Organic Photochemistry. I. The Synthesis of 2-Oxo-2,3,4,5-tetrahydro-1*H*-naphth[1,8-*de*]azocine by the Photolysis of *N*-Chloroacetyl-2-(α-naphthyl)ethylamine

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N-Chloroacetyl-2-(α-naphthyl)ethylamine (2) on irradiation in methanol–water solution (1:1) with a high-pressure mercury vapor lamp fitted with a Vycor filter was converted to the tricyclic lactam 3, 2-oxo-2,3,4,5-tetrahydro-1*H*-naphth[1,8-*de*]azocine, in yields up to 47%. The lactam was converted to the amine 4, 2,3,4,5-tetrahydro-1*H*-naphth[1,8-*de*]azocine, which was acetylated to produce the amide 5, *N*-acetyl-2,3,4,5-tetra-hydro-1*H*-naphth[1,8-*de*]azocine. The results of some phototitrations of 2 are also reported and discussed.

In 1966 the facile photocyclization of *N*-chloroacetyl-L-tryptophan to a tricyclic eight-membered lactam was reported.[1] Interesting applications of the reaction to certain benzene derivatives such as tyrosines, tyramines, catecholamines, and normescaline[2] and 3,4-dimethoxyphenethylamine[3] have since been reported. As a part of our continuing study of this reaction, it was of interest to apply the reaction to *N*-chloroacetyl-2-(α-naphthyl)ethylamine (2) as a prototype of aromatic polycyclic systems.

2-(α-Naphthyl)ethylamine (1) was prepared in 78% yield by reduction of 1-naphthylacetonitrile with lithium aluminum hydride and converted to 2. Irradiation of 2 in methanol–water solution (1:1, v/v) with a high-pressure mercury vapor lamp fitted with a Vycor filter resulted in photolysis of 2 and the formation of a tricyclic eight-membered lactam 3, 2-oxo-2,3,4,5-tetrahydro-1*H*-naphth[1,8-*de*]azocine, which was isolated in 47% yield.

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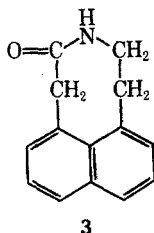
The mass spectrum and combustion analysis indicated that 3 had been formed with the loss of the elements of hydrogen chloride. The ir [(Nujol) 1666 cm^{-1}, C=O of a lactam with six or more members], uv (typical naphthalene spectrum with a shift of λ_{max} from 282 to 288 mμ on going from 2 to 3),[4] and nmr (six aromatic protons) spectra established that 3 was a disubstituted naphthalene. The second position of substitution of the naphthalene moiety could be assigned on the basis of the nmr spectra. In order to obtain symmetrical compounds (in the case of the 1,8 derivative) with improved solubilities, 3 was reduced with diborane to the amine 4, 2,3,4,5-tetrahydro-1*H*-naphth[1,8-*de*]-azocine, which was acetylated to obtain 5, *N*-acetyl-2,-3,4,5-tetrahydro-1*H*-naphth[1,8-*de*]azocine. The nmr

spectra of 3, 4, and 5 exhibit ABX-type spectra for the six aromatic protons with a multiplet of intensity four protons (naphthalene β protons) occurring upfield from a multiplet of intensity two protons (naphthalene α protons) (Figure 1). In the spectrum of 4, these multiplets consist of two overlapping quartets and an isolated quartet, respectively. This spectrum could be analyzed algebraically as an ABX system[5] (δ_A 7.36, δ_B 7.24, δ_X 7.75 ppm; J_{AB} = 6.9, J_{AX} = 8.4, J_{BX} = 1.4 Hz). These values are in good agreement with those reported

