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PHOTO-INDUCED ADDITION OF IMIDES TO OLEFINS
— REMARKABLE DIFFERENCE BETWEEN PHTHALIMIDES AND SUCCINIMIDES

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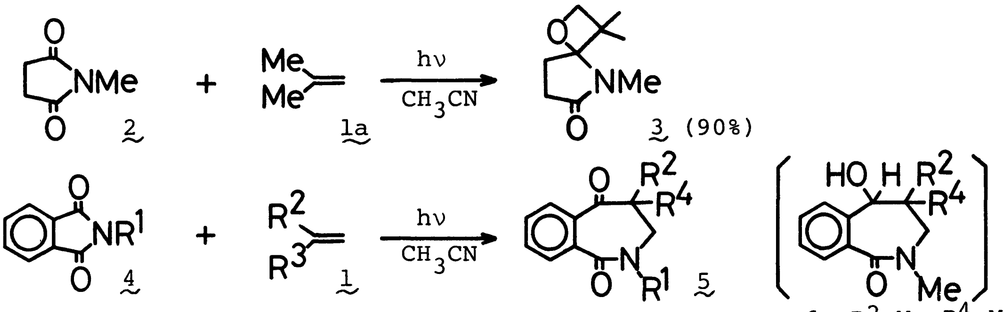
On irradiation, phthalimides 4 dissolved in acetonitrile reacted with various olefins 1 to give 5, while the reaction of succinimides with the corresponding olefins resulted in the formation of oxetanes. Photolysis of N-alkenylphthalimides 8 in acetonitrile afforded 9. The presence of N-alkenyl δ,ε double bond (counted from N atom) is extremely preferable for the formation of 9.

We reported recently the photochemical oxetane formation of alicyclic imides with olefins, especially in the cases of N-2-alkenyl alicyclic imides.1) However, it was found that the photochemical reaction of phthalimides with olefins was widely different from that of alicyclic imides (succinimides), despite the similar behavior in their photochemical hydrogen abstraction reaction.2) In this letter, we wish to report on the photochemical reaction of phthalimides with olefins in comparison with that of succinimide derivatives with olefins.

Typically, in the photo-reaction with 2-methylpropene 1a in acetonitrile N-methylsuccinimide 2 gave oxetane 3 as the exclusive product (90%).3) In contrast N-methylphthalimide 4a afforded a different type of adduct 5a in the reaction with the same olefin 1a as a sole isolable product (67%).4) 5a: mp 74-5 °C; ^{1}H NMR ($CDCl_3$) δ 1.27 (s, 6H), 3.23 (s, 3H), 3.47 (s, 2H), 7.4-8.0 (m, 4H); IR (KBr) 1692, 1642 cm^{-1}; MS (20 eV), m/e (rel intensity), 217 (M^+, 4), 174 (100). By treating with sodium borohydride in methanol, 5a gave an alcohol 6a (70%): mp 188-9 °C; ^{1}H NMR ($CDCl_3$) δ 1.14 (s, 3H), 2.10 (s, 3H), 2.62 (d, J=14 Hz, 1H), 2.90 (d, J=14 Hz, 1H), 3.08 (s, 3H), 3.57 (s, 1H), 4.20 (s, 1H, OH), 7.2-8 (m, 4H); IR (KBr) 3305, 1625 cm^{-1}; MS (20 eV), m/e (rel intensity), 219 (M^+, 100), 190 (61), 161 (56).



6a, R^2=Me, R^4=Me
6b, R^2=H, R^4=Ph

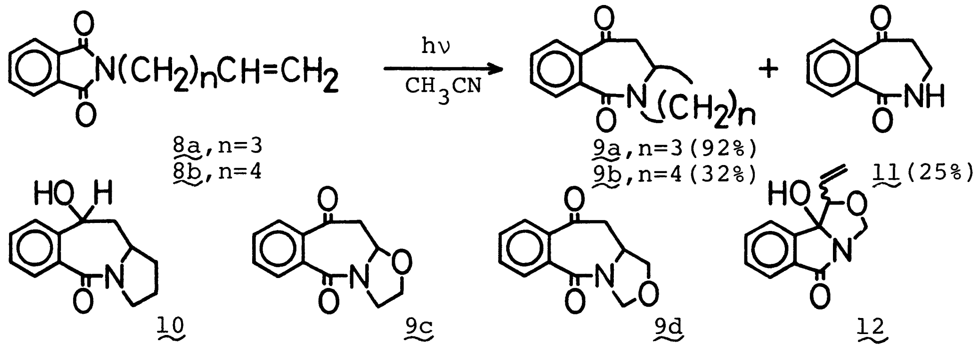
Table

4 R^1	1 R^2	R^3	5 R^4,	yield(%),	mp(°C)
4a,Me	1a,Me,	Me	5a,Me,	67,	74-5
	1b,Me,	n-C_3H_7	5b, H,	42,	oil
	1c, H,	n-C_3H_7	5c, H,	25,	oil
	1d, H,	Ph	5d,Ph,	37,	oil
	1e,Me,	Ph	5e,Ph,	40,	oil
4b, H	1d, H,	Ph	5f,Ph,	32,	127-30
	1e,Me,	Ph	5g,Ph,	41,	137-8

