enough water to make a total volume of 3.2 l. The solution (0.00328 M, pH >11) was filtered into a Pyrex immersion well. Purified nitrogen was passed through for 1.5 hr.

The solution was irradiated for 19.5 hr with a Hanovia Type A, medium-pressure, mercury arc lamp. The highest temperature that the filter solution reached was 55°. The solution was filtered. The solid (0.28 g, 12% of the sample weight) was chromatographed on 45 g of silica gel giving anthracene (0.02 g, 1%, mp 196–203°), anthraquinone (0.15 g, 6.7%, mp 230–239°), and 10,10'-bianthrone (0.09 g, 4.2%, mp 253–256°).

The filtrate was continuously extracted with ether for 3 days. The solid (0.2 g) from the evaporation of the ether was chromatographed on 20 g of silica gel giving anthracene (0.03 g, 1.5%, mp 185–190°), anthraquinone (0.09 g, 4.0%, mp 232–243°), and crude 10,10'-bianthrone (0.05 g, 2.4%, mp 235–240°). The total yields of the three products were anthracene (2.5%), anthraquinone (11%), and 10,10'-bianthrone (6.6%).

The filtrate was acidified with 10 ml of concentrated hydrochloric acid and continuously extracted with ether for 3 days. The ether solution was evaporated to dryness. The solid was recrystallized from benzene. Filtration of the hot benzene solution gave the photodimer of 9-anthroic acid (0.25 g, 11%). Upon cooling, the benzene solution gave crystals of 9-anthroic acid (1.4 g, 54%).

Irradiation of Sodium 9-Anthroate in a Sealed Tube. The ampoule was made from a test tube (13 × 100 mm) and a standard taper inner joint (14/20). The ampoule was filled with 5 ml of sodium 9-anthroate (0.003 M) in water. The ampoule was frozen in a Dry Ice–trichloroethylene bath, evacuated to 0.025 mm, closed, and allowed to thaw. This process was repeated except before being thawed the second time it was sealed off. The ampoule was irradiated for 5 hr with a Hanovia Type A, medium-pressure, mercury arc lamp using the nickel sulfate–cobalt sulfate filter solution described above. The ultraviolet spectrum (Figure 1) of the solution shows the presence of the anthrol anion.

Irradiation of Sodium 9-Anthroate in a Sealed Tube to Identify Carbon Monoxide. 9-Anthroic acid (2.00 g, 0.009 mole) and 10% sodium hydroxide (50 ml) were diluted to 75 ml. The solution (0.12 M) was put in a heavy-walled, Pyrex, 100-ml capacity tube fitted with a vacuum stopcock. The tube was frozen, evacuated to 0.02 mm, closed, and thawed. This process was repeated four times. The tube was irradiated for 19 hr with a Hanovia Type A, medium-pressure, mercury arc lamp using the nickel sulfate–cobalt sulfate filter solution described above. After irradiation the product gases were expanded into an infrared gas cell. The infrared spectrum showed, in addition to the bands for the water present, a broad band at 4.7 μ (lit.[15] for carbon monoxide 4.67 μ).

The solution was filtered giving a solid (0.02 g) which by infrared comparison was shown to be a mixture of anthraquinone and 10,10'-bianthrone. No further attempt at separation was made.

Irradiation of the Disodium Salt of the Photodimer of 9-Anthroic Acid in a Sealed Tube. The dimer of 9-anthroic acid (0.222 g, 0.0005 mole) was dissolved in 10% sodium hydroxide (20 ml) and diluted to 25 ml (0.02 M). An ampoule containing 6 ml of the solution was prepared in the manner previously described and irradiated. The ultraviolet spectrum of the solution showed the presence of sodium 9-anthroate and the anthrol anion. Filtration of the solution gave water-insoluble compounds (0.006 g, 11% of starting material). The filtrate was acidified and continuously extracted with ether. Filtration of the ether solution gave dimer (0.038 g, 71% yield) and evaporation gave 9-anthroic acid (0.007 g, 13% yield).

(15) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.
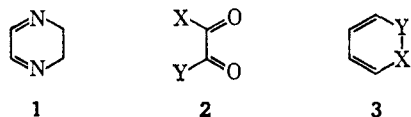
The Photorearrangement of 2,3-Dihydropyrazines

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Contribution from the W. A. Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois. Received November 28, 1966

Abstract: Six 2,3-dihydropyrazines have been found to rearrange to imidazoles upon photolysis. Data are presented in support of the proposal that the reaction proceeds through an irreversibly formed enediimine intermediate.

Formal comparison of the photolysis of the 2,3-dihydropyrazine system **1** with the photochemistry of the structurally related and extensively studied α-dicarbonyl systems **2** and six-membered cyclic dienes **3** could be of practical and theoretical interest.[2] Analogy

with **2** suggests 1,4[3] and 1,2[4] additions, reduction,[5] oxi-

dation,[4c,5] and radical formation[6] might occur upon photolysis of **1**. If **3** is allowed as an analogy, ring opening to a triunsaturated system,[7] ring closure to a bicyclo[2.2.0] system,[8] formation of a bicyclo[3.1.0] system,[7g,9] dimerization,[10] or aromatization[11] might

(1) National Science Foundation Fellow, 1962–1964; University of Illinois Fellow, 1964–1965; Union Carbide Fellow, 1965–1966.

(2) The formal aspects of these comparisons must be emphasized. Different systems are involved and the details of the processes may be very different. *Cf.* J. G. Calvert and J. N. Pitts, "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, pp 528–530.

(3) (a) A. Schonberg and A. Mustafa, *J. Chem. Soc.*, 551 (1945); (b) R. Moore and W. Waters, *ibid.*, 238 (1953); (c) M. Rubin, *J. Org. Chem.*, **28**, 1949 (1963); (d) J. J. Bohning and K. Weiss, *J. Am. Chem. Soc.*, **88**, 2893 (1966), and references cited therein.

(4) (a) M. B. Rubin and P. Zwitkowits, *J. Org. Chem.*, **29**, 2362 (1964); (b) C. H. Krauch, S. Farid, and G. O. Schenk, *Ber.*, **98**, 3102 (1965); (c) M. B. Rubin and R. G. LaBarge, *J. Org. Chem.*, **31**, 3283 (1966).

(5) (a) W. Urry and D. J. Trecker, *J. Am. Chem. Soc.*, **84**, 118 (1962); (b) J. Meinwald and H. Klingle, *ibid.*, **88**, 2807 (1966); (c) P. W. Jolly and P. de Mayo, *Can. J. Chem.*, **42**, 170 (1964).

(6) Calvert and Pitts, ref 2, p 421.

(7) (a) D. H. R. Barton, *Helv. Chim. Acta*, **42**, 2604 (1959); (b) E. Havinga and J. L. M. A. Schlatmann, *Tetrahedron*, **16**, 146 (1961); (c) R. L. Autrey, D. H. R. Barton, A. K. Ganguly, and W. H. Reusch, *J. Chem. Soc.*, 3313 (1961); (d) R. Srinivisan, *J. Chem. Phys.*, **38**, 1039 (1963); (e) G. J. Fonken and K. Mehrotra, *Chem. Ind.* (London), 1025 (1964); (f) W. G. Dauben and R. M. Coates, *J. Org. Chem.*, **29**, 2761 (1964); (g) J. Meinwald and P. H. Mazzocchi, *J. Am. Chem. Soc.*, **88**, 2851 (1966), and references cited therein.

(8) (a) W. G. Dauben and G. J. Fonken, *ibid.*, **81**, 4060 (1959); (b) W. H. Schuller, R. N. Moore, J. E. Hawkins, and R. V. Lawrence, *J. Org. Chem.*, **27**, 1178 (1962); (c) H. Prinzbach and J. H. Hartenstein, *Angew. Chem. Intern. Ed. Engl.*, **2**, 471 (1963); (d) E. J. Corey and J. Streith, *J. Am. Chem. Soc.*, **86**, 950 (1964); (e) W. G. Dauben and R. M. Coates, *ibid.*, **86**, 2490 (1964).

(9) (a) G. R. Evanega, W. Bergmann, and J. English, Jr., *J. Org. Chem.*, **27**, 13 (1962); (b) H. Prinzbach and E. Druckrey, *Tetrahedron*

be expected from the irradiation of **1**. Previous study of the photochemistry of imines has shown this functional group resembles the carbonyl group in its photoreactions of reduction,[12] addition,[13] and prototropy.[14] On the other hand photoisomerization of anils,[15] novel photoaddition and cyclization reactions,[16] and photooxidation[17] have been observed for the imine function. Pyrazine, a heteroaromatic imine, has been reported to photoisomerize to pyrimidine[18a] and to undergo photofragmentation to acetylene and hydrogen cyanide.[18b] Many of the possibilities suggested for the 2,3-dihydropyrazines by these analogies are intriguing. This synthetic potential and an interest in the chemical consequences of n → π* excitation of diunsaturated system constrained to a six-membered ring[19] prompted this study.

In this paper we report a new reaction, the photorearrangement of 2,3-dihydropyrazines to imidazoles.[20] Evidence is presented which suggests an enediimine, formed irreversibly after n → π* excitation, is an intermediate in this reaction.

Results and Discussion

Spectral Properties. The low-intensity n → π* bands expected for a dihydropyrazine[21] could not be resolved for 2,3-dihydro-5,6-dimethylpyrazine (**4**) or 2,3-dihydro-5,6-diphenylpyrazine (**5**). These absorptions appear as the longest wavelength band in each

Letters, 2959 (1965); (c) H. Hart and A. J. Waring, *ibid.*, 325 (1965). In most cases these products are considered to arise from photochemical reaction of the triene produced by ring opening although it is recognized that such an intermediate is not obligatory. *Cf.* D. H. R. Barton, R. Bernasconi, and J. Klein, *J. Chem. Soc.*, 511 (1960).

(10) (a) L. A. Paquette and G. Slomp, *J. Am. Chem. Soc.*, **85**, 765 (1963); E. C. Taylor and R. O. Kan, *ibid.*, **85**, 776 (1963); W. Ayer, R. Hagatsu, P. de Mayo, J. T. Reid, and J. B. Stothers, *Tetrahedron Letters*, 648 (1961); (b) D. J. Valentine, N. J. Turro, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 5202 (1964); G. O. Schenk, S. P. Mannsfeld, G. Schonberg, and C. H. Krauch, *Z. Naturforsch.*, **19b**, 18 (1964).

(11) R. Srinivisan, *J. Am. Chem. Soc.*, **82**, 5063 (1960).

(12) (a) J. Rennert and J. Weisenfeld, *Photochem. Photobiol.*, **5**, 337 (1966); (b) S. Kato, S. Minagawa, and M. Koizumi, *Bull. Chem. Soc. Japan*, **34**, 1026 (1961); (c) C. DuFraisse and E. Toromanoff, *Compt. Rend.*, **235**, 759 (1952).

