

1.4 g (93%) of the remaining crystalline product was shown to be the mixture given in Table IX. Recrystallization (EtOH-hexane) gave 1.3 g (87%) of the product, mp 52–54°.

1-(2-Phenylethylsulfonyl)-2-(ethylenimino)propene.—To 1.1 g (0.0043 mol) of a mixture of 36% *cis*- and 64% *trans*-1-(2-phenylethylsulfonyl)-2-(ethylenimino)propene in 50 ml of THF was added 6.0 g (0.11 mol) of KOH. After stirring, filtration, and concentration, the mixture (1.0 g, 91%) given in Table IX was present. Recrystallization (EtOH-hexane) gave 0.80 g (73%) of product, mp 60–61°.

Infrared Data.¹⁶—The 3-propynyl sulfides exhibit the characteristic strong carbon-hydrogen stretch at 3300 cm⁻¹ and a very weak carbon-carbon triple bond stretch in the 2100–2200-cm⁻¹ region. The corresponding 3-propynyl sulfones and sulfoxides show in addition to the acetylenes carbon-hydrogen stretch and the carbon-carbon triple bond stretch, the characteristic strong sulfone absorption in the 1300–1350- and 1120–1150-cm⁻¹ regions and the strong sulfoxide absorption in the 1020–1060-cm⁻¹ region, respectively. The 1-propynyl sulfides exhibit a weak carbon-carbon triple bond stretch at 2180 cm⁻¹. The corresponding sulfones and sulfoxides, however, show a very strong band at 2180–2200 cm⁻¹. The ethylsulfonylpropadiene and ethylsulfinylpropadiene exhibit a strong carbon-carbon double-bond stretch in the 1940–1980-cm⁻¹ region which appears as a singlet. As previously published⁵ the *p*-tolylsulfonylpropadiene shows a strong doublet at 1960 and 1920 cm⁻¹. The conjugated ethylenimine adducts exhibit strong olefinic absorption in the 1560–1640-cm⁻¹ region in addition to the characteristic sulfone and sulfoxide bands which are shifted slightly lower. The non-conjugated ethylenimine adducts exhibit similar absorptions

(16) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1962.

as the conjugated adducts with the olefinic band shifted ~50 cm⁻¹ higher in the nonconjugated adduct from that in the conjugated.

Registry No.—1, Z = SOEt, 25557-97-5; 1, Z = SO₂Et, 25557-98-6; 1, Z = SO₂C₆H₄CH₃-*p*, 25557-99-7; 2, Z = SOEt, 25558-40-1; 2, Z = SO₂Et, 13894-33-2; 2, Z = SO₂C₆H₄CH₃-*p*, 25558-42-3; 2, Z = SO₂CH₂-C₆H₅, 25558-43-4; 2, Z = SO₂CH₂CH₂C₆H₅, 25558-44-5; 3, Z = SOEt, 25558-45-6; 3, Z = SO₂Et, 13894-50-3; 3, Z = SO₂C₆H₄CH₃-*p*, 25558-47-8; 3, Z = SO₂-CH₂C₆H₅, 25558-48-9; 3, Z = SO₂CH₂CH₂C₆H₅, 25558-49-0; HC≡CCH₂SR, R = CH₂CH₂C₆H₅, 25558-00-3; CH₃C≡CSR, R = CH₂C₆H₅, 22582-35-0; CH₃C≡CSR, R = CH₂CH₂C₆H₅, 25558-02-5; 1-benzylsulfonylpropyne, 25558-03-6; 1-(2-phenylethylsulfonyl)propyne, 25558-04-7; 3-ethylsulfinylpropyne, 25558-05-8; 1-ethylsulfinylpropyne, 25558-06-9; ethylsulfinylpropadiene, 25558-07-0; *cis*-1-ethylsulfonyl-2-(ethylenimino)-1-butene, 25558-50-3; *trans*-1-ethylsulfonyl-2-(ethylenimino)-1-butene, 25558-51-4.

