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Photoreactions of 3,4,5,6-Tetrafluoro-*N*-methylphthalimide with Alkenes. Effect of Fluoro Substituents on Photoreaction Pathway

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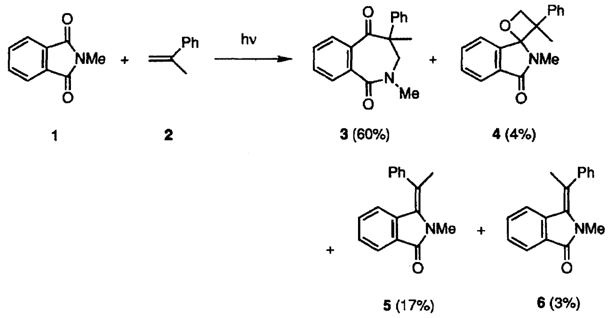
Photoreactions of 3,4,5,6-tetrafluoro-*N*-methylphthalimide (**7**) with styrene (**8**), α-methylstyrene (**2**), and 1,1-diphenylethylene (**11**) have been investigated in order to clarify the effect of fluoro substituents on the reaction pathway. The irradiation of **7** with **2**, **8**, and **11** in benzene under N_2 gave oxetanes as exclusive products. The irradiation of **7** with **11** under O_2 afforded benzophenone (**13**) together with the oxetane. The methanol-incorporated addition of **2** and **8** to **7** proceeded in photoreactions of **7** with **2** and **8** in methanol. A consideration of the energy levels of the excited triplet states of **7** and the alkenes, the quenching of the fluorescence of **7** by **8**, and the concentration effects of the alkenes indicate that all of the reactions occur from the singlet excited state of **7**. The difference between the exclusive oxetane formation of **7** and the preferred insertion of alkenes into the C–N bond of phthalimides is discussed regarding the nature of the singlet excited states of the imides. The methanol-incorporated addition and formation of **13** are rationalized in terms of mechanisms involving electron-transfer. The calculated ΔG_{et} values associated with electron-transfer support the electron-transfer process.

The photochemistry of imides has received much attention during the last two decades.[1)] Concerning the photochemistry of imides with alkenes, oxetane formation was found to be the most typical process in photolyses of the alicyclic imides with alkenes, illustrating its normal $n\pi^*$ carbonyl photoreactivity.[2)] On the other hand, photoreactions of phthalimides with alkenes are quite different from those of alicyclic imides. The most typical reactions of phthalimides with alkenes were found to be the insertion of alkenes into the C–N bond of the imide function[3)] and an alcohol-incorporated addition of the alkenes to the imides via an initial electron transfer from the alkenes to the singlet excited state of the imides.[4)] A small number of examples of ox etane formation of phthalimides have been reported so far.[4h,5)] For example, the photoreaction of *N*-methylphthalimide (**1**) and α-methylstyrene (**2**) in acetonitrile has been reported to give oxetane **4** and its decomposition products, **5** and **6**, as minor products (Eq. 1).[5c)]



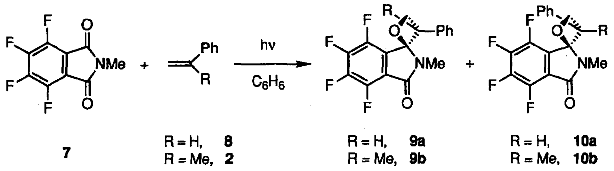
(1)

Our attention has been focused on the photoreactions of 3,4,5,6-tetrafluoro-*N*-methylphthalimide (**7**) with alkenes, since the introduction of fluorine atoms on the aromatic ring has been expected to change the photoreaction pathway through a variation of the energy and character of the excited states, thus offering some useful information for clarifying the complicated photochemistry of the phthalimides. Some investigations concerning the photoreactions of phthalimides with one and two substituents on the aromatic ring have already been reported.[6)]

This paper describes the photoreactions of **7** in the presence of alkenes with phenyl substituent groups. The exclusive photoreaction of **7** with the alkenes in benzene has been found to be oxetane formation; no insertion of the alkenes into the C–N bond of the imide function has been observed, in contrast to the photoreactions of **1**. The methanol-incorporated addition of alkenes to **7** has proceeded in a manner similar to that of **1**.

