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PHOTO-DEAROMATIZATION OF N-METHYLPHTHALIMIDES: AN EXAMPLE OF NUCLEOPHILIC AROMATIC PHOTOADDITION OF ALCOHOL[1,2]

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Abstract—Dearomatization of N-methylphthalimide and its 3- and 4-methyl derivatives occurs upon irradiation of alcohol solutions. The X-ray crystal structure analysis of the product revealed the complete structure of a multi-substituted cyclohexene system. No evidence for formation of the photo-enol in the phthalimide system has been found during the study of the possible course of the photodearomatization. Unexpected deuterium incorporation at the N-methyl group is also reported.

One typical approach to overcome the resonance energy of benzenoids and to dearomatize them is by electronic excitation, a transformation for which there exist many precedents.[3] In this way various nucleophiles such as amine,[4] cyanide[5] and hydride[6] have been observed to add photochemically to benzenoids. We have briefly reported an unusual dearomatization of N,3-dimethylphthalimide on UV irradiation in alcohol,[7] and full details are now presented in this paper.

RESULTS AND DISCUSSION

Irradiation of a solution of N,3-dimethylphthalimide **1** in methanol gave, besides two isomeric reduction products **2** and addition products **3**, consistent with the general photochemical pattern of phthalimides,[8,9] a dearomatized compound **4a**, which was apparently formed by the addition of methanol to the benzene moiety followed by reduction. Similarly, irradiation of **1** in ethanol and isopropanol led to the products **4b** and **c**, while no detectable amount of the product was formed in t-butanol. Yields of the dearomatized products **4** increase in the order of the reactivity of alcohols in the α-hydrogen abstraction. Irradiation of N,4-dimethyl- **5** and N-methylphthalimide **6** in isopropanol also gave the dearomatized products **7** and **8**, respectively. The results are summarized in Table 1.

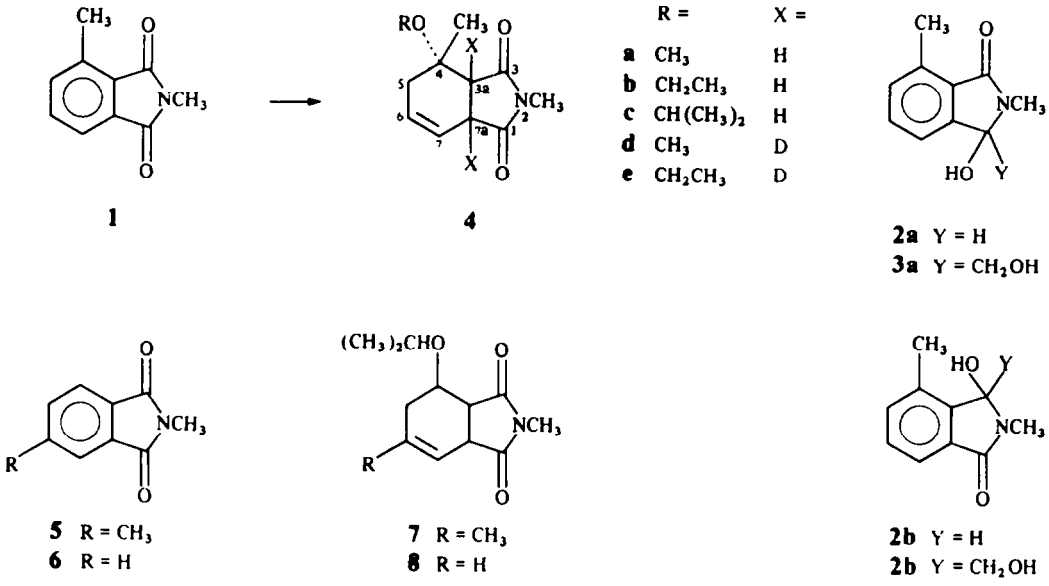
The complete structure and the stereochemical configuration at the three new asymmetric centres of **4b** were established by X-ray analysis. Fractional coordinates and thermal factors for the C, N and O atoms are listed in Table 2,† bond lengths and angles are shown in Fig. 1† and the configuration and the conformation for one arbitrarily chosen antipode is shown in Fig. 2.

