Photochemical Rearrangements of 1,2-Benzisoxazolinones

LARRY J. DARLAGE, THOMAS H. KINSTLE,* AND C. L. MCINTOSH

Department of Chemistry, Iowa State University, Ames, Iowa 50010

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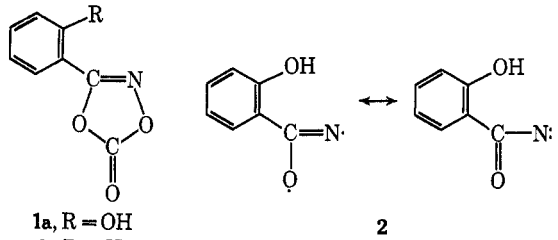
Irradiation of 3-hydroxy-1,2-benzisoxazole (**3**) results in the formation of benzoxazolinone (**4**). This photoisomerization is shown to occur predominantly *via* the keto tautomer **3b** since facile rearrangements of the *N*-alkyl-1,2-benzisoxazolinones (**19**) occur under similar photolytic conditions. A mechanism involving a diradical species is proposed for this reaction. Low temperature photolysis–infrared measurements support this mechanism while arguing against an isocyanate (**12**) or a spiro-α-lactam (**13**) intermediate. Sensitization studies conducted on **3** and **19a** indicate that the rearrangement occurs predominantly from the triplet state.

As part of our research program in mechanistic organic mass spectrometry, we have recently been engaged in investigating the behavior upon electron impact of a variety of hydroxamic acids and heterocyclic compounds. Our mechanistic interpretations have often been hampered by our lack of structural knowledge of gas phase ions, and indeed this is a most formidable problem in most mass spectral mechanistic studies.[1] In a particular instance, we were concerned with the nature of the major fragmentation pathway (loss of CO_2) of **1a**; *i.e.*, did the product ion have an ionized nitrene structure (**2**), or did cyclization to ion-



1a, R = OH
b, R = H

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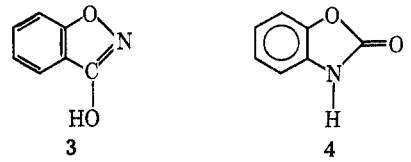
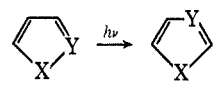


3 **4**

ized **3** occur?[2] Our approach included comparing the mass spectral behavior of authentic **3** with that of the $M - CO_2$ ion of **1a**. An interesting reaction of **3** was the loss of CO_2, a fragmentation reminiscent of the behavior of cyclic imides,[3] and indeed we discovered that the mass spectra of **3** and **4** were quite similar, both qualitatively and quantitatively. There often exist photochemical[4] and/or thermal[5] analogies to mass spectral processes, and indeed these analogies often provide valuable inferred information concerning the structures of mass spectral ions. We therefore embarked on investigations of the thermal[6] and photochemical behavior of **3** and **4** and describe here the results of our photolysis studies.

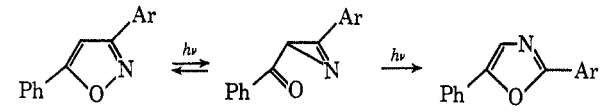
The photochemical behavior of five-membered aromatic compounds containing two heteroatoms has been described for a variety of systems. A general rearrangement process involving the formal interchange of two adjacent atoms has been found to occur as shown in Scheme I. Singh and Ullman[7] have documented a ring

SCHEME I



5 **6**

contraction–ring expansion sequence in the photoisomerization of 3,5-diarylisoxazoles to 2,5-diaryloxazoles by isolating the corresponding azirine intermediates (**7**).



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Other examples of this general mechanistic type have been postulated for additional isoxazoles,[8,9] and pyrazole derivatives.[10-12]

An alternate isomerization mechanism involving bicyclic intermediates such as **8** and **9** has been postu-

8 **9**

lated to explain the rearrangements of alkyl pyrazoles and imidazoles[13] and 2,5-diphenyloxazoles.[14] The various other heterocyclic rearrangements,[15] including condensed ring heterocycles,[10,12,16,17] have not yet been

* To whom correspondnce should be addressed: Department of Chemistry, Bowling Green State University, Bowling Green, Ohio 43403.

(1) (a) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden Day, San Francisco, Calif., 1967; (b) R. G. Cooks, *Org. Mass Spectrom.*, **2**, 481 (1969); (c) I. Howe, D. H. Williams, and R. G. Cooks, *ibid.*, **2**, 137 (1969).

(2) J. Sauer and K. K. Mayer, *Tetrahedron Lett.*, 319 (1968).

(3) J. L. Cotter and R. A. Dine-Hart, *ibid.*, **1**, 915 (1968), and references cited therein.

(4) (a) C. Fenselau, J. L. Young, S. Meyerson, W. R. Landis, E. Selke, and L. C. Leitch, *J. Amer. Chem. Soc.*, **91**, 6847 (1969). (b) H. Nakata, H. Sakurai, H. Yoshizumi, and A. Tatematsu, *Org. Mass. Spectrom.*, **1**, 199 (1968), and references cited therein. (c) F. L. Bach, J. Karliner, and G. E. Van Lear, *Chem. Commun.*, 1110 (1969).

(5) E. K. Fields and S. Meyerson, *Accounts Chem. Res.*, **2**, 273 (1969).

(6) T. H. Kinstle and L. J. Darlage, *J. Heterocycl. Chem.*, **6**, 123 (1969).

