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Photosensitized Anaerobic Oxidation of Dibutyl Sulfide

Marye Anne Fox,* Paul K. Miller, and Michael D. Reiner

Department of Chemistry, University of Texas at Austin, Austin, Texas 78712

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Upon photoexcitation, acetone can function as an oxidant for dibutyl sulfide by a low quantum yield route ($\phi = \sim 0.016$). A complex mixture of photoproducts results. Solvent effects, kinetics, product distributions, and quenching studies indicate that a radical pathway is important. Unlike the analogous oxidation of methionine, both sulfoxide and sulfone are produced along with smaller quantities of sulfur-containing products produced from radical fragments. In addition to acting as an oxygen source, acetone undergoes normal solution-phase photoreactions and significant polymerization. A mechanism for the oxygen-transfer process is suggested, and experiments which examine the generality of this photoprocess are described.

Although the conversion of dialkyl sulfides to the corresponding sulfoxides is very easily achieved with a variety of oxidants,¹ one technique (the photosensitized transfer of carbonyl oxygen from a ketone to a sulfide) struck us as particularly novel and as worthy of mechanistic investigation. Gennari and Jori have shown that methionine can be cleanly oxidized to methionine sulfoxide (>95% yield) when a *deaerated* solution of methionine in acetone is irradiated at 311 nm.² They suggested that acetone acts both as a sensitizer and as an oxygen donor in this photooxidation. Subsequently, it was demonstrated,^{3,4} *even in the absence of oxygen*, that biacetyl can similarly act as a photosensitizer and oxygen source. Since only amino acid photoproducts were analyzed in these studies, the fate of the sensitizer after oxygen transfer was unknown. Molecular oxygen was found to *inhibit* these photoreactions. This is a curious observation since in addition to interrupting a radical chain, oxygen itself could also function as an oxidant. Dye-sensitized photooxidation of sulfides proceeding with the participation of singlet oxygen are well-known.^{1b,5} Although n, π^* sensitizers apparently function in complex fashion with some substrates,⁶ such sensitizers have been shown to generate singlet oxygen⁷ and therefore, presumably, to function as a source of an effective oxidant.

Since the cleavage of the σ and π bonds of a carbonyl double bond requires ~ 180 kcal/mol,⁸ the discovery of an efficient photoprocess for oxygen transfer from carbonyl groups is most interesting. Furthermore, the possibility of employing sulfides as a photochemical deoxygenation reagent with ketones would provide an intriguing synthetic reaction should such photolyses prove to be general and to be capable of producing useful quantities of deoxygenation product in a wide variety of ke-

tones. With these thoughts in mind, we undertook a mechanistic study of the reaction of some photoexcited ketones with dialkyl sulfides, choosing the reaction of acetone with dibutyl sulfide (1) as a convenient model system.

Results

Photolysis of Acetone in the Presence of Dibutyl Sulfide (1). Irradiation for 6 h with RPR 3000-Å lamps of degassed Pyrex ampules containing a solution of 1 (0.025 M) in neat, dry acetone gives about 15% disappearance of 1 and a complex mixture of photoproducts. Identifiable products and typical yields (with respect to reacted dibutyl sulfide) from the analogous preparative scale irradiation are listed in Chart I. Significant polymer formation is also evident. Continued irradiation results in further conversion of sulfoxide 2 to sulfone 3 and to the disappearance of sulfur-containing product. The quantum yield for disappearance of 1 is $\sim 1.6 \times 10^{-2}$.

If the photolysis is conducted in cyclohexane (0.025 M 1, 5 M acetone), the reaction is slower (about 6% conversion in 6 h) but somewhat cleaner: the major products are bicyclohexyl (81%),⁹ 9 (28%), 2 (58%), 3 (25%), 11 (6%), and 4 (5%). Again, significant photopolymerization occurs.

The rate of sulfoxide production in the photolysis of 0.025 M dibutyl sulfide in a 50% acetone–50% solvent mixture was followed by gas chromatography. Table I summarizes the relative rates observed. The results of an analogous experiment in which the rate of sulfoxide formation was monitored as a function of the initial concentrations of each reactant are tabulated in Table II.

