Acknowledgment. The work reported has been supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We gratefully acknowledge the generosity of the donors of this fund.

Registry No.—**12,** 500-05-0; **12a,** 6018-41-3; **12b,** 61752-09-8; **12c,** 61752-10-1; **13a,** 61752-11-2; **13b,** 61752-12-3; **13c,** 61752-13-4; **14a,** 61752-14-5; **14b,** 61752-15-6; **17,** 61752-16-7; **18,** 61752-17-8; **19,** 61752-18-9; **20,** 61787-98-2; **21,** 61752-19-0; coumaloyl chloride, 23090-18-8.

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Photochemistry of 3-Ethoxy-3-methylpent-4-en-2-one, an α-Alkoxy β,γ-Unsaturated Ketone

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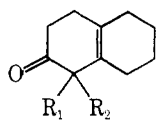
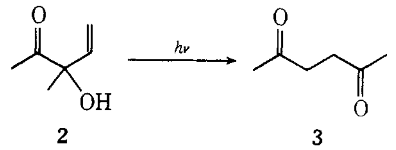
Irradiation of 3-ethoxy-3-methylpent-4-en-2-one gives (*E*)- and (*Z*)-5-ethoxyhex-4-en-2-one by 1,3-acyl shift; acetaldehyde, 3-methylpent-4-en-2-one, (*Z*)- and (*E*)-3-methylpent-3-en-2-one by Norrish type II cleavage; 2,3,4-trimethyl-2-vinyloxetan-3-ol (two isomers) by type II cyclization; and 3,4-dimethylhexane-2,5-dione (*dl*- and *meso*-) and 5-ethoxyhex-5-en-2-one by secondary reactions. Disappearance of 3-ethoxy-3-methylpent-4-en-2-one is neither sensitized by xanthone nor quenched by piperylene. The 1,3 shift is reversible. Mechanisms and relevance to other α-substituted β,γ-unsaturated ketones are discussed; isolation of γ-keto enol ethers from photolysis of α-ethoxy β,γ-unsaturated ketones provides circumstantial evidence that a γ-keto enol is the likely intermediate in photochemical conversion of α-hydroxy β,γ-unsaturated ketones to 1,4-diketones.

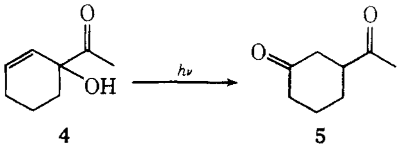
It has recently become apparent that α-substitution can cause dramatic alterations in the photochemical behavior of β,γ-unsaturated ketones.[1] For example, Engel et al.[2] have shown that α-methylation of **1a** enhances the likelihood of 1,3-shift (α-cleavage) at the expense of 1,2-shift products, although the multiplicity of the reactive excited state is uncertain.[3] Sasaki,[4] Carlson,[5] McMurry,[6] and we[7,8] have shown that α-hydroxylation introduces a synthetically useful modification to the usual reaction pattern of 1,3-acyl shifts. We previously reported the photochemistry of the two α-hydroxy β,γ-unsaturated ketones **2** and **4** which, on direct irradiation or with triplet sensitization, gave the 1,4-diketones **3** and **5**.[7,8] The rearrangements of **2** and **4** were suggested to involve a 1,3-acyl shift (probably via discrete acetyl and allyl radicals), followed by tautomerization of the resultant γ-keto enol. The (inefficient) sensitized 1,3-acyl shift of both **2** and **4**, though not unprecedented,[9] is highly unusual in β,γ-unsaturated ketone photochemistry.



1a, $R_1 = R_2 = H$
b, $R_1 = CH_3$; $R_2 = H$
c, $R_1 = R_2 = CH_3$

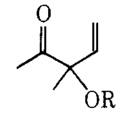


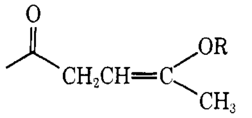
2 **3**



4 **5**

This report describes the photochemistry of a related molecule, 3-ethoxy-3-methylpent-4-en-2-one (**6a**), whose excited state reactivity is unusually complex and substantially different from that of the hydroxy analogue **2**.[10] The reasons for extending our study of α-hydroxy substituted β,γ-unsaturated ketones to α-alkoxy analogues (**6b**) were several. First,


6a, R = CH_2CH_3
b, R = alkyl

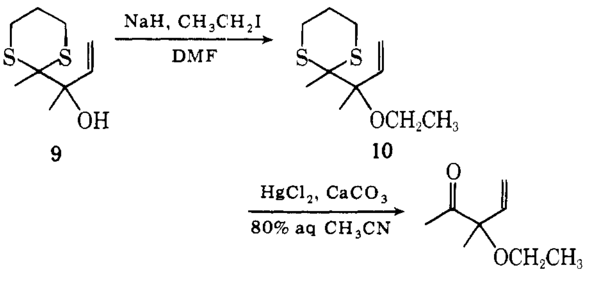

7, R = H
8, R = alkyl

it is possible to write alternative mechanisms for the **2** → **3** and **4** → **5** transformations. For example, although the 1,3-acyl shift/enol ketonization mechanism for the photorearrangement of **2** is well precedented,[1] the intermediacy of enol **7** was not proven by physical detection. An α-alkoxy analogue such as **6b** could provide circumstantial evidence for the validity of the **2** → **7** → **3** mechanism since an analogous 1,3-acyl shift in **6b** should halt at the stage of an (isolable) enol ether **8**. A complication attending this idea is the γ hydrogens available in all but tertiary alkoxy substituents, which would be susceptible to competing Norrish type II reactions. However, assessing the competition between the 1,3 shift and γ-H abstraction was also of fundamental interest.[11]

From a synthetic point of view, were the **6b** → **8** transformation to proceed in reasonable yield, it would provide a useful synthetic route to γ-keto enol ethers. Such half-protected 1,4-diketones would have considerable utility as synthetic intermediates.

Results

Synthesis. The synthesis of 3-ethoxy-3-methylpent-4-en-2-one (**6a**) was accomplished using three different synthetic schemes, the most efficacious of which is summarized in eq 1. The dithiane **9** was available from an intermediate step in the synthesis of **2**.[7,12,13] Addition of sodium hydride to a solution of the dithioketal **9** and ethyl iodide in dry dimethylformamide at 0 °C gave 92% of the ether **10**. Mercuric chloride cleavage[12] of the dithiane **10** afforded the desired ether (**6a**) in 33% yield after careful purification by distillation and preparative gas chromatography.



