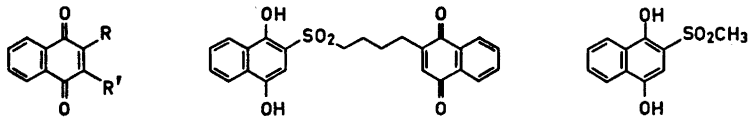



(3)

*Table 1.* Radical alkylation of aromatics by sulphoxides and Fenton's reagent (0.2 equiv. $Fe^{2+}$).

| Sulphoxide | Substrate | Reaction time h | Equiv. $H_2O_2$ | Temp. °C | Products (%) |
|---|---|---|---|---|---|
| DMSO | 1,3,5-trinitrobenzene | 2 | 1.5 | 25 | trinitrotoluene (67) |
| — | 1,3,5-trinitrobenzene | 2 | 3 | 25 | trinitrotoluene (75), trinitroxylene(25) |
| — | *m*-dinitrobenzene | 1 | 1.5 | 25 | 2,6-dinitrotoluene (10), 2,4-dinitrotoluene(40) |
| — | nitrobenzene | 1 | 3 | 80 | *o*-nitrotoluene (10) |
| — | 3-nitrobenzoic acid | 1 | 3 | 80 | two isomers (20) |
| — | *p*-quinone | 0.5 | 2 | 16 | I + II + III (16), IV (1), V (1), VI (1) |
| — | *p*-quinone | 0.5 | 6 | 16 | duroquinone (8) |
| — | 1,4-naphthoquinone | 2 | 1.3 | 25 | VII (15), XI (6) |
| — | pyridine | 1 | 1.5 | 80 | 2—:3—:4—:2,6— = 8:1:4:0.5 ($\sum$ 25) |
| — | quinoline | 1 | 3 | 60 | 2—:4—: unknown = 1.5:1:2 ($\sum$ 45) |
| — | thiophene | 1 | 1.5 | 80 | 2-methylthiophene (20) |
| — | furan | 1 | 1.5 | 60 | 2-methylfuran (6) |
| — | 2-furoic acid | 0.75 | 4 | 60 | methyl 5-methylfuroate (50) |
| — | 2-nitrothiophene | 1.5 | 1.5 | 60 | 3-methyl-2-nitrothiophene (32) |
| — | naphthalene | 1 | 5 | 85 | 1—:2— = 10:1 ($\sum$ 45) |
| — | anthracene | 2 | 3 | 85 | 9-methylanthracene (34) |
| $(C_2H_5)_2SO$ | pyridine | 1 | 1.5 | 70 | 2—:4— = 2:1 ($\sum$ 26) |
| — | 2-furoic acid | 1 | 3 | 85 | 5-ethyl furoic acid (66) |
| — | naphthalene | 1.5 | 3 | 65 | trace of ethylated product |
| — | 1,3,5-trinitrobenzene | 0.75 | 3 | 20 | 2-ethyl-1,3,5-trinitrobenzene ($\sim$30 %) |
| — | 1,4-naphthoquinone | 1.5 | 1.1 | 10 | VIII + IX ($\sum$ 30) |
| $(n\text{-}C_4H_9)_2SO$ | 2-furoic acid | 1.5 | 3 | 60 | 5-butyl-furoic acid (22) |
| tetramethylene-sulphoxide | 1,4-naphthoquinone | 0.5 | 1.1 | 15 | X (13) |

dihydroxynaphthyl)methyl sulphone, XI (6 %). Phenanthraquinone was not methylated under the same conditions. The results are summarized in Table 1.




VII R = R' = $CH_3$
VIII R = $C_2H_5$, R' = H
IX R = R' = $C_2H_5$

X

XI

The condensed aromatic hydrocarbons, naphthalene, and anthracene, were methylated in a yield of 45 % and 34 %, respectively.

