7 and 11c the hydrogen atoms are placed at the calculated positions and treated as riding on their parent carbon atom. In structure 8b all hydrogens except one of each water molecule were located by difference Fourier synthesis and they were refined with isotropic thermal parameters. In structure 11b the hydrogens were placed on their calculated positions and all but two were treated as riding on their parent carbon atom. The remaining two hydrogens were, for reasons of calculation efficiency, refined with isotropic thermal parameters. Parameters refined were the overall scale factor, an isotropic extinction parameter g [$F_o = F_c/(1 + gI_c)$] for 11c, positional and isotropic cq anisotropic thermal parameters for non-hydrogen atoms, and positional and isotropic thermal parameters for hydrogen atoms (if included). Refinements converged with shift/error ratios less than unity, except for 7, where convergence in the parameters of one highly disordered anion was poor. Final difference Fourier maps showed no significant features. All calculation were done using SDP.[24]

Electrochemistry. The polarographic measurements were carried out with a Metrohm E505 polarograph. This polarograph was operated in a three-electrode mode with a dropping mercury electrode (DME) as cathode, a platinum wire as auxiliary electrode, and an Ag/AgCl electrode (Metrohm EA 441/5) as reference. The reference electrode was filled with 1 M $Et_4N^+Cl^-$ (Merck, synthetic quality, recrystallized from ethyl acetate/$CHCl_3$) in MeOH (Merck, pa quality). The measurements were performed at 20 °C in a 0.1 M solution of TEAP ($Et_4N^+ClO_4^-$, Fluka, purum, recrystallized from EtOH) in DMSO (pa quality of Merck, max 0.03% H_2O). The reference electrode was brought into contact with the sample via a double salt bridge of the following configuration:

Ag; AgCl, $Et_4N^+Cl^-$ – MeOH:TEAP–DMSO:sample.

The characteristics of the DME electrode were m = 1.065 mg/s, natural drop time = 5.30 s, and height of the mercury colomn 64 cm^{-1}. A mechanical drop time of 1.000 s was maintained during all experiments. The sample concentrations were 1.14–1.82 mM. Oxygen was expelled by bubbling with nitrogen (Hoekloos, very pure) for at least 10 min. Polarograms were recorded and evaluated by a computerized method described by Zollinger et al.[17] The nickel/barium complex 1b[2] was used as a reference and measured several times during the day to detect fluctuations ($\Delta E_{1/2} < 3$ mV).

Cyclic voltammetry was carried out with an AUTOLAB computerized system for electrochemistry (ECO CHEMIE, Utrecht, The Netherlands). The measurements were performed at a stationary hanging mercury drop electrode (Metrohm, 663 VA Stand). The same reference and auxiliary electrode were used as in the polarographic experiments. The solvent and the supporting electrolyte were also the same as used in the polarography.

Coulometry was carried out with a Metrohm coulostat E524 and a Metrohm integrator E525. The measurements were carried out in the same solvent and supporting electrolyte as were used for the polarographic experiments. A mercury pool was used as cathode and it was seperated from the platinum counterelectrode by one salt bridge. The reference electrode was the same as used for the other electrochemical experiments. The coulostat was operated with a constant potential (potentiostatic coulometry).

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Registry No. 2, 115142-66-0; 3, 5470-11-1; 4, 119655-83-3; 5a, 119655-84-4; 5b, 119655-86-6; 5c, 119655-88-8; 6, 5627-11-2; 7, 119655-90-2; 8a[Ni(II)], 119655-97-9; 8a[Ni(I)], 119656-07-4; 8b[Cu(II)], 119655-93-5; 8b[Cu(I)], 119656-04-1; 8c, 119655-95-7; 9, 593-56-6; 10, 119638-40-3; 11a[Ni(II)], 119655-99-1; 11a[Ni(I)], 119656-08-5; 11b[Cu(II)], 119656-01-8; 11b[Cu(I)], 119656-06-3; 11b[Cu(0)], 119656-05-2; 11c, 119656-03-0.

Supplementary Material Available: Tables of positional and thermal parameters of all atoms, bond distances, and bond angles in the complexes 7, 8b·2H_2O, 11b, and 11c (18 pages). Ordering information is given on any current masthead page.

(24) *Structure Determination Package*; B. A. Frenz and Associates Inc.; College Station, TX, and Enraf-Nonius, Delft, 1983.

Photochemical Reactions of *N,N'*-Dimethylimidazolidinetrione with Alkenes. Solvent-Incorporated Addition via Hydrogen Abstraction

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Photoreactions of *N,N'*-dimethylimidazolidinetrione (1) with alkenes in benzene gave oxetanes in high yields. The reaction of 1 with stilbene proceeded via excitation of the alkene rather than 1, whereas that with 2,5-dimethylhexadiene took place via excitation of the ground-state complex of 1 with the diene. On irradiation in hydrogen-donating solvents such as alcohols, toluene, or cyclohexane, 1 underwent a quite rare solvent-incorporated addition to the alkenes via intermolecular hydrogen abstraction.

The photochemical reactivity of 1 is of interest in connection with that of extensively investigated cyclic imides[1] and acylureas,[2] since imidazolidinetriones may be viewed as a composite of (a) one imide and one amide and (b) urea and *cis*-glyoxal.[3] In relation to our studies on photoreactions of nitrogen-containing α-dicarbonyl compounds,[4] we have reported photochemical intramolecular hydrogen abstraction of *N,N'*-dialkylimidazolidinetriones.[5] Kanaoka et al. have independently reported intermolecular hydro-

(1) (a) Kanaoka, Y. *Acc. Chem. Res.* **1978**, *11*, 407. (b) Mazzocchi, P. H. *Org. Photochem.* **1981**, *5*, 421. (c) Coyle, J. D. *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum: New York, 1984; pp 259–284.

(2) (a) Kondo, Y.; Witkop, B. *J. Am. Chem. Soc.* **1968**, *90*, 3258. (b) Coyle, J. D.; Bryant, L. R. B. *J. Chem. Soc., Perkin Trans. 1* **1983**, 531. (c) Aoyama, H.; Sakamoto, M.; Ohnota, M.; Omote, Y. *Chem. Lett.* **1983**, 1905.

(3) For composite molecule description of imidazolidinetriones, see: Larson, D. B.; Arnett, J. F.; McGlynn, S. P. *J. Am. Chem. Soc.* **1973**, *95*, 6928.

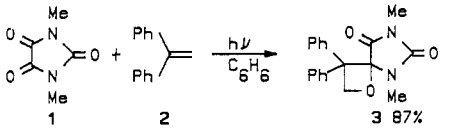
(4) (a) Aoyama, H.; Sakamoto, M.; Kuwabara, K.; Yoshida, K.; Omote, Y. *J. Am. Chem. Soc.* **1983**, *105*, 1958. (b) Aoyama, H.; Sakamoto, M.; Omote, Y. *J. Chem. Soc., Chem. Commun.* **1982**, 119. (c) Aoyama, H.; Ohnota, M.; Sakamoto, M.; Omote, Y. *J. Org. Chem.* **1986**, *51*, 247.

