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PHOTO-INDUCED SOLVENT-INCORPORATED ADDITION OF N-METHYLPHTHALIMIDE TO OLEFINS. REACTIONS PROMOTED BY WAY OF INITIAL ONE ELECTRON TRANSFER

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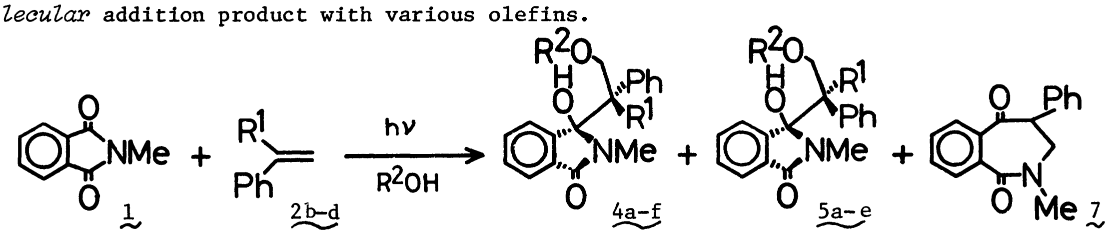
Irradiation of N-methylphthalimide 1 and styrene 2b in methanol gave two solvent-incorporated isomeric adducts 4a and 5a. The corresponding solvent-incorporated adducts (1 : olefin : alcohol = 1 : 1 : 1) were obtained in the photochemical reaction of 1 with several olefins 2a-f in alcohols. A mechanism involving one electron transfer from 2b to 1 is proposed.

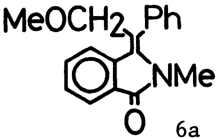
Although it is well known that photochemically excited imides abstract hydrogen from various hydrogen donors,1) photochemical reaction of imides with olefins has been remained unexplored till recent year and now becomes the subject of active works.2) On the photolysis in acetonitrile N-methylphthalimide 1 reacted with 2-methylpropene 2a to give 1,6,6-trimethyl-3,4-benzo-6,7-dihydroazepine-2,5-dione 3, whereas under similar conditions N-methylsuccinimide reacted with the same olefin to give an oxetane.2c) Further, it has been reported that N-alkenylphthalimides cyclized photochemically to give solvent-incorporated *intramolecular* cycloaddition products.2d) In this letter we wish to disclose that irradiation of 1 dissolved in an alcohol gives solvent-incorporated *intermolecular* addition product with various olefins.



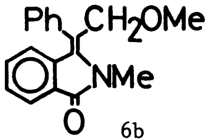
Table

1	2,	R1	R2	4 (yield,%)	5 (yield,%)	7 (yield,%)
1	2b,	H	Me	4a, 40	5a, 34	-
1	2b,	H	Et	4b, 38	5b, 31	7, trace
1	2b,	H	isoPr	4c, 32	5c, 25	7, 18
1	2b,	H	t-Bu	4d, 28	5d, 26	7, 30
1	2c,	Me	Me	4e, 40	5e, 30	-
1	2d,	Ph	Me	4f, 83	-	-

After irradiation of a methanol solution of 1 and styrene 2b,[3)] chromatography of the products on silica gel gave 4a (40%), 5a (34%), and other products derived from 2b. 4a: mp 131-2 °C; ^{1}H NMR ($CDCl_3$) δ 2.89 (s, 3H, NMe), 3.50 (s, 3H, OMe), 3.6-3.9 (m, 2H), 4.0-4.3 (m, 1H), 5.29 (s, 1H, OH), 6.4-6.6 (m, 2H), 6.9-7.2 (m, 3H), 7.3-7.7 (m, 4H); IR (KBr) 3280, 1673 cm^{-1}; MS (20 eV), m/e (rel intensity), 279 (M^+-H_2O, 6), 162 (42), 104 (100); Elemental Analysis ($C_{18}H_{19}NO_3$). 5a: mp 159-62 °C; ^{1}H NMR ($CDCl_3$) δ 3.05 (s, 3H, NMe), 3.31 (s, 3H, OMe), 3.4-3.8 (m, 3H), 5.10 (s, 1H, OH), 6.9-7.3 (m, 9H); IR (KBr) 3210, 1684 cm^{-1}; MS (20 eV), m/e (rel intensity), 279 (M^+-H_2O, 9), 162 (35), 104 (100); Elemental Analysis ($C_{18}H_{19}NO_3$). The structure of the isomeric products 4a and 5a was deduced from their dehydration. By refluxing with sodium acetate in acetic anhydride each of 4a and 5a was easily dehydrated to give a respective mixture of 6a (mp 146-7 °C) and 6b (mp 148.5-151 °C). The stereochemistry of 4a and 5a was assigned on the basis of their ^{1}H NMR spectra. Based on the assumption that the intramolecular hydrogen bonding between hydroxy group and methoxy group fixes the molecule in a particular conformation,[4)] the higher field shift of phenyl ring protons of 4a compared with those of 5a is explicable in terms of the anisotropic shielding effect of the fixed phenyl ring. This is supported by a resemblance of ^{1}H NMR pattern in the region of δ 6.4-7.7 in a series of products. Irradiating 1 and 2b in various alcohols we obtained similarly the corresponding solvent-incorporated adducts (ethanol, isopropanol, or tert-butanol). However, the yield of the adducts 4a-d and 5a-d decreased with the decreasing polarity of the solvents. Another product was 7. α-Methylstyrene 2c or 1,1-diphenylethylene 2d added similarly to 1 on irradiation in methanol, giving the corresponding solvent-incorporated products 4e+5e or 4f as shown in a table.