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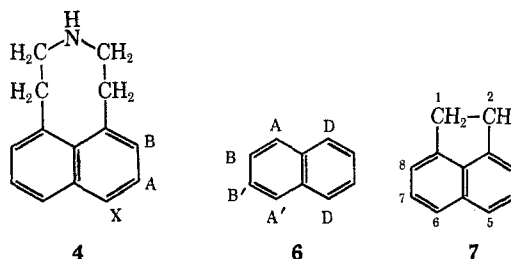
for 1,4-dideuterionaphthalene (6) (100 MHz, CCl$_4$, TMS internal reference; δ_A 7.67, δ_B 7.32 ppm; $J_{BB'}$ = 6.86, J_{AB} = 8.29, $J_{AB'}$ = 1.22 Hz)[6] and acenaphthene (7) (40 MHz, CCl$_4$, TMS internal reference; δ_4 7.32, δ_3 7.11, δ_5 7.46 ppm; J_{34} = 6.7, J_{45} = 8.1, J_{35} = 1.2 Hz).[7] The nmr spectrum of 4 thus establishes the fact that the aromatic protons of 4 exist as two similar groups of three protons, the members of each group of which have different chemical shifts and are mutually spin coupled. The protons of the 1,2-disubstituted naphthalene do not meet these criteria and the spectrum of the aromatic protons of 1,2-dimethylnaphthalene (CDCl$_3$, δ 7.10–8.08 ppm, complex multiplet), determined as a reference spectrum, is more complex and of a different character from those of 3, 4, and 5. Of the disubstituted naphthalenes only the 1,5 and 1,8 derivatives possess the required groupings of protons. The results of an nmr study of dimethylnaphthalenes[3] support this conclusion. In the case of the compounds under consideration, the length of the chloroacetamidoethyl group of 2, as indicated by molecular models and by the intramolecular acylation studies with ω-(1-naphthyl)alkanoyl halides,[9] is clearly insufficient to allow the formation of a 1,5-

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(2) O. Yonemitsu, T. Tokuyama, M. Chaykovsky, and B. Witkop, *ibid.*, **90**, 776 (1968).

(3) O. Yonemitsu, Y. Okuno, Y. Kanaoka, I. Karle, and B. Witkop, *ibid.*, **90**, 6522 (1968).

(4) H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, p 303.

(5) E. D. Becker, "High Resolution NMR, Theory and Chemical Applications," Academic Press, New York, N. Y., 1969, p 157.

(6) M. A. Cooper and S. L. Manatt, *J. Amer. Chem. Soc.*, **91**, 6325 (1969).

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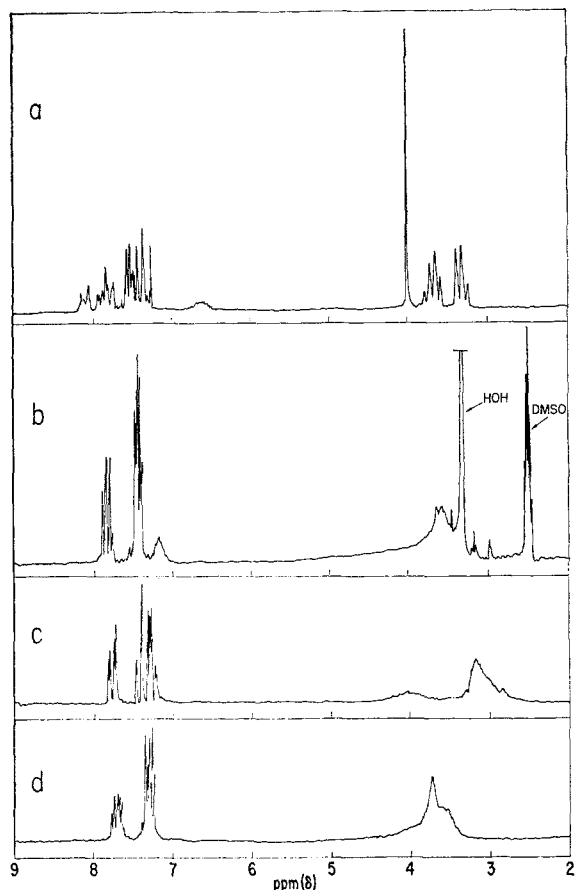(9) R. Huisgen and U. Rietz, *Tetrahedron*, **2**, 271 (1958).

Figure 1.—100-MHz nmr spectra: (a) compound 2 in CDCl₃, (b) compound 3 in DMSO-d₆, (c) compound 4 in CDCl₃, and (d) compound 5 in CDCl₃.