(13) (a) A. Schönberg and W. Awad, *J. Chem. Soc.*, 651 (1947); (b) A. Mustafa, A. K. Mansour, and A. F. A. M. Shalaby, *J. Am. Chem. Soc.*, **81**, 3409 (1959); (c) G. Pfundt and W. M. Hardham, *Tetrahedron Letters*, 2411 (1965).

(14) (a) M. G. Cohen and G. M. J. Schmidt, *J. Phys. Chem.*, **66**, 2442 (1962); (b) D. G. Anderson and G. Wettermark, *J. Am. Chem. Soc.*, **87**, 1443 (1965).

(15) (a) E. Fischer and Y. Frei, *J. Chem. Phys.*, **27**, 808 (1957); (b) ref 11, p 460.

(16) (a) P. Cerutti and H. Schmid, *Helv. Chim. Acta*, **47**, 203 (1964); (b) *ibid.*, **48**, 1359 (1965); (c) J. S. Shannon, H. Silberman, and S. Sternhell, *Tetrahedron Letters*, 659 (1964); (d) P. J. Collin, H. Silberman, S. Sternhell, and G. Sugowicz, *ibid.*, 2063 (1965); (e) S. Searles and R. Clasen, *ibid.*, 1627 (1965); (f) E. C. Taylor, B. Forth, and M. Pfau, *J. Am. Chem. Soc.*, **87**, 1400 (1965).

(17) R. O. Kan and R. C. Furey, *Tetrahedron Letters*, 2573 (1966).

(18) (a) F. Lahmani, N. Ivanhoff, and M. M. Mayat, *Compt. Rend.*, **263**, 1005 (1966); (b) K. K. Innes, quoted in ref 2, p 460.

(19) The useful concept of electrons largely localized in σ, π, and nonbonding orbitals is retained in the present discussion except for the extended Hückel calculations. Recent comments on the localized approximation for azines have been made by R. Hoffmann, *J. Chem. Phys.*, **40**, 2745 (1964).

(20) (a) P. Beak and J. Miesel, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 95. (b) Dr. D. R. Arnold has independently discovered this reaction; D. R. Arnold, personal communication. We wish to thank Dr. Arnold for this information and for valuable discussion of this manuscript.

(21) Analogous absorptions in related molecules are of low intensity although allowed by local symmetry and affected by molecular symmetry; (a) for a general discussion see J. W. Sidman, *Chem. Rev.*, **58**, 689 (1958); M. Kasha, *Discussions Faraday Soc.*, **9**, 14 (1950); (b) for an example see K. K. Innes, J. D. Simons, and S. G. Tilford, *J. Mol. Spectry.*, **11**, 257 (1963).
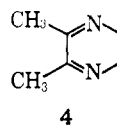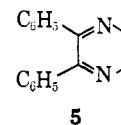
4   5

case with a broad featureless structure. By the empirical criteria of low intensity, absence of absorptions in the hydrocarbon analogs, and the shift of the absorption to shorter wavelengths in hydrogen-bonding solvents (Table I), this absorption is clearly of the n → π* type.[19,21,22] Attempts to demonstrate the disappearance of the long-wavelength band in acid were precluded by the instability of the compounds under these conditions.

Table I. The n → π* Absorptions of 2,3-Dihydro-5,6-dimethylpyrazine (**4**) and 2,3-Dihydro-5,6-diphenylpyrazine (**5**)

Compound	Solvent	λ_{max}, mμ	ε
4	95% ethanol	337	200
	Methylene chloride	349	240
	Cyclohexane	352	215
5	95% ethanol	364	440
	Methylene chloride	371	425
	Cyclohexane	378	315

In the ultraviolet spectrum of **4** the n → π* band is the only absorption above 290 mμ; in the case of **5** there is a tailing absorption from 290 to 310 mμ from an absorption shoulder at 280 mμ. Accordingly the use of a Pyrex filter in photochemical experiments would allow only excitation of the n → π* band for **4** and mainly n → π* excitation for **5**. 2,3-Dihydro-5,6-diphenylpyrazine (**5**) did not show fluorescence in methanol at room temperature or phosphorescence in an ethanol–glycerol glass at 77°K.

Photolyses. Irradiation of 2,3-dihydro-5,6-dimethylpyrazine (**4**) in absolute ethanol using a 450-w high-pressure mercury resonance lamp with a Pyrex filter[23] for 5 hr yields 71% 1,4,5-trimethylimidazole (**6**).
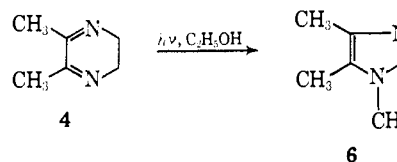

4   6

The product was identified by spectral comparison with an authentic sample and by preparation of the picrate.

Photolysis of 2,3-dihydro-5,6-diphenylpyrazine gives 4,5-diphenyl-1-methylimidazole (**7**) in 75% yield. In some photolyses 4,5-diphenyl-1-ethoxymethylimidazole (**8**) may also be isolated in about 10% yield. The major product was identified as **7** by spectral and melting point comparisons with an authentic sample. The structure of **8** is based on analytical, infrared, ultra-

(22) The short-wavelength shift caused by conjugative substituents for the n → π* band of carbonyl groups[21a] appears to be altogether reversed in comparing the n → π* absorptions of **4** with **5**. The reliability of this correlation for imines is somewhat compromised by its failure to predict the "conjugative" shifts of the n → π* absorptions of azo compounds: H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, pp 185, 430.

(23) In the following discussion these conditions should be presumed unless otherwise stated.

5

C6H5—N / CH3 (7) + C6H5—N / CH2OC2H5 (8)
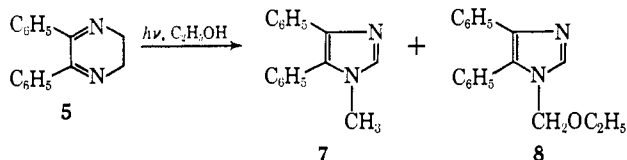
violet, nmr, and mass spectral data as well as its conversion to 4,5-diphenylimidazole (9) in 70% yield on treatment with refluxing hydriodic acid. The quantum yields for the disappearance of 2,3-dihydro-5,6-diphenylpyrazine (5) and the appearance of 4,5-diphenyl-

C6H5, N, CH2OC2H5 (8) → HI → C6H5, N, H (9)
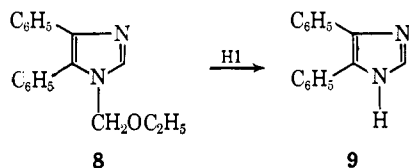
1-methylimidazole (7) are about 0.1. Photolyses of 5 in hexane and benzene[23] or in absolute ethanol using a 23-w low-pressure mercury resonance lamp for 3 to 6 hr leads to 7 in yields ranging from 70 to 90%. The use of 95% ethanol as a solvent for 5 with the high-pressure lamp and a Pyrex filter gives 7 (4%), 8 (8%), and 9 (33%).

In effect this reaction provides a method for the transfer of substituents from the 2 and 3 positions of a 2,3-dihydropyrazine to the 2 position and the exocyclic carbon bonded to nitrogen of an N-substituted imidazole.[24] The availability of 2,3-dihydropyrazines from diketone and diamine precursors suggests the reaction may offer some synthetic convenience over present procedures for the preparation of substituted imidazoles.

The synthetic potential and the variation in products observed in the reaction may be illustrated by the photolysis of *trans*-2,3-diphenyl-5,6,7,8,9,10-hexahydroquinoxaline (10). In absolute ethanol the prod-

**10** → hv, C2H5OH → **11** + **12**

↓ hv, cyclohexane

↘ H2–PdC

11 + **13**
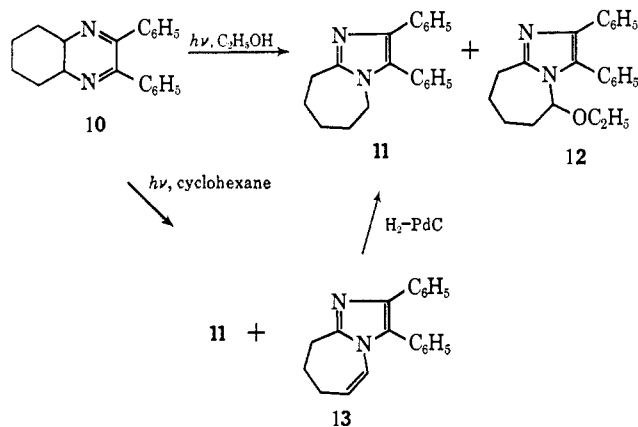
ucts are 2,3-diphenyl-6,7,8,9-tetrahydro-5H-imidazo-[1,2-a]azepine (11) in 9% yield and 2,3-diphenyl-5-ethoxy-6,7,8,9-tetrahydro-5H-imidazo[1,2-a]azepine (12) in 62% yield. In cyclohexane 11 was produced in 8% yield and 2,3-diphenyl-8,9-dihydro-7H-imidazo[1,2-a]-azepine (13) in 19% yield. The structural assignments are based on analytical data, consistency of ultraviolet, infrared, nmr, and mass spectral data with the expected values, using 7 and 8 as model compounds, and the con-

(24) Synthetically this reaction compliments the conversion of 5 to 2-phenyl-2-imidazoline with hydrogen peroxide: H. I. X. Mager and W. Berends, *Rec. Trav. Chim.*, **84**, 314 (1965).

version of 13 to 11 on catalytic hydrogenation. This appears to be the second synthesis of this type of imidazoazepine ring system.[25]

Additional cases are provided by photolyses of 2,3-dihydro-2,3-dimethyl-5,6-diphenylpyrazine (14), 2,3-dihydro-2-methyl-5,6-diphenylpyrazine (15), and 2,3-dihydro-2-isobutyl-5,6-diphenylpyrazine (16). Irradiation of an ethanolic solution of 14[26] for 10 min gave 4,5-diphenyl-1-(1-ethoxyethyl)-2-methylimidazole (17) in 55% yield.[27] Reaction of 15 under these conditions for 8 hr gave 1,2 dimethyl-4,5-diphenylimidazole (18) (42%) and an unresolved mixture of 4,5-diphenyl-1 ethoxymethyl-2-methylimidazole (19) and 4,5-diphenyl-1-(1-ethoxyethyl)imidazole (20) (20%). Photolysis of 16 for 10 min gave 2-isobutyl-4,5-diphenyl-1-methylimidazole (21) (50%)[27] as well as material characterized by its spectral properties as 2-isobutyl-4,5-diphenyl-1-ethoxymethylimidazole (22) (6%)[27] and 1-(1-ethoxy-3-methylbutyl)-4,5-diphenylimidazole (23) (20%).[27] Conversion of 17 to 4,5-diphenyl-2-methylimidazole was achieved with hydriodic acid while 18 was identified by direct comparison with an authentic sample.
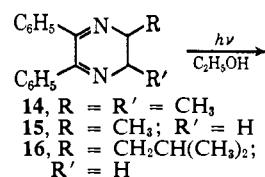
14, R = R' = CH3
15, R = CH3; R' = H
16, R = CH2CH(CH3)2; R' = H

