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# Photochemistry of Succinimides with a Cycloalkenylalkyl Group in the Side Chain. Competitive Norrish Type II and Paterno–Büchi Reactions[1)]

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Photolysis of *N*-[ω-(cycloalken-1-yl)alkyl]succinimides (**9c—f**) ($m \geqq 2$) afforded mainly azepinediones (**13c—f**) with ring enlargement as the Norrish type II cyclization products. In the case of $m=1$, spiro-azepinedione derivatives (**11a, b**) were obtained in addition to tricyclic nitrogen heterocycles (**10a, b**), the Norrish type II products. These spiro-azepinediones are probably formed *via* imide-oxetanes by the intramolecular Paterno–Büchi reaction of these succinimides in competition with the type II processes.

**Keywords**——*N*-[ω-(cycloalken-1-yl)alkyl]succinimide; Norrish type II reaction; oxetane formation; azepinedione; spiro compound; photochemistry

The photoreactions of cyclic imides (**1**) have been extensively studied and much information has been obtained on their photochemical behavior;[2,3)] one feature is a difference between the photoreactions of alicyclic imides and aromatic cyclic imides (*i.e.* phthalimides) with alkenes. In general, on irradiation with alkenes, alicyclic imides give oxetanes (**2** and **4**)[4)] but phthalimides give benzazepinedione (**3**)[3)] with ring enlargement by a two-carbon unit derived from the alkenes (Chart 1), except for the indole-phthalimide system which gives oxetanes.[5)] As for intramolecular oxetane formation in the succinimide system, however, only one example has been reported.[6)] Oxetanes are potentially useful intermediates in general synthesis,[7)] and in particular, intramolecular imide oxetanes are interesting candidates as intermediates for the synthesis of nitrogen-heterocycles in view of their complex structures containing a nitrogen atom. Thus, attempts to find oxetane formation (Paterno–Büchi reaction) are of continuing interest in the photochemistry of alicyclic imides. We now report the photochemical behavior of a series of *N*-[ω-(cycloalken-1-yl)alkyl]succinimides (**9**).

