Photochemical Reactivity of Conjugated Imino Ethers. II. 6,7-Dihydro-2-methoxy-4,6,6-trimethyl-5*H*-azepine

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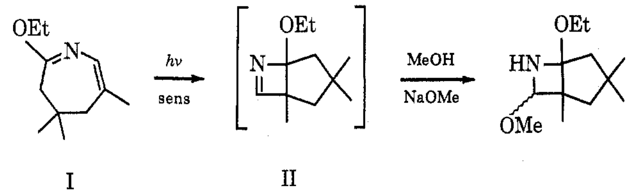
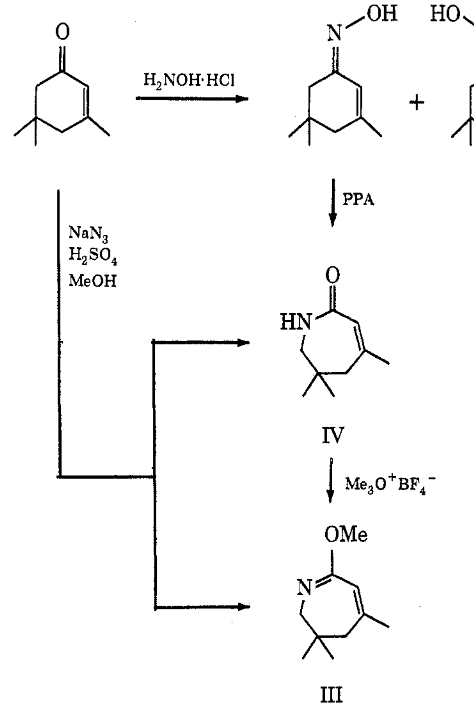
The sensitized photochemical reactivity of 6,7-dihydro-2-methoxy-4,6,6-trimethyl-5*H*-azepine (III) is described. In benzene solvent with acetophenone sensitization, III dimerizes to form a linear dimer V, and in methanol solvent with xanthone sensitization, III undergoes ionic solvent addition. Both reactions are rationalized in terms of a highly strained trans intermediate.

Recently we reported the photochemical valence isomerization of a cyclic conjugated imino ether (I) to an unstable 1-azetine derivative (II).[1] We now wish to report on the photochemical reactivity of 6,7-dihydro-2-methoxy-4,6,6-trimethyl-5*H*-azepine (III), a system structurally related to I which contains a permutation of the imino ether functional group.



Azepine III was prepared by the Schmidt rearrangement of isophorone in absolute methanol. From the Schmidt reaction both the azepine and the corresponding lactam, 6,7-dihydro-4,6,6-trimethyl-5*H*-azepin-2-one (IV), were isolated. Treatment of lactam IV, which could also be prepared by Beckmann rearrangement of isophorone syn oxime,[2] with trimethyloxonium fluoroborate likewise yielded the desired conjugated imino ether. The structure of III is unambiguously established by the spectroscopic data. In the infrared III shows strong absorption at 1670 and 1640 cm^{-1} for carbon–nitrogen and carbon–carbon double bond stretching bands, respectively. The nmr spectrum, shown in Table I, has a characteristic methoxyl singlet at δ 3.57 ppm. A mass spectral parent ion occurs at *m/e* 167 (16% of base), and a strong $\pi-\pi^*$ band appears at 212 nm (ε 8700) in the ultraviolet.



Irradiation of the unsaturated imino ether in *n*-heptane solvent with a 450-W mercury lamp through a Vycor filter for 2 hr resulted in about 60% destruction of starting material. Gas chromatographic analysis of the reaction mixture showed 19 products, each in less than 5% yield. Because of the complexity, no attempt was made to isolate and identify the photoproducts from the direct irradiation.

When acetophenone was employed as a photosensitizer in the irradiation of III in benzene solvent with a Pyrex filter, a single photoproduct was observed in the gas chromatogram. Mass spectral analysis of the isolated product indicated that it was dimeric, with a parent ion at *m/e* 334 (57% of base) and not the expected valence isomer, 7-methoxy-3,3,5-trimethylazabicyclo[3.2.0]hept-6-ene.[3] The photoproduct was assigned the linear dimeric structure V based upon the molecular weight and the following evidence. In the infrared spectrum strong carbon–nitrogen double bond stretching bands, characteristic of imino ether functional groups, appear at 1650 and 1675 cm^{-1}. A band of medium intensity appears at 1640 cm^{-1} and is assigned as a carbon–carbon double bond stretching band. The carbon–carbon double bond is further characterized as geminally disubstituted by the appearance of a strong C–H bending vibration at 1130 cm^{-1}. The absence of conjugated functional groups is established by the observation of only end absorption in the uv spectrum.

