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# Synthesis and Photochemistry of Heterocyclic Norbornenyl Ketones

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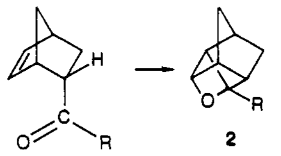
A series of *endo*-5-norbornenyl ketones 1 was prepared which contained the following heterocyclic rings: 2-furyl, 2-thienyl, *N*-methyl-2-pyrryl, 3,5-dimethyl-4-isoxazolyl, 5-methyl-3-isoxazolyl and 2,5-dimethyl-4-oxazolyl groups. Oxetanes 2 were produced from the ketones either by direct irradiation ($\lambda > 300$ nm) or by use of photosensitizers. The two isoxazolyl systems were irradiated at 254 nm and found to lead to additional products, two of which were identified as 2*H*-azirines 16. It is probable that the latter were formed from an upper level excited state.

Since its initial discovery by Srinivasin[2] in 1961, the intramolecular oxetane reaction has evolved from the status of an arcane, low-efficiency photoisomerization to that of a versatile synthetic strategem. For example, two recent reviews[3] cite more than a hundred examples involving an impressive variety of substrates. Early work by Yang and Morrison and their co-workers[4] highlighted complexities in the mechanistic details of these reacttions. These studies stimulated our interest in the synthetic potential of this reaction, and we undertook a detailed study of the photochemistry of a series of *endo*-5-acylnorbornenes 1.[5] This choice of substrate turned out to be fortuitous because only a single regioisomer 2 is formed and, in most cases, no byproducts are formed. Thus, high yields of oxetanes with a wide variety of substituents can be obtained.



1 2

The high chemical efficiencies of these reactions are attributable to the very fast rates of interaction between the excited carbonyl groups and the double bonds. We have estimated rates of exciplex formation as fast as $10^{11}$ $s^{-1}$ for aliphatic substituents, for example. Clearly, very few other events can compete with oxetane formation, and we have exploited this aspect of the reaction to study the kinetics of other fast reactions that cannot be readily monitored by conventional means.[5,6]

We now report on another unexplored realm in this series, namely, the photochemistry of heterocyclic derivatives of 5-acylnorbornenes. As a class, these systems present some novel aspects, both from photochemical as well as photophysical viewpoints. They are of interest synthetically because some intermolecular analogues have been shown to lead to photocycloadditions which involve both the carbonyl groups (oxetane formation) and the heterocyclic rings (cyclobutane formation).[7] Another intriguing aspect concerns the role that ring-rearrangement reactions might play before or after oxetane formation.[8,9]

For these and other reasons we synthesized and irradiated the following derivatives of 1: R = 2-furyl (3), 2-thienyl (4), 1-methyl-2-pyrrolyl (5), 3,5-dimethyl-4-isoxazolyl (6), 5-methyl-3-isoxazolyl (7), and 2.5-dimethyl-4-oxazolyl (8).

## Syntheses

It was anticipated that ketones 3–7 would be sensitive to strong acids and bases, given the possibilities for epimerization and cleavage. We therefore developed several mild procedures for their preparation.

The furyl ketone 3 was obtained by reaction of 5-norbornene-2-carboxylic acid with a cold solution of 2-furyllithium (eq 1). The pure endo isomer was obtained in 28% yield by flash chromatography. A mild acylation proce-

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[7] (a) Arnold, D. R.; Clarke, B. M. Jr. *Can. J. Chem.* **1975**, *53*, 1. (b) Cantrell, T. S. *J. Org. Chem.* **1977**, *42*, 3744.

[8] Salem, L. *J. Am. Chem. Soc.* **1974**, *96*, 3486.

[9] For a review, see: Padwa, A., *Rearrangements in Ground and Excited States*: De Mayo, P., Ed.; Academic: New York, 1980; Vol. 3, pp 518–529.

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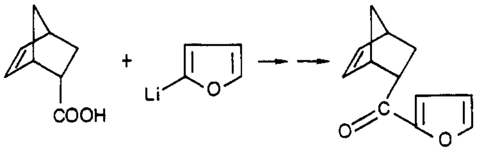

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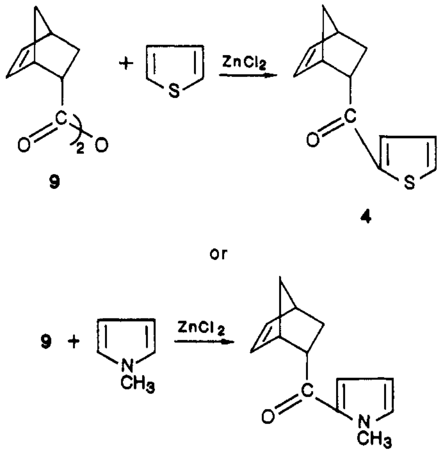
(1)

dure was developed for the preparation of the thienyl and *N*-methylpyrrolyl ketones **4** and **5**. This sequence involved treatment of the heterocycles with a zinc chloride: 5-norbornene-2-carboxylic anhydride (**9**) complex (eq 2). The pure endo isomers were isolated in low yields (~10%) by flash chromatography.