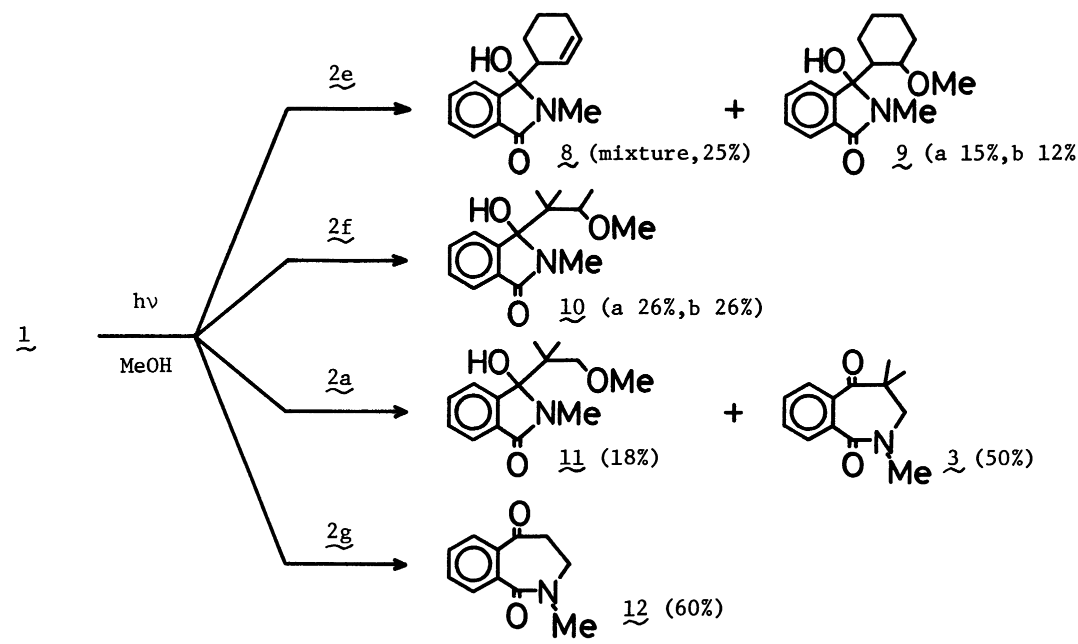
6a



6b

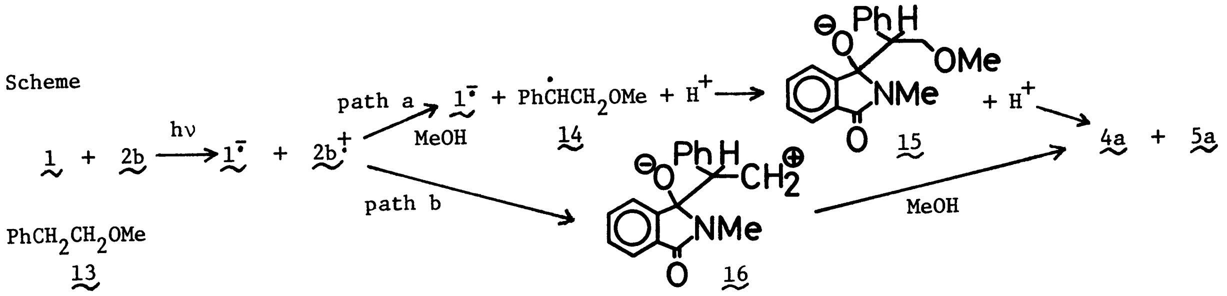
In the photo-reaction of 1 with aliphatic olefins, photo-hydrogen abstraction reaction from cycloalkenes was reported.[1a)] Although photolysis of 1 and cyclohexene 2e in acetonitrile yielded only the adducts 8 derived probably *via* allyl hydrogen abstraction reaction,[1a)] in methanol irradiation of a mixture of 1 and 2e gave solvent-incorporated adducts 9 together with 8. Irradiation of a methanol solution of 1 and 2-methyl-2-butene 2f (or 2a) gave adducts 10 (or 11, though in this case the main product was cycloaddition product 3). However, 1-pentene 2g gave none of the solvent-incorporated adducts in the reaction with 1 under similar conditions, resulting in the formation of product 12.[2b,c)]