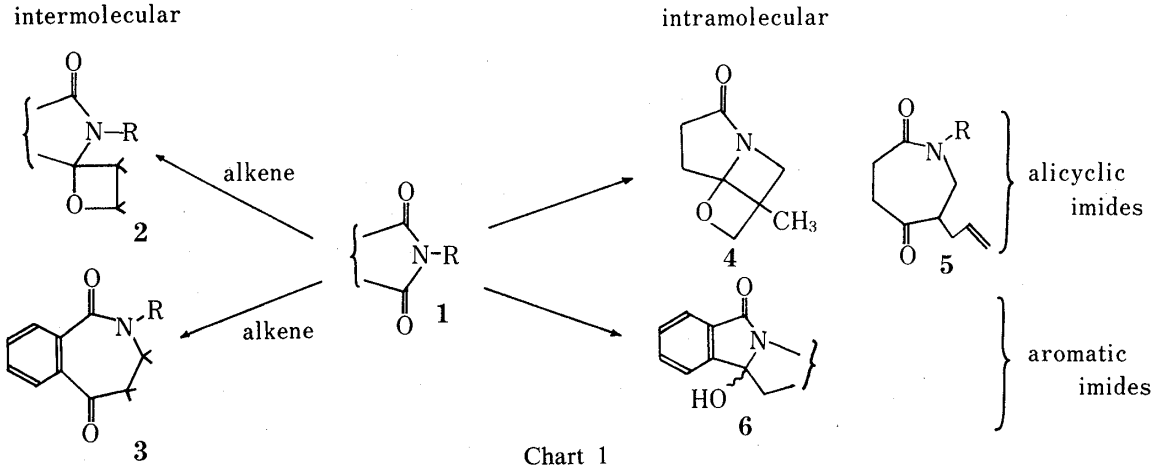


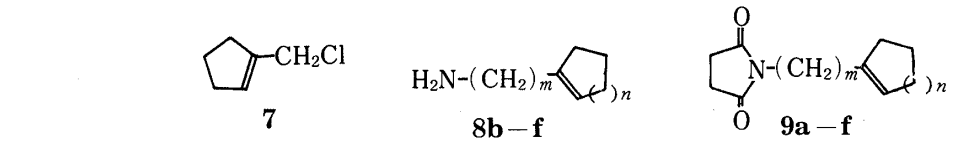

Chart 1

TABLE I. Preparation of the *N*-[ω-(Cycloalken-1-yl)alkyl]succinimides **9**

| Succinimide | Yield (%) | mp (°C) | Formula | Analysis (%) Calcd (Found) | | |
|---|---|---|---|---|---|---|
| | | | | C | H | N |
| **9a** | 68 | 66—67.5 | $C_{10}H_{13}NO_2$ | 67.02 | 7.31 | 7.82 |
| | | | | (66.88 | 7.46 | 7.65) |
| **9b** | 78 | 62—64 | $C_{11}H_{15}NO_2$ | 68.37 | 7.82 | 7.25 |
| | | | | (68.19 | 7.80 | 7.28) |
| **9c** | 82 | 52—53 | $C_{11}H_{15}NO_2$ | 68.37 | 7.82 | 7.25 |
| | | | | (68.18 | 7.76 | 7.32) |
| **9d** | 86 | 56—58 | $C_{12}H_{17}NO_2$ | 69.54 | 8.27 | 6.76 |
| | | | | (69.66 | 8.15 | 6.66) |
| **9e** | 89 | 48—50 | $C_{12}H_{17}NO_2$ | 69.54 | 8.27 | 6.76 |
| | | | | (69.39 | 8.25 | 6.55) |
| **9f** | 76 | 46—48 | $C_{13}H_{19}NO_2$ | 70.56 | 8.65 | 6.33 |
| | | | | (70.36 | 8.38 | 6.55) |

A series of succinimide derivatives **9b—f** (Chart 2) was prepared by melting a mixture of a corresponding amine (**8b—f**) and succinic anhydride in a usual manner, except in the case of **9a**, which was derived from succinimide and 1-(chloromethyl)cyclopent-1-ene (**7**). Melting points and analytical data of these imides (**9**) are listed in Table I. Representative photolysis of **9** was carried out in acetonitrile solution (10 mM) using a 120 W low-pressure mercury lamp at room temperature for 8 h.

In acetonitrile, photolysis of **9c—f** afforded mainly azepinedione derivatives (**13**), with ring enlargement by a two-carbon unit derived from the side chain. Irradiation of **9a, b** in acetonitrile was carried out in a similar manner for 20 h, but the substrate (**9a, b**) was recovered quantitatively. However, photolysis in an acetonitrile solution containing water (8 : 1, v/v) gave rise to tricyclic compounds (**10a, b**) and spiro compounds (**11a, b**) in moderate yields. Similarly, irradiation of **9b** in methanol afforded a spiro compound (**12**). Interestingly, the photolysis of **9d** in acetonitrile (or methanol) provided compound **14** as a major product in addition to **13d** (Chart 2). These results are collected in Table II, and melting points and




| | a | b | c | d | e | f |
|---|---|---|---|---|---|---|
| *m* | 1 | 1 | 2 | 2 | 3 | 3 |
| *n* | 1 | 2 | 1 | 2 | 1 | 2 |