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Reductive Dimerization of Difunctional Aryl Imines on Photolysis

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Irradiations of aryl imines which have a nitrile, amide, double bond, or hydroxyl group suitably positioned for interaction with the imine give the *meso*- and *dl*-1,2-diamines resulting from reductive dimerization. Nonconjugated diimines give polymeric products. In the case of 2-cyanoethylamine-*N*-benzylidene, the mechanism involves initial formation of α -hydroxy radicals by transfer of a hydrogen atom from the alcoholic solvent to the benzaldehyde sensitizer, sequentially followed by production of α -amino radicals by hydrogen transfer from the α -hydroxy radical to the imine and dimerization of the α -amino radicals. One anil and three imidates were found to be unreactive under the specified photolysis conditions.

Recent studies of the photochemistry of imines suggest that many of the reported reactions actually do not involve a photoexcited state of the imine. Aryl imines have been shown to undergo reduction^{1,2} and reductive dimerization³ on photolysis *via* an α -amino radical formed by hydrogen atom transfer to the imine from an α -hydroxy radical initially formed by abstraction of a hydrogen atom from the solvent by the sensitizer. Padwa, Bergmark, and Pashayan have noted the potential generality of this type of reaction for imines in the presence of added or adventitious sensitizers.³ However, intramolecular reactions not usually explicable in terms of an α -amino radical are observed in some imine photolyses.^{4,5}

We have investigated the photochemistry of some acyclic imines which have a second functional group suitably situated for intramolecular reaction with the imine. Although the photochemistry of analogous olefins and ketones suggests that intramolecular reaction might be expected,⁶ only reductive dimerization involving conversion of the imine to a substituted 1,2-diamine is observed.

(1) W. F. Smith and B. W. Rossiter, *J. Amer. Chem. Soc.*, **89**, 717 (1967).

(2) M. Fischer, *Chem. Ber.*, **100**, 3599 (1967).

(3) A. Padwa, W. Bergmark, and D. Pashayan, *J. Amer. Chem. Soc.*, **91**, 2653 (1969), and references cited therein.

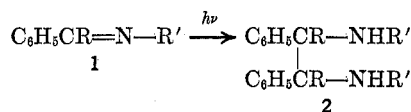
(4) (a) P. Beak and J. L. Miesel, *ibid.*, **89**, 2375 (1967); (b) B. Singh and E. F. Ullman, *ibid.*, **90**, 6911 (1969); (c) J. L. Derocque, W. T. Theuer, and J. A. Moore, *J. Org. Chem.*, **33**, 4381 (1968); (d) G. M. Badger, C. P. Joshua, and G. E. Lewis, *Tetrahedron Lett.*, 3711 (1964); (e) F. B. Mallory and C. S. Wood, *ibid.*, 2643 (1965); (f) A. Padwa, S. Clough, and E. Glazer, *J. Amer. Chem. Soc.*, **92**, 1778 (1970); (g) W. M. Moore and C. Baylor, Jr., *ibid.*, **91**, 7170 (1969); (h) M. Green and G. Tollin, *Photochem. Photobiol.*, **7**,

129, 145 (1968), and references cited therein; (i) K. H. Grellmann and E. Tauer, *Tetrahedron Lett.*, 1901 (1967); (j) R. W. Binkley, *J. Org. Chem.*, **34**, 2072 (1969); (k) J. Rennert and J. Wiesenfeld, *Photochem. Photobiol.*, **5**, 337 (1966); (l) E. C. Taylor, B. Furth, and M. Pfau, *J. Amer. Chem. Soc.*, **87**, 1400 (1965); (m) W. F. Richey and R. S. Becker, *J. Chem. Phys.*, **49**, 2092 (1968), and references cited therein; (n) M. P. Cava and R. H. Schlesinger, *Tetrahedron Lett.*, 2109 (1964).

(5) Exceptions to intramolecularity include photochemical cycloadditions [F. P. Woerner, H. Reimlinger, and D. R. Arnold, *Angew. Chem., Int. Ed. Engl.*, **7**, 130 (1968); L. A. Singer and P. D. Bartlett, *Tetrahedron Lett.*, 1887 (1964), and subsequent work; S. Searles, Jr., and R. A. Clasen, *ibid.*, 1627 (1965); J. C. Sheehan and I. Lengyel, *J. Org. Chem.*, **28**, 3252 (1963)] and possibly reactions which involved the direct formation of radicals [R. W. Binkley, *ibid.*, **34**, 931 (1969); J. H. Boyer and P. A. J. Frints, *Tetrahedron Lett.*, 3211 (1968)].