The crystal structure analysis confirmed the *cis* ring-junction, and established that the CH_3 group on C-4 is on the same side as the *cis* hydrogen atoms on C-3a and C-7a. The name of the compound is 3a*β*,4,5,7a*β*-tetrahydro-2,4*β*-dimethyl-4*α*-ethoxy-1H-isoindole-1,3(2H)-dione. The conformation of the molecule has the following features: an equatorial CH_3 and axial O-ethyl on C-4; O-ethyl *trans* to C-3a; a six-membered ring with five atoms lying in a plane (deviations of ±0.02 Å) and C-4 bent out of that plane by 0.70 Å; a slightly twisted five-membered ring essentially co-planar with the two carbonyl oxygens and the N-methyl carbon (C-3a and C-7a have by far the largest deviations from the plane, ±0.21 Å); and a dihedral angle of 135° between the planes of the two rings.

Table 1. Yields of the dearomatized products

Imide	Solvent	Time (h)		Yield (%)
1	MeOH	8	**4a**	14
	EtOH	1	**4b**	27
	iso-PrOH	1	**4c**	31
	t-BuOH	8		—
5	iso-PrOH	3.5	**7**	17
6	iso-PrOH	0.75	**8**	13

† Following numbering of **4b** is adopted in Table 2 and Fig. 1; 3a,6,7,7a-tetrahydro-2,7-dimethyl-7-ethoxy-1H-isoindole-1,3(2H)-dione.



Scheme 1.

In 1961 Yang and Rivas found that 2-methyl- and 2-benzyl-benzophenones **9** on irradiation form the dienol intermediates **10**, sufficiently long lived to allow chemical trapping, either by cycloaddition or by incorporation of deuterium into the *ortho*-alkyl substituents (Scheme 2).[10] Now the photoenolization process is a general phenomenon which occurs with a wide variety of substrates. Similarly it was anticipated that the behavior of 3-methylphthalimide such as **1** would differ from that of the benzene-unsubstituted imides in that the presence of the 3-methyl group would allow intramolecular hydrogen abstraction to compete with other reactions. For the abstraction, the excited imide carbonyl would lead to the diradical **11**, which would collapse to ground state species forming a dienol **12**. Therefore, one attractive explanation for the formation of **4** from **1** could be addition of alcohol to the photo-generated enol **12**. To test this possibility, reduction of **1** under thermal conditions was first examined. When **1** was reduced with sodium borohydride, the isomer ratio of the reduction products **2a** and **b** was approximately equal to the value (3 : 2) observed in the above photoreaction. So there seems to be no significant intramolecular photoenolization in competition with intermolecular photoreduction.[10,11]

To confirm this, photolysis of **1** in CH_3OD or CH_3CH_2OD was examined. Based on PMR spectrometry, the recovered imide **1** incorporated no detectable amount of deuterium at the aromatic methyl group. In contrast to this, the products **4d** and **e** were found to contain significant amounts of deuterium at the ring fused carbons: **4d** and **e** contained nearly quantitative and *ca* 60% deuterium, at the 3a position and at the 7a position, respectively. The results are listed in Table 3.

Although intramolecular hydrogen abstraction requires a *syn*-conformation between the carbonyl group and the γ-hydrogen source, collapse to the ground state dienol would allow rotation so that the two isomers, the (*E*)-dienol **13** and the (*Z*)-dienol **14**, might form. However, in simple ketone systems, strong