(5) Aoyama, H.; Ohnota, M.; Sakamoto, M.; Omote, Y. *Tetrahedron Lett.* **1984**, *25*, 3327.

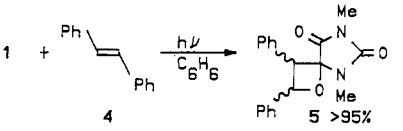
0022-3263/89/1954-2359$01.50/0

gen abstraction of *N,N'*-dimethylimidazolidinetrione (**1**).[6] We report here the photochemical reactions of **1** with alkenes.

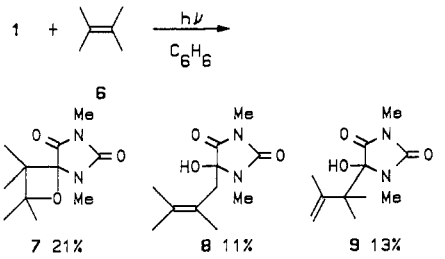
Photoreaction in Benzene. When a solution of **1** and 1,1-diphenylethylene (**2**) in benzene was irradiated with a high pressure mercury lamp through a Pyrex filter, an oxetane (**3**) was obtained in high yield. The structure of **3** was determined on the spectral data. The IR spectrum of **3** showed absorptions (1770 and 1700 cm^{-1}) characteristic of a hydantoin. The ^{13}C NMR spectrum exhibited a peak at δ 73.5 assignable to the OCH_2 unit.



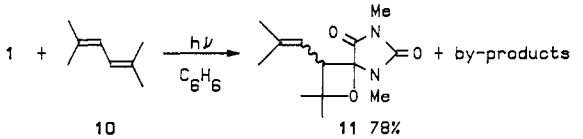
Irradiation of a benzene solution of **1** and (*E*)-stilbene (**4**) yielded the corresponding oxetanes (**5**) almost quantitatively. The product was a mixture of three stereoisomers, which could not be separated.



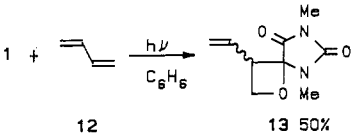
Photoreaction of **1** with 2,3-dimethyl-2-butene (**6**) in benzene afforded an oxetane (**7**) and two adducts (**8** and **9**) formed via intermolecular hydrogen transfer.



Photoreaction of **1** with 2,5-dimethyl-2,4-hexadiene (**10**) also gave oxetanes (**11**) accompanied by some byproducts. The oxetane was a mixture of two stereoisomers. The major isomer was isolated by recrystallization but the minor one cannot be obtained in pure form by this method. The NMR and IR spectra of the byproducts suggested that they were the 1:1 adducts produced by intermolecular hydrogen transfer (as with **8** and **9**) but the complete purification of them was not achieved.



The reaction of **1** and butadiene (**12**) in benzene was quite slow compared with the reactions with other alkenes, and oxetanes (**13**) (mixture of stereoisomers) were obtained in 50% yield on prolonged irradiation along with many unidentified byproducts.



(6) Sato, E.; Kanaoka, Y. *Chem. Pharm. Bull.* **1985**, *33*, 3006.

The photoreaction of **1** with ethyl vinyl ether gave an intractable mixture and that with acrylonitrile yielded only polyacrylonitrile.

Mechanism of the Photoreactions in Benzene. Although the mechanism of the Paterno–Büchi reactions is well understood,[7] the photoreaction of **1** with **4**, **6**, or **10** is worth noting. The reaction of **1** with stilbene (**4**) apparently proceeds via excitation of **4** rather than **1**, in view of the extinction coefficients (**1**, $\epsilon_{313} = 80$; **4**, $\epsilon_{313} = 17\,000$), the molar ratio in the photoreaction (**4**/**1** = 10), and the quantum yield (0.009). This finding is of interest since Paterno–Büchi reactions via excitation of alkenes are rare.[8]

The UV spectrum of a benzene solution of a 1:4 mixture of **1** and **10** showed a broad end absorption in the range of 340–400 nm, whereas a solution of the each compound in benzene was transparent in the above range. This fact indicated the formation of a ground-state complex of **1** with **10**. Selective excitation of the complex with the 366-nm line resulted in efficient formation of the adducts. This observation is interesting because the Paterno–Büchi reactions via excitation of ground-state CT complexes are quite rare.[9] The formation of ground-state CT complexes was not observed in the case of other alkenes **2**, **4**, **6**, and **12**. These findings are understandable since **10** is a stronger donor than these alkenes.[10]

Formation of the intermolecular hydrogen transfer products **8** and **9** in the reaction of **1** with **6** may proceed via rapid electron transfer followed by proton transfer instead of direct hydrogen atom transfer because (a) formation of analogous products in the photoreaction of phthalimides with **6** in benzene is reported to proceed via initial electron transfer,[11] and (b) the adducts **8** and **9** were obtained even in the reaction in toluene, which is a hydrogen donor comparable to **6**[12] (see the next section).

The triplet energy of **1** (78.4 kcal)[3] is higher than those of the alkenes[13] that are present in large excess in the reaction solutions, and hence usual sensitization and quenching experiments could not be achieved. This situation makes it difficult to determine the multiplicities of the reactive excited states in the photoreactions. However it is known that triplet state Paterno–Büchi reactions do not proceed (or are extremely inefficient) when the triplet energies of alkenes are lower than those of carbonyl compounds.[7] The present reactions are therefore most reasonably explained in terms of singlet reactions via exciplexes with charge-transfer character.[7] The low reactivity of butadiene may be attributable to the fact that the diene is the weakest donor among the alkenes studied here.[10]

Photoreactions in Hydrogen-Donating Solvents. When a solution of **1** and 1,1-diphenylethylene (**2**) in

(7) (a) Jones, G. II *Org. Photochem.* **1981**, *5*, 1. (b) Carless, H. A. J. ref 1c, pp 425–487. (c) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978.

(8) (a) Albone, E. S. *J. Am. Chem. Soc.* **1968**, *90*, 4663. (b) Nozaki, H.; Otani, I.; Noyori, R.; Kawanishi, W. *Tetrahedron* **1968**, *24*, 2183. (c) DeBoer, C. *Tetrahedron Lett.* **1971**, 4977. (d) Farid, S.; Hartman, S. E.; Doty, J. C.; Williams, J. L. R. *J. Am. Chem. Soc.* **1975**, *97*, 3697.