(6) (a) R. Srinivasan, *J. Amer. Chem. Soc.*, **82**, 775 (1960); (b) N. C. Yang, M. Nussim, and D. R. Coulson, *Tetrahedron Lett.*, 1525 (1965); (c) J. Meinwald and R. A. Chapman, *J. Amer. Chem. Soc.*, **90**, 3218 (1968); (d) R. R. Sauers and J. A. Whittle, *J. Org. Chem.*, **34**, 3579 (1969).

On photolysis with light from a high-pressure mercury lamp passed through a Pyrex filter, degassed ethanol solutions of the imines **1a-f** give a 50–70% yield of the 1,2-diamines **2a-f** expected for reductive dimerization. For **2a** and **2d**, only *meso*-diamines are



- a, R = H, R' = (CH₂)₂CN
 b, R = H, R' = (CH₂)₂CH=CH₂
 c, R = H, R' = (CH₂)₂NHCOCH₃
 d, R = H, R' = (CH₂)₂NHCOCH₂C₆H₅
 e, R = H, R' = (CH₂)CH(OH)C₆H₅
 f, R = CH₃, R' = (CH₂)₂CN

isolated but comparable amounts of *dl* and *meso* compounds are obtained for **2b** and **2c**. For **2e** and **2f**, stereochemistry is not assigned; the instability of **2e** precluded preparation of an analytical sample.

The products are identified by a combination of spectral and chemical methods. In addition to the ir, nmr, and uv spectra expected for **2a-f**, mass spectrometry establishes the molecular weight and shows the major fragmentation to be the expected α cleavage.⁷ Authentic *meso*-diamine **2a** was synthesized by reaction of *meso*-1,2-diamino-1,2-diphenylethane with acrylonitrile and is identical with the photoproduct. Lithium aluminum hydride reduction of **2a** gives the same tetraamine as does hydrolysis of *meso* **2c** and, establishing the stereochemistry of the latter, aluminum amalgam reduction of **1a** and **1d** also gives the *meso*-diamines **2a** and **2d**.^{8,8}

On the basis of previous work,¹⁻³ the pathway for conversion of **1** to **2** could be anticipated to involve hydrogen transfer from an α -hydroxy radical, formed by abstraction of hydrogen from the solvent by a sensitizer, to the imine followed by dimerization of the relatively stable α -amino radicals. The sensitizer in the photolyses of **2a-e** would be benzaldehyde, either present in trace amounts as in the imine or formed during the irradiation. The contrast of the high sensitizer efficiency of *m*-methoxyacetophenone, which does not abstract hydrogen readily, has been used as a test for "chemical sensitization" by Monroe and Wiener.⁹ Consistent with the expected mechanism, the conversion of **1a** to **2a** is efficiently sensitized by benzaldehyde but not by *m*-methoxyacetophenone (Table I). An attempt to intercept the α -hydroxy radicals with 2-mercaptomesitylene¹⁰ and thus increase the probability of observing photoreactions of the imine **1a** was unsuccessful. In fact, retardation of the reductive dimerization, as expected if α -hydroxy radicals are involved in the reaction, was observed (Table I).

Photolyses of ethanol solutions of ethylenediamine-*N,N'*-dibenzylidene [**1**, R = (CH₂)₂N=CHC₆H₅] and propylenediamine-*N,N'*-dibenzylidene [**1**, R = (CH₂)₃N=CHC₆H₅] gave polymeric products,¹¹ thus providing

(7) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, San Francisco, Calif., 1964, p 63.

(8) R. Jaunin, *Helv. Chim. Acta*, **39**, 111 (1956).

(9) B. Monroe and S. Wiener, *J. Amer. Chem. Soc.*, **91**, 450 (1969).

(10) S. G. Cohen, D. A. Laufer, and W. V. Sherman, *ibid.*, **86**, 3060 (1964).

(11) Polymer formation on photolyses of a number of diimines has previously been reported by M. P. Cava, "Report by The Ohio State University Research Foundation," cited in *Sci-Tech Aerosp. Rep.*, **4**, 1614 (1966). In the present case, attempts to detect the reduced amine or products of [3,3] rearrangements were not successful.