(7) (a) B. Singh and E. F. Ullman, *J. Amer. Chem. Soc.*, **88**, 1844 (1966); (b) B. Singh and E. F. Ullman, *ibid.*, **89**, 6911 (1967).

(8) D. W. Kurtz and H. Schechter, *Chem. Commun.*, 689 (1966).

(9) H. Göth, A. R. Gagneux, C. H. Eugster, and H. Schmid, *Helv. Chim. Acta*, **50**, 137 (1967).

(10) H. Göth, H. Tiefenthaler, and W. Dörschein, *Chimia*, **19**, 596 (1965).

(11) (a) J. Reisch, *Chim. Ther.*, 335 (1966); (b) J. Reisch and R. Pagnucco, *Chem. Ind. (London)*, 1646 (1967); (c) J. Reisch and A. Fitzek, *Tetrahedron Lett.*, 4513 (1967); (d) S. N. Ege, *Chem. Commun.*, 488 (1967); *J. Chem. Soc. C*, 2624 (1969).

(12) H. Tiefenthaler, W. Dörscheln, H. Göth, and H. Schmid, *Helv. Chim. Acta*, **50**, 2244 (1967).

(13) (a) P. Beak, J. L. Miesel, and W. R. Messer, *Tetrahedron Lett.*, 5315 (1967); (b) P. Beak and W. Messer, *Tetrahedron*, **25**, 3287 (1969).

(14) M. Kojima and M. Maeda, *Tetrahedron Lett.*, 2379 (1969).

(15) J. P. Catteau, A. Lablanche-Combier, and A. Pollet, *Chem. Commun.*, 1018 (1969).

(16) (a) H. Tiefenthaler, W. Dörscheln, H. Göth, and H. Schmid, *Tetrahedron Lett.*, 2999 (1964); (b) H. Göth and H. Schmid, *Chimia*, **20**, 148 (1966).

(17) J. P. Dubois and H. Labhart, *ibid.*, **23**, 109 (1969).

clarified. In fact, with the exception of some recent work of Ogata, *et al.*,[18] on photolysis of anthranils, our results reported and discussed in the next section represent the first detailed mechanistic study of any condensed ring heterocyclic rearrangement.

Results and Discussion

Irradiation of a 0.005 *M* solution of 3-hydroxy-1,2-benzisoxazole (**3**) in ether for 1 hr with Corex-filtered ultraviolet light resulted in the formation of benzoxazolinone (**4**) in 80% yield. Sublimation of the crude photolysate yielded a white crystalline solid whose physical and spectral properties were identical with those of **4** synthesized by an independent route.[6] Irradiation of **3** for more than 1 hr under similar conditions resulted in lower yields of **4** (see Table I) with concurrent formation of a resinous precipitate due to photodecomposition of **4**. Table I contains the relative yields of **3** and **4** obtained using various photolysis reaction conditions. In each case the products were characterized by infrared and nmr spectroscopy.

TABLE I

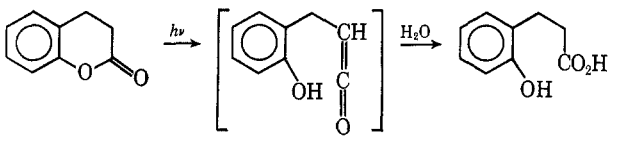
PHOTOLYSIS OF 3-HYDROXY-1,2-BENZISOXAZOLE (**3**)

Temp, °C	Filter	Solvent	Time, min	% of **3**	% of **4**
20	Corex	Ether	60	0	80[a]
20	Corex	Ether	180	0	60[a]
20	Vycor	Ether	210	0	59[a]
20	Corex	Methanol	15	~20	73[b]
−72	Vycor	Methanol	120	38	62[c]
20	Pyrex	Acetone	180	49	24[b]
20	Vycor	0.1 *M* piperylene in ether	180	0	37[d]

[a] Purified by sublimation. [b] Isolated by column chromatography. [c] Ratio of products determined by nmr spectroscopy. [d] Extracted from the concentrated ether solution with aqueous Na_2CO_3.

Possible mechanisms for this photoisomerization are presented in Scheme II. Enol **3a**–keto **3b** equilibria in **3** follows from an infrared spectral analysis which indicated that the enol form **3a** is preferred in the solid state (strong O–H absorption at 3000–2500 cm^{-1} and no carbonyl absorption), and both forms are present in chloroform solution (O–H absorption as above and carbonyl absorption at 1670 cm^{-1}). Methylation of **3** with methyl halide or diazomethane yielded both 3-methoxy-1,2-benzisoxazole (**22**) and 2-methyl-1,2-benzisoxazolin-3-one (**19a**).[19]

The first step in the photoisomerization of **3** to **4** presumably involves homolytic cleavage of the weak N–O bond to form the diradical species **10** (Scheme II). Hydrogen migration followed by a Curtius rearrangement would produce 2-hydroxyphenyl isocyanate (**12**), as shown in mechanism A. This isocyanate is known to undergo an intramolecular cyclization to form benzoxazolinone (**4**).[20,21] **12** is analogous to the ketene intermediate (**15**) generated at −190° in the photolysis of dihydrocoumarin and observed by infrared spectroscopy.[22] The photodecomposition of 3-(2-hydroxyphenyl)-Δ^2-1,4,2-dioxazolin-5-one (**1a**) has also been



