The Reaction of 2-Methylpent-2-ene with *p*-Nitrosophenol and with *NN*-Dimethyl-*p*-nitrosoaniline

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Summary Identification of minor reaction products in the reaction of 2-methylpent-2-ene (I) with *p*-nitrosophenol (II) and with *NN*-dimethyl-*p*-nitrosoaniline (III) indicates a possible mechanism.

RECENT commercial interest[1–3] has centred around the title reactions which are attractive synthetic routes to *p*-phenylenediamines and *p*-aminophenols. We now report the minor products of the reaction which have significance with regard to a possible mechanism.

Both (II) and (III) react with (I) under an inert atmosphere at moderate temperatures (20—140°) in a variety of organic solvents to yield the corresponding *p*-substituted-*N*-(1-ethyl-2-methylprop-2-enyl)anilines (IVa) and (IVb) as major products; 36% and 31%, respectively for the reaction of a twelvefold excess of olefin with 1% solution of the nitroso-compound in tetrahydrofuran at 65° during 24 h. Minor products ($\leqslant$12%) include the respective *p*-substituted primary anilines, azoxybenzenes, and azobenzenes.† Of greater significance is the isolation of *N*-(1-ethyl-2-methylprop-2-enyl)quinoneimine *N*-oxide (V)‡ (14% maximum yield after one reaction half-life) from the reaction of (I) with (II). The reaction of aromatic *C*-nitroso-compounds with olefins containing α-methylenic hydrogen atoms has recently been shown to proceed *via* an 'ene' addition to give *N*-alkenyl-*N*-arylhydroxyl-

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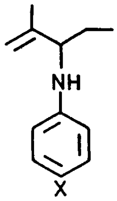
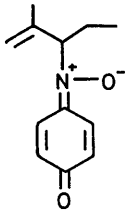
† The products were isolated by distillation (IVb), column chromatography on neutral alumina (IVa), and preparative t.l.c. on silica gel (V). New compounds were characterised by i.r., n.m.r., and u.v. spectroscopy and elemental analysis.

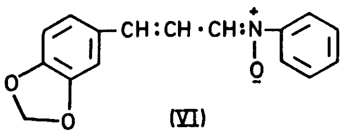
‡ Oxidation of (IVa) according to the method of Pederson[5] gives, as expected, (V) in good yield.

amines [6,7] We suggest that decomposition of these alkenyl arylhydroxylamines could give rise to the observed alkenyl arylamines (IVa,b) and would also give α-alkenyl-*N*-aryl-nitrones as products, in a manner analogous to that previously reported[7,8] for alkyl aryl hydroxylamines However, only when these nitrones possess special structural features can they be detected and isolated Such structural features include either the ability to tautomerise to a more stable form, or the possession of a high degree of resonance stability An example of the former is found in the isolation of (V) from the reaction of (I) and (II), while the latter is illustrated by the isolation by early workers[4] of (VI) from the reaction of nitrosobenzene with safrole The general instability of α-alkenyl-*N*-aryl-nitrones is not unexpected since they are known to undergo cyclisation,[9] and reaction with further nitrosoarene is possible[10] both in the open nitrone and cyclic forms These reactions would give rise to more complex products, and could ultimately produce 'tar-like' residues The large amounts (45% by weight in each case under the conditions quoted earlier) of tarry material isolated from the reaction of (I) with (II) or with (III) could thus be made up of condensed nitrone structures Elemental analysis indicates that this material contains both alkyl and aryl moieties and this is confirmed by n m r and i r spectroscopy Also in support of this suggestion is the observation that treatment of the tars with dilute acid liberates the appropriate *p*-substituted aniline


X = OH (a)
NMe$_2$ (b)

(IV)


(V)


(VI)

The formation of azoxybenzenes, azobenzenes, and primary anilines in the reaction of (I) with (II) or (III) appears not to occur *via* the main reaction pathway but can be explained by the nitrosoarene undergoing a reductive side-reaction *via* the *N*-arylhydroxylamine, and indeed evidence for such a reaction has been obtained [7]

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