As is well known, in polar solvents photolysis of electron donor-acceptor pairs often produces a pair of radical ions.[5)] Thus, the formation of the solvent-incorporated adduct 4a and 5a in our reaction will involve one electron transfer from 2b to 1 as the initial step.[6)] This is supported by the observed tendency that the yield of solvent-incorporated adducts increased with the increas-



ing polarity of solvents and with the decreasing oxidation potential of the olefin. In addition, the estimated free energy change (ΔG) in this electron transfer process is negative.[7)]

Scheme



Since protonation of the radical anion $1^{\cdot-}$ in methanol seems to be unfavorable,[7b)] two mechanisms (path a and b) are conceivable for the formation of the 4a and 5a. Nucleophilic attack of methanol to $2b^{\cdot+}$ may occur initially, followed by coupling of the resulted radical 14 and radical anion $1^{\cdot-}$ leading to the formation of 15 to which protonation occurs (path a). Alternatively, initial coupling of the radical anion-radical cation pair may occur, resulting in the formation of zwitterion 16 to which methanol finally adds (path b). Since no phenyl migration was observed in the photolysis of a methanol solution of 1 and 2d, the contribution of the latter seems to be less important for our reactions.

It is reported that the irradiation of methyl p-cyanobenzoate (aromatic ester) and 2d in methanol formed radical ions through one electron transfer, resulting in anti-Markownikoff addition of the solvent to 2d.[5c-e)] In the photolysis of 1 and 2b, methyl 2-phenylethyl ether 13 was detected a little by means of glc. As another possible process, the solvent-incorporated adduct 4a and 5a might be produced *via* hydrogen abstraction from 13 by photo-excited 1, and subsequent addition of the resulting radicals. However, photolysis of an ethanol solution containing 1 (0.04 M), 2b

(0.06 M), and 13 (0.06 M) resulted in the formation of adducts 4a + 5a / 4b + 5b < 1 / 100 at the low conversion of 1 (< 20%). Thus, we conclude that the solvent-incorporated adducts could not be formed *via* the intermediate 13 or at least in the major parts.

In the photolyses of electron donor-acceptor pairs, to our knowledge, there have been a few examples of solvent-incorporated adduct formation.8) However, those examples are limited to cyanated aromatics acting as an electron acceptor. The present photochemical reactions of phthalimides with olefins are the first example of the solvent-incorporated olefin addition to the carbonyl system.

Further investigation is now in progress.

References and Notes

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3) A methanol solution containing 1 (0.014 M) and 2b (0.1 M) was irradiated with a 300-W high-pressure Hg-lamp under N_2 for 3h. The yield was based on the consumed imide.

4) IR spectra in chloroform supported the presence of the intramolecular hydrogen bonding. The similar structural analysis of photo-adducts was performed by Y. Kanaoka and Y. Hatanaka.1a)

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6) In the photo-hydrogen abstraction reaction of phthalimides electron transfer (or CT) mechanisms were proposed in some cases.1b-e)

7) Using Weller's equation,7a) we can estimate ΔG is negative even if the electron transfer occur from the lowest excited state of this system (T^1 of 2a). The reported half-wave reduction potential of 1 (-1.22 V)7b) and oxidation potential of 2b (+1.38 V)7c) were applied in the above estimation. (a) D. Rehn and A. Weller, Isr. J. Chem., 8, 259 (1970); (b) O. R. Brown, S. Fletcher, and J. A. Harrison, J. Electroanal. Chem. Interfacial. Electrochem., 57, 351 (1974); (c) K. Mizuno, R. Kaji, H. Okada, and Y. Otsuji, 37rd Annual Meeting of the Chemical Society of Japan, Yokohama, April 1978, Abstracts of papers II, p. 1052.

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