Figure 2.—Phototitrations of 2, 0.15×10^{-3} mol in 20 ml of methanol and 80 ml of water in each case, with a high-pressure mercury vapor lamp. Titrations were carried out under the following conditions: under N₂ with a Vycor filter (—), $t_{1/2}$ = 2.6 min; under N₂ with a Pyrex filter (· · ·), $t_{1/2}$ = 17.6 min; under O₂ with a Vycor filter (---), $t_{1/2}$ = 2.9 min; under O₂ with a Pyrex filter (-· · ·), $t_{1/2}$ = 16.6 min.

disubstituted naphthalene. Compounds 3, 4, and 5 are thus shown to be 1,8-disubstituted naphthalenes.

The nmr signals of the aliphatic protons of 3, 4, and 5 occur as broad structureless overlapping bands (Figure 1). The nature of the temperature dependence of the spectrum of 5 indicates that the character of these signals is primarily a result of incomplete averaging produced by a slow rate of inversion of the eight-membered ring on the nmr time scale;[10] at 117° the signals, which are broad and structureless at 40°, appear as two triplets, each of intensity four protons. These results undoubtedly are a manifestation of restraints placed on the eight-membered ring by the 1,8 substitution of the rigid naphthalene system and are in accord with the assignment of cyclization to the 8 position of the naphthalene moiety. Such broadening was not observed with the tricyclic eight-membered lactam derived from N-chloroacetyl-L-tryptophan[1] or with the tricyclic 2,3-disubstituted naphthalene, 3-methoxycarbonyl-2,3,4,5-tetrahydro-1H-naphth[2,3-d]azepine.[11]

Automatic titration of the protons generated during photolysis has been found to be a useful technique for following the course of this photodehydrohalogenation and for studying its scope. This technique affords a measure of the rate of photolysis from the initiation of irradiation of the substrate. Some titration results al-
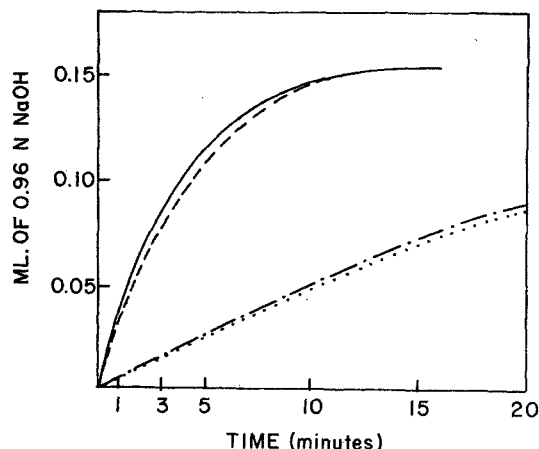
ready have been reported[2] and similar results had been found with N-chloroacetyl derivatives of tryptamine and analogs of tryptamine.[12] Results of phototitrations of 2 are given in Figure 2. The rate of photolysis of 2 under nitrogen with a Vycor filter ($t_{1/2}$ = 2.8 min) is comparable to that of N-chloroacetyltryptamine ($t_{1/2}$ = 2.6 min), which was used as a reference substrate. Careful tlc and uv spectroscopy of the titration mixtures indicated that the products of the reactions conducted with a given filter under nitrogen or oxygen were nearly indistinguishable and that the products obtained using a Vycor or a Pyrex filter were qualitatively the same with small differences in the relative amounts of several of the components. These results suggest that similar reactions take place with both filters. The fact that the reaction proceeds well in the presence of oxygen and that the rates for the reactions under nitrogen or oxygen are similar may indicate that free-radical intermediates or triplet states are not important to the course of the reaction. The reaction rates indicate that the Pyrex filter (30% transmission at 300, 10% at 290, and 0% at 280 mμ)[13] greatly reduced the amount of effective radiation reaching the substrate and suggest that the effective radiation may be acting through excitation of the naphthalene band which is labeled ¹Lₐ in the system of Platt[4] [for this band 2 has $\lambda\lambda_{max}^{MeOH}$ 272 mμ (log ε 3.78), 282 (3.86), 289 (3.69), 293 (3.69)] and which is considered to be transversely polarized. Results obtained so far show that the nature of the aromatic moiety affects the rate as well as the course of the reaction[1–3] and suggest that a photoexcited state of the aromatic portion of the molecule may a play a key role. The fact that photolysis of chloroacetamide itself in aqueous methanol produces protons at a much slower rate than photolysis of 2 may point to such a mechanism.[12] However, cyclization actually may be a concerted reaction in which photoexcitation of the chloroacetamido function also is involved. It has been pointed out that the n–π* excited state of an α-halocarbonyl group has the potential to facilitate the homolysis

