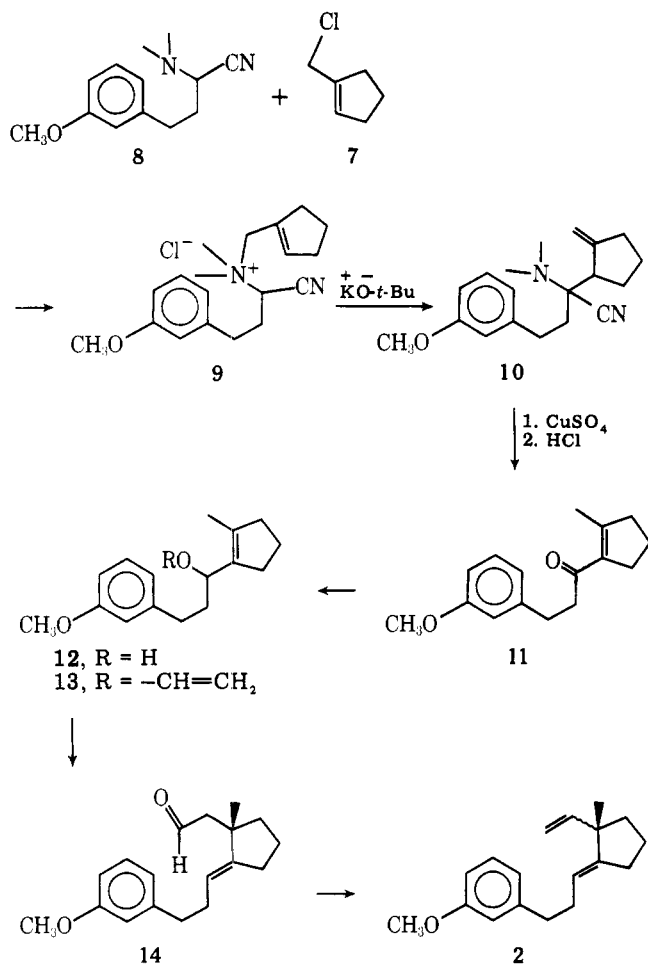


Scheme II



aqueous in THF, 8 h) forms enone **11** [46% from **8**: IR 1680, 1650 cm^{-1} ; $^1\text{H NMR}$ δ 2.05 (allylic CH_3)]. Reduction (**11** to **12**, LiAlH_4 , ether, 15 min), vinyl ether exchange [**12** to **13**, ethyl vinyl ether, $\text{Hg}(\text{OAc})_2$], and Claisen rearrangement affords aldehyde **14** [55% from **11**; IR 2740, 1725 cm^{-1} ; $^1\text{H NMR}$ δ 9.51, 5.12 (aldehyde and vinyl H's)] with the transoid geometry of the trisubstituted olefin in **14** (Scheme II) resulting from this rearrangement. Diene **2** was cleanly formed by reduction (LiAlH_4 , THF) and dehydration using the multiple step procedure of Sharpless (MsCl , $o\text{-NO}_2\text{C}_6\text{H}_4\text{SeNa}$, H_2O_2 , Δ).¹⁴

The ease with which we have been able to prepare steroid **1** with the all trans natural configuration starting from simple starting materials via stitching and riveting has encouraged us to pursue more complex natural products, the report of which will be forthcoming.

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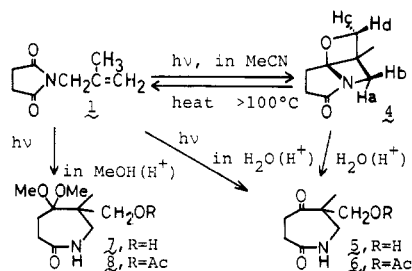
Formation of Intramolecular Oxetanes in the Photolysis of *N*-2-Alkenyl Alicyclic Imides

Summary: On irradiation in acetonitrile, *N*-(2-methylallyl)-succinimide (**1**) underwent intramolecular ring closure to give oxetane **4**. On the other hand, in weakly acidified methanol (or water) **1** gave the corresponding ring-enlarged compound **7** (or **5**) via oxetane **4**.

Sir: We wish to report on the first example of intramolecular oxetane formation in the photolysis of imides.^{1,2} *N*-(2-Methylallyl)succinimide (**1**), *N*-allylsuccinimide (**2**), and *N*-allylglutarimide (**3**) were examined in this work.