Results and Discussion

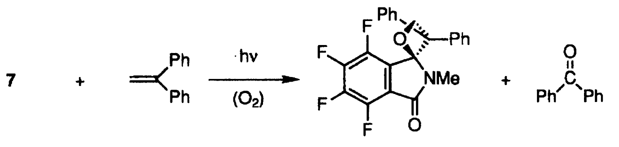
The irradiation of a benzene solution of **7** (1.7 mM, 1 M=1 mol dm^{-3}) and styrene (**8**) (170 mM) by light that was >320 nm (uranium filter) under N_2 resulted in the formation of oxetanes **9a** (40%) and **10a** (36%) (Eq. 2). The irradiation of **7** (1.7 mM) with **2** (150 mM) in benzene under N_2 also gave oxetanes **9b** (28%) and **10b** (38%). No insertion products of **2** into the C–N bond of the imide function of **7**, corresponding to **3**, and no decomposition products of **9b** and **10b**, corresponding to **5** and **6**, were observed, in contrast to the



(2)

photoreaction of **1** and **2** (Eq. 1).[5c)] The structures of **9a,b** and **10a,b** were deduced from the ^{1}H NMR and IR spectra. The stereochemistry of **9a,b** and **10a,b** is assigned mainly based on the high field shift of the NMe protons in **9a** and **9b** (δ=2.54 and 2.34), compared with those in **10a** and **10b** (δ=3.33 and 3.38), respectively, caused by an anisotropic shielding effect of the phenyl ring. Products **9a,b** and **10a,b** were photostable under the irradiation conditions, and the ratios of **9a**/**10a** and **9b**/**10b** were kept constant in the course of the reaction. The ratio of **9a**/**10a** also remained almost constant over the concentration region of 3 mM to 350 mM of **8**. The result of the concentration effect may indicate that **9a** and **10a** arise from the same excited state of **7**, since in the photoreactions of phthalimides and alkenes a marked concentration dependency on the yields of the products was reported when the products were generated from distinct excited states.[5d)]

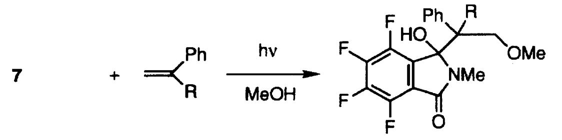
The irradiation of a benzene solution of **7** (1.7 mM) and 1,1-diphenylethylene (**11**) (35 mM) under N_2 also gave oxetane **12** (68%) (Eq. 3). On the other hand, irradiation under O_2 resulted in formation of benzophenone (**13**) together with **12**, as shown in Table 1. The Table shows that the formation of **13** is efficient in acetonitrile, a polar solvent, compared with that in benzene.



11 12 13

(3)

The irradiation of a methanol solution of **7** (1.7 mM) and **8** (170 mM) under N_2 resulted in the formation of a mixture of two diastereomers of the methanol-incorporated adduct **14a** (84%, ratio of the two diastereomers=1.1) (Eq. 4). The irradiation of **7** (1.7 mM) with **2** (150 mM) in methanol under N_2 also gave a mixture of two diastereomers of the methanol-incorporated adduct **14b** (90%, ratio of the two diastereomers=1.1). The structures of **14a,b** were supported by their spectral resemblance to analogous adducts obtained by photoreactions of **1** with **2** and **8** in methanol.[4h)] The products **14a,b** were also photostable under the irradiation conditions. The ratios of the two diastereomers were kept constant over the course of the reaction, as well as over the concentration region of 3 mM to 350 mM of **8**.