Some heteroaromatics were successfully methylated. The isomer distribution from pyridine was, 2-$CH_3$:3-$CH_3$:4-$CH_3$:2,6-di$CH_3$ = 8:1:4:0.5 (total yield ~25 %), ratio of 2:4 substitution = 2.0, a value in agreement with earlier investigations on radical substitutions of pyridine (see Ref. 5 for references).

In quinoline the isomer distribution was 2:4:unknown = 1.5:1:2. No 6-, 7-, 8-methyl, or 4-dimethyl derivatives were present, but a trace of the 3-isomer was detected. The unknown compound could conceivably be the 5-methyl derivative. 2-Furoic acid was alkylated in the 5-position. Contrary to predictions,[6] 2-nitrothiophene was alkylated in the 3-position (32 %); no 5-derivative was detected. This matter will be investigated further and presented in a forthcoming paper.

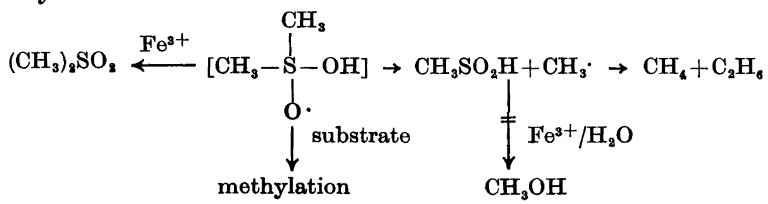
## ALKYLATION WITH OTHER SULPHOXIDES

Ethyl radicals were produced on a preparative scale from diethyl sulphoxide and were trapped by suitable substrates. Ethylpyridines (2-ethyl:4-ethyl = 2.0) were formed in a yield of 26 %, 2-furoic acid gave 5-ethylfuroic acid-2 (66 %) and from 1,4-naphthoquinone a mixture of 2-ethyl- and 2,3-diethylnaphthoquinones, VIII and IX, (30 %) was obtained, Table 1. Radicals from the higher homologues of alkyl sulphoxides underwent intramolecular rearrangements and reacted easier with their parent solvent. No butylpyridines could be isolated, but from 2-furoic acid the 5-butyl derivative was obtained in a yield of 22 %. The compound X was formed from tetramethylenesulphoxide and naphthoquinone *via* a ring opening of the sulphoxide, radical attack on the quinone and addition of the sulphinic group to another molecule of naphthoquinone.

## THE MECHANISM OF THE REACTION

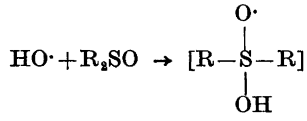
The methyl radicals produced in the absence of a substrate should give methane and ethane but the gases evolved amounted to only 20 – 30 % of the theoretical yield. A mass spectrographic investigation of the gases from DMSO, $d_6$, showed the presence of $C_2D_6$, $C_2D_5H$, $CD_4$, and $CD_3H$, *i.e.*, dimerization and proton abstraction must take place to some extent. Small

amounts of protonated gases were formed *via* proton abstraction from hydrogen peroxide or water. The sulphone formation increased considerably in the absence of a substrate meaning that an intermediate sulphone radical as indicated in (4) was formed, which either reacted with the substrate, fragmented to alkyl radicals, or gave the sulphone. The fact that radicals generated by the present method are more selective in their reactions than methyl radicals produced by other methods favours an intermediate deactivated complex radical as alkylating agent. The oxidation potential of ferric ions is too low for affecting carbonium ion formation and, in fact, no methanol was detected in the reaction mixture by GC.

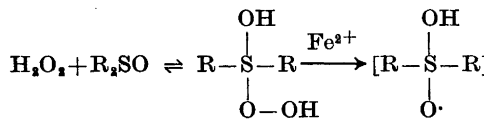



(4)

The formation of the complex radical can be visualized by the radical addition (5) or fragmentation (6). The latter formulation is the most probable on the following grounds. There were no sign of alkyl radical and sulphinic ester formation when hydroxyl radicals were replaced by *t*-butoxy radicals generated by several methods (7). Methylated products were formed but it was proved by labelling (DMSO, $d_6$) and ESR measurements [7,8] that the methyl radicals originated from butoxy radicals *via* (8).