Table 2. Fractional coordinates and thermal factors of **4b**

Atom	x	y	z	B_{eq}
C1	0.7004	0.4659	0.0295	5.0
O1	0.7666	0.5096	0.1329	6.5
N2	0.6702	0.4585	−0.1690	5.0
C3	0.5810	0.4068	−0.2582	5.0
O3	0.5560	0.3882	−0.4221	6.7
C3A	0.5166	0.3804	−0.1161	5.2
C4	0.5136	0.3149	−0.1134	5.9
C5	0.6139	0.2854	0.0600	6.7
C6	0.7459	0.3137	0.2631	6.7
C7	0.8186	0.3729	0.2358	5.1
O7	0.9141	0.3685	0.1164	4.6
C7A	0.6430	0.4104	0.0941	4.9
C8	0.9446	0.4017	0.4453	7.1
C9	1.0689	0.3291	0.1842	6.3
C10	1.1385	0.3314	0.0338	7.6
C11	0.7421	0.4994	−0.2650	6.9

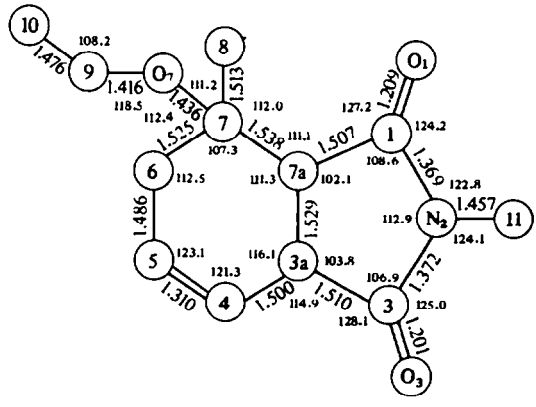


Fig. 1. Bond lengths and angles of **4b**. Additional values not shown in the drawing are: ∠ O(7)C(7)C(7a) = 102.6° and ∠ C(6)C(7)C(8) = 111.0°. Standard deviations, based on the least-squares refinement, are near 0.006 Å for the bond lengths and near 0.3° for the bond angles.

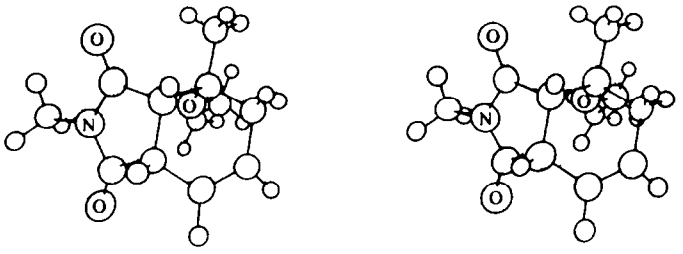
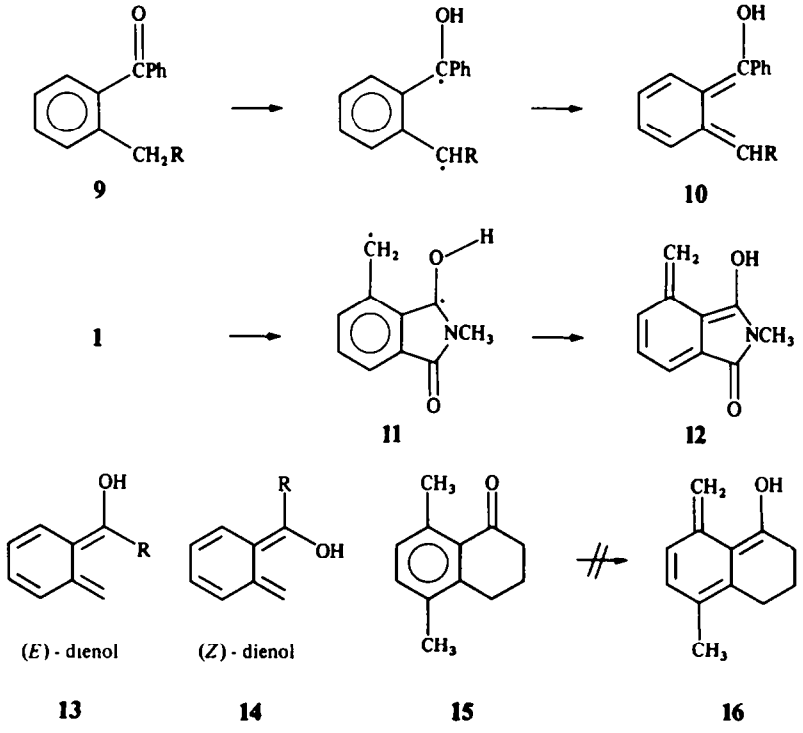