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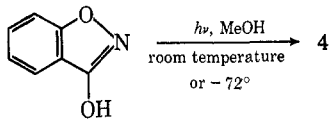
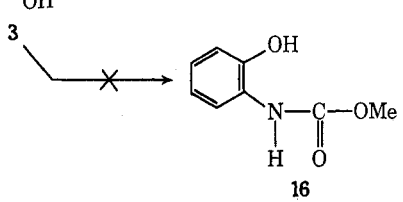
shown to yield benzoxazolinone (**4**), presumably *via* the intermediate isocyanate **12**, since the photolysis of **1b** produces phenyl isocyanate.[2]





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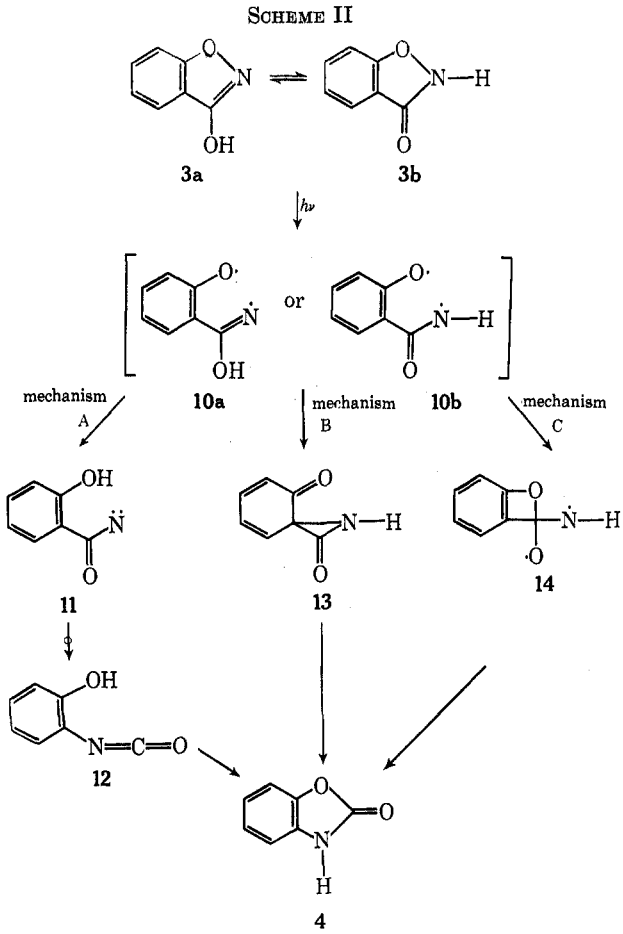
Our attempts to trap the isocyanate **12**, however, were unsuccessful. Irradiation of **3** in absolute methanol either at room temperature or at −72° resulted in the formation of only **4** (see Table I). None of the methyl carbamate **16** could be detected by infrared or nmr analysis of the photolysis products. These results are somewhat inconclusive evidence for the absence of

SCHEME II



(18) M. Ogato, H. Matsumoto, and H. Kano, *Tetrahedron*, **25**, 5205, 5217 (1969).

(19) H. Böshagen, *Chem. Ber.*, **100**, 954 (1967).

(20) J. W. Cornforth, *Heterocycl. Compounds*, **5**, 442 (1957).

(21) K. H. Wünsch and A. J. Boulton, *Advan. Heterocycl. Chem.*, **8**, 285 (1967).

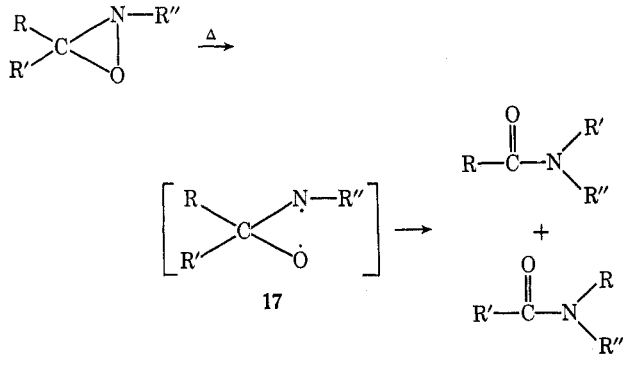
(22) O. L. Chapman and C. L. McIntosh, *J. Amer. Chem. Soc.*, **91**, 4309 (1969).

12 as a reactive intermediate in the photoisomerization of **3** to **4**, since we were also unable to detect **16** from the photolysis of salicyloyl azide in absolute methanol at room temperature.[23,24]

Mechanism B (Scheme II) involves a ring contraction–ring expansion sequence[26] analogous to the one documented by Singh and Ullman[7] for the photoisomerization of diarylisoxazole. A similar α lactam has also been suggested as an intermediate in the photochemical transformation of 3-hydroxyisoxazole to 2(3*H*)-oxazolone.[9] Thus **13** is a plausible, though expectedly unstable,[27] intermediate, which would rearrange under the reaction conditions to benzoxazolinone (**4**).

Finally, one must also consider a mechanism in which **4** is the primary photoproduct in the reaction. One possibility is mechanism C which involves a series of free-radical rearrangements. Attack of the phenoxide radical upon the carbonyl moiety in **10b** would produce the diradical species **14**, and then subsequent migration of the phenyl group to nitrogen would result in the formation of **4**.