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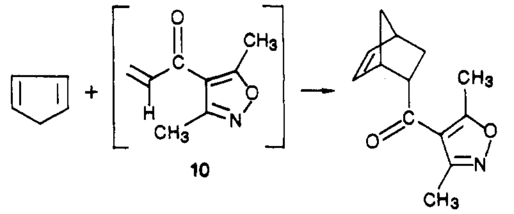
(2)

Both of the isoxazole ketones **6** and **7** were prepared more efficiently by a third method that involved Diels–Alder reactions between 1,3-cyclopentadiene and the appropriate vinyl ketones **10** and **11** (eq 3 and 4). Vinyl ketone **10** was prepared by oxidation of the vinyl alcohol **12** formed from the reaction of 3,5-dimethylisoxazole-4-carbaldehyde (**13**) and vinylmagnesium bromide (eq 5). An analogous synthesis of **11** was investigated but proved to be difficult to scale-up. Instead, vinyl ketone **11** was generated in situ by pyrolysis of the Mannich base **14** of methyl 5-methylisoxazolyl ketone **15** (eq 6).



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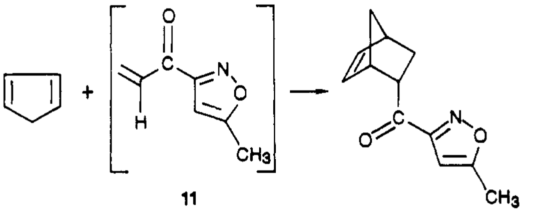

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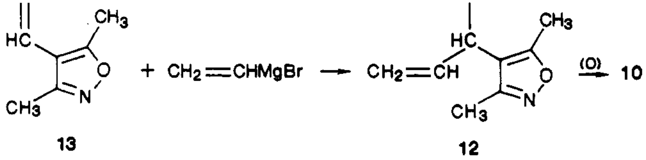

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12

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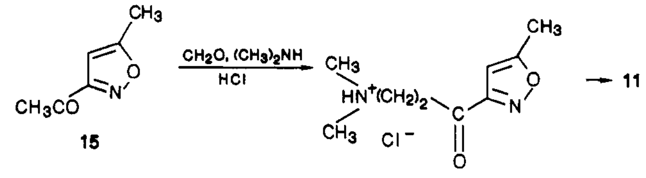

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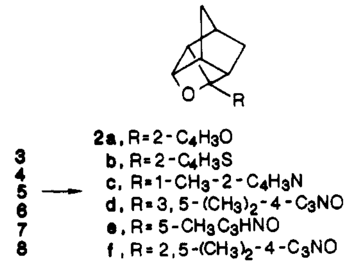
14

(6)

## Results and Discussion

Compounds **5**, **6**, and **7** cleanly formed oxetanes assigned structures **2c**, **2d**, and **2e**, respectively, upon irradiation with long-wavelength UV light (λ > 300 nm) (eq 7). The furyl and thienyl systems **3** and **4** formed oxetanes **2a** and **2b** only under sensitized irradiation conditions using acetophenone or fluorene[10] ($E_T$ = 68 kcal/mol) as donor. In no case was any evidence found for other kinds of cycloadducts. Although **2a–c** could not be isolated due to instability, $^1$H NMR spectra[5] taken during irradiations clearly indicated their presence. Oxetanes **2d,e** were stable and could be characterized as pure products.



(7)

Formation of oxetanes to the exclusion of other cycloadducts is a further reflection of the high efficiency of oxetane formation in 5-acylnorbornenes.[11] The lack of reactivity of the singlet states of the thienyl and furyl ketones may be a reflection of the zwitterionic nature of these states.[7,8] In any event, the triplet states of these ketones appear to react normally to give oxetanes.

