Photochemical Valence Isomerization of a Conjugated Imino Ether

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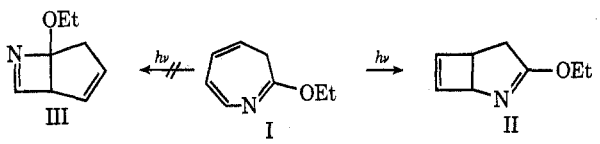
A photochemical valence isomerization of a heterodiene, 4,5-dihydro-2-ethoxy-4,4,6-trimethyl-3*H*-azepine (IV), to a 1-azetine derivative VI is described. The heterodiene is photostable in the excited singlet state and the valence isomerization reaction only occurs under conditions of photosensitization.

Photochemical valence isomerization of cisoid 1,3-dienes is a generally useful method for the preparation of cyclobutene derivatives. Examples have been reported for acyclic, cyclic, and heterocyclic dienes.[1,2] Few cases, however, are known in which a heteroatom is part of the diene chromophore.[3-5] Odum and Schmall recently reported that irradiation of 2-ethoxy-3*H*-azepine (I) yields 3-ethoxy-2-azabicyclo[3.2.0]-hepta-2,6-diene (II) as the exclusive valence isomerization product. The product of participation of the imino ether, 5-ethoxy-6-azabicyclo[3.2.0]hepta-2,6-diene (III), was not observed.[6] In this paper we

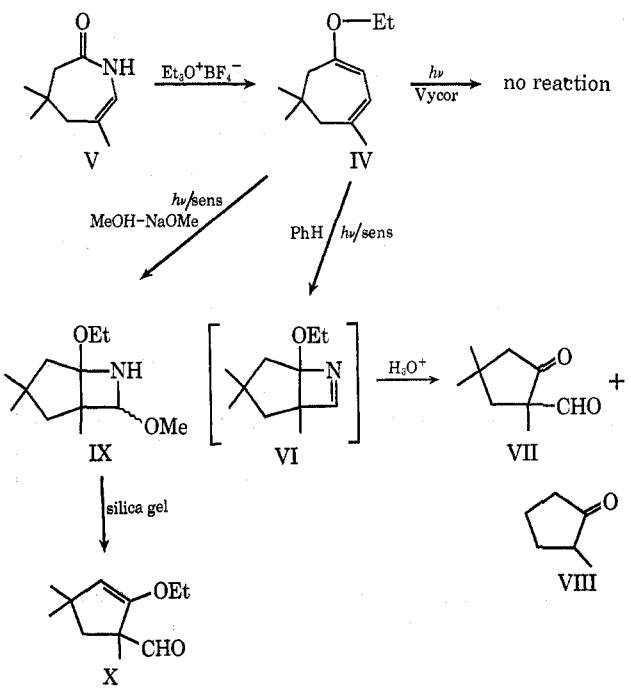


report evidence for the participation of an imino ether group in a valence isomerization reaction.

In our investigations of the photochemical reactivity of conjugated imines and imino ethers,[7] we have looked at the photochemical reactivity of 4,5-dihydro-4,4,6-trimethyl-3*H*-azepine (IV). The dihydroazepine was prepared in 86% yield by the O-alkylation of 4,5-dihydro-4,4,6-trimethyl-2(3*H*)-azepin-2-one (V) with Meerwein's salt. The structure of IV is established by the spectroscopic data. The unsaturated imino ether shows strong infrared absorption at 6.15 μ and ultraviolet absorption at 252 nm (ϵ 3900). In the nmr IV exhibits a six-proton singlet at δ 1.00 for the gem dimethyl group, a three-proton triplet (J = 7 Hz) at δ 1.25 and a two-proton quartet (J = 7 Hz) at δ 4.11 for the ethoxy group, an allylic methylene absorption at δ 1.71 (singlet), a three-proton doublet (J = 1.5 Hz) at δ 1.79 for the allylic methyl, a two-proton singlet at δ 2.03 for the methylene adjacent to the imino ether group, and an olefinic absorption (broad) at δ 6.02. Coupling between the allylic and olefinic protons was demonstrated by double resonance.