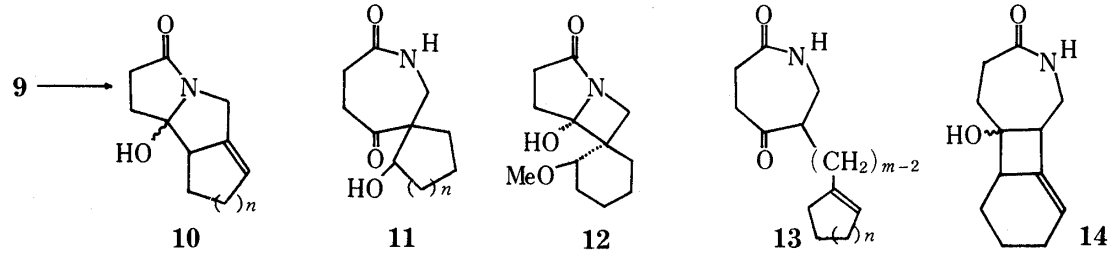



Chart 2

TABLE II. Distribution of the Photoproducts

| Substrate | | Solvent | Time (h) | Photoproduct yield (%) | |
|---|---|---|---|---|---|
| | | | | H-Abstraction | Oxetane |
| **9a** | $m=1$ $n=1$ | $CH_3CN$–$H_2O$ | 8 | **10a**: 17 ($\delta$) | **11a**: 43 |
| **9b** | $m=1$ $n=2$ | $CH_3CN$–$H_2O$ | 8 | **10b**: 12 ($\delta$) | **11b**: 49 |
| | | MeOH | 6 | — | **12**: 40 |
| **9c** | $m=2$ $n=1$ | $CH_3CN$ | 8 | **13c**: 18 ($\gamma$) | — |
| **9d** | $m=2$ $n=2$ | $CH_3CN$ | 8 | **13d**: 17 ($\gamma$)+**14**: 53[a] ($\gamma'$) | — |
| **9e** | $m=3$ $n=1$ | $CH_3CN$ | 8 | **13e**: 12 ($\gamma$) | — |
| **9f** | $m=3$ $n=2$ | $CH_3CN$ | 8 | **13f**: 14 ($\gamma$) | — |

a) Two-fold Norrish type II reaction.

TABLE III. Photoproducts from **9**

| Product | mp (°C) | Appearance (Recryst. solvent) | Formula | Analysis (%) Calcd (Found) | | |
|---|---|---|---|---|---|---|
| | | | | C | H | N |
| **10a** | 52—53.5 | Colorless needles (Benzene–hexane) | $C_{10}H_{13}NO_3$ | 67.02 (67.18 | 7.31 7.22 | 7.82 7.65) |
| **11a** | 121—124 | Colorless plates (Ethyl acetate) | $C_{10}H_{15}NO_3$ | 60.89 (60.88 | 7.67 7.62 | 7.10 7.22) |
| **10b** | 58—60 | Colorless plates (Benzene–hexane) | $C_{11}H_{15}NO_2$ | 68.37 (68.21 | 7.82 7.60 | 7.25 7.10) |
| **11b** | 118—120 | Colorless needles (Ethyl acetate) | $C_{11}H_{17}NO_3$ | 62.54 (62.28 | 8.11 8.01 | 6.63 6.57) |
| **12** | 176—178 | Colorless needles (Acetone) | $C_{12}H_{19}NO_3$ | 63.98 (63.88 | 8.50 8.36 | 6.22 6.46) |
| **13c** | 158—161 | Colorless plates (Ethyl acetate) | $C_{11}H_{15}NO_2$ | 68.37 (68.56 | 7.82 7.90 | 7.25 7.45) |
| **13d** | 169—171 | Colorless needles (Ethyl acetate) | $C_{12}H_{17}NO_2$ | 69.54 (69.68 | 8.27 8.44 | 6.76 6.88) |
| **14** | 190 (dec.) | Colorless plates (Ethyl acetate) | $C_{12}H_{17}NO_2$ | 69.54 (69.80 | 8.27 8.50 | 6.76 6.66) |
| **13e** | 148—150 | Colorless plates (Ethyl acetate) | $C_{12}H_{17}NO_2$ | 69.54 (69.62 | 8.27 8.32 | 6.76 6.88) |
| **13f** | 142—144 | Colorless plates (Ethyl acetate) | $C_{13}H_{19}NO_2$ | 70.56 (70.70 | 8.65 8.56 | 6.33 6.28) |

analytical data of the photoproducts are given in Table III.