(1)

Direct alkylation of **2** afforded **6a** in modest yield, but the anticipated α-alkylation side products diminished the yield substantially. Synthesis of **6a** from **2** by successive ketalization, ether oxygen alkylation, and acid-catalyzed cleavage of the ketal in acetone was successful, but the more direct approach shown in eq 1 gave better overall yields. The structural assignment for **6a** was supported by its UV, NMR, and mass spectra (cf. Experimental Section).

Direct Irradiation. To avoid photoproduct hydrolysis (symptoms: ethanol and 2,5-hexanedione as products, variable product yields) during irradiation and GLC analysis, several precautions were necessary: (1) ethoxide-washed and oven-dried photolysis and collection tubes; (2) sample preparation in a drybox; (3) scrupulously and freshly dried solvents; (4) double septums over and molecular sieves in photolysis tubes; and (5) glass GLC columns and a high-pH support (Chromosorb G-NAW). Carbon disulfide and sodium-dried benzene-d_6 were used rather than chlorocarbons for IR and NMR spectra of the most moisture-sensitive samples.

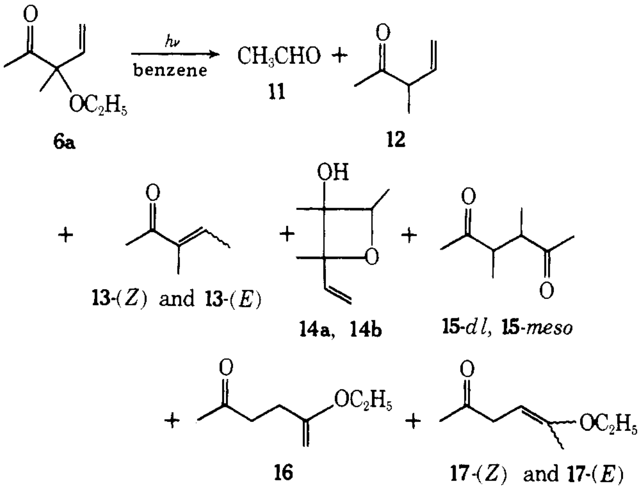
Table I. Photoproducts from Irradiations of 3-Ethoxy-3-methylpent-4-en-2-one

Compd	Retention time, min[a]	Yield, %[b] direct	Yield, %,[b,c] with piperylene
11	2.6	4	4
12	9.1	2	7
13-(*Z*)	12.4	4	7
13-(*E*)	16.2	5	9
14a[d]	28.6	6	7
14b[d]	35.4	3	3
15a[e]	47.9	2	0
15b[e]	55.7	2	0
16	58.1	3	5
17a[f]	71.2	2	4
17b[f]	76.1	3	5

[a] On a 20 ft × 9 mm o.d. glass column of 5% SE-30 on 60/80 Chromosorb G-NAW at 85 °C, 95 mL/min. [b] Uncorrected for detector response. [c] 0.3 M piperylene and 0.3 M **6** in benzene. [d] One of four possible stereoisomers, absolute stereochemistry undetermined. [e] *dl* and meso stereoisomers; correspondence to individual GLC fractions undetermined. [f] *E* and *Z* isomers; absolute stereochemistry not unambiguously determined.

When samples of **6a** (0.2 M in benzene, *tert*-butylbenzene as standard) were prepared, irradiated, and analyzed with the precautions indicated, the GLC trace revealed (after 2 h of irradiation) that 11 principal photoproducts[14] and numerous trace products were formed (Scheme I). The hydrolysis products, ethanol and 2,5-hexanedione (**3**), were not observed under rigorously dry and acid-free conditions.

Scheme I. Direct Photolysis of 3-Ethoxy-3-methylpent-4-en-2-one



The 11 principal photoproducts were isolated by preparative GLC (cf. Table I for yields and retention times). Comparison of IR and NMR spectra with published ones identified acetaldehyde (**11**), 3-methylpent-4-en-2-one (**12**),[15] and (*Z*)- and (*E*)-3-methylpent-3-en-2-one [**13**-(*Z*), **13**-(*E*)].[15–18] The next two fractions were identified as two of the four possible racemic stereoisomers of 2,3,4-trimethyl-2-vinyloxetan-3-ol (**14a**, **14b**) based on NMR (two methyl singlets, methyl doublet, methine quartet, vinyl ABX), IR (hydroxyl, vinyl, and oxetane bands), and mass spectra (cf. Experimental Section).

The *dl* and meso modifications of 3,4-dimethylhexane-2,5-dione (**15a,b**) were identified by comparison of IR, NMR, and mass spectra[19] and GLC retention times to those of the authentic materials prepared as a *dl*–meso mixture from 2-butanone and lead dioxide according to Wolf.[20]

Three enol ethers were identified on the basis of IR, NMR, and mass spectra, and by their particular susceptibility to hydrolysis to 2,5-hexanedione and ethanol. 5-Ethoxyhex-5-en-2-one (**16**) was distinguished from the others by the terminal methylene–enol ether moiety (NMR δ 3.83 and 3.91 doublets; IR 975 and 795 cm^{-1}). Two GLC fractions (**17a, 17b**) were identified from IR, NMR, and mass spectra as 5-ethoxyhex-4-en-2-one. Both had enol ether IR bands (in CS_2: **17a,** 790 cm^{-1}; **17b,** 810 cm^{-1}) and, in the NMR (C_6D_6), 1-H vinyl triplets (**17a,** δ 4.70; **17b,** δ 4.57) coupled (J = 7 Hz) to a methylene doublet (**17a,** δ 3.11; **17b,** δ 2.77). More fine spin-spin splitting between methylene, vinyl H, and vinyl methyl could be seen in **17a.** Since **17**-(Z) should be expected to have the more shielded vinyl hydrogen, less shielded vinyl methyl, and the larger allylic coupling,[21–23] the NMR contradictions precluded unambiguous distinction as to which fraction of **17a,b** was **17**-(E) and which was **17**-(Z).

Plots of product yields vs. irradiation time showed clear induction periods for the 3,4-dimethylhexane-2,5-diones **15,** indicating that they were secondary photoproducts. The plot for **16** was ambiguous. No induction periods were seen in formation of photoproducts **11, 12, 13, 14,** and **17.**

In addition to the identified photoproducts, ca. 25 additional trace products could be seen in the GLC trace when the temperature was programmed to 200 °C. Quantification and identification were not feasible.

Photolyses of 3-Ethoxy-3-methylpent-4-en-2-one with Added Sensitizers or Quenchers. Two solutions of 0.3 M 3-ethoxy-3-methylpent-4-en-2-one (**6a**) in dry benzene with *tert*-butylbenzene as standard, with 0.9 M piperylene added to one sample, were degassed and irradiated in parallel with a 450-W Hanovia medium-pressure mercury arc lamp for a total of 3 h. Aliquots were withdrawn at regular intervals for GLC analysis (5% SE-30, 85 °C, 95 mL/min). No quenching of the disappearance of **6a** could be observed.