R=H, **8**
R= Me, **2**

R=H, **14a**
R= Me, **14b**

(4)

The irradiation of a methanol-benzene (vol/vol= 2/23) solution of **7** (1.7 mM) and **8** (170 mM) under N_2 was found to give the methanol-incorporated adducts **14a** (46%, ratio of the two diastereomers=1.1) as well as oxetanes **9a** (19%) and **10a** (18%) at the same time. The ratios of **14a**/(**9a**+**10a**) were almost constant during the course of the photoreaction, and remained almost constant over the concentration region of 3 mM to 350 mM of **8**. The result of the concentration effect may indicate that both the methanol-incorporated adducts **14a** and the oxetanes, **9a** and **10a**, arise from the same excited state of **7**.

To obtain information concerning the excited states of **7**, the spectroscopic properties of **7** were measured. The absorption spectrum of **7** in methanol showed strong bands at around 295 nm (ε 2000). Although **7** showed no fluorescence in aprotic solvents, such as benzene and acetonitrile, very weak fluorescence was observed in protic solvents, such as water and methanol (Table 2). The fluorescence behavior of **7** is similar to that of phthalimides, and the fluorescence spectra of **7** in protic solvents are almost identical with those of *N*-propylphthalimide.[7)] The fluorescence quantum yields of **7** are, however, remarkably small. The small fluorescence quantum yields of **7** may indicate the closer proximity of the first singlet excited state (S_1) in nπ^* character and the second singlet excited state (S_2) in

Table 1. Yields of Photoproducts **12** and **13** in the Photoreactions of 3,4,5,6-Tetrafluoro-*N*-methylphthalimide (**7**) with 1,1-Diphenylethylene (**11**) under O_2[a)]

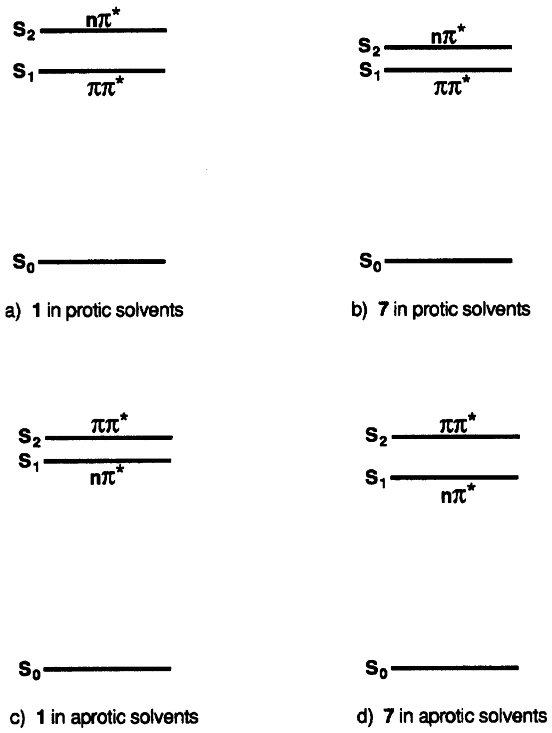
Solvent	Irradiation time/h	Yield/%		
		7[b)]	**12**[c)]	**13**[c)]
C_6H_6	12	85	10	78
	24	77	15	179
CH_3CN	12	91	3	232
	24	86	5	355

a) Reaction conditions: [**7**]=1.7 mM, [**11**]=35 mM, $h\nu$ (λ>340 nm), under O_2. b) Recovered yields based on used **7**. c) Yields based on used **7**.

Table 2. Fluorescence Spectral Properties of *N*-Propylphthalimide and 3,4,5,6-Tetrafluoro-*N*-methylphthalimide (**7**)[a)]

Imide	Solvent	$\lambda_{\max}$/nm	Φ
N-Propylphthalimide	H_2O	420[b)]	0.050[b)]
	MeOH	408[b)]	0.010[b)]
7	H_2O	420	0.001
	MeOH	410	0.002

a) Conditions: [**7**]=1.0×10^{-4} M, in air saturated solvents, at 25°C. b) Ref. 7.



a) **1** in protic solvents b) **7** in protic solvents

c) **1** in aprotic solvents d) **7** in aprotic solvents

Fig. 1. Estimated energy levels of *N*-methylphthalimide (**1**) and 3,4,5,6-tetrafluoro-*N*-methylphthalimide (**7**) in protic and aprotic solvents.