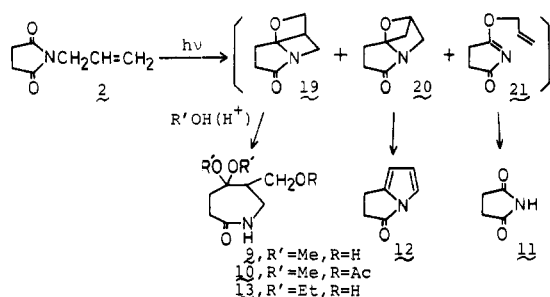
Irradiation of **1** (0.05 M) in acetonitrile with a 120-W low-pressure Hg-arc lamp for about 120 h gave, after evaporation of the solvent, an oily product **4** almost quantitatively. After a prolonged heating at about 100 °C, **4** decomposed into the starting material **1**. The structure of **4** (oxetane) is assigned on the basis of its ^{13}C and ^1H NMR spectra.³ The ^{13}C NMR spectrum of **4** revealed the presence of eight different carbon atoms: δ (CDCl₃) 14, 15, 27, 30, 50 (NCC), 59 (OCC), 79 (NCO), 181 (NC=O). In the ^1H NMR spectrum the observed long-range coupling between H_a and H_c , which is confirmed by the spin decoupling, clearly demonstrates the fixed W configuration ($\text{H}_a\text{C}(\text{CCH}_2)_c$) for **4**: δ (CDCl₃) 1.32 (s, 3 H, CH_3), 1.9–2.9 (m, 4 H, $-\text{CH}_2\text{CH}_2-$), 3.68 (dd, $J = 2, 9$ Hz, 1 H, H_a), 4.10 (d, $J = 9$ Hz, 1 H, H_b), 4.36 (dd, $J = 2, 6$ Hz, 1 H, H_c), 4.69 (d, $J = 6$ Hz, 1 H, H_d). By treatment with aqueous acid, **4** was converted to **5** (oil), then to acetate **6**: mp 111.0–112.5 °C; $^1\text{H NMR}$ (CDCl₃) δ 1.02 (s, 3 H, CH_3), 2.04 (s, 3 H, OAc), 2.4–3.0 (m, 4 H), 3.24 (dd, $J = 6, 16$ Hz, 1 H), 3.44 (dd, $J = 6, 16$ Hz, 1 H), 4.20 (br s, 2 H, CH_2OAc), 7.20 (br t, 1 H, NH); IR (KBr) 3320, 3090 (NH), 1737 (ester), 1706 (keto), 1663 (amide) cm^{-1} . Irradiation of **1** in water acidified with a trace of hydrochloric acid also gave **5** in a good yield. On the other hand, irradiation of **1** (0.05 M) in acidic methanol acidified with a trace of hydrochloric acid for about 20 h afforded a ketal **7** (88%): mp 160.0–161.0 °C; $^1\text{H NMR}$ (CDCl₃) δ 0.98 (s, 3 H, CH_3), 1.8–2.6 (m, 4 H, $-\text{CH}_2\text{CH}_2-$), 3.34 (s, 3 H, OCH₃), 3.39 (s, 3 H, OCH₃), 2.8–4.0 (m, 5 H), 6.80 (br t, 1 H, NH); IR (KBr) 3400 (OH), 3240, 3070 (NH), 1655 (amide) cm^{-1} . Acetate of **7** (**8**): mp 124.0–126.0 °C; $^1\text{H NMR}$ (CDCl₃) δ 1.02 (s, 3 H, CH_3), 2.06 (s, 3 H, OAc), 1.8–2.6 (m, 4 H, $-\text{CH}_2\text{CH}_2-$), 3.28 (s, 3 H, OCH₃), 3.34 (s, 3 H, OCH₃), 2.8–3.5 (m, 2 H), 4.02 (d, $J = 12$ Hz, 1 H), 4.23 (d, $J = 12$ Hz, 1 H), 6.36 (br t, 1 H, NH); IR (KBr) 3200, 3080 (NH), 1735 (ester), 1670 (amide) cm^{-1} (Scheme I).