On the contrary, irradiation of 4a and 2-methyl-1-pentene 1b in acetonitrile gave a product 5b, probably via the formation of adduct followed by successive Type II cleavage reaction of the initial adduct.[2,5] Similarly, irradiation of 4a and 1-pentene 1c gave the Type II cleavage product 5c.[5] In the latter two cases, we could not obtain the primary photo-adduct.

When styrene 1d was employed as an olefin in the above reaction, the corresponding product 5d was obtained together with other unidentified minor products. 5d: oil; ^{1}H NMR (CDCl$_3$) δ 3.06 (s, 3H), 3.6-4.3 (m, 3H), 7.0-8.1 (m, 9H); IR (oil) 1688, 1643 cm^{-1}; MS (20 eV), m/e (rel intensity), 265 (M$^+$, 6), 222 (100), 104 (75). The alcohol 6b, was obtained by the reduction of 5d by sodium borohydride, mp 176-8 °C; ^{1}H NMR (CDCl$_3$) δ 3.24 (s, 3H), 3.1-5 (m, 2H), 3.60 (dd, J=13, 15 Hz, 1H), 3.94 (m, 1H), 4.84 (d, J=8 Hz, 1H), 7.0-8.1 (m, 9H); IR (KBr) 3280, 1621 cm^{-1}; MS (20 eV), m/e (rel intensity), 267 (M$^+$, 20), 84 (72), 49 (100). Other examples of the intermolecular photo-addition reactions are shown in a table.

In the photochemical reaction of N-alkenylsuccinimides, N-2-alkenylsuccinimides gave intramolecularly cyclized oxetanes,[1] whereas N-3-butenylsuccinimide 7a and N-4-pentenylsuccinimide 7b afforded only hydrogen abstraction products.[6] On the contrary, the photolysis of N-alkenylphthalimides 8a and 8b in acetonitrile gave 9a and 9b resulted from intramolecular skeltal reorganization via N-C bond scission and cyclization. That is, irradiation of 8a (0.1 M) in acetonitrile



8a, n=3
8b, n=4

9a, n=3 (92%)
9b, n=4 (32%)

11 (25%)

10

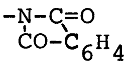
9c

9d

12

gave a product 9a in a high yield (92%). 9a: mp 129.5-130.5 °C; ^1H NMR (CCl_4) δ 1.6-2.5 (m, 4H), 2.72 (dd, J=3, 18 Hz, 1H), 2.98 (dd, J=12, 18 Hz, 1H), 3.6-8 (m, 2H), 4.18 (m, 1H), 7.4-8.0 (m, 4H); IR (KBr) 1675, 1625 cm^{-1}; MS (20 eV), m/e (rel intensity), 215 (M^+, 95), 146 (100). By treating with sodium borohydride, 9a gave an alcohol 10 (70%): mp 151-3 °C; ^1H NMR ($CDCl_3$) δ 1.5-2.5 (m, 6H), 3.2-3.7 (m, 3H), 3.92 (dd, J=8, 10 Hz, 1H), 4.48 (s, 1H, OH), 7.2-7.8 (m, 4H); IR (KBr) 3320, 1619 cm^{-1}; MS (20 eV), m/e (rel intensity), 217 (M^+, 51), 199 (34), 70 (100). Likewise, the photolysis of 8b in acetonitrile gave 9b (32%), mp 126-8 °C, accompanied by 11 (25%), a product resulted from the two-fold Type II reactions (cyclization and elimination).[2)] Irradiation of N-(2-vinyloxyethyl)phthalimide 8c or N-allyloxymethylphthalimide 8d, oxa derivatives of 8a, afforded similarly 9c (62%, mp 100-1 °C) or 9d (15%, mp 124-5.5 °C), respectively. However, the major product in the latter reaction was δ-hydrogen abstraction product 12 (60%).