Structural assignments of the photoproducts were made on the basis of spectroscopic data (Table IV). In the infrared (IR) spectra of **10a**, **b**, the bands at 3300 and 1670 $cm^{-1}$ indicated the presence of cyclol and lactam moieties, respectively.[8] In the proton nuclear magnetic resonance ($^1$H-NMR) spectra of **10a**, **b**, the presence of two doublets at 3.8 and 4.2 ppm with a coupling constant of 15 Hz suggested the presence of a methylene group adjacent to the nitrogen atom on the five-membered ring, indicating the ring closure of **9a**, **b**. Such a methylene group with a large coupling constant was absent in the substrates (**9a**, **b**), which gave singlet signals. The presence of a one-proton broad singlet at 5.7 ppm and a one-proton singlet at 6.4—6.8 ppm exchangeable with deuterium oxide ($D_2O$) suggested the presence of a vinyl proton and a hydroxyl group, respectively. The IR spectra of spiro

TABLE IV. Spectral Data for the Photoproducts

| Product | IR ($cm^{-1}$) | | MS ($m/z$) | $^1$H-NMR (in $CDCl_3$ $\delta$) |
|---|---|---|---|---|
| **10a** | 3300 | 1670 | 179 ($M^+$) | 1.0—2.2 (9H, m), 3.8, 4.2 (1H×2, d×2, $J$=15 Hz, NH–C$\underline{H}_2$), 5.7 (1H, br s, CH=), 6.4 (1H, s, –OH) |
| **11a** | 3200 | 1700 | 179 ($M^+-18$) | 0.9—2.5 (12H, m), 2.7—3.1, 2.2—2.5 (1H×2, |
| | 3050 | 1670 | | dd×2, $J$=6, 16 Hz, NH–C$\underline{H}_2$), 3.7 (1H, s, –OH), 4.0 (1H, m, –C$\underline{H}$–OH), 7.7 (1H, br s, –NH) |
| **10b** | 3300 | 1670 | 193 ($M^+$) | 1.0—2.3 (11H, m), 3.8, 4.2 (1H×2, d×2, $J$=15 Hz, NH–C$\underline{H}_2$), 5.7 (1H, br s, CH=), 6.8 (1H, s, –OH) |
| **11b** | 3260 | 1700 | 193 ($M^+-18$) | 0.9—2.7 (14H, m), 2.7—3.1, 2.2—2.5 (1H×2, |
| | 3200 | 1670 | | dd×2, $J$=6, 16 Hz, NH–C$\underline{H}_2$), 3.8 (1H, s, –OH), 4.0 (1H, m, C$\underline{H}$–OH), 7.7 (1H, br s, –NH) |
| **12** | 3350 | 1680 | 225 ($M^+$) | 1.0—3.0 (12H, m), 3.4 (3H, s, –OMe), 3.4—3.8 (3H, m, N–C$\underline{H}_2$+$H_3$CO–C$\underline{H}$), 4.2 (1H, s, –OH) |
| **13c** | 3200 | 1700 | 193 ($M^+$) | 1.4—2.3 (6H, m), 2.4—3.0 (4H, m), 3.1 (1H, m), 3.3— |
| | 3050 | 1670 | | 3.8 (2H, m, NH–C$\underline{H}_2$), 5.5 (1H, br s, CH=), 7.2 (1H, br s, NH) |
| **13d** | 3200 | 1700 | 207 ($M^+$) | 1.4—2.2 (8H, m), 2.4—3.0 (4H, m), 3.1 (1H, m), 3.3— |
| | 3050 | 1670 | | 3.8 (2H, m, NH–C$\underline{H}_2$), 5.5 (1H, br s, CH=), 7.2 (1H, br s, NH) |
| **14** | 3330 | 3180 | 207 ($M^+$) | 1.0—2.9 (12H, m), 3.1—3.6 (2H, m, NH–C$\underline{H}_2$), 3.5 (1H, |
| | 3250 | 1650 | | s, –OH), 5.4 (1H, s, CH=), 7.4 (1H, s, NH) |
| **13e** | 3200 | 1700 | 207 ($M^+$) | 1.1—2.9 (13H, s), 3.3—3.8 (2H, m, NH–C$\underline{H}_2$), 5.5 (1H, |
| | 3050 | 1670 | | br s, CH=), 7.2 (1H, br s, NH) |
| **13f** | 3200 | 1700 | 221 ($M^+$) | 1.1—3.0 (15H, m), 3.3—3.8 (2H, m, NH–C$\underline{H}_2$), 5.5 (1H, |
| | 3050 | 1670 | | br s, CH=), 7.4 (1H, br s, NH) |