If the photolysis (0.025 M dibutyl sulfide in neat degassed acetone) is conducted in the presence of hydroquinone, nearly

Chart I. Photolysis of Acetone in the Presence of Dibutyl Sulfide

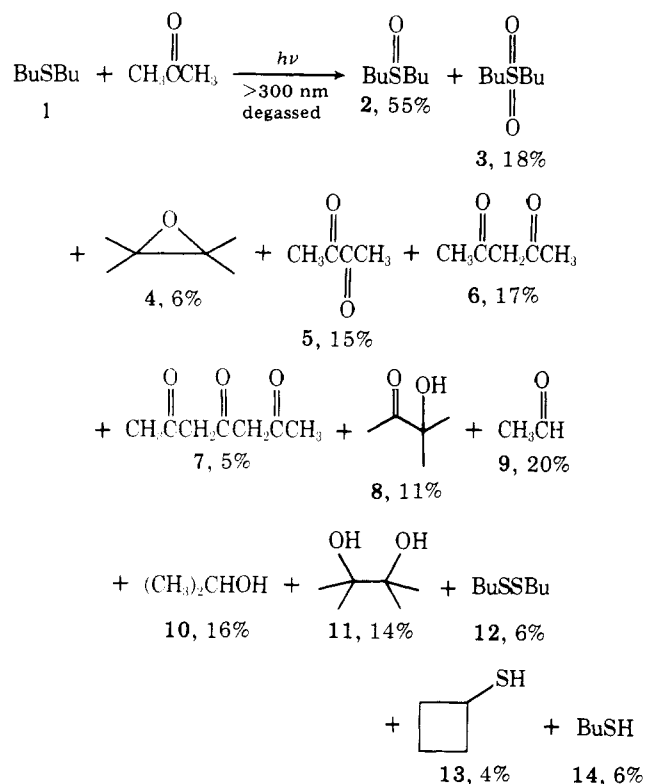


Table I. Solvent Dependence of the Relative Rates for Production of Sulfoxide in the Photolysis of Acetone in the Presence of Dibutyl Sulfide

solvent	rate ^a
cyclohexane	1.0
benzene	1.0
tetrahydrofuran	1.2
acetone	(2.7) ^b
methanol	1.6
water	1.5

^a Average of three runs. ^b Note that initial acetone concentration is doubled in this determination compared to the other runs.

Table II. Dependence of the Relative Rates of Sulfide Production on Initial Reactant Concentrations in the Photolysis of Acetone in the Presence of Dibutyl Sulfide

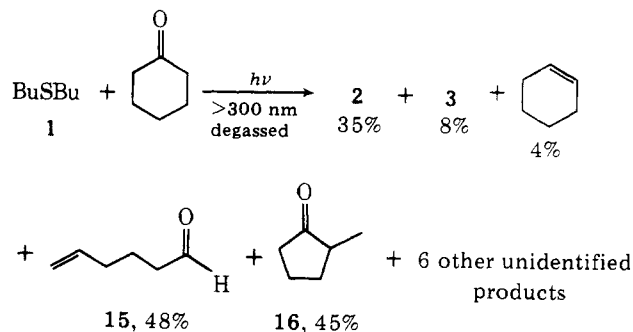
[acetone] ₀ , M	[dibutyl sulfide] ₀ , M × 10 ²	rel rate ^a
13.6 (neat)	1	1.0
13.6	2	1.8
13.6	5	5.2
6.8	1	0.45
2.7	1	0.21
1.4	1	0.13

^a Average of three runs.

complete inhibition of sulfoxide formation occurs. (The initial rate of sulfoxide formation is reduced by a factor greater than 100.) In aerated solution, the rate of sulfoxide formation is comparable to that observed in degassed solution and the production of products 4–11 is reduced.

Photolysis of Other Carbonyl Compounds in the Presence of Dibutyl Sulfide (1). Irradiation of a degassed

Chart II. Photolysis of Cyclohexanone in the Presence of Dibutyl Sulfide



solution of 1 (0.025 M) in dry cyclohexanone with a Pyrex-filtered medium-pressure lamp for 16 h gives about 10% disappearance of 1 and the mixture of photoproducts listed in Chart II. If the photolysis is conducted in benzene (2 M cyclohexanone, 0.25 M sulfide), similar product distributions are observed although the mass balance for cyclohexanone is poor. Apparently, polymerization is also significant in this reaction.

The effectiveness of other carbonyl compounds as photooxygen-transfer reagents was evaluated by monitoring the formation of sulfoxide in degassed methanol solutions. Significant ($\geq 20\%$) yields of dibutyl sulfoxide were observed with acetone, cyclohexanone (vide supra), biacetyl, acetophenone, and 3-pentanone. No sulfoxide formation could be observed with photosensitization with isobutyraldehyde, benzaldehyde, or benzophenone.

Photolysis of Acetone in the Presence of Other Sulfides. Degassed acetone solutions of several sulfides (0.05 M) were irradiated in Pyrex ampules to about 20% disappearance of sulfide. The resulting complex mixtures were subjected to GC-MS analysis with the resulting spectra searched for oxidation products. Significant peaks ($>10\%$) with molecular weights corresponding to sulfoxide were observed with diethyl sulfide, ethyl allyl sulfide, and methyl allyl sulfide. No monooxidation products could be observed with dibenzyl sulfide, thiophene, diphenyl sulfide, or dibutyl disulfide.