Irradiation of dihydroazepine IV in anhydrous ether with a 450-W mercury lamp equipped with a Vycor filter resulted in virtually no destruction of starting material. However, when a photosensitizer (either benzophenone or acetophenone) was employed, efficient photodestruction of IV occurred. Evaporation of the irradiation solvent (benzene) yielded an oil which polymerized upon standing or upon attempted distillation. Immediate treatment of the oil with 3 *N* hydrochloric acid at 50° yielded two stable, volatile products which were extracted and isolated by preparative gas chromatography. The products were identified as 2-formyl-2,4,4-trimethylcyclopentanone (VII) and 3,4,4-trimethylcyclopentanone (VIII) by comparison of ir and nmr spectra with those of authentic samples prepared by acid-catalyzed isomerization of isophorone oxide.[8] Formation of the β-ketoaldehyde VII upon hydrolysis of the irradiation mixture suggests that the photoproduct of the dihydroazepine IV is in fact the valence isomer, 1-ethoxy-3,3,5-trimethyl-7-azabicyclo-[3.2.0]hept-6-ene (VI). The trimethylcyclopentanone hydrolysis product VIII occurs by a reverse aldol condensation of the β-ketoaldehyde (Scheme I).

SCHEME I



Photochemical valence isomerization of IV was further substantiated by irradiation in anhydrous methanol solution in the presence of 1% sodium methoxide and a photosensitizer, benzophenone. Under these conditions a solvent addition product of the valence isomer, 1-ethoxy-6-methoxy-3,3,5-trimethyl-7-azabicyclo[3.2.0]heptane (IX), was isolated. The sol-

(1) R. Srinivasan, *Advan. Photochem.*, **4**, 113 (1966).

(2) G. J. Fonken in "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, p 197.

(3) 1-Azetine derivatives have been reported by C. Lohse, *Tetrahedron Lett.*, 5625 (1968); bicyclic 2-azetines have been obtained by J. Derocque, W. J. Theiser, and J. A. Moore, *J. Org. Chem.*, **33**, 4381 (1968).

(4) 1-Oxetenes have been reported by O. L. Chapman and W. R. Adams, *J. Amer. Chem. Soc.*, **90**, 233 (1968); J. M. Holouka, P. D. Gardner, C. B. Strow, M. L. Hill, and T. V. Van Auken, *ibid.*, **90**, 5041 (1968); and L. E. Friedrich and G. B. Schuster, *ibid.*, **91**, 7204 (1969).

(5) A four-membered-ring azoxy compound has been reported by W. R. Dolbier, Jr., and W. M. Williams, *ibid.*, **91**, 2818 (1969).

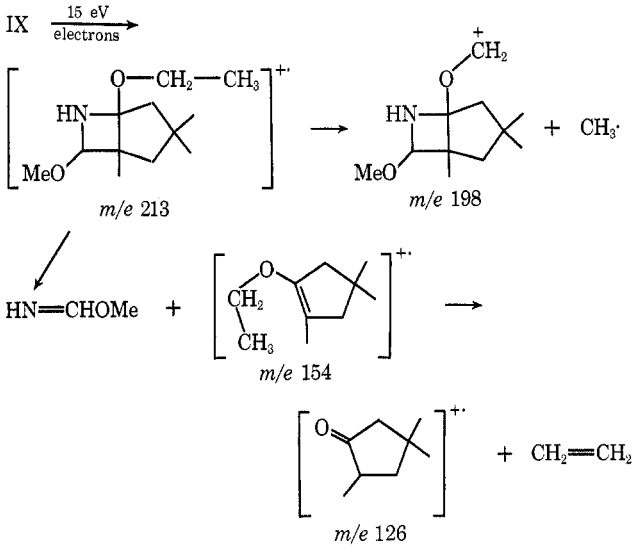
(6) R. A. Odum and B. Schmall, *Chem. Commun.*, 1299 (1969).