→ hv / C2H5OH →
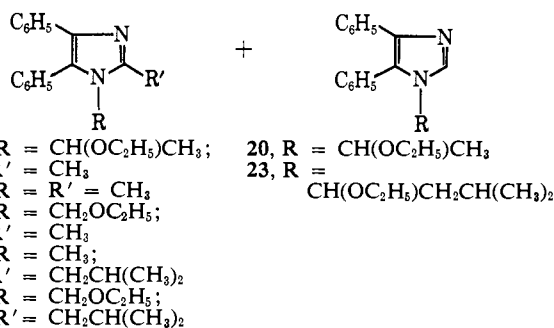
17, R = CH(OC2H5)CH3; R' = CH3
18, R = R' = CH3
19, R = CH2OC2H5; R' = CH3
21, R = CH3; R' = CH2CH(CH3)2
22, R = CH2OC2H5; R' = CH2CH(CH3)2

+

20, R = CH(OC2H5)CH3
23, R = CH(OC2H5)CH2CH(CH3)2

Irradiation of 2,3-dihydro-2-isobutyl-5,6-diphenylpyrazine (16) in cyclohexane took an unexpected course and produced 1,2-di(2-isobutyl-4,5-diphenylimidazoyl)-ethane (24) (43%) in addition to the expected product 21 (26%). The infrared and ultraviolet spectra of this compound are very similar to that of 21, but the extinction coefficient in the ultraviolet was approximately

24
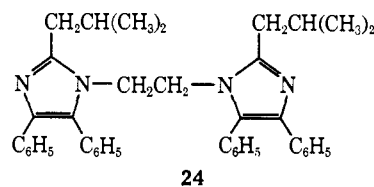
twice that of 21. The singlet assigned to the N-substituted methylene protons of 24 appears at δ 3.78 and this value compares well with the chemical shift of δ 3.30 for the N-methyl group in 21 and of δ 3.94 for the methylene of the N-ethyl group in 4,5-diphenyl-1-ethyl-imidazole. The mass spectrum of 24 confirmed the

(25) R. G. Glushov and O. Y. Mayidson, *Dokl. Akad. Nauk SSSR*, **133**, 585 (1960).

(26) The *cis* isomer and a mixture of *cis* and *trans* isomers gave the same product in separate experiments.

(27) This is based on starting material consumed.

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molecular weight of 578 and gave major fragments at m/e 303 (metastable for 578 → 303 observed at 158.5; calcd, 159) and 289, consistent with species a and b which can be envisioned to arise from **24**.


a   b
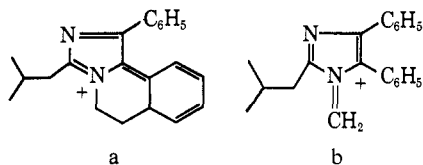
Intermediates. These conversions of 2,3-dihydro-pyrazines to imidazoles may be formulated for the general case as proceeding *via* an enediimene **25** formed by photolytic ring opening. Subsequent ring closure of **25** to **26** would generate an intermediate which could lead to an N-alkylimidazole (**27**) by proton transfer or to an N-ethoxyalkylimidazole (**29a**) by addition

1

28   a, R = C₂H₅   29
             b, R = H
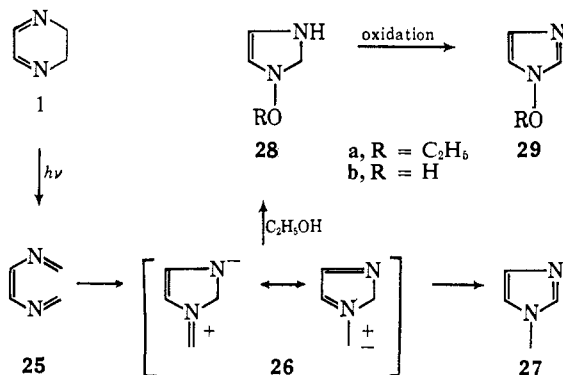
of ethanol followed by oxidation[28] of the resulting imidazoline **28**.

The generality of the photochemical ring opening reactions for systems isoelectronic with 1,3-cyclo-hexadienes was predicted by Barton 8 years ago.[7a] Despite the formidable uncertainties involved in drawing formal analogies for photochemical reactions,[2,29] the present case can be considered to support the empirical utility of Barton's prediction. The cyclization of **25** to **26** as a nonphotochemical reaction has reasonable precedent.[30]

This proposal outlines the general nature of the intermediates, and the involvement of different tautomers and timing of the reactions are open to discussion. At least two species, **30** and **31**, which could fulfill the function of **25**, can be envisioned. Analogy[2,29] clearly favors **25**, however, and for the lack of definative


30   31
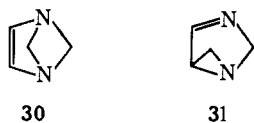
information about the alternatives, **25** will be provisionally preferred.[31]

(28) The facility of the proposed reaction is suggested by the ready oxidation of aryl-2-imidazolines: K. Hoffmann, "Imidazole and Its Derivatives," Part 1, Interscience Publishers, Inc., New York, N. Y., 1953, p 42. The oxidation could be a photoreaction due to traces of unremoved oxygen in the nitrogen used for purging or a subsequent reaction occurring in the work-up. M. Busch, *Ber.*, **64**, 1816 (1931), claims the preparation of a 4-imidazoline bearing hydrogens on both nitrogen atoms and reports this compound is readily oxidized to the corresponding imidazole.

(29) See the discussion by F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Am. Chem. Soc.*, **86**, 3094 (1964), for a cautionary note on the use of analogy for photochemical processes.

(30) G. McCoy and A. Day, *ibid.*, **65**, 2159 (1943).

The results of the photolyses of **10** can be accommodated in the proposed mechanistic framework. Production of 2,3-diphenyl-8,9-dihydro-6H-imidazo[1,2-a]azepine (**13**) from **10** under these conditions could occur by proton transfer of **32** to give **33** followed by oxidation.
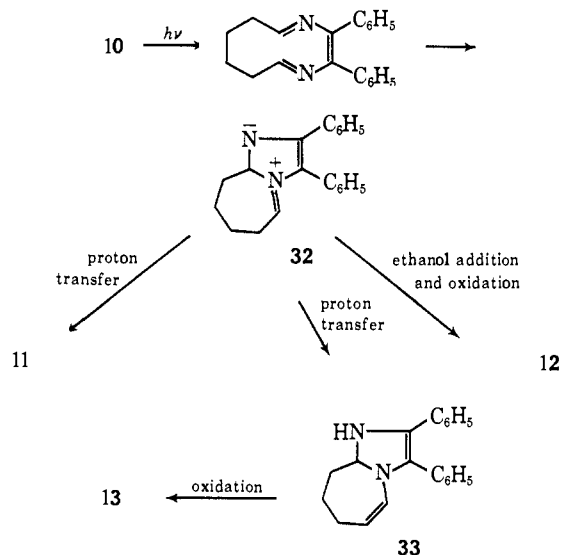
The formation of 4,5-diphenylimidazole (**9**) in the photolysis of 2,3-dihydro-5,6-diphenylpyrazine (**5**) in 95% ethanol could result from the loss of the elements of formaldehyde from **28b** or **29b** formed by addition of water to **26** or by exchange with the corresponding ethers.

The product distributions in the cases of the unsymmetrically 2,3-substituted 2,3-dihydropyrazines **15** and **16** can be rationalized if the intermediates corresponding to **25** and **26** are considered to lead predominantly to imidazole products resulting from intramolecular nucleophilic addition at the most substituted imine carbon atom.[33] For example, 1,2-dimethyl-4,5-diphenylimidazole (**18**) is formed in the photolysis of 2,3-dihydro-2-methyl-5,6-diphenylpyrazine (**15**) rather than 1-ethyl-4,5-diphenylimidazole.

The formation of 1,2-di(2-isobutyl-4,5-diphenylimidazoyl)ethane (**24**) on photolysis of **16** in cyclohexane may result from the condensation of two molecules of **34** to give **35**, a species which could undergo ring closure and proton transfer to yield **37**, followed by oxidation. Tautomeric variants of this scheme can be envisioned. A different possibility is photoreaction of **34** to form the diazetidene **36** followed by ring closure,

(31) The assumption that changes in bond orders or overlap populations on transformation from the ground to the excited state indicate positions of bond formation and bond breaking in the excited state[32a] may be applied to the present case by use of the extended Hückel method.[32b] In agreement with the suggested intermediacy of the enediimine **25**, bond overlap populations obtained from the calculations show a bond weakening of the 2,3 and 1,6 bonds and a bond strengthening of the 1,2 and 5,6 bonds on promotion of an electron from the highest occupied to the lowest unoccupied orbital of 2,3-dihydropyrazine (**1**). In contrast to this a strengthening of the 2,3 bond is obtained on promotion of an electron from the second highest occupied to the lowest unoccupied orbital of **1**.

(32) (a) H. E. Zimmerman, *Pure Appl. Chem.*, **9**, 493 (1964); J. P. Malrieu, *Photochem. Photobiol.*, **5**, 291,301 (1966); R. Hoffmann, private communication. (b) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); the program used was kindly provided by Mr. Donald Dugre. We are grateful to Mr. Dugre and Professor Hoffmann for use of the program and for advice.

(33) Although rationales can be constructed for this proposal, the limited data, as well as the fact that small energy differences of subtle origin may be involved, suggest that further speculation is not warranted.

ring opening, and proton transfer to give **37**. The intermediacy of **36** is suggested by analogy to the proposals of Searles and Clasen for the photolytic conversion of anils to stilbenes and azobenzenes.[16e] These rationales, however, do not explain the apparently anomalous formation of **24**.