The 100-MHz nmr spectrum of V is reported in Table I in two different solvents, carbon tetrachloride and benzonitrile, and in benzonitrile at two different temperatures, 40 and 180°. At 40° in both solvents four methyl singlets, one methyl doublet, and two methoxyl singlets are distinct. The methoxyl chemical shifts are consistent with imino ether type methoxyls (see nmr spectrum of VIa for a comparison of methoxyl chemical shifts). The chemical shifts of the olefinic protons suggest an exocyclic methylene, in agreement with the ir evidence. The protons at positions 3 and 3′ appear as the AB portion of an ABX type pattern. The X proton at position 4′ is further split by the methyl protons at 4′ and the methylene protons at 5′ and appears as a complex multiplet.

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[1] T. H. Koch and D. A. Brown, *J. Org. Chem.*, **36**, 1934 (1971).

[2] R. H. Mazur, *ibid.*, **26**, 1289 (1961).

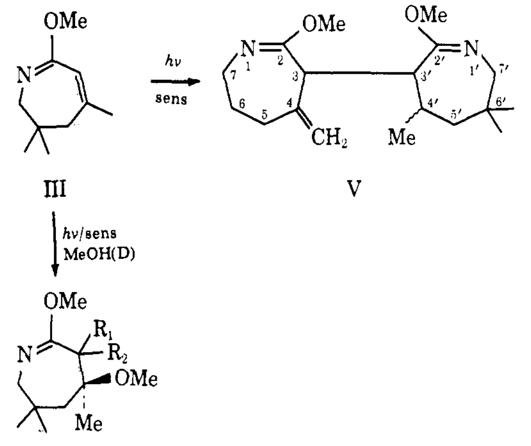
[3] Photochemical valence isomerization has been reported for structurally similar molecules: J.-L. Derocque, W. J. Theuer, and J. A. Moore, *J. Org. Chem.*, **33**, 4381 (1968).

TABLE I
NMR DATA[a]

Compd	Solvent	Temp, °C	Ring positions 2,2′	3,3′	4,4′	5,5′	6,6′	7,7′
III	CCl_4	Ambient	3.57 s (3 H)	5.5–5.7 m (1 H)	1.88 d (3 H) $J = 1$ Hz	1.95 s (2 H)	0.95 s (6 H)	3.08 s (2 H)
VIa	CCl_4	Ambient	3.52 s (3 H)	2.43 d (1 H) 2.52 d (1 H) $J = 14$ Hz	1.10 s (3 H) 3.15 s (3 H)	1.15 d (1 H) 1.87 d (1 H) $J = 15$ Hz	0.87 s (3 H) 0.97 s (3 H)	3.12 s (2 H)
V	CCl_4	40	3.42 s (3 H) 3.48 s (3 H)	3.3–3.7 (2 H)[b]	4.70 s (1 H) 4.75 s (1 H) 0.74 d (3 H) $J = 7$ Hz 1.8–2.1 m (1 H)	2.05 s (2 H)[c] 1.1–1.4 m (2 H)	0.75 s (3 H) 0.87 s (3 H) 0.89 s (3 H) 0.93 s (3 H)	3.22 s (2 H) 3.22 d (1 H) 3.40 d (1 H) $J = 13$ Hz
V	PhCN	40	3.57 s (3 H) 3.67 s (3 H)	3.76 c (1 H)[b] 3.94 c (1 H)	4.90 s (1 H) 4.97 s (1 H) 0.88 d (3 H) $J = 8$ Hz 1.9–2.3 m (1 H)	2.22 s (2 H)[c] 1.2–1.6 m (2 H)	0.89 s (3 H) 0.95 s (3 H) 0.98 s (3 H) 1.03 s (3 H)	3.47 s (2 H) 3.43 d (1 H) 3.63 d (1 H) $J = 14$ Hz
V	PhCN	180	3.60 s (3 H) 3.67 s (3 H)	3.76 c (1 H)[b] 3.94 c (1 H)	4.96 s (2 H) 0.89 d (3 H) $J = 8$ Hz 1.9–2.3 m (1 H)	2.20 d (1 H)[c] 2.33 d (1 H) $J = 14$ Hz 1.39 d (2 H) $J = 7$ Hz	0.90 s (3 H) 0.94 s (6 H) 1.02 s (3 H)	3.46 s (2 H) 3.55 s (2 H)

[a] The nmr spectrum of III was measured at 60 MHz and the nmr spectra of VIa and V at 100 MHz. Chemical shifts are given in parts per million relative to TMS on the δ scale and coupling constants are given in hertz. The following abbreviations are used: s, singlet; d, doublet; m, multiplet; c, complex. [b] These protons appear as the AB portion of an ABX pattern. The X portion of the pattern is complicated by further coupling to adjacent protons at positions 4′ and 5′. In CCl_4 an insufficient portion of the pattern is visible for the calculation of chemical shifts and coupling constants. In PhCN $J_{AB} = 12.2$, $J_{AX} = 3.9$, and $J_{BX} = 0.1$ Hz and J_{AX} and J_{BX} are of opposite sign. [c] The protons at position 5 appear as a slightly broadened singlet in CCl_4 and PhCN at ambient temperature but appear as an AB pattern at 180° in PhCN.