The second phase of these studies dealt with the effects of short wavelength irradiation on the isoxazole ketones **6** and **7**. Others[9] have shown that related ketones undergo ring contraction to form 2*H*-azirines on excitation at 254 nm. It was of interest to determine whether this rearrangement could compete with oxetane formation and whether or not the proximate norbornene double bond would serve as a trap for intermediate(s), e.g., nitrenes, in these rearrangements.[9] Further, a detailed MO study[12] of this rearrangement led to the conclusion that this photoreaction might be adiabatic; i.e., the lowest excited singlet state of isoxazole can lead to the lowest excited singlet state (carbonyl, n,π*) of the 2*H*-azirine. Because our system has an additional carbonyl group in conjugation with the heteroring, the analogy is imperfect, but we were nevertheless intrigued by the possibility of direct, i.e., one photon, formation of the oxetane of the 2*H*-azirine via excitation of the isoxazolyl ketone.

In the event, irradiation of **7** at 254 nm led to a complex mixture and a small amount of **2e**. Irradiation of **6** at 254 nm produced a constant mixture of isomers identified as diastereomeric 2*H*-azirines **16** and oxetane **2d**. The

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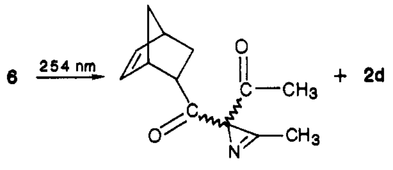
[10] Engel, P. S.; Monroe, B. M. *Adv. Photochem.* **1971**, *8*, 297.

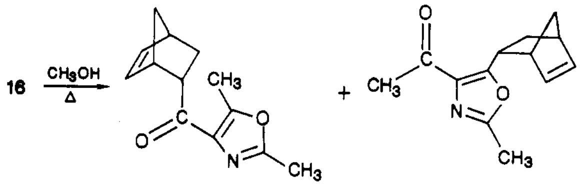
[11] In earlier studies we calculated an effective molarity (EM) for this reaction of ca. $10^4$: Sauers, R. R.; Valenti, P. C.; Crichlow, C. A. *J. Am. Chem. Soc.* **1982**, *104*, 6378.

[12] Tanaka, H.; Matsushita, T.; Osamura, Y.; Nishimoto, K. *Int. J. Quantum Chem.* **1980**, *18*, 463.



**16**

structures of **16** were assigned on the basis of a characteristic infrared absorption at 5.56 μm[13] and high-field paired methyl resonances in the $^1$H NMR at δ 2.13, 2.20 and 2.53, 2.56. In addition, heating the mixture in methanol effected conversion to a mixture of two new isomers that are believed to be oxazoles **8** and **17**. This reaction appears to be general for 3-acyl-2*H*-azirines.[13a] Isomer **8** was characterized by its rapid conversion to an oxetane **2f** on irradiation at 300 nm.



**8** **17**

The photochemistry of **6** was further characterized by measurement of the following quantum yields: $\phi^{300}{}_{2d}$ = 0.11 ± 0.01; $\phi^{254}{}_{2d}$ = 0.024 ± 0.03; $\phi^{254}{}_{16}$ = 0.024 ± 0.003. Attempts to quench the efficiency of oxetane formation at 350 nm by use of 0.1 M DABCO or 0.1 M *trans*-dicyanoethylene were unfruitful (±10%). In addition, irradiation at 254 nm in benzene (70% absorption) led to the same mixture of products that was obtained in acetonitrile.

The remarkable wavelength effect on the photochemistry of **6** can most simply be interpreted in terms of two excited states. Evidently, an upper state produced at 254-nm partitions between formation of 2*H*-azirines and conversion to a carbonyl n,π* state that leads to oxetane **2d**. If it is assumed that the oxetane is formed from the same reactive stated in both cases, it can be calculated that about 22% of the upper states decay to the oxetane-forming state. In other words, the inefficiency associated with the reaction leading to 2*H*-azirines is *not* limited by oxetane formation. Some other radiationless process must be involved, possibly the revertible formation of a diradical or nitrene formed by cleavage of the N–O bond.[9,13,14] If this species is formed, it must be short-lived because we did not observe formation of an isomeric isoxazole as a consequence of bond rotation and reclosure at the other oxygen atom.[9,14] The question regarding adiabaticity cannot yet be answered until more is known about the intervention of these intermediates.

In summary, we have extended the generality of the photochemical oxetane synthesis **1** → **2** to include heterocyclic ketones **3**–**8**. In addition, we have described a novel wavelength effect in the photochemistry of **6** and **7**. This phenomenon is rare,[15] and we plan to investigate the photochemistry of model systems in more detail to gain a better understanding of these isomerizations.

## Experimental Section

Infrared spectra were determined on a Perkin-Elmer Model 727B spectrometer. Proton magnetic resonance spectra ($^1$H NMR) were determined in $CDCl_3$ on a Varian Model T-60 spectrometer using tetramethylsilane as internal standard. Integration data is consistent with the assigned structures (±10%). Absorption spectra were obtained on a Cary spectrometer, Model 17D, or a Perkin-Elmer Model 559 UV-vis spectrophotometer.