(10) For recent reviews, see J. E. Anderson, *Quart. Rev. (London)*, **19**, 426 (1966); G. Binsch in "Topics in Stereochemistry," Vol. 3, E. L. Eliel and N. L. Allinger, Ed., Interscience, New York, N. Y., 1968, p 97.

(11) L. A. Paquette, D. E. Kuhla, J. H. Barrett, and L. M. Leichter, *J. Org. Chem.*, **34**, 2888 (1969).

(12) Unpublished results of C. M. Foltz.

(13) Specifications of the supplier of the filter.

or the heterolysis of the carbon–chlorine bond and that the polarity of the medium might be expected to favor one process or the other.[14] This has been found to be the case in the case of the photolysis of certain α-tosyloxy ketones.[15] On the basis of these results and observations, a reasonable mechanism for the reaction would seem to be one in which photoexcitation of the naphthalene moiety of the substrate results in the formation of a π–π* singlet state with increased electron density at the 8 position. Such an intermediate could displace chloride ion from the side chain, which also may have been predisposed to reaction by photoexcitation, to produce a tricyclic lactam which could lose a proton to complete the reaction. Studies of the acidities of a number of naphthalene derivatives[16] and phenols[17] indicate that in such compounds the contributions of polar structures are much greater in the lowest excited singlet state than in the lowest excited triplet state. Among recently reported photochemical reactions of aromatic compounds, which are believed to proceed in part or largely by ionic mechanisms, are the following: the photohydrolysis of *m*-nitrophenyl phosphates and sulfates,[18] the photosolvolyses of *m*-methoxybenzyl acetates,[19] and the photocyclization of certain ortho-substituted biphenyls.[20] Further studies on the scope and mechanism of this photocyclodehydrohalogenation reaction are in progress.

Experimental Section

All melting points were determined with a Kofler micro hot stage and are uncorrected. Spectra were measured with a Cary recording spectrophotometer, Model 15, using hexane (spectrograde, Matheson Coleman and Bell) and methanol (analytical reagent, Baker) as solvents; with a Perkin-Elmer 421 grating infrared spectrophotometer; with a Varian Associates Model HA-100 instrument using the frequency sweep mode of operation, probe temperatures were 32.4–36° depending on the season, chemical shifts were recorded as δ values (ppm) relative to tetramethylsilane as an internal reference; and with a Hitachi Perkin-Elmer RMU-7 mass spectrometer. The high-pressure mercury vapor lamp (200 W, No. 654A-36), water-cooled quartz immersion well, and glass filter sleeves (Vycor 7910 and Pyrex 7740) were obtained from Engelhard Hanovia, Inc., Newark, N. J. *N*-Chloroacetyltryptamine was synthesized by chloroacetylating tryptamine (Aldrich Chemical Co.).

2-(α-Naphthyl)ethylamine Hydrochloride (1).—An ethereal solution of 13.9 g (0.083 mol) of 1-naphthylacetonitrile (Aldrich Chemical Co.) was added dropwise under nitrogen to a stirred suspension of 5.7 g (0.15 mol) of lithium aluminum hydride (Alfa Inorganics, Inc.) in ether. The mixture was stirred an additional hour and then treated with 100 ml of ether saturated with water, 22 ml of water, and 4.5 ml of 20% sodium hydroxide solution. The ether was decanted and the solid was extracted by trituration with ether. A 1 *N* hydrochloric acid extract of the ethereal solution was alkalinized with sodium hydroxide and extracted with ether. The ethereal extract was washed, dried, and treated with hydrogen chloride to obtain 1, 13.5 g (78%), mp 240–245° (lit.[21] mp 243–248°).