Several patterns in the spectrum in benzonitrile simplify upon heating; the changes were reversible on cooling. The absorptions assigned to the methylene protons at positions 7 and 7′ appear as singlets at 180°; the absorption assigned to the methylene protons at position 5 changes from a broad singlet at 40° to an AB pattern at 180°; and the pattern assigned to the methylene protons at position 5′ collapses from a multiplet to a doublet. Some of the simplifications observed upon heating are more dramatic than expected. More complex patterns might be anticipated for the three methylene groups at positions 7, 7′, and 5′. A similar simplicity, however, is observed for the methylene protons at position 7 of VIa (*vide infra*).



III

V

VIa, $R_1 = R_2 = H$
b, $R_1 = H$; $R_2 = D$
c, $R_1 = D$; $R_2 = H$

The 70-eV mass spectral fragmentation provides further evidence for the assigned structure. The base peak appears at *m/e* 167, corresponding to a reverse ene reaction. Fragments are also observed at *m/e* 168 (46%) and 166 (22%) corresponding to a simple fragmentation of the 3–3′ bond with charge retention alternately in both fragments. Fragment ions at *m/e* 167 (67%) and 168 (10%) are still observed at 15 eV. At this ionization potential the base peak is the parent ion. The assigned structure is consistent with a single-crystal X-ray analysis.[4]

The quantum yields of dimerization have been determined with acetophenone, triphenylamine, and triphenylene sensitization and are reported in Table II.

TABLE II[a]
QUANTUM YIELD DATA

Sensitizer	E_T[b]	ϕisc[c]	[Sens]	[Azepine]	ϕ Dimer	ϕ Destruction
Acetophenone	74	1.0	0.20	0.021	0.032	0.06
Triphenylamine	70	0.88	0.0013	0.022	0.011	0.03
Triphenylene	67	0.96	0.0038	0.022	0.012	0.03

[a] Quantum yields were measured at 3000 A with potassium ferrioxalate actinometry at 30°: C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956). [b] W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964). [c] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

When the sensitized irradiation of III is conducted in absolute methanol as solvent, the photodimerization is no longer observed. Under these conditions a methanol solvent adduct is formed and assigned structure VIa, 2,4-dimethoxy-4,5,6,7-tetrahydro-4,6,6-trimethyl-3*H*-azepine, based upon the spectroscopic evidence. The 100-MHz nmr spectrum shown in Table I is the most definitive, with two characteristic singlets at δ 3.15 and 3.52 ppm. The mass spectrum

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(4) T. H. Koch and C. Tsai, unpublished work.

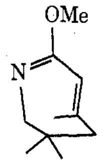
shows a weak parent ion at m/e 199 (2% of base), and in the infrared only a carbon–nitrogen double bond stretching band is observed (1680 cm^{-1}).

With methanol-*O-d* solvent and xanthone sensitization, deuterium is incorporated in the photoproduct at position 3, giving a mixture of VIb and VIc. The nonstereospecific addition of methanol is shown by the nmr pattern for the proton at position 3, which appears as a complex multiplet. For stereospecific addition the pattern would have appeared as a 1:1:1 triplet resulting from coupling to deuterium.

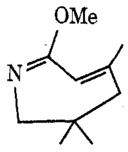
When the irradiation of 6,7-dihydro-2-methoxy-4,6,6-trimethyl-5*H*-azepine is carried out in two parts benzene and one part methanol, both solvent addition and dimerization are observed in the ratio of approximately 12:1. In this medium solvent addition and dimerization appear to be in competition, occurring from a common intermediate. A possible intermediate that is consistent with the experimental results and with evidence in hydrocarbon systems is a trans isomer of III.

Cyclohexenes and cycloheptenes commonly add methanol in an ionic fashion under photosensitized conditions.[5] Twisted or trans isomers have been proposed as probable intermediates. Upon direct irradiation, 2-cycloheptenone also adds alcohols in an ionic fasion to the carbon–carbon double bond,[6] most likely *via* a trans isomer.[7,8] With cyclic olefins smaller than six carbons for which twisted or trans isomers are highly improbable, free-radical addition of alcohol is observed.[5]

There are two possible trans isomers of III, one in which the unsaturated functional groups are cisoid (VII) and one in which they are transoid (VIII). The cisoid isomer would be expected to undergo conrotatory ring closure to yield the valence isomer, 7-methoxy-3,3,5-trimethylazabicyclo[3.2.0]hept-6-ene.[9] Since this is not an observed reaction of III, we favor the transoid intermediate VIII. Reaction of VIII with methanol could occur by initial protonation at position 3, relieving the ring strain and generating a tertiary carbonium ion subsequently trapped by methoxide. Consistent with observation, this mechanism would give a nonstereospecific addition of methanol-*O-d*. The dimerization could occur from VIII by a symmetry-allowed ${}_{\pi}2_s + {}_{\pi}2_s + {}_{\sigma}2_s$[10] ene reaction. The low quantum efficiency observed for dimerization (Table II) could result in part from a triplet decay ratio favoring III as well as from competitive thermal relaxation of VIII.