(9) (a) Farid, S.; Shealer, S. E. *J. Chem. Soc., Chem. Commun.* **1973**, 296. (b) Green, B. S.; Rejtoe, M.; Johnson, D. E.; Hoyle, C. E.; Simpson, J. T.; Correa, P. E.; Ho, T.-I.; Mccoy, F.; Lewis, F. D. *J. Am. Chem. Soc.* **1979**, *101*, 3325. (c) Silber, E.; Park, S.; Herdon, W. C. *Tetrahedron* **1979**, *35*, 2485.

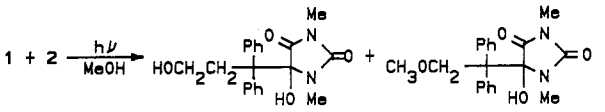
(10) (a) Mariano, P. S.; Stavinoha, J. L. ref 1c, pp 145–257. (b) Kubo, Y.; Suto, M.; Araki, T.; Mazzocchi, P. H.; Klingler, L.; Shook, D.; Somich, C. *J. Org. Chem.* **1986**, *51*, 4404.

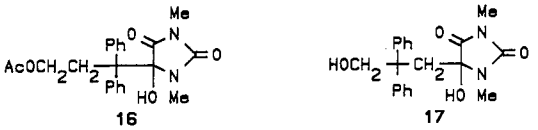
(11) Mazzocchi, P. H.; Klingler, L. *J. Am. Chem. Soc.* **1984**, *106*, 7567. See also ref 10b.

(12) Russell, G. A. *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; pp 275–331.

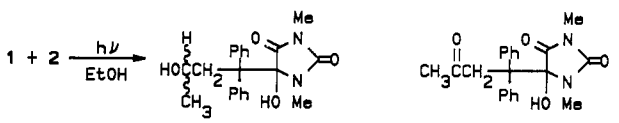
(13) (a) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973. (b) Reference 7c; p 292. (c) Goerner, H. *J. Phys. Chem.* **1982**, *86*, 2028.

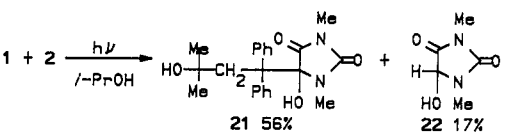
methanol was irradiated with a high-pressure mercury lamp, two methanol-incorporated adducts, **14** and **15**, were obtained. The quantum yield of this reaction was 0.20. The structure of **14** was determined by elemental analysis and spectral data (NMR, IR, and MS). The presence of a primary hydroxy group was confirmed by formation of the corresponding acetate (**16**). An alternative structure (**17**) was eliminated on the basis of the fact that the ^1H NMR spectrum (500 MHz) of **16** showed each of the proton resonances of the two methylene groups as complex multiplets. The structure of **15** was also determined by the spectral data.



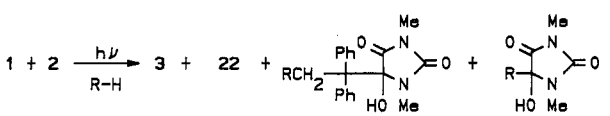


Irradiation of a solution of **1** and **2** in ethanol gave two ethanol-incorporated adducts, **18** and **19**. These products were stereoisomers, which gave the same ketone (**20**) on oxidation with chromic trioxide in pyridine. The two isomers could be separated by chromatography, but their stereochemistry could not be assigned. In this reaction, products analogous to **15** formed by polar addition of ethanol were not detected. Similarly, photolysis of **1** and **2** in 2-propanol gave a solvent-incorporated adduct (**21**) accompanied by a small amount of a photoreduction product (**22**).



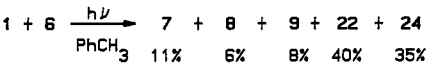


Photoreactions of **1** and **2** in other hydrogen-donating solvents such as toluene or cyclohexane–benzene (1:1)[14] also gave the corresponding solvent-incorporated adducts (**23** or **25**) as a major products accompanied by solvent adducts (**24** or **26**), the oxetane **3** and **22**.

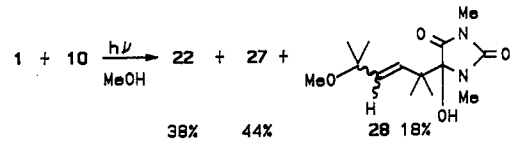


Photoreaction of **1** with stilbene (**4**) in methanol was quite sluggish, and prolonged irradiation resulted in the slight decomposition of the reactants, whereas the reaction in toluene yielded the oxetane **5** (84%), the same product obtained for reaction in benzene.

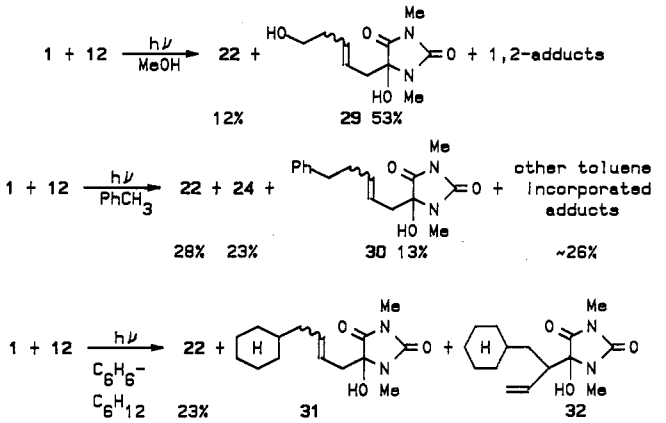
Irradiation of a methanol solution of **1** and the dimethylbutene **6** gave the oxetane **7** and the hydrogen-abstraction products **8** and **9** along with a methanol adduct **27** and **22**. The latter products are obtained in the photoreaction of **1** in methanol.[6] The reaction in toluene gave a similar result. In these cases, the reaction with the alkene and that with the solvent took place competitively, and no new reactions occurred.



When a solution of **1** and the diene **10** in methanol was irradiated, the methanol adduct **27** and the reduction product **22** were obtained as major products together with a methanol-incorporated adduct (**28**), which was formed via polar addition of methanol. Irradiation of a solution of **1** and **10** in cyclohexane–benzene (1:1) afforded the oxetane **11** (77%) and the cyclohexane adduct **26** (13%).



Photoreaction of **1** with butadiene in methanol afforded a methanol-incorporated 1,4-adduct (**29**) as a mixture of *E* and *Z* isomers along with the reduction product **22**. A 1,2-adduct (like **32**) was also formed in this reaction but could not be purified. The reaction in toluene gave **22**, the toluene adduct **24**, and a mixture of toluene-incorporated adducts. Among these isomers, an *E* isomer of a 1,4-adduct (**30**) was purified by means of repeated chromatography. Irradiation of **1** and butadiene in cyclohexane–benzene (1:1) gave **22** and a mixture of cyclohexane-incorporated adducts **31** and **32**, which were not separated (the combined yield is 44%).