Fig. 2. Stereodrawing of an arbitrarily chosen optical antipode of **4b**. The drawing was made by a computer program using the experimentally determined coordinates listed in Table 2.

evidence has been obtained only for the formation of (*E*)-dienols **13**, and the corresponding (*Z*)-isomers **14** appear to be forbidden.[11] For example, no evidence for formation of the photo-enol was found in a tetralone system **15**, for which formation of (*E*)-dienol is restricted.[12] In a similar manner, in the bicyclic system like the phthalimide **1**, ring strain dictates that only the (*Z*)-dienol **12** should be possible, and the desirable (*E*)-dienol is no longer capable of existence. Thus the imide carbonyl of **1** may be unable to photoenolize.

Involvement of an electron transfer step has been reported for the addition of amines[4] and ethers[13] to benzene. The phthalimide group can be an electron acceptor, and in fact proposed to play such a role in photolyses of certain donor–acceptor pair systems.[9,14] Therefore, it is likely that electron-transfer from solvent alcohols to an excited phthalimide, leading to the intermediate **18**, is mechanistically important (Scheme 3). Coupling of the radical ion pair affords enol **19** which will readily lead to its keto-form **20**. A preferred addition of alkoxy group to the C-4 position rather than C-7 might be explained by a radical stabilization effect of the methyl substituent for the formation of **4**. On the other hand, a steric hindrance of the methyl on the C-6 position would prevent the addition at C-7 for the formation of **7**. Another possible intermediate **21** which differed in the addition site would be less favored than a fully conjugated dienone **20**. Photoreduction of the dienone **20** by hydrogen abstraction from the α-H of a solvent alcohol gives rise to **22**, consistent with the fact that no dearomatized product was found upon irradiation in t-butanol. At the C-5 position of the products (**4d** and **e**), no deuterium was incorporated. This result also supports the above interpretation of the photoreduction. Reversion of the enol **22** to the keto-form results in partial incorporation of the solvent deuterium at the C-7a position of **4d** and **e**.

During the course of the study of deuterium incorporation, it was observed that appreciable amounts of deuterium were located at the N-methyl carbon of the recovered imide **1** (Table 3). In an attempt to elucidate the mechanism of this unexpected N-



Scheme 2.

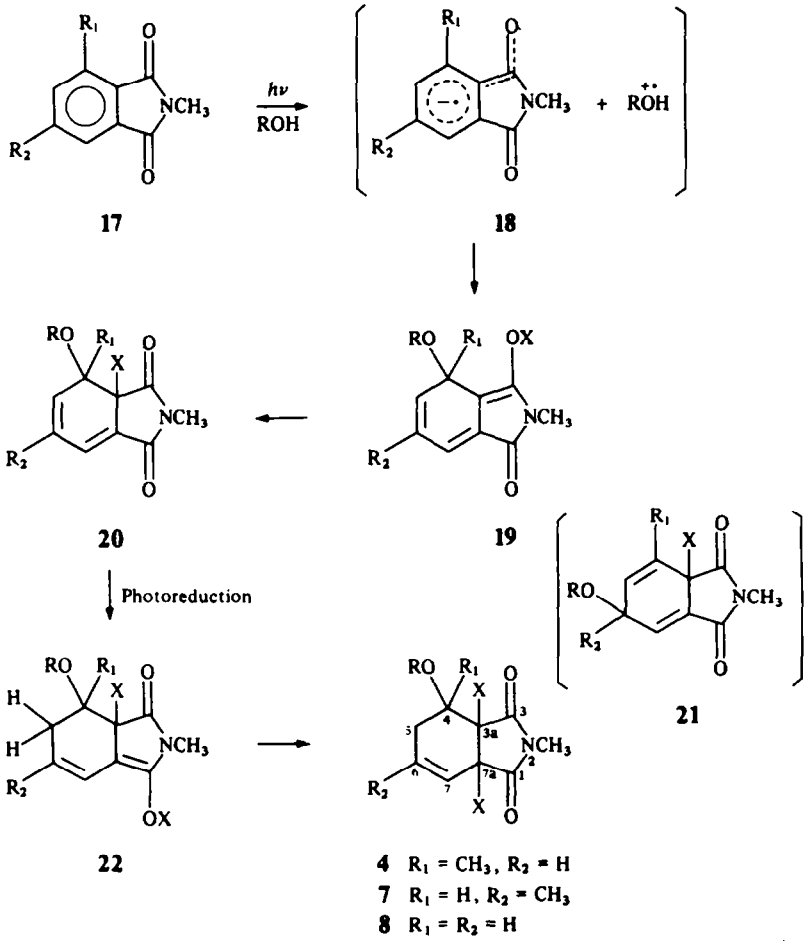
Table 3. Irradiation of 1 in deuterated alcohols