C₆H₅ N
16 —hν→ 34 —hν→ 36

35

37

oxidation → 24
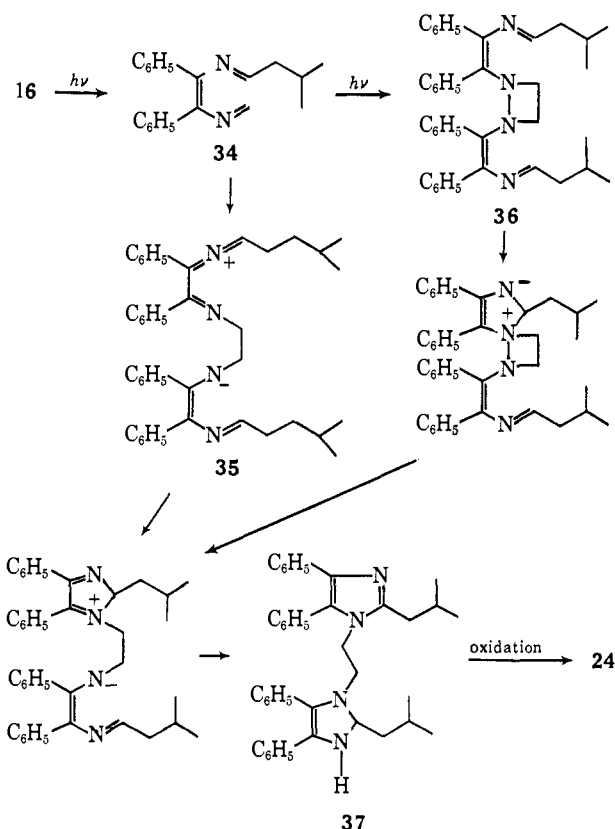
Support for the proposed intermediates is provided by the deuterium incorporation observed in the course of photolysis. Irradiation of **5** in ethanol-*d* (95% *d*), followed by heating the products in ethanol-*d* to complete the exchange of the liable imidazole C-2 proton, gave 4,5-diphenyl-1-methyl-*d*-imidazole-2-*d* (**38**) which has a minimum of 90% dideuterium incorporation. The extent of deuterium incorporation was determined by mass spectrometry, and the position of deuteration was determined by nmr analysis. Direct comparison of the spectrum of **38** with that of **7** showed the expected ratio, 10:2, of proton resonances, and the signal for the N-deuteriomethyl group at δ 3.42 had an unresolved triplet shape.[34] Isolation of unreacted **5** demonstrated that it did not exchange under the conditions of the experiment, while control experiments with 4,5-diphenyl-1-methylimidazole (**7**) showed that exchange of only the C-2 proton occurred on treatment with ethanol-*d* under

5 —hν, C₂H₅OD→ 38
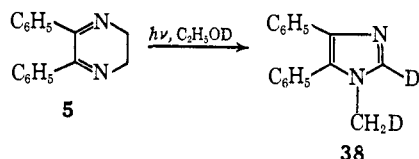
the photolysis conditions.[35] The incorporation of deu-

(34) The hydrogen–deuterium coupling constant would be expected to be on the order of 1–2 cps.

(35) H. A. Staab, M. Th. Wu, A. Mannschreck, and G. Schwalbach, *Tetrahedron Letters*, 845 (1964); T. M. Harris and J. L. Randall, *Chem. Ind.* (London), 1728 (1965); R. O. Olofson, private communication.

terium into the N-methyl group of the product imidazole is expected for an intermediate corresponding to **26** in this reaction.

In an attempt to generate a relatively stable enediimine, the irradiation of 2,3-dihydro-5,6-diphenyl-2,2,3,3-tetramethylpyrazine (**39**) was investigated. The expected enediimine intermediate in this case would not be capable of imidazole formation by the prescribed pathway. Photolysis of **39** in absolute ethanol for 2.5 hr gave 2,2-dimethyl-4,5-diphenyl-3-imidazoline (**40**) (60%) and 2,2-dimethyl-4,5-diphenylisoimidazole (**41**) (9%). The imidazoline **40** was identified by

39 —hν, C₂H₅OH→ 40 + 41
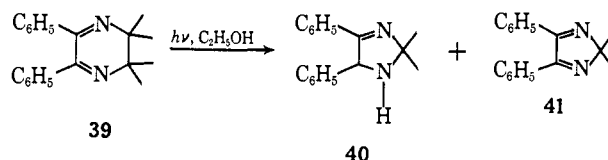
analytical, infrared, ultraviolet, nmr, and mass spectral data. The ultraviolet spectrum of **40**, λ_{max} 245 mμ (ε 12,500), is characteristic of phenyl-substituted Schiff bases.[36] The nmr resonances of two methyl groups at δ 1.62 and 1.48 are consistent with the assigned structure and indicate that alternative structures bearing methyl groups on a carbon doubly bonded to nitrogen can be ruled out.[37] The mass spectrum shows that losses of hydrogen, a methyl group, and benzonitrile from the molecular ion, as expected for **40**, are favorable processes. Chemical confirmation of this assignment was provided by the oxidation of **40** to **41** with sulfur at 125° in high yield and by the hydrolysis of **40** to desyl-

$$\text{41} \xleftarrow[125°]{S} \text{40} \xrightarrow{acid} C_6H_5-\overset{O}{\overset{\|}{C}}-\overset{NH_2}{\underset{|}{C}}H-C_6H_5$$
42
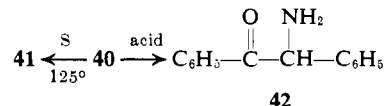
amine (**42**) by dilute acid. The structure of **41** was established by spectral and physical comparison with an authentic sample.

Although detection of the presumed intermediate **43** has not been possible,[38] the observed products are consistent with its transient existence. Ring closure

39 —hν→ 43 →

—C₂H₅OH→ (CH₃)₂COC₂H₅ —C₂H₅OH→

40 + (CH₃)₂C(OC₂H₅)
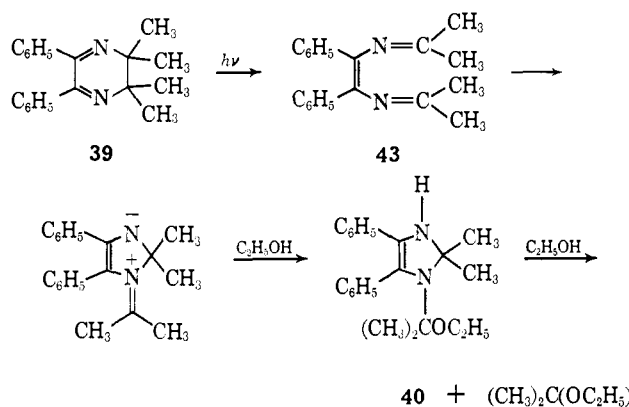
of **43** followed by loss of the nitrogen substituent, presumably with formation of acetone or acetone diethyl ketal, would lead to **40**. The formation of 2,2-di-

(36) G. E. McCasland and E. C. Horswill, *J. Am. Chem. Soc.*, **73**, 3923 (1951).

(37) E. Arnal, J. Elyuero, R. Jacquier, C. Marzin, and J. Wylde, *Bull. Soc. Chim. France*, 877 (1965).

(38) A number of experiments, under a variety of conditions, were carried out and attempts were made to detect **43** as a nonisolable species.

methyl-4,5-diphenylisoimidazole (41) in this reaction may be due to photooxidation of 40 by minor products or impurities in the system.

If the photolytic conversion of the 2,3-dihydropyrazines to imidazoles proceeds *via* an enediimine corresponding to 25, there is a reasonable possibility that the photochemical ring opening is reversible, *i.e.*, that the enediimine can re-form a 2,3-dihydropyrazine.[39] In principle, this process could be detected by partial photolysis of a 2,3-dihydropyrazine which is optically active by virtue of an asymmetric center at position 2 and isolation of the starting material to determine if racemization, requisite in ring closure of the planar enediimine intermediate, has occurred. Photolysis of optically active 2,3-dihydro-2-isobutyl-5,6-diphenylpyrazine (16) for 10 min in absolute ethanol or cyclohexane followed by recovery of starting material in 55 and 44% yields showed that less than 5% racemization had occurred. Accordingly, the photochemical ring opening is not reversible within the limits of detection.[40]
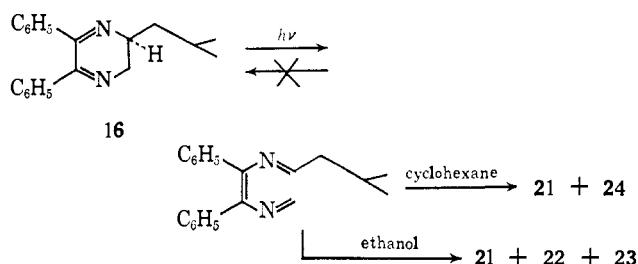
Excited Species. On the basis of the spectral data for 4 the reaction may be formulated as occurring after n → π* excitation. The photolysis of 2,3-dihydro-2,3-diphenylpyrazine (5) to give 4,5-diphenyl-1-methylimidazole (7) does not appear to be sensitized or quenched by benzophenone,[41] triphenylene,[41] *trans*-stilbene,[42] naphthalene, or piperylene, even when the latter is the reaction solvent. These results suggest, but do not require, that a triplet species is not an intermediate in the conversion of 5 to 7.[43] The reaction may provisionally be formulated as occurring in an n,π* singlet. It is possible that a triplet which lies less than *ca.* 60 kcal/mole above its ground state could be in-

volved as could a triplet which is inefficient in energy transfer. Observation of the phosphoresence spectrum of 4 and 5 in conjunction with a quantitative study of quenching and sensitization could settle this point. Investigation of the nature of the n → π* absorptions of 4 and 5 would also be of interest for a further understanding of these reactions.

Experimental Section[44,46]

2,3-Dihydro-5,6-dimethylpyrazine (4) was prepared by the method of Ishiguru and Matsumurra[47] bp 60–62° (18 mm) (lit.[47] 60–63° (18 mm)), n^{22}D 1.4826. The nmr spectrum consists of singlets at δ 3.28 (relative area 2), CH_2, and 2.10 (relative area 3), C-CH_3. The infrared and ultraviolet (λ_{max} 230 (ε 1740) and 337 mμ (ε 200)) are consistent with the established structure. 2,3-Dihydro-5,6-dimethylpyrazine is unstable to standing in air but is stable for several weeks if stored under nitrogen in the refrigerator.

Anal. Calcd for $C_6H_{12}N_2$: C, 65.42; H, 9.15; N, 25.43. Found C, 65.24; H, 9.07; N, 25.35.

2,3-Dihydro-5,6-diphenylpyrazine (5) was prepared according to Amundsen,[48] mp 162.5–163.5° (lit.[48] 161.5–162.5°). The nmr spectrum consists of an unsymmetrical multiplet centered at δ 7.3 (relative area 5), Ar-*H*, and a singlet at δ 3.7 (relative area 2), C*H*₂. The infrared and ultraviolet (λ_{max} 224 (ε 15,100), 288 (ε 5740), and 363.5 mμ (ε 440)) are consistent with the established structure. The mass spectrum showed major fragment peaks at m/e 131 and 103 corresponding to the loss of the elements of benzonitrile. No fluorescence of 2,3-dihydro-5,6-diphenylpyrazine was observed in methanol solution at room temperature under conditions such that a fluorescence quantum yield of 0.01 would have been detected. No phosphorescence of 5 in a 1:1 ethanol-glycerol glass at 77°K was observed.

trans-**2,3-Diphenyl-5,6,7,8,9,10-hexahydroquinoxaline (10).** To a solution of 2.9 g of benzil in 10 ml of absolute ethanol was added 2.18 g of *trans*-1,2-diaminocyclohexane-CO_2 adduct in 5 ml of absolute ethanol. The solution was heated at reflux on a steam bath under a positive pressure of nitrogen for 45 min. After 5–10 min, yellow plates precipitated. The reaction mixture was cooled in ice and filtered, and the solid collected was washed with portions of cold 95% ethanol. The product consisted of 3.82 g of yellow plates, mp 170.5–173° (lit.[49] 167–168°). The product was sublimed at 110° (0.1 mm) to give yellow needles, mp 171–172°. The nmr spectrum consisted of a multiplet at δ 7.24 (relative area 10), Ar*H*, a series of multiplets at 1.20–3.00 (relative area 10), C-*H*. The infrared, mass (molecular ion at m/e 288), and ultraviolet spectra (λ_{max} 223 (ε 15,000), 260 (ε 5100), 290 (ε 5300), and 369 mμ (ε 450)) were consistent with the expected values.