VII

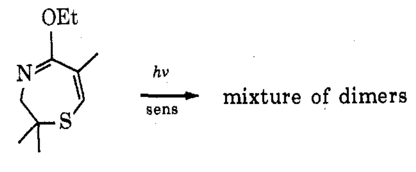


VIII

An alternative mechanism for dimerization, although not applicable to solvent addition, would involve initial hydrogen atom abstraction from the allylic methyl group of III by the sensitizer followed by radical addition or radical–radical combination. This mechanism is rendered unlikely because of the stereospecificity observed for the dimerization. Moreover, π,π^* sensitizers such as triphenylamine and triphenylene would not be expected to abstract hydrogen atoms from azepine.

Attempts to observe or trap (except by irradiation in methanol) a transient such as VIII have been unsuccessful. In trapping experiments, if dienes such as furan are added directly to the irradiation solution, they serve as efficient quenchers of the photosensitizer. Addition of furan to a cold (−78°) solution of III and acetophenone after irradiation did not yield an adduct but only photodimer. Low-temperature irradiation at −75° in *n*-heptane with triphenylamine sensitization and at −190° as a glass with acetophenone sensitization, both followed by ir analysis,[11] revealed only the presence of starting material, photodimer, and sensitizer. It is not surprising that an intermediate such as VIII with four sp^2 atoms in a seven-membered ring would not be observed even at −190°. *trans*-2-Cycloheptenone, which has only three sp^2 atoms in a seven membered ring, is unstable at −120°.[8]

The photochemical reactivity of 5-ethoxy-2,3-dihydro-2,2,6-trimethyl-1,4-thiazepine (IX), a molecule structurally related to III, has recently been reported.[12] Irradiation of IX in aprotic solvents with thioxanthone sensitization gave a mixture of dimers of unspecified structures. In methanol solvent again with thioxanthone sensitization no solvent addition occurred and only dimers were isolated. The difference in triplet state reactivity between III and IX may result from the electronic effects of the sulfur and/or the position of the allylic methyl group. Certainly for III the allylic methyl group is ideally located for an ene reaction from an intermediate such as VIII.



IX

Experimental Section

Melting points and boiling points are uncorrected. Melting points were measured with a Thomas-Hoover Unimelt apparatus. Perkin-Elmer Model 337 and Cary 14 spectrophotometers were used to determine ir and uv spectra, respectively. Nmr spectra were recorded with Varian A-60A and HA-100 and JEOL PS-100 spectrometers and chemical shifts are reported in δ units from internal tetramethylsilane. The mass spectra were obtained with Varian Mat CH-5 and CH-7 spectrometers. Glpc analyses and isolations were performed with a Varian Aerograph (Model 200) gas chromatograph equipped with a thermal conductivity detector, and peak areas were measured by Disc integration. Microanalyses were performed by Spang Microanalytical

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[10] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

[11] O. L. Chapman and J. D. Lassila, *J. Amer. Chem. Soc.*, **90**, 2449 (1968).

[12] M. F. Semmelhack, S. Kunkes, and C. S. Lee, *Chem. Commun.*, 698 (1971).

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***syn*-Isophorone Oxime.**—Freshly distilled isophorone (138 g, 1 mol), bp 80–82° (9 mm), was added to a solution of 68 g (1 mol) of hydroxylamine hydrochloride, 275 ml (1.38 mol) of 20% sodium hydroxide, and 413 ml of water. Enough ethanol (126 ml) was added to make a homogeneous solution which was refluxed for 3 hr and allowed to stand overnight. The ethanol was evaporated and the oxime was collected by vacuum filtration, yielding 130 g (84%), mp 98–100°. The nmr spectrum indicated that the oxime was a mixture of 90% syn and 10% anti oxime. Recrystallization of the mixture from petroleum ether (bp 30–60°) yielded 115 g (75%) of syn oxime, mp 101–102°. The observed melting point is in disagreement with the literature melting point, 77–78.5.[2] The material isolated by Mazur was shown by nmr to be a mixture of isophorone oximes. Nmr (CCl$_4$) showed δ 1.00 (s, 6 H), 1.85 (broad s, 3 H), 1.94 (broad s, 2 H), 2.08 (s, 3 H, syn oxime), 2.35 (s, 3 H, anti oxime), 5.90 (broad s, 1 H, anti oxime), 6.65 (broad s, 1 H, syn oxime), 9.65 ppm (s, 1 H).

