

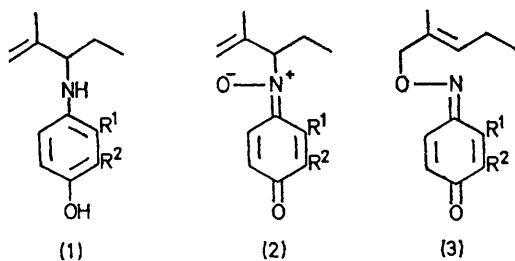
## O-Alkenyl Oxime Ethers: a New Product Type from Nitrosophenol-Olefin Reactions

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**Summary** The *N*-(1-ethyl-2-methylprop-2-enyl)quinone imine *N*-oxides (**2**), formed by reaction of 2-methylpent-2-ene with *p*-nitrosophenols, rearrange on heating to *O*-2-methylpent-2-enyl *p*-benzoquinone mono-oxime ethers.

THE major olefin-derived products obtained on reaction of *p*-nitrosophenol with 2-methylpent-2-ene are compounds (**1a**) and (**2a**).<sup>1</sup> This reaction is thought<sup>2,3</sup> to involve initial 'ene' addition of the nitroso-group to the olefin to give an unstable *N*-alkenylhydroxylamine which may either disproportionate to (**1a**) and (**2a**) or reduce the nitroso-compound giving (**2a**) and other products such as 4,4'-dihydroxyazoxybenzene.



- a;  $R^1 = R^2 = H$   
 b;  $R^1 = H, R^2 = Me$   
 c;  $R^1 = Me, R^2 = H$

Although 2-methyl-4-nitrosophenol and 3-methyl-4-nitrosophenol exist nearly completely as their *p*-benzoquinone mono-oxime tautomers in dioxan at 20° (98 and

97%, respectively; cf. 14–16% for *p*-nitrosophenol)<sup>4</sup> they reacted readily in tetrahydrofuran solution with 2-methylpent-2-ene at 100–120°, although more slowly than *p*-nitrosophenol does (*t*<sub>r</sub> at 100°: 4.5 and 11.5 h, respectively; cf. 0.4 h for *p*-nitrosophenol). In each case, the principal characterizable products were the alkenylaminophenols (**1b**; yield 33% at 120°; **1c**; yield 20% at 120°). The quinone imine *N*-oxide (**2b**) was formed in 25–30% yield from the reaction of 2-methyl-4-nitrosophenol with 2-methylpent-2-ene at 120° but the corresponding product could not be detected from 3-methyl-4-nitrosophenol.

TABLE. Yields of *O*-alkenyl oxime ethers (**3**) at reaction times corresponding to complete reaction of the nitrosophenol

|               | Yield (%) | Reaction time/h | Reaction temp. |
|---------------|-----------|-----------------|----------------|
| ( <b>3b</b> ) | <2        | 24              | 100°           |
|               | 6         | 6               | 120°           |
| ( <b>3c</b> ) | 5         | 30              | 100°           |
|               | 12        | 20              | 120°           |

However, significant minor products of the two reaction systems (see Table) were the *O*-alkenyl oxime ethers (**3b**) and (**3c**), characterized by reference to authentic materials synthesized from 1-chloro-2-methylpent-2-ene and the silver salt of the appropriate *p*-benzoquinone mono-oxime.

We ascribe the formation of (**3**) to thermal rearrangement of the quinone imine *N*-oxide (**2**) since heating (**2a**) in *n*-heptane for 4 h at 120° afforded (**3a**)† in 11% yield, together with (**1a**) (32%) and other, unidentified, products. Similar products were formed, but in higher yields, on heating (**2a**) with 2-methylpent-2-ene under the same conditions. Failure to detect (**3a**) in the reaction products of

† Synthesized similarly to (**3b**) and (**3c**).

*p*-nitrosophenol and 2-methylpent-2-ene<sup>3</sup> is therefore probably due to use of reaction temperatures lower than 120°.

The conversion of (2) into (3) is analogous to the thermal rearrangement of allylically unsaturated amine oxides to *O*-alkenylhydroxylamines<sup>5</sup> and of nitrones to *O*-alkenyl oxime ethers.<sup>6</sup> Although there is now good evidence that the general Meisenheimer<sup>7</sup> and Martynoff<sup>8</sup> rearrangements proceed by a dissociation-recombination mechanism in-

volving caged free radicals, this evidence does not bear directly on migration of allylic groups and we formulate the present transformation as a [2,3] sigmatropic rearrangement by analogy with the conversion of (+)-*N*-*trans*-but-2-enyl-*N*-ethyl-*p*-toluidine oxide into (+)-*O*-1-methylprop-2-enyl-*N*-ethyl-*p*-tolylhydroxylamine.<sup>9</sup>

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<sup>3</sup> B. Pepper, Ph.D. Thesis, University of London, 1973.

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<sup>5</sup> J. Meisenheimer, *Chem. Ber.*, 1919, **52**, 1667.

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<sup>7</sup> R. A. W. Johnstone in 'Mechanisms of Molecular Migrations,' ed., B. S. Thyagarajan, Interscience, New York, 1969, vol. **2**, p. 249; J. P. Lorand, R. W. Grant, P. A. Samuel, E. O'Connell, and J. Zaro, *Tetrahedron Letters*, 1969, 4087; A. R. Lepley, P. M. Cook, and G. F. Willard, *J. Amer. Chem. Soc.*, 1970, **92**, 1101.

<sup>8</sup> D. G. Morris, *Chem. Comm.*, 1971, 221 and refs. therein.

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