Enamide Photochemistry. Stereochemistry of Photocyclization of 1-Ethylidene and 1-Benzylidene 2-Benzoyltetrahydroisoquinolines

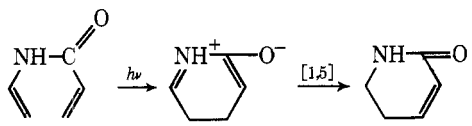
George R. Lenz

Division of Chemical Research, Searle Laboratories, P. O. Box 5110, Chicago, Illinois 60680

Received January 6, 1976

The syntheses of 2-aroyl-1-isopropylidene, (*Z*)-1-ethylidene, and (*Z*)-1-benzylidene enamides have been accomplished and their photochemistry studied. Irradiation of the enamides gave an intermediate via the aza analogue of hexatriene–cyclohexadiene ring closure which, as shown by deuterium labeling, undergoes a [1,5]-hydrogen shift to form 8-oxoberbines. The (*Z*)-ethylidene and (*Z*)-benzylidene enamides form a photoequilibrium with their respective *E* isomers but photocyclize stereospecifically from the *Z* isomer to the 5,6,13,13a-tetrahydro 13-substituted 8-oxoberbines where the 13 substituent is axial and the 13,13a hydrogens are cis.

The photocyclization reactions of enamides have been extensively studied over the last few years and have proven to be valuable in building polycyclic ring systems from easily accessible precursors.[1] This photocyclization is generally viewed as proceeding through the aza analogue of hexatriene–cyclohexadiene photocyclization to form an intermediate which undergoes a [1,5]-hydrogen shift.[1a,2] The [1,5]-

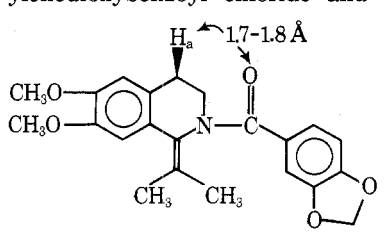


hydride shift, although postulated, has never been demonstrated. Additionally, the reaction has been reported to be stereospecific,[3] as well as nonstereospecific.[4] The reason for the stereospecificity may well be that virtually all of the reported cyclizations have utilized an aromatic double bond and an olefinic bond constrained in a ring. The only report where stereochemistry was investigated in an enamide where the olefinic double bond was noncyclic was by Chapman, who found a nonstereospecific cyclization in acrylic acid anilides.[5] We would like to report here on our further studies on the stereochemistry of the formation of 13-substituted 8-oxoberbines as well as a deuterium labeling experiment.

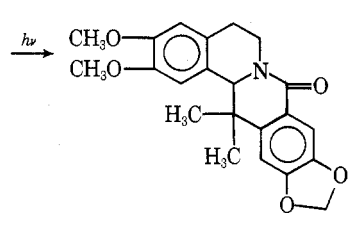
Results and Discussion

The isopropylidene enamide **1** was synthesized to determine whether the two methyl groups would cause sufficient steric interference in the photocyclization to allow a [1,3]-acyl shift to become competitive.[6] Additionally, if the photocyclization did occur, the 13,13-*gem*-dimethyl group should allow observation of the low-field 13a hydrogen as a singlet and the second low-field resonance as the C-6 equatorial hydrogen.[7] The enamide **1** was readily synthesized from 3,4-methylenedioxybenzoyl chloride and 3,4-dihydro-1-isopropyl-6,7-dimethoxyisoquinoline. The acid chlorides give better yields in cases where the 1 substituent is other than methylene.[8] The NMR spectrum of **1** showed that the C-3–C-4 ethylene bridge no longer appeared as two triplets as in the equivalent 1-methylene enamide,[7] but that the 1-isopropylidene group forced the benzoyl group into a conformation where it was within 1.7–1.8 Å of the axial C-4 hydrogen. This deshielding effect caused this proton to shift downfield to δ 4.33 as opposed to the equatorial C-4 proton which resonated at δ 3.58.[9] Irradiation of **1** proceeded smoothly to give a single product in 96.5% yield. The product **2** was identified as a 13,13-dimethyl-8-oxoberbine on the basis of its characteristic spectral properties. The NMR spectrum of **2** was particularly instructive as it again showed the two low-field resonances found in the unsubstituted 8-oxoberbines. The lower field resonance occurred as a doublet of quartets at δ 4.95 which is what would be expected for equatorial C-3 proton, thus confirming our original assignment.[7] The other resonance was separated from the δ 4.95 signal and occurred as a singlet at δ 4.80, and was assigned to the C-13a proton.

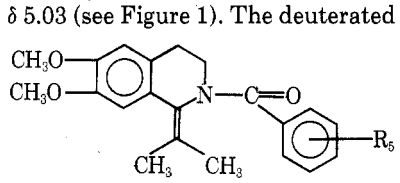
Since the C-13a proton in **2** was well resolved and easily identified, it appeared that this type of enamide was a good candidate for demonstrating the [1,5]-hydrogen shift by deuterium labeling. Since deuterated benzoyl chloride was easily accessible, the benzoyl derivatives were synthesized and irradiated. The unlabeled derivative **3** was irradiated and, after extensive chromatography, the berbine derivative **4** was isolated in 43% yield. 8-Oxoberbine **4** showed the C-13a proton as a singlet at δ 4.78, well resolved from the C-6 multiplet at δ 5.03 (see Figure 1). The deuterated analogue **5** was next ir-



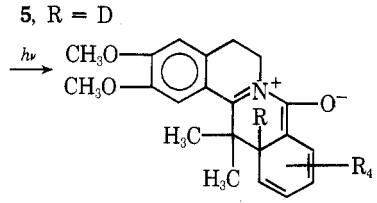
1

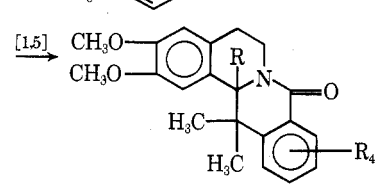


2



3, R = H
5, R = D





4, R = H
6, R = D

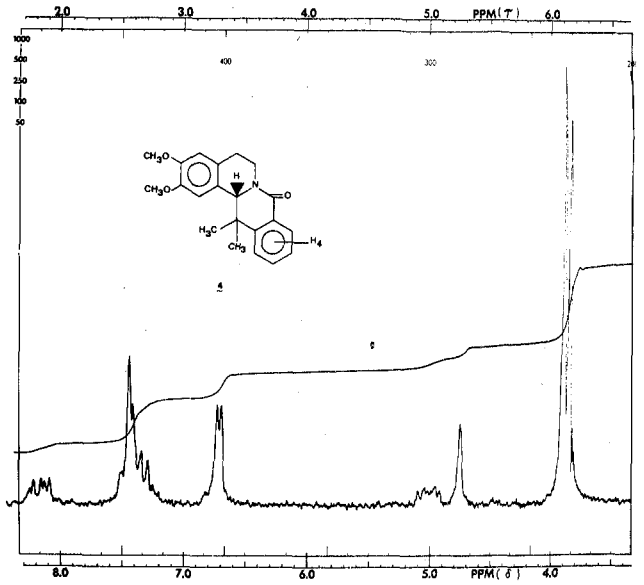


Figure 1a. The ^1H NMR spectrum of compound **4** from 200 to 500 Hz.