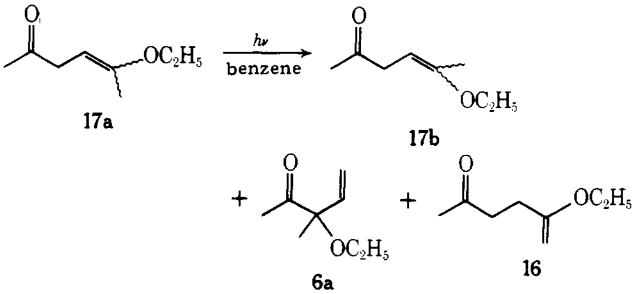
Although no change in the rate of keto ether loss was observed, many other differences were apparent in the GLC traces of the two photolysates. Most notable was the complete lack of either isomer of 3,4-dimethylhexane-2,5-dione (**15**) in the piperylene-quenched photolysis. Most other photoproducts appeared more rapidly and rose to a greater overall yield in the piperylene-quenched photolysis (cf. Table I).

Parallel photolyses were also run on two 0.5 M solutions of **6a** in benzene containing *tert*-butylbenzene standard, which were identical except that one was saturated with xanthone (0.19 M). A 6-h irradiation at 365 nm and a bandwidth of 23 nm, obtained with a 1000-W Osram super-pressure mercury arc lamp with a Schoeffel GM-250 grating monochromator (conditions under which the xanthone would absorb virtually 100% of the light), was monitored by GLC.

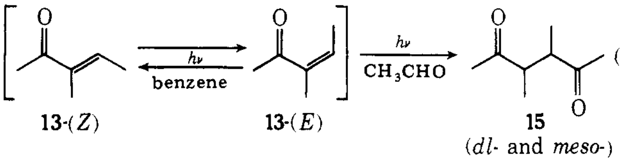
At the end of the irradiation no loss of **6a** could be observed in either photolysis. Using trans–cis piperylene isomerization (Φ = 0.44)[24–26] as actinometer, and assuming that no more than 5% of **6a** could have reacted without detection, an upper limit for the quantum yield for sensitized disappearance of **6a** would be 4×10^{-3}.

Direct Photolysis of 5-Ethoxyhex-4-en-2-one in Benzene. A sample of 5-ethoxyhex-4-en-2-one (**17a**), isolated by preparative GLC and dissolved to make a 1% solution in dry benzene-d_6 according to the precautions presented earlier (vide ante), was irradiated with a Corex D-filtered mercury arc lamp, and reaction was monitored by GLC. After 30 min three new GLC peaks were apparent, having identical retention times with **17b,** the other isomer of 5-ethoxyhex-4-en-2-one, 3-ethoxy-3-methylpent-4-en-2-one (**6a**), and 5-ethoxyhex-5-en-2-one (**16**) (Scheme II). The remaining photolysate was diluted and analyzed by FT NMR, which clearly showed that both isomers of **17** were present. No photoequilibrium could be established because of the gradual accumulation of secondary photoproducts. From the relative rates of production of **6a** and **17b,** it appears likely that the latter is a secondary photoproduct.

Scheme II. Photolysis of 5-Ethoxyhex-4-en-2-one in Benzene



Photolysis of (*E*)-3-Methylpent-3-en-2-one with Acetaldehyde in Benzene-d_6. A 1% solution of (*E*)-3-methylpent-3-en-2-one [**13**-(*E*)], with an eightfold excess of acetaldehyde, and *tert*-butylbenzene as standard, in sodium-dried benzene-d_6 was irradiated for 2.5 h with a Corex-filtered mercury arc lamp; progress of the reaction was followed by GLC. After 15 min of irradiation a GLC peak representing (*Z*)-3-methylpent-3-en-2-one [**13**-(*Z*)] was the only detectable photoproduct. Morrison and Rodriquez[27] have previously documented this example of photochemical cis–trans isomerization. The photolysis was continued for 150 min, at which time more than 95% of the (*E*)- and (*Z*)-3-methylpent-3-en-2-ones had disappeared and two new products had appeared, which were identified at *dl*- and *meso*-3,4-dimethylhexane-2,5-dione (**15a,b**) on the basis of GLC retention times (eq 2).

 (2)

Discussion

Primary Photochemistry of 3-Ethoxy-3-methylpent-4-en-2-one. The photochemistry of the α-ethoxy β,γ-unsaturated ketone **6a** proved significantly more complicated than that of the α-hydroxy analogue **2**,[7] as the 11 principal photoproducts,[14] two hydrolysis products, and numerous trace products attest. However, all of the primary photoproducts can be accounted for in terms of competing 1,3-acyl shift (**11, 17a,b**) and Norrish type II [**11, 12, 13**-(*Z,E*), and **14a,b**] processes. The other products (**15a,b** and **16**) arise via secondary photochemical reactions (vide infra).

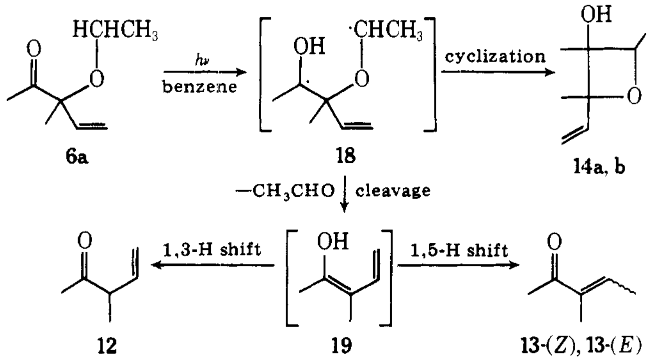
Both sets of primary photoreactions can be rationalized as originating in either the n–π^* singlet (S_1) or n–π^* triplet (T_2)[3] of **6a.** The α-ethoxy ketone **6a** showed a normal hypsochromic shift of the n–π^* absorption band in polar solvents [λ_{max} 297, 305, 315 (sh), and 325 nm (sh) in c-C_6H_{12}; 295 (sh), 302, 313 (sh), and 325 nm (sh) in acetonitrile]. The analogous α-hydroxy ketone **2** showed a *bathochromic* polar solvent shift of the long wavelength absorption band.[7] Comparison of the spectra of **2** and **6a** supports previous conclusions[4,7,28,29] that internal hydrogen bonding of α-hydroxy ketones in nonpolar solvents is the cause of their atypical bathochromic n–π^* polar solvent shifts.