(7) For the previous paper in this series, see T. H. Koch and R. J. Sluski, *Tetrahedron Lett.*, 2391 (1970).

(8) H. O. House and R. L. Wasson, *J. Amer. Chem. Soc.*, **79**, 1488 (1957).

vent addition product exhibits an N–H stretching vibration at μ 3.02 and no olefinic or imino ether stretching vibrations in the infrared spectrum. In the nmr three methyl singlets appear at δ 1.02, 1.07, and 1.15. The two sets of methylene protons occur as two AB patterns with chemical shifts of δ 1.52 and 1.72 (J = 14 Hz) and 1.63 and 1.83 (J = 14 Hz). The ethoxy group appears as a triplet at δ 1.12 and a quartet at δ 3.57 (J = 7 Hz), and the methoxy protons appear as a three-proton singlet at δ 3.16. The methine proton is shifted by the two adjacent heteroatoms to δ 4.20, and the N–H proton appears as a broad absorption at δ 2.88. The mass spectrum (direct probe, 15 eV) exhibits only a weak parent ion at m/e 213 (2% of base). The three most intense fragments occur at m/e 198 (20% of base), 154 (37% of base), and 126 (base), and the fragment at m/e 154 is related to the peak of m/e 126 by a metastable ion at m/e 103 (calcd 103). The fragmentation sequence can be explained as indicated in Scheme II.

SCHEME II



The methanol addition product is not stable to silica gel chromatography. When IX was eluted from a column of tlc grade silica gel at 100 psi with 30% chloroform–70% benzene solvent, a product of partial hydrolysis, 2-ethoxy-3-formyl-3,5,5-trimethylcyclopentene, was isolated. This product was also identified spectroscopically. In the infrared, aldehydic and olefinic stretching vibrations occur at 5.78 and 6.09 μ, respectively. Methyl singlets are observed at δ 1.08, 1.13, and 1.23, the methylene protons at δ 1.42 and 2.15 (AB pattern, J = 14 Hz), and the ethoxy group at δ 1.30 (triplet, J = 7 Hz) and 3.76 (quartet, J = 7 Hz). The olefinic proton appears as a one-proton singlet at δ 4.44, characteristic of olefinic protons of vinyl ethers. We note that a geminal coupling constant of 14 Hz is consistently observed in the five-membered ring compounds VIII, IX, and X.

We feel that the structural evidence firmly supports the fact that IV is undergoing an electrocyclic reaction to form an unstable 1-azetine derivative. Electrocyclic reactions of cisoid dienes in excited states are symmetry allowed for the disrotatory mode of closure. Alternatively, photochemical cis–trans isomerization followed by thermal conrotatory ring closure is also a symmetry-allowed process, both mechanisms yielding the same product.[9] Since our reaction occurs exclusively from the triplet state, it is especially important to consider the latter mechanism. Sensitized and unsensitized cis–trans isomerizations have been reported in seven- and eight-membered carbocyclic systems.[10–18] Conrotatory ring closure was sometimes a subsequent reaction.[17,18] In an effort to distinguish between the two modes of ring closure, we attempted to trap a possible geometric isomer with furan, a method proved successful by other research groups.[12,18] A mixture of acetophenone and dihydroazepine was sprayed on an aluminum plate at −190° within a vacuum shroud and irradiated through a Pyrex filter with an external, 200-W super pressure mercury lamp for 30 min. While still at liquid nitrogen temperature, furan was then sprayed on the plate and the mixture slowly allowed to warm to room temperature. No furan addition products were isolated from the irradiated mixture. Although the experiment does not eliminate the possibility of geometrical isomerization prior to ring closure, it does suggest that, if cis–trans isomers are formed, they are not stable at liquid nitrogen temperature. A high degree of instability is predicted for a cis–trans isomer since the isomerization would force a methyl group toward the center of the ring.