Discussion

It is apparent that several ketones can indeed function as both photosensitizers and oxygen-transfer reagents to simple dialkyl sulfides, although the quantum efficiency of transfer in our model system (acetone–1) is fairly low. It is equally clear, however, that such transfers apparently compete with normal solution-phase photochemistry so that the majority of the isolable photoproducts are compounds which might have been expected from photolysis of the ketone itself. For example, acetone is known to undergo α cleavage upon photoexcitation in the gas phase and has been shown to undergo hydrogen abstraction in solution.^{10,12} Products 5–14 obtained in our reactions can easily be derived by normal hydrogen abstraction and radical combination reactions of the radicals so formed. The radical nature of the processes leading to these products is clearly demonstrated by the shift in product distribution observed when cyclohexane, a well-known radical scavenger, is present. The quenching effects of hydroquinone and molecular oxygen are also consistent with radical pathways for the formation of these products. The observation that these two radical quenchers differ in their quenching effectiveness allows the possibility that a shift in mechanism occurs in the presence of oxygen so that sulfoxidation in aerated solution can occur through an alternate reaction path.

Normal photochemistry is also observed when cyclohexanone functions as the photosensitizer. In particular, 15 and

16 are the normally isolated products obtained upon solution-phase irradiation of cyclohexanone.¹¹

Since normal ketone photoreactions still proceed and since such processes consume ketone without effecting deoxygenation, the product yield of sulfoxide is relatively low with respect to the amount of carbonyl compound consumed. As such, the photochemical technique seems unable to function as a synthetically useful ketone deoxygenation reaction despite the fact that sulfoxide represents a large fraction of sulfur-containing photoproduct.

In the photolysis of acetone in the presence of dibutyl sulfide, most of the reacted sulfide can be accounted for by the two oxidation products 2 and 3. It can be demonstrated that irradiation of a solution of 2 in degassed acetone results in production of 3 and that the relative yield of 3:2 increases as conversion of starting material progresses. We assume, therefore, that 3 is formed in our reaction by secondary oxidation of 2, a primary photoproduct. Finding significant quantities of 3 at low conversion of starting material suggests that the photoconversion of 2 to 3 is more facile than the original oxidation of 1 to 2. Products 12 and 14 are presumably derived from $\cdot\text{SBU}$, a species which can reasonably be postulated by the reaction of 1 in the presence of the radical chains discussed above.

The mechanism for the formation of sulfoxide, which is presumably formed in a pathway competitive with normal ketone photochemistry, must begin with the ketone excited state since only the ketone absorbs light with Pyrex-filtered UV irradiation. The triplet state formed by rapid intersystem crossing from the initially formed n, π singlet¹² could conceivably interact with sulfide in several ways: energy transfer, atom (oxygen) transfer, charge transfer, or bond formation.

The possibility that sulfoxidation results solely from energy transfer from the n, π^* ketone triplet to produce sulfide triplet excited states is unlikely. Although the triplet energies of only a few sulfides are known,¹³ the observed apparent efficiency

