HETEROCYCLES, Vol. 3, No. 9, 1975

PHOTOADDITION REACTIONS OF N-METHYLPHTHALIMIDE WITH TOLUENES AND AMINES [1,2]

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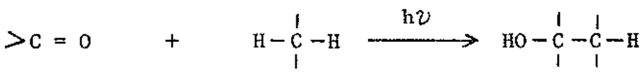
Photoreactions of N-methylphthalimide 1 were examined in presence of substituted toluenes and tertiary amines. Together with the reduced products 3,5,6, the addition products 2,4, were obtained. It has been shown that the imide carbonyl is capable of photochemically adding the methylene adjacent to benzene and nitrogen.

In photoaddition reactions of carbonyl compounds, referred to as "photo-aldol condensation",[3,4] the methylene group activated by an adjacent group such as double bond or hetero atoms are prone to the reactions leading to carbinols (Scheme I).[3,4] In the course of our systematic studies on the photochemistry of imide carbonyls, we reported that phthalimides undergo photochemical carbinol formation in the presence of alcohol,[5] ether,[3] and olefin.[3] As an extension of this work, we wish to report in the present communication our results on such a photo-aldol condensation of N-methylphthalimide 1 with aromatic hydrocarbons possessing benzyl hydrogens, and with some tertiary amines.



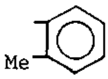
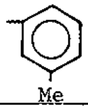
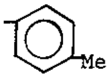
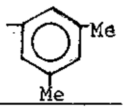
$$>C=O \quad + \quad H-\overset{|}{\underset{|}{C}}-H \xrightarrow{h\nu} HO-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-H$$

Scheme I

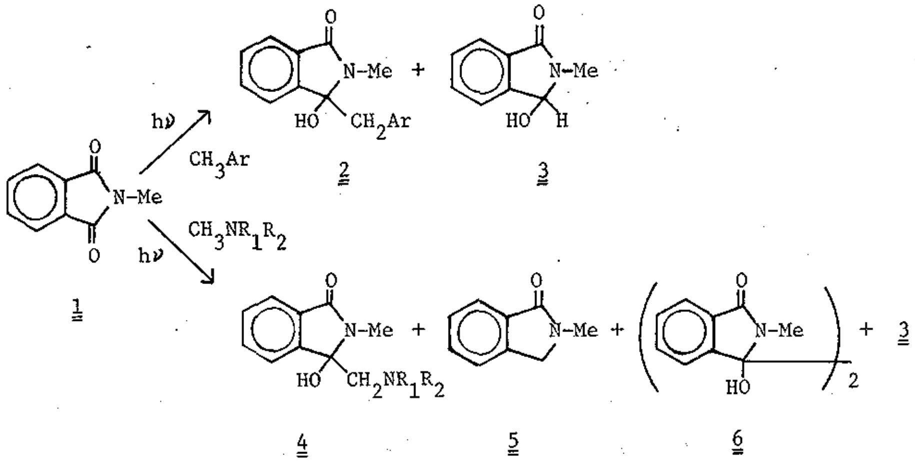
Photoreaction of 1 was examined in a set of several toluene derivatives, and the results are summarized in Table I.[6] The addition products 2 were isolated, though in rather low yields, accompanied by the reduced product 3 and recovered 1. Presumably the benzyl hydrogen is abstracted by the excited imide carbonyl followed by combination of the two radicals formed. This inference is supported by identification of bibenzyl (20 %) from the reaction mixture of toluene, which is formed probably by coupling of benzyl radicals.

In preliminary experiments a survey was made of the reactivity of 1 toward triethylamine, N,N-dimethylcyclohexylamine and N,N-dimethylaniline[7]. It has been recently known that amines are efficient photoreducing agents for aromatic ketones[8]. Parallel to this, triethylamine and N,N-dimethylcyclohexylamine led to photoreduction to give N-methylphthalimidine 5, a highly reduced product, which is not found in the reduction with alcohol.[5] Results under various conditions are compared in Table II[6]. In the most cases the amino carbinols 4 were isolated, which are the crossed coupling products of the amine-derived and the imide-derived radicals. It is worth noting that pinacol 6, common photoreduced products of ketone triplets, is generally formed in this amine-mediated photoreduction (Scheme II) in contrast to that 6 has not been

Table I Photoreaction Products with Toluenes[a)]; Yield (%)

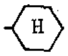
Ar					
2 (mp°C)	5(166-7)	23(182-3)	7(114.5-5)	35(151-1.5)	24(175-5.5)
3	2	3	2	4	1
Recovered 1	70	21	41	42	33
time (hr)	4	2	7	1	1

a) A solution (~20mM) in the hydrocarbon was irradiated with a 1Kw high pressure mercury lamp.



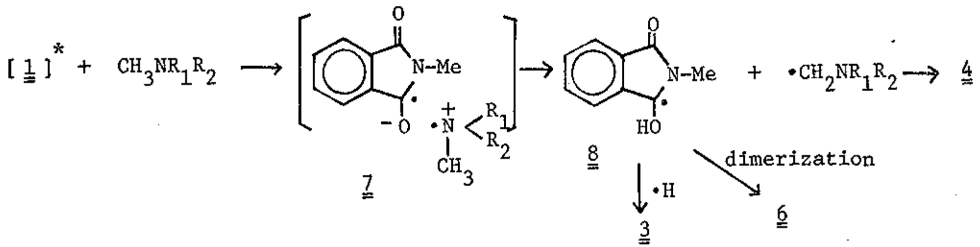
Scheme II

Table II Photoreaction Products with Amines[a]; Yields (%)

R$_1$	R$_2$	Conditions	Yield(%)	3	4	5	6	1
Me		10eq 500w CH$_3$CN 2hr (hp)		–	9	–	14	32
		2 " " 4		–	4	–	14	63
			mp(°C)	130-1	157-8	113-4.5	231-5	132-3
Me		10 " " 1		–	–	23	–	–
		11 500w[b) " 2 (hp)		20	37[e)]	–	16	20
		2 " " "		20	11[e)]	–	44	19 d)
		2 500w[c)] C$_6$H$_6$ " (hp)		56	4[e)]	–	16	6

a) A solution (10mM) was irradiated as stated. b) Pyrex tube, merry-go-round.

c) Quartz tube, merry-go-round. d) A solution (10mM ; 10ml) was irradiated and the product analysis was performed with a TLC-autodetector (IATRON Thinchrograph TFG-10). e) mp 86-7.5°



Scheme III

detected in the photoreduction of 1 by alcohol.[5]

Photoreduction of ketone triplets by amines proceeds generally by way of a charge transfer complex followed by transfer of α-hydrogen of the amine and formation of the radicals.[8] Analogously, the similar intermediates 7,8 may be postulated in the photoreaction of 1 with amines to lead to the addition products 4, hydroxyphthalimidine 3, and pinacol 6 (Scheme III).

It has now been shown that the imide carbonyl of 1 is capable of adding the methylene adjacent to benzene and nitrogen. In conclusion, the photoreactions of the phthalimide system in the presence of alcohol[5], ether[3], olefine[3], aromatic hydrocarbon and amine generally include the carbinol formation (Scheme I). Synthetic scope of these reactions is under investigation.

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6 New compounds gave satisfactory analyses and their structures were supported by spectral (uv, ir, nmr, mass) data.

7 A solution of 1 containing an amine (10 eq.) in acetonitrile (10mM) was irradiated with a 500w high pressure mercury lamp.

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Received 31st July, 1975