6,7-Dihydro-4,6,6-trimethyl-5*H*-azepin-2-one (IV).—6,7-Dihydro-4,6,6-trimethyl-5*H*-azepin-2-one (IV) was prepared by the Beckman rearrangement of the syn oxime of isophorone with polyphosphoric acid according to the procedure reported by Mazur.[2] The yield of azepinone (mp 112–113°) was a good deal higher (64%) since pure syn oxime was used. Nmr (CCl$_4$) showed δ 0.98 (s, 6 H), 1.94 (d, J = 1 Hz, 3 H), 2.02 (s, 2 H), 2.83 (d, J = 5 Hz, 2 H), 5.58–5.78 (m, 1 H), 8.16 (broad absorption, 1 H); ir (KBr) 3180, 3020, 1660, and 1620 cm^{-1}.

6,7-Dihydro-2-methoxy-4,6,6-trimethyl-5*H*-azepine (III). Schmidt Reaction.—Distilled isophorone (55.2 g, 0.40 mol), sodium azide (39.0 g, 0.60 mol), and 500 ml of absolute methanol were placed in a three-neck reaction flask equipped with mechanical stirrer, addition funnel, and thermometer. Concentrated sulfuric acid (120 ml) was added dropwise at a rate to maintain the temperature at less than 35°. The solution became very viscous and an additional 200 ml of absolute methanol was added. The solution was stirred overnight and then brought to pH 10 with 10% aqueous sodium hydroxide solution (350 ml). The precipitate was removed by filtration and the filtrate was extracted with 3 × 100 ml of ether. The combined ether extracts were dried with magnesium sulfate and the ether was removed by rotary evaporation. 6,7-Dihydro-4,6,6-trimethyl-5*H*-azepin-2-one (IV) (9.6 g, 16% yield) precipitated from the residual oil (34 g, 51% yield). The physical and spectroscopic properties of the azepinone were identical with those of the authentic sample prepared by the Beckman rearrangement of the syn oxime of isophorone. Distillation of the residual oil, bp 55–57° (2 mm), yielded 25.8 g (39%) of 6,7-dihydro-2-methoxy-4,6,6-trimethyl-5*H*-azepine (III). The azepine was separated from residual lactam by chromatography on a 0.5 in. × 2 ft column of thin layer grade Woelm neutral alumina at 50 psi, eluting with 80 ml of benzene. To remove a 5% impurity of similar boiling point the azepine was then distilled at 10.5 mm pressure through a Nester-Faust Teflon annular spinning band column which had been rinsed with 3% ammonium hydroxide, distilled water, and acetone. The column was allowed to equilibrate with a pot temperature of 120° for 2 hr after reflux had begun. About 2-g fractions were then collected at a 1:1 reflux ratio. The per cent of the impurity in each fraction was analyzed by glpc with Disc integration on a 0.25 in. × 7 ft column of 5% SE-30 on 60/80 mesh Chromosorb W at 140° (He flow 60 cc/min). The first fraction contained 20% of the impurity; the second, 2%; and the remainder, less than 0.5%. A sample of the impurity (80% pure) was collected by glpc with the 0.25-in. SE-30 column at 90° (He flow 60 cc/min). Spectroscopic analysis indicated that the impurity was 6,7-dihydro-2-methoxy-4,6,6-trimethyl-3*H*-azepine. Nmr (CCl$_4$) showed δ 0.93 (s, 6 H), 1.65 (d, J = 1 Hz, 3 H), 2.87 (s, 2 H), 3.25 (d, J = 1 Hz, 2 H), 3.55 (s, 3 H), 4.85–5.07 (m, 1 H); ir (neat) 2960, 1690, 1645 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 167 (16), 166 (16), 154 (16), 153 (23), 152 (62), 124 (32), 110 (24), 96 (28), 95 (30), 56 (49), 55 (53), 53 (58), 42 (30), 41 (base). An analytical sample of 6,7-dihydro-2-methoxy-4,6,6-trimethyl-5*H*-azepine was collected by glpc under the same conditions. Nmr (CCl$_4$) showed δ 0.95 (s, 6 H), 1.88 (d, J = 1 Hz, 3 H), 1.95 (s, 2 H), 3.08 (s, 2 H), 3.57 (s, 3 H), 5.54–5.67 (m, 1 H); ir (neat) 2940, 1670, and 1640 cm^{-1}; uv $\lambda_{\max}$ (EtOH) 212 nm (ϵ 8700); mass spectrum (70 eV) *m/e* (rel intensity) 167 (21), 152 (base), 137 (9), 134 (14), 110 (11), 96 (29), 81 (16), 67 (18), 42 (21).

Anal. Calcd for $C_{10}H_{17}NO$: C, 71.81; H, 10.25; N, 8.37. Found: C, 71.59; H, 10.07; N, 8.27.