Solvent	Time (h)	4 Yield (%)	Yield (%)	1 (recovered) C—CH_3/arom-H[a]	NCH_3/arom-H[a]
(before irradiation)		—	—	0.89	0.93
MeOD	50	d 3	63	0.89	0.68
EtOD	8	e 5	34	0.88	0.83

[a] Ratio of integrals of PMR signals.

methyl deuteration, irradiations of **5**, **6** and N,N-dimethylbenzamide in CH_3OD were further examined. Mass spectrometric analyses of the recovered samples were performed by comparison of signal intensities of $M^+ + 1$, $M^+ + 2$, and $M^+ + 3$ with that of M^+. The results are listed in Table 4.

All the imides were found to contain deuterium, while the amide was not. No substantial incorporation took place when the same solutions were refluxed without irradiation, indicative of involvement of the excited states in this process. In the presence of appropriate acceptors, photochemical deprotonation of α-hydrogen of amines may occur via the electron transfer step.[15] Although the details of the mechanism of the above N-methyl deuteration are yet unknown, the results implicate that the phthalimide skeleton, as a good electron acceptor, is on irradiation capable of undergoing photochemical H–D exchange at the N-methyl group probably by way of a radical cation ($^+\dot{N}$—CH_3). Photoinduced hydrogen isotope exchange of aromatic compounds in the presence of acid[16,17] and amine[18] are known. Hydrogens attached on the saturated carbon are also exchangeable by photolysis with metal catalysts such as organometallic compounds[19] and semiconductors.[20] An advantage of the photodeuteration of phthalimides is in that this is a rather mild and simple hydrogen isotope exchange process without catalysts under neutral conditions. Since a phthaloyl group is one of the common and easily removable protecting groups of an amino



Scheme 3.

Table 4. Mass spectrometric analyses of deuterium incorporation

Compound	Solvent	Conditions[a]	Time (h)	M^{+b}	$M^{+}+1^{b}$	$M^{+}+2^{b}$	$M^{+}+3^{b}$
1	(before irradiation)		—	100.0	11.7	1.1	<0.1
	MeOD	ir	50	100.0	40.5	7.2	0.9
	EtOD	ir	8	100.0	22.1	2.7	0.3
	MeOD	rf	50	100.0	11.7	1.2	<0.1
6	(before irradiation)		—	100.0	10.7	0.9	<0.1
	MeOD	ir	50	100.0	36.7	6.4	0.7
	MeOD	rf	50	100.0	10.7	1.0	<0.1
5	(before irradiation)	—	100.0	11.6	1.1	<0.1	
	MeOD	ir	50	100.0	30.3	4.9	0.5
	MeOD	rf	50	100.0	11.7	1.1	<0.1
N,N-dimethylbenzamide	(before irradiation)	—	100.0	10.0	0.7	<0.1	
	MeOD	ir	50	100.0	10.2	0.7	<0.1
	MeOD	rf	50	100.0	10.0	0.7	<0.1

[a] ir, irradiated; rf, refluxed.
[b] Relative intensities (%) for M^{+} as standard.

function, this photodeuteration would be refined to a method to prepare "labeled" amines.