The disappearance of **6a** could neither be sensitized with xanthone (E_T = 74 kcal mol^{-1}) nor quenched with piperylene. The absence of any discernible triplet-sensitized reactivity in **6a** (other than inefficient long-term decomposition) is probably attributable to an invisible free-rotor effect.[21] Since xanthone's triplet energy is probably too low to sensitize the T_2 of **6a**, these results are compatible with very fast reaction from either T_2 or S_1 on direct irradiation.

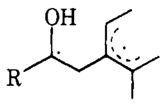
The 1,3-shift products, enol ethers **17**-(*Z*) and **17**-(*E*), are the analogues of the γ-keto enol **7**, which had been postulated as an undetected intermediate in the **2** → **3** rearrangement. Whether the 1,3 shift in **6a** is concerted or stepwise is hard to assess. Acetaldehyde (**11**) and traces of biacetyl were the only α-cleavage products detected, and most of the **11** more likely originates in Norrish type II cleavage as companion to the Δ^4- and Δ^3-3-methylpenten-2-ones **12** and **13**. In either case, isolation of enol ethers **17** from photolysis of the α-alkoxy ketone **6a** provides strong circumstantial evidence for intermediacy of enol **7** in the photolysis of the α-hydroxy analogue **2**. Tautomerization of **17** is blocked by the ether function, but diketone **3** is readily obtained by hydrolysis. The low yields of enol ethers **17** obviate any synthetic utility in this system as a half-protected 1,4-diketone.

The origins of acetaldehyde (**11**), unsaturated ketones **12**, **13**-(*E*), and **13**-(*Z*), and oxetanol isomers **14a,b** are in Norrish type II pathways (Scheme III) which compete with the 1,3-acyl shift. γ-Hydrogen abstraction can be followed by cyclization of the biradical **18** to give the oxetanols (**14**) or by cleavage to give acetaldehyde and the transient enol **19**. Tautomerization of the enol by 1,3- and 1,5-hydrogen shifts leads to **12** and **13**, respectively.

Scheme III. Norrish Type II Reactions of 3-Ethoxy-3-methylpent-4-en-2-one



There are many examples of type II reactions in β,γ-unsaturated ketones which have involved hydrogen abstraction from a β-alkyl group to give a diradical of type **20** and subsequent cyclization rather than cleavage.[1,9,11] Wagner has explained the absence of type II elimination as a result of the orthogonality of the allylic π radical to the C_2–C_3 bond.[30] This rationale does not apply to **6a**, in which H abstraction is from a β'-alkyl group to give the quite different diradical **18** (Scheme III).

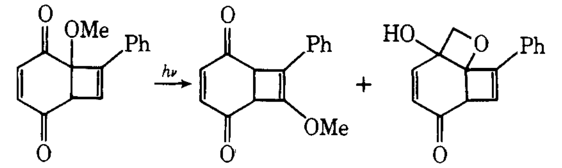


20

The photochemistry of **6a** more closely resembles results of Yates and Szabo,[31] LaCount and Griffin,[32] and Lewis and Turro[33] for various α-alkoxy ketones and acetophenones, in which both type II cleavage and cyclization occur competitively.

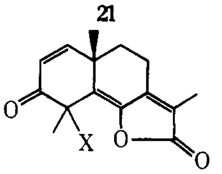
It is difficult to gauge precisely the partitioning of **6a** between the several available pathways because of the number of minor, unidentified products. However, that the n-π^* singlet of **6a** is partitioned between 1,3 shift and γ-H abstraction, whereas the photochemistry of the hydroxy analogue **2** was uncomplicated by type II reactions, demonstrates the significant γ-hydrogen substituent effect. Dramatic enhancement of γ-H abstraction by adjacent alkoxy functionality has been demonstrated previously by several groups,[33-35] and quantified and explained by Wagner.[34] In **6a**, the best estimates of the proportioning are the product yields in runs with added piperylene which was shown not to quench disappearance of **6a** or appearance of any primary photoproducts, but which did quench secondary triplet decompositions of the primary products. Under these conditions the yield ratio (**12** + **13** + **14**):(**17**) gauges the γ-H abstraction:1,3-shift partitioning as ca. 4:1 (a typical value[33-35]). Similarly, the (**12** + **13**):(**14**) ratio measures the type II cleavage:cyclization ratio as ca. 2:1 (cf. Table I). These values, of course, measure only products, not reactivities, since reversion to **6a** from reaction intermediates has not been measured.

Few closely related systems have been studied.[1] Anet and Mullis[36] did report the photochemistry of the α-methoxy β,γ-unsaturated ketone **21**, which partitioned about 3:1 between 1,3 shift (**22**) and type II cyclization (**23**), with no type II cleavage and apparently no 1,3 shift reversal (eq 3). McMurry[37] has recently reported the photochemistry of 4-hydroxy- (**24a**)[6] and 4-acetoxysantonene (**24b**).[37] Hydroxy ketone **24a** gives the *A*-nor-6-acetyl compound **25** (by 1,2 shift and cyclopropanol rearrangement) as the major direct and sole triplet-sensitized product. In contrast to **24a** and **6a**, the α-acetoxy β,γ-unsaturated ketone **24b** gives decarboxylation product **24c** and double bond migration isomers in the triplet state, and enone-type rearrangements to **26** in the singlet.[37] The sensitized photolyses of the 1,2-dihydro analogues of **24a** and **24b** gave analogous triplet photochemistry, but the singlet photochemistry was not reported.[36,37] The diverging reactions of the α-oxy ketones such as **2**, **4**, **6a**, **24a**, and **24b** leave many unanswered questions about the role of α-alkoxy substituents in β,γ-unsaturated ketone photochemistry.

