Thermal 2,5-Cycloaddition of *N*-Arylmaleimides to Phenols

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Phenol undergoes thermal 2,5-cycloaddition of *N*-phenylmaleimide to give *endo*- and *exo*-bicyclo-octenones (**3**) and (**4**) respectively, and a homopolymer of the maleimide; use of *N*-(*p*-methoxyphenyl)maleimide minimises polymer formation, and gives a combined cycloadduct yield of 60% in the case of *p*-cresol.

Diels–Alder additions of maleic anhydride to hydroquinone and some of its simple ring-alkylated derivatives giving *e.g.* (**1**) offer in principle a useful one-step route to the bicyclo[2.2.2]octane system (Scheme 1),[1,2] but the very poor yields and the failure to extend the reaction to phenol and substituted phenols have evidently rendered this approach unattractive in practice. By using *N*-phenylmaleimide and its derivatives as the dienophile, we have found that monohydric phenols will also form cycloadducts, thereby providing easy access to bicyclo[2.2.2]octenones, *e.g.* (**2**), from phenol.

Thus phenol (2 mol) and *N*-phenylmaleimide (1 mol) at 170 °C for 3 days give the *endo*- and *exo*-isomeric bicyclo[2.2.2]octenone adducts, (**3**) and (**4**), in isolated yields of 31 and 5% respectively, based on the 0.65 mol of *N*-phenylmaleimide consumed. The acyclic adduct (**5**) was also isolated in 3% yield.

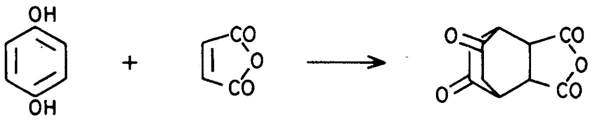
The stereochemistry of the isomers (**3**) and (**4**) has been established by detailed analysis of their 220 MHz ^{1}H n.m.r. spectra. In particular, the carbonyl group at C-10 of the *endo* isomer (**3**) acts differentially on the chemical shift of the imide ring protons (2- and 6-H) which therefore appear as two double doublets at δ 3.42 (1H; $J_{2,6}$ 8.5, $J_{1,2}$ 3.0 Hz) and δ 3.33 (1H; $J_{6,7}$ 8.5, $J_{2,6}$ 3.0 Hz). In the spectrum of this isomer, the methylene group at C-11 appears as a singlet with fine structure. Complementary effects are observed in the case of the *exo*-isomer (**4**). Thus, the two hydrogens of the methylene group are differently affected by the proximity of an imide carbonyl group and hence resonate as two double doublets (J_{gem} 19 Hz) at δ 2.12 (1H; $J_{7,11}$ 2 Hz) and 2.28 (1H; $J_{7,11}$ 3 Hz). The imide ring protons of this isomer appear as a broad multiplet, showing much line perturbation, at δ 3.20—3.36. These data confirm the assigned configurations.

Mixing solutions of phenol and *N*-phenylmaleimide in acetonitrile produces an intensification of the yellow colour of the maleimide through increased tailing into the visible region; this is suggestive of charge-transfer complexation, even though no new absorption maximum is observed.

A major by-product of the reaction between phenol and *N*-phenylmaleimide is a homopolymer of the imide (51% yield). This is not formed in the absence of the phenol under the conditions employed. Spectral evidence (n.m.r. and i.r.), together with elemental analysis, indicates that this polymer is of type (**6**), rather than a polyamide of type [–COCH=CH-CONPh–]$_n$. Thus, the ^{1}H n.m.r. spectrum showed the absence of ethylenic protons (broad absorptions centred at δ 7.4 and 3.4). The i.r. spectrum showed $\nu_{max.}$ 1715 cm^{-1} (C=O stretch, as for *N*-substituted succinimides). Efforts to prevent or reduce the polymerisation by performing the reaction in the dark, under nitrogen, or by use of radical traps proved wholly unsuccessful, despite the fact that *N*-phenylmaleimide readily undergoes radical polymerisation.[3] We have however observed that *N*-phenylmaleimide readily forms a polymer of type (**6**) in the presence of weak bases such as pyridine; the spectroscopic properties are identical with those of the above polymer formed by *N*-phenylmaleimide in the presence of phenol. This finding, coupled with the insensitivity towards radical traps and the indications of charge-transfer complexation, suggests that the negative moiety of a charge-transfer complex between the imide and the phenol may be initiating an essentially base-catalysed polymerisation of the free and/or complexed maleimide. Alternatively, the process may represent a type of zwitterionic polymerisation.

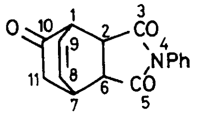
The spectroscopic properties of the poly(*N*-phenylmaleimide) indicate that it is a polymer of different type from the structurally complex maleic anhydride polymers formed in the presence of catalysts such as triphenylphosphine.[4]

Experiments using derivatives of *N*-phenylmaleimide having diminished acceptor properties are consistent with charge-transfer catalysis of the polymerisation. Thus *N*-(*p*-methoxyphenyl)maleimide suffers much reduced polymerisation, with no significant loss of reactivity in the cycloaddition. *p*-Cresol forms the two stereoisomeric cycloadducts (**7**) and (**8**) with *N*-(*p*-methoxyphenyl)maleimide in yields of 42 and 18% respectively, together with the acyclic adduct analogous to (**5**) (7%), and the maleimide polymer (20%). The good yields of cycloadducts obtainable suggest that reactions of this type may have practical value for

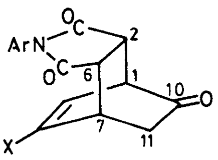


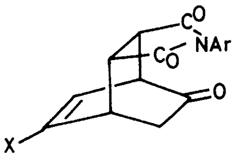
(**1**)

Scheme 1

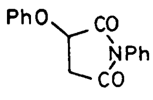


(**2**)

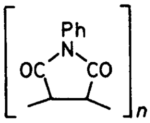




(**3**) X = H; Ar = Ph (**4**)
(**7**) X = Me; Ar = C_6H_4OMe-*p* (**8**)



(**5**)



(**6**)

synthesis of bicyclo[2.2.2]octanes not readily accessible by other procedures.

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