TABLE I
EFFECTS OF ADDED SENSITIZERS AND INHIBITORS ON THE PHOTOLYSES OF 2-CYANOETHYLAMINE-*N*-BENZYLIDENE (**1a**)

Time, hr	% 2-cyanoethylamine- <i>N</i> -benzylidene remaining in the presence of			
	Blank	PhCHO ^a	MAP ^b	MMS ^c
0.5		56		
1	96	3	89	100
2	74		73	
3	54	0	65	94
4	38		30	92
9				81
15				59

^a 1:1 *M* benzaldehyde; benzaldehyde absorbs 50% of incident light. ^b *m*-Methoxyacetophenone absorbs 95% of incident light. ^c 0.1 *M* 2-mercaptomesitylene relative to imine; 2-mercaptomesitylene absorbs 5% of incident light.

further support for the formation of 1,2-diamines by dimerization of α -amino radicals³ rather than by combination of α -amino radicals with an imine group.

Solutions of **1a-d**, **1f**, and the 1,2-diimines in alkane or benzene solvents do not show reactions upon irradiation. Presumably because the alcohol function served to provide a hydrogen atom for a trace of sensitizer, the alcohol imine **1e** gives a low yield of **2e** under these conditions.

Experimental Section¹²

2-Cyanoethylamine-*N*-benzylidene (1a).—A benzene solution of 15 g (0.21 mol) of 3-aminopropionitrile¹³ and 22.2 g (0.21 mol) of benzaldehyde was heated at reflux for 6 hr. The benzene was evaporated and the residue was distilled to give 27.9 g (84%) of **1a**: bp 128° (2.0 mm); uv max (95% ethanol) 248 m μ (ϵ 1.68 \times 10⁴); uv shoulder 280 m μ (ϵ 1.70 \times 10³), 288 (1.11 \times 10³); ir (neat) 2210 (C \equiv N) and 1620 cm⁻¹ (C \equiv N); nmr (CDCl₃) δ 8.17 (s, 1, CH \equiv N), 7.79–7.15 (m, 5, ArH), 3.64 (t, 2, *J* = 6.8 Hz, CH₂); mass spectrum (70 eV) *m/e* (rel intensity) 158 (38, molecular ion), 118 (100), 104 (20), 91 (74), 77 (20). A series of molecular distillations gave analytically pure **1a**.

Anal. Calcd for C₁₀H₁₀N₂: C, 75.92; H, 6.37; N, 17.71. Found: C, 76.07; H, 6.57; N, 17.65.

Acetophenone-*N*-(2-Cyano)ethylimine (1f).—A xylene solution (40 ml) of 2.65 g (0.02 mol) of acetophenone, 1.57 g (0.02 mol) of aminopropionitrile,¹³ and 0.5 ml of 48% HBr was heated at reflux for 34 hr. Vacuum distillation gave 1.5 g (40%) of **1f**: bp 135° (0.4 mm); uv max (95% ethanol) 242 m μ (ϵ 1.07 \times 10⁴); ir (neat) 2220 (C \equiv N); nmr (CDCl₃) δ 8.0–7.2 (m, 5, ArH), 3.65 (t, 2, *J* = 6.5 Hz, CH₂), 2.77 (t, 2, *J* = 6.5 Hz, CH₂), and 2.24 ppm (s, 3, CH₃); mass spectrum (70 eV) *m/e* (rel intensity) 172 (15, molecular ion), 132 (19), 91 (51), 77 (100). A series of molecular distillations gave a colorless liquid.

Anal. Calcd for C₁₁H₁₂N₂: C, 75.71; H, 7.02; N, 16.27. Found: C, 75.17; H, 7.02; N, 16.57.

3-Butenylamine-*N*-benzylidene (1b).—Benzaldehyde, 4.5 g (0.043 mol), 3-butenylamine,¹⁴ 3.0 g (0.043 mol), obtained from 4.5 g of 3-butenylamine hydrochloride, and sodium sulfate, 2 g, were shaken in ether (150 ml) for 11 hr at 25°. After the sodium

(12) All melting points (corrected) were taken on a Büchi capillary melting point apparatus. Ir spectra were run on Perkin-Elmer Model 521 and 137B ir spectrometers, and uv spectra were obtained on a Cary 14 uv-visible spectrometer. Varian Associates T-60, A-60A, A-56/60A, and HA-100 spectrometers were used to determine the nmr spectra, and chemical shifts are reported in δ (parts per million) relative to the internal standard TMS (TMS). The mass spectra were measured on an Atlas CH4 mass spectrometer and relative intensities are reported as per cent of the base peak of the mass spectrum. Preparative tlc plates (2000 m μ) were made of Merck silica gel (PF₂₅₄). Elemental analyses were provided by Mr. J. Nemeth and associates.