Anal. Calcd for $C_{20}H_{20}N_2$: C, 83.29; H, 6.99; N, 9.71; mol wt, 288. Found: C, 83.26; H, 7.04; N, 9.33; mol wt, 280 (benzene).

cis-**2,3-Dihydro-2,3-dimethyl-5,6-diphenylpyrazine (14).** *meso*-2,3-Diaminobutane was isolated from commercial 2,3-diaminobutane by the method of Dickey, Fickett, and Lucas.[50] A solu-

(39) A number of analogies for such a process may be found in the photochemistry of 1,3,5-hexatrienes. For examples, see ref 7b; R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 2806 (1961); G. J. Fonken, *Tetrahedron Letters*, 549 (1962).

(40) Application of the Woodward–Hoffmann concepts to the two n → π* states presumed for these purposes to be involved in the interconversions of a 2,3-disubstituted dihydropyrazine and its isomeric enediimine reveals that concerted ring opening and ring closure are allowed both as conrotatory and disrotatory processes: R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965); H. Longuet-Higgens and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965). In this case, unlike that of 1,3 cyclohexadienes, the symmetry rules allow a photolytic interconversion of *cis*- and *trans*-2,3-dihydro-2,3-disubstituted pyrazines by concerted processes. Experimental demonstration of this would assume both transitions occur, the enediimine to be photostable, and photochemical ring closure of the presumed enediimine intermediate. The latter reaction was not detectable with 16. Consistent with these results, no racemization of optically active 14 or photochemical interconversion of *cis* and *trans* isomers of 14 was found in incomplete reactions.

(41) Quantitative studies were complicated by competitive absorptions.

(42) The conversion of 5 to 7 in the presence of *trans*-stilbene provides a marked contrast to the photoaddition of *o*-quinones to *trans*-stilbene *via* a triplet species.[3]

(43) G. S. Hammond and N. J. Turro, *Science*, **142**, 1541 (1963); G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962); H. E. Zimmerman and J. S. Swenton, *J. Am. Chem. Soc.*, **86**, 1436 (1964); G. W. Griffin and E. J. O'Connel, *ibid.*, **84**, 4148 (1962).

(45) G. Weber and B. Bablovzian, *J. Biol. Chem.*, **241**, 2558 (1966).

(46) The microanalyses were performed by Mr. Joseph Nemeth and associates.

(47) T. Ishiguru and M. Matsumurra, *Yakugaku Zasshi*, **78**, 229 (1958); *Chem. Abstr.*, **54**, 11862 (1958).

(48) L. Amundsen, *J. Chem. Educ.*, **16**, 567 (1939).

(49) A. Einhorn and B. Bull, *Ann.*, **295**, 209 (1897).

(50) F. Dickey, W. Fickett, and H. Lucas, *J. Am. Chem. Soc.*, **74**, 944 (1952).

tion containing 199 mg of *meso*-2,3-diaminobutane in benzene was added to a solution of 445 mg of benzil (94% of theoretical) in 5 ml of absolute ethanol. The solution was heated at reflux under a positive pressure of nitrogen for 2 hr. A total of 440 mg of fine, light yellow crystals precipitated on cooling and scratching the reaction solution. Second and third crops totaling 103 mg were obtained by concentrating the mother liquors.

The combined crude products were chromatographed on a column of 20 g of silica gel. Elution with 25% benzene-Skelly B gave unreacted benzil. Elution with 25% ether-benzene gave *cis*-2,3-dihydro-2,3-dimethyl-5,6-diphenylpyrazine (14). The solid was sublimed at 90–100° (0.15 mm) to give 400 mg of yellow needles, mp 96.5–98.5°. The nmr consisted of a multiplet at δ 7.38 (relative area 5), Ar*H*, a quartet at 3.92 (relative area 1, *J* = 6 cps), C*H*–CH₃, and a doublet at 1.26 (relative area, 3, *J* = 6 cps). The infrared and ultraviolet (λ_{max} 224 (ε 14,850), 290 (ε 5700), and 375 mμ (ε 350)) spectra were consistent with the assigned structure.

Anal. Calcd for $C_{18}H_{18}N_2$: C, 82.40; H, 6.92; N, 10.68; mol wt, 262. Found: C, 82.56; H, 6.96; N, 10.91; mol wt, 270.

A partially resolved mixture of *cis*- and *trans*-2,3-dihydro-2,3-dimethyl-5,6-diphenylpyrazines (15) was also prepared. Racemic 2,3-diaminobutane was resolved using *d*-tartaric acid following the method of Dickey, Fickett, and Lucas.[50] A tartrate salt of constant optical rotation of +0.90° was obtained and decomposed in strong aqueous sodium hydroxide. The amine was isolated by continuous extraction of the aqueous solution with benzene.

To a solution of 1.35 g of benzil (90% of theoretical) in 5 ml of absolute ethanol was added a benzene solution containing 625 mg of partially resolved *l*-2,3-diaminobutane by titration. The reaction and purification were carried out as above.

Sublimation gave light yellow needles, mp 88–94°. The sublimed crystals were ground with a mortar and pestle to ensure sample homogeneity. The nmr spectrum showed two different C–C*H₃* doublets at δ 1.24 and 1.48 and was consistent with a mixture of *cis*- and *trans*-2,3-dihydro-2,3-dimethyl-5,6-diphenylpyrazines containing about 26% *trans* isomer.

The optical rotation was determined using a solution of 219 mg of the dihydropyrazine. The mixture in 10 ml of 95% ethanol gave αD −0.63 ± 0.03°, [α]D −28.7 ± 4.75%.

2,3-Dihydro-5,6-diphenyl-2-methylpyrazine (15) was prepared by the method of Strache,[51] mp 116–118° (lit.[51] 111–112°). The nmr (multiplets at δ 7.28 (relative area 10), Ar*H*, 4.20–2.84 (relative area 3), –C*H*–CH₂–, and a doublet at 1.44 (relative area 3), C–C*H₃*), infrared, and ultraviolet spectra were consistent with the established structure.

d-2-Isobutyl-2,3-dihydro-5,6-diphenylpyrazine (16). To a solution of 1.84 g of benzil in 5 ml of absolute ethanol was added 1.07 g of L-1,2-diamino-4-methylpentane.[52] The mixture was heated at reflux under a positive pressure of nitrogen for 2.5 hr. After sufficient ethanol to clarify the solution was added, the solution was cooled with Dry Ice and precipitation occurred. A total of 1.84 g (73% yield) of light yellow crystals, mp 66–69°, was collected by filtration.

The crude product was chromatographed on silica gel. Elution with 25% ether-benzene gave a yellow oil which crystallized on scratching to light yellow needles, mp 68–70°. This solid was sublimed at 60° (0.12 mm) to give light yellow needles, mp 69–71°. The nmr spectrum consisted of a multiplet centered at δ 7.28 (relative area 10), Ar*H*, a multiplet centered at 4.00 (relative area 1), –NC*H*–, multiplets centered at 3.26 (relative area 2), NC*H*–, a series of multiplets at 1.30–2.20 (relative area 3), –C*H₂*CH–, and a doublet at 1.00 (relative area 6), –(C*H₃*)₂.

The infrared spectrum had strong absorptions at 2970, 1510, and 980 cm⁻¹. The ultraviolet spectrum (λ_{max} 224 (ε 15,450), 288 (ε 5800), and 369 mμ (ε 440)) and the mass spectrum were consistent with the structure assigned. The optical rotation was determined on a solution of 231 mg of sublimed material in 10 ml of 95% ethanol, αD +2.13 ± 0.07°, [α]D 91.90 ± 3.3%.

Anal. Calcd for $C_{20}H_{22}N_2$: C, 82.72; H, 7.64; N, 9.65; mol wt, 290. Found: C, 82.63; H, 7.57; N, 9.47; mol wt, 283 (benzene).

2,3-Diphenyl-5,5,6,6-tetramethylpyrazine (39). To a solution of 2.75 g of benzil in toluene was added 1.65 g of 2,3-diamino-2,3-dimethylbutane.[53] Anhydrous sodium sulfate and a trace of *p*-toluenesulfonic acid were added and the mixture was heated at reflux under a drying tube. After 10-days heating at reflux the solvent was removed under reduced pressure and the residue was

chromatographed on a column of 40 g of Florisil. Elution with 50% benzene-Skelly B gave fractions which contained both benzil (1660-cm⁻¹ band) and 2,3-diphenyl-5,5,6,6-tetramethylpyrazine (975-cm⁻¹ band) by infrared analysis. These fractions were recrystallized from ice-cold acetone solution by the addition of water. This solid was sublimed to give 1.1 g of light yellow needles, mp 92–110° (29% yield). The nmr spectrum consisted of two resonances at δ 7.40 (relative area 5), Ar*H*, and 1.42 (relative area 6), CC*H₃*. The infrared spectrum showed strong absorptions at 2880, 1545, 1450, 1160, and 975 cm⁻¹. The ultraviolet spectrum (λ_{max} 223 (ε 12,100), 290 (ε 4150), and 365 mμ (ε 420)) was also consistent with the assigned structure.

Anal. Calcd for $C_{20}H_{22}N_2$: C, 82.72; H, 7.64; N, 9.65; mol wt, 290. Found: C, 82.46; H, 7.61; N, 9.49; mol wt, 285 (benzene).

1,4,5-Trimethylimidazole (6). Crude 4,5-dimethylimidazole[54] (3.0 g) was methylated with 5.0 g of dimethyl sulfate. The product was distilled under reduced pressure to give a colorless oil which became semicrystalline during the distillation, bp 107–109° (18 mm) (lit.[55] 117° (20 mm)). The nmr spectrum consisted of singlets at δ 7.70 (relative area 1), N=C*H*N, 3.62 (relative area 3), N–C*H₃*, and 2.38 and 2.29 (relative area 3 each), C–C*H₃*. The nmr resonances of the methyl groups in benzene solution appear at δ 2.80, 2.20, and 1.72, and these compare relatively well with reported values of δ 2.63, 2.21, and 1.65.[56a] The infrared and mass spectrum were consistent with the established structure,[56] with the latter showing a large molecular ion − 1 peak. The picrate, mp 219–220° (lit.[56b] mp 218–219°), and methiodide, mp 158–160° (lit.[56b] mp 158°), derivatives were prepared.