nπ* character of **7** in protic solvents, compared with that of **1**, as shown in Fig. 1. In aprotic solvents, the nonemitting nature of **7** indicates the S_1 in nπ* character. Furthermore, the energy differences between nπ*-S_1 and the ππ*-S_2 of **7** is expected to be larger than those of **1** in aprotic solvents. The energy of the S_1 of **7** in methanol estimated from the absorption and the fluorescence spectra was 87.7 kcal mol^{-1} (1 cal=4.184 J). On the other hand, strong phosphorescence bands of **7** were observed at λ_{max} 434 nm in EPA (ether isopentane alcohol) (1×10^{-4} M) at 77 K. The long lifetime (2.3 s) suggests that the lowest triplet state is ππ* in character. The energy of the triplet state (E_T) calculated from the 0-0 band of the phosphorescence (410 nm) was 69.7 kcal mol^{-1}. The lifetime and E_T (in EtOH, 77 K) of **1** have been reported to be 1.0 s and 68.5 kcal mol^{-1}, respectively.[8)]

There was no evidence from the absorption spectra for a preformed ground-state complex between **7** and alkenes **2**, **8**, and **11**. Since the fluorescence of **7** was quenched by **8** in methanol, the methanol-incorporated addition can be concluded to proceed from S_1 of **7**. The quenching occurred without varying the shape or wavelength of the maximum emission. Stern-Volmer plots of the quenching by **8** gave a straight line against the concentration of **8** up to 100 mM; the slope was 15 M^{-1}. The oxetane formation observed in benzene may also occur from S_1 of **7** (Scheme 1), since the concentration effect of **8** indicates that both methanol-incorporated addition and oxetane formation arise from the same excited state of **7**, and that alkenes **2**, **8**, and **11** have lower triplet energies, i.e., E_T (**2**)=61.7 kcal mol^{-1},[9)] than that of **7**.

The results obtained in this study clearly indicate that oxetane formation is a characteristic photoreaction of **7** in aprotic solvents in marked contrast to the photoreactions of **1**, in which the insertion of alkenes into the C–N bond of **1** predominates. This difference can be explained by the larger energy differences between the nπ*-S_1 and ππ*-S_2 of **7**, compared with those of **1** in aprotic solvents (Fig. 1). Thus, the nπ*-S_1 of **7** can interact weakly with the ππ*-S_2, compared with that of **1**, and S_1 of **7** may have a purer nπ* character compared with that of **1**. This nature of S_1 may be responsible for the exclusive oxetane formation of **7**.

The methanol-incorporated addition to give **14a,b** can be rationalized by an analogous mechanism involving an electron transfer from alkenes **2** and **8** to S_1 of **7** (Scheme 1), to that of the methanol-incorporated addition of alkenes to **1**.[4)] The electron-transfer mechanism may be strongly supported by the large negative free-energy changes (ΔG_{et}) associated with electron transfer from alkenes **2**, **8**, and **11** to S_1 of **7**, calculated roughly by using[10)]

$$\Delta G_{et} = 23.06[E(D/D^+) - E(A^-/A)] - E_S. \qquad (5)$$

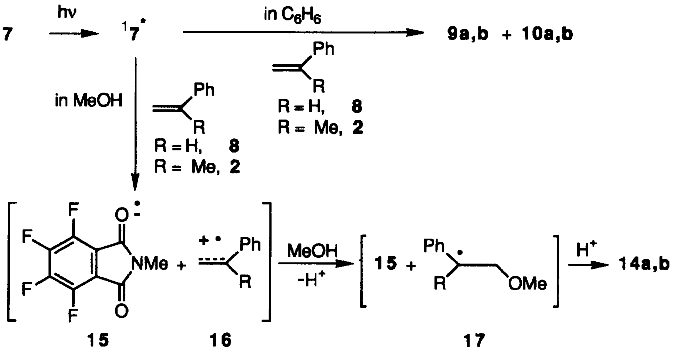
In this equation $E(D/D^+)$ is the one-electron oxidation potential for the alkenes (in volts), $E(A^-/A)$ is the one-electron reduction potential for **7** (in volts), and E_S is the energy of S_1 of **7** (87.7 kcal mol^{-1}). The $E(A^-/A)$ value for **7** determined by cyclic voltammetry (conditions; [**7**]=1×10^{-3} M in 0.1 M Bu_4NClO_4/acetonitrile, at ambient temperature, with a platinum electrode vs. Ag/0.01 M $AgClO_4$) was −1.01 V; the calculated ΔG_{et} values are summarized in Table 3.