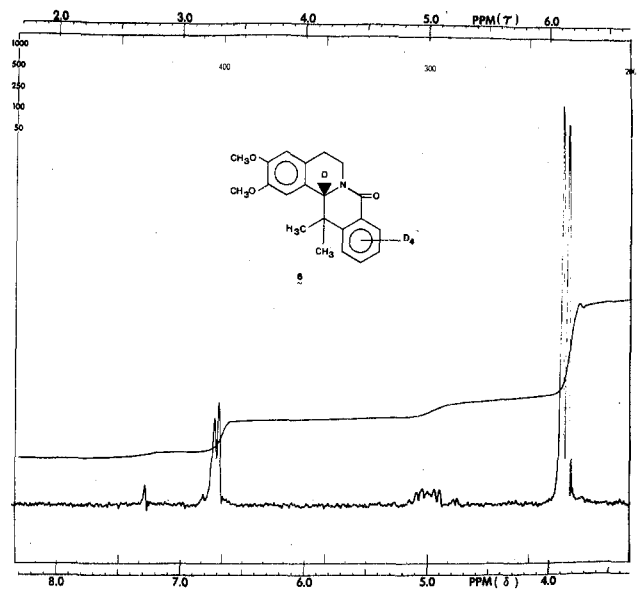
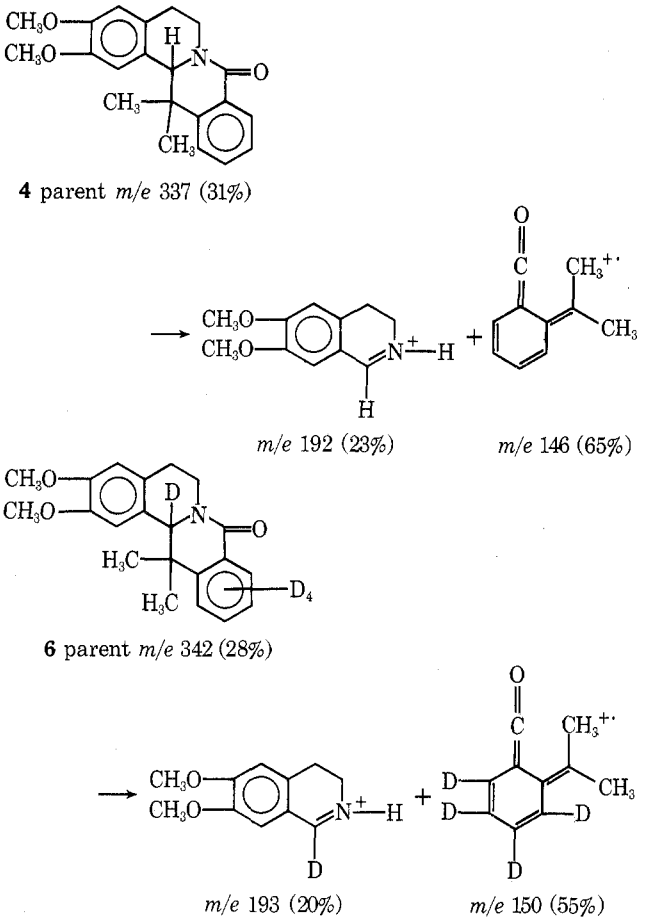


Figure 1b. The ^1H NMR spectrum of compound **6** showing the replacement of the C-13a proton at δ 4.78 by a deuterium from the perdeuteriobenzoyl group of **5**.

radiated, and, after equivalent workup, the deuterated berbine **6** was isolated. The NMR spectrum clearly showed the absence of the C-13a proton at δ 4.78 as well as four of the six remaining aromatic protons. This indicated that upon irradiation the enamide **5** underwent the 6-π electron electrocyclic ring closure to generate the intermediate indicated, which subsequently undergoes a sigmatropic [1,5]-hydrogen shift to generate the 8-oxoberbine. We also studied the mass spectral fragmentation patterns of berbines **4** and **6** (Chart I). Both berbines showed significant parent ions and the only significant fragmentation was a retro-Diels–Alder with a concomitant hydrogen transfer.[10] The base peak was at *m/e* 131 in **4** which corresponded to a loss of methyl from the fragment at *m/e* 146. The occurrence of deuterium in the peak corresponding to the AB rings of the berbine (dihydroisoquinolinium ion) served to confirm the position of deuterium indicated by the NMR spectrum.

We next turned our attention to the question of stereospecificity. Virtually nothing was known about enamide photocyclizations where either one or both double bonds were

Chart I. Mass Spectral Fragmentation Patterns of Undeuterated (4) and Deuterated (6) 8-Oxoberbines



4 parent *m/e* 337 (31%)

m/e 192 (23%) *m/e* 146 (65%)

6 parent *m/e* 342 (28%)

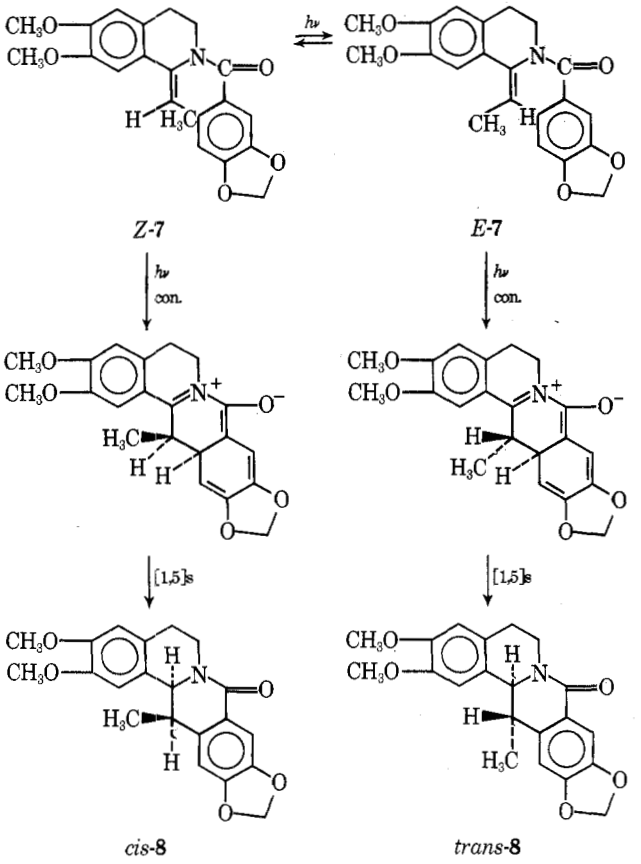
m/e 193 (20%) *m/e* 150 (55%)

alicyclic, excepting Chapman's report on acrylic acid anilides.[5] Chapman found the photocyclization in that series to be nonstereospecific. If the enamide photocyclization is analogous to the hexatriene–cyclohexadiene interconversion, then it should be concerted in a conrotatory fashion[11] to yield an intermediate. This intermediate then undergoes a [1,5]-hydrogen shift to give the product. The [1,5] shift must be suprafacial since antarafacial migrations are prohibited in cyclohexadiene systems for steric reasons.[12] This implies that electron demotion to ground state has occurred in the intermediate since [1,5]-suprafacial shifts are ground state allowed.

Considering the ethylidene enamide **7**, irradiation (Chart II) sets up a photoequilibrium between the *E* and *Z* forms. Then irradiation of the *Z* isomer **7** causes photocyclization in a conrotatory mode to generate an intermediate where the two hydrogens which govern the stereochemistry are cis to one another. A [1,5] shift then gives the 8-oxoberbine where the 13 and 13α hydrogens are cis (*cis*-**8**). Conversely, photocyclization of *E*-**7** forms *trans*-**8** via the same rationale. Then an ethylidene enamide **7** can form either *cis*-**8** or *trans*-**8** or a mixture of both, depending on whether there is an equilibrium between *E*-**7** and *Z*-**7** or if either *E*-**7** or *Z*-**7** selectively photocyclizes.

Enamide **7** was synthesized from 3,4-methylenedioxybenzoyl chloride and 1-ethyl-3,4-dihydro-6,7-dimethoxyisoquinoline. Only one isomer was formed and this was assigned the *Z* configuration based on its NMR spectrum which showed a shielded vinyl methyl group as a doublet at δ 1.42. Additionally a short irradiation furnished a mixture of *E* and *Z* isomers. This was indicated by the appearance in the NMR spectrum of a new doublet for a vinyl methyl group at δ 1.76. These methyl resonances may be compared with those of the isopropylidene enamide **1** which occur at δ 1.80 and 1.48. Since

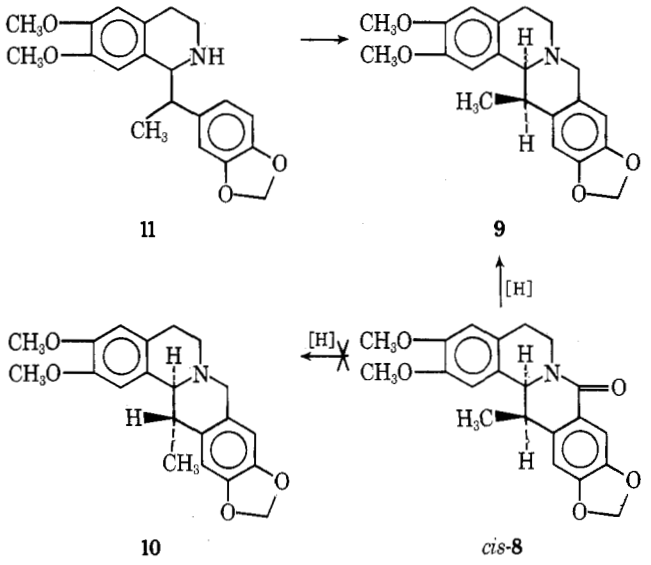
Chart II. Stereochemical Relationships between *E*- and *Z*-7 and the Resultant 8-Oxoberbines



it had already been shown that benzylidene enamides formed a photoequilibrium after a short irradiation period and the isomers could be separated,[12] the above experiment was taken as good evidence that *E*-7 and *Z*-7 were in photoequilibrium.