Additional studies on photochemical reactivity of other conjugated imine and imino ether systems are currently under way.

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 spectrometers and chemical shifts are reported in δ units from internal tetramethylsilane. The mass spectra were obtained with Varian Mat CH-4 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 Laboratories, Ann Arbor, Mich.

Materials.—4,5-Dihydro-4,4,6-trimethyl-2(3*H*)-azepine was prepared by the Beckman rearrangement of the anti oxime of isophorone according to the procedure of Mazur.[19] Reagent grade benzene was purified for irradiation purposes by stirring with concentrated sulfuric acid for several days, extracting with water and saturated sodium bicarbonate solution, drying over sodium hydroxide, and distilling from phosphorus pentoxide.

4,5-Dihydro-2-ethoxy-4,4,6-trimethyl-3*H*-azepine (IV).—A procedure analogous to that reported by Paquette for the prep-

(9) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).
(10) E. J. Corey, M. Tada, R. LeMahieu, and L. Libit, *J. Amer. Chem. Soc.*, **87**, 2051 (1965).
(11) P. Eaton and K. Lin, *ibid.*, **86**, 2087 (1964).
(12) P. Eaton and K. Lin, *ibid.*, **87**, 2052 (1965).
(13) P. Datta, T. D. Goldfarb, and R. J. Beikess, *ibid.*, **91**, 5429 (1969).
(14) E. H. White, E. W. Friend, Jr., R. L. Stern, and H. Maskill, *ibid.*, **91**, 523 (1969).
(15) G. M. Whitesides, G. L. Goe, and A. C. Cope, *ibid.*, **91**, 2608 (1969).
(16) W. J. Nebe and G. J. Fonken, *ibid.*, **91**, 1249 (1969).
(17) R. S. H. Liu, *ibid.*, **89**, 112 (1967).
(18) L. L. Barber, O. L. Chapman, and J. D. Lassila, *ibid.*, **91**, 537 (1969).
(19) R. H. Mazur, *J. Org. Chem.*, **26**, 1289 (1961).

aration of 2-ethoxy-3,5,5-trimethyl-3*H*-azepine was followed.[20] All glassware was oven-dried prior to use. A 500-ml three-neck flask was charged with 41 g (0.28 mol) of freshly distilled boron trifluoride etherate and 135 ml of anhydrous ether (distilled from lithium aluminum hydride). The reaction vessel was equipped with addition funnel, condenser, stirring apparatus, and drying tube. Epichlorohydrin (20 g, 0.22 mol) was added dropwise with stirring. Upon completion of the addition, the reaction mixture was stirred at room temperature for an additional 3 hr. At this time the triethyloxonium fluoroborate was crystalline. The ether was pipetted off and the crystals were washed three times with anhydrous ether. The triethyloxonium fluoroborate was partially dissolved in 20 ml of dry methylene chloride (freshly distilled from calcium hydride), and a solution of 27.8 g (0.20 mol) of 4,5-dihydro-4,4,6-trimethyl-2(3*H*)-azepin-2-one [mp 90–91° (lit.[19] 89–91°)] in 90 ml of dry methylene chloride was added dropwise while the reaction mixture was maintained at 10–15 with a water bath. The resulting solution was stirred at room temperature for 1 hr and allowed to stand overnight. The reaction was then hydrolyzed by dropwise addition of 35 g of 50% potassium hydroxide solution. The precipitate was removed by filtration and the filtrate dried with anhydrous sodium sulfate. After rotary evaporation of the methylene chloride, the residual oil was fractionally distilled at 9 mm as follows: fraction 1, 3.4 g, bp 66–69°; fraction 2, 7.9 g, bp 69–83°; and fraction 3, 21.0 g, bp 83°. The fractions were analyzed with a 7 ft × 0.25 in. column of 10% Carbowax 20M on 60–80 mesh Chromosorb W at 140°, helium flow 60 cc/min. Fractions 1 and 2 were found to consist of three products and to have the following compositions in order of retention time 20, 44, 31, and 8, 76, 18%, respectively. The compositions are uncorrected for differences in thermal conductivity. The second peak in the chromatogram was identified as the desired oxygen alkylation product, 4,5-dihydro-2-ethoxy-4,4,6-trimethyl-3*H*-azepine. Distillation fraction 3 consisted entirely of this product. The first and third peaks were collected from the gas chromatograph (10 ft × 3/8 in. column of 10% Carbowax 20M on 60–80 mesh Chromosorb W at 155°, helium 60 cc/min) and identified as 1-chloro-2,3-diethoxypropane and 3-chloro-2-ethoxypropanol, respectively. The total yield of the dihydroazepine product IV including fractions 1 and 2 was 86%. An analytical sample of IV was collected from the gas chromatograph as described above for the by-products: nmr (CCl_4) δ 1.00 (singlet, 6 H), 1.25 (triplet, J = 7 Hz, 3 H), 1.71 (singlet, 2 H), 1.79 (doublet, J = 1.5 Hz, 3 H), 2.03 (singlet, 2 H), 4.11 (quartet, J = 7 Hz, 2 H), 6.02 (multiplet, 1 H); ir (neat) 3.40, 6.15, 7.32, 7.67, 8.10, 8.50, 9.0, and 9.6 μ; uv λ_{max}^{EtOH} 252 nm (ϵ 3900).