compounds **11a**, **b** showed a carbonyl (1700 $cm^{-1}$) band and an amide carbonyl (1670 $cm^{-1}$) band. In the $^1$H-NMR spectra of **11a**, **b**, two doublet-of-doublet signals at 2.7—3.1 and 2.2—2.5 ppm ($J$=6 and 16 Hz) collapsed into two doublets ($J$=16 Hz) on addition of $D_2O$, suggesting the presence of a methylene group adjacent to NH on a ring. The presence of two protons exchangeable with $D_2O$ required NH (7.7 ppm, 1H, br s) and OH (3.7—3.8 ppm, 1H, s) groups. From the carbon-13 nuclear magnetic resonance ($^{13}$C-NMR) spectra of **11a**, **b**, the presence of a quaternary carbon as a singlet at 55—56 ppm was inferred, suggesting a spiro compound.[9,10] In addition, signals at 66—69, 175, and 212 ppm were assigned to a secondary carbon with a hydroxyl group, an amide carbonyl, and a carbonyl, respectively. The structure of **12** was similarly determined from the $^1$H- and $^{13}$C-NMR spectra. The $^1$H-NMR spectrum showed the presence of a methoxyl group and a hydroxyl group at 3.35 and 4.20 ppm, respectively. The $^{13}$C-NMR spectrum showed signals due to a quaternary carbon (s), a secondary carbon (d) with a methoxyl, a tertiary carbon (s) with a hydroxyl, and an amide carbonyl (s) at 57, 58, 102, and 176 ppm, respectively.

The structure of **13** was determined on the basis of the similarity of the spectral data to those of **11**. The structure of the tricyclic azepinone (**14**) was supported by the spectral data, which showed the presence of an amide carbonyl, a hydroxyl group, a one-proton vinyl, and two methine protons. The stereochemistry of these photoproducts is not yet known. However, the stereochemistry of **12** could be inferred by considering the involvement of an oxetane intermediate (**15**), as discussed later.

On the basis of the structural determination and the distribution of the products, plausible photochemical reaction pathways of the *N*-[$\omega$-(cycloalken-1-yl)alkyl]succinimides