A number of photochemical aromatic substitutions have been reported including nucleophilic substitution with alkoxy groups.[16] Photoaddition of alcohols to double bonds in olefin[21] and enone[22] is also well known. However, nucleophilic photoaddition of alcohols to benzenoids has not been reported. Phthalimides **1** belong to a multi-substituted benzenoid, and it is worth noting that in such a system as **1**, the addition of alcohol to a benzene moiety effectively competes with the usual addition to the imide carbonyl.[8,9] Thus multi-substituted benzenoid systems will be a family of substrates for a variety of photoaddition and photosubstitution reactions.

EXPERIMENTAL

M.ps and b.ps are uncorrected. IR spectra were recorded on a JASCO IRA-1 spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were obtained from a JEOL JNM-FX100 spectrometer. Low- and high-resolution mass spectra were measured on a JEOL JMS-D300 spectrometer. The light source for irradiation experiments was a 500 W Eikosha EHB-WI mercury lamp contained in a water-cooled quartz immersion well.

Silica gel used for preparative thin layer chromatography was Merck Kieselgel 60 GF254. Commercial grade solvents were used without further purification. Deuterated alcohols (99%) were purchased from Aldrich Chemical Co., Tokyo N-Methylphthalimides were prepared according to the literature procedures.[23,24]

Preparative irradiation. Solutions of imides (3 mmol) in alcohols (300 ml) were irradiated through a Pyrex filter in an immersion apparatus under continuous bubbling of N_2 at room temp. Products obtained on removal of the solvent were purified by silica gel preparative thin layer chromatography (benzene–ethanol 10:1). Except the irradiation of **1** in MeOH, photoreduction **2** and photoaddition **3** products were obtained as complex mixtures, and were not isolated.

Photoreduction products **2a** *and* **b**. One isomer (72 mg, 14%), colorless needles m.p. 108–109° (ether); IR (nujol) 3300, 1670 cm^{-1}; ^{1}H-NMR (DMSO) δ 2.57 (3H, s), 2.91 (3H, s), 6.02 (2H, AB system, J = 8 Hz), 7.1–7.6 (3H, m); mass spectrum, *m/e* 177 (M^{+}). (Found: C, 67.82; H, 6.35; N, 7.94. Calc for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.91%.) The other (44 mg, 8%), colorless prisms m.p. 179–181° (ethyl acetate); IR (nujol) 300, 1675 cm^{-1}; ^{1}H-NMR (DMSO) δ 240 (3H, s), 2.93 (3H, s), 6.07 (2H, AB system, J = 9 Hz), 7.3–7.5 (3H, m); mass spectrum, *m/e* 177 (M^{+}). (Found: C, 67.94; H, 6.28; N, 8.03.)

Photoaddition products **3a** *and* **b**. One isomer (109 mg, 18%), colorless needles m.p. 129–131° (MeOH–ether); IR (nujol) 3400, 3320, 1660 cm^{-1}; ^{1}H-NMR (DMSO) δ 2.58 (3H, s), 2.81 (3H, s), 3.6–3.7 (2H, m), 4.76 (1H, t, J = 6 Hz), 6.24 (1H, s), 7.2–7.5 (3H, m); mass spectrum, *m/e* 189 ($M^{+}-18$). (Found: C, 63.75; H, 6.28; N, 6.90. Calc for $C_{11}H_{13}NO_3$: C, 63.75; H, 6.32; N, 6.76%.) The other (76 mg, 12%), colorless needles m.p. 172–174° (MeOH–ether); IR (nujol) 3400, 3300, 1660 cm^{-1}; ^{1}H-NMR (DMSO) δ 2.46 (3H, s), 2.82 (3H, s), 3.6–4.0 (2H, m), 4.78 (1H, t, J = 6 Hz), 6.37 (1H, s), 7.3–7.4 (3H, m); mass spectrum, *m/e* 189 ($M^{+}-18$). (Found: C, 63.67; H, 6.29; N, 6.93.)