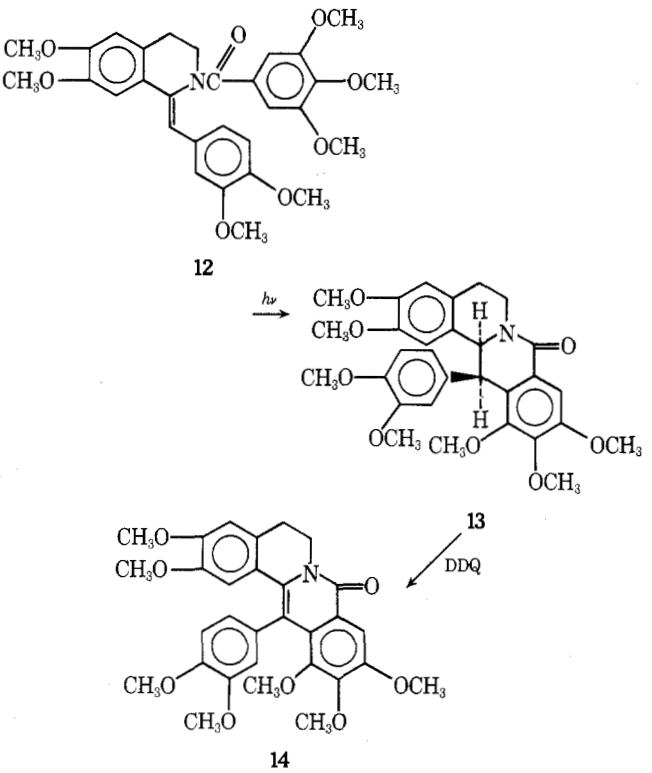
Irradiation of a degassed dioxane solution of **7** furnished a single photoproduct in 97.5% yield by direct crystallization, unaccompanied by any other products. The NMR spectrum of the photoproduct **8** in deuteriochloroform did not allow analysis of the coupling between the C-13 and C-13a protons. They were resolved, however, in deuteriobenzene, which showed the C-13a proton as a doublet (J = 3.5 Hz) at δ 4.72 with the C-13 methyl group as a doublet (J = 7 Hz) at δ 0.90. In the 13-methylberbines, the coupling constant between the C-13 and C-13a protons has been determined to be 3 Hz when the protons are cis and 7 Hz when they are trans. Additionally, the C-13 methyl group appears as a doublet at δ 0.95–1.00 when C-13 and C-13a protons are cis, and at δ 1.4–1.5 when the protons are trans. Both have a coupling constant of 7.0–8.0 Hz.[13] On this basis the photoproduct can be assigned the structure where the C-13 and C-13a protons are cis (*cis*-**8**). Additionally, Shamma has prepared both *cis*- and *trans*-13-methylberbines **9** and **10** with identical oxygenation patterns with **8** by reaction of the benzylisoquinoline **11** with formaldehyde.[14] Reduction of the photoproduct *cis*-**8** with sodium bis(methoxyethoxy)aluminum hydride gave the berbine identical in all respects with an authentic sample of *cis*-berbine **9**. This confirmed the structure of the photoproduct as *cis*-**8** and correlated the coupling constants between the 13-substituted 8-oxoberbines and the 13-substituted berbines.[15] The results show that enamide **7** undergoes an *E*–*Z* photoequilibrium but stereospecifically forms only the cis isomer *cis*-**8**.

The 2-benzoyl-1-benzylidene enamides were next investigated. These had previously been investigated cursively as a precursor to *N*-benzoylnoraporphanes by irradiation in the



presence of iodine as an oxidizing agent.[12] Based on the data of Cava, the structure was revised to that of a 13-aryloxyprotoberberine.[17] Therefore it seemed as though a 13-aryl-8-oxoberbine was being formed which was being dehydrogenated to the 13-aryloxyprotoberberine, and if the oxidizing agent were omitted the 8-oxoberbine could be isolated and the stereochemistry determined.

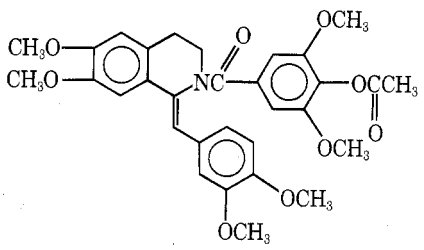
The enamide **12** was synthesized from dihydropapaverine and 3,4,5-trimethoxybenzoyl chloride and assigned the *Z* configuration by analogy with **7** and the appearance of the C-4 axial proton at δ 5.08 due to deshielding by the carbonyl of the benzoyl group. A model shows that the carbonyl of the benzoyl group is within 1.6–1.7 Å of the C-4 axial proton. Irradiation of a degassed solution of **12** in dioxane led to a single product



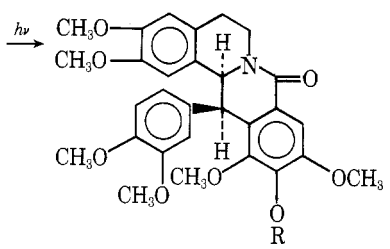
13 in 88% yield. This was identified as a 13-aryl-8-oxoberbine on the basis of its spectral characteristics and its ready dehydrogenation by dichlorodicyanobenzoquinone to the 13-aryloxyprotoberberine **14**.[17] The NMR spectrum of **13** allowed the straightforward assignment of stereochemistry. The C-13a proton appeared as a doublet (J = 3.5 Hz) at δ 5.18 while the

C-13 proton appeared as a doublet (J = 3.5 Hz) at δ 4.52. Additionally the C-6 equatorial proton again appeared as a very broad multiplet at δ 4.41–4.92. On this basis, the C-13, C-13a protons in **13** were assigned the cis configuration, exactly the same as in the 13-methyl case (**8**). Inspection of a model of **13** indicates that the BC-ring junction is pseudotrans (due to ready inversion of the amide nitrogen) and that the angle between the C-13 and C-13a protons is 60°, equivalent to a coupling constant of 3.5 Hz using the Karplus equation.[18] Comparison of a model of **13** with one in which the protons are trans to one another indicates that **13** is the more stable. In the trans compound where the 13-phenyl group would be equatorial, there are severe steric interactions between it and the C-1 hydrogen and methoxyl group at C-12. These interactions are alleviated in **13** where the phenyl group is axial. This had previously been pointed out in the 13-methylberbines.[13,14]

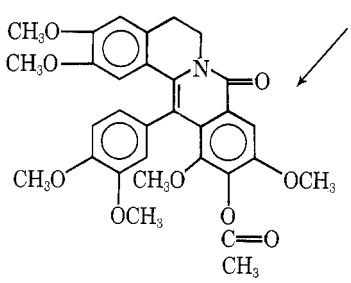
The final enamide studied was the acetoxy enamide **15** with the Z configuration. Photocyclization gave the 13-aryl-8-



15



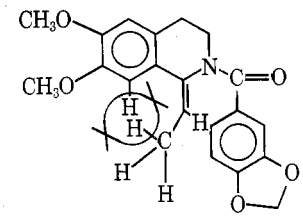
16, R = CH_3CO
17, R = H



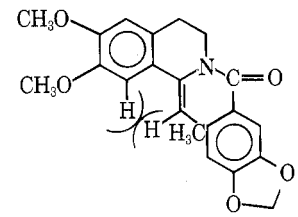
18

oxoberbine **16** in 84% yield. The stereochemistry was again assigned by the 3-Hz coupling constant between the C-13 and C-13a protons. Transesterification under argon gave the free phenol **17** while DDQ dehydrogenation gave the oxyprotoberberine **18**.