4,5-Diphenylimidazole was prepared by the method of Davidson, Weiss, and Jelling.[57] The crude product was recrystallized from ethanol-water to give colorless needles, mp 230–231° (lit. 249°,[57] 232–233°[58]).

4,5-Diphenyl-1-methylimidazole (5) was prepared by the method of Simonev and Garnovskii,[59] mp 157.5–158° (lit.[59] 158°). The nmr spectrum consisted of a multiplet at *ca.* δ 7.35 (relative area 11), Ar*H* and N=C*H*N, and a singlet at 3.37 (relative area 3), N–C*H₃*. The infrared, ultraviolet, and mass spectra were consistent with the established structure.

1,2-Dimethyl-4,5-diphenylimidazole (18). To 2 g of solid 4,5-diphenyl-2-methylimidazole[57] was added 0.9 ml of dimethyl sulfate (10% excess). The mixture was heated on a steam bath for 24 hr and cooled. A solution of methanol-ammonium hydroxide was added before the solution was poured into sodium hydroxide solution. The aqueous solution was extracted with chloroform, and the chloroform extracts were combined, washed with water, and dried over anhydrous sodium sulfate. After filtration, the solvent was removed under reduced pressure. The residue was recrystallized from ether to give colorless rectangles, mp 121–24°. The nmr spectrum consisted of a multiplet at δ 7.30 (relative area 10), Ar*H*, a singlet at 3.30 (relative area 3), N–C*H₃*, and a singlet at 2.44 (relative area 3), C–C*H₃*. The infrared spectrum had strong bands at 2950, 1605, and 1400 cm⁻¹.

Anal. Calcd for $C_{17}H_{16}N_2$: C, 82.22; H, 6.49; N, 11.28. Found: C, 82.16; H, 6.31; N, 11.08.

2,2-Dimethyl-4,5-diphenylisoimidazole (41) was prepared according to the method of Weiss,[60] mp 78–79° (lit.[60] 79–80°). The nmr (δ 7.46 (relative area 10), Ar*H*, singlet at 1.64 (relative area 5.7), CC*H₃*), infrared, and mass spectra were consistent with the established structure.

General Procedure for Photolysis. The solutions were photolyzed in a Pyrex container into which the high-pressure mercury vapor lamp and filter in a quartz immersion well or the low-pressure mercury vapor lamp without a filter had been previously placed. The solution was deaerated by a stream of nitrogen before and during photolysis. The nitrogen was purified by passage through two traps of Fieser solution,[61] a lead acetate solution trap, and a drying tower of mixed Molecular Sieve and indicating Drierite. The photolyses were terminated when starting material could not be detected by infrared or ultraviolet spectroscopy.

(51) H. Strache, *Ber.*, **21**, 2358 (1888).
(52) S. Schnell and P. Karrer, *Helv. Chim. Acta*, **38**, 2036 (1955).
(53) R. Syre, *J. Am. Chem. Soc.*, **77**, 6689 (1955).

(54) H. Brederick and G. Thielig, *Ber.*, **86**, 88 (1953).
(55) H. Jowett, *J. Chem. Soc.*, **87**, 405 (1905).
(56) (a) J. Imbach and R. Jacquier, *Compt. Rend.*, **257**, 2683 (1963); (b) R. Grindley and T. Pyman, *J. Chem. Soc.*, 3128 (1927).
(57) D. Davidson, M. Weiss, and M. Jelling, *J. Org. Chem.*, **2**, 319 (1937).
(58) I. Lamb and F. Pyman, *J. Chem. Soc.*, **125**, 706 (1924).
(59) A. Simonov and A. Garnovskii, *Zh. Obshch. Khim.*, **31**, 114 (1961).
(60) M. Weiss, *J. Am. Chem. Soc.*, **74**, 5193 (1952).
(61) L. Fieser, *ibid.*, **46**, 2639 (1924).

The crude photolysis mixtures were usually worked up by evaporation of the solvent at reduced pressure, followed by column chromatography on either Florisil (Floridian Co.) or silica gel (E. Merck AG, 0.05–0.20 mm). Unless otherwise noted, the column was eluted with solvents in the following order: 50% benzene–Skelly B, benzene, benzene–1% ether, benzene–2% ether, benzene–5% ether, benzene–10% ether, benzene–25% ether, benzene–50% ether, ether, and more polar solvents as needed. The Skelly B used for chromatography was predistilled; all other solvents used in the chromatographies were reagent grade.

Light Sources. The light sources used for photolysis were an Hanovia Type L 450-w high-pressure quartz mercury vapor immersion lamp and an Hanovia 23-w Type SC-2537 low-pressure Vycor mercury vapor immersion lamp. The Pyrex filter sleeve used to restrict the light absorbed by the sample transmits 1, 30, and 70% of the incident light at 280, 300, and 320 mμ.

Photolysis of 2,3-Dihydro-5,6-dimethylpyrazine (4). A solution of 1.27 g of 2,3-dihydro-5,6-dimethylpyrazine (4) in 420 ml of absolute ethanol was photolyzed using a Pyrex-filtered high-pressure lamp. The solvent was removed under reduced pressure and the residue distilled to give 902 mg (71% yield) of clear, colorless oil, bp 107–109° (18 mm), which crystallized on standing. The nmr in deuteriochloroform and benzene, the infrared and ultraviolet spectra, and the melting point of the picrate derivative were identcial with those of authentic 1,4,5-trimethylimidazole (6).

Photolysis of 2,3-Dihydro-5,6-diphenylpyrazine (5). A solution of 1.00 g of 2,3-dihydro-5,6-diphenylpyrazine (5) in 420 ml of absolute ethanol was photolyzed using a Pyrex-filtered high-pressure mercury vapor lamp. The yellowish solid obtained by evaporation of the solvent was chromatographed on a column of 40 g of Florisil. Elution with benzene–5% ether gave 746 mg (75% yield) of light tan crystals. Recrystallization of this solid from ether gave colorless rectangular crystals, mp 159–160°. This material was identical with authentic 4,5-diphenyl-1-methylimidazole (7) by nmr, infrared, ultraviolet, mass spectral, and mixture melting point criteria.

In a later photolysis of a solution of 1.14 g of 2,3-dihydro-5,6-diphenylpyrazine in 420 ml of absolute ethanol using a Pyrex-filtered high-pressure lamp the crude product was chromatographed on a column of 20 g of silica gel. Elution with 10% ether–benzene gave a crystalline fraction (244 mg) which was rechromatographed on a column of 20 g of silica gel. Elution with 25% ether–benzene gave 100 mg of crystalline material in the first fractions, and this was recrystallized from ether to give colorless rectangles, mp 89.5–91.5°. The compound was identified as 4,5-diphenyl-1-ethoxymethylimidazole (8). The nmr spectrum consisted of a singlet at δ 7.80 (relative area 1), N=CHN, a broad multiplet centered at 7.25 (relative area 10), ArH, a singlet at 5.08 (relative area 2), N-CH$_2$-O, a quartet at 3.44 (relative area 2, J = 7 cps), CH$_2$CH$_3$, and a triplet at 1.12 (relative area 3, J = 7 cps), CH$_2$CH$_3$. The infrared, ultraviolet, and mass spectra were also consistent with the structure assigned.

Anal. Calcd for C$_{17}$H$_{16}$N$_2$O: C, 77.67; H, 6.52; N, 10.07. Found: C, 77.58; H, 6.40; N, 9.90.

A solution of 76.7 mg of 4,5-diphenyl-1-ethoxymethylimidazole in several milliliters of concentrated HI was refluxed for 7 hr. The acid solution was diluted with distilled water and neutralized with concentrated ammonium hydroxide. The colorless precipitate collected by suction filtration was 44 mg (70% yield) of impure 4,5-diphenylimidazole, mp 205–220°. The crude product was recrystallized from ethanol–water to give colorless needles, mp 228–230°, undepressed upon mixture melting point with authentic 4,5-diphenylimidazole. The infrared and mass spectra of the cleavage product were identical with those of the authentic material.

The photolysis of 5 was carried out in Skelly B, benzene, and 95% ethanol and found to give 7 in yields of 67, 90, and 4%. In the latter case 8 (8%) and 9 (33%) were also obtained. Irradiation of 5 in ethanol for 6 hr using the low-pressure mercury resonance lamp gave 7 in 80% yield.

Approximate quantum yields for the disappearance of 5 and the combined appearance of 7 and 8 were determined to be 0.13 ± 0.03 in ethanol at 25° by ultraviolet analysis with a Pyrex-filtered high-pressure mercury resonance lamp in a thermostated rotating reactor[62] using the photoreduction of benzophenone as an actinometer.[63] The semiquantitative nature of this result should be

noted.[64] The ultraviolet spectra used for the determination of quantum yields did not show an isosbestic point.

Attempts were made to sensitize the photoreaction of 5 in ethanol with benzophenone, triphenylene, and *trans*-stilbene and to quench the reaction with naphthalene or by using piperylene as solvent. In all cases the reaction appeared to give the yield of 7 expected in the absence of sensitization or quenching.

Photolysis of 5 in Ethanol-*d*. About 250 ml of ethanol-*d* was prepared by the hydrolysis of diethyl sulfite with D$_2$O.[65] The ethanol-*d* was distilled, stored over anhydrous sodium carbonate, and redistilled. The pH of the sample was approximately that of absolute ethanol as determined with a Corning pH meter and glass microelectrodes. The deuterium incorporation was determined using the falling drop method.

Anal. Calcd for C$_2$H$_5$DO: 16.6 atom % excess deuterium. Found: 16.6 atom % excess deuterium.

A solution of 852 mg of 2,3-dihydro-5,6-diphenylpyrazine (5) in about 250 ml of ethanol-*d* was photolyzed using a Pyrex-filtered high-pressure lamp for 1.5 hr. After removal of the solvent the semisolid deep yellow residue was chromatographed on a column of 20 g of silica gel. Elution with 5% ether–benzene gave 215 mg of starting material 5. The mass spectrum at low ionizing voltage indicated no incorporation of deuterium. Elution with 25% ether–benzene gave 85 mg of colorless needles identified by nmr and infrared spectra as a slightly impure sample of 4,5-diphenyl-1-ethoxymethylimidazole (8). Elution with 50% ether–benzene gave 135 mg of colorless crystalline solid which was recrystallized from ether to give colorless rectangles, mp 156–159°. The nmr (multiplet at δ 7.28 (relative area 5), ArH, unresolved triplet at 3.42 (relative area 1), -CH$_2$-D) and infrared spectra were consistent with the expected product, 2-deuterio-4,5-diphenyl-1-methyl-*d*-imidazole (36). The sample of the recrystallized imidazole 36 was heated at reflux overnight in ethanol-*d* under a drying tube to ensure complete exchange of the labile imidazole ring proton[35] before mass spectral analysis. At low ionizing voltage the ratio of the molecular ion peaks of this material indicated 8.6% C$_{16}$H$_{13}$N$_2$D and 91.4% C$_{16}$H$_{12}$N$_2$D$_2$. Further elution of the chromatography column with ether gave an additional 103 mg of solid, which was seen by nmr spectroscopy to be composed of about 70% dideuterated imidazole 36. Elution with ethanol gave 204 mg of light yellow solid, mp 212–228°, identified by its nmr, infrared, and mass spectra as 4,5-diphenylimidazole (9). The formation of these products suggests the deuterioethanol contained a small amount of deuterium oxide.