Trimethyloxonium Fluoroborate.—Trimethyloxonium fluoroborate was prepared by the procedure described by Meerwein.[13] To a solution of 10 g of trimethyloxonium fluoroborate in 500 ml of dry methylene chloride was added a solution of 10 g of 6,7-dihydro-4,6,6-trimethyl-5*H*-azepin-2-one in 50 ml of dry methylene chloride. The reaction mixture was refluxed for 12 hr and then hydrolyzed by slowly adding 18 g of 50% aqueous potassium carbonate solution. The precipitate was removed by filtration and the filtrate was dried over magnesium sulfate, filtered, and rotary evaporated. Nmr analysis of the crude oil showed 65% unreacted azepinone and 35% 6,7-dihydro-2-methoxy-4,6,6-trimethyl-5*H*-azepine (III). An analytical sample of the azepine was collected by glpc (0.37 in. × 10 ft column of 5% FS-1265 on 60/80 mesh Chromosorb W at 110°, He flow 60 cc/min) and was identical by nmr and ir analyses with that prepared by the Schmidt reaction.

Irradiation of 6,7-Dihydro-2-methoxy-4,6,6-trimethyl-5*H*-azepine (III) in the Absence of Sensitizer.—6,7-Dihydro-2-methoxy-4,6,6-trimethyl-5*H*-azepine (0.3 g) in 190 ml of *n*-heptane was irradiated with a 450-W mercury lamp through a Vycor filter for 2 hr. Gas chromatographic analysis of the crude reaction mixture with a 5% SE-30 on 60/80 mesh Chromosorb W column temperature programmed from 100 to 250° showed about 60% destruction of starting material and formation of 19 products each in less than 5% yield.

Photosensitized Dimerization of 6,7-Dihydro-2-methoxy-4,6,6-trimethyl-5*H*-azepine (III).—6,7-Dihydro-2-methoxy-4,6,6-trimethyl-5*H*-azepine (10 g) and 0.72 g of acetophenone in 450 ml of reagent grade benzene were irradiated with a 450-W mercury lamp in a Pyrex immersion well for 8 hr. After rotary evaporation of the solvent, crude dimer (10 g) was recrystallized successively from *n*-heptane and absolute ethanol and sublimed at 70° (0.05 mm), yielding 3.0 g (30%) of 3-(2′-methoxy-4′,5′,6′,7′-tetrahydro-4′,6′,6′-trimethyl-3′(3′*H*)azepinyl)-6,6-dimethyl-2-methoxy-4-methylene-4,5,6,7-tetrahydro-3*H*-azepine (V): mp 120–121°; nmr (100 MHz, CCl$_4$) δ 0.75 (s, 3 H), 0.74 (d, J = 7 Hz, 3 H), 0.87 (s, 3 H), 0.89 (s, 3 H), 0.93 (s, 3 H), 1.1–1.4 (m, 2 H), 2.05 (broad s, 2 H), 1.8–2.1 (m, 1 H), 3.22 (s, 2 H), 3.22 (d, J = 13 Hz, 1 H), 3.40 (d, J = 13 Hz, 1 H), 3.42 (s, 3 H), 3.48 (s, 3 H), 3.3–3.7 (m, 2 H), 4.70 (s, 1 H), 4.75 ppm (s, 1 H); nmr (PhCN, 40°) δ 0.89 (s, 3 H), 0.88 (d, J = 8 Hz, 3 H), 0.95 (s, 3 H), 0.98 (s, 3 H), 1.03 (s, 3 H), 1.2–1.6 (m, 2 H), 1.9–2.3 (m, 1 H), 2.22 (broad s, 2 H), 3.47 (s, 2 H), 3.43 (d, J = 14 Hz, 1 H), 3.63 (d, J = 14 Hz, 1 H), 3.57 (s, 3 H), 3.67 (s, 3 H), 3.76 and 3.94 (AB portion of an ABX pattern, J_{AX} = 3.9, J_{BX} = 0.1, J_{AB} = 12.2 Hz, J_{AX} and J_{BX} are of opposite sign), 4.90 (s, 1 H), 4.97 (s, 1 H); nmr (PhCN, 180°) δ 0.90 (s, 3 H), 0.89 (d, J = 8 Hz, 3 H), 0.94 (s, 6 H), 1.02 (s, 3 H), 1.39 (d, J = 7 Hz, 2 H), 1.9–2.3 (m, 1 H), 2.20 (d, J = 14 Hz, 1 H), 2.33 (d, J = 14 Hz, 1 H), 3.46 (s, 2 H), 3.55 (s, 2 H), 3.60 (s, 3 H), 3.67 (s, 3 H), 3.76 and 3.94 (AB portion of an ABX pattern as described), 4.96 ppm (s, 2 H); ir (KBr) 2950, 2775, 1675, 1650, 1640 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 335 (13), 334 (57), 320 (11), 319 (48), 225 (13), 224 (83), 169 (31), 168 (46), 167 (base), 166 (22), 152 (96), 124 (22), 112 (48), 82 (31), 55 (35); mass spectrum (15 ev) *m/e* (rel intensity) 335 (28), 334 (base), 319 (13), 224 (65), 169 (28), 168 (10), 167 (65); metastables at *m/e* 303 and 138 relate fragment 319 to the parent ion and fragment ion 152 to 167, respectively.