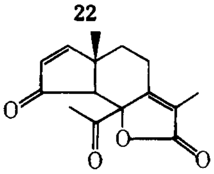


(3)

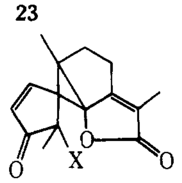
21 **22** **23**



24a, X = OH
b, X = OAc
c, X = CH$_3$

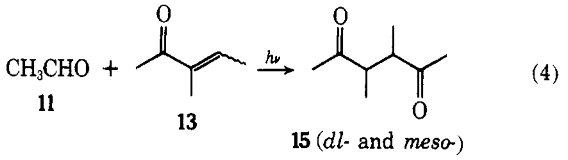


25



26a, X = OAc
b, X = CH$_3$

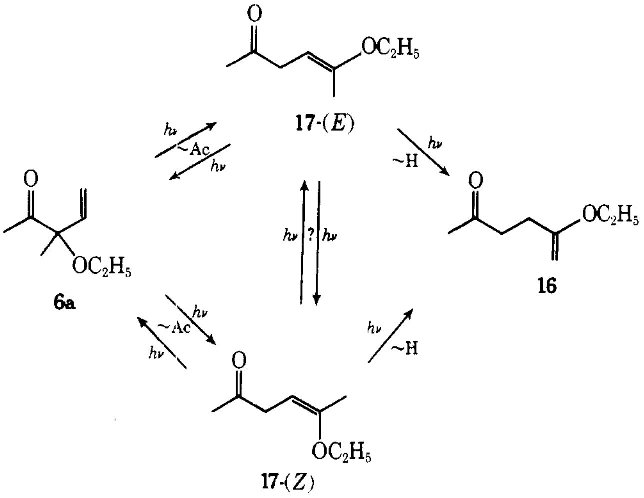
Secondary Photochemical Reactions. The *dl*- and *meso*-3,4-dimethylhexane-2,5-diones **15** were identified as secondary photoproducts from the observations that (a) buildup of diketones **15** shows an induction period, accelerating when photolysis of **6a** is about 30% complete; and (b) production of diketones **15** is totally quenched by 0.9 M piperylene (Table I), while disappearance of **6a** is not. The likely source of diketones **15** was shown by an independent photolysis to be photoaddition of acetaldehyde (**11**) to 3-methylpent-3-en-2-one (**13**) under the photolysis conditions for **6a** (eq 4). Fraser-Reid et al. have also recently reported photosynthesizing 1,4-diketones by photoaddition of aldehydes to enones[38] under conditions comparable to those employed here.



11 13 15 (*dl*- and *meso*-)

The origin of 5-ethoxyhex-5-en-2-one (**16**) can be traced to further rearrangement of the enol ethers **17**, as suggested by the rise in yield of **16** at the expense of **17** during photolysis of **6a**. Photolysis of isolated **17** gave **16** via a 1,3-H shift and **6a** via a 1,3-acyl shift (Scheme IV). Both are presumed singlet reaction products since their formation was not quenched by piperylene. In addition, **17** undergoes cis–trans isomerization under the photolysis conditions. Although olefin isomerization is often seen in unconstrained β,γ-unsaturated ketones as a triplet process,[1,21] the **17**-(E) $\rightleftharpoons$ **17**-(Z) isomerization more likely results from sequential 1,3-acyl shifts, since **6a** appeared more rapidly than **17b** in photolyses of **17a**.

Scheme IV. Photochemistry of 5-Ethoxyhex-4-en-2-one



17-(E)

6a

16

17-(Z)

Although the secondary photochemistry of the other primary products was not explored, the oxetanols **14** appeared photolytically stable since their yields were not affected by added piperylene. The oxetanols also were stable to hydrolysis under normal conditions.

Experimental Section[39]

2-Methyl-2-(1-ethoxy-1-methylprop-2-en-1-yl)-1,3-dithiane. To an oven-dried 500-mL three-neck round-bottomed flask equipped with a mechanical stirrer, nitrogen inlet, and dry addition funnel were added 200 mL of dimethylformamide, dried by distillation over calcium hydride, and 27.3 g (0.175 mol) of ethyl iodide. Sodium hydride (7.38 g of a 57% oil dispersion, 0.175 mol) was washed free of oil with pentane and added to the reaction flask all at once. 2-Methyl-2-(1-hydroxy-1-methylprop-2-en-1-yl)-1,3-dithiane[7] (20.4 g, 0.100 mol) dissolved in 80 mL of dry DMF was added with stirring to the reaction flask which was cooled in an ice bath. The reaction mixture was warmed and stirred at room temperature for 20 h. The reaction mixture was diluted with 330 mL of water and extracted with ether (5 × 100 mL), and the combined ether extracts were washed with 250 mL of brine. The ethereal solution was dried over anhydrous sodium sulfate and concentrated in vacuo to give 23.1 g of a pale yellow liquid. Simple distillation afforded 21.5 g (93%) of clear, colorless 2-methyl-2-(1-ethoxy-1-methylprop-2-en-1-yl)-1,3-dithiane: bp 107–108 °C (0.5 Torr); infrared (neat film) absorptions at 3089 (vinyl), 2985, 2932, 1440, 1410, 1385, 1365, 1275, 1240, 1111, 1074, 1038, 996 (vinyl), and 924 cm^{-1} (vinyl); NMR (CCl_4) resonances at δ 1.17 (3 H, triplet, J = 6.5 Hz, CH_3CH_2–), 1.40 (3 H, singlet, methyl), 1.47 (3 H, singlet, methyl), 1.67–2.20 (2 H, multiplet, C-5 methylene), 2.28–3.00 (4 H, multiplet, C-4 and C-6 methylenes), 3.33 (2 H, quartet, J = 6.5 Hz, CH_3CH_2–), 5.08, 5.22, and 6.24 (3 H, ABX pattern, cis terminal H, trans terminal H, and single vinyl H, respectively, J_{AX} = 17, J_{BX} = 11, J_{AB} = 2 Hz).

3-Ethoxy-3-methylpent-4-en-2-one. To a 2-L three-neck round-bottomed flask fitted with mechanical stirrer, 1-L addition funnel, condenser, and dry nitrogen inlet were added 900 mL of 80% aqueous acetonitrile, 53.2 g (0.196 mol) of mercuric chloride, and 22.2 g (0.222 mol) of calcium carbonate (to buffer the solution near pH 7). 2-Methyl-2-(1-ethoxy-1-methylprop-2-en-1-yl)-1,3-dithiane (20.7 g, 0.0891 mol) dissolved in 600 mL of 80% aqueous acetonitrile was added dropwise to the reaction mixture. After stirring at room temperature for 1 h, the reaction mixture was refluxed for an additional 16 h. A tan solid which began to form after 1 h was removed after reflux by suction filtration through a pad of Celite 512 (AW). The filter cake was washed thoroughly with ether. The combined filtrate and ether solutions were diluted with 1 L of additional ether and this solution was washed with 5 M ammonium acetate (2 × 600 mL). The organic layer was dried over anhydrous sodium sulfate and then concentrated to ca. 60 mL by distillation through a 4-ft vacuum-jacketed fractionating column of glass helices. Preparative GLC (6.5 ft × 0.75 in. 20% UC-W98 on 60/80 Chromosorb P-DMCS, 93 °C) followed by simple distillation afforded 4.1 g (33%) of clear, colorless 3-ethoxy-3-methylpent-4-en-2-one: bp 159–161 °C; infrared (CCl_4) absorptions at 3092 (vinyl), 2990, 2938, 2905, 2885, 1716 (carbonyl), 1628 (vinyl), 1438, 1403, 1390, 1350, 1190, 1124 (ether), 1065, and 928 cm^{-1} (vinyl); NMR (benzene-d_6) resonances at δ 1.17 (3 H, triplet, J = 7 Hz, CH_3CH_2–), 1.43 (3 H, singlet, α-methyl), 2.16 (3 H, singlet, acetyl methyl), 3.20 and 3.28 (2 H, overlapping quartets, J = 7 Hz, nonequivalent O-methylene hydrogens), 5.10, 5.37, and 5.88 (3 H, ABX pattern, cis vinyl H, trans vinyl H, single vinyl H, respectively, J_{AX} = 17, J_{BX} = 10, J_{AB} = 2.5 Hz); ultraviolet λ_{max} at 297 nm (ϵ 141), 305 (139), 315 (sh), and 325 (sh) in cyclohexane, λ_{max} at 295 nm (sh), 302 (ϵ 137), 313 (sh), 325 (sh) in acetonitrile; significant mass spectral fragmentations (with rel intensities) at m/e 142 (0.02, P), 99 (90), 78 (32), 71 (92), 43 (100), 41 (23), 39 (21), 29 (32), 27 (53), and 15 (42).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.31; H, 9.92.