The results obtained indicate that alkylidene enamides undergo E–Z isomerization followed by apparent specific photocyclization of the Z isomer to form an intermediate with defined stereochemistry and which determines the conformation of the resultant 13-alkyl-8-oxoberbine. This intermediate then undergoes a suprafacial [1,5]-hydrogen shift to form a berbine where the 13-alkyl group is axial and the C-13 and C-13a hydrogens are cis. The reason for the observed stereospecifity appears to be steric in origin. Examination of Dreiding models of E- and Z-**7** shows that in the approach of the phenyl ring to the exocyclic double bond to form the transition state for the conrotatory electrocyclic ring closure there is little difference between the E and Z configurations.



E-**7**



Z-**7**

This occurs because as the intermediate (Chart II) is being formed, a conrotatory cyclization rotates both the E hydrogen and the Z methyl away from the approaching phenyl ring thus minimizing steric interactions. This difference is certainly not enough to cause the observed stereospecificity. On the other hand, when the influence of the C-8 hydrogen of the A ring on ring formation is considered, the reason for the stereospecificity becomes apparent. In the E isomer, during electrocyclic ring closure, the methyl group must rotate past the C-8 hydrogen. Inspection of a Dreiding model equipped with van der Waals radii indicates that the methyl hydrogens overlap the C-8 hydrogen to the extent of about 80% which causes extreme steric hindrance in the rotation of the methyl group past the C-8 hydrogen during cyclization. In the Z isomer, rotation of the vinylic hydrogen past the C-8 hydrogen is favored since van der Waals interactions are minimal. This steric inhibition to rotation is of course exacerbated when the methyl group is replaced by phenyl in **12** and **15**.

The steric explanation for the observed stereospecifity is amenable to experimental proof. Since **1**, which photocyclized readily, contains a vinylic *gem*-dimethyl group, it is stereochemically equivalent to the E-ethylidene isomer E-**7** which indicates that the methyl group, despite the severe steric interactions, is capable of rotating past the C-8 hydrogen. Then the ratio of the quantum yields of formation of **2** and **8** would reflect the undesirable steric interactions in the photocyclization of **1**. This will be true provided that the processes which deactivate the excited states of the intermediates which form **2** and **8** are very close or identical. This means, for example, that the rates of the reverse reaction to form starting materials from the intermediates must be identical, if they indeed occur. Also the rate of the 1,5-hydrogen shift in both intermediates must be equal, as well as radiationless decay to form these intermediates. Although this is a large caveat, it is not unreasonable for the following reasons. We are attempting to determine the reason why a reaction which, in the other reported cases[4,5] was nonstereospecific, becomes completely stereospecific in the photocyclization of the isoquinoline enamides. Secondly, if only the approach of the benzoyl group to the substituted exocyclic double is considered, it would be predicted that photocyclization would occur from the less sterically congested isomer, namely the E isomer. This then leads to the prediction that the predominant or exclusive photoproduct will possess a trans arrangement of the 13,13a hydrogens. This is, of course, contrary to the observed results where photocyclization occurs exclusively from the Z isomer to generate an 8-oxoberbine where the 13,13a hydrogens are cis. So if the ratio of the quantum yields of formation of **2** and **8** yields a number which indicates that the Z isomer would cyclize exclusively, or very nearly so, then this experiment will lend strong support for the steric inhibition to photocyclization in the E isomer. When the experiment was performed the relative quantum yield at 3000 Å was determined to be ϕ_8/ϕ_2 = 20, indicating that a methyl group in the E configuration retarded the rate of photocyclization by a factor of 20. This predicts that photocyclization should occur almost exclusively from the Z isomer. In fact, it occurs exclusively and the small difference between the observed and predicted stereospecificity vs. stereoselectivity probably occurs as a result of some

of the rates in the aforementioned approximations not being identical. It appears, therefore, that as a result of these experiments stereospecific formation of only a single 13-alkyl-8-oxoberbine is not the result of inherent stereospecificity in the photocyclization of enamides but, rather, is the result of steric interference by the C-8 substituent of the isoquinoline ring on the conrotatory electrocyclic cyclization of the enamide *E* isomers.

Experimental Section

General. The general experimental is the same as has been previously described.[7]

2-(3′,4′-Methylenedioxybenzoyl)-1,2,3,4-tetrahydro-1-isopropylidene-6,7-dimethoxyisoquinoline (1). To a solution of 8.7 g (37.4 mmol) of 3,4-dihydro-1-isopropyl-6,7-dimethoxyisoquinoline[19] in 200 ml of dry pyridine under nitrogen, 8.3 g (45 mmol) of 3,4-methylenedioxybenzoyl chloride[20] was added and the mixture heated at 65 °C for 16 h. The majority of the pyridine was removed under vacuum and the residue dissolved in 500 ml of chloroform. The chloroform solution was washed with water (twice), extracted with 5% sodium bicarbonate, and dried with sodium sulfate. The solvent was removed and the residue dissolved in the minimum amount of ethyl acetate. An equal amount of ether was added and the solution filtered from a small amount of gummy material. Petroleum ether was added to cloudiness and after scratching 10.75 g (28.3 mmol, 75%) of 1 crystallized: mp 153–155 °C; ir 1640, 1630, 1615, 1515 cm^{-1}; uv 220 nm (end, ϵ 39 000), 238 (min, 14 500), 254 (17 500), 278 (min, 8500), 292 (11 500); NMR δ 6.98 (s, 2 H), 6.65–6.86 (m, 3 H), 5.98 (s, 2 H), 4.33 (m, 1 H), 3.93 (s, 6 H), 3.58 (m, 1 H), 3.50–4.00 (m, 2 H), 1.80 (s, 3 H), 1.48 (s, 3 H).

Anal. Calcd for $C_{21}H_{21}NO_5$: C, 69.27; H, 6.08; N, 3.67. Found: C, 68.98; H, 6.05; N, 3.37.

2,3-Dimethoxy-13,13-dimethyl-9,10-methylenedioxy-8-oxoberbine (2). A solution of 3.0 g (7.8 mmol) of 1 in 190 ml of toluene was flushed with argon and irradiated (Pyrex filter) for 10 h with a 450-W Hanovia medium pressure mercury arc. The reaction was best monitored by NMR as there was no difference in TLC behavior between starting material and product. The solvent was removed to yield an oil which was dissolved in 40 ml of ether and filtered to remove a small amount of impurities. Scratching yielded 2.87 g (7.53 mmol, 96.5%) of 5,6,13,13a-tetrahydro-2,3-dimethoxy-13,13-dimethyl-8*H*-benzo[*a*][1,3]benzodioxolo[5,6-*g*]quinolizin-8-one: mp 176–178 °C; ir 1645, 1620, 1525 cm^{-1}; uv 221 nm (ϵ 34 000), 258 (min, 6750), 274 (8000), 289 (8500), 304 (7000); NMR δ 7.61 (s, 1 H), 6.88 (s, 1 H), 6.73 (s, 1 H), 6.70 (s, 1 H), 6.01 (s, 2 H), 4.95 (dq, $J \cong 8$ Hz, 1 H), 4.80 (s, 1 H), 3.90 (s, 3 H), 3.85 (s, 3 H), 2.5–3.2 (m, 3 H), 1.40 (s, 3 H), 0.86 (s, 3 H).

Anal. Calcd for $C_{22}H_{23}NO_5$: C, 69.27; H, 6.08; N, 3.67. Found: C, 69.03; H, 6.24; N, 3.37.