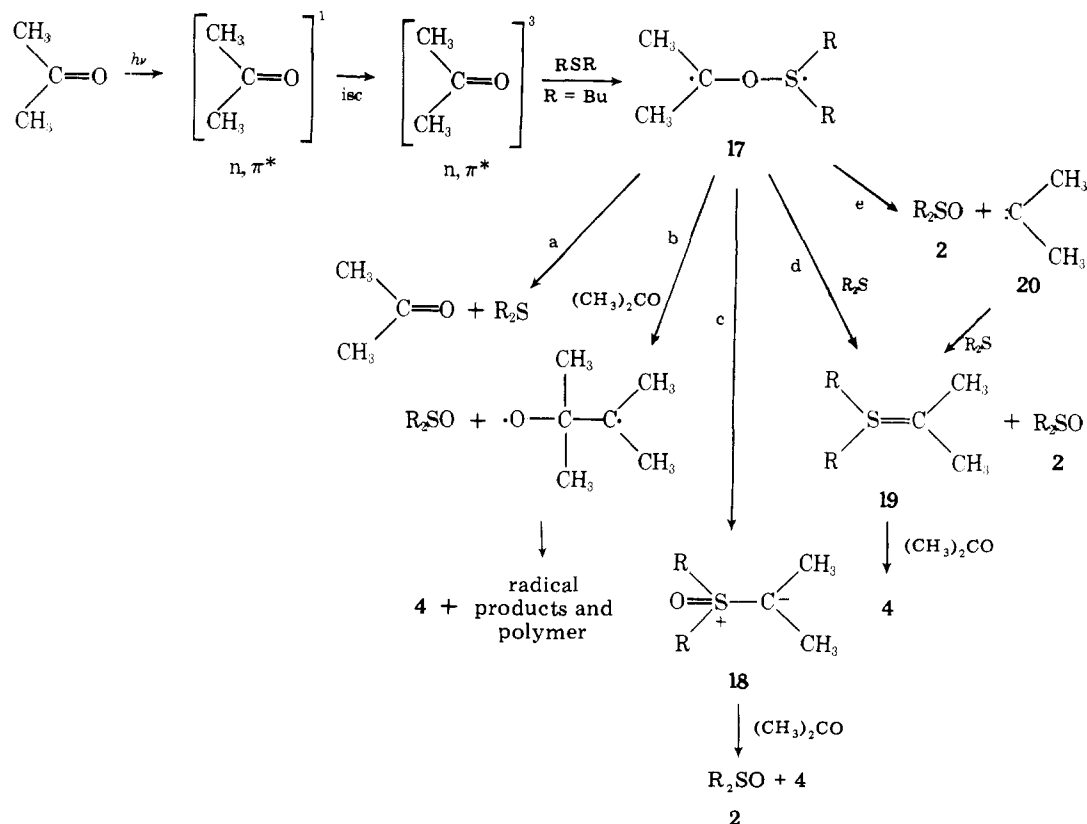
of intersystem crossing in simple dialkyl sulfides¹⁴ together with the positions of their UV maxima suggest that E_T for sulfides should lie at fairly high energies. The ability of S-heterocycles to sensitize biacetyl phosphorescence¹⁵ clearly places their E_T above that of biacetyl, a compound known to sensitize the sulfoxidation. Furthermore, from the known triplet photochemistry of sulfides,¹⁶ one might expect significantly higher quantum yields for the disappearance of sulfide and higher chemical yields of products 12–14 should sulfide triplet states be involved.

The second pathway, oxygen transfer, is also improbable. Since the cleavage of a carbonyl $\text{C}=\text{O}$ double bond requires about 180 kcal/mol⁸ and the formation of a sulfoxide $\text{S}=\text{O}$ bond releases only ~ 89 kcal/mol,¹⁷ only the most high-lying triplet excited states should allow such a transfer reaction even with marginal exothermicity. Even the triplet state of simple dialkyl ketones may be insufficiently high-lying (triplet acetone lying ~ 80 kcal/mol above its ground state) to transfer oxygen in one step. Biacetyl, which also functions as photosensitizer–oxygen-transfer reagent,³ has a triplet energy of 56 kcal/mol¹⁸ and is clearly incapable of simple exothermic atom transfer in its triplet excited state.

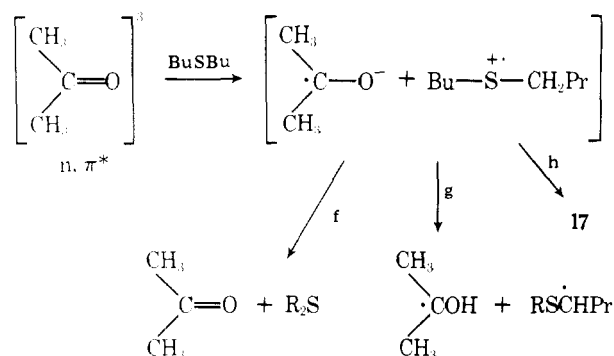
The remaining two pathways, initial charge-transfer interaction and bond formation, are both reasonable and may in fact both be significant in the sulfoxidation. The identification of 4 in the product mixture may be important mechanistically despite its low yield, for it represents the sole isolable deoxygenation product of these reactions.

In Scheme I, photoexcitation of acetone at ~ 3000 Å gives the n, π^* singlet which undergoes a rapid intersystem crossing with near unit efficiency to the n, π^* triplet. Such an excited state might be intercepted by sulfide to form a 1,3-diradical 17, which may react further by several pathways. In path a, cleavage of the weak, newly formed O–S bond results in an energy-dissipating return to ground state reactants. In view of the low quantum efficiency for sulfide disappearance, such