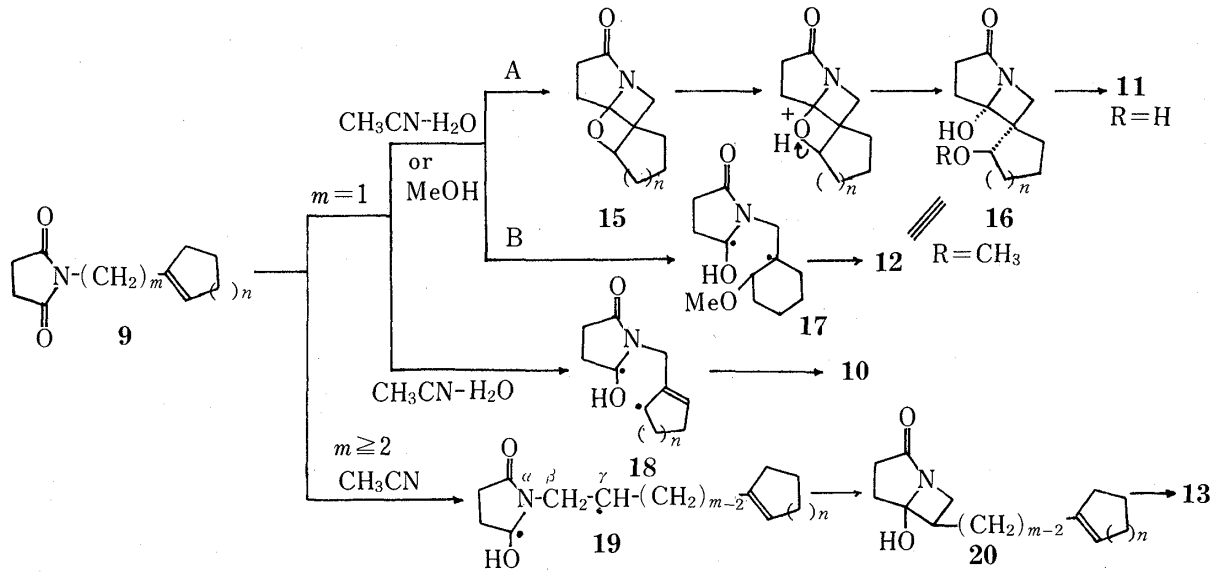


Chart 3

(**9**) are summarized in Chart 3. In the photoreactions of a series of *N*-[ω-(cycloalken-1-yl)alkyl]phthalimides[10] (the aromatic counterparts), when $m=1$, δ-hydrogen abstraction proceeds by way of an initial electron transfer (**21**) followed by biradical formation (**22**) to give a tetracyclic product (**23**) (Chart 4). In the case of the photolysis of *N*-(cycloalken-1-

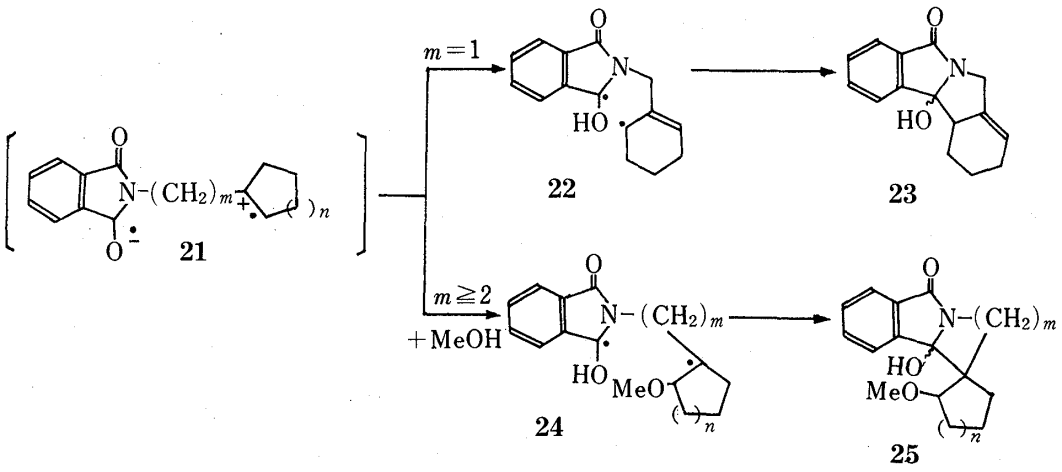


Chart 4

yl)methylsuccinimides (**9a**, **b**), $m=1$, in acetonitrile-water, the formation of the tricyclic compounds (**10a**, **b**) indicates formally similar photochemical behavior of δ-hydrogen abstraction, possibly by way of a biradical (**18**). In contrast, the formation of the spiro-azepinediones (**11a**, **b**) can reasonably be explained by an initial formation of intramolecular oxetanes **15** (A) followed by a sequence of reactions; heterolytic cleavage of oxetane, and retro-transannular ring opening of the spiro-azetidine intermediate (**16**). In methanol solution, a strained spiro compound (**12**) was isolated as a sole product, for which the pathway A may be considered. However, pathway B *via* a biradical intermediate (**17**) is also conceivable. In the reactions of a series of *N*-[ω-(cycloalken-1-yl)alkyl]phthalimides ($m\geqq 2$), pairs of stereoisomers were obtained, supporting the involvement of the biradical inter-