The rearrangement of **14** to **4** is analogous to the transformation observed in the gas phase pyrolysis of oxaziridines.[28] The suggested mechanism for the formation of the two amide products involves migration



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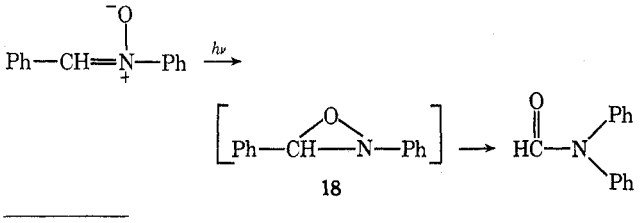
of either R or R′ to the nitrogen radical in species **17**. A similar migration has been reported in the photolysis of *N*-oxides[29] and nitrones.[30] For example, the irradiation product of *N*,α-diphenylnitrone is *N*,*N*-diphenylformamide, consistent with an oxaziridine intermediate (**18**), and indeed this intermediate has been isolated in certain systems.[30]



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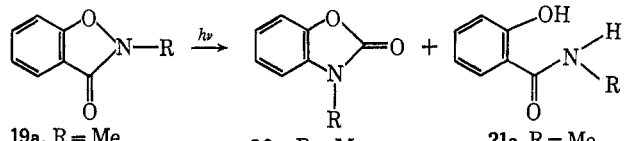
Substituted 1,2-Benzisoxazolinones.—In order to examine the mechanistic aspects of the photoisomerization of **3** to **4** in greater detail, we investigated the photolysis of alkyl derivatives (**19** and **22**). Table II

TABLE II
PHOTOLYSIS OF
2-METHYL-1,2-BENZISOXAZOLINONE (19a)

Filter	Solvent	Time, min	% of 19a	% of 20a	% of 21a
Vycor	Ether	180	50	23	~3
Vycor	Pentane	180	31	25	5
Vycor	Methanol	60	4	17	39
Pyrex	Acetone	180		92	
Pyrex	0.01 *M* acetophenone in benzene	180	67	29	
Pyrex	0.01 *M* benzophenone in benzene	180	>95[a]	<5[a]	
Vycor	0.1 *M* piperylene in ether	180	25	13	3

[a] Determined by nmr spectroscopy of the photolysis product mixture.

contains the results of the photolysis of **19a**, describing the percentage yields of recovered starting material, rearrangement product (**20a**), and hydrogen abstraction product (**21a**).



19a, R = Me
b, R = allyl
c, R = *tert*-butyl

20a, R = Me
b, R = allyl
c, R = *tert*-butyl

21a, R = Me

The products were isolated by column chromatography and were characterized by comparing their physical and spectral properties with those of **20a** and **21a** synthesized by independent methods (see Experimental Section).

Irradiation of **19a** in ether or pentane solution using a Vycor filter produced a considerable amount of insoluble material, presumably from photodecomposition of the rearrangement product **20a**, since under identical photolytic conditions **20a** produced a dark precipitate after only 15-min irradiation. Vastly different results were obtained by irradiating **19a** in absolute methanol.[31] After 1 hr almost all of the starting material had disappeared, and the major product isolated was *N*-methylsalicylamide (**21a**). The formation of **21a** provides evidence for the initial formation of a diradical species (see Scheme II) and is somewhat analogous to the intramolecular hydrogen abstraction products obtained in the photolysis of benzisoxazole[16b] and indazole.[12]

The highest yield of the rearrangement product **20a** was obtained by photolysis of **19a** in acetone. In this case no *N*-methylsalicylamide was detected, and **20a** was isolated in 92% yield. Photolysis of **19b** in acetone under similar conditions for 3 hr produced 3-allylbenzoxazolinone (**20b**) in an isolated yield of 82%. The spectral and physical properties of **20b** were identical with those of an authentic sample of 3-allylbenzoxazo-

(23) A urethane corresponding to **16** has been reported in the pyrolysis of salicyloyl azide in alcohol by H. Lindemann and W. Schultheis, *Justus Liebigs Ann. Chem.*, **451**, 241 (1927).

(24) Photolysis of **3** as a thin film at 77°K (see ref 22) led to no detectable infrared absorption in the region 2240–2260 cm^{-1} characteristic for phenyl isocyanate.[25] There was observed the formation of **4** (C=O doublet at 1740–1780 cm^{-1}).

(25) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962, p 131.

(26) For a review, see P. Beak and W. Messer in "Organic Photochemistry," Vol. 2, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1969, pp 136–143.

(27) I. Lengyel and J. C. Sheehan, *Angew. Chem., Int. Ed. Engl.*, **7**, 25 (1968).

(28) E. Schmitz, *Advan. Heterocycl. Chem.*, **2**, 100 (1963).

(29) R. O. Kan, "Organic Photochemistry," McGraw-Hill, New York, N. Y., 1966, pp 147–150.

(30) J. S. Splitter and M. Calvin, *J. Org. Chem.*, **23**, 651 (1958); *ibid.*, **30**, 3427 (1965).

(31) Similar solvent effects have been reported for the photolysis of isothiazole (ref 15).

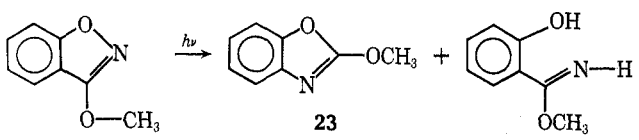
linone. Finally, 3-*tert*-butylbenzoxazolinone (**20c**) was obtained in a 50% yield upon irradiation of **19c** in acetone for 6 hr with Corex-filtered ultraviolet light. **20c** was shown by mass spectroscopy and chemical analysis to be isomeric with 2-*tert*-butyl-1,2-benzisoxazolinone (**19c**), and its nmr and infrared spectra were consistent with the assigned structure (see Experimental Section).