N-Chloroacetyl-2-(α-naphthyl)ethylamine (2).—A mixture of 4.15 g (0.02 mol) of 1, 250 ml of ether, and 20 ml of 1 *N* sodium hydroxide was stirred vigorously and treated dropwise with 2.83

g (0.025 mol) of chloroacetyl chloride with concurrent addition of portions of 30 ml of 1 *N* sodium hydroxide. The mixture was stirred 15 min more, acidified with 2 *N* sulfuric acid, and extracted with ether. The extract was washed with 5% sodium bicarbonate solution and water and dried; 4.0 g (80%) of **2** crystallized from the concentrated solution. Recrystallization from ether–petroleum ether (30–60°) afforded the analytical sample: mp 111–113°; ir (Nujol) 3258 (NH), 3078, 1642 (amide I), 1565 cm⁻¹ (amide II); uv (hexane) 225 mμ (log ε 4.95), 283 (3.87), 315 (2.6); uv (methanol) 225 (4.92), 282 (3.86), 314 (2.58); nmr (CDCl₃) δ 3.22–3.44, 3.56–3.84 (4 H, two multiplets, –CH₂CH₂–), 4.01 (2 H, singlet, –CH₂Cl), 7.2–8.2 (7 H, multiplet, aromatic protons) (Figure 1); mass spectrum, molecular ion *m/e* 247.

Anal. Calcd for C₁₄H₁₄NOCl: C, 67.88; H, 5.70; N, 5.65. Found: C, 67.45; H, 5.76; N, 5.38.

Photolysis of *N*-Chloroacetyl-2-(α-naphthyl)ethylamine (2). Synthesis of 2-Oxo-2,3,4,5-tetrahydro-1*H*-naphth[1,8-*de*]azocine (3).—A solution of 0.91 g of **2** in 350 ml of methanol and 350 ml of water was irradiated for 2.5 hr with a high-pressure mercury vapor lamp fitted with a Vycor filter. Tlc (0.25 mm silica gel, ether–methanol 9:1) at that point indicated complete conversion of the starting material. The volume of the mixture was reduced to about 250 ml at reduced pressure. The mixture was adjusted to pH 6 with sodium bicarbonate and taken to dryness *in vacuo*. Two additional photolyses were carried out in the same way. Each residue was extracted several times with hot ethanol and the extracts were combined, diluted with 2 vol of ether, and allowed to stand overnight at room temperature. The mixture was then filtered and concentrated *in vacuo*. The crystals which separated from the concentrated solution were collected and washed with cold methanol, 1.09 g (47%) of tan crystals, mp 272–276°. Treatment with charcoal and recrystallization from methanol afforded the analytical sample: mp 276–279°; ir (Nujol) 3180 (NH), 3062 and 1666 cm⁻¹ (C=O in a large lactam); uv (methanol) 230 mμ (log ε 4.66), 288 (3.85), 317 (2.73), 322 (2.55); nmr (DMSO-*d₆*) δ 3.6 (center of a very broad signal, aliphatic protons), 7.17 (broad singlet, –C(=O)NH–), 7.28–7.56 (4 H, multiplet, naphthalene β protons), 7.70–7.94 (2 H, multiplet, naphthalene α protons) (Figure 1); mass spectrum, molecular ion *m/e* 211.

Anal. Calcd for C₁₄H₁₃NO: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.52; H, 6.03; N, 6.80.

Reduction of 2-Oxo-2,3,4,5-tetrahydro-1*H*-naphth[1,8-*de*]azocine (3) with Diborane. A. Preparation of 2,3,4,5-Tetrahydro-1*H*-naphth[1,8-*de*]azocine (4).—A solution of diborane (50 ml) in tetrahydrofuran (1 *M* BH₃, Alfa Inorganics, Inc.) was added to a solution of 1.055 g (0.005 mol) of **3** in 800 ml of dry tetrahydrofuran. The mixture was boiled under reflux under nitrogen for 5 hr and then treated with 50 ml of 6 *N* hydrochloric acid and boiled under nitrogen for 1.25 hr. The resulting mixture was concentrated *in vacuo* to 50 ml, alkalinized with sodium hydroxide, and extracted with ether. Ether was removed from the dried extract and the oil which remained was boiled under reflux under nitrogen for 3 hr with a mixture of 50 ml of ethanol, 2 g of potassium hydroxide, and 10 ml of water. The mixture was then concentrated *in vacuo* and extracted with ether. The extract was washed, dried, and concentrated *in vacuo*. The residue was a brown oil which was dissolved in ether and decolorized with charcoal. Removal of the ether yielded an oil which was redissolved in ether and treated with hydrogen chloride. The amine hydrochloride was 0.75 g of a white solid which was recrystallized from ethanol and from methanol–ether, mp 245–247°.