Product **13** has been reported to be formed by the photooxygenation of **11** using electron transfer sensitizers, such as 9,10-anthracenedicarbonitrile.[11)] In the photoreaction of **7** with **11** under O_2, **7** seems to act catalytically as an electron-transfer sensitizer.

Experimental

NMR spectra were determined on a JEOL JNM-GX-270 (270 MHz) instrument. IR spectra were obtained with a Hitachi 260-50 spectrophotometer. Mass spectra (EI) were measured on a Hitachi M-80B mass spectrometer. Fluorescence and phosphorescence spectra were obtained with a Hitachi 850 spectrophotometer. The reduction potential was determined using a Yanaco cyclic polarograph P-900. The mp were measured using a Yanagimoto micromelting point apparatus, and are uncorrected. Microanalyses were performed on a Yanagimoto CHN corder MT-5.

Materials. 3,4,5,6-Tetrafluoro-*N*-methylphthalimide (**7**) was prepared according to a method described in the literature,[13)] and was purified by recrystallization from methanol: Mp 161.0—162.0°C (lit, 160—161°C).[13)] Alkenes **2**, **8**, and **11** were commercially available and were purified



Scheme 1.

Table 3. Calculated Free-Energy Changes (ΔG_{et}) Associated with Electron-Transfer from Styrene (**8**), α-Methylstyrene (**2**), and 1,1-Diphenylethylene (**11**) to the Singlet Excited State of 3,4,5,6-Tetrafluoro-*N*-methylphthalimide (**7**)

Alkene	$E(D/D^+)/V$	ΔG_{et},[a]/kcal mol^{-1}
Styrene (**8**)	+1.90[b]	−20.6
α-Methylstyrene (**2**)	+1.76[b]	−23.8
1,1-Diphenylethylene (**11**)	+1.52[b]	−29.4

a) Calculated by Eq. 5. b) Ref. 12.

by distillation. The solvents were purified by distillation after dehydration.

General Procedure for Irradiation and Product Isolation. UV irradiation of 25 ml of N_2 purged (or O_2 purged) solutions containing 10 mg (1.7 mM) of **7** and alkenes **2**, **8**, and **11** was carried out with an Eikosha EHB-WI-300 high-pressure Hg-lamp through a uranium filter (>320 nm) at ambient temperature. The reaction was monitored by ^{1}H NMR measurements, and was conducted to >95% conversion, except for reactions under O_2. After evaporation of the solvent, the residue was subjected to column chromatography (Wakogel C-200). Hexane-benzene or benzene-ether was used as the eluant for separating the products. The yields of the products, based on the consumed **7**, are given in the text and in Table 1.

Irradiation 7 and Styrene (8) in Benzene. (3′*RS*)-4,5,6,7-Tetrafluoro-2-methyl-3′-phenyl-(1*RS*)-spiro[1*H*-isoindole-1,2′-oxetan]-3(2*H*)-one (9a): Mp 130.0—132.0°C; ^{1}H NMR ($CDCl_3$) δ=2.56 (s, 3H, NMe), 5.0—5.3 (m, 3H), 6.9—7.0 (m, 2H, Ph), and 7.2—7.4 (m, 3H, Ph); IR (KBr) 1727, 1520, 1506, 1428, 1404, 1040, and 958 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 337 (M^+, 2), 234 (56), 202 (5), 177 (8), 149 (8), 104 (100), and 101 (16). Found: C, 60.39; H, 3.52; N, 4.08%. Calcd for $C_{17}F_4H_{11}NO_2$: C, 60.54; H, 3.29; N, 4.15%.