The facile photoisomerization of **19** to **20** suggests that 3-hydroxy-1,2-benzisoxazole (**3**) undergoes photochemical rearrangement *via* the keto tautomer (**3b**). Further evidence for this is shown by the extremely slow rate of isomerization of 3-methoxy-1,2-benzisoxazole (**22**) under similar photolytic conditions (see Table III). Irradiation of **22** in ether for 6 hr produced only

TABLE III
PHOTOLYSIS OF 3-METHOXY-1,2-BENZISOXAZOLE (22)

Filter	Solvent	Time, min	% of 22	% of 23	% of 24
Vycor	Ether	360	19	3	33
Vycor	Methanol	60	18	24	11
Pyrex	Acetone	180	>95		
Pyrex	Acetone	540	60		

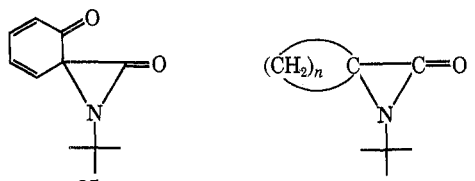
about 3% of the rearrangement product **23** and a relatively high yield of the imido ester **24**. In acetone **22**



22 23 24

remained unreactive, and even after 9 hr of irradiation only starting material was recovered. A surprising solvent effect[31] again was exhibited in the photolysis of **22** in absolute methanol which yielded **23** as the major product.[32]

The photoisomerization of the *N*-alkyl-1,2-benzisoxazolinones (**19**) to **20** clearly cannot occur *via* a mechanism analogous to mechanism A (Scheme II). Mechanism B (H = alkyl) is plausible in view of the evidence for a ring contraction–ring expansion sequence in corresponding monocyclic systems.[7] According to mechanism B, the spiro-α-lactam **25** would be the primary



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photoproduct upon irradiation of **19c**. The unsubstituted α lactam **13** was undetected in previous low temperature experiments (ref 24), but *N*-*tert*-butyl derivatives are known to be more stable. Spiro-α-lactams stabilized by an *N*-*tert*-butyl group have been isolated for systems (**26**) in which n = 4, 5, and 7,[27] and even the highly strained species **26** (n = 3) has been observed at 0° but could not be isolated.[27]

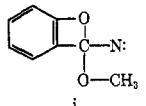
In attempts to detect this intermediate, 2-*tert*-butyl-1,2-benzisoxazolinone (**19c**) was photolyzed at −70° in methylene chloride. The progress of the photolysis was followed by infrared spectroscopy. After 60 min of irradiation, carbonyl absorption appeared at 1750 cm^{-1} corresponding to the rearrangement product **20c**. The intensity of this band at 1750 cm^{-1} increased at the expense of carbonyl absorption due to starting material upon further irradiation. Likewise, photolysis of **19c** at −70° in methanol or of **19a** at 77°K in a methanol matrix did not yield an intermediate α lactam by infrared detection techniques. Absorption in the region 1820–1850 cm^{-1} was never observed, thus ruling out the α lactam **25** as an intermediate under these photolytic conditions.

Sensitization and Quenching.—In order to gain a better understanding regarding the mechanism of these photoisomerizations, sensitization and quenching studies were conducted on **19a** (Table II) and **3** (Table I). Irradiation of **19a** in benzene containing 0.01 *M* benzophenone (E_T = 69 kcal)[33] resulted in less than 5% conversion to **20a**. In the presence of 0.01 *M* acetophenone (E_T = 74 kcal)[33] in benzene, **19a** under similar conditions rearranged to **20a** which was isolated in a 29% yield. The transformation of **19a** to **20a** was essentially quantitative when the photolysis was conducted in acetone (neat) (E_T = 79 kcal).[33] These results indicate that the energy of the triplet state of **19a** lies between 69 and 74 kcal, which is somewhat higher than the values reported for isoxazoles.[7b] The photoisomerization of **19a** to **20a**, however, could not be quenched in the presence of 0.1 *M* piperylene, a triplet quencher (see Table II), suggesting that the reaction can occur by both a singlet and a triplet mechanism. Similar results were obtained for 3-hydroxy-1,2-benzisoxazole (**3**) as shown in Table I.[34]

Summary

The photolysis of 3-hydroxy-1,2-benzisoxazole (**3**) produces benzoxazolinone (**4**) as a *primary* photoproduct. Mechanisms A and B (Scheme II) which involve the reactive intermediates **12** and **13**, respectively, are probably unimportant pathways in this photoisomerization. This conclusion is based on the facile rearrangement observed for the *N*-alkyl compounds (**19**), which cannot proceed *via* mechanism A, and on the photolysis of **3** at 77°K, in which neither **12** nor **13** could be detected by infrared spectroscopy. Furthermore, **25** was not detected by ir upon irradiation of **19c** at −70°. It is possible that the loss of the benzene resonance imposes too great a barrier for the formation of **13** or **25**. More likely, α lactams are never formed in photochemical heterocyclic rearrangements contrary to our intuitive feelings and the suggestion of Schmid.[9]

(32) The photoisomerization of **22** to **23** has not been studied in detail but possibly involves the intermediate formation of i by a mechanism analogous to C (Scheme II).