Scheme I



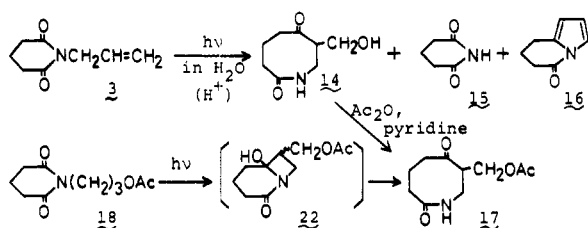
In acetonitrile, photolysis of **2** gave no detectable products even after irradiation for 160 h. However, irradiation of **2** (0.05 M) in acidified methanol for 50 h gave, after chromatography (SiO_2), a crystalline compound **9** (70%), mp 123.5–124.5 °C, as the major product. Acetate of **9** (**10**): mp 153.0–154.0 °C. The minor products were succinimide **11** (~5%) and 1,2-dihydro-3*H*-pyrrolizin-3-one **12** (~5%). **12**: mp 72.5–74.0 °C (lit. 71 °C);⁴ $^1\text{H NMR}$ (CDCl_3) δ 3.02 (s, 4 H), 6.02 (d, 1 H), 6.50 (t, 1 H), 7.10 (d, 1 H); IR (KBr) 1730 (C=O), 1565 (C=C), 1280 cm^{-1} . Similarly, irradiation of **2** in ethanol gave **13** (70%), mp 132.0–133.5 °C, together with **11** (~10%) and **12** (~10%) (Scheme II).

Scheme II



Again, irradiation of **3** in acetonitrile gave no products, but photolysis of it (0.05 M) in acidified water for about 50 h gave **14** (~65%), glutarimide **15** (~2%), and an oily product **16** (~15%) after chromatography (SiO_2). **14**: mp 110.0–113.0 °C. Acetate of **14** (**17**): mp 145.0–147.0 °C. We obtained the same compound, **17**, by another route: photolysis of *N*-(3-acetoxypyrrol)glutarimide (**18**) in acetonitrile in a yield of 30%^{2a,b} (Scheme III).

Scheme III



These results unambiguously disclose the formation of intramolecular oxetanes in the photolysis of *N*-2-alkenyl alicyclic imides. Oxetane **4** obtained in the photolysis of **1** is the initial photoproduct without doubt. By treating in methanol or water it converts to **7** or **5**. Similarly, in the photolysis of **2** or **3**, we can safely conclude that oxetanes could be possible intermediates. For example, in the photolysis of **2** in acidified methanol oxetane **19** converts to the final product **9**, and the formation of **12** may be explainable in terms of the decomposition of oxetane **20**. To support our conclusion, it was reported that 5-oxa-1-methylbicyclo[2.1.1]hexane, which is one of the oxetanes obtained from the photolysis of 5-hexen-2-one, easily decomposed to a mixture of methylcyclopentadienes even under mild conditions.^{1c} In the photolysis of **2** in methanol, **11** was also obtained. The formation of **11** we may reasonably explain taking into account that the nucleophilic attack of solvent to **21** resulted from the "photo-Cope reaction".^{1e,5}

So far as our researches are concerned the oxetane formation reaction should be regarded as one of the most typical photochemical reactions of imides. The detailed mechanism of this reaction is under investigation.

References and Notes

- (1) It is well known that a wide variety of carbonyl compounds undergo photocycloaddition with olefins to form oxetane.^{1a} Especially, photochemical reaction of γ,δ -unsaturated carbonyl compounds often results in formation of intramolecular oxetanes.^{1b-c} In addition, oxetane formation of some types of esters has been recently reported, and its mechanisms have been investigated in detail.^{1d-e} (a) N. J. Turro, "Molecular Photochemistry", W. A. Benjamin, New York, N.Y., 1966, Chapter 6; (b) R. Srinivasan, *J. Am. Chem. Soc.*, **82**, 775 (1960); (c) N. C. Yang, M. Nussim, and D. R. Coulson, *Tetrahedron Lett.*, 1525 (1965); (d) S. R. Kurowsky and H. Morrison, *J. Am. Chem. Soc.*, **94**, 507 (1972); (e) J. D. Dalton and S. J. Tremont, *ibid.*, **97**, 6916 (1975), and papers cited therein; (f) Y. Odaira, T. Shimadaira, and S. Tsutsumi, *Chem. Commun.*, 757 (1967); (g) T. Tominaga, Y. Odaira, and S. Tsutsumi, *Bull. Chem. Soc. Jpn.*, **40**, 2451 (1967); (h) Y. Shigemitsu, H. Nakai, and Y. Odaira, *Tetrahedron*, **25**, 3039 (1969); (i) Y. Shigemitsu and Y. Odaira, *Tetrahedron Lett.*, 2887 (1971); (j) Y. Katsuhara, Y. Shigemitsu, and Y. Odaira, *Bull. Chem. Soc. Jpn.*, **44**, 1169 (1971); (k) R. A. Neunteufel and D. R. Arnold, *J. Am. Chem. Soc.*, **95**, 4080 (1973); (l) T. S. Cantrell, *J. Chem. Soc., Chem. Commun.*, 468 (1973).
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