***endo*-Bicyclo[2.2.1]hept-2-en-5-yl 2-Furyl Ketone (3).** A solution of 2-furyllithium in ether was prepared by addition of anhydrous furan (11.28 g, 0.166 mol) to the butyllithium prepared from 3.44 g (0.496 mol) of lithium wire and 26.6 g (0.194 mol) of 1-bromobutane in 45 mL of dry ether in a nitrogen atmosphere. The reaction temperature was held at −20 °C during the addition (2.5 min), after which the reaction mixture was allowed to warm to 25 °C followed by heating at reflux for 4 h. Bicyclo[2.2.1]hept-2-ene-5-carboxylic acid (10.39 g, 0.075 mol) in 95 mL of dry ether was added over 22 min to the cold (−2 to +5 °C) solution of furyllithium. The resulting mixture was stirred at 0 °C for 10 min followed by rapid quenching by addition of 100 mL of water. The aqueous layer was extracted with ether (3X), and the organic extracts were combined and washed with aqueous $NaHCO_3$. The dried ($MgSO_4$) extracts were evaporated to yield 8.24 g (58.4%) of a viscous orange oil. Flash chromatography (90:10 petroleum ether/ethyl acetate) gave 5.30 g of pure endo ketone **3** and other fractions which contained the exo isomer. The endo isomer **3** was distilled at 70 °C (0.020 Torr) to give 3.93 g (27.8%) of a colorless oil: IR 5.99 μm; $^1$H NMR δ 1.42–2.24 (m, 4 H), 2.95 (m, 2 H), 3.38–3.78 (m, 1 H), 6.0 (m, 2 H), 6.56 (m, 1 H), 7.15 (t, *J* = 3 Hz, 1 H), 7.62 (br s, 1 H).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.87; H, 6.59.

***endo*/*exo*-Bicyclo[2.2.1]hept-2-ene-5-carboxylic Anhydrides (9).**[16] A mixture of 25 g (0.181 mol) of 5-bicycloheptene-2-carboxylic acid (ca. 75% endo isomer by $^1$H NMR analysis) and 18.32 g (0.181 mol) of triethylamine in 362 mL of anhydrous ether was stirred at room temperature for 10 min under a dry nitrogen atmosphere. To the yellow solution was added 61.28 g (0.229 mol) of phenyl *N*-phenylphosphoroamidochloridate in one portion. The reaction mixture was stirred at room temperature for 30 min. The reaction was accompanied by the formation of a light gray precipitate. Evaporation of the ether in vacuo gave 19.35 g (82.5%) of an oily, off-white solid. The crude product was dissolved in $CCl_4$, and the insoluble material was removed by filtration. After removal of the $CCl_4$, there was left 17.85 g (75.8%) of anhydride **9** as an off-white solid.

***endo*-Bicyclo[2.2.1]hept-2-en-5-yl 2-Thienyl Ketone (4).** To a solution of 11.61 g (0.138 mol) of anhydrous thiophene in 29 mL of anhydrous ether was added 3.13 g (0.023 mol) of freshly fused, finely pulverized $ZnCl_2$ under a stream of dry nitrogen. To the stirred suspension was added 6 g (0.023 mol) of the carboxylic anhydrides **9** in one portion. Reaction was indicated by the appearance of a yellow-orange color within 5 min of the anhydride addition. The reaction was quenched after a 45-min reaction time by the addition of 30 mL of saturated $Na_2CO_3$ solution followed by stirring with the ether layer for 5 min. After separation of the layers, the ether layer was extracted twice with 30 mL of saturated $Na_2CO_3$ solution, dried over $MgSO_4$, and evaporated in vacuo to yield 3.61 g (76.8%) of a viscous orange oil. The crude product was redissolved in ether and extracted several times with 10% NaOH solution until infrared analysis indicated complete removal of anhydride. The etheral layer was dried over $MgSO_4$ and evaporated in vacuo to yield 1.99 g (42.4%) of a viscous orange oil. The crude product was distilled in vacuo (0.025 Torr) through a short-path still to yield 0.62 g (13.2%) of the endo/exo thienyl ketone as a viscous, colorless oil (84°C). Alternatively, endo thienyl ketone was isolated from the crude product by flash chromatography; yield, 1.00 g.