Anal. Calcd for $C_{11}H_{19}NO$: C, 72.88; H, 10.57; N, 7.73. Found: C, 73.09; H, 10.52; N, 7.80; mol wt, 181 (mass spectrum).

Irradiation in the Absence of a Sensitizer.—A solution of 1.0 g of 4,5-dihydro-2-ethoxy-4,4,6-trimethyl-3*H*-azepine in 120 ml of anhydrous ether was irradiated for 4 hr with a Hanovia 450-W lamp equipped with a Vycor filter. Destruction of the starting dihydroazepine IV was monitored by glpc with a column of 10% Carbowax 20M on 60–80 mesh Chromosorb W at 140° (He 60 cc/min). The gas chromatographic analysis indicated no photodestruction of starting material. Upon evaporation of the solvent, 4,5-dihydro-2-ethoxy-4,4,6-trimethyl-3*H*-azepine (0.95 g) was recovered, pure by glpc and nmr.

Irradiation in the Presence of Acetophenone.—A solution of 2.0 g of 4,5-dihydro-2-ethoxy-4,4,6-trimethyl-3*H*-azepine and 0.23 g of acetophenone in 100 ml of purified benzene was irradiated for 2.25 hr with a 450-W Hanovia lamp equipped with a Corex filter. The destruction of starting material was followed by glpc. After rotary evaporation of the solvent, 10 ml of 3 *N* hydrochloric acid was added and the mixture was heated with stirring at 50° for 0.5 hr. The reaction mixture was cooled, neutralized with saturated sodium bicarbonate solution, and extracted three times with ether. The combined ether extracts were dried with magnesium sulfate, and the ether was removed by rotary evaporation. The resulting oil was distilled at 15-mm pressure by Kugelrohr distillation and three fractions were collected: fraction 1, room temperature (0.10 g); fraction 2, room temperature to 91° (0.36 g); and fraction 3, 92–125° (0.33 g). Each fraction was analyzed on glpc with a 10% Carbowax 20M on 60–80 mesh Chromosorb W column at 150° (He, 67 cc/min) and found to contain the following per cent composition of 2,4,4-trimethylcyclopentanone, 2-formyl-2,4,4-trimethylcyclopentanone, and acetophenone, respectively: fraction 1, 89, 7, 4%; fraction 2, 39, 43, 18%; fraction 3, 14, 60, 26%. The percent compositions are uncorrected for differences in thermal conductivity. The uncorrected yields for 2,4,4-trimethylcyclopentanone and 2-formyl-2,4,4-trimethylcyclopentanone were both 21%, giving a total yield of 42% hydrolysis products. The yield of recovered acetophenone was 67%. 2,4,4-Trimethylcyclopentanone shows nmr (CCl_4) absorptions at δ 1.05 (doublet, J = 7 Hz, 3 H), 1.10 (singlet, 3 H), 1.18 (singlet, 3 H), 1.98 (singlet, 2 H), 1.2–2.7 (complex pattern, 3 H). 2-Formyl-2,4,4-trimethylcyclopentanone shows nmr (CCl_4) absorptions at δ 1.05 (singlet, 3 H), 1.17 (singlet, 3 H), 1.34 (singlet, 3 H), 1.50 and 2.62 (AB pattern, J = 14 Hz, 2 H), 2.12 (singlet, 2 H), 8.71 (singlet, 1 H). Both hydrolysis products were unambiguously identified by comparison of their nmr and ir spectra with samples prepared by boron trifluoride etherate catalyzed rearrangement of isophorone oxide.[8]

