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Suggested mechanism for the formation of 3-hydroxy-2-methylbenzoic acid from 3-aminonaphthalene-1,5-disulphonic acid

R. SANGAIAH AND G. S. KRISHNA RAO*
Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012, India.

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Abstract

A mechanism has been suggested for the formation of 3-hydroxy-2-methylbenzoic acid (1), obtained from 3-aminonaphthalene-1, 5-disulphonic acid (3) by alkali fusion in an autoclave. The various steps involved are discussed and the possible mode of degradation of one of the naphthalene rings to give the final benzenoid product is delineated.

Key words : 3-Hydroxy-2-methylbenzoic acid, 3-aminonaphthalene-1, 5-disulphonic acid, β-iminoketone, β-diketone, vinylogous β-ketoacid.

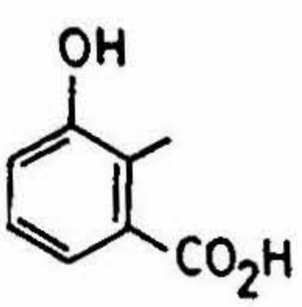
1. Introduction

In a recent communication from this laboratory[1] we reported the use of 3-hydroxy-2-methylbenzoic acid (1) in the synthesis of 2-methyl-3-isopropenylanisole (2), a structure assigned to a naturally occurring monoterpene from *Piqueria trinervia*[2]. The starting benzoic acid (1) was originally obtained by Baudisch and Perkin[3] in an interesting reaction from a dye intermediate, 3-aminonaphthalene-1,5-disulphonic acid (3) by heating with aqueous sodium hydroxide (50%) in an autoclave. Subsequently the experiment was repeated by two groups of workers[4,5] with substantial improvement in the yield of the benzoic acid from 27% to 76% by carrying out the reaction using nitrogen under pressure. In spite of three groups of investigators[3–5] having handled this reaction, no one has discussed the mechanism of formation of the benzoic acid (1) from its naphthalenic precursor (3) to date. In this communication a plausible mechanism is suggested for the various steps occurring under the one-pot reaction conditions prevailing in the autoclave.

2. Discussion

The sulphonic acid groups of the aminonaphthalene disulphonic acid (3) are expected to be converted under the conditions of caustic fusion[6] to the dianion of the dihydroxy

naphthylamine (4) which in turn would tautomerize to the β-iminoketone (5). The iminoketone undergoes hydrolysis to give ammonia and the diketone[6] (6)*, followed by cleavage of the unstable β-diketone to give the anion of the vinylogous β-ketoacid (7), as depicted in Chart I. This would undergo ketonic fission by attack of ^-OH on the ketonic carbonyl with loss of acetic acid (as sodium acetate) to give finally the trianion (8) which would furnish 3-hydroxy-2-methylbenzoic acid (1) on acidification of the contents of the autoclave with concentrated hydrochloric acid.



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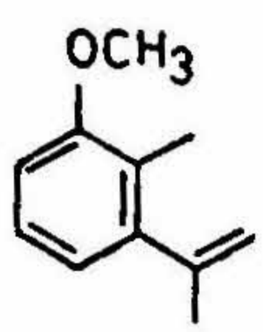

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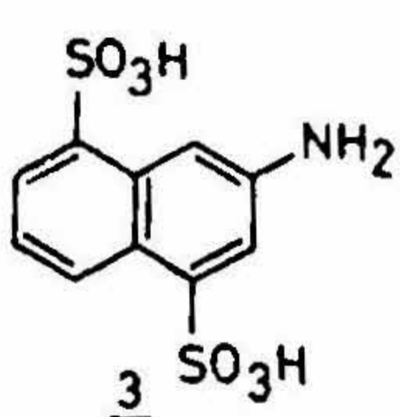

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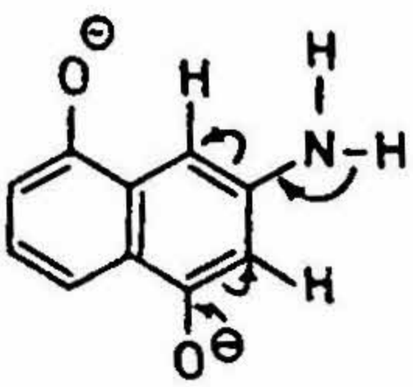