2-Benzoyl-1,2,3,4-tetrahydro-1-isopropylidene-6,7-dimethoxyisoquinoline (3). 3,4-Dihydro-1-isopropyl-6,7-dimethoxyisoquinoline (8.3 g, 35.6 mmol) and benzoyl chloride (5.0 g, 36 mmol) were allowed to react as for 1 to give 9.8 g (29.1 mmol, 81%) of 3: mp 125–127 °C (ether–petroleum ether); ir 1630, 1575, 1505 cm^{-1}; uv 220 nm (end, ϵ 27 500), 237.5 (min, 14 000), 252 (17 000), 279 (5750), 290 (6250); NMR δ 7.38 (m, 5 H), 6.83 (s, 1 H), 6.78 (s, 1 H), 4.38 (dd, with secondary splitting, J = 11.5, 7 Hz, 1 H), 3.92 (s, 6 H), 3.58 (dd, with secondary splitting, J =12, 6.5 Hz, 1 H), 2.97 (m, 2 H), 1.73 (s, 3 H), 1.44 (s, 3 H).

Anal. Calcd for $C_{21}H_{23}NO_3$: C, 74.75; H, 6.87; N, 4.15. Found: C, 74.45; H, 6.99; N, 4.24.

2,3-Dimethoxy-13,13-dimethyl-8-oxoberbine (4). A solution of 1.00 g of 3 (2.97 mmol) in 180 ml of dioxane was degassed by two freeze–thaw cycles and then irradiated in a Rayonet preparative photoreactor with eight 3000-Å lamps for 27 h when the NMR spectrum of an aliquot indicated completion. Owing to the tendency of 4 to gum or oil out of recrystallization solvents in the presence of small amounts of impurities, it was subjected to high-pressure liquid chromatography (HPLC) on Woelm alumina. Elution with ethyl acetate–benzene (15:85) gave a glass. Crystallization was effected by dissolving the glass in a minimal amount of ether and adding petroleum ether. The ether was then removed on a rotary evaporator without using a heating bath. Evaporative cooling gave, from petroleum ether, 431 mg (1.28 mmol, 43%) of 5,6,13,13a-tetrahydro-2,3-dimethoxy-13,13-dimethyl-8*H*-dibenzo[*a*,*g*]quinolizin-8-one: mp 124.5–126 °C; ir 1660, 1525 cm^{-1}; uv 230 nm (ϵ 20 500), 254 (7500), 268 (6250), 275 (min, 5750), 280 (6000), 289 (sh, 5000); NMR δ 8.18 (m, 1 H), 7.47 (m, 3 H), 6.76 (s, 1 H), 6.73 (s, 1 H), 5.03 (m, 1 H), 4.78 (s, 1 H), 3.92 (s, 3 H), 3.87 (s, 3 H), 2.87 (m, 3 H), 1.47 (s, 3 H), 0.93 (s, 3 H).

Anal. Calcd for $C_{21}H_{23}NO_3$: C, 74.75; H, 6.87; N, 4.15. Found: C, 77.41; H, 7.08; N, 4.00.

2-Benzoyl-1,2,3,4-tetrahydro-1-isopropylidene-6,7-dimethoxyisoquinoline-*2′,3′,4′,5′,6′-d*$_5$ (5). Compound 5 was prepared analogously to 3 from 3,4-dihydro-1-isopropyl-6,7-dimethoxyisoquinoline and perdeuteriobenzoyl chloride[21] in 51% yield: mp 124.5–126 °C (ether–petroleum ether); ir 1635, 1515 cm^{-1}; uv 237 nm (min, 14 500), 252 (17 000), 279 (min, 5500), 290 (6250); NMR δ 6.83 (s, 1 H), 6.78 (s, 1 H), 4.42 (dt, J = 12, 7 Hz, 1 H), 3.92 (s, 6 H), 3.58 (dq, J = 12, 8, 6 Hz, 1 H), 2.93 (m, 2 H), 1.72 (s, 3 H), 1.43 (s, 3 H).

Anal. Calcd for $C_{21}H_{18}D_5NO_3$: C, 73.67; H + D, 6.87; N, 4.09. Found: C, 73.62; H + D, 6.76; N, 3.80.

Irradiation of the Deuterated Enamide (5). A solution of 1.00 g of 5 (2.90 mmol) in 180 ml of dioxane was degassed and irradiated under the same conditions and monitoring as 4 for 51 h. Workup analogous to 4 gave 377 mg (1.10 mmol, 38%) of 5,6,13,13a-tetrahydro-2,3-dimethoxy-13,13-dimethyl-8*H*-dibenzo[*a*,*g*]quinolizin-8-one-*9,10,11,12,13a-d*$_5$ (6): mp 126–128 °C; ir 1650, 1520 cm^{-1}; uv 230 nm (ϵ 20 000), 255 (6500), 266 (5750), 280 (5500), 289 (4500); NMR δ 6.75 (s, 1 H), 6.71 (s, 1 H), 5.03 (m, 1 H), 3.92 (s, 3 H), 3.87 (s, 3 H), 2.75–3.17 (m, 3 H), 1.47 (s, 3 H), 0.93 (s, 3 H).

Anal. Calcd for $C_{21}H_{18}D_5NO_3$: C, 73.67; H + D, 6.87; N, 4.09. Found: C, 73.38; H + D, 7.00; N, 3.93.

(*Z*)-2-(3′,4′-Methylenedioxybenzoyl)-1-ethylidene-1,2,3,4-tetrahydro-6,7-dimethoxyisoquinoline (7). A solution of 8.3 g (37.8 mmol) of 1-ethyl-3,4-dihydro-6,7-dimethoxyisoquinoline[22] was treated with 10.0 g of 3,4-methylenedioxybenzoyl chloride (54.6 mmol) as described for 1 to yield 9.2 g (25.0 mmol, 66%) of 7: mp 153–154 °C (ether); ir 1640, 1625, 1615, 1520 cm^{-1}; uv 220 nm (end, ϵ 40 000), 242 (13 500), 261 (20 000), 282 (9000), 297 (12 000); NMR δ 6.95 (s, 3 H), 6.75 (s, 1 H), 6.63 (s, 1 H), 5.95 (s, 2 H), 5.75 (q, J = 7 Hz, 1 H), 3.92 (s, 6 H), 2.92 (broad s, 4 H), 1.42 (d, J = 7 Hz, 3 H).

Anal. Calcd for $C_{21}H_{21}NO_6$: C, 68.65; H, 5.76; N, 3.81. Found: C, 68.38; H, 5.82; N, 4.08.

13,13a-*cis*-5,6,13,13a-Tetrahydro-2,3-dimethoxy-13-methyl-8*H*-benzo[*a*][1,3]benzodioxolo[5,6-*g*]quinolizin-8-one (8). A solution of 3.00 g (8.10 mmol) of 7 was dissolved in 600 ml of dioxane and degassed by four successive freeze–thaw cycles. The solution was irradiated as described for 3 for 20 h. The solvent was removed and the residue crystallized from ethyl acetate–petroleum ether to yield 2.90 g (7.80 mmol, 97.5%) of 8: mp 217–218 °C; ir 1650, 1620, 1520 cm^{-1}; uv 222 nm (ϵ 41 000), 254 (min, 7000), 272 (8000), 291 (8500), 303 (7250); NMR δ 7.43 (s, 1 H), 6.70 (s, 2 H), 6.10 (s, 1 H), 6.02 (s, 2 H), 5.00 (m, 2 H), 3.90 (s, 6 H), 2.50–3.33 (m, 4 H), 0.78 (d, J = 7 Hz, 3 H); (C_6D_6) 8.10 (s, 1 H), 6.43 (s, 2 H), 6.37 (s, 1 H), 5.37 (d, $J \simeq 1.5$ Hz, 1 H), 5.32 (d, $J \simeq 1.5$ Hz, 1 H), 5.18 (dq, J = 8 Hz, 1 H), 4.72 (d, J = 3.5 Hz, 1 H), 3.53 (s, 3 H), 3.45 (s, 3 H), 3.33–5.00 (m, 5 H), 0.90 (d, J = 7 Hz, 3 H).

Anal. Calcd for $C_{21}H_{21}NO_5$: C, 68.65; H, 5.76; N, 3.81. Found: C, 68.33; H, 5.98; N, 4.01.