Irradiation in the Presence of Methanol and Sodium Methoxide.—A dry Pyrex tube 18 cm × 7 mm o.d. was charged with 0.212 g of benzophenone (sublimed), 0.249 g of 4,5-dihydro-2-ethoxy-4,4,6-trimethyl-3*H*-azepine, and 3.3 ml of 1.1% sodium methoxide anhydrous methanol solution (methanol distilled from magnesium methoxide prior to use). The tube was attached to a vacuum line with an Ultratorr union and degassed by three freeze (liquid nitrogen), pump (10^{-5} mm), thaw cycles. Upon completion of the degassing, the vacuum line and irradiation tube were filled to 1 atm of prepurified nitrogen. The solution was irradiated for 11 hr at 3500 Å with three external low-pressure mercury lamps (Southern New England Ultraviolet Co.). The irradiated solution was distilled by trap-to-trap distillation on the vacuum line at 7 × 10^{-6} mm. For the distillation, traps of ice, Dry Ice, and liquid nitrogen were employed. The irradiation tube was maintained at 21° with a cold water bath throughout the distillation. In the ice trap was collected 0.051 g of material which consisted of roughly 23% benzophenone and 77% 1-ethoxy-6-methoxy-3,3,5-trimethyl-7-azabicyclo[3.2.0]heptane by nmr analysis. The Dry Ice trap contained methanol and additional azabicyclic product. Redistillation of this fraction on the vacuum line yielded an additional 0.080 g of product. The total yield of product was 0.13 g (45%). An analytical sample of the azabicyclic product was obtained by redistillation of the fraction contaminated with benzophenone: nmr (CCl_4) δ 1.02 (singlet, 3 H), 1.07 (singlet, 3 H), 1.12 (triplet, J = 7 Hz, 3 H), 1.15 (singlet, 3 H), 1.52 and 1.72 (AB pattern, J = 14 Hz), 1.63 and 1.83 (AB pattern, J = 14 Hz), 2.88 (broad absorption, 1 H), 3.16 (singlet, 3 H), 3.57 (quartet, J = 7 Hz, 2 H), 4.20 (singlet, 1 H); ir (neat) 3.02, 3.45, and 8.61 μ; mass spectrum (15 eV) m/e 213 (2% of base), 198 (20% of base), 154 (37% of base), and 126 (base).

Anal. Calcd for $C_{12}H_{23}O_2N$: C, 67.56; H, 10.87; N, 6.57. Found: C, 67.69; H, 10.79; N, 6.70.