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(33) N. J. Turro, J. C. Dalton, and D. S. Weiss in "Organic Photochemistry," Vol 2, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1969, p 12.

(34) Phosphorescence spectra were taken of 2-methyl-1,2-benzisoxazolinone (**20a**) and 3-hydroxy-1,2-benzisoxazole (**3**) in a MTHF glass at 77°K. The results of these spectra were inconclusive due to the extremely weak emission observed. We are grateful to G. Wampfler for making these measurements.

Experiments with monocyclic heterocycles are underway to test this latter point.

Therefore, the likely pathway for photoisomerization of **3** is mechanism C (Scheme II) which involves the diradical species **10** and **14**. Evidence for **10** is furnished by the formation of the hydrogen abstraction product **21a** during the photolysis of **19a**. **14** is analogous to the intermediate proposed for the photoisomerization of indazole and *N*-(2)-alkylated indazoles.[12,17]

Experimental Section

The 450-W Hanover lamp (no. 679A36) used in all photolyses was contained in a water-cooled quartz immersion well equipped with the appropriate filter. All solutions were degassed with nitrogen for ~20 min prior to irradiation. The photochemical reactions were monitored by tlc. Products were isolated by sublimation or chromatography on silica gel columns and characterized by comparison with authentic samples using nmr, ir, and mass spectrometry.

3-Hydroxy-1,2-benzisoxazole (**3**) was prepared from 3-(2-hydroxyphenyl)-Δ^2-1,4,2-dioxazolin-5-one (**1a**) and triethylamine as described previously[6] and was recrystallized from 30% aqueous methanol: mp 144–145°; ir (KBr) 3000–2500 (OH) and 1615 cm^{-1} (C=N); nmr ($CDCl_3$) 7.15–7.95 (m, 4 H) and ~11.0 ppm (s, 1 H); uv (CH_3OH) has been reported.[19]

Benzoxazolinone (**4**), synthesized from *o*-aminophenol and urea,[35] had mp 143–144°; ir (KBr) 3250 (NH) and 1740–1780 cm^{-1} (C=O, doublet); nmr ($CDCl_3$) 7.12 (s, 4 H) and ~10.0 ppm (broad s, 1 H).

2-Methyl-1,2-benzisoxazolinone (**19a**) and **3-methoxy-1,2-benzisoxazole** (**22**) were prepared according to the literature procedure[19] using acetone as solvent. A 1:3 mixture (89% yield) of **22** and **19a** was obtained. Fractional distillation of the mixture produced **22**: bp 27–28° (0.07 mm); ir (film) 1615 cm^{-1} (C=N); nmr (CCl_4) 4.12 (s, 3 H) and 7.00–7.65 ppm (m, 4 H); uv (CH_3OH) 288 mμ (log ε 3.58), 282 (3.57), 278 (3.57), 273 (sh) (3.45), and 236 (3.76). **19a** was obtained by fractional crystallization from hexane–ethyl acetate of the solid residue from the distillation: mp 74.5–75.5° (lit.[19] mp 74–75°); ir (KBr) 1675 cm^{-1} (C=O); nmr ($CDCl_3$) 3.63 (s, 3 H) and 7.16–7.92 ppm (m, 4 H); uv (CH_3OH) 294 mμ (log ε 3.73), 287 (3.73), 254 (sh) (3.45), 242 (sh) (3.73), and end absorption.

2-Allyl-1,2-benzisoxazolinone (**19b**).—To a solution of 6.75 g (0.05 mol) of **3** in 50 ml of acetone containing 6.8 g (0.05 mol) of anhydrous, granular K_2CO_3 was added 6.5 g (0.054 mol) of allyl bromide. The mixture was stirred at 50° for 6 hr, filtered, concentrated at reduced pressure, and chromatographed on a column of silica gel. 3-Allyloxy-1,2-benzisoxazole (3.2 g, 37%) was obtained by elution with 15% ethyl acetate in petroleum ether, and 3.4 g (39%) of **19b** was isolated by further elution with 20% ethyl acetate in petroleum ether and purified by recrystallization from hexane: mp 32–33°; ir (KBr) 1670 cm^{-1} (C=O); nmr (CCl_4) 4.45–4.65 (m, 2 H), 5.08–5.53 (m, 2 H), 5.60–6.30 (m, 1 H), and 7.00–7.90 ppm (m, 4 H); uv (CH_3OH) 295 mμ (log ε 3.73), 289 (3.72), 255 (sh) (3.50), 244 (sh) (3.76), and end absorption. *Anal.* Calcd for $C_{10}H_9NO_2$: C, 68.56; H, 5.18. Found: C, 68.51; H, 5.19.

2-*tert*-Butyl-1,2-benzisoxazolinone (**19c**).—A sealed tube containing 1.35 g (0.01 mol) of **3**, 7.4 g (0.08 mol) of *tert*-butyl chloride, and 10 ml of absolute methanol was heated in an oil bath at 100–105° for 4 hr. Evaporation of the methanol and excess *tert*-butyl chloride at reduced pressure returned 1.9 g of a dark oil which was chromatographed on a column of silica gel to yield 0.9 g (47%) of **19c**: mp 48–49° (from pentane); ir (KBr) 1670 (C=O) and 2975 cm^{-1} (CH); nmr (CCl_4) 1.62 (s, 9 H) and 7.00–7.82 ppm (m, 4 H); uv (CH_3OH) 294 mμ (log ε 3.63), 287 (3.62), 255 (sh) (3.41), 242 (sh) (3.65), and end absorption; parent ion at *m/e* 191. *Anal.* Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85. Found: C, 69.34; H, 6.70.