(5)

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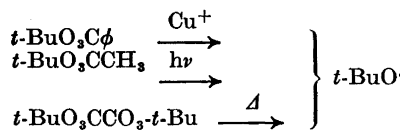



(7)



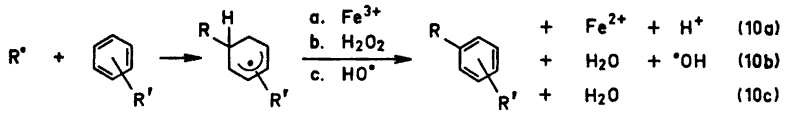

(8)

When *t*-butyl peroxalate was decomposed in acetonitrile in the presence of trinitrobenzene, trinitrotoluene was obtained in a relatively good yield. It was shown, too, by mass spectrometry that no methyl scrambling had occurred in the solvent which was composed of 50 % DMSO and 50 % DMSO,$d_6$, *i.e.*, the possible reaction (9) does not occur. On the whole, radical addition, (5), does not seem plausible.

$$CH_3^{\cdot} + (CD_3)_2SO \longrightarrow CH_3-\underset{\displaystyle CD_3}{\overset{\displaystyle CD_3}{\underset{|}{\overset{|}{S}}}}-O^{\cdot} \rightarrow CD_3^{\cdot} + CD_3-\overset{\displaystyle O}{\underset{|}{S}}-CH_3 \qquad (9)$$

*t*-Butyl hydrogen peroxide, which is able to associate or form a bond with DMSO, gave on photolysis in DMSO minor amounts of methyl radicals originating from the solvent that could be shown by the radical trapping method. The association of hydroxylic solvents to DMSO can be demonstrated by the large shift of the methyl groups in NMR; $\delta_{(CH_3)_2SO} = 2.56$ ($CDCl_3$), $\delta_{(CH_3)_2SO} = 3.17$ ($D_2O$). In (6) the preformed peroxide bond is split by the ferrous ions, this reaction having its analogue in the fragmentation of ketones by hydrogen peroxide and ferrous ions. All facts taken together speak in favour of reaction (6).

We are dealing with a chain reaction initiated by ferrous ions. The oxidant in the propagation step could either be ferric ions (10a) or hydrogen peroxide (10b).




A low concentration of ferrous salt (0.05 equiv.) produced only minor amounts of methylated products; 0.2 equiv. were necessary for obtaining satisfactory yields. Part of the ferrous ions could be substituted by ferric ions without affecting the yield, but the reaction was somewhat slower. If only ferric ions were present, practically no TNT was found after 1 h. This indicated that ferric ions were responsible for the oxidation step (10) and ferrous ions for the initiation. Oxalic acid, which complexes with ferric but not with ferrous ions, inhibited the reaction. Hydrogen peroxide was decomposed to an extent corresponding to the ferrous ions added.

Oxidation by hydrogen peroxide (10b) and by hydroxyl radicals (10c) – a termination reaction – are unimportant in comparison with (10a). However, they are able to oxidize radicals as was shown by a photolytic generation of hydroxyl radicals in the presence of TNB. A low yield of TNT was obtained. The mechanistic reaction sequence is thus described by eqns. (6), (4), and (10a).

## EXPERIMENTAL

*Methylation of 1,3,5-trinitrobenzene.* a) 1,3,5-Trinitrobenzene (1 g) and $FeSO_4 \cdot 7H_2O$ (280 mg, 0.2 equiv) were dissolved in DMSO (8 ml) and hydrogen peroxide (0.75 ml, 35 %, 1.5 equiv) in DMSO (2 ml) was added drop by drop at room temperature with good stirring. After 2 h the mixture was poured into ice-water (30 ml) and extracted with chloroform (3 × 10 ml). The combined extracts were washed with water, dried and evaporated. The crude product was analyzed by NMR. Trinitrotoluene was formed in a yield of 67 %. Traces of trinitroxylene was detected together with unreacted trinitrobenzene.