Distillation at 80–82 °C (0.025 Torr) gave 0.52 g (11%) of pure ketone **4**: IR 6.06 μm; $^1$H NMR δ 1.22–3.0, (m, 7 H), 3.6 (m, 1 H), 5.92 (m, 2 H), 7.08 (dd, *J* = 6, 4 Hz, 2 H), 7.5 (dd, *J* = 5, 2

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[13] (a) Singh, B.; Ullman, E. F. *J. Am. Chem. Soc.* **1967**, *89*, 6911. (b) Ferris, J. P.; Trimmer, R. W. *J. Org. Chem.* **1976**, *41*, 13. (c) Sato, T.; Yamamoto, K.; Fukui, K.; Saito, K.; Hayakawa, K.; Yoshiie, S. *J. Chem. Soc., Perkin Trans. 1* **1976**, 783.

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[15] Turro, N. J.; Ramamurthy, V.; Cherry, W.; Farneth, W. *Chem. Rev.* **1978** *78*, 125.

[16] Mestres, R.; Paloma, C. *Synthesis* **1981**, 218.

Hz, 1 H), 7.6 (dd, $J = 4$, 2 Hz, 1 H).

Anal. Calcd for $C_{12}H_{12}OS$: C. 70.55; H, 5.92; S, 15.70. Found: C, 70.34; H, 5.75; S, 15.97.

***endo*-Bicyclo[2.2.1]bicyclohept-2-en-5-yl 2-*N*-Methylpyrryl Ketone (5).** To a solution of 11.86 g (0.046 mol) of the anhydrides **9** in 60 mL of anhydrous ether in a three-necked, round-bottomed flask was added 6.27 g (0.046 mol) of freshly fused, finely pulverized anhydrous $ZnCl_2$ under a stream of dry nitrogen. The reaction mixture was stirred at room temperature for 10 min. Complexation of the $ZnCl_2$ with the norbornenyl anhydride was evident by the immediate appearance of a deep yellow color. To the rapidly stirred reaction was added 11.19 g (0.138 mol, 3 equiv) of anhydrous *N*-methylpyrrole in one portion. Stirring was continued at room temperature under a nitrogen atmosphere for 5 h. Hydrolysis was effected by the addition of 60 mL of $H_2O$. After separation of the two layers, the ether solution was extracted with 20 mL each of a 10% NaOH solution (3X), washed with water (3X), dried over $MgSO_4$, and evaporated in vacuo to yield 8.42 g (91%) of a viscous yellow-orange oil. Partial decolorization to a yellow oil was effected by stirring the crude product as a solution in 100 mL of dry ether with 0.2 g of activated charcoal under a dry nitrogen atmosphere for 12 h at room temperature. Removal of the ether followed by distillation in vacuo 76–79 °C (0.030 Torr) through a Vigreux column gave 3.30 g (35%) of a viscous, colorless oil.

Purification by flash chromatography gave 2.69 g of pure endo ketone **5** from 8.19 g of crude product: IR 6.06 μm; $^1$H NMR $\delta$ 1.36–2.0 (m, 4 H), 2.82 (br s, 1 H), 3.15 (br s, 1 H), 3.55 (m, 1 H), 3.8 (s, 3 H), 5.95 (m, 3 H), 6.68 (t, 1 H), 6.9 (dd, $J = 4$, 2 Hz, 1 H).

Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.88; H, 7.74; N, 7.00.

**Vinyl(3,5-dimethyl-4-isoxazolyl)carbinol (12).** A solution of 15.43 g (0.123 mol) of aldehyde[17] **13** in 180 mL of dry ether was cooled in an ice bath and treated with 240 mL of a solution of vinylmagnesium bromide in tetrahydrofuran (1.0 M, 0.24 mol) under a nitrogen atmosphere. After the addition, the mixture was allowed to warm to room temperature followed by heating at reflux for 1.5 h. The reaction was quenched with saturated aqueous ammonium chloride and extracted with ether. The dried ($MgSO_4$) extracts were evaporated and distilled to give 15.28 g (81%) of alcohol **12**; bp 96–101 °C (0.075 Torr); $^1$H NMR $\delta$ 2.20 (s, 3 H), 2.33 (s, 3 H), 3.93 (b, 1 H), 5.07–5.40 (m, 3 H), 5.73–6.30 (m, 1 H).

***endo*-Bicyclo[2.2.1]hept-2-en-5-yl 3,5-Dimethyl-4-isoxazolyl Ketone (6).** The crude alcohol **12** (4.6 g, 0.030 mol) was dissolved in 40 mL of acetone, cooled to 0 °C, and treated with 8.6 mL of a 3.2 M solution of chromium trioxide in 4 M sulfuric acid. After oxidation was completed (TLC), brine was added, and the chromium salts were removed by filtration. The salts were washed with ether, and the filtrate was extracted with ether. The combined extracts were washed with aqueous sodium bicarbonate and brine and dried over $MgSO_4$. Cyclopentadiene (3.98 g, 0.060 mol) was added to the ether solution and the reaction mixture was kept at 25 °C for 15 h. The mixed ketones (endo/exo 85:15) were obtained as a yellow oil after evaporation of the solvents: yield, 5.55 g (85%).