3-Methylbenzoxazolinone (**20a**) and **3-Allylbenzoxazolinone** (**20b**) were synthesized by reacting benzoxazolinone (**4**) with methyl iodide and allyl bromide, respectively, using a procedure analogous to those described for the preparation of **19a** and **19b**. 3-Methylbenzoxazolinone (**20a**) was purified by recrystallization from a hexane–ethyl acetate solution: mp 83.0–83.5;[36] ir (KBr) 1765 cm^{-1} (C=O); nmr ($CDCl_3$) 3.37 (s, 3 H) and 6.80–7.30 ppm (m, 4 H). 3-Allylbenzoxazolinone (**20b**) was purified by vacuum distillation: bp 75–76° (0.07 mm);[36] ir (KBr) 1756 cm^{-1} (C=O); nmr ($CDCl_3$) 4.33–4.55 (m, 2 H), 5.06–5.48 (m, 2 H), 5.60–6.30 (m, 1 H), and 6.83–7.26 ppm (m, 4 H).

2-Methoxybenzoxazole (**23**) was prepared from 2-chlorobenzoxazole and sodium methoxide by a procedure analogous to that described:[37] mp 32–33° (from pentane); ir (CCl_4) 1588 and 1640 cm^{-1}; nmr (CCl_4) 4.13 (s, 3 H) and 6.97–7.53 ppm (m, 4 H); parent ion at *m/e* 149.

Methyl Salicylimidate (**24**) was synthesized from salicylonitrile,[38] methanol, and dry HCl by the general method described for related esters.[39,40] It had mp 75.5–76.5° (from pentane); ir (CCl_4) 3380 (OH) and 1645 cm^{-1} (C=N); nmr (CCl_4) 3.73 (s, 3 H), 6.53–7.78 (m, 4 H), and ~10 ppm (broad s, 2 H); parent ion at *m/e* 151. *Anal.* Calcd for $C_8H_9NO_2$: C, 63.56; H, 6.00. Found: C, 63.80; H, 5.66.

Irradiation of 3-Hydroxy-1,2-benzisoxazole (**3**). **A. In Ether.**—A degassed solution of 135 mg of **3** in 200 ml of ether was photolyzed for 1 hr with Corex-filtered ultraviolet light. Evaporation of the solvent and sublimation yielded 107 mg (80%) of **4**, indistinguishable from authentic material by melting point, ir, nmr, and mass spectral criteria. Yields of **4** decreased upon longer irradiation (see Table I). Irradiation through Vycor for 3 hr of a degassed ether solution of **3** which was 0.1 *M* in piperylene produced a 37% yield of **4**.

B. Irradiation of 3 in Methanol.—A solution of 270 mg of **3** in 180 ml of absolute methanol was degassed and photolyzed (Corex) for 15 min. The residue obtained upon evaporation of the methanol was chromatographed on a column of silica gel. Elution with 25–35% ethyl acetate in petroleum ether yielded 197 mg (73%) of **4**. Approximately 20% of **3** was recovered by elution with 40–50% ethyl acetate in petroleum ether. Irradiation of a methanol solution of **3** for 2 hr at a temperature of −72° resulted in a product mixture of only **3** and **4** in a ratio of 38:62.

C. Irradiation of 3 in Acetone.—A degassed solution containing 270 mg of **3** in 180 ml of acetone was irradiated with Pyrex-filtered uv light for 3 hr. Solvent removal and elution from a silica gel column returned 65 mg (24%) of **4** and 133 mg of starting material.

Photolysis of Salicyloyl Azide.—A solution of 163 mg of salicyloyl azide[41] in 200 ml of absolute methanol was degassed and photolyzed with Pyrex-filtered uv light until effervescence resulting from nitrogen expulsion had ended (30 min). Evaporation of the methanol produced an essentially quantitative yield of **4**.

Photolysis of 2-Methyl-1,2-benzisoxazolinone (**19a**). **A. Direct Irradiation.**—Photolysis (Vycor, 3 hr) of a degassed solution of 0.5 g of **19a** in 180 ml of ether, followed by evaporation and silica gel column chromatography yielded 114 mg (23%) **20a** and 267 mg of a mixture (17:1 by nmr) of **19a** and **21a**. **21a**, separated from this mixture by tlc, showed a molecular ion at *m/e* 151. Similar results (see Table II) were obtained by irradiating (Vycor) a 0.006 *M* solution of **19a** in pentane for 3 hr. *N*-Methylsalicylamide (**21a**)[42] was obtained by preparative tlc as the major product (39%) upon irradiation of a solution of 149 mg of **19a** in 180 ml of absolute methanol for 1 hr.

B. Sensitized Photolysis of 19a.—A degassed solution of **19a** (149 mg) in 180 ml of benzene containing 0.01 *M* benzophenone was irradiated 3 hr with Pyrex-filtered uv light. The concentrated photolysate was analyzed by nmr spectroscopy which indicated <5% conversion of **19a** to **20a**. A photolysis carried out under identical conditions using 0.01 *M* acetophenone as sensitizer yielded 43 mg (29%) of **20a** and 100 mg (67%) of recovered **19a**. Irradiation of **19a** (149 mg) in 180 ml of acetone

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for 3 hr using a Pyrex filter resulted in an almost quantitative conversion (>92%) to **20a**.