*Table 2.* The effect of the $Fe^{2+}$ and the $Fe^{3+}$ concentration on the methylation of trinitrobenzene, TNB.

| TNB[a] equiv. | $FeSO_4$ equiv. | $FeCl_3$ equiv. | $H_2O_2$ equiv. | % Trinitrotoluene, TNT[b] | | |
|---|---|---|---|---|---|---|
| | | | | 23 min | 67 min | 24 h |
| 2 | 0.2 | — | 1 | 50 | 54 | 60 |
| 2 | 0.01 | 0.2 | 1 | 8 | — | — |
| 2 | 0.05 | — | 1 | | <10 | |
| 2 | — | 0.2 | 1 | ~0 | ~ 0 | |

[a] TNB, 4 g, and the iron salts were dissolved in DMSO, 25 ml. The calculated amount of hydrogen peroxide (~35 %) was added. The yield of TNT was determined by NMR spectroscopy.
[b] Calculated with respect to hydrogen peroxide.

b) By adding 0.2 equiv. of conc. sulphuric acid to the solution and using 3 equiv. of hydrogen peroxide, the yield of trinitrotoluene increased to 75 %. In addition, 25 % of 1,3,5-trinitroxylene was formed.

***Ethylation of 1,3,5-trinitrobenzene*** with three equivalents of hydrogen peroxide in diethyl sulfoxide gave an oily product when the reaction mixture was poured into water. The water phase was decanted and unreacted trinitrobenzene crystallized out on addition of some methanol. The ethyl derivative remained in the solution. Evaporation followed by NMR analysis of the remainder showed that it was a mixture of the starting material and 2-ethyl-1,3,5-trinitrobenzene (yield *ca.* 30 %).

*General procedure for radical methylation of aromatics and hetero-aromatics.* About 10 ml DMSO and 0.2 equiv. $FeSO_4 \cdot 7H_2O$ were used for each gramme of substrate. A small amount of conc. sulphuric acid occasionally increased the yield. The methyl radicals were generated by slow addition of hydrogen peroxide (35 %) dissolved in a small volume of cold DMSO with stirring. The products were precipitated by addition of water after an hour. The yields were determined by GC, NMR, and/or in some cases by isolation.

The same procedure was followed for the other sulphoxides.

*Methylation of* p-*benzoquinone.* a) *p*-Benzoquinone (2 g) and $FeSO_4 \cdot 7H_2O$ (1.0 g) were dissolved in DMSO (20 ml). Hydrogen peroxide (2 ml, 35 %, 2 equiv.) with conc. sulphuric acid (0.11 ml) in DMSO (3 ml) were added at 16°C over a period of 15 min with stirring. The reaction mixture was left for a further 10 min and then poured into icewater and extracted with ether (4 × 10 ml). The combined extracts were washed with water (10 ml), dried, and evaporated. The crude product (1.6 g) was chromatographed on silica (chloroform + 1 % methanol). The first fraction contained a mixture of mono-, di-, and trimethylated quinones (16 %). We were not able to separate the three different dimethyl-*p*-benzoquinones by GC.

Fraction 2 proved to be 3,6-dihydroxy-2-methylphenyl methyl sulphone, V, m.p. 126°C, (from toluene). NMR (acetone $d_6$): $\delta$ 2.21 ($Ar-CH_3$, s), 3.18 ($SO_2-CH_3$, s), 7.01 (2 H, s), 8.17 (OH, broad), 8.50 (OH, broad). MS: *m/e* (rel.int.) 203 (10), 202 $M^+$ (100), 139 (37), 123 (17), 95 (9), 94 (9), 69 (17), 67 (35), 53 (58). IR: 3450, 3385, 1350, 1320, 1140, 1110 $cm^{-1}$.