Anal. Calcd for $C_{20}H_{34}N_2O_2$: C, 71.81; H, 10.25; N, 8.34. Found: C, 71.86; H, 10.06; N, 8.39.

Photosensitized Irradiation of 6,7-Dihydro-2-methoxy-4,6,6-trimethyl-5*H*-azepine (III) in Methanol.—6,7-Dihydro-2-methoxy-4,6,6-trimethyl-5*H*-azepine (0.289 g) and xanthone (0.103 g) in 120 ml of absolute methanol (freshly distilled from magnesium methoxide) were degassed with nitrogen and irradiated in a Pyrex immersion well with a 450-W mercury lamp for 40 min. Gas chromatographic analysis of the irradiated solution with a column of 5% SE-30 on 60/80 mesh Chromosorb W temperature programmed from 100 to 200° at 4 deg/min indicated the absence of photodimer, the presence of a small quantity of starting azepine, and a new photoproduct as well as xanthone. The solvent was rotary evaporated and the residual oil was molecularly distilled at 60° (2 mm), yielding 0.105 g of a colorless oil. Gas chromatographic analysis of the oil with the SE-30 column at 125° showed that it consisted of 22% starting azepine

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[13] H. Meerwein, *Org. Syn.*, **46**, 120 (1966).

and 65% product, identified as 2,4-dimethoxy-4,5,6,7-tetrahydro-4,6,6-trimethyl-3*H*-azepine (VIa, 21% yield). An analytical sample of the solvent addition product was collected by glpc with a 0.37 in. × 10 ft column of 5% SE-30 on 60/80 mesh Chromosorb W at 155°, helium 60 cc/min. Nmr (100 MHz, CCl_4) showed δ 0.87 (s, 3 H), 0.97 (s, 3 H), 1.10 (s, 3 H), 1.15 (d, J = 15 Hz, 1 H), 1.87 (d, J = 15 Hz, 1 H), 2.43 (d, J = 14 Hz, 1 H), 2.52 (d, J = 14 Hz, 1 H), 3.12 (s, 2 H), 3.15 (s, 3 H), 3.52 ppm (s, 3 H); ir (neat) 2950 and 1680 cm^{-1}; mass spectrum m/e (rel intensity) 199 (2), 184 (13), 169 (14), 168 (30), 152 (15), 128 (17), 113 (13), 112 (24), 111 (base), 110 (12), 99 (41), 86 (14), 55 (18), 43 (15), 41 (19).

Anal. Calcd for $C_{11}H_{21}NO_2$: C, 66.29; H, 10.62; N, 7.03. Found: C, 66.33; H, 10.66; N, 7.04.

The irradiation was also performed on a 10-ml scale in 99.5% methanol-*O-d*. The nmr spectrum of the solvent adduct (VIb and VIc) isolated by preparative glpc was identical with that of the methanol adduct (VIa) except in the region δ 2.40–2.60 ppm. Here the absorption appears as a 1 H multiplet.

Formation of Methanol Addition Product and Dimer in Methanol–Benzene Solvent Mixture.—To each of two 13-mm test tubes was added 2.0 ml of a benzene solution 0.02 *M* in 6,7-dihydro-2-methoxy-4,6,6-trimethyl-5*H*-azepine (III) and 0.007 *M* in xanthone. To each tube was then added 1.0 ml of anhydrous methanol. The tubes were degassed by four freeze (liquid nitrogen), pump (2 × 10^{-5} mm), thaw cycles and sealed. One of the tubes was irradiated for 24 hr at 3500 A in a Rayonet reactor. The second tube was kept in the dark for the same length of time. Destruction of azepine and formation of methanol addition product were analyzed relative to external phenyl acetate by glpc with a column of 5% SE-30 on 60/80 mesh Chromosorb W at 100°, helium 70 cc/min. Formation of dimer and destruction of xanthone were analyzed relative to external anthracene with the same column at 195°. Reaction mixture compositions are corrected for differences in thermal conductivity and are as follows.