Scheme I. Possible Reaction Pathways in the Dibutyl Sulfide–Acetone Mixtures



Scheme II. Conceivable Charge-Transfer Intermediates

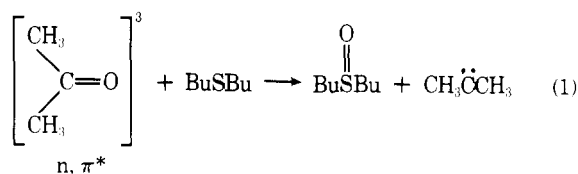


a pathway may be a major fate of 17. If 17 is intercepted at the C-radical center by a ground state acetone molecule, C-O bond cleavage could ensue (path b) to give the observed sulfoxide and a non-sulfur-containing biradical which could close to 4 or fragment to radical products and/or polymer. If 17 rearranges (path c), possibly by a ring closure-opening sequence, the sulfoxonium ylide 18 might form. On reaction with acetone, the observed products would be formed. Interception of 17 by a second molecule of sulfide (path d) at the C-radical center would directly give sulfoxide accompanied by sulfonium ylide 19. Upon reaction with acetone, 4 and ground state sulfide may be generated. An alternate pathway (e) to ylide 19 results if 17 fragments to sulfoxide and dimethylcarbene 20. Ylide 19 could be formed if 20 were to be captured by sulfide at a rate competitive with intramolecular C-H insertion.

In this scheme, production of n, π^* triplet is well documented. The interception of ketone excited states, by sulfides, has also been shown to occur at rates approaching diffusion control.¹⁹ Charge transfer from sulfide to the excited ketone is undoubtedly important in this rapid interaction and may accompany or, in fact, precede the O-S bond formation required for sulfoxide formation. Thus, formation of biradical 17 conceivably could be achieved as in Scheme II. Since the UV spectrum of acetone-1 mixtures is nearly identically a sum of the individual components, such charge transfer must be an excited state, rather than ground state, phenomenon. Reverse electron transfer (path f) from this charge-transfer geminate radical pair provides an alternative to path a in Scheme I for energy wastage. Partial charge transfer has also been shown to enhance intersystem crossing from excited triplet to ground state singlet states.²⁰ Transfer of α -H (path g) allows for entry into radical chain pathways discussed above, and the collapse of the geminate pair could lead to 17. Although the observed solvent dependence observed in the reaction is in the correct direction for the intervention of charged intermediates, the magnitude of the change is modest (less than a factor of 2) for a fairly large change in solvent dielectric.²¹

Whether 17 is formed either directly (relying on the excited ketone's known chemical mimicry of alkoxy radicals²²) or via these charge-transfer intermediates, it would be expected to be extremely reactive. It could exist as a biradical (as shown in Scheme I), as ring-closed species, or as a zwitterionic form of biradical 17.

The available kinetic data for production of sulfoxide show near first-order dependence on both sulfide and ketone. Since the rate of production of the excited state of acetone should show, of itself, dependence only on the intensity of illumination in light opaque solution, such a kinetic order requires that, in addition to acting as the photosensitizer, a second molecule of acetone must be involved before sulfoxide for-



mation results. Thus, direct oxygen transfer as in eq 1 is ruled out, not only by energetic arguments but also by kinetic behavior. Paths d and e in Scheme I are also rendered kinetically unimportant for they should show kinetic independence on acetone for the production of sulfoxide.

The multiplicity of the carbene potentially formed in path e is unknown as is the multiplicity of its biradical precursor 17. Despite the fact that 17 is presumably formed from an encounter complex with a triplet excited acetone molecule, crossover to the singlet manifold within such a complex or as 17 is easily conceivable. Path e (which we have shown above to be unlikely from kinetic considerations) could be followed only if the carbene formed in this reaction mode were triplet. With singlet carbenes, intramolecular CH insertion has nearly universally been shown to dominate any intermolecular carbene interceptions.^{23,24}

If path c (or paths d or e) is followed, equivalent quantities of 2 and 4 should be isolated since they are produced from a common intermediate. The experimental observation that 2 is formed in yields nearly 10 times larger than 4 suggests that path c, if operative, cannot be the sole route to 2. Furthermore, paths c, d, and e involve the production of highly colored ylide intermediates whose absorption spectra should be observable,^{25,26} at least on a short timescale. The absence of any absorptive transients (400-750 nm) of lifetimes $>1 \mu\text{s}$ upon flash photolysis of a deaerated solution of dibutyl sulfide in acetone at 337 nm, when coupled with typical reaction rates for such ylides,²⁶ suggests that paths c, d, and e are probably of minor importance in the photosulfoxidation. Hence, among the routes considered, our mechanistic preference for sulfoxide production is path b.

Since the lifetimes of 1,4-biradicals which have been detected directly (from Norrish type II abstraction) range from 30 to 100 ns,²⁷ the absence of microsecond-lived transients in this photolysis does not rule out the involvement of diradical 17, but it does suggest that this 1,3-diradical must be short-lived and/or weakly absorptive.

Upon excitation a variety of dialkyl ketones and biacetyl have been found to act as oxygen-transfer agents, but with aldehydes and with diaryl ketones a marked drop in reaction efficiency was observed. With benzophenone, benzpinacol is formed in high yield, presumably through path g, Scheme II.