Isomerization of 7. A solution of 510 mg of 7 was dissolved in 190 ml of ethyl acetate and irradiated, under argon, with a 450-W mercury arc (Pyrex filter) for 45 min. The NMR spectrum of an evaporated aliquot of the irradiation solution showed that approximately two-thirds had been converted to 8 by integration of the aliphatic methyl peak. The remainder consisted of an *E*–*Z* mixture as shown by two vinylic doublets for the olefinic methyl groups at δ 1.76 (*E*) and 1.42 (*Z*) in the ratio of 1:2. The olefinic methyl groups in 1 resonate at δ 1.80 and 1.48.

Reduction of 8-Oxoberbine (8). A solution of 1.00 g of 8 in 55 ml of dry benzene was reduced with 4 ml of a 70% solution of sodium bis(methoxyethoxy)aluminum hydride in toluene for 18 h. The excess reducing agent was destroyed by the addition of 50 ml of saturated Rochelle salt. The organic layer was dried with sodium sulfate and evaporated. Crystallization from 10 ml of methanol gave 763 mg (2.16 mmol, 81%) of 13,13a-*cis*-5,6,13,13a-tetrahydro-2,3-dimethoxy-13-methyl-8*H*-benzo[*a*][1,3]benzodioxolo[5,6-*g*]quinolizine (9), identical in every respect (ir, TLC, NMR, melting point, mixture melting point) with an authentic sample.[14] The ir, TLC, melting point, and mixture melting point comparisons were carried out by Professor M. Shamma at Pennsylvania State University.

(*Z*)-2-(3′,4′,5′-Trimethoxybenzoyl)-1-(3″,4″-dimethoxybenzylidene)-1,2,3,4-tetrahydro-6,7-dimethoxyisoquinoline (12). A solution of 4.0 g of dihydropapaverine[23] (11.7 mmol) in 50 ml of dry pyridine was treated with 6 g (26 mmol) of 3,4,5-trimethoxybenzoyl chloride (Aldrich). Workup as for 1 and crystallization from methylene chloride–ethyl acetate–ether gave 3.34 g (6.24 mmol, 53%) of 12: mp 195–200 °C; ir 1640, 1590, 1520 cm^{-1}; uv 230 nm (ϵ 32 000), 281

(18 500), 322 (19 500); NMR δ 6.33–7.08 (m, 6 H), 6.08 (s, 1 H), 5.08 (m, 1 H), 3.88 (s, 6 H), 3.82 (s, 3 H), 3.77 (s, 3 H), 3.73 (s, 3 H), 3.48 (s, 6 H), 2.58–3.42 (broad m, 3 H).

Anal. Calcd for $C_{30}H_{33}NO_8$: C, 67.27; H, 6.21, N, 2.62. Found: C, 66.98; H, 6.14; N, 2.77.

Isomerization of 12. A solution of 500 mg of **12** in ethyl acetate was irradiated for 20 min analogous to **7**. At this time very little of the 8-oxoberbine **13** had formed. Subtraction of the methoxy resonances for **7** and **13** allowed the identification of the *E* isomer methoxyl resonances at δ 4.00, 3.97 (2), 3.87, 3.78, 3.50. Integration of the separated low-field methoxyl intensities for *E*- and *Z*-**12** and **13** furnished a ratio of *E*-**12**:*Z*-**12**:**13** of 47:36:17.

Irradiation of 12. A solution of 2.75 g (5.1 mmol) in 700 ml of dioxane in a Pyrex vessel was degassed by four successive freeze–thaw cycles. Irradiation in a Rayonet preparative photoreactor with eight 3000-Å lamps for 89 h furnished, after evaporation of solvent and crystallization from ethyl acetate–ether, 2.50 g (4.6 mmol, 88%) of 13,13a-*cis*-5,6,13,13a-tetrahydro-2,3,10,11,12-pentamethoxy-13-(3′,4′-dimethoxyphenyl)-8*H*-dibenzo[*a*,*g*]quinolizin-8-one (**13**): mp 177–178 °C; ir 1660, 1600, 1515 cm^{-1}; uv 220 nm (ε 56 000), 250 (min, 10 000), 262 (sh, 12 000), 276 (13 000), 310 (3000); NMR δ 7.63 (s, 1 H), 6.92 (s, 1 H), 6.55 (d, *J* = 6.5 Hz, 1 H), 6.45 (s, 1 H), 6.22 (d, *J* = 1.5 Hz, 1 H), 5.85 (dd, *J* = 6.5, 1.5 Hz, 1 H), 5.18 (d, *J* = 3.5 Hz 1 H), 4.41–4.92 (broad m, 1 H), 4.52 (d, *J* = 3.5 Hz, 1 H), 3.98 (s, 6 H), 3.96 (s, 3 H), 3.83 (s, 3 H), 3.74 (s, 3 H), 3.46 (s, 6 H), 1.67–3.17 (m, 3 H).

Anal. Calcd for $C_{30}H_{33}NO_8$: C, 67.27; H, 6.21; N, 2.62. Found: C, 67.01; H, 6.36; N, 2.51.

Dehydrogenation of 13. To a stirred solution of 334 mg (0.62 mmol) in 50 ml of toluene, 165 mg (0.73 mmol) of recrystallized 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) was added and the mixture stirred overnight. A few drops of 1,4-dihydrobenzene were added to quench the excess DDQ, the solution turning light yellow after 15 min. The DDQ hydroquinone was filtered and the mother liquors filtered through a short alumina column. The column was washed with 250 ml of toluene and the product was eluted with 250 ml of ethyl acetate–toluene (1:1). Evaporation of solvent and crystallization from ethyl acetate–petroleum ether gave 295 mg (0.55 mmol, 89%) of 5,6-dihydro-2,3,10,11,12-pentamethoxy-13-(3′,4′-dimethoxyphenyl)-8*H*-dibenzo[*a*,*g*]quinolizin-8-one (**14**): mp 208–210 °C; ir 1640, 1605, 1590, 1510 cm^{-1}; uv 231 nm (ε 40 000), 252 (34 000), 295 (min, 10 000), 334 (23 000), 354 (sh, 17 000), 370 (sh, 11 000); NMR δ 7.87 (s, 1 H), 6.93 (m, 1 H), 6.77 (s, 2 H), 6.65 (s, 1 H), 6.43 (s, 1 H), 4.50 (broad m, 1 H), 4.00 (s, 3 H), 3.90 (s, 6 H), 3.87 (s, 3 H), 3.78 (s, 3 H), 3.30 (s, 3 H), 3.17 (s, 3 H), 2.83 (t, 2 H). The other ethylene bridge proton (C-6) is under the δ 3.17–3.30 methoxyls by NMR signal integration. The deuteriobenzene NMR spectrum separates this signal: (C_6D_6) 8.35 (s, 1 H), 6.95 (d, *J* = 2 Hz, 1 H), 6.71 (d, *J* = 2 Hz, 1 H), 6.63 (s, 1 H), 6.57 (s, 1 H), 6.30 (s, 1 H), 4.67 (very broad m, 1 H), 4.00 (very broad m, 1 H), 3.93 (s, 3 H), 3.52 (s, 3 H), 3.43 (s, 3 H), 3.40 (s, 3 H), 2.85 (s, 3 H), 2.83 (s, 3 H), 2.45 (t, 2 H).

Anal. Calcd for $C_{30}H_{31}NO_8$: C, 67.53; H, 5.86; N, 2.63. Found: C, 67.62; H, 5.78; N, 2.54.

(*Z*)-2-(4′-Acetoxy-3′,5′-dimethoxybenzoyl)-1-(3″,4″-dimethoxybenzylidene)-1,2,3,4-tetrahydro-6,7-dimethoxyisoquinoline (15). Compound **15** was prepared in 62% yield (10.3 g, 18.2 mmol) from 10.0 g (29.3 mmol) of dihydropapaverine and 15 g (58.3 mmol) of acetylsyringoyl chloride[24] according to the procedure outlined for **1**: mp 223.5–226 °C; ir 1780, 1640, 1610, 1520 cm^{-1}; uv 220 nm (end, ε 28 000), 257 (min, 14 000), 281 (16 000), 321 (20 000); NMR δ 7.05 (s, 1 H), 6.72 (m, 3 H), 6.48 (s, 1 H), 6.40 (3, 1 H), 6.07 (s, 2 H), 5.08 (m, 1 H), 3.90 (s, 6 H), 3.83 (s, 6 H), 3.80 (s, 3 H), 3.47 (s, 6 H), 2.83–3.67 (m, 3 H), 2.27 (s, 3 H).