(3′*SR*)-4,5,6,7-Tetrafluoro-2-methyl-3′-phenyl-(1*RS*)-spiro[1*H*-isoindole-1,2′-oxetan]-3(2*H*)-one (10a): Mp 88.0—90.0°C; ^{1}H NMR ($CDCl_3$) δ=3.33 (s, 3H, NMe), 4.82 (ddd, *J*=4.2, 5.4, and 9.3 Hz, 1H), 5.01 (dd, *J*=8.1 and 9.3 Hz, 1H), 5.24 (ddd, *J*=1.7, 5.4, and 8.1 Hz, 1H), 6.8—6.9 (m, 2H, Ph), and 7.1—7.3 (m, 3H, Ph); IR (KBr) 1742, 1506, 1426, 1404, 1022, 954, and 804 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 337 (M^+, 2), 307 (7), 234 (14), 189 (4), 148 (9), 104 (100), and 103 (13). Found: C, 60.44; H, 3.57; N, 4.22%. Calcd for $C_{17}F_4H_{11}NO_2$: C, 60.54; H, 3.29; N, 4.15%.

Irradiation of 7 and α-Methylstyrene (2) in Benzene. (3′*RS*)-4,5,6,7-Tetrafluoro-2,3′-dimethyl-3′-phenyl-(1*RS*)-spiro[1*H*-isoindole-1,2′-oxetan]-3(2*H*)-one (9b): Mp 132.0—134.0°C; ^{1}H NMR ($CDCl_3$) δ=1.74 (d, *J*=1.2 Hz, 3H, CMe), 2.34 (s, 3H, NMe), 4.76 and 5.32 (ABq, *J*=6.1 Hz, 2H, CH_2), 6.9—7.1 (m, 2H, Ph), and 7.2—7.4 (m, 3H, Ph); IR (KBr) 1722, 1524, 1504, 1400, and 974 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 351 (M^+, 1), 321 (4), 189 (7), 148 (12), 118 (100), 117 (38), and 103 (25). Found: C, 61.29; H, 3.90; N, 3.85%. Calcd for $C_{18}F_4H_{13}NO_2$: C, 61.54; H, 3.73; N, 3.99%.

(3′*SR*)-4,5,6,7-Tetrafluoro-2,3′-dimethyl-3′-phenyl-(1*RS*)-spiro[1*H*-isoindole-1,2′-oxetan]-3(2*H*)-one (10b): Mp 168.5—170.0°C; ^{1}H NMR ($CDCl_3$) δ=1.83 (s, 3H, CMe), 3.38 (s, 3H, NMe), 4.52 (dd, *J*=4.8 and 5.4 Hz, 1H), 5.42 (d, *J*=4.8 Hz, 1H), 6.6—6.8 (m, 2H, Ph), and 7.1—7.2 (m, 3H, Ph); IR (KBr) 1728, 1510, 1500, 1420, 1030, and 966 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 351 (M^+, 1), 321, (3), 189 (4), 148 (11), 118 (100), 117 (38), and 103 (27). Found: C, 61.62; H, 4.02; N, 4.05%. Calcd for $C_{18}F_4H_{13}NO_2$: C, 61.54; H, 3.73; N, 3.99%.

Irradiation of 7 and 1,1-Diphenylethylene (11) in Benzene and in Acetonitrile. 4,5,6,7-Tetrafluoro-2-methyl-3′,3′-diphenylspiro[1*H*-isoindole-1,2′-oxetan]-3(2*H*)-one (12): Mp 186.0—188.0°C; ^{1}H NMR ($CDCl_3$) δ=2.44 (s, 3H, NMe), 5.58 (s, 2H, CH_2), 6.7—6.9 (m, 2H, Ph), and 7.0—7.4 (m, 8H, Ph); ^{13}C NMR ($CDCl_3$) δ=26.9 (NCH_3), 62.3 (C), 73.2 (CH_2), 96.1 (C), 102.9 (C), 113.9 (C), 125.4 (CH), 126.2 (CH), 127.0 (CH), 127.4 (CH), 128.9 (CH), 129.2 (CH), 141.1 (C), 142.2 (CF), 142.9 (CF), 143.3 (CF), 143.5 (CF), 143.8 (C), 162.1 (C=O); IR (KBr) 1734, 1518, 1506, 1430, 1402, 1038, and 976 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 383 (7), 233 (18), 205 (7), 119 (18), 180 (100), 179 (59), 175 (69), and 148 (38). Found: C, 66.57; H, 3.77; N, 3.26%. Calcd for $C_{23}F_4H_{15}NO_2$: C, 66.83; H, 3.66; N, 3.39%.