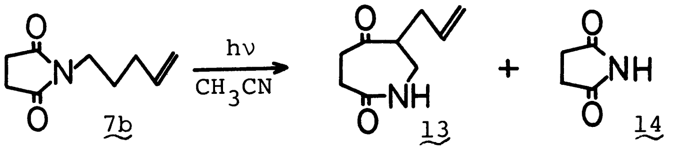
In the observed difference between the photo-reaction of phthalimides and of succinimides, the behavior of the former is novel in the widely known organic photochemistry, although that of the latter resembles to those of normal carbonyl compounds (having $n\pi^*$ excited states). Recently, P. H. Mazzocchi et al. have reported on the photolysis of N-methylphthalimide and dienes.[5)] However, we will emphasize herewith the wide generality of this type of reaction in the photochemical reaction of phthalimides not only with dienes but with various simple olefins. We will further point out the special preference for the N-alkenyl δ,ε double bond (counted from N atom) in the photolysis of N-alkenylphthalimides. On the photolysis of simple carbonyl compounds the most favorable double bond for intramolecular oxetane formation is at γ,δ-position counted from the carbonyl carbon. However, in the photochemical reactions of N-alkenylphthalimides the presence of N-alkenyl δ,ε double bond is extremely preferable for the clean and fast intramolecular cyclization, resulting in the formation of 9. Otherwise, the reaction is

slow and dirty.[7)] This is implying the unique behavior of the photo-excited phthalimide grouping, 
$-\underset{\mathrm{CO-C_6H_4}}{\mathrm{N-C{=}O}}$
, to the olefinic double bonds.

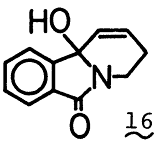
The scope and the limitation as well as the mechanism of these reactions are under investigation.

References and Notes

1) K. Maruyama and Y. Kubo, J. Org. Chem., 42, 3215 (1977).
2) (a) Y. Kanaoka, Yuki Gosei Kagaku Kyokai Shi, 33, 949 (1975) and papers cited therein; (b) Y. Kanaoka and Y. Hatanaka, J. Org. Chem., 41, 400 (1976).
3) Photolysis of an acetonitrile solution of N-methylsuccinimide 2 (0.4 M) and 2-methylpropene 1a (1 M) with a 120-W low-pressure Hg-lamp gave oxetane 3 (90 %). 3: oil; ^{1}H NMR (CCl_4) δ 1.20 (s, 3H), 1.36 (s, 3H), 1.6-2.6 (m, 4H), 2.98 (s, 3H), 3.94 (d, J=5 Hz, 1H), 4.22 (d, J=5 Hz, 1H); IR (oil) 1700, 963 cm^{-1}; MS (20 eV), m/e (rel intensity), 169 (M^+, 5), 139 ($M^+-CH_2=O$, 100), 124 (64).
4) An acetonitrile solution containing N-methylphthalimide 4a (0.03 M) and 2-methylpropene 1a (0.1 M) was irradiated with a 300-W high-pressure Hg-lamp for 8h. The yield was based on the consumed imide 4a. The photochemical reaction of phthalimides with olefins is profoundly dependent on solvents used. When we used a protic solvent, the addition products were quite different from those described in this letter. We will report on it elsewhere in near future.
5) P. H. Mazzocchi, M. J. Bowen, and N. K. Narain, J. Am. Chem. Soc., 99, 7063 (1977).
6) Irradiation of N-4-pentenylsuccinimide 7b (0.1 M) in acetonitrile gave 13 (78%) together with a trace of succinimide 14. 13: mp 100.5-102.0 °C; ^{1}H NMR



($CDCl_3$) δ 2.0-9 (m, 7H), 3.0-6 (m, 2H, these signals changed to two dd, 3.20 J=8, 16 Hz, 3.44 J=12, 16 Hz, by shaking with D_2O), 4.9-5.3 (m, 2H), 5.4-6.0 (m, 1H), 6.84 (br s, 1H, NH); IR (KBr) 4220, 1700, 1666 cm^{-1}; MS (20 eV), m/e (rel intensity), 167 (M^+, 32), 138 (83), 96 (100). The formation of 13 was rationalized by taking account of Type II cyclization followed by rearrangement.[2)] Similarly, irradiation of N-3-butenylsuccinimide 7a gave 6-vinylperhydroazepine-2,5-dione 15 (67%), mp 107-9.5 °C, and succinimide 14 (8%).
7) Photo-reactions of N-allylphthalimide 8e and N-3-butenylphthalimide 8f in acetonitrile were slow compared with that of 8a. On the prolonged irradiation 8e gave N-1-propenylphthalimide (10%) and phthalimide 4b (25%), and 8f similarly gave 16 (27%).[8)]



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8) M. Machida, K. Oda, and Y. Kanaoka, private communication.

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