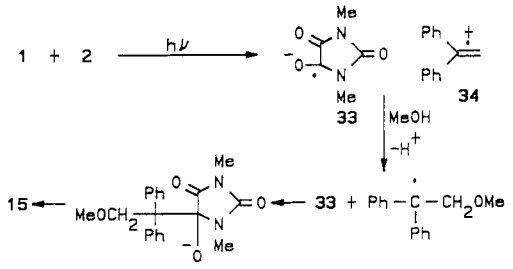
Mechanisms of the Photoreactions in the Hydrogen-Donating Solvents. Alcohol-incorporated addition of alkenes to multiple bonds which involves polar addition of alcohols is well-known in the photochemistry of cyclic imides,[1] iminium salts,[15] and cyanoarenes.[16] These reactions proceed via electron transfer from alkenes. The

(14) Benzene was added because of the low solubility of **1** to cyclohexane.

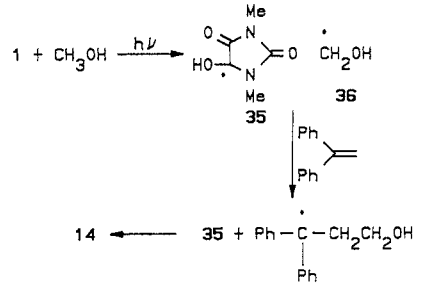
(15) Mariano, P. S. *Org. Photochem.* **1987**, *9*, 1–128.

(16) (a) McCullough, J. J.; Miller, R. C.; Wu, W. S. *Can. J. Chem.* **1977**, *55*, 2909 and references cited therein. (b) Mizuno, K.; Pac, C.; Sakurai, H. *J. Am. Chem. Soc.* **1974**, *96*, 2993. (c) Lewis, N. A.; De Voe, R. J. *Tetrahedron* **1982**, *38*, 1069.

Scheme I



Scheme II



formation of **15** or **28** is also explainable by the mechanism involving electron transfer and subsequent addition of methanol to the resulting cation radical of the alkene (Scheme I).

It is known that the cation radical (**34**) reacts with **2** in the absence of nucleophiles (e.g. in acetonitrile) to give two kinds dimers of **2**.[17] In confirmation of the intermediacy of **34** in the formation of **15**, the photoreaction of **1** and **2** (0.25 M) in acetonitrile was carried out. However, the reaction yielded the oxetane **3** almost quantitatively, and the dimers of **2** were not detected. This finding suggests that the deactivation of the radical ion pair (**33** and **34**) via back electron transfer and/or the oxetane formation from the radical ion pair[18] is faster than addition of diphenylethylene to the cation radical **34**.

On the other hand, formation of the adduct, **14**, apparently proceeds via hydrogen abstraction from methanol and the addition of the resulting radical (**36**) to the alkene (Scheme II). The formation of other solvent-incorporated adducts **18**, **19**, **21**, **23**, **25**, **29**, **30**, **31**, and **32** is also explainable by similar mechanisms.

Although it is difficult to determine the multiplicity of the reactive excited states involved in the present reaction experimentally (vide supra), it is sure that the hydrogen abstraction proceeds from the triplet state of **1** because the photochemical hydrogen abstraction of **1** from hydrogen-donating solvents (alcohols, toluene, and cyclohexane) has been reported to take place from the triplet state.[6] This triplet mechanism is also consistent with the fact that Norrish type II reaction of *N,N'*-dialkylimidazolidinetriones takes place from the triplet states.[5] The intermolecular hydrogen abstraction of **1** from the solvents should be extremely rapid since it can take place even in the presence of the alkenes which can behave as triplet quenchers.

The solvent-incorporated adducts formed via hydrogen abstraction were obtained only in the case of 1,1-diphenylethylene and butadiene. This observation is quite reasonably explained in terms of the high reactivity of these alkenes toward carbon radicals.[19] Meanwhile, in the case of the polysubstituted alkenes **6** and **10** such products were not produced, and **22** and **27** were obtained instead. This is apparently due to the low reactivity of the alkenes toward radicals, since it is known that increasing the degree of substitution around the double bond significantly decreases the rate of radical addition owing to steric hindrance.[19] Thus the radical **36**, which does not react with these alkenes, should undergo coupling or disproportionation with **35** to give **27** and **22**, respectively. The reduction product, **22**, can also be produced by hydrogen abstraction of **35** from the solvents.

Only in the case of stilbene were no hydrogen-abstraction products produced. This is quite reasonable because the alkene rather than **1** is excited on irradiation as described above.

Oxetane formation was completely suppressed in reactions where alcohols are used as solvent except for the inefficient formation of **7** (6%) in the reaction with **6**. In contrast considerable amounts of the oxetanes were formed in the reactions in toluene, which is a hydrogen donor stronger than (or comparable to) methanol.[12] It is known that the oxetane formation of α-dicarbonyl compounds in nonpolar solvents are more efficient than those in polar solvents.[20] In fact, the reaction of **1** with stilbene in acetonitrile was extremely inefficient as with that in methanol. However, it is also conceivable that solvation of **1** with the alcohols through hydrogen bonding makes the formation of the intermediate exciplex inefficient, since the reaction of **1** with **2** proceeds even in acetonitrile as described above.

Solvent-incorporated addition of carbonyl compounds to alkenes via hydrogen abstraction is extremely rare in the photochemistry of carbonyl compounds. Only one example has been reported so far to our knowledge. Pfau et al. reported a 2-propanol-incorporated addition of benzophenone to methacrylic acid.[21] The prerequisites for this type of addition are presumed to be as follows. The carbonyl compounds should undergo hydrogen abstraction from solvents even in the presence of the alkenes: the hydrogen abstraction should be able to compete with other reactions such as the Paterno–Büchi reaction and with quenching by the alkenes.[22] Moreover, the alkenes should possess high reactivity toward radicals because the radical addition to the alkenes should compete with other rapid reactions of radicals such as coupling, hydrogen abstraction, or disproportionation. The generality of this type of photoaddition is under investigation by use of other carbonyl compounds.

Experimental Section

Melting points were taken on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were measured on a JASCO IRA-1 infrared spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q or FX-100 spectrometer. UV spectra were obtained on a Shimadzu UV-365 spectrometer. Mass spectra were recorded on a Hitachi RMU-6MG spectrometer. Elemental analyses were performed by a Perkin-Elmer Model 240 elemental analyzer.

General Procedure for the Photolysis in Benzene. A solution of 200 mg (1.4 mmol) of **1** and 14 mmol of olefins in benzene (100 mL) was deaerated by bubbling through argon and irradiated with a high-pressure mercury lamp through a Pyrex

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filter for 20–30 h. After evaporation of the solvent, products were isolated by flash chromatography on silica gel followed by distillation or recrystallization.