3a,4,5,7a - *Tetrahydro* - 2,4 - *dimethyl* - 4 - *methoxy* - 1H - *isoindole* - 1,3(2H) - *dione* (**4a**, 90 mg, 14%), colorless needles m.p. 119–120° (n-hexane); IR (nujol) 1760, 1700 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.47 (3H, s), 1.8–2.5 (2H, m), 2.87 (1H, d, J = 8.5 Hz), 2.96 (6H, s), 3.2–3.5 (1H, m), 5.6–5.9 (1H, m), 6.0–6.2 (1H, m); ^{13}C-NMR ($CDCl_3$) δ 21.4 (q), 24.4 (q), 31.6 (t), 41.0 (d), 48.9 (q), 49.5 (d), 72.4 (s), 121.9 (d), 123.9 (d), 176.7 (s), 177.1 (s); mass spectrum, *m/e* 209 (M^{+}). (Found: C, 63.08; H, 7.20; N, 6.78. Calc for $C_{11}H_{15}NO_3$: C, 63.14; H, 7.23; N, 6.69%.)

3a,4,4,7a - *Tetrahydro* - 2,4 - *dimethyl* - 4 - *ethoxy* - 1H - *isoindole* - 1,3(2H) - *dione* (**4b**, 180 mg, 27%), colorless prisms m.p. 103–104° (n-hexane); IR (nujol) 1770, 1710 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.93 (3H, t, J = 7 Hz), 1.47 (3H, s), 1.8–2.5 (2H, m), 2.83 (1H, d, J = 8 Hz), 2.94 (3H, s), 3.17 (2H, q, J = 7 Hz), 3.2–3.4 (1H, m), 5.6–5.8 (1H, m), 5.9–6.2 (1H, m); ^{13}C-NMR ($CDCl_3$) δ 15.4 (q), 21.9 (q), 24.2 (q), 32.3 (t), 41.1 (d), 49.8 (d), 56.1 (t), 72.2 (s), 121.8 (d), 124.0 (d), 176.9 (s), 177.2 (s); mass spectrum, *m/e* 223 (M^{+}). (Found: C, 64.22; H, 7.73; N, 6.20. Calc for $C_{12}H_{17}NO_3$: C, 64.55; H, 7.68; N, 6.27%.)

3a,4,5,7a - *Tetrahydro* - 2,4 - *dimethyl* - 4 - *isopropoxy* - 1H - *isoindole* - 1,3(2H) - *dione* (**4c**, 219 mg, 31%), colorless prisms m.p. 65–66° (n-pentane); IR (nujol) 1770, 1700 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.88 (3H, d, J = 6 Hz), 0.94 (3H, d, J = 6 Hz), 1.50 (3H, s), 1.8–2.5 (2H, m), 2.78 (1H, d, J = 8 Hz), 2.93 (3H, s), 3.1–3.4 (1H, m), 3.61 (1H, septet, J = 6 Hz), 5.6–5.8 (1H, m), 5.9–6.2 (1H, m); ^{13}C-NMR ($CDCl_3$) δ 23.4 (q), 23.9 (q), 24.1 (q), 24.7 (q), 33.1 (t), 41.0 (d), 50.2 (d), 63.9 (d), 72.5 (s), 121.1 (d), 124.8 (d), 177.0 (s), 177.2 (s); mass spectrum, *m/e* 237 (M^{+}). (Found: C, 65.99; H, 8.16; N, 6.02. Calc for $C_{13}H_{19}NO_3$: C, 65.80; H, 8.07; N, 5.90%.)

