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Directive Effects of Substituents on the Electron Transfer Photoreduction of N-Methylphthalimide by 2,3-Dimethyl-2-butene

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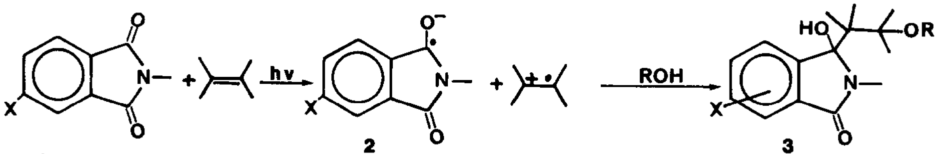
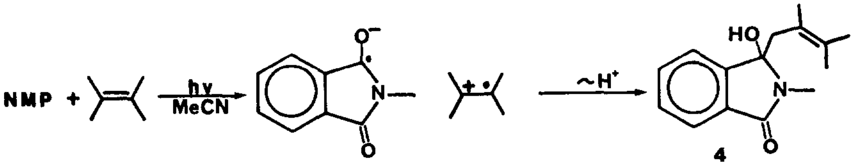
Summary. Irradiation of a series of aryl substituted phthalimides in the presence of 2,3-dimethyl-2-butene results in a single regiochemical photoreduction product for each substituent. The results are consistent with substituent stabilization effects on the intermediate phthalimide radical anion.

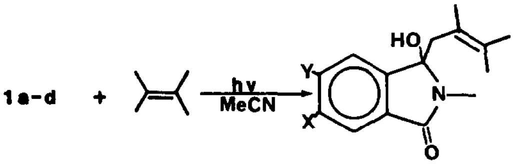
The photochemical reactions of phthalimides with various alkenes have been the subject of numerous recent investigations.[1] The processes involved include [2+2] addition to the C(O)N bond,[2] the Paterno-Buchi reaction,[3] and inter-and intramolecular electron transfer reactions.[4] Recently we reported on the directive effects of aryl substituents on the regiochemistry of trapping of the photochemically generated ion pair from N-methylphtalimide (NMP) and 2,3-dimethyl-2-butene.[5] Those results indicated that strong acceptor (CO_2Me) groups direct the incoming substituent in the predicted manner, however other substituents (Me, Cl, OMe) gave essentially equal product mixtures. Our initial thought was that the observed lack of regiochemical preference might be due to the protic nature of the solvent i.e. preferential protonation of one of the carbonyl groups in the ground state could affect the regiochemistry of the reaction.



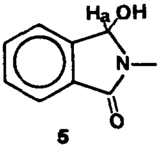
1a, X = OMe
b, X = Me
c, X = Cl
d, X = COOMe

We have obtained convincing evidence that the photoreduction observed on prolonged irradiation of NMP in the presence of 2,3-dimethyl-2-butene occurs by initial electron transfer[6] followed by proton transfer and coupling of the resultant radical pair. This reaction now allowed us to conduct a study in the aprotic solvent system. Irradiation of each of the 4 substituted phthalimides 1a-d resulted in a single product.[7] We were able to ascertain the regiochemistry of the products by lanthanide shift reagent (LSR) studies and were able to show that the site of LSR complexation was at the carbonyl rather than the OH oxygen by studies on 5 which showed that the NCH_3 and *ortho* aromatic proton were shifted more than Ha. The structures of 4a-d follow from examination of their LSR doped spectra which shows the most shifted aromatic proton as a *meta* coupled doublet for 4d and as *ortho* coupled doublets for 4a-c. Obviously the directive effects of the aryl substituents are more clearly manifested in the aprotic solvent since we observe a single product in all cases. However the observed regiochemistry is at first glance somewhat surprising e.g. *a priori* we would have expected acceptors to direct *para* and donors to direct *meta* consistent with what is found for electrochemical reductions of substituted benzaldehydes.[8] The Cl substituent should be considered as an acceptor but it directs *meta*. Examination of the contributing structures 6 + 7 and the relevant σ values[9] provides a ready answer. In contributing structure 6 x is *para* to the radical anion whereas in 7 it is *meta*. Whether the radical anion most resembles 6 or 7 is a function of the relative magnitudes and signs of the σ_p and σ_m values for the various





4a,Y=OMe
b,Y=Me
c,Y=Cl
d,X=COOMe



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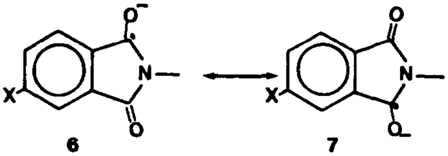

substituents. For the para situation the important value is the resultant σ_r value $\sigma_r = \sigma_p - \sigma_\pi$

The appropriate values of σr for the substituents in question are listed below. Clearly the σ_r values are in the appropriate order with OMe, Me, and Cl predicting meta orientation and CO_2Me predicting para orientation as observed.

Substituent	σ_r		σ_p	$- \sigma_m$
OMe	-0.383	=	-0.268	-(0.115)
Me	-0.101	=	-0.170	-(-0.069)
Cl	-0.146	=	0.227	(0.373)
CO_2Me	+0.07	=	0.39	(0.32)

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