Anal. Calcd for $C_{31}H_{33}NO_9$: C, 66.06; H, 5.90; N, 2.49. Found: C, 66.00; H, 5.96; N, 2.65.

Irradiation of Enamide 15. A solution of 2.15 g (3.8 mmol) of **15** in 400 ml of dioxane was irradiated, under argon, with a 450-W mercury arc (Pyrex) for 16 h. Evaporation of solvent and crystallization from a small amount of methanol furnished 1.85 g (3.2 mmol, 84%) of 13,13a-*cis*-11-acetoxy-5,6,13,13a-tetrahydro-2,3,10,12-tetramethoxy-13-(3′,4′-dimethoxyphenyl)-8*H*-dibenzo[*a*,*g*]quinolizin-8-one (**16**): softens 129–130 °C, melts 169–170 °C; ir 1780, 1660, 1610, 1525 cm^{-1}; uv 220 nm (end, ε 64 000), 237 (sh, 25 000), 280 (11 000), 293 (7500), 308 (3500); NMR δ 7.67 (s, 1 H), 6.90 (s, 1 H), 6.52 (d, *J* = 8.5 Hz, 1 H), 6.47 (s, 1 H), 6.13 (dd, *J* = 8.5, 2 Hz, 1 H), 5.92 (d, *J* = 2 Hz, 1 H), 5.18 (d, *J* = 3 Hz, 1 H), 4.50–4.83 (m, 1 H), 4.52 (d, *J* = 3 Hz, 1 H), 3.93 (s, 6 H), 3.82 (s, 3 H), 3.33 (s, 3 H), 2.50–2.92 (m, 1 H), 2.33 (s, 3 H), 1.70 (m, 1 H).

Anal. Calcd for $C_{31}H_{33}NO_9$: C, 66.06; H, 5.90; N, 2.49. Found: C, 65.98; H, 6.00; N, 2.21.

Transesterification of 522 mg (0.93 mmol) of **16** with 250 mg of *p*-toluenesulfonic acid in 50 ml of methanol under argon for 15.5 h gave 341 mg (0.62 mmol, 64%) of the 11-phenol **17** as the hemihydrate, mp 123–125 °C.

Anal. Calcd for $C_{29}H_{31}NO_8 \cdot 0.5H_2O$: C, 63.49; H, 6.25; N, 2.55. Found: C, 63.78; H, 5.98; N, 2.57.

Dehydrogenation of 16. Compound **16** (508 mg, 0.91 mmol) was treated with 227 mg (0.1 mmol) of DDQ and worked up as described for **14** to give 334 mg (0.61 mmol, 66%) of **18**: mp 210–211 °C; ir 1785, 1780 sh, 1645, 1610, 1520 cm^{-1}; uv 230 nm (ε 44 000), 246 (sh, 33 000), 284 (min, 8000), 335 (22 000), 360 (sh, 15 000), 378 (sh, 9500); NMR δ 7.95 (s, 1 H), 6.95 (m, 1 H), 6.80 (m, 2 H), 6.68 (s, 1 H), 6.43 (s, 1 H), 4.17–4.75 (m, 2 H by integration, signal is barely above baseline), 4.00 (s, 3 H), 3.90 (s, 6 H), 3.80 (s, 3 H), 3.32 (s, 3 H), 3.27 (s, 3 H), 2.90 (t, 2 H), 2.33 (s, 3 H).

Anal. Calcd for $C_{31}H_{31}NO_9$: C, 66.30; H, 5.56; N, 2.49. Found: C, 66.73; H, 5.59; N, 2.34.

Relative Rates of Formation of 1 and 7. Solutions of **1** (5.25×10^{-3} mol/l.) and **7** (5.60×10^{-3} mol/l.) in ethyl acetate were prepared in a nitrogen glove box and transferred to Pyrex tubes. The samples were irradiated concurrently in a merry-go-round apparatus in a Rayonet photoreactor equipped with 3000Å lamps. Samples were removed as a function of time and analyzed by VPC on a Hewlett-Packard HP-5711A using a 6-ft 1.5% OV-17 column. The conversion of **1** was followed to 10% formation of **2** and **7** until 40% conversion to **8**. There was no change in the slope of rate of formation of **8** over the range studied. The ratio of the quantum yields of formation of **8** to **2** was determined to be 20 (Φ_8/Φ_2).

Acknowledgments. The author would like to thank Mr. John Schulz of the Searle Laboratories for preparing the deuterated benzoyl chloride and Mrs. Mildred Bruhn of the Searle Laboratories and the Chemical Notation Society for aid in nomenclature.

Registry No.—**1**, 58735-30-1; **2**, 58735-31-2; **3**, 58735-32-3; **4**, 58735-33-4; **5**, 58735-34-5; **6**, 58735-35-6; **7**, 58735-36-7; **7** *E* isomer, 58735-37-8; **8**, 58735-38-9; **9**, 24306-61-4; **12**, 58735-39-0; **12** *E* isomer, 58735-40-3; **13**, 58735-46-9; **14**, 58735-41-4; **15**, 58735-42-5; **16**, 58735-43-6; **17**, 58735-44-7; **18**, 58735-45-8; 3,4-dihydro-1-isopropyl-6,7-dimethoxyisoquinoline, 58735-47-0; 3,4-methylenedioxybenzoyl chloride, 25054-53-9; benzoyl chlroide, 98-88-4; perdeuteriobenzoyl chlroide, 43019-90-5; 1-ethyl-3,4-dihydro-6,7-dimethoxyisoquinoline, 51665-55-5; dihydropapaverine, 6957-27-3; acetylsyringoyl chloride, 39657-47-1.

References and Notes

(1) Inter alia: (a) N. C. Yang, A. Shani, and G. R. Lenz, *J. Am. Chem. Soc.*, **88**, 5369 (1966); (b) G. R. Lenz and N. C. Yang, *Chem. Commun.*, 1136 (1967); E. Winterfeld and H. J. Altman, *Angew. Chem.*, **80**, 486 (1968); *Angew. Chem., Int. Ed. Engl.*, **7**, 466 (1968); (c) I. Ninomiya, T. Naito, and T. Mori, *Tetrahedron Lett.*, 2259 (1969); (d) M. P. Cava, P. Stern, and K. Wakisaka, *Tetrahedron*, **29**, 2245 (1973); (e) S. V. Kessar, G. Singh, and P. Balakrishnan, *Tetrahedron Lett.*, 2269 (1974); (f) H. Iida, S. Aoyagi, and C. Kibayashi, *J. Chem. Soc., Chem. Commun.*, 499 (1974).

(2) (a) I. Ninomiya, T. Naito, and T. Mori, *J. Chem. Soc., Perkin Trans. 1*, 505 (1973); (b) G. R. Lenz, *Tetrahedron Lett.*, 1963 (1973).

(3) (a) I. Ninomiya, T. Naito, and T. Mori, *Tetrahedron Lett.*, 3643 (1969); (b) I. Ninomiya, T. Naito, and T. Kiguchi, *Ibid.*, 4451 (1970).

(4) I. Ninomiya, S. Yamaguchi, T. Kiguchi, A. Shinohara, and T. Naito, *J. Chem. Soc., Perkin Trans. 1*, 1747 (1974).

(5) P. G. Cleveland and O. L. Chapman, *Chem. Commun.*, 1064 (1967).

(6) (a) N. C. Yang and G. R. Lenz, *Tetrahedron Lett.*, 4897 (1967); (b) R. W. Hoffmann and K. R. Eichen, *Chem. Ber.*, **102**, 2987 (1969); (c) D. Bellus, *Adv. Photochem.*, **8**, 109 (1971).

(7) G. R. Lenz, *J. Org. Chem.*, **39**, 2846 (1974).

(8) G. R. Lenz, *J. Org. Chem.*, **39**, 2839 (1974).

(9) This is one extremum of the well-known hindered rotation of tetrahydroisoquinoline amides: (a) G. Fraenkel, M. P. Cava, and D. R. Dalton, *J. Am. Chem. Soc.*, **89**, 329 (1967); (b) D. R. Dalton, K. C. Ramey, H. J. Gisler, Jr., L. J. Lendvay, and A. Abraham, *Ibid.*, **91**, 6367 (1969).