C. Quenching Experiment.—A 0.1 *M* solution of piperylene in ether (200 ml) failed to quench the photoisomerization of **19a** (164 mg) to **20a**. The photolysis was carried out for 3 hr using a Vycor filter, and the products were isolated by column chromatography (see Table II).

Photolysis of 2-Allyl-1,2-benzisoxazolinone (19b).—A degassed solution of 175 mg of **19b** in 180 ml of acetone was photolyzed 3 hr using Pyrex-filtered uv light. The residue obtained after acetone evaporation was chromatographed on a silica gel column. Elution with 15–20% ethyl acetate in petroleum ether yielded 143 mg (82%) of **20b**.

Photolysis of 2-*tert*-Butyl-1,2-benzisoxazolinone (19c).—A degassed solution of 191 mg of **19c** in 180 ml of acetone was photolyzed with Corex-filtered uv light for 6 hr. Elution through a silical gel column with 2–4% ethyl acetate in petroleum ether separated 95 mg (50%) of **20c**: mp 74–75°; ir (KBr) 1750 cm^{-1} (C=O); nmr (CCl_4) 1.72 (s, 9 H) and 6.85–7.35 ppm (m, 4 H); parent ion at *m/e* 191. *Anal.* Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85. Found: C, 68.90; H, 6.79.

Further elution with 5–15% ethyl acetate in petroleum ether yielded 75 mg (39%) of **19c**.

Photolysis of 3-Methylbenzoxazolinone (20a).—A solution of 0.5 g of **20a** in 160 ml of pentane containing ~20 ml of ether was degassed and irradiated with Vycor-filtered uv light for 3 hr. A large amount of dark, insoluble material was obtained. Extensive chromatography of the photolysate on a column of silica gel yielded **20a** (375 mg, 65%) as the only elutable product.

Irradiation of 3-Methoxy-1,2-benzisoxazole (22).—A degassed solution of 149 mg of **22** in 180 ml of ether was photolyzed with Vycor-filtered uv light for 6 hr. The products were isolated by chromatography on a silica gel column. Elution with 5–10% ethyl acetate in petroleum ether yielded 33 mg of an oil whose nmr spectrum was consistent with a 6:1 mixture of **22** and **23**. Compound **24** was obtained by eluting with 15–25% ethyl acetate in petroleum ether, mp 74.5–76° (from pentane). The mass spectrum of **24** showed a molecular ion at *m/e* 151, and its ir and nmr spectra were identical with those of authentic **24**. Irradiation of **22** under identical conditions in absolute methanol followed by chromatography of the photolysate yielded 27 mg (18%) of **22**, 16 mg (11%) of **24**, and 36 mg (24%) of **23**. The mass spectrum of **23** had a parent ion at *m/e* 149, and its ir and nmr spectra were identical with those of authentic **23**. Irradiation of **22** (148 mg) in acetone 180 ml for up to 9 hr using a Pyrex filter resulted in a quantitative recovery of starting material.

Registry No.—**3**, 21725-69-9; **4**, 59-49-4; **19a**, 24963-20-0; **19b**, 26384-70-3; **19c**, 26384-71-4; **20a**, 21892-80-8; **20b**, 13444-14-9; **20c**, 26384-73-6; **22**, 26384-74-7; **23**, 26384-75-8; **24**, 26384-76-9.

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The Photochemistry of 4-Methyl-4-alkoxy-2-pentanones

L. M. STEPHENSON* AND J. L. PARLETT

Department of Chemistry, Stanford University, Stanford, California 94305

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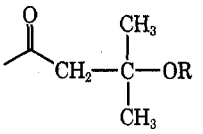
The mechanism of the formation of five-membered ring ethers by irradiation of β-alkoxy ketones has been investigated using deuterium labeling. A pathway involving δ-hydrogen abstraction by electronically excited carbonyl is implicated.

The photoreaction of aliphatic ketones to give smaller ketones and olefins, known as the Norrish type II photocleavage, is one of the most extensively studied areas of photochemistry. The field has been reviewed recently[1-3] and remains a subject of current interest.[4-6]

It is now well established that the reaction proceeds *via* γ-hydrogen abstraction to give 1,4 diradicals which can either cleave to olefins,[1] ring close to cyclobutanes,[1] or return to starting material.[4] Recent work of Turro and Weiss[7] has established that the geometry of the species which precedes hydrogen abstraction resembles that of a cyclic olefin; *i.e.*, γ hydrogens which lie in the plane of the carbonyl group, are easily transferred. The increased strain energy of the five and seven carbon cyclic olefins over that of cyclohexene (4.5 and 4.0 kcal/mol, respectively)[8] clearly accounts, at least qualitatively, for the high selectivity toward γ abstraction.

We have investigated the photochemistry of several ethers of diacetone alcohol (**1a–c**) in an attempt to understand those features which might lead to hydrogen abstraction *via* seven-membered ring transition states (δ abstraction) and wish to report these results below.



1a, R = CH_3
b, R = CH_2CH_3
c, R = CD_3

Results and Discussion

When irradiated in pentane, both **1a** and **1b** yield mesityl oxide **2**, an alcohol **3**, and a tetrahydrofuranol **4** (see Scheme I). In these systems γ-hydrogen abstraction enjoys a two- or threefold statistical advantage over δ abstraction. Despite this and the fact that no obvious geometrical constraints are operative,[9] *no* products of γ-hydrogen abstraction (acetone, olefin, or cyclobutanol) could be found. This result, first reported by

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