3a,4,5,7a - *Tetrahydro* - 2,6 - *dimethyl* - 4 - *isopropoxy* - 1H - *isoindole* - 1,3(2H) - *dione* (**7**, 120 mg, 17%), colorless oil b.p.$_1$ 100° (bath temp); IR (neat) 1770, 1700 cm^{-1}; ^{1}H-NMR

($CDCl_3$) δ 0.96 (3H, d, J = 6 Hz), 1.00 (3H, d, J = 6 Hz), 1.76 (3H, m), 2.14 (2H, m), 2.94 (3H, s), 2.99 (1H, dd), 3.1–3.4 (1H, m), 3.51 (1H, septet, J = 6 Hz), 4.15 (1H, m), 5.76 (1H, m); ^{13}C-NMR ($CDCl_3$) δ 22.0 (q), 23.0 (q), 24.1 (q), 24.2 (q), 33.6 (t), 40.0 (d), 44.1 (d), 69.8 (d), 70.8 (d), 114.1 (d), 132.9 (s), 177.5 (s), 177.6 (s); mass spectrum, *m/e* calc for $C_{13}H_{19}NO_3$: 237.1365; found: 237.1348.

3a,4,5,7a - *Tetrahydro* - 4 - *isopropoxy* - 2 - *methyl* - 1H - *isoindole* - 1,3(2H) - *dione* (**8**, 88 mg, 13%), colorless needles m.p. 66–67° (n-pentane); IR (nujol) 1770, 1690 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.97 (3H, d, J = 6 Hz), 1.00 (3H, d, J = 6 Hz), 2.0–2.6 (2H, m), 2.95 (3H, s), 3.07 (1H, dd), 3.2–3.4 (1H, m), 3.53 (1H, septet, J = 6 Hz), 4.16 (1H, m), 5.7–5.9 (1H, m), 6.0–6.2 (1H, m); ^{13}C-NMR ($CDCl_3$) δ 21.9 (q), 22.9 (q), 24.3 (q), 28.4 (t), 39.5 (d), 44.6 (d), 68.9 (d), 70.6 (d), 121.0 (d), 125.1 (d), 177.0 (s), 177.6 (s); mass spectrum, *m/e* 223 (M^+). (Found: C, 64.69; H, 7.77; N, 6.15. Calc for $C_{12}H_{17}NO_3$: C, 64.55; H, 7.68; N, 6.27%.)

Irradiation in deuterated alcohols. A soln of **1** (10 mM) in CH_3OD or CH_3CH_2OD was introduced to a Pyrex tube (12 mm i.d.), and degassed by five freeze–pump–thaw cycles to a reduced pressure of less than 10^{-3} Torr. Tubes were placed approximately 1 cm from the immersion well and irradiated at room temp. Characteristic features on ^{1}H-NMR spectra of **4d** and **e** were as follows; doublets at 2.87 (for **4a**) and 2.83 (for **4b**) disappeared; the intensities of multiplet at *ca* 3.3 were decreased for about 40% of those observed for **4a** and **b**; other signals were almost intact. The results are listed in Tables 3 and 4.

Irradiations of **5**, **6** and N,N-dimethylbenzamide in CH_3OD were performed in a similar manner for 50 h. Yields of recovery of **5**, **6** and the amide were 65%, 69% and quantitative, respectively. The results are listed in Table 4.

X-Ray crystallography. Compound **4b** crystallizes in space group $P2_1/c$; hence it is a racemate. The cell parameters are; a = 8.088(3) Å, b = 22.855(15) Å, c = 7.381(3) Å, β = 119.9(1)°, V = 1182.7 Å^3 and d_{calc} = 1.25 g cm^{-3} for a molecular weight of 223.28 for $C_{12}H_{17}NO_3$. Nickel-filtered copper radiation (λ = 1.5418 Å) was used to measure 1944 independent reflections on an automatic four-circle diffractometer ($2\theta_{max}$ = 126°). The structure was obtained with the symbolic addition procedure for determining phases. Least-squares refinement of 1714 data with (F) > 3σ resulted in an agreement factor R_F = 9.0%.

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