Spiro[*N*,*N*'-dimethylhydantoin-5,2'-3',3'-diphenyloxetane] (3): mp 176–177 °C; IR ($CHCl_3$) 1770, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.25 (s, 3 H, NMe), 3.02 (s, 3 H, NMe), 5.30 and 5.45 (AB q, 2 H, J = 5.9 Hz, CH_2), 6.9–6.7 (m, 2 H, Ph), 7.1–7.5 (m, 8 H, Ph); ^{13}C NMR δ 24.7 (q), 26.2 (q), 62.5 (s), 73.5 (t), 96.8 (s), 125.7 (d), 126.9 (d), 127.5 (d), 127.7 (d), 128.5 (d), 128.9 (d), 138.6 (s), 142.3 (s), 156.0 (s), 171.0 (s). Anal. Calcd for $C_{19}H_{18}H_2O_3$: C, 70.79; H, 5.62; N, 8.69. Found: C, 70.60; H, 5.60; N, 8.68.

Spiro[*N*,*N*'-dimethylhydantoin-5,2'-3',4'-diphenyloxetane] (5) was a mixture of three stereoisomers: IR ($CHCl_3$) 1780, 1715 cm^{-1}; characteristic signals ^1H NMR ($CDCl_3$) δ 2.69 (s), 2.71 (s), 2.91 (s), 3.10 (s), 3.12 (s), 3.26 (s), 4.53 (d, J = 8.3 Hz), 4.91 (d, J = 8.3 Hz), 5.11 (d, J = 8.3 Hz), 6.11 (d, J = 8.3 Hz), 6.26 (d, J = 8.3 Hz), 6.40 (d, J = 8.3 Hz), 6.63–7.90 (m); ^{13}C NMR δ 24.5 (q), 24.7 (q), 24.9 (q), 25.0 (q), 25.9 (q), 26.7 (q), 52.9 (d), 53.5 (d), 55.4 (d), 78.0 (d), 78.9 (d), 82.2 (d), 91.9 (s), 92.0 (s), 92.8 (s), 155.4 (s), 155.6 (s), 156.1 (s), 169.9 (s), 170.4 (s), 172.4 (s); MS (CI) m/z 323 (M + 1). Anal. Calcd for $C_{19}H_{18}N_2O_3$: C, 70.79; H, 5.62; N, 8.69. Found (for a mixture of the isomers): C, 70.60; H, 5.49; N, 8.30.

Spiro[*N*,*N*'-dimethylhydantoin-5,2'-3',3',4',4'-tetramethyloxetane] (7): mp 121–122 °C; IR ($CHCl_3$) 1775, 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21 (s, 3 H, Me), 1.27 (s, 3 H, Me), 1.64 (s, 3 H, Me), 1.83 (s, 3 H, Me), 2.98 (s, 3 H, NMe), 3.14 (s, 3 H, NMe); ^{13}C NMR δ 20.1 (q), 20.7 (q), 24.4 (q), 25.2 (q) × 2, 27.8 (q), 48.8 (s), 85.6 (s), 94.5 (s), 156.6 (s), 171.3 (s). Anal. Calcd for $C_{11}H_{18}N_2O_3$: C, 58.38; H, 8.01; N, 12.38. Found: C, 58.36; H, 8.01; N, 12.43.

***N*,*N*'-Dimethyl-5-(2,3-dimethyl-2-butenyl)-5-hydroxyhydantoin (8)**: bp 90 °C (10^{-3} Torr); IR ($CHCl_3$) 3300, 1770, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.57 (s, 3 H, Me), 1.63 (s, 3 H, Me), 1.70 (s, 3 H, Me), 2.61 and 2.88 (AB q, 2 H, J = 14 Hz, CH_2), 2.90 (s, 3 H, NMe), 2.95 (s, 3 H, NMe), 4.77 (s, 1 H, OH); ^{13}C NMR δ 18.8 (q), 21.0 (q), 24.5 (q) × 2, 39.1 (t), 86.6 (s), 119.9 (s), 131.2 (s), 155.7 (s), 174.3 (s). Anal. Calcd for $C_{11}H_{18}N_2O_3$: C, 58.38; H, 8.01; N, 12.38. Found: C, 58.06; H, 8.09; N, 12.06.

***N*,*N*'-Dimethyl-5-hydroxy-5-(1,1,2-trimethyl-2-propenyl)hydantoin (9)**: mp 71–72 °C; IR ($CHCl_3$) 3300, 1765, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.19 (s, 3 H, Me), 1.31 (s, 3 H, Me), 1.90 (s, 3 H, Me), 2.94 (s, 6 H, NMe), 4.23 (s, 1 H, OH), 4.9–5.0 (m, 2 H, $=CH_2$); ^{13}C NMR δ 22.1 (q) × 2, 23.1 (q), 24.4 (q), 27.3 (q), 46.0 (s), 90.2 (s), 115.0 (t), 148.2 (s), 156.9 (s), 173.9 (s). Anal. Calcd for $C_{11}H_{18}N_2O_3$: C, 58.38; H, 8.01; N, 12.38. Found: C, 58.75; H, 8.07; N, 11.98.

Spiro[*N*,*N*'-dimethylhydantoin-5,2'-4',4'-dimethyl-3'-isobutenyloxetane] (11) was a mixture of two stereoisomers, and the major isomer was isolated by recrystallization: mp 109–110 °C; IR ($CHCl_3$) 1780, 1715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.48 (s, 6 H, Me), 1.71 (s, 3 H, Me), 1.76 (s, 3 H, Me), 3.01 (s, 3 H, NMe), 3.10 (s, 3 H, NMe), 4.02 (d, 1 H, J = 8.3 Hz, CH), 5.39 (d, 1 H, J = 8.3 Hz, =CH); ^{13}C NMR δ 18.7 (q), 24.7 (q), 25.0 (q), 25.8 (q), 26.8 (q), 29.6 (q), 50.2 (d), 83.6 (s), 90.6 (s), 115.6 (d), 139.0 (s), 156.0 (s), 172.0 (s). Anal. Calcd for $C_{13}H_{20}N_2O_3$: C, 61.88; H, 7.99; N, 11.10. Found: C, 61.84; H, 8.06; N, 11.04. The minor isomer could not be completely purified: characteristic signals ^1H NMR ($CDCl_3$) δ 2.98 (s), 3.12 (s); ^{13}C NMR ($CDCl_3$) δ 82.6 (s), 116.1 (d).