When the solvent addition product was chromatographed on a high-pressure (100 psi) silica gel column 0.5-in. i.d. by 23 in. (Chromatronix) eluting with 30% chloroform–70% benzene solvent, a product of partial hydrolysis, 2-ethoxy-3-formyl-3,5,5-trimethylcyclopentene, was isolated: nmr (CCl_4) δ 1.08 (singlet, 3 H), 1.13 (singlet, 3 H), 1.23 (singlet, 3 H), 1.30 (triplet, J = 7 Hz, 3 H), 1.42 and 2.15 (AB pattern, J = 14 Hz), 3.76 (quartet, J = 7 Hz, 2 H), 4.44 (singlet, 1 H), 9.47 (singlet, 1 H); ir (CCl_4) 3.28, 3.40, 3.51, 3.58, 3.71, 5.78, 6.09, 6.92, 7.50, 7.85, 8.37 μ.

Irradiation at Low Temperature.—An aluminum disk attached to a stainless steel dewar within a vacuum shroud (Air Products) was cooled to liquid nitrogen temperature and alternately sprayed with acetophenone and 4,5-dihydro-4,4,6-trimethyl-3*H*-azepine. The mixture was irradiated at liquid nitrogen temperature with an external 200-W super pressure mercury lamp (Bausch and Lomb) through a Pyrex filter for 30 min. While still at liquid nitrogen temperature, the aluminum disk was sprayed with furan and the entire mixture was gradually allowed to warm to room temperature. Tlc analysis of the reaction mixture suggested that furan addition products were not formed. Only dihydroazepine, acetophenone, and polymeric products were observed. Photoreaction of 4,5-dihydro-4,4,6-trimethyl-3*H*-azepine in the presence of acetophenone at liquid nitrogen temperature has been observed by infrared analysis.

Registry No.—IV, 29431-21-8; IX, 29431-22-9; X, 29431-23-0.

(20) L. A. Paquette, *J. Amer. Chem. Soc.*, **86**, 4096 (1964).

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3-Monosubstituted 1-Benzoyl-2,2-dichloroaziridines. Methanolysis, Thermolysis, and Benzoylation

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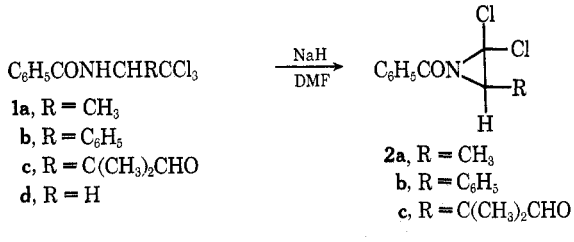
Three 3-monosubstituted 1-benzoyl-2,2-dichloroaziridines **2** have been prepared by cyclization of the corresponding trichloroethylamides **1**. Their behavior on methanolysis and thermolysis was examined. Unlike the corresponding 1-arylaziridines, acid catalysis is required for the methanolysis of the 1-benzoylaziridines. The course of this reaction is sensitive to the nature of the 3 substituent. Like many other 1-acyl-3-arylaziridines, **2b** rearranges thermally giving the oxazole derivative **8**. In contrast, the 3-alkylaziridines **2a** and **2c** are thermally stable in the absence of acid. A novel ring-opening reaction of **2a** occurs with benzoyl chloride. It is concluded that ring cleavage of the 1-benzoyl-3-alkylaziridines is generally initiated by electrophilic attack at the amide oxygen atom. Curiously, however, acid catalysis leads to C-2–N bond cleavage of the aziridine ring of **2a**, whereas benzoylation results in C-3–N bond rupture.

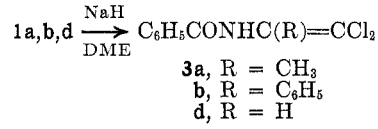
Previous work[1] has demonstrated the ready accessibility of *N*-trichloroethylbenzamides of type **1**. If



the proximity of the amido group could be utilized to facilitate displacement of halogen from the normally inert trichloromethyl group, these compounds might serve as intermediates for a new general synthesis of α-amino acids. While exploring this possibility it was found that treatment with sodium hydride in dimethylformamide (DMF) did indeed lead to the 1-benzoyl-2,2-dichloroaziridines **2** in three examples tried.[2]