3,4-Dimethylhexane-2,5-dione. Using a procedure outlined by Wolf,[20] 60 g (0.83 mol) of 2-butanone and 20 g (0.083 mol) of lead dioxide were refluxed for 28 h in a 300-mL three-neck round-bottomed flask equipped with a condenser and dry nitrogen inlet. After ca. 3 h, the black solid had become yellow. The solid was removed by suction filtration upon completion of reflux. Distillation of the filtrate through a 10-cm Vigreux column gave a low-boiling fraction (bp <80 °C) and 3.88 g (33% based on PbO_2 used) of 3,4-dimethylhexane-2,5-dione, bp 85–95 °C (17–20 Torr), as a mixture of the *dl* and meso isomers. Separation of the isomers was accomplished by preparative GLC (20 ft × 9 mm o.d. glass, 4% SE-30 on 60/80 Chromosorb G-NAW, 85 °C): fraction 1 (retention time 41.3 min) had infrared (CCl_4) absorptions at 2985, 2947, 2890, 1710 (carbonyl), 1454, 1421, 1355, 1280, 1195, 1163, 1088, and 945 cm^{-1}; NMR (CCl_4) resonances at δ 1.02 (6 H, doublet, J = 6.5 Hz, 3,4-dimethyls), 2.10 (6 H, singlet, terminal methyls), and 2.40–3.00 (2 H, multiplet, methines); fraction 2 (retention time 48.2 min) had infrared (CCl_4) absorptions at 2985, 2948, 2890, 1710 (carbonyl), 1460, 1423, 1355, 1158, 1082, and 955 cm^{-1}; NMR identical with that of fraction 1. No attempt was made to identify which GLC fraction was the *dl* mixture and which was the meso component.

Direct Irradiation of 3-Ethoxy-3-methylpent-4-en-2-one. Photolysis samples were prepared in oven-dried, ethoxide-washed thin-walled Pyrex NMR tubes under a dry nitrogen atmosphere. In a typical experiment, 100 μL (0.0912 g, 0.642 mmol) of 3-ethoxy-3-methylpent-4-en-2-one, 6.0 μL of *tert*-butylbenzene as standard, 1.90 mL of sodium-dried spectrograde benzene, and ca. 25 Linde 4-A molecular sieves were added to the NMR tube. The photolysis tube was sealed by first wiring on one and then a second (larger) serum cap. Samples were degassed by three freeze–pump–thaw cycles at 10^{-4} Torr, and irradiated with a Corex-D filtered 450-W, medium pressure Hanovia mercury arc lamp for periods up to 6 h. Photolysis was followed by GLC analysis on a 20 ft × 9 mm o.d. glass column packed with either 4 or 5% SE-30 on 60/80 Chromosorb G-NAW. In analytical studies 100-μL aliquots were removed from the photolysis tube every 15 min; GLC analysis revealed the immediate buildup of 11 major[14] and many minor photoproducts with the concomitant loss of the 3-ethoxy-3-methylpent-4-en-2-one peak. Two peaks (corresponding to the 3,4-dimethylhexane-2,5-diones) appeared more slowly, but grew to be major photoproducts after ca. 1.5 h of irradiation. The major photoproducts were isolated by preparative GLC after irradiation periods of ca. 1.5 h, using oven-dried and base-washed collection devices. The principal photoproducts, in order of their GLC retention times, are listed below with their respective GLC elution times (20 ft × 9 mm o.d. glass 5% SE-30 on 60/80 Chromosorb G-NAW, 85 °C, 95 mL/min) and maximum percent yields.[14]

1. **Acetaldehyde** (2.6 min, yield 4%) was characterized by comparison of its GLC retention time, NMR, and IR spectra with those of authentic material.

2. **3-Methylpent-4-en-2-one** (9.1 min, yield 2%) was characterized by comparison of its IR and NMR spectra to published data:[15] NMR (CCl_4) resonances at δ 1.16 (3 H, doublet, $J = 7$ Hz, C-3 methyl), 2.04 (3 H, singlet, acetyl methyl), 2.75–3.40 (1 H, five-peak multiplet with fine splitting, methine), and 4.65–6.0 (3 H, ABX pattern, vinyl H's) [lit.[15] NMR δ 1.19 (doublet, $J = 6.9$ Hz), 2.07 (singlet), 3.12 (pentet, $J = 7$ Hz), and 5–6 (multiplet)].

3. **(*Z*)-3-Methylpent-3-en-2-one** (12.4 min, yield 4%) was characterized by comparison of NMR and infrared spectra to spectra of authentic material.[15–18]

4. **(*E*)-3-Methylpent-3-en-2-one** (16.2 min, yield 5%) was characterized by comparison of NMR and infrared spectra to those of authentic material.[15–18]

5. **2,3,4-Trimethyl-2-vinyloxetan-3-ol A** (28.6 min, yield 6%), one of four possible racemic stereoisomers, absolute stereochemistry undetermined, was characterized by its infrared, NMR, and mass spectra: infrared (CCl_4) absorptions at 3575 (hydroxyl), 3093 (vinyl), 2982, 2940, 2900, 1630 (vinyl), 1441, 1391, 1376, 1332, 1260 (oxetane), 1217, 1142, 1097, 1054, 987, 952 (oxetane), 940, and 886 cm^{-1}; NMR ($CDCl_3$) resonances at δ 1.18 (3 H, doublet, $J = 7$ Hz, C-4 methyl), 1.30 and 1.38 (3 H each, singlets, C-2 and C-3 methyls), 2.26 (1 H, singlet, hydroxy), 4.53 (1 H, quartet, $J = 7$ Hz, methine), 5.34, 5.53, and 5.91 (3 H, ABX pattern, cis terminal H, trans terminal H, single vinyl H, respectively, $J_{AX} = 17$, $J_{BX} = 10$, $J_{AB} = 2.5$ Hz).