Benzophenone (**13**) was identified by comparing its IR and ^{1}H NMR spectra with those of the commercially available sample.

Irradiation of 7 and Styrene (8) in Methanol. A Mixture (1 : 1) of Diastereomers of 4,5,6,7-Tetrafluoro-1-hydroxy-1-(2-methoxy-1-phenylethyl)-2-methyl-1*H*-isoindol-3(2*H*)-one (14a): Mp 38.0—40.5°C; ^{1}H NMR ($CDCl_3$) of one diastereomer δ=3.29 (s, 3H, NMe), 3.56 (s, 3H, OMe), 3.77 (dd, *J*=2.4 and 9.4 Hz, 1H), 4.08

(dd, J=4.4 and 11.9 Hz, 1H), 4.21 (dd, J=9.4 and 11.9 Hz, 1H), 6.37 (s, 1H, OH), 6.6—6.7 (m, 2H, Ph), and 6.9—7.0 (m, 3H, Ph); ^{1}H NMR (CDCl$_3$) of the other dia stereomer δ=3.06 (s, 3H, NMe), 3.56 (s, 3H, OMe), 3.7—3.9 (m, 2H), 4.34 (ddd, J=1.7, 9.5, and 11.2 Hz, 1H), 6.39 (s, 1H, OH), and 7.0—7.3 (m, 5H, Ph); IR (KBr) 1698, 1514, 1500, 1455, 1398, 1100, and 1034 cm^{-1}; MS (70 eV) m/z (rel intensity) 234 (16), 149 (3), 104 (100), and 103 (12). Found: C, 58.32; H, 4.38; N, 3.65%. Calcd for $C_{18}F_4H_{15}NO_3$: C, 58.54; H, 4.09; N, 3.79%.

Irradiation of 7 and α-Methylstyrene (2) in Methanol. A Mixture (3 : 2) of Diastereomeres of 4,5,6,7-Tetrafluoro-1-hydroxy-1-(2-methoxy-1-methyl-1-phenylethyl)-2-methyl-1*H*-isoindol-3(2*H*)-one (14b): Mp 135.0—138.0°C; ^{1}H NMR (CDCl$_3$) of one diastereomer δ=1.58 (s, 3H, CMe), 3.15 (s, 3H, NMe), 3.60 (s, 3H, OMe), 3.64 (dd, J=2.7 and 9.8 Hz, 1H), 4.41 (d, J=9.8 Hz, 1H), 6.29 (s, 1H, OH), 6.9—7.1 (m, 2H, Ph), and 7.1—7.3 (m, 3H, Ph); ^{1}H NMR (CDCl$_3$) of the other diastereomer δ=1.65 (s, 3H, CMe), 2.79 (s, 3H, NMe), 3.57 (s, 3H, OMe), 3.63 and 4.17 (ABq, J=9.7 Hz, 2H, CH$_2$), 6.11 (s, 1H, OH), and 7.1—7.4 (m, 5H, Ph); IR (KBr) 1696, 1514, 1504, 1426, 1396, 1108, and 1036 cm^{-1}; MS (70 eV) m/z (rel intensity) 234 (44), 202 (3), 177 (6), 149 (11), 118 (100), and 117 (32). Found: C, 59.63; H, 4.71; N, 3.44%. Calcd for $C_{19}F_4H_{17}NO_3$: C, 59.53; H, 4.47; N, 3.65%.

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