Although this photoinduced sulfoxidation seems to occur for several dialkyl sulfides, no oxygen transfer could be observed with several other sulfides listed above. With dibenzyl sulfide, the ease of abstraction of benzylic hydrogen may favor reduction of the photoexcited ketone either directly or via path g. Alternately, because of the stability of the benzyl radical formed, the cleavage of the sulfoxide produced²⁸ may be more efficient than its photoproduction. With thiophene, diphenyl sulfide, and dibutyl disulfide, formation of the initial charge-transfer complex is more difficult.^{19b} It should be noted that these same sulfides are also inert to sulfoxidation by singlet oxygen.²⁹ The product mixture obtained from the disulfide indicates that significant S-S bond cleavage has occurred.

Thus, it appears that, as with intramolecular photoreactions of keto sulfides,³⁰ intermolecular photoreactions of ketones with sulfides are exceedingly complex. Several ketones of

relatively high reduction potential can, in their excited state, transfer oxygen to several alkyl sulfides. The reaction is probably not useful, however, as a general, efficient method for carbonyl deoxygenation.

Experimental Section

Photolysis Methods. All small-scale photolyses were conducted in rigorously degassed (three freeze-pump-thaw cycles) solutions contained in sealed Pyrex ampules inserted in a merry-go-round support inside a Rayonet photochemical reactor equipped with RPR 3000-Å lamps. Preparative-scale photoreactions were conducted in a quartz immersion well using a Pyrex-filtered Hanovin 450-W medium-pressure lamp. All solutions were purged with dry purified nitrogen or argon for 1.0 h before and during each photolysis. Quantum yields were obtained in a double-baffle merry-go-round by ferrioxalate actinometry.³¹

Analytical Techniques. Analytical gas chromatography (GLC) was accomplished on an Antek 400 flame ionization detector gas chromatograph on a 10 ft × 1/8 in. 20% SE-30 on 80–100 mesh Chromosorb P stainless steel column (column A). Preparative gas chromatographic separations were achieved on a Varian 3700 gas chromatograph on 1/4 in. stainless steel columns: 3 ft 10% Carbowax 20M on 60–80 mesh Chromosorb W (column B); 5 ft 10% OV-1 on 60–80 mesh Chromosorb W (column C); and 3 ft 5% SE-30 on 80–100 mesh Chromosorb P (column D). A Finnegan 4023 automated gas chromatograph-mass spectrometer equipped with a 6 ft × 1/4 in. 3% OV-1 on Chromosorb W glass column was used for GC-MS analyses (column E). Ultraviolet spectra were obtained on a Cary 14 spectrophotometer.

Materials. Spectral grade acetone (Mallinckrodt) was dried over molecular sieves and distilled from KMnO₄. Cyclohexanone (Aldrich) was distilled through a spinning band column. A middle fraction was shown to be pure (>99%) by gas-liquid chromatography (column A). Solvents employed were spectral grade reagents and were used without further purification. Water was triply distilled in glass. Dibutyl sulfide (Aldrich) was distilled in a short spinning band column and shown to be pure by GLC.

Photolysis of Acetone-1. Dibutyl sulfide (1.09 g, 7.5 mmol) was dissolved in 300 mL of acetone. Several aliquots of the resulting solution were transferred to Pyrex ampules and were rigorously degassed by a three-cycle freeze-pump-thaw sequence. The ampules were then sealed and suspended in the Rayonet photochemical reactor and irradiated for 6 h with RPR 3000-Å lamps. The remaining solution was purged with purified nitrogen for 1.0 h before and during the photolysis. The solution was irradiated for 4 h through a 2-mm Pyrex filter using a Hanovia 450-W medium-pressure lamp. In subsequent runs, purging was accomplished with dry argon.

The resulting mixtures were analyzed, with minimal exposure to air, by GLC on column A (150 °C). Quantitative determination of 1 with respect to a dodecane internal standard (added after the photoreaction) revealed about 15% disappearance of 1 in the photolysis. Nearly identical chromatograms were obtained in the ampules and in the larger scale photolyses. GC-MS analysis of the mixture on column D (50 → 150 °C, 10 °C/min) revealed a complex mixture of products of which several could be conclusively matched with good reliability with library mass spectra; yields of these products are listed in Chart I.