In a control experiment it was shown that 3,4-diphenyl-1-methylimidazole (7) gave only 2-deuterio-4,5-diphenyl-1-methylimidazole on photolysis under these conditions.

Photolysis of *trans*-2,3-Diphenyl-5,6,7,8,9,10-hexahydroquinoxaline (10). A solution of 1.10 g of *trans*-2,3-diphenyl-5,6,7,8,9,10-hexahydroquinoxaline (10) in 420 ml of absolute ethanol was photolyzed for 7 hr using a Pyrex-filtered high-pressure lamp. The solvent was removed under reduced pressure and the residue was chromatographed on a column of 20 g of silica gel.

Elution with 1% ether–benzene gave 356 mg (32.5% recovery) of light yellow crystals, found to be unreacted 10.

Elution with 2% ether–benzene gave 460 mg (53% yield) of colorless solid which was purified by sublimation at 110° (0.15 mm) to give fine colorless needles, mp 121–123°. The nmr spectrum consisted of a multiplet at δ 7.28 (relative area 10), ArH, a multiplet at 5.12 (relative area 1), O–CH–N, a multiplet at 3.18 (relative area 4), CH$_2$CH$_3$ and -CH$_2$C(=)N, a series of multiplets at 1.20–2.50 (relative area 6), (-CH$_2$)$_3$-, and a triplet at 1.06 (relative area 3), CH$_2$CH$_3$. The infrared spectrum had strong bands at 2970, 1600, 1443, 1350, 1110, 1090, and 1065 cm^{-1}. The ultraviolet (λ_{max} 256 (ϵ 11,400) and 269 (sh) mμ (ϵ 10,200)) and mass spectra are in qualitative agreement with the structural assignment as 2,3-diphenyl-5-ethoxy-6,7,8,9-tetrahydro-5H-imidazo[1,2-*a*]azepine (12).

Anal. Calcd for C$_{22}$H$_{24}$N$_2$O: C, 79.48; H, 7.28; N, 8.43; mol wt, 332. Found: C, 79.32; H, 7.55; N, 8.56; mol wt, 332 (benzene).

Elution with 10% ether–benzene gave 70 mg (9% yield) of colorless solid. This material was purified by sublimation at 120–130° (0.15 mm) to give colorless crystals, mp 138–140°. The nmr spectrum consisted of a multiplet at δ 7.30 (relative area 10), ArH, a multiplet at 3.74 (relative area 2), CH$_2$–N–, a multiplet at 3.02 (relative area 2), -CH$_2$C(=)-, and a multiplet at 1.82 (relative

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(64) Reference 2, p 723 and Chapter 7.
(65) E. de Salas and C. Wilson, *J. Chem. Soc.*, 319 (1938).

area 6), (-C*H*₂)₃-. The infrared spectrum showed strong absorptions at 2910, 1600, and 1350 cm⁻¹. The ultraviolet and mass spectra were consistent with the assigned structure, 2,3-diphenyl-6,7,8,9-tetrahydro-5H-imidazo[1,2-*a*]azepine (**11**).

Anal. Calcd for C₂₀H₂₀N₂: C, 83.29; H, 6.99; N, 9.71; mol wt, 288. Found: C, 83.04; H, 6.96; N, 9.56; mol wt, 282 (benzene).

Irradiation of 1.06 g of **10** in 420 ml of cyclohexane for 5 hr under the same conditions followed by the same work-up gave 205 mg (19%) of a crystalline material in the benzene-2% ether fractions. This was sublimed to give colorless needles, mp 120-121°. The nuclear magnetic resonance consisted of a multiplet at δ 7.30 (relative area 10), Ar*H*, a doublet (with additional fine structure) at 6.24 (relative area 1, *J* = 10 cps), NC*H*=CH-, a multiplet at 5.24 (relative area 1), -C=C*H*CH₂, a multiplet at 3.10 (relative area 2), -C*H*₂C(=)-, and multiplets at 1.76-2.60 (relative area 4), -C*H*₂-C*H*₂. The infrared spectrum had strong absorptions at 2960, 1600, and 1410 cm⁻¹. The ultraviolet (λ 280 sh m*μ* (ε 12,900); end absorption 255-220 m*μ*) and mass spectra were consistent with the structure assigned as 2,3-diphenyl-8,9-dihydro-7H-imidazo[1,2-*a*]azepine (**13**).

Anal. Calcd for C₂₀H₁₈N₂: C, 83.88; H, 6.34; N, 9.78. Found: C, 83.58; H, 6.18; N, 9.42.

Elution with benzene-10% ether gave 90 mg of **11**. Elution with more polar solvents gave other unidentified products.

Catalytic hydrogenation of 76 mg of **13** in ethanol over 10% palladium on charcoal gave, after *ca.* 1 equiv uptake of hydrogen and chromatography, 20 mg of starting material and 31 mg of **11** identified by infrared, nmr, and melting point comparison.

Photolysis of *cis*-2,3-Dihydro-2,3-dimethyl-5,6-diphenylpyrazine (14). A solution of 917 mg of *cis*-2,3-dihydro-2,3-dimethyl-5,6-diphenylpyrazine (**14**) in 420 ml of absolute ethanol was photolyzed using a Pyrex-filtered high-pressure lamp for 10 min. The crude product was chromatographed on a column of 20 g of silica gel.

Elution with 1% ether-benzene gave 474 mg of *cis*-2,3-dihydro-2,3-dimethyl-5,6-diphenylpyrazine. No *trans*-dihydropyrazine was detected in the nmr spectrum.

Elution with 5% ether-benzene gave 239 mg (26%) of a crystalline solid purified by vacuum sublimation to give colorless crystals, mp 79-85°. The nmr spectrum consisted of a multiplet at δ 7.40 (relative area 10), Ar*H*, a quartet at 5.16, quartet (relative area 1, *J* = 7 cps), OC*H*-CH₃, two overlapping quartets at 3.30 (relative area 2, *J* = 7 cps), C*H*₂CH₃, a singlet at 2.66 (relative area 3), -C-C*H*₃, a doublet at 1.60 (relative area 3, *J* = 7 cps), -CHC*H*₃, and a triplet at 1.14 (relative area 3, *J* = 7 cps), CH₂C*H*₃. The infrared spectrum had strong absorptions at 2950, 1600, 1385, 1340, and 1125 cm⁻¹. The ultraviolet and mass spectra were consistent with the structure assigned as 4,5-diphenyl-1-(1-ethoxyethyl)-2-methylimidazole (**17**).

Anal. Calcd for C₂₀H₂₂N₂O: C, 78.40; H, 7.24; N, 9.14; mol wt, 305. Found: C, 78.14; H, 7.38; N, 9.14; mol wt, 319 (benzene).

Photolysis of the partially resolved *cis-trans* mixture of **14** ([α]D −28.7 ± 4.75%) for 9 min in ethanol gave **17** (25%) and **14** (57%). The recovered starting material contained 27% *trans* isomer by nmr and had optical activity of αD −0.68 ± 0.02°, [α]D −29.78° ± 3.0%.

A solution of 190 mg of **17** in 10 ml of concentrated hydriodic acid was heated at reflux for 2 days. After cooling the mixture was poured into water and neutralized with concentrated ammonium hydroxide. The precipitate was collected by suction filtration to give 147 mg (97% yield) of 4,5-diphenyl-2-methylimidazole, mp 238-240°, identified by nmr, infrared, and melting point comparison with an authentic sample.

Photolysis of 2,3-Dihydro-5,6-diphenyl-2-methylpyrazine (15). A solution of 1.5 g of 2,3-dihydro-5,6-diphenyl-2-methylpyrazine (**15**) in a 420 ml of absolute ethanol was photolyzed using a Pyrex-filtered high-pressure lamp for 8 hr. The crude product was chromatographed on a column of 20 g of silica gel.

Elution with 1% ether-benzene gave 232 mg (15% recovery) of **15**.

Elution with 5% ether-benzene gave 272 mg of oil. This oil was sublimed at 70-90° (0.15 mm) to give a colorless viscous oil. The nmr spectrum showed this to be a mixture of 4,5-diphenyl-1-(1-ethoxyethyl)imidazole (**20**) (singlet at δ 7.84, NC*H*=N, multiplets at 7.30, Ar*H*, 5.12, O-C*H*CH₃, and 3.30, OC*H*₂CH₃, doublet at 1.58, -C*H*CH₃, and triplet at 1.08, CH₂C*H*₃) and 4,5-diphenyl-1-ethoxymethyl-2-methylimidazole (**19**) (multiplet at δ 7.30, Ar*H*, singlet at 5.00, N-C*H*₂-O-, multiplet at 3.30, O-C*H*₂CH₃, singlet at 2.54, C*H*₃, and triplet at 1.08, CH₂C*H*₃) in a ratio of 4:3. The infrared and mass spectra were consistent with the assigned mixture.

Anal. Calcd for C₁₉H₂₀N₂O: C, 78.05; H, 6.90; N, 9.58. Found: C, 77.70; H, 7.11; N, 9.39.

Elution with 10% ether-benzene gave 125 mg of oil. The nmr spectrum of this oil was consistent with a mixture of 4,5-diphenyl-1-ethoxymethyl-2-methylimidazole (**19**) and 1,2-dimethyl-4,5-diphenylimidazole (**18**) in a ratio of 2:3. The infrared spectrum was consistent with this mixture.

Elution with 25% ether-benzene gave 627 mg (42% yield) of crystalline material identified as 1,2-dimethyl-4,5-diphenylimidazole (**18**) by comparison of the nmr and infrared spectra with those of authentic material. Sublimation of the imidazole gave colorless needles, mp 125-127°; a mixture melting point with authentic material was undepressed.

Photolysis of *d*-2-Isobutyl-2,3-dihydro-5,6-diphenylpyrazine (16). A solution of 931 mg of *d*-2-isobutyl-2,3-dihydro-5,6-diphenylpyrazine ([α]D 91.9° ± 3.3%) in 420 ml of absolute ethanol was photolyzed using a Pyrex-filtered high-pressure lamp for 10 min. The crude product was chromatographed on a column of 20 g of silica gel.