Fraction 3 contained an isomer with the methyl group in the 4- or 5-position, VI, (m.p. 176—177°C (from toluene). NMR (acetone $d_6$) $\delta$ 2.22 ($Ar-CH_3$, s), 3.17 ($SO_2-CH_3$, s), 6.84 (1 H, s), 7.20 (1 H, s), 8.67 (OH, broad). MS: *m/e* (rel. int.) 203 (10), 202 $M^+$ (100), 139 (70), 123 (13), 95 (9), 69 (15), 53 (16). IR: 3450, 3390, 1320, 1285, 1160, 1130 $cm^{-1}$. The yield of each sulphone was about 1 %.

Fraction 4 gave 1 % of 2,5-dihydroxyphenyl methyl sulphone, IV, (m.p. 138°C. NMR (acetone $d_6$): $\delta$ 3.24 ($Ar-CH_3$, s), 7.00 (2 H, m), 7.28 (1 H, s broad), 8.33 (OH, broad). MS: *m/e* (rel.int.) 189 (10), 188 $M^+$ (85), 125 (100), 109 (35), 97 (28), 81 (53), 53 (38).

Fraction 5 gave a small amount of hydroquinone.

b) When *p*-benzoquinone (1 g) was treated with 6 equiv. of hydrogen peroxide under the same conditions, duroquinone was obtained by crystallization of the crude product

from methanol giving yellow needles, m.p. 109—110°C (0.13 g, 8 %) identical with a reference specimen. No *p*-benzoquinone and toluquinone were detected by GC, but traces of dimethylated products and possibly a trimethylated derivative (intensity ~20 % of the duroquinone peak) were found.

*Methylation of 1,4-naphthoquinone.* To a solution of 1,4-naphthoquinone (1 g) and $FeSO_4 \cdot 7H_2O$ (0.35 g) in DMSO (10 ml) were added drop by drop a mixture of hydrogen peroxide (35 %, 1.02 g) conc. sulphuric acid (0.035 ml) and DMSO (3 ml) with stirring at room temperature. After 2 h the reaction mixture was poured into ice-water and extracted with chloroform (3 × 12 ml). The combined extracts were washed with water, dried, and evaporated. One ml of chloroform was added to the remainder and undissolved material (0.36 g) was separated by filtration. This material gave 90 mg (6 %) of white crystals, m.p. 195—196°C from chloroform which proved to be 2-(1,4-dihydroxynaphthyl)methyl sulphone, XI, NMR (acetone $d_6$): $\delta$ 3.25 ($SO_2-CH_3$, s), 7.08 (1 H, s), 7.66 (2 H, m) 8.31 (2 H, m), 9.24 (OH, broad). MS: *m/e* (rel.int.) 239 (14), 238 $M^+$ (100), 175 (19), 158 (14), 130 (11), 102 (20), IR: 3450, 3400, 1330, 1320, 1155, 1120 $cm^{-1}$. UV: (ethanol) pH ~ 10, $\lambda_{max}$ 269 (7600), $\lambda_{sh}$ 333 (1200); pH ~2, $\lambda_{max}$ 250 (14800), $\lambda_{max}$ 280 (6000), $\lambda_{max}$ 341 (3000). The compound was unaffected by base (under argon). The filtrate was chromatographed on silica ($CHCl_3$) and gave a yellow crystalline compound (0.26 g, 15 %), m.p. 127°C from methanol, identical with 2,3-dimethyl 1,4-naphthoquinone.

*Ethylation of 1,4-naphthoquinone* with diethyl sulphoxide (10 ml solvent/g naphthoquinone) according to the same procedure gave 2,3-diethyl-1,4-naphthoquinone, IX, and 2-ethyl-1,4-naphthoquinone, VIII, m.p. 88°C (from methanol, yield 10 %, pure material) which could be partly separated on a silica column (benzene). The total yield of crude quinones was ~30 %; practically no starting material was present in the product.