Pure *endo*-**6** was obtained by flash chromatography (hexane-/ethyl acetate, 80:20): mp 44–46 °C; IR ($CCl_4$), 5.39 (s), 14.2 (m) μm; $^1$H NMR $\delta$ 1.20–3.5 (m, 7 H), 2.46 (s, 3 H), 2.66 (s, 3 H), 5.6–6.26 (m, 2 H); UV $\lambda_{max}$ ($CH_3CN$) 306 ($\epsilon$ 118), 228 nm ($\epsilon$ 6800).

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.81; H, 6.74; N, 6.19.

**$\beta$-(Dimethylamino)ethyl 5-Methyl-3-isoxazolyl Ketone Hydrochloride (14).** A mixture containing 12.51 g (0.10 mol) of 3-acetyl-5-methylisoxazole[18] (**15**), 8.93 g (0.11 mol) of 37% formalin, 8.16 g (0.10 mol) of dimethylamine hydrochloride, and 1.0 mL of concentrated hydrochloric acid was heated at reflux for 1 h. After cooling, water was removed by azeotropic distillation with ethanol. The hydrochloride salt **14** (9.42 g, 43%) precipitated and was removed by filtration; mp 128–131 °C dec; $^1$H NMR $\delta$ 2.50 (s, 3 H), 2.80 (s, 3 H), 2.87 (s, 3 H), 3.63 (m, 5 H), 6.27 (s, 1 H).

***endo*-Bicyclo[2.2.1]hept-2-en-5-yl 5-Methyl-3-isoxazolyl Ketone (7).** A solution of 2.18 g (0.010 mol) of the hydrochloride salt **14**, 2.00 g (0.030 mol) of cyclopentadiene, and 0.04 g of hydroquinone in 20 mL of methanol was heated in a sealed tube at 80–81 °C for 21 h. The methanol and excess cyclopentadiene were removed by evaporation, and the residue was purified by flash chromatography using an 80:20 mixture of hexane/ethyl acetate. There was obtained 1.84 g (89%) of a mixture of exo/endo isomers of **7**. Pure *endo*-**7** was obtained by successive crystallization from hexanes: mp 60–61 °C; IR ($CCl_4$) 5.88 (s), 13.9 (m) μm; $^1$H NMR $\delta$ 1.33–4.03 (m, 7 H), 2.50 (s, 3 H), 5.67–6.33 (q, 2 H), 6.33 (s, 1 H); UV ($CH_3CN$) $\lambda_{max}$ 320 ($\epsilon$ 77.5), 245 nm ($\epsilon$ 2940).

Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.90. Found: C, 71.09; H, 6.59; N, 6.77.

**Irradiations. a. Analytical.** The appearance of oxetanes during irradiation was monitored by $^1$H NMR spectroscopy by making use of the rate of appearance of doubled doublets at $\delta$ ~4.5[5] (HCO protons) and septets at $\delta$ ~3.4 (bridgehead protons). A new methyl resonance appeared at $\delta$ 3.7 during irradiation of **5**.

**b. Direct Irradiations.** Solutions 0.5–1.5 M in endo ketone in benzene or acetonitrile were purged with dry nitrogen or sealed under vacuum in 5-mm Pyrex or quartz NMR tubes. Irradiations were carried out in a Rayonet photoreactor using the 253.7-, 300-, or 350-nm bulbs.

**c. Sensitized Irradiations.** Sensitized irradiations of **3** and **4** were carried out at 300 nm by using sufficient quantities of fluorene or acetophenone to absorb >99% of the light.

**d. Results.** Direct irradiations of ketones **5**–**7** at 300 nm (Pyrex vessels) led to substantial amounts of oxetanes after a few hours time, and all eventually led to complete consumption of ketone. Long-term irradiations of **3** and **4** did not lead to any observable changes in the $^1$H NMR spectra.

Sensitized reactions on **3** and **4** rapidly led to new absorptions at $\delta$ 4.6, but with **4** these absorptions began to disappear on longer term irradiation. With **3** a ~70% conversion to **2a** could be realized. Irradiation of **6** in benzene at 254 nm produced **2d** and **16** in essentially the same ratio as was formed in acetonitrile.

**e. Product Isolation. Irradiation at 300 or 350 nm.** Attempts to isolate oxetanes **2a**–**c** led to intractable polymeric materials in all cases. In some experiments, oxetanes began to decompose during irradiation even when attempts were made to rigorously exclude oxygen and traces of acids.