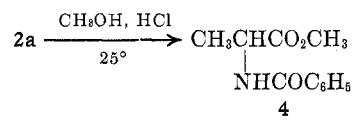
Unfortunately, cyclization was not the exclusive reaction. Some decomposition occurred and elimination of HCl from **1** was not completely preventable. Indeed, in 1,2-dimethoxyethane (DME) as solvent in place of DMF, the amides **1a**, **1b**, and **1d** gave the products of elimination **3a** (27%), **3b** (83%), and **3d** (79%), respectively.[4]

Although achievement of the original objective of this work was clearly thwarted by the poor yields



(45–60%) of **2** obtainable even under the best conditions, further study of the chemistry of these aziridines was of interest. 1-Aryl-2,2-dichloroaziridines have been thoroughly studied,[5,6] and at least one report of 1-benzoyl-monochloroaziridines has appeared.[7] However, the 1-benzoyl-2,2-dichloroaziridines **2** represent a new type worthy of study in view of the reports[8] that 1-aryl-monochloroaziridines differ chemically from their 2,2-dichloro analogs.

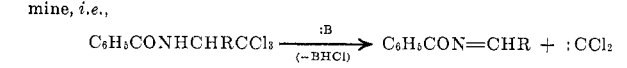
Two reactions were chosen: acid-catalyzed methanolysis and thermolysis. Treatment of the methylaziridine **2a** with methanolic hydrogen chloride at room temperature for 1 week gave two products: *N*-benzoyl-*dl*-alanine methyl ester (**4**) (39% yield, partly hydrolyzed to the acid during isolation) and the trichloroethylamide **1a** (13% yield). Similar treatment of the



phenylaziridine **2b** resulted in more radical rupture of the molecule. Essentially all of the nitrogen was converted to ammonium chloride (93% yield), the 1-benzoyl group appeared as methyl benzoate (90% yield), and the rest of the molecule emerged as a mixture of the chloro ester **5** (53% yield) and the methoxy ester **6**

(1) H. E. Zaugg, *Syn.*, **2**, 49 (1970).

(2) That these cyclizations result from intramolecular nucleophilic displacement of halide ion and not by addition of dichlorocarbene to an acylimine, *i.e.*,



is indicated by experiments in which the yield of **2b** in the presence of tetramethylethylene, although reduced somewhat, is no poorer than the yield obtained in the presence of an equal volume of cyclohexane.[3]

(3) Compare J. A. Deyrup and R. B. Greenwald, *Tetrahedron Lett.*, 321 (1965).

(4) An attractive rationalization for this marked solvent effect involves the reasonable assumption that the sodium derivatives of the amides **1** are largely contact ion pairs in DME and either solvent-separated ion pairs or free ions in DMF. The proximity of the sodium ion in the contact ion pairs could lower the nucleophilic reactivity of the amide anion as well as assist in the removal of chloride ion through a cyclic transition state, with both effects favoring elimination.

(5) (a) E. K. Fields and J. M. Sandri, *Chem. Ind. (London)*, 1216 (1959); A. G. Cook and E. K. Fields, *J. Org. Chem.*, **27**, 3686 (1962); (b) P. K. Kadaba and J. O. Edwards, *ibid.*, **25**, 1431 (1960); (c) H. W. Heine and A. B. Smith, III, *Angew. Chem., Int. Ed. Engl.*, **2**, 400 (1963); (d) K. Ichimura and M. Ohta, *Tetrahedron Lett.*, 807 (1966); *Bull. Chem. Soc. Jap.*, **40**, 1933 (1967).

(6) R. E. Brooks, J. O. Edwards, G. Levey, and F. Smyth, *Tetrahedron*, **22**, 1279 (1966).

(7) F. W. Fowler and A. Hassner, *J. Amer. Chem. Soc.*, **90**, 2875 (1968).

(8) J. A. Deyrup and R. B. Greenwald, *Tetrahedron Lett.*, 5091 (1966); *J. Amer. Chem. Soc.*, **87**, 4538 (1965).