*Preparation of methyl 5-methylfuroate-2.* Furoic acid (6 g) and $FeSO_4 \cdot 7H_2O$ (3 g, 0.2 equiv.) were dissolved in DMSO (50 ml). A chilled solution of hydrogen peroxide (23.5 g, 31 %, 4 equiv.) and conc. sulphuric acid (0.3 ml) in DMSO (10 ml) were added during 45 min with stirring at 60—65°C. After a further 30 min the mixture was poured into ice-water (180 ml) and extracted with ether (3 × 25 ml). The extract was washed with water (10 ml) and dried over magnesium sulphate. The crude acid was esterified with diazomethane and distilled *in vacuo*. A forerun gave some esterified starting material. The main fraction, b.p. 78—84°/11, consisted of methyl 5-methylfuroate-2, yield 50 %. NMR: ($CDCl_3$) $\delta$ 2.39 ($CCH_3$, s), 3.86 ($OCH_3$, s), 6.11 ($H_4$, d, $J$ 3.4; q, $J$ ~ 0.9), 7.08 ($H_3$, d, $J$ 3.4).

*Methylation of pyridine.* Pyridine was methylated with 1.5 equiv. of hydrogen peroxide at 80°C. The reaction mixture was poured into ice-water, basified with sodium hydrogen carbonate, and filtered with some active carbon. Extraction with ether afforded a crude product which according to NMR and GC contained four methyl derivatives: 2-methyl, 3-methyl, 4-methyl, and 2,6-dimethylpyridine (8:1:4:0.5; $\sum$ 25 % yield).

*Quinoline* was methylated according to the same procedure.

*Reaction of tetramethylene sulphoxide with 1,4-naphthoquinone. Preparation of X.* 1,4-Naphthoquinone (0.74 g) and $FeSO_4 \cdot 7H_2O$ (0.26 g) were dissolved in tetramethylene sulphoxide (5 ml) and a solution of hydrogen peroxide (35 %, 0.45 g), and conc. sulphuric acid (0.026 ml) in tetramethylene sulphoxide (0.5 ml) was added drop by drop with stirring at 15°C. After standing for 15 min, the mixture was poured into ice-water (20 ml). The water solution was decanted from the oily precipitate. Chloroform (2 ml) was added to the residue and the undissolved material, which consisted of impure X, was filtered off and crystallized three times from acetonitrile, m.p. 194—195°C, 0.14 g, 13 %. NMR (DMSO-$d_6$): $\delta$ 1.69 (4 H, m), 3.30 (2 H, m), 3.55 (2 H, m), 6.83 (1 H, t), 7.12 (1 H, s), 7.5—8.3 (8 H, m), 10.15 (2 H, broad). MS: *m/e* (rel.int.) 436 $M^+$ (4), 278 (37), 214 (50), 173, (90), 158 (87), 130 (40), 104 (81), 102 (55), 76 (100). IR: (KBr) 3420, 3350, 1670, 1460, 1340, 1310, 1270, 1125, 1110 $cm^{-1}$. UV (ethanol): pH ~ 10, $\lambda_{max}$ 266 (28 200), $\lambda_{sh}$ 323 (7300) pH ~ 2, $\lambda_{max}$ 251 (39 300), $\lambda_{sh}$ 266 (17 500), $\lambda_{max}$ 339 (6900).

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## REFERENCES

1. Lagercrantz, C. and Forshult, S. *Acta Chem. Scand.* **23** (1969) 811.
2. Dixon, W. T., Norman, R. O. C. and Buley, A. L. *J. Chem. Soc.* **1964** 3625.
3. Damerau, W., Lassman, G. and Lohs, K. *Z. Chem.* **9** (1969) 343.
4. Fieser, L. F., Clapp, R. C. and Daudt, W. H. *J. Am. Chem. Soc.* **64** (1942) 2052.
5. Norman, R. O. C. and Radda, G. K. *Advan. Heterocyclic Chem.* **2** (1963) 131.
6. Melander, L. *Arkiv Kemi* **11** (1957) 397.
7. Forshult, S., Lagercrantz, C. and Torssell, K. *Acta Chem. Scand.* **23** (1969) 522.
8. Torssell, K. *Tetrahedron* **26** (1970) 2759.

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