Spiro[*N*,*N*'-dimethylhydantoin-5,2'-3'-vinyloxetane] (13) was a mixture of two stereoisomers: bp 20 °C (10^{-3} Torr); IR ($CHCl_3$) 1780, 1720 cm^{-1}; characteristic signals ^1H NMR ($CDCl_3$) δ 2.99 (s, NMe), 3.02 (s, NMe), 3.11 (s, NMe), 3.12 (s, NMe), 3.8–4.3 (m, 3'-CH), 4.4–4.9 (m, 4'-CH_2), 5.0–5.4 (m, $=CH_2$), 5.9–6.4 (m, CH=); ^{13}C NMR δ 24.3 (q), 24.4 (q), 24.8 (q), 26.7 (q), 45.8 (d), 46.0 (d), 69.5 (t), 70.5 (t), 94.5 (s), 95.0 (s), 119.9 (t), 120.2 (t), 131.6 (d), 132.0 (d), 155.1 (s), 155.8 (s), 169.6 (s), 170.9 (s). Anal. Calcd for $C_9H_{12}N_2O_3$: C, 55.09; H, 6.16; N, 14.28. Found (for a mixture of the isomers): C, 54.69; H, 6.19; N, 14.07.

General Procedure for Photolysis in Hydrogen-Donating Solvents. A solution of 200 mg (1.4 mmol) of 1 and 14 mmol of olefins in 40 mL of solvent was irradiated for 10–15 h and done as described above.

***N*,*N*'-Dimethyl-5-hydroxy-5-(3-hydroxy-1,1-diphenylpropyl)hydantoin (14)**: mp 209–210 °C; IR (KBr) 3300, 1760, 1685 cm^{-1}; ^1H NMR (C_5D_5N) δ 2.27 (s, 3 H, NMe), 2.90 (s, 3 H, NMe), 3.22–3.84 (m, 4 H, CH_2CH_2), 5.53 (br s, 1 H, OH), 7.2–7.4 (m, 8 H, Ph), 7.5–7.7 (m, 2 H, Ph), 9.76 (br s, 1 H, OH); ^{13}C NMR δ 23.6 (q), 27.5 (q), 38.1 (t), 57.9 (s), 58.7 (t), 92.0 (s), 127.4 (d), 127.6 (d), 127.7 (d), 130.5 (d), 131.2 (d), 139.0 (s), 142.8 (s), 150.8 (s), 173.2 (s); MS (CI) m/z 355 (M + 1). Anal. Calcd for $C_{20}H_{22}N_2O_4$: C, 67.78; H, 6.25; N, 7.90. Found: C, 67.70; H, 6.24; N, 7.87.

***N*,*N*'-Dimethyl-5-hydroxy-5-(2-methoxy-1,1-diphenylethyl)hydantoin (15)**: mp 177–178 °C; IR ($CHCl_3$) 3280, 1760, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.44 (s, 3 H, NMe), 2.95 (s, 3 H, NMe), 3.37 (s, 3 H, OMe), 3.82 and 5.32 (AB q, 2 H, J = 9.3 Hz, CH_2), 6.83 (s, 1 H, OH), 7.2–7.3 (m, 8 H), 7.4–7.6 (m, 2 H); ^{13}C NMR δ 23.9 (q), 28.1 (q), 56.3 (s), 59.6 (q), 77.7 (t), 92.0 (s), 127.2 (d), 127.3 (d), 129.8 (d), 127.9 (d), 129.2 (d), 130.6 (d), 138.6 (s), 141.8 (s), 155.9 (s), 172.7 (s); MS (CI) m/z 355 (M + 1). Anal. Calcd for $C_{20}H_{22}N_2O_4$: C, 67.78; H, 6.25; N, 7.90. Found: C, 67.38; H, 6.18; N, 7.76.

***N*,*N*'-Dimethyl-5-hydroxy-5-(3-acetoxy-1,1-diphenylpropyl)hydantoin (16).** A solution of 14 (50 mg) in 5 mL of pyridine–acetic anhydride mixture (1:1) was heated to 100 °C for 4 h. After evaporation in vacuo, the residue was chromatographed on silica gel. Compound 16 (42 mg) showed the following: mp 187–188 °C dec; IR ($CHCl_3$) 3250, 1760, 1700 cm^{-1}; 500-MHz ^1H NMR ($CDCl_3$) δ 1.94 (s, 3 H, COMe), 2.36 (s, 3 H, NMe), 2.70 (s, 3 H, NMe), 2.846–2.905 (m, 1 H), 3.312–3.368 (m, 1 H), 3.389–3.441 (m, 1 H), 3.956–4.006 (m, 1 H), 3.99 (s, 1 H, OH), 7.26–7.37 (m, 8 H, Ph), 7.65–7.82 (m, 2 H, Ph); ^{13}C NMR δ 20.8 (q), 23.8 (q), 27.6 (q), 32.5 (t), 56.9 (s), 61.7 (t), 91.4 (s), 127.4 (d), 127.7 (d), 127.9 (d), 129.9 (d), 130.3 (d), 136.4 (s), 140.6 (s), 155.6 (s), 171.2 (s), 172.6 (s). Anal. Calcd for $C_{22}H_{24}N_2O_5$: C, 66.65; H, 6.10; N, 7.06. Found: C, 66.39; H, 6.03; N, 7.01.

***N*,*N*'-Dimethyl-5-hydroxy-5-(3-hydroxy-1,1-diphenylbutyl)hydantoin (18)**: mp 168–169 °C dec (in a sealed tube); IR (KBr) 3350, 3100, 1770, 1700 cm^{-1}; ^1H NMR (DMSO-d_6, at 76 °C) δ 0.53 (d, 3 H, J = 5.9 Hz, Me), 2.23 (s, 3 H, NMe), 2.65 (s, 3 H, NMe), 2.3–2.5 (m, 1 H), 3.0–3.4 (m, 2 H), 7.2–7.3 (m, 6 H, Ph), 7.5–7.6 (m, 4 H, Ph); ^{13}C NMR (DMSO-d_6) δ 23.3 (q), 25.0 (q), 27.2 (q), 44.3 (t), 58.2 (s), 63.5 (d), 91.0 (s), 126.7 (d), 127.2 (d), 129.4 (d), 130.9 (d), 138.2 (s), 142.5 (s), 155.1 (s), 171.8 (s); MS (CI) m/z 369 (M + 1). Anal. Calcd for $C_{21}H_{24}N_2O_4$: C, 68.46; H, 6.56; N, 7.60. Found: C, 68.11; H, 6.52; N, 7.58. **19**: mp 167–168 °C dec (in a sealed tube); IR (KBr) 3400, 3050, 1770, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20 (d, 3 H, J = 6.4 Hz, Me), 1.91 (d, 1 H, J = 14.7 Hz, CH_2), 2.45 (s, 3 H, NMe), 2.99 (s, 3 H, NMe), 3.4–3.5 (m, 1 H, CH), 3.80 (dd, 1 H, J = 9.8, 14.7 Hz, CH_2), 7.2–7.3 (m, 8 H, Ph), 7.6–7.7 (m, 2 H, Ph); ^{13}C NMR δ 24.0 (q), 25.1 (q), 28.4 (q), 46.8 (t), 58.2 (s), 65.5 (d), 91.0 (s), 126.9 (d), 127.4 (d), 127.7 (d), 129.5 (d), 130.8 (d), 143.0 (s), 142.6 (s), 173.8 (s); MS (CI) m/z 369 (M + 1). Anal. Calcd for $C_{21}H_{24}N_2O_4$: C, 68.46; H, 6.56; N, 7.60. Found: C, 68.19; H, 6.61; N, 7.58.