Coinjection of known samples of compounds 2–6, 9–12, and 14 with the photolysis mixture on columns A (150 °C) and C (150 °C) caused enhancement of the appropriate peaks and confirmed the identities of these compounds. Because of their importance to the study, 2–4 were isolated from the photolysis mixture by GLC (column D, 50 → 150 °C, 5 °C/min) after stripping the solvent on a rotary evaporator. The fraction containing 4 required further GLC purification (column B, 100 °C). The isolated compounds had identical chromatographic behavior and IR, NMR, and mass spectra with those of authentic samples. Authentic samples of 2 and 3 were obtained from Aldrich. 4 was synthesized by the method of Price and Carmelite.³²

The quantum yield for disappearance of 1 was determined by irradiating sealed Pyrex ampules of solutions of 1 (0.025 M) in degassed acetone in a double-baffle merry-go-round in the Rayonet photochemical reactor for 8 h. Irradiation of two Pyrex ampules containing potassium ferrioxalate for 2.0 min at the beginning and end of the irradiation period showed that light intensity was invariant over the period. Thus, quantitative determination of the disappearance of 1 as discussed above, coupled with light flux measurements from ferrioxalate actinometry,³⁰ formed the basis for quantum yield determinations.

If one of the ampules described above contains a small crystal of

hydroquinone, no formation of 2 can be observed by GLC (column A). If one of the ampules is capped (air-saturated) rather than degassed, 2 is still formed in comparable yield (GLC analysis, column A) but the complexity of the mixtures obtained is reduced. The UV absorption spectrum of acetone-1 mixtures proved to be a strict sum of the absorption spectra of the individual components in hexane or in methanol for 1 M acetone and 0.01–0.1 M 1 concentration ranges. No additional absorption beyond the 277-nm acetone maximum could be observed in the 250–700 nm range.

Photolysis of Acetone-1 in Cyclohexane. A solution of 0.18 g of dibutyl sulfide in 18.5 mL of acetone (14.6 g, 0.25 mol) was diluted to 50 mL with spectral grade cyclohexane (Aldrich Gold Label). The solution was transferred to Pyrex ampules, rigorously degassed, and irradiated with the RPR 3000-Å lamp array for 6 h. Upon GLC analysis on column A with dodecane as an internal standard, 6% disappearance of 1 had occurred. GC-MS analysis, with library search for spectral matches, revealed the product distribution listed in the text. (Yields are reported with respect to 1 consumed.) Significant reduction of acetone concentration was also observed.

Rate Dependence in Photolysis of Acetone-1. To a mixture of 5 mL of acetone and 5 mL of each of the following solvents was added 36 mg (0.25 mmol) of 1: cyclohexane (Aldrich Gold Label spectroscopic grade), benzene (Mallinckrodt SpectrAR grade), tetrahydrofuran (Fisher certified, redistilled from benzophenone ketyl), methanol (Fisher certified, dried over molecular sieves), and water (distilled from KMnO₄ and doubly distilled in glass). The respective solutions were transferred to Pyrex ampules, degassed, and suspended for simultaneous irradiation for 6 h with the RPR 3000-Å lamp array. After irradiation, the dodecane internal standard was added and the quantity of 2 + 3 produced was determined by GLC on column A by peak triangulation. The ratios of the areas so obtained, having established comparable chemical yields of 2 + 3 in these solvents, were used directly to obtain the relative rates listed in the text. The ratios listed are the average of three such determinations.

An analogous procedure was employed in the experiments in which the initial concentrations of 1 and acetone were varied. Water was the solvent diluent. Kinetic analysis was again achieved by GLC on column A. The reported values are the averages of four such runs.

Photolysis of Cyclohexanone-1. Dibutyl sulfide (0.11 g, 0.75 mmol) was dissolved in 30 mL of cyclohexanone. The resulting solution was transferred to Pyrex ampules, rigorously degassed, and suspended on the outside of the quartz water-cooling jacket of a 450-W medium-pressure mercury lamp for 16 h. Upon GLC analysis on column A, ~10% disappearance of 1 had occurred and peaks corresponding to the retention times of 2 and 3 were easily discernible. Other major products are also formed. GC-MS analysis on column E led to the identification of the products listed in Chart II as well as six other products formed in 5–15% yield for which no satisfactory correspondence with reference mass spectra could be obtained.

To 6.75 mL of cyclohexanone was added 180 mg (1.25 mmol) of 1. The resulting solution was diluted to 50 mL with spectral grade benzene (Mallinckrodt). After degassing and photolysis as above, a nearly identical chromatogram was obtained by GLC (column A) as in the neat irradiation. Upon diluting the photolysate so that quantitative analysis of cyclohexanone could be achieved, GLC (column A) indicated that a fraction of the cyclohexanone (~3%) had disappeared. Thus, about 25 molecules of cyclohexanone react for each molecule of 1 that disappears.