mediate (**24**). In contrast, from the photolysis of **9b** only one spiro compound (**12**) was isolated. This stereoselectivity can again be interpreted in terms of the intermediate oxetane (**15**), whose ring opening mode should control the conformation of the incoming nucleophile. Given the above interpretation, the stereochemistry of **12** can be formulated as in **16** (R= $CH_3$), which results from the rigid multicyclic structure of the precursor oxetane (**15**).

When there is a $\gamma$-hydrogen on the N-alkyl group as in the succinimides (**9c—f**), $m \geqq 2$, the major process appears to be the Norrish type II reaction forming an intermediate (**20**) by way of the biradical (**19**), which eventually leads to the ring-expanded compounds (**13c—f**). Such a phenomenon has been observed previously for certain succinimides,[11] and frequently for a number of phthalimides.[2] Further, formation of the tricyclic cyclobutane derivative (**14**) suggests the involvement of two-fold Norrish type II processes (Chart 5; **13d**→**14**).[12]

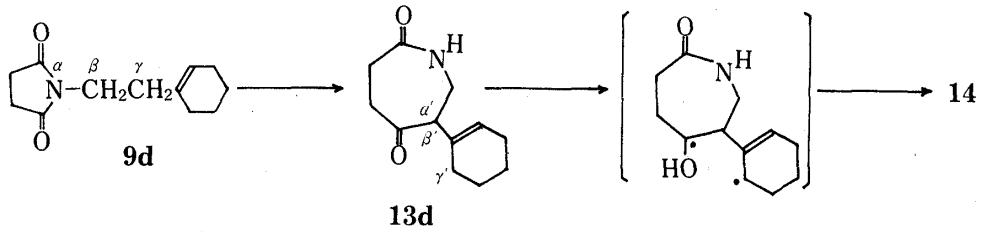



Chart 5

Irradiation of **13d** in acetonitrile for 2 h gave **14** quantitatively, supporting this assumption. Meanwhile, irradiation of the homologous derivatives (**13c**, **e**) gave no products such as **14**, resulting in recovery of the starting azepinediones in good yields. It is worth noting that the two-fold Norrish type II cyclization is controlled by such subtle structural differences. These results may be rationalized by considering the nature of the carbonyl group involved, reflecting an unfavorable distance between the carbonyl group and the $\gamma$-hydrogen to be abstracted compared with that in the homologue (**13d**). In this secondary Norrish type II reaction, the group involved is not an imide group but a simple (cyclic) ketone moiety, and photochemically[13] the $\gamma$-hydrogen abstraction (in **13d**) is greatly predominant over $\delta$-abstraction (in **13e**). The difference between **13d** and **13c** may be ascribed to the greater distance between the $\gamma$-hydrogen and the carbonyl oxygen in **13c**, which precludes $\gamma$-hydrogen abstraction.[14]

The above results, coupled with those reported in the previous papers,[1a,6,9,15] suggest that in the photoreactions of *N*-[$\omega$-(cycloalken-1-yl)alkyl]succinimides (**9**), $\gamma$- and $\delta$-hydrogen abstraction processes (Norrish type II) proceed predominantly over electron transfer processes which are common in the corresponding phthalimide series, even when there is an alkenyl group on the N-alkyl side chains. In competition with such type II processes, intramolecular oxetane formation is probably also a major process although the oxetanes themselves were not directly isolated, probably due to the instability inherent in their strained tetracyclic structure.