***N*,*N*'-Dimethyl-5-hydroxy-5-(2-acetyl-1,1-diphenylethyl)hydantoin (20).** Compound 18 or 19 (35 mg) was dissolved in pyridine (5 mL) containing CrO_3 (70 mg). The mixture was set aside for 24 h and then treated as usual. The product was isolated by chromatography. **20**: mp 160–162 °C dec; IR ($CHCl_3$) 3450, 1770, 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.79 (s, 3 H, CH_3CO), 2.12 (s, 3 H, NMe), 3.00 (s, 3 H, NMe), 3.21 (br s, 1 H, OH), 3.52 (s, 2 H, CH_2), 7.6–7.4 (m, 8 H, Ph), 7.6–7.8 (m, 2 H, Ph); ^{13}C NMR δ 24.5 (q), 27.2 (q), 30.5 (q), 48.2 (t), 58.4 (s), 104.0 (s), 126.3 (d), 126.8 (d), 127.2 (d), 127.5 (d), 127.7 (d), 128.0 (d), 128.3 (d), 128.5 (d), 129.2 (d), 130.1 (d), 140.5 (s), 145.8 (s), 158.1 (s), 172.3 (s). Anal. Calcd for $C_{21}H_{22}N_2O_4$: C, 68.83; H, 6.05; N, 7.64. Found: C, 68.70; H, 6.09; N, 7.65.

***N*,*N*'-Dimethyl-5-hydroxy-5-(3-hydroxy-3-methyl-1,1-diphenylbutyl)hydantoin (21)**: mp 155–156 °C dec; IR ($CHCl_3$) 3400, 3100, 1770, 1700 cm^{-1}; ^1H NMR (DMSO-d_6, at 76 °C) δ 0.56 (s, 3 H, Me), 0.84 (s, 3 H, Me), 2.22 (s, 3 H, NMe), 2.76 (s, 3 H, NMe), 2.74 and 3.14 (AB q, 2 H, J = 15.1 Hz, CH_2), 7.1–7.3 (m, 6 H, Ph), 7.5–7.6 (m, 4 H, Ph); ^{13}C NMR ($CDCl_3$) δ 24.1 (q), 28.9 (q), 49.6 (t), 72.2 (s), 91.9 (s), 127.0 (d), 127.1 (d), 127.4 (d), 128.3 (d) and broad peaks at 35.3, 58.6, 131.7, 144.1, 143.5, 155.5, 174.2. Anal. Calcd for $C_{22}H_{26}N_2O_4$: C, 69.09; H, 6.85; N, 7.32. Found: C, 68.72; H, 6.88; N, 7.21.

***N*,*N*'-Dimethyl-5-hydroxyhydantoin (22)** was identified by direct comparison with an authentic sample.[6]

N,N'-Dimethyl-5-hydroxy-5-(1,1,3-triphenylpropyl)hydantoin (23): mp 192–195 °C dec; IR ($CHCl_3$) 3300, 1770, 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.6–1.8 (m, 1 H), 2.0–2.8 (m, 2 H), 2.19 (s, 3 H, NMe), 2.57 (s, 3 H, NMe), 3.3–3.5 (m, 1 H), 4.77 (br s, 1 H, OH), 6.9–7.4 (m, 13 H, Ph), 7.6–7.8 (m, 2 H, Ph); ^{13}C NMR δ 23.8 (q), 27.7 (q), 30.4 (t), 35.4 (t), 58.7 (s), 91.7 (s), 125.7 (d), 127.1 (d), 127.7 (d), 128.2 (d), 130.2 (d), 130.7 (d), 136.5 (s), 141.1 (s), 142.3 (s), 155.6 (s), 172.9 (s). Anal. Calcd for $C_{26}H_{26}N_2O_3$: C, 75.34; H, 6.32; N, 6.76. Found: C, 75.02; H, 6.38; N, 6.68.

N,N'-Dimethyl-5-hydroxy-5-(2-cyclohexyl-1,1-diphenylethyl)hydantoin (25): mp 202–203 °C dec; IR ($CHCl_3$) 3300, 1770, 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.3–1.7 (m, 11 H, cyclohexyl), 2.0–2.3 (m, 1 H, CH_2), 2.23 (s, 3 H, NMe), 2.66 (s, 3 H, NMe), 3.01 (br d, 1 H, J = 14.7 Hz, CH_2), 4.77 (s, 1 H, OH), 7.2–7.3 (m, 8 H, Ph), 7.6–7.8 (m, 2 H, Ph); ^{13}C NMR δ 23.9 (q), 26.2 (t), 26.8 (t), 28.1 (q), 34.0 (d), 34.5 (t), 35.8 (t), 40.2 (t), 59.7 (s), 91.9 (s), 127.0 (d), 127.4 (d), 130.5 (d), 130.8 (d), 137.8 (s), 141.7 (s), 155.6 (s), 173.1 (s). Anal. Calcd for $C_{25}H_{30}N_2O_3$: C, 73.86; H, 7.44; N, 6.89. Found: C, 73.79; H, 7.54; N, 6.77.

N,N'-Dimethyl-5-hydroxy-5-benzylhydantoin (24), N,N'-dimethyl-5-hydroxy-5-cyclohexylhydantoin (26), and N,N'-dimethyl-5-hydroxy-5-(hydroxymethyl)hydantoin (27) were identified by direct comparison with authentic samples.[6]

N,N'-Dimethyl-5-hydroxy-5-(4-methoxy-1,1,4,4-tetramethyl-2-butenyl)hydantoin (28) was a mixture of *E* and *Z* isomers. The major *E* isomer was isolated by recrystallization: mp 89–90 °C; IR ($CHCl_3$) 3350, 1770, 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.15 (s, 3 H), 1.22 (s, 3 H), 1.25 (s, 3 H × 2), 2.92 (s, 3 H, NMe), 2.96 (3 H, NMe), 3.12 (s, 3 H, OMe), 4.43 (s, 1 H, OH), 5.48 (AB q, 1 H, J = 16.4 Hz, CH=), 5.85 (AB q, 1 H, J = 16.4 Hz, =CH); ^{13}C NMR δ 21.5 (q), 23.1 (q), 24.4 (q), 25.4 (q), 26.0 (q), 27.6 (q), 43.8 (s), 50.2 (q), 74.9 (s), 89.6 (s), 133.2 (d), 135.4 (d), 156.6 (s), 173.5 (s). Anal. Calcd for $C_{14}H_{24}N_2O_4$: C, 59.13; H, 8.50; N, 9.85. Found: C, 59.03; H, 8.63; N, 9.77. The minor *Z* isomer could not be purified: characteristic signals ^{13}C NMR ($CDCl_3$) δ 50.1 (s, OMe), 131.8 (d, CH=), 137.5 (d, CH=).