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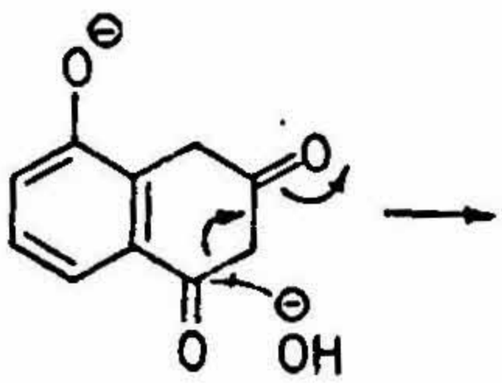

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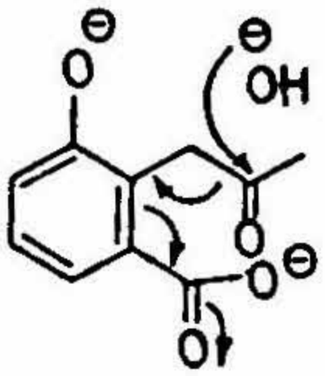

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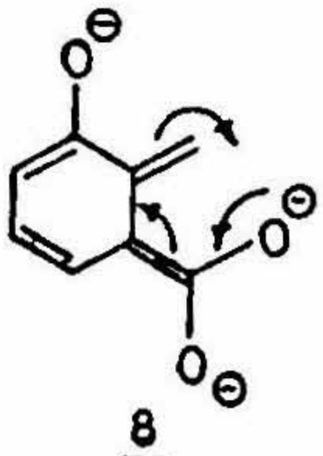

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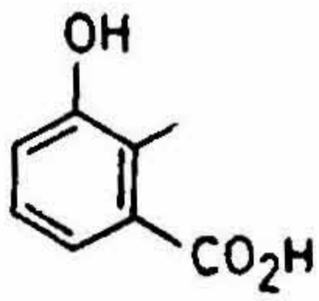

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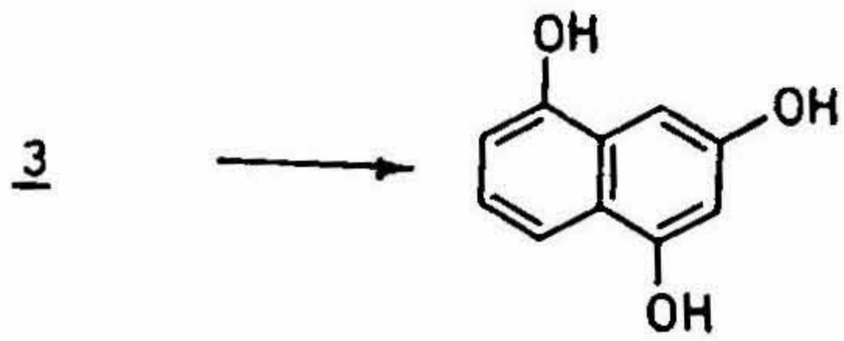

3 → (i) → 6

(i)

* Alternatively, the conversion of (3) to (6) may also be visualized *via* the intermediate (i) derived from (3) directly. We thank the referee for this suggestion.

3. Acknowledgement

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References

1. SANGAIAH, R. AND KRISHNA RAO, G. S. — *Tetrahedron Lett.*, 1981, 22, 1843.

2. BOHLMANN, F. AND SUWITA, A. — *Phytochem.*, 1978, 17, 560.

3. BAUDISCH, O. AND PERKIN, JT., W. H. — *J. Chem. Soc.*, 1909, 95, 1883.

4. FIESER, L. F. AND LOTHROP, W. C. — *J. Am. Chem. Soc.*, 1936, 58, 749.

5. DEAN, R. E., MIDGLEY, A., WHITE, E. N. AND MCNEIL, D. — *J. Chem. Soc.*, 1961, 2773.

6. MARCH, J. — *Advanced organic chemistry : reactions, mechanism, and structure*, (International student's edition), McGraw-Hill, Kogakusha, Japan, 1977, pp. 596–600.