Solution	% Destruction of azepine	% Methanol adduct VIa	% Dimer V	% Destruction of xanthone
MeOH/PhH, dark	0	0	0	0
MeOH/PhH, $h\nu$	89	37	3	66

Attempted Trapping of an Intermediate with Furan.—A Pyrex test tube was charged with 0.25 g of 6,7-dihydro-2-methoxy-4,6,6-trimethyl-5*H*-azepine (III) and 0.060 g of acetophenone in 15 ml of heptane. After degassing with nitrogen, the test tube was placed in a quartz dewar cooled with Dry Ice–ethanol. The reaction mixture was irradiated for 4 hr with a 450-W mercury lamp through a window in the Dewar. After the irradiation 1.0 g of furan was immediately added and the reaction mixture was allowed to warm to room temperature. The solvent was removed by rotary evaporation. Nmr and glpc analysis of the residual oil indicated that only starting materials and photodimer were present.

Attempted Infrared Observation of an Intermediate.—An infrared solution cell with a 0.20-mm path length was filled with a *n*-heptane solution of 6,7-dihydro-2-methoxy-4,6,6-trimethyl-5*H*-azepine (III) and triphenylamine of appropriate concentration for ir spectroscopy. The ratio of the carbon-carbon double bond stretch of the azepine (1640 cm^{-1}) to the stretching band of the phenyl groups of triphenylamine (1590 cm^{-1}) was approximately 9:1. The solution cell was attached to the base of a stainless steel dewar, enclosed in a shroud (Air Products), and cooled to −75° by charging the dewar with Dry Ice–acetone. After a low-temperature ir spectrum was obtained, the solution was irradiated for 2000 sec with an external 200-W super pressure mercury lamp (Bausch and Lomb) through a Corning CS-054 filter. While still at −75° a terminal ir spectrum was obtained. Comparison of the 12 peaks between 2000 and 1200 cm^{-1} in the terminal spectrum with peaks in the initial spectrum and with peaks in an ir spectrum of photodimer in *n*-heptane indicated that only starting materials and photodimers were present to any observable extent in the cold irradiated solution. During the irradiation approximately 75% of the azepine was destroyed.

A thin film of approximately five parts azepine (III) and one part acetophenone was cooled to −190° with liquid nitrogen in an Air Products cell and similarly irradiated for 1200 sec. Infrared analysis of the irradiated film (at −190°) showed that at least 50% of the azepine had been destroyed. Warming the cell to room temperature resulted in no distinguishable changes. The terminal infrared spectrum was consistent with a mixture of azepine, dimer, and acetophenone.

Reagents Used for Quantum Yield.—Acetophenone from Matheson Coleman and Bell was distilled at 81–81.5° (11 mm) prior to use. Triphenylamine (194–196°) was used without further purification. Spectrograde benzene was used as the solvent without further purification.

Quantum Yield Measurements.—Quantum yield experiments were performed in a Rayonet photochemical reactor Model RPR-100 using RPR-3000A lamps equipped with a rotating wheel. The wheel was constructed from an aluminum drum, 7 in. in diameter and 2.25 in. thick, mounted on a central shaft of 0.75 in. aluminum rod. On the perimeter of the drum were located 30 cylindrical compartments 13 mm in diameter. Each compartment was exposed to the lamps through a 0.25 × 0.75 in. slit. At the base and top of the shaft are ball bearings which are rigidly attached to the Rayonet reactor. The wheel was rotated at 48 rpm. The quantum yield apparatus was cooled with air which had passed through a water-cooled heat exchanger. The apparatus equilibrated at 30°. Calibration of the compartments of the wheel with potassium ferrioxalate actinometer[14] demonstrated that each compartment received identical quantities of light (±1%).

Samples (3.0 ml) of the appropriate concentration (Table I) of sensitizer and azepine (III) were placed in 13-mm Pyrex test tubes and degassed by four freeze (liquid nitrogen), pump (2 × 10^{-5} mm), thaw cycles and sealed. Sensitizer concentrations were selected such that greater than 99% of the incident light below 4000 A was absorbed. During the irradiation the lamp intensity was monitored with potassium ferrioxalate actinometry and averaged 2.5 × 10^{15} quanta/sec (uncorrected for the low intensity at wavelengths greater than 4000 A). Analyses were performed with a 0.25 in. × 7 ft gas chromatographic column of 5% SE-30 on nonacid-washed, 60/80 mesh Chromosorb W with helium flow at 60 cc/min. Destruction of starting material was analyzed at 100° relative to external triglyme and formation of dimer, at 190° relative to external anthracene. Areas of azepine (III) and dimer (V) were corrected for differences in thermal conductivity.

Registry No.—III, 37991-60-9; IV, 23137-74-8; V, 37991-62-1; VIa, 37991-63-2; isophorone, 78-59-1; *syn*-isophorone oxime, 28052-11-1; *anti*-isophorone oxime, 26358-61-2; 6,7-dihydro-2-methoxy-4,6,6-trimethyl-3*H*-azepine, 37991-64-3; trimethyloxonium fluoroborate, 420-37-1.

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[14] See Table II, footnote c.