Anal. Calcd for $C_8H_{14}O_2$: $M^{+\cdot}$ 142.0994. Found: 142.1016.

6. **2,3,4-Trimethyl-2-vinyloxetan-3-ol B** (35.4 min, yield 3%), one of four possible racemic stereoisomers, absolute stereochemistry undetermined, was characterized by infrared, NMR, and mass spectra: infrared (CS_2) absorptions at 3620 (hydroxyl), 3110 (vinyl), 2980, 2930, 2915, 1370, 1325, 1260 (oxetane), 1230, 1185, 1065, 1100, 957 (oxetane), 890, and 860 cm^{-1}; NMR ($CDCl_3$) resonances at δ 1.24 (3 H, singlet, methyl), 1.27 (3 H, doublet, $J = 6$ Hz, C-4 methyl), 1.32 (3 H, singlet, methyl), 1.82 (1 H, singlet, hydroxy), 4.42 (1 H, quartet, $J = 6$ Hz, methine), 5.11, 5.31, and 5.91 (3 H, ABX pattern, cis terminal H, trans terminal H, single vinyl H, respectively, $J_{AX} = 17$, $J_{BX} = 10$, $J_{AB} = 2$ Hz); significant mass spectral fragmentations (with relative intensities) at *m/e* 124 (1, P − 18), 58 (22), 43 (100), and 15 (16).

7 **and** 8. **3,4-Dimethylhexane-2,5-dione** was isolated as two GLC fractions corresponding to indistinguishable *dl* and meso modifications, identified by IR, NMR, and mass spectra[19] identical with those of authentic material prepared according to Wolf:[20] fraction 7 (47.9 min, yield 2%) and fraction 8 (55.7 min, yield 2%).

9. **5-Ethoxyhex-5-en-2-one** (58.1 min, yield 3%) was characterized by infrared (CS_2) absorptions at 3120 (vinyl), 2980, 2925, 1725 (carbonyl), 1660 (vinyl), 1362, 1300, 1280, 1272, 1160, 1082, 975 ($OCH{=}CH_2$), and 795 cm^{-1} ($OCH{=}CH_2$); NMR (benzene-d_6) resonances at δ 1.07 (3 H, triplet, $J = 7$ Hz, ethoxy methyl), 1.65 (3 H, singlet, acetyl methyl), 2.20–2.49 (4 H, multiplet, methylenes), 3.44 (2 H, quartet, $J = 7$ Hz, ethoxy methylene), 3.83 (1 H, doublet, $J = 1$ Hz, vinyl H), and 3.91 (1 H, doublet, $J = 1$ Hz, vinyl H); significant mass spectral fragmentations (with relative intensities) at *m/e* 142 (5, P), 99 (40), 71 (72), and 43 (100).

Anal. Calcd for $C_8H_{14}O_2$: $M^{+\cdot}$ 142.0994. Found: 142.1026.

10 and 11. 5-Ethoxyhex-4-en-2-one was isolable as two GLC fractions corresponding to the *E* and *Z* stereoisomers, which were not unambiguously distinguishable on the basis of spectral data (vide infra).

10. **5-Ethoxyhex-4-en-2-one A** (71.2 min, yield 2%) was characterized by infrared (CS_2) absorptions at 3050 (sh, vinyl), 2980, 2920, 1715 (carbonyl), 1370, 1238, 1210, 1168, 1128, 1070, 962, and 790 cm^{-1}; NMR (benzene-d_6) resonances at δ 1.02 (3 H, triplet, $J = 7$ Hz, ethoxy methyl), 1.57 (3 H, singlet, vinyl methyl), 1.82 (3 H, singlet, acetyl methyl), 3.11 (2 H, doublet with unresolved fine splitting, $J = 7$ Hz, α-methylene), 3.45 (2 H, quartet, $J = 7$ Hz, ethoxy methylene), and 4.70 (1 H, broad triplet with unresolved fine splitting, $J = 7$ Hz, vinyl H); significant mass spectral fragmentations (with relative intensities) at *m/e* 142 (4, P), 99 (26), 71 (54), 43 (100), 29 (18), 31 (29), 27 (27), and 15 (19).

Anal. Calcd for $C_8H_{14}O_2$: $M^{+\cdot}$ 142.0994. Found: 142.0976.

11. **5-Ethoxyhex-4-en-2-one B** (76.1 min, yield 3%) was characterized by infrared (CS_2) absorptions at 3080 (sh, vinyl), 2975, 2925, 2875, 1715 (carbonyl), 1660 (vinyl), 1385, 1360, 1313, 1240, 1215, 1163, 1127, 1080, 975, and 810 cm^{-1}; NMR (benzene-d_6) resonances at δ 1.14 (3 H, triplet, $J = 7$ Hz, ethoxy methyl), 1.75 (3 H, singlet, vinyl methyl), 1.78 (3 H, singlet, acetyl methyl), 2.77 (2 H, doublet, $J = 7$ Hz, α-methylene), 3.52 (2 H, quartet, $J = 7$ Hz, ethoxy methylene), and 4.57 (1 H, triplet with unresolved fine splitting, $J = 7$ Hz, vinyl); significant mass spectral fragmentations (with relative intensities) at *m/e* 142 (6, P) 99 (36), 71 (84), 43 (100), 29 (18), 27 (26), and 15 (19).

Anal. Calcd for $C_8H_{14}O_2$: $M^{+\cdot}$ 142.0994. Found: 142.1026.

Effects of Sensitizers and Quenchers. Samples were prepared and analyzed as for direct irradiations without additives (vide supra), except for addition of xanthone (0.19 M) or piperylene (0.9 M). Irradiation of xanthone-containing samples at 365 nm (Osram 1000-W super-pressure lamp, Schoeffel GM-250 monochromator, 23-nm bandwidth, xanthone absorbing all incident light) caused no reaction in 6.5 h. Using xanthone-sensitized piperylene isomerization as actinometer,[24–26] an upper limit for the quantum yield of disappearance of 3-ethoxy-3-methylpent-4-en-2-one was 4×10^{-3} mol/einstein.