N,N'-Dimethyl-5-hydroxy-5-(5-hydroxy-2-pentenyl)hydantoin (29) was a mixture of *E* and *Z* isomers: bp 80 °C (10^{-3} Torr); IR ($CHCl_3$) 3400, 1780, 1720 cm^{-1}; characteristic signals ^1H NMR ($CDCl_3$) δ 2.0–2.4 (m), 2.60 (t, J = 6.1 Hz), 2.90 (s), 2.95 (s), 3.4–3.6 (m), 5.1–5.7 (m), 5.86 (br s); ^{13}C NMR δ 24.0 (q), 24.5 (q), 35.6 (t), 37.3 (t), 61.6 (t), 86.5 (s), 123.3 (d), 133.4 (d), 155.7 (s), 173.6 (s); weak signals at δ 86.4 (s), 122.2 (d), 131.7 (d). Anal. Calcd for $C_{10}H_{16}N_2O_4$: C, 52.62; H, 7.07; N, 12.27. Found (for a mixture of the isomers): C, 52.40; H, 7.03; N, 11.98. **N,N'-Dimethyl-5-hydroxy-5-(3-hydroxy-1-vinylpropyl)hydantoin** (a 1,2-adduct) was separated from **29** by chromatography but could not be completely purified and did not give satisfactory analytical data: characteristic signals ^{13}C NMR ($CDCl_3$) δ 23.9 (q), 24.4 (q), 24.6 (q), 25.0 (q), 30.4 (t), 30.6 (t), 46.2 (d), 59.8 (t), 60.5 (t), 86.5 (s), 87.1 (s), 120.1 (t), 120.9 (t), 134.1 (d), 134.3 (d), 155.6 (s), 156.2 (s), 173.0 (s), 173.6 (s).

(E)-N,N'-Dimethyl-5-hydroxy-5-(5-phenyl-2-pentenyl)hydantoin (30): bp 130 °C (10^{-3} Torr); IR ($CHCl_3$) 3350, 1780, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.30 (t, 2 H, J = 7.3 Hz), 2.5–2.7 (m, 4 H), 2.86 (s, 3 H, NMe), 2.92 (s, 3 H, NMe), 4.85 (br s, 1 H, OH), 4.9–5.8 (m, 2 H), 7.1–7.4 (m, 5 H); ^{13}C NMR δ 24.0 (q), 24.5 (q), 34.1 (t), 35.5 (t), 37.2 (t), 86.5 (s), 120.7 (d), 125.9 (d), 128.3 (d), 136.8 (d), 141.3 (s), 155.5 (s), 173.6 (s). Anal. Calcd for $C_{16}H_{20}N_2O_3$: C, 66.65; H, 6.99; N, 9.72. Found: C, 66.57; H, 7.25; N, 9.40.

(E)- and (Z)-N,N'-dimethyl-5-hydroxy-5-(4-cyclohexyl-2-butenyl)hydantoin (31) and N,N'-dimethyl-5-hydroxy-5-(2-cyclohexyl-1-vinylethyl)hydantoin (32) could not be separated: bp 110 °C (10^{-3} Torr); IR ($CHCl_3$) 3350, 1780, 1710 cm^{-1}; characteristic signals ^{13}C NMR ($CDCl_3$) δ 24.0 (q), 24.5 (q), 37.1 (t), 40.4 (t), 86.7 (s), 120.9 (d), 136.6 (d), 155.5 (s), 173.6 (s); weak signals at 46.8 (d), 46.9 (d), 121.0 (t), 121.2 (t), 134.7 (d), 135.4 (d). Anal. Calcd for $C_{15}H_{24}N_2O_3$: C, 64.26; H, 8.63; N, 9.99. Found (for a mixture of the isomers): C, 64.44; H, 8.95; N, 9.75.

Quantum Yield Determination. Valerophenone actinometry[23] was used. Irradiation was performed with a 300-W high-pressure mercury lamp in a merry-go-round apparatus. The 313-nm line was isolated with a filter solution containing 0.002 M potassium chromate in 5% aqueous potassium carbonate. The sample in a Pyrex tube was degassed to ca. 10^{-3} Torr in three freeze–thaw cycles. After irradiation, the degree of reaction (consumption of **1**) was determined by gas chromatography.

Registry No. **1**, 5176-82-9; **2**, 530-48-3; **3**, 119695-55-5; **4**, 103-30-0; **5**, 119846-69-4; **6**, 563-79-1; **7**, 119695-56-6; **8**, 119695-57-7; **9**, 119695-58-8; **10**, 164-13-6; **11** (isomer 1), 119695-59-9; **11** (isomer 2), 119695-75-9; **12**, 106-99-0; **13** (isomer 1), 119695-60-2; **13** (isomer 2), 119695-76-0; **14**, 119695-61-3; **15**, 119695-62-4; **16**, 119695-63-5; **18**, 119695-64-6; **19**, 119695-65-7; **20**, 119695-66-8; **21**, 119695-67-9; **22**, 64732-10-1; **23**, 119695-68-0; **24**, 98619-34-2; **25**, 119695-69-1; **26**, 98619-36-4; **27**, 98619-35-3; **28** (isomer 1), 119695-70-4; **28** (isomer 2), 119695-77-1; **29** (isomer 1), 119695-71-5; **29** (isomer 2), 119695-78-2; **30**, 119695-72-6; **31** (isomer 1), 119695-73-7; **31** (isomer 2), 119695-80-6; **32**, 119695-74-8; ethyl vinyl ether, 109-92-2; acrylonitrile, 107-13-1; *N,N'*-dimethyl-5-hydroxy-5-(3-hydroxy-1-vinylpropyl)hydantoin, 119695-79-3.

(23) Wagner, P. J.; Kelso, P. A.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7480.

Studies toward the Syntheses of Functionally Substituted γ-Butyrolactones and Spiro-γ-butyrolactones and Their Reaction with Strong Acids: A Novel Route to α-Pyrones

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A general strategy for the conversion of 5-keto carboxylic acids, **6** (via their enol–lactones **7**), to a variety of γ-lactones, **8a–c**, and spiro-γ-lactones, **8d–g**, is described. Lactones **8b** and **8d,e** may be further converted into the corresponding α-pyrones, **17b** and **17d,e**, respectively, in the presence of strong acids.

The synthesis of γ-lactones and spiro-γ-lactones has been the focus of recent interest thanks to their presence in a large number of natural products.[1] Of particular importance, however, is the preparation of functionalized

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