Elution with 1% ether-benzene gave 508 mg of light yellow solid purified by sublimation to give 446 mg (50% recovery) of **16**, mp 66.5-69.5°. The nmr and infrared spectra of the sublimed solid were identical with those of starting material. The optical rotation of this material determined using a solution of 228.4 mg of sublimed material in 10 ml of 95% ethanol was αD +2.11 ± 0.07°, [α]D +92.2° ± 3.3%.

Elution with 2% ether-benzene gave 30 mg of an oil whose infrared spectrum suggested an ethoxyimidazole. The nmr spectrum consisted of a multiplet at δ 7.30, Ar*H*, singlet at 5.04, NC*H*₂-O, quartet at 3.28, -C*H*₂CH₃, multiplet at 2.70, C*H*₂-CH, multiplet at 2.30, CH₂C*H*(CH₃)₂, doublet and triplet at 1.10, CH(C*H*₃)₂ and CH₂C*H*₃, and is consistent with the structure assigned as 2-isobutyl-4,5-diphenyl-1-ethoxymethylimidazole (**22**).

Elution with 5% ether-benzene gave 194 mg of crystalline solid. The nmr (multiplet at δ 7.28 (relative area 10), Ar*H*, singlet at 3.30 (relative area 3), NC*H*₃, multiplet at 2.68 (relative area 2), C*H*₂-CH, multiplet at 2.18 (relative area 1), -C*H*₂CH(CH₃)₂, and doublet at 1.08 (relative area 6), -CH(C*H*₃)₂) spectrum was consistent with 2-isobutyl-4,5-diphenyl-1-methylimidazole (**21**). The imidazole was purified by sublimation at 100° (0.12 mm) to give fine colorless needles, mp 104-107°. The mass, infrared (KBr disk strong absorptions at 2980, 1600, 770, and 695 cm⁻¹), and ultraviolet spectra were consistent with the assigned structure.

Anal. Calcd for C₂₀H₂₂N₂: C, 82.72; H, 7.64; N, 9.65. Found: C, 82.57; H, 7.54; N, 9.49.

Elution with 10% ether-benzene gave 60 mg of partially crystalline material which was composed of 30-40% of **21**. The remainder of the material was assigned the structure 4,5-diphenyl-1-(1-ethoxy-4-methylbutyl)imidazole (**23**) discussed below.

Further elution with 10% ether-benzene gave 93 mg of an oil which was apparently an ethoxyimidazole. The nmr spectrum (singlet at δ 7.78 (relative area 1), NC*H*N, multiplet at 7.28 (relative area 10), Ar*H*, multiplet at 4.98 (relative area 1), O-C*H*(N)-CH₂-, quartet at 3.30 (relative area 2), O-C*H*₂CH₃, multiplet at 2.68 (relative area 1), CH-C*H*(CH₃)₂, multiplet at 1.78 (relative area 2), CHC*H*₂CH, doublet at 1.08, (relative area 6), CH(C*H*₃)₂, triplet at 0.80 (relative area 3), CH₂C*H*₃) was consistent with an impure sample of 4,5-diphenyl-1-(1-ethoxy-4-methylbutyl)imidazole (**23**). Attempts to obtain analytical samples of **22** and **23** were not successful.

Photolysis of *d*-2-Isobutyl-2,3-dihydro-5,6-diphenylpyrazine (16) in Cyclohexane. A solution of 903 mg of sublimed *d*-2-isobutyl-2,3-dihydro-5,6-diphenylpyrazine (**16**) in 420 ml of cyclohexane (Fisher Spectral Grade) was photolyzed using a Pyrex-filtered high-pressure lamp for 10 min. The crude product was chromatographed on a column of 22 g of silica gel.

Elution with benzene gave 397 mg (40% recovery) of light yellow crystals sublimed to give 336 mg of **16**, mp 68.5-70.5°. The infrared spectrum was identical with that of the starting dihydropyrazine **16**. The optical rotation was determined using a 10-ml solution of 228.3 mg of the sublimed solid in 95% ethanol, αD +2.08 ± 0.08°, [α]D +91.2° ± 3.8%.

Elution with 1% ether-benzene gave 22 mg of yellow oil which was identified as slightly impure **16** from its infrared spectrum.

Elution with 2% ether-benzene gave 107 mg of off-white solid. The infrared and nmr spectra were identical with those of 2-isobutyl-4,5-diphenyl-1-methylimidazole (**21**).

Further elution with 5% ether-benzene gave 218 mg of solid, mp 230-270° dec. Although the compound was only slightly soluble in all common organic solvents, it was found that it could be re-

Table II. Partial Mass Spectrum of
1,2-Di(2-isobutyl-4,5-diphenylimidazoyl)ethane (24) at 70 ev

m/e	% of largest peak	m/e	% of largest peak	Metastable peaks and transition assignments m/e	Transition
579	44.7	269	20.8	550	578 → 563
578	100.0	261	49.0	505–506	563 → 535
523	20.4	260	51.2	495–496	578 → 535
304	26.0	259	83.0	158.5	578 → 303
303	81.0	247	23.4		
302	39.5	246	38.2		
301	20.4	245	37.4		
289	33.6	244	24.6		
288	20.0	234	76.7		
287	24.2	233	81.0		
276	22.9	232	34.0		

Table III. Partial Mass Spectrum of
2,2-Dimethyl-4,5-diphenyl-3-imidazoline at 13 ev

m/e	% of largest peak
250	2.8
248	3.1
235	4.7
148	12.7
147	100.0
145	10.0

crystallized from acetone to give colorless rectangles, mp 269–271°. The nmr (multiplet at δ 7.26, ArH, singlet at 3.78, N–CH_2–, multiplets at 1.80–2.30, CHCH_2, doublet at 0.90, CH(CH_3)$_2$), infrared (KBr disk, strong absorptions at 2970, 1600, 760, and 690 cm^{-1}), and ultraviolet (λ_{max} 257.5 mμ (ε 23,400), λ shoulder 268 mμ (ε 21,100)) spectra were consistent with a 1-substituted 4,5-diphenylimidazole dimer, assigned the structure 1,2-di(2-isobutyl-4,5-diphenylimidazoyl)ethane (24). The mass spectrum (Table II) at 70 ev was consistent with the structure assigned.

Anal. Calcd for C$_{42}$H$_{42}$N$_4$: C, 83.06; H, 7.37; N, 9.68; mol wt, 578. Found: C, 82.93; H, 7.31; N, 9.81; mol wt, 523 (chloroform).

Photolysis of 2,3-Diphenyl-5,5,6,6-tetramethylpyrazine (39). A solution of 915 mg of 2,3-diphenyl-5,5,6,6-tetramethylpyrazine (39) in 420 ml of absolute ethanol was photolyzed using a Pyrex-filtered high-pressure lamp for 2.5 hr. The residue remaining after solvent evaporation was chromatographed on 15 g of silica gel.

Elution with 2% ether–benzene gave 71 mg (9% recovery) of 39. Elution with 5% ether–benzene gave 474 mg (60% yield) of crystalline solid which was recrystallized from Skelly B and sublimed at 80° (0.15 mm) to give colorless needles, mp 86.5–88.5°. The nmr (multiplet at δ 7.40 (relative area 10), ArH, singlet at 5.48 (relative area 1), CH, broad singlet (removed by shaking with D$_2$O) at 3.14 (relative area 1), NH, singlet at 1.62 (relative area 3), CH_3, and singlet at 1.48 (relative area 3), CH_3), infrared (strong absorptions at 2980, 1635, 1500, and 1450 cm^{-1}), and ultraviolet (λ_{max} 245 mμ (ε 12,500)) spectra of the photoproduct are consistent with the assigned structure, 2,2-dimethyl-4,5-diphenyl-3-imidazoline

(40). The mass spectrum (Table III) was consistent with the assigned imidazoline structure.

Anal. Calcd for C$_{17}$H$_{18}$N$_2$: C, 81.56; H, 7.25; N, 11.19; mol wt, 250. Found: C, 81.70; H, 7.38; N, 11.06; mol wt, 271.

The presence of *ca.* 9% 2,2-dimethyl-4,5-diphenylisoimidazole was shown by nmr analysis of the crude reaction mixture.

Dehydrogenation of 2,2-Dimethyl-4,5-diphenyl-3-imidazoline (40). A sample of 120 mg of purified 2,2-dimethyl-4,5-diphenyl-3-imidazoline was heated with an equimolar quantity of elemental sulfur for 3 hr at 95° and 1 hr at 125°.[66] The sample was dissolved in ether, the unreacted sulfur was removed by filtration, and the solvent was removed under reduced pressure to leave 100 mg (83% yield) of pinkish crystals. The nmr, infrared, and ultraviolet spectra were identical with those of 2,2-dimethyl-4,5-diphenylisoimidazole (41). The compound was sublimed to give colorless needles, mp 78–79.5° (lit.[62] 78–79°). A mixture melting point with authentic 41 was undepressed.

Acid Hydrolysis of 2,2-Dimethyl-4,5-diphenyl-3-imidazoline (40). A sample of 220 mg of 2,2-dimethyl-4,5-diphenyl-3-imidazoline was hydrolyzed by heating for 1 hr in a few milliliters of 2 N hydrochloric acid. The solution was neutralized with sodium carbonate and the impure desylamine was collected by filtration; mp 85–90° (lit.[66] 109°).

A sample of the hydrolysis product was dissolved in warm dilute hydrochloric acid and aqueous picric acid was added. The precipitate was recrystallized from water to give yellow needles, mp 185–186° dec. A mixture melting point with authentic desylamine picrate was undepressed.[67] The infrared spectrum of this picrate was identical with that of the authentic sample.

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Thermal Reactions of Azidoformates

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Abstract: Kinetic studies have shown that azidoformates decompose thermally in a variety of solvents in a clean first-order reaction, the rate-determining step being evolution of nitrogen and formation of a nitrene. The nitrene reacts with saturated hydrocarbons by insertion into a C–H bond and by abstraction of two hydrogen atoms from adjacent carbons. The insertion reaction is highly selective, the primary:secondary:tertiary reactivity being in the ratio of 1:10:32. The mechanisms of these reactions are discussed.

I n a search for new reactions of saturated hydrocarbons, our attention was focused on the reactions of several of Curtius's "starre" or nonrearranging azides: azidoformates, sulfonyl azides, and aryl azides.[1] It was felt that, if these compounds decompose by loss of nitrogen and formation of an electron-deficient nitrene

species, the nitrene might insert into a carbon–hydrogen bond, in analogy to the well-known carbene reaction. If the reaction followed this course, monofunctional compounds could be used to introduce polar groups into saturated hydrocarbon polymers, such as polyethylene and polypropylene, while difunctional derivatives could be used as cross-linking agents for these polymers as

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