(10) Berbine alkaloids show a similar type of fragmentation: M. Ohashi, J. M. Wilson, H. Budzikiewicz, M. Shamma, W. A. Slusarchyk, and C. Djerassi, *J. Am. Chem. Soc.*, **85**, 2807 (1963).

(11) R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry", Verlag Chemie, Weinheim/Bergstr., Germany, 1970, p 51.

(12) N. C. Yang, A. Shani, and G. R. Lenz, *Tetrahedron Lett.*, 2941 (1966).

(13) (a) C. K. Yu, D. B. MacLean, R. G. A. Rodrigo, and R. H. F. Manske, *Can. J. Chem.*, **48**, 3673 (1970); (b) T. R. Govindachari, K. Nagarajan, R. Charubala, B. R. Pai, and P. S. Subramanian, *Indian J. Chem.*, **8**, 769 (1970).

(14) M. Shamma, C. D. Jones, and J. A. Weiss, *Tetrahedron*, **25**, 4347 (1969).

(15) Ninomiya, who independently discovered the formation of 8-oxoberbines by the irradiation of enamides, indicated that cyclization of a ethylidene enamide gave a *cis*-8-oxoberbine but gave no evidence for either the structure of the ethylidene enamide nor the 13-methyl-8-oxoberbine.[16]

(16) (a) I. Ninomiya and T. Naito, *J. Chem. Soc., Chem. Commun.*, 137 (1973).

(b) After this manuscript was completed, the full article by Ninomiya appeared in *J. Chem. Soc., Perkin Trans. 1*, 1791 (1975). Their structural assignments to the enamide *E–Z* isomers and the structure of the resultant 8-oxoberbine for methyl substituents are in agreement with ours.
(17) M. P. Cava and S. C. Havlicek, *Tetrahedron Lett.*, 2625 (1967).
(18) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).
(19) P. N. Craig, F. P. Nabenhauer, P. M. Williams, E. Macko, and J. Toner, *J. Am. Chem. Soc.*, **74**, 1316 (1952).
(20) G. Barger, *J. Chem. Soc.*, **93**, 563 (1908).
(21) Prepared from deuteriobenzene (Aldrich) following the procedure for the preparation of benzoyl chloride from benzene given in E. Vogel, "Textbook of Practical Organic Chemistry", Wiley, New York, N.Y., 1956, p 792.
(22) B. B. Dey and T. R. Govindachari, *Arch. Pharm. (Weinheim, Ger.)*, **277**, 177 (1939).
(23) J. M. Gulland and R. D. Haworth, *J. Chem. Soc.*, 581 (1928).
(24) W. M. McCord, *J. Am. Chem. Soc.*, **53**, 4181 (1931).

Sulfoximines. 2. New Method for the Preparation of *N*-Arylsulfoximines

Richard W. Heintzelman, Robert B. Bailey, and Daniel Swern*

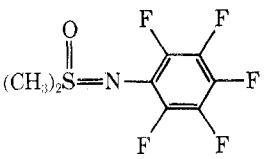
Fels Research Institute and Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122

Received January 23, 1976

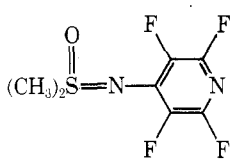
A new method for the preparation of *N*-aryl-*S,S*-dimethylsulfoximines (**8a–l**) is reported. The method involves formation of a complex (**6**) between Me_2SO and *tert*-butyl hypochlorite at low temperatures (−60 °C), followed by reaction of the complex with arylamines to give *N*-aryl-*S,S*-dimethylazasulfoxonium chlorides (**7a–l**). Upon treatment of the salts with base, the corresponding *N*-aryl-*S,S*-dimethylsulfoximines (**8a–l**) are obtained (25–70%-yields). Limitations of the reaction and possible mechanistic pathways are discussed.

At the start of this investigation (1974), a survey of the literature[1,2] showed that no general method existed for the synthesis of *N*-arylsulfoximines, $R_2S(=O)$–N–aryl, and only several *N*-arylsulfoximines were known.

Banks and co-workers[3] prepared *S,S*-dimethyl-*N*-perfluorophenylsulfoximine (**1**) and *S,S*-dimethyl-*N*-tetrafluoropyridylsulfoximine (**2**) by decomposition of the corresponding



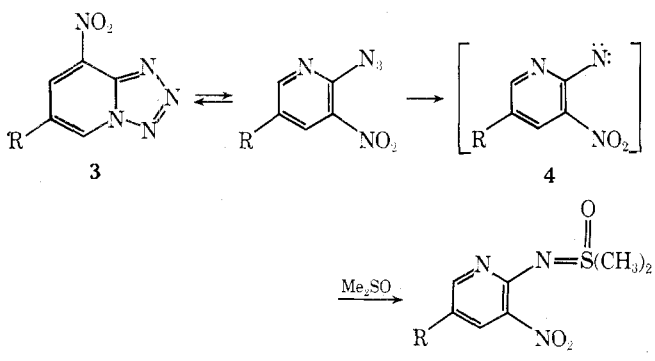
1



2

azides in dimethyl sulfoxide solution. A nitrene intermediate was proposed. However, the chemistry of perfluoroarylnitrenes is vastly different from the chemistry of other arylnitrenes.[3,4] Therefore, this method would appear to be inapplicable to the preparation of other (nonfluorinated) *N*-arylsulfoximines.

Pollack et al.[5] prepared sulfoximines **5a** and **5b** in extremely low yields from the corresponding tetrazolo[1,5-*a*]pyridines **3a** and **3b.** The reaction was reported to proceed via the nitrene **4** which reacts with dimethyl sulfoxide to give the sulfoximines. Sulfoximine **5a** was prepared in only 4% yield, and **5b** was merely identified in situ by NMR but not isolated.



3 4 5

a, R = H
b, R = NO_2

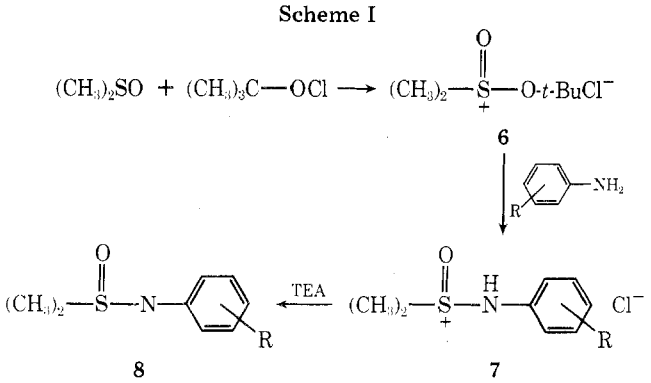
After our investigation was well under way, Claus and coworkers[6] reported the preparation of *N*-arylsulfoximines in good yields by the oxidation of the corresponding iminosulfuranes (sulfilimines) with aqueous potassium permanganate–dioxane. This procedure is an improvement over the original potassium permanganate oxidation of iminosulfuranes reported by Bentley and Whitehead,[7] although it requires that the oxidation be conducted in quite dilute solution. These investigators also reported the preparation of two *N*-arylsulfoximines from Me_2SO, *t*-BuOCl, and aniline or *p*-chloroaniline, respectively, but with lower yields and purity.

Since no convenient general method existed for the preparation of *N*-arylsulfoximines using readily available "off-the-shelf" reactants, and in view of our interest in organic sulfur–nitrogen compounds, we have been investigating new methods for the preparation of these interesting compounds. This paper describes the preparation of a series of previously unreported (see ref 6) *N*-aryl-*S,S*-dimethylsulfoximines (**8a–l**) by a new procedure using readily available reactants (Me_2SO, *t*-BuOCl, arylamines). We also describe experimental results which suggest possible reaction pathways.

Results

Scheme I shows the method of preparation of *N*-arylsulfoximines (**8a–l**). The initial step involves formation of a complex between Me_2SO and *tert*-butyl hypochlorite at low temperatures (−60 °C). This complex, which has pseudohalogen characteristics, i.e., it oxidizes I^- to I_2, is represented as a salt (**6**). Other structures are possible, however, and will be discussed later. Reaction of this complex with arylamines

Scheme I



6 8 7