Anal. Calcd for C₁₄H₁₅N·HCl: C, 71.95; H, 6.90; N, 5.99. Found: C, 72.13; H, 6.68; N, 6.17.

The amine **4** was prepared from the hydrochloride as needed and sublimed at 1 mm at bath temperatures of 50–68°. The sublimate was a white solid, mp 111–114°, which was the analytically pure amine: ir (KBr) 3435 cm⁻¹ (NH); uv (hexane) 229 mμ (log ε 4.84), 288 (3.86), 318 (2.8), 323 (2.8); nmr (CDCl₃) δ 1.49 (about 1 H, broad singlet, removed on D₂O treatment, NH), 2.3–4.4 (8 H, broad overlapping bands, two –CH₂CH₂– groups), 7.18–7.48 (4 H, octet, naphthalene β protons, AB part of an ABX system), 7.66–7.84 (2 H, quartet, naphthalene α protons, X part of an ABX system with the following constants:[5] δ_A 7.36, δ_B 7.24, δ_X 7.75; J_{AB} = 6.9, J_{AX} = 8.4, J_{BX} = 1.4 Hz) (Figure 1); mass spectrum, molecular ion *m/e* 197.

Anal. Calcd for C₁₄H₁₅N: C, 85.24; H, 7.66; N, 7.10. Found: C, 85.39; H, 7.50; N, 6.81.

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B. Preparation of *N*-Acetyl-2,3,4,5-tetrahydro-1*H*-naphth-[1,8-*de*]azocine (5).—In another reduction 0.51 g (0.0024 mol) of 3 in tetrahydrofuran was boiled under reflux under nitrogen for 5 hr with 35 ml of a solution of diborane in tetrahydrofuran (1 *M* BH₃, Ventron Corp.). Boiling the mixture under reflux with hydrochloric acid and the usual work-up yielded a crystalline product, 80% of which was dissolved in ether and acetylated with 1.11 g (0.014 mol) of acetyl chloride added in portions to the stirred solution with concurrent additions of 1 *N* sodium hydroxide. The usual isolation and recrystallization of the product from ether yielded 5 as white crystals: 0.25 g; mp 133–135°; ir (Nujol) 1630 cm⁻¹ (amide C=O); uv (hexane) 228 mμ (log ε 4.78), 287 (3.87), 317 (2.7), 322 (2.65); nmr (CDCl₃) δ 1.30 [3 H, singlet, CH₃C(=O), the Dreiding molecular model shows that the methyl group is held over by naphthalene moiety with the result that the methyl group is shielded by the diamagnetic ring current], 3.72 (8 H, center of broad overlapping signals, two –CH₂CH₂– groups), 7.14–7.48 (4 H, multiplet, naphthalene β protons), 7.52–7.84 (2 H, multiplet, naphthalene α protons) (Figure 1); nmr [toluene-*d*₈, 40°, (Me₃Si)₂ internal reference] δ 3.1 and 3.8 (broad overlapping signals, aliphatic protons); nmr (toluene-*d*₈, 117°) δ 3.18 (4 H, triplet, two –CH₂– groups), 3.54 (4 H, triplet, two –CH₂– groups); mass spectrum, molecular ion *m/e* 239.

Anal. Calcd for C₁₆H₁₇NO: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.34; H, 7.27; N, 5.85.