## Experimental

All melting points were determined on a Yamato melting point apparatus, model MP-21, and are uncorrected. Infrared (IR) spectra were recorded on a Shimadzu IR-400 spectrometer. Nuclear magnetic resonance (NMR) spectra were taken on a Hitachi R-40 spectrometer and a JEOL FX 60 spectrometer. Chemical shifts are reported in parts per million ($\delta$) relative to tetramethylsilane (TMS, 0.0 ppm) as an internal standard. The abbreviations used are as follows: s, singlet; d, doublet; t, triplet; m, multiplet. Mass spectra (MS) were determined with a Shimadzu-LKB 9000 gas chromatograph-mass spectrometer equipped with a direct inlet system.

Irradiations of succinimide derivatives in 10 mM solution were conducted using a 120 W low-pressure mercury lamp and a water-cooled quartz immersion well (Eikosha EL-J-120). Stirring of the reaction mixture was effected by

the introduction of a stream of nitrogen at the bottom of the outer jacket. All column chromatography was conducted using silica gel (Merck, Kieselgel 60, 70—230 mesh).

**1-(Chloromethyl)cyclopent-1-ene 7**——Compound **7** was prepared from 2-methylenecyclopentanol and thionyl chloride according to the procedure of Sato,[16] bp 62—64 °C (11 mmHg) [lit.[16] bp 58—59 °C (11 mmHg)].

**1-Cyclohexene-1-methanamine 8b**——Cyclohexenecarbonitrile prepared from cyclohexanone cyanohydrin was reduced with $LiAlH_4$ to give the amine **8b**, bp 62—65 °C (18 mmHg) [lit.[17] bp 55—57 °C (12 mmHg)].

**1-Cyclopentene-1-ethanamine 8c**——1-Cyclopenteneacetonitrile prepared from cyclopentanone and cyanoacetic acid was reduced with $LiAlH_4$ to give **8c**, bp 66—68 °C (14 mmHg) [lit.[18] bp 49—50 °C (10 mmHg)].

**1-Cyclohexene-1-ethanamine 8d**——1-Cyclohexeneacetonitrile prepared from cyclohexanone and cyanoacetic acid was reduced with $LiAlH_4$ to give **8d**, bp 82—84 °C (18 mmHg) [lit.[18] bp 53—54 °C (2.5 mmHg)].

**1-Cyclopentene-1-propanamine 8e**——The amine (**8e**) was prepared from 2-(cyclopenten-1-yl)propionitrile according to the procedure of Wittekind *et al.*,[19] bp 105—106 °C (20 mmHg). IR $\nu_{max}^{neat}$ $cm^{-1}$: 3400 (NH). MS *m/z*: 125 ($M^+$). $^1$H-NMR ($CDCl_3$) $\delta$: 1.2—1.8 (10H, m), 2.8 (2H, t, $J$=8 Hz), 4.6 (2H, br s, $-NH_2$), 5.5 (1H, br s, a vinyl proton).

**1-Cyclohexene-1-propanamine 8f**——The amine **8f** was prepared from 2-(cyclohexen-1-yl)propionitrile using the method described above for **8e**, bp 100—102 °C (18 mmHg) [lit.[19] bp 103—104 °C (20 mmHg)].

**Synthesis of Succinimide Derivatives 9**——General Procedure: The succinimide **9a** was obtained as follows. A mixture of succinimide, $K_2CO_3$, and **7** in *N,N*-dimethylformamide was stirred for 15 h at room temperature. After removal of the solvent, the residue was treated with chloroform and water. The chloroform layer was further washed with water, dried over anhydrous $Na_2SO_4$, and concentrated *in vacuo*. The other succinimide derivatives **9b—f** were obtained by fusion of a mixture of the corresponding amine and succinic anhydride in the usual manner. The melting points of these imides are listed in Table I.

**Irradiation of 9**——General Procedure: A solution of **9** in acetonitrile (10 mM) was irradiated with a 120 W low-pressure mercury lamp for 8 h under a nitrogen atmosphere. After removal of the solvent *in vacuo*, the residue was chromatographed over silica gel and the products were purified by recrystallization. The properties of photoproducts are listed in Table III.

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