With **6**, **7** and **17** the derived oxetanes were stable; they were isolated by evaporation of the solvent and purified by flash chromatography.

Oxetane **2d** was a colorless oil in 58% yield: IR ($CCl_4$) 6.94, 10.31 μm; $^1$H NMR $\delta$ 1.7 (br s, 4 H), 2.2 (m, 1 H), 2.33 (s, 3 H), 2.40 (s, 3 H), 2.8 (br, 2 H), 3.5 (m, 1 H), 4.78 (m, 1 H).

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.67; H, 6.92; N, 6.43.

Oxetane **2e** was obtained as a colorless oil, bp 43–45 °C (0.075 Torr), in 88% yield; IR (neat) 6.25, 10.2, 10.6 μm; $^1$H NMR $\delta$ 1.4–3.5 (m, 8 H), 2.45 (s, 3 H), 4.70 (m, 1 H), 6.07 (s, 1 H).

Anal. Calcd for $C_{12}H_{13}NO_2$; C, 70.91; H, 6.45; N, 6.89. Found: C, 70.73; H, 6.46; N, 6.88.

Oxetane **2f** was obtained as an oil, bp 50 °C (0.05 Torr): IR (film) 6.29 (s), 7.69 (s), 10.42 (s) μm; $^1$H NMR $\delta$ 1.33–3.60 (m, 8 H), 2.33 (s, 3 H), 2.36 (s, 3 H), 4.70 (q, 1 H).

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.67; H, 7.21; N, 6.62.

**f. Product Isolation Irradiation of 6 at 254 nm. 2-(5-Bicyclo[2.2.1]hepten-2-ylcarbonyl)-2-acetyl-3-methyl-2*H*-azirine (16).** Flash chromatography (80:20 benzene/ethyl acetate) of the photolysate gave oxetane **2d** (27%), azirine **16** (25%), and unreacted starting material (9%). The azirine was molecularly distilled: bp 52 °C (0.0125 Torr); IR ($CCl_4$) 5.56 (w), 5.93 (s), 14.3 (m) μm; $^1$H NMR $\delta$ 1.10–3.67 (m, 7 H), 2.13, 2.20 (2 s, 3 H), 2.53, 2.56 (2 s, 3 H), 5.60–6.20 (q, 2 H).

Anal. Calcd for $C_{13}H_{15}NO_2$; C, 71.86; H, 6.96; N, 6.45. Found: C, 71.77; H, 7.22; N, 6.75.

**Thermolysis of 16.** A solution of 0.17 g (0.078 mmol) of azirine **16** in 10 mL of methanol was heated at reflux for 9 h. Evaporation of the solvent gave a residue which was subjected to flash chro-

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(17) Natale, N. R.; Quincy, D. A. *Synth. Commun.* **1983**, *13*, 817.

(18) Cusmano, S. *Gazz. Chim. Ital.* **1948**, *78*, 622. A more efficacious route to this ketone has been developed and will be published separately.[19]

matography using an 80:20 mixture of hexane/ethyl acetate. *endo*-Bicyclo[2.2.1]hept-2-en-5-yl 2,5-dimethyl-4-oxazolyl ketone (**8**) was obtained as a white solid: mp 66-68°C; yield, 0.070 g (41%); IR ($CCl_4$) 5.90 (s) 13.9 (m) $\mu$m; $^1$H NMR $\delta$ 1.10-4.00 (m, 7 H), 2.50 (s, 3 H), 2.56 (s, 3 H), 5.67-6.27 (q, 2 H).

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.97; H, 7.26; N, 6.29.

**5-(Bicyclo[2.2.1]hept-2-en-5-yl)-2-methyl-4-acetyloxazole (17)** was obtained as an oil: yield, 0.050 g (29%); IR ($CCl_4$) 5.93 (s), 14.1 (w) $\mu$m; $^1$H NMR $\delta$ 1.10-4.16 (m, 7 H), 2.33 (s, 3 H), 2.46 (s, 3 H), 5.60-6.27 (q, 2 H).

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 68.10, 72.64, 73.18; H, 6.64, 7.99, 7.76; N, 6.07, 5.26, 4.07.

**Irradiation of 16.** Degassed solutions of 2*H*-azirine **16** in $CD_3CN$ were irradiated at 254, 300, and 350 nm for long periods with no significant change as monitored by $^1$H NMR. Under comparable conditions at 254 nm isoxazole **6** was consumed to the extent of ca. 85%.