Continuous Titration of Protons Generated during Photolyses of Compound 2.—In all cases 0.15 × 10⁻³ mol of the substrate was dissolved in 20 ml of methanol and that solution was diluted with 80 ml of water. The solution was placed in a semicircular two-neck quartz cell with an inner radius of 3.8 cm and a distance between inner cell walls of 0.7–1 cm. The electrode was introduced through one opening and the other was available for withdrawal of aliquots, etc. The cell was placed in a stainless steel cylinder with a polished inner surface with inner diameter of 15 cm and was supported by hooks on the wall of the cylinder. The water-cooled well containing the lamp and filter was also placed within the cylinder. The substrate solution was agitated by a vigorous stream of a gas which was introduced through two polyethylene tubes. A steel shield supported in grooves on the inner surface of the metal cylinder was positioned between the substrate cell and the immersion well. This shield could be removed rapidly after the lamp had been allowed a warm-up period of 3 min. In doing a series of phototitrations, a given arrangement of equipment could be reproduced precisely. During irradiation the protons produced were titrated with a Radiometer Titrator, type TTT1C, fitted with an Ole Dich No. 38 recorder and a Radiometer GK 2302C glass electrode which was immersed in the substrate solution. The titration curves obtained with this equipment indicate that relative rates of production of protons under various conditions. Reaction half-lives were taken from the curves (Figure 2). Each reaction was allowed to continue nearly to completion and then was taken to dryness *in vacuo*. Examination of the residues in methanol solution by uv spectroscopy and tlc afforded information on the character of the product mixtures. Tlc plates (0.25 mm, silica gel GF, Analtech, Inc.) were developed with ether–methanol (9:1, v/v) or benzene–methanol (3:1, v/v). Developing solvents were allowed to evaporate before visualization with a uv lamp or iodine vapor.

Some Unusual Oxidation Reactions of
# 1,3-Diaryl-3,4-dihydro-7-methoxy-2(1*H*)-quinoxalinones

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Acid-catalyzed air oxidation of 3-aryl-3,4-dihydro-7-methoxy-1-(*p*-methoxyphenyl)-2(1*H*)-quinoxalinones (4) proceeded rapidly to give the corresponding 3,4-dehydro compounds 5. In contrast, a similar oxidation of the 4-methyl derivative 9 afforded anisic acid and 5-methoxy-3-(*p*-methoxyphenyl)-1-methyl-2(3*H*)-benzimidazolone (10). Photolytic oxidation of 3,4-dihydroquinoxalinones by 4,4′-dimethoxyazobenzene proceeded smoothly to give the quinoxalinones 5 and *p*-anisidine.

The acid-catalyzed ortho-semidine type of rearrangement of 4-aryl-1,2-diphenyldiazetidinones (*e.g.*, 1) to 3-aryl-1-phenyl-2(1*H*)-quinoxalinones (2) was reported
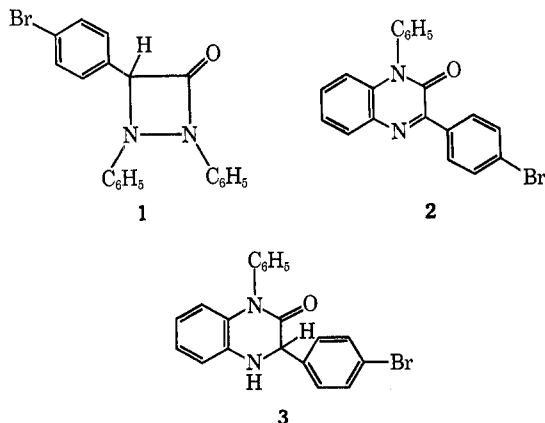
1   2

3

in 1967 by Fischer and Fahr.[2] Surprisingly, no notice appeared to be taken at that time of the unusual oxidation of the expected product, a 3,4-dihydro-2(1*H*)-quinoxalinone (3), to the compound which was actually isolated. We have investigated this reaction and found that, in the absence of air, none of the quinoxalinone 2 was formed, and that 3-aryl-3,4-dihydro-2(1*H*)-quinoxalinones readily undergo a novel acid-catalyzed air oxidation.

We have prepared a series of 7-methoxydihydroquinoxalinones (4) in good yield by catalytic reduction of the corresponding quinoxalinones 5. These compounds were found to be stable to air in the presence of small amounts of base (*e.g.*, triethylamine or sodium bicarbonate), but in slightly acidic solutions were rapidly reoxidized to the quinoxalinones by air. The dihydro compounds were also stable to acid in the absence of air and were recovered unchanged under these conditions. The *N*-acetyl derivative of the dihydroquinoxalinone 6

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