With 0.9 M piperylene, samples irradiated with a Corex-D-filtered mercury lamp (Hanovia, 450 W) gave disappearance of 3-ethoxy-3-methylpent-4-en-2-one at a rate identical with that in parallel control samples. However, product yields were: acetaldehyde, 4%; 3-methylpent-4-en-2-one, 7%; (*Z*)-3-methylpent-3-en-2-one, 7%; (*E*)-3-methylpent-3-en-2-one, 9%; 2,3,4-trimethyl-2-vinyloxetanol A, 7%; 2,3,4-trimethyl-2-vinyloxetanol B, 3%; *dl*- and *meso*-3,4-dimethylhexane-2,5-diones, absent; 5-ethoxyhex-5-en-2-one, 5%; 5-ethoxyhex-4-en-2-one A, 4%; and 5-ethoxyhex-4-en-2-one B, 5%.

Photolysis of (*E*)-3-Methylpent-3-en-2-one with Acetaldehyde. A 1% solution of (*E*)-3-methylpent-3-en-2-one, 8 equiv of acetaldehyde, and 2% of *tert*-butylbenzene as standard in sodium-dried benzene-d_6 was irradiated with a Corex D-filtered 450-W medium-pressure Hanovia mercury arc lamp. Progress of the photolysis was followed by GLC (20 ft × 9 mm o.d. glass column, 5% SE-30 on 60/80 Chromosorb G-NAW, 85 °C, 95 mL/min) at 0, 15, 45, 90, and 150 min. After 15 min of irradiation the only photoproduct was (*Z*)-3-methylpent-3-en-2-one, identifiable by its GLC retention time.[15–18] After 150 min of irradiation more than 95% of the (*E*)- and (*Z*)-3-methylpent-3-en-2-ones had been destroyed and two products appeared which were *dl*- and *meso*-3,4-dimethylhexane-2,5-dione.

Photolysis of 5-Ethoxyhex-4-en-2-one A in Benzene-d_6. A 1% solution of 5-ethoxyhex-4-en-2-one A in sodium-dried benzene-d_6 was irradiated for 30 min with a Corex D-filtered medium-pressure Hanovia mercury arc lamp. Aliquots were analyzed at 0, 15, and 30 min of irradiation by GLC (20 ft × 9 mm o.d. glass column, 5% SE-30 on 60/80 Chromosorb G-NAW, 85 °C, 95 mL/min). After 30 min of irradiation three new GLC peaks were apparent, corresponding to 5-ethoxyhex-4-en-2-one B, 3-ethoxy-3-methylpent-4-en-2-one, and 5-ethoxyhex-5-en-2-one (64% of the A isomer had been destroyed). Integration of the GLC trace gave 5-ethoxyhex-4-en-2-one A, 3-ethoxy-3-methylpent-4-en-2-one, 5-ethoxyhex-4-en-2-one B, and 5-ethoxyhex-5-en-2-one in a ratio of 5.6:2.0:1.0:1.0. The GLC analysis was confirmed by ^1H FT NMR on an additional photolysate aliquot appropriately diluted with benzene-d_6.

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Registry No.—**6a**, 61769-86-6; **9**, 61769-87-7; **10**, 61769-88-8; **11**, 75-07-0; **12**, 758-87-2; *Z*-**13**, 1567-72-2; *E*-**13**, 1567-73-3; **14**, 61769-89-9; *dl*-**15**, 28895-03-6; *meso*-**15**, 28895-02-5; **16**, 61769-90-2; *Z*-**17**, 61769-91-3; *E*-**17**, 61769-92-4; ethyl iodide, 75-03-6.

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(8) K. G. Hancock, J. T. Lau, and P. L. Wylie, *Tetrahedron Lett.*, 4149

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General Photochemical Synthesis of 1*H*-1,2-Benzodiazepines from *N*-Iminoquinolinium Ylide Dimers[1]

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Irradiation of *N*-iminoquinolinium ylide dimers **7a–i**, prepared from *N*-aminoquinolinium mesitylenesulfonates **5a–i** by treatment with base, in methylene chloride solution containing acetic acid afforded the fully unsaturated 1*H*-1,2-benzodiazepines **8a–i** in moderate yields. The photoproducts **8a** and **8c** were reduced with lithium aluminum hydride to the 2,3-dihydrobenzodiazepines **12a** and **12c**, which were further hydrogenated over palladium/carbon to give the 2,3,4,5-tetrahydrodiazepines **13a** and **13c**, respectively. The reduced 1,2-benzodiazepines gave the corresponding mono- (**14**, **15**) and diacetyl (**16**, **17**) derivatives. Based on NMR studies in $CDCl_3$–acetic acid solution which demonstrate an equilibrium between the dimers **7** and the corresponding *N*-iminoquinolinium ylides **6**, a mechanism for the formation of the 1,2-benzodiazepines **8** via the diaziridine (**25**) and 2*H*-1,2-benzodiazepine (**9**) intermediates is proposed.

Streith[2] first showed in 1968 that the photolysis of *N*-acyliminopyridinium ylides (**1**) yields the previously unknown 1*H*-1,2-diazepines (**2**) (Scheme I). Concurrent investigations by Sasaki[3] and by Snieckus,[4] and more recently by Abramovitch,[5] provided additional examples of this photoinduced ring expansion reaction. At present, this constitutes the only general route to simple, fully unsaturated 1*H*-1,2-diazepines.[6-8]

In contrast, the analogous *N*-acyliminoquinolinium (**3**)[9-11] and -isoquinolinium[10-12] ylides have been shown to rearrange upon irradiation into 2-aminoquinoline and 1-aminoisoquinoline derivatives, respectively, as well as to undergo N–N fragmentation to the respective parent heterocycles.[13] The formation of 1,2-benzodiazepines **4** from ylides **3** (Scheme I) as a result of photochemical ring expansion and solvent incorporation represents the two isolated exceptions to the above generalization.[9,10]

We report on the general photochemical synthesis of the hitherto unknown fully unsaturated 1*H*-1,2-benzodiazepines **8** from the *N*-iminoquinolinium ylide dimers **7**. Of the six theoretically possible benzodiazepines,[14] the 1,4-benzodiazepines have been most widely investigated owing to their useful biological activity.[15] The 1,5-benzodiazepines have also received substantial attention,[16] whereas the corresponding 1,3, 2,4, and 2,3 isomers have been neglected in comparison.[14,17] As for the 1,2 isomers, prior to the present work, only fused cyclopentano-3*H*-1,2-benzodiazepines had been reported.[18]