**Quantum Yields.** Quantum yields were determined in the Rayonet reactor at 253.7 and 300 nm in degassed 1.0 M solutions in $CD_3CN$.[19] The rate of disappearance of ketone **6** was measured by $^1$H NMR or absorption spectroscopy and assumed to be equal to the rate of formation of oxetane **2d** and 2*H*-azirine **16** because no other productts (±5%) were seen. Light intensities were monitored by use of 0.15 M potassium ferric oxalate[20] ($\phi^{300\text{nm}} = 1.24$) and by 4-acetyl-3,5-dimethylisoxazole[21] ($\phi^{254\text{nm}}{}_{K} = 0.18 \pm 0.02$). Potassium ferric oxalate was freshly recrystallized before use, and all manipulations with actinometer solutions were done in the dark. After irradiation, an aliquot of the photolysate was added to a premixed solution of 2 mL of 0.1% *o*-phenanthroline, 0.5 mL of buffer, and 0.9 mL of 0.1 M $H_2SO_4$. After 1 h in the dark the concentration of $Fe^{2+}$ was calculated from the absorbance of the complex at 540 nm.

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**Registry No.** 1 (R = OH), 1195-12-6; **2a**, 110773-83-6; **2b**, 110773-84-7; **2c**, 110773-85-8; **2d**, 110773-86-9; **2e**, 110773-87-0; **2f**, 110773-88-1; **3**, 110773-89-2; **4**, 110773-90-5; **5**, 110773-91-6; *endo*-**6**, 110773-92-7; *exo*-**6**, 110773-93-8; *endo*-**7**, 110773-94-9; *exo*-**7**, 110773-95-0; **8**, 110773-96-1; **9**, 110773-97-2; **12**, 110773-98-3; **13**, 54593-26-9; **14**, 110773-99-4; **16**, 110774-00-0; **17**, 110796-29-7; furan, 110-00-9; thiophene, 110-02-1; *N*-methylpyrrole, 96-54-8; 3-formyl-5-methylisoxazole, 24068-54-0; cyclopentadiene, 542-92-7.

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[19] For more details, see: Van Arnum, S. D. Thesis, Rutgers University, 1987.

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# Photochemical and Thermal Transformations of 3-Benzyl-2(3*H*)-furanones and Related Substrates[1]

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Photochemical and thermal transformations of several 2(3*H*)-furanones are reported. Steady-state irradiations of 3-benzyl-3,5-diphenyl-2(3*H*)-furanone (**1a**) in benzene or methanol, for example, gave a mixture of 2,3,5-triphenylfuran (**3a**) (8-9%) and 1,3,5-triphenylbut-3-en-1-one (**6a**) (26-34%), along with 34-37% recovery of the unchanged starting material. Similar results were obtained with 3-benzyl-3-(4-methylphenyl)-5-phenyl-2-(3*H*)-furanone (**1b**) and 3-benzyl-3-(4-methoxyphenyl)-5-phenyl-2(3*H*)-furanone (**1c**) under analogous conditions. Upon direct irradiation, 3,3-dibenzyl-5-phenyl-2(3*H*)-furanone (**1d**), however, gave only 3-benzyl-1,4-diphenylbut-3-en-1-one (**6d**) (80-83%), whereas 3-benzyl-3-phenylphenanthro[9,10-*b*]furan-2(3*H*)-one (**1e**) gave only 2,3-diphenylphenanthro[9,10-*b*]furan (**3e**) (15-21%). On the other hand, 3-benzoyl-3,5-diphenyl-2(3*H*)-furanone (**1f**) gave only the bis lactone **10a** (72-75%) under direct photolysis. The bis lactones **10a-c** and the rearranged 5-benzyl-3,5-diaryl-2(5*H*)-furanones **9a-d** were the major products in the course of sensitized irradiation of **1a-d** in the presence of acetophenone in benzene. The thermolysis of **1a-d** also led to the formation of the rearrangement products **9a-d** in high yields (60-80%). Possible mechanisms of these various photochemical and thermal reactions are discussed in terms of singlet-mediated decarbonylation, triplet-sensitized homolysis of the benzyl-to-furanone bond and probable thermal [1,3]-sigmatropic shift of the benzyl group. The laser pulse photoexcitation (337.1 nm) of benzophenone in the presence of **1a-d** in benzene of acetonitrile produces the short-lived triplets of the 2(3*H*)-furanones ($\tau_T$ = 0.5-3.0 $\mu$s), which subsequently undergo bond cleavage leading to furanoxy radicals. The spectral and kinetic features of the triplets and the radicals are presented.

## Introduction

Photochemical and thermal transformations of several unsaturated lactones have been extensively investigated.[3-29] It has been observed that these lactones undergo a of phototransformations, namely, decarbonylation,[4,5,9,24,26]

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