Photolysis of Carbonyls-1. Aliquots (10-mL) of a solution of 365 mg (2.5 mmol) of 1 in dry methanol (100 mL) were made 1 M in each of the following ketones: acetone (580 mg, Aldrich, distilled), cyclohexanone (980 mg, Aldrich, distilled), biacetyl (860 mg, Aldrich, vacuum distilled twice in the absence of light), acetophenone (1.2 g, Aldrich, distilled) and 3-pentanone (860 mg, Aldrich, vacuum distilled), isobutyraldehyde (720 mg, Aldrich, distilled), benzaldehyde (1.1 g, Aldrich, distilled), and benzophenone (1.82 g, Aldrich, recrystallized from ether). Each of the solutions was transferred to Pyrex ampules, rigorously degassed, and irradiated with the RPR 3000-Å lamp array for 6 h. The resulting solutions were analyzed by GLC (column A) for 2. 2 was absent from the aldehyde and benzophenone solutions.

Photolysis of Acetone-Sulfides. Aliquots (10-mL) of acetone were made 0.05 M in each of the following distilled sulfides: diethyl sulfide (45 mg, Aldrich), ethyl allyl sulfide and methyl allyl sulfide (res, collectively, 51 and 44 mg, Columbia Organic Chem.), dibenzyl sulfide (107 mg, Pfalz and Bauer, recrystallized from benzene), thiophene (42 mg, Aldrich Gold Label), phenyl sulfide (93 mg, Aldrich Gold Label), and butyl disulfide (89 mg, Aldrich). After degassing and irradiation as above, the photolysis mixtures were analyzed by GC-MS. The resulting spectra were each scanned for a peak corresponding to the parent of the monoxidation product. Such a peak was present for the

monoxides of diethyl sulfide (*m/e* 106), ethyl allyl sulfide (*m/e* 118), and methyl allyl sulfide (*m/e* 164). More detailed analyses of the complex mixtures obtained were not attempted except with butyl disulfide, where butanethiol could easily be identified as a major product.

Flash Photolysis of Acetone-1. A 50% acetone-D₂O solution was placed in a 5-mm rectangular quartz cuvette which had been modified to accept a serum cap through which a hypodermic needle was inserted for in situ gas purging. After a 10-min purge with purified nitrogen, the solution was excited by the emission (337 nm) from a nitrogen gas laser (8-ns pulse) with a maximum energy of 5 mJ/pulse. Transient absorptions were monitored at right angles to the exciting beam. Transient lifetimes could be monitored; the photodetection equipment, digitization, and computer-controlled data acquisition and processing array have been described.³³ Under such conditions, a very short-lived transient could be observed upon monitoring at 360 nm. This transient, as might be expected if it were the acetone triplet,³⁴ disappeared when the solution was made 0.1 M in I. No new transient absorptions (of microsecond lifetime) could be detected in the 360–450 nm range in the quenched solution.

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Registry No.—1, 544-40-1; 2, 2168-93-6; 3, 598-04-9; 4, 5076-20-0; 5, 431-03-8; 6, 123-54-6; 7, 626-53-9; 8, 115-22-0; 9, 75-07-0; 10, 67-63-0; 11, 76-09-5; 12, 629-45-8; 13, 6861-61-6; 14, 109-79-5; 15, 764-59-0; 16, 1120-72-5; acetone, 67-64-1; cyclohexanone, 108-94-1; cyclohexene, 110-83-8.

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Simplified Analogues of Lysergic Acid. 6. Derivatives of 1-Methyl-1,2,3,9a-tetrahydro-9H-indeno[2,1-b]pyridine

J. Cymerman Craig* and Stephen D. Hurt

Department of Pharmaceutical Chemistry, School of Pharmacy, University of California, San Francisco, California 94143

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The synthesis of a series of simplified analogues 6–10 of the ergot alkaloids 11–15, in which the ergoline A, B, and C rings have been replaced by the indan ring system, is described. The key intermediate, 1-methyl-3-oxo-1,2,3,9a-tetrahydro-9H-indeno[2,1-b]pyridine (20), was prepared and then elaborated to the corresponding analogues of lysergol, setoclavine, isetoclavine, lysergene, and decarboxylsergic acid. Both the primary alcohol 1-methyl-3-(hydroxymethyl)-1,2,3,9a-tetrahydro-9H-indeno[2,1-b]pyridine (6) and the corresponding aldehyde (26), which was found to exist entirely in the enolic form, were extremely resistant to oxidation.

The naturally occurring ergot alkaloids exhibit marked central and peripheral pharmacological effects, including serotonin antagonism, vasoconstriction, oxytocic activity, and psychotropic activity.¹ These compounds have recently received considerable attention since they also inhibit the pituitary secretion of the hormone prolactin;^{2,3} such activity may be useful in the treatment of human breast cancer.⁴

The ergot alkaloids may be classified into two structural groups,¹ the lysergamide alkaloids and the clavine alkaloids.