A Hanovia Type L, 450-W, high-pressure quartz mercury-vapor immersion lamp fitted with a Pyrex filter was used for most photolyses. A Hanovia 23-W, Type SC-2537, low-pressure Vycor mercury immersion lamp was employed for irradiations with <300-m μ light.

(13) S. R. Buc, J. H. Ford, and E. C. Wise, *J. Amer. Chem. Soc.*, **67**, 92 (1945).

(14) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509 (1951).

sulfate had been removed, fresh sodium sulfate was added and the mixture was heated at reflux for 40 hr. Low-boiling components were removed by distillation at atmospheric pressure and the residue was vacuum distilled three times to give 3.6 g (54%) of **1b**: bp 75–80° (0.18 mm); uv max (95% ethanol) 248 m μ (ϵ 2.05 \times 10⁴); uv shoulder 270 m μ (ϵ 1.71 \times 10³), and 279 (1.09 \times 10³); ir (neat) 1656 (C=C) and 1647 cm⁻¹ (C=N); nmr (CDCl₃) δ 8.21 (t, 1, J = 1 Hz, CH=N), 7.52 (m, 5, ArH), 5.83 (m, 1, C=CH-), 5.07 (m, 2, CH₂=), 3.65 (t, d, 2, J = 7.5, 1 Hz, -CH₂-N=), and 2.46 ppm (m, 2, J = 7.5 Hz, =CCH₂-); mass spectrum (70 eV) m/e (rel intensity) 159 (18 molecular ion), 118 (65), 104 (10), 91 (100), 77 (15).

Anal. Calcd for C₁₁H₁₃N: C, 82.97; H, 8.23; N, 8.80. Found: C, 83.22; H, 8.08; N, 8.62.

N-Acetyl-N'-benzylidene-1,3-propanediamine (1c).—Benzaldehyde, 6.7 g (0.064 mol), and N-(3-aminopropyl)acetamide,¹⁵ 7.3 g (0.064 mol), were heated at reflux in benzene (50 ml) for 26 hr. The benzene and unreacted benzaldehyde were removed by vacuum distillation, and the residue was purified by a series of molecular distillations to give a clear oil. Cooling gave a white solid which was recrystallized from ether to give 2.3 g (17%) of **1c**: mp 61.5–62.5°; uv max (95% ethanol) 248 m μ (ϵ 1.62 \times 10⁴); uv shoulder 279 m μ (ϵ 1.41 \times 10³) and 288 (9.0 \times 10³); ir (CHCl₃) 3450, 3320 (NH) and 1650 cm⁻¹ (C=O and C=N); nmr (CDCl₃) δ 8.24 (t, 1, J = 1 Hz, CH=N), 7.80–7.25 (m, 5, ArH), 6.80 (broad, 1, CONH), 3.66 (t, d, 2, J = 6, 1 Hz, CH₂-N), 3.33 (m, 2, N-CH₂-), 1.95 (s, 3, CH₃), and 1.94 ppm (quintet, 2, J = 6 Hz, C-CH₂-C); mass spectrum (70 eV) m/e (rel intensity) 204 (13, molecular ion), 145 (32), 132 (100), 118 (43), 91 (34), 43 (48).

Anal. Calcd for C₁₂H₁₆N₂O: C, 70.56; H, 7.90; N, 13.71. Found: C, 70.71; H, 7.81; N, 13.95.

N-Benzylidene-N'-benzoyl-1,2-ethanediamine (1d).—N-(2-Aminoethyl)benzamide,¹⁶ 2.85 g (0.018 mol), and benzaldehyde, 1.84 g (0.018 mol), were heated at reflux in benzene (40 ml) for 12 hr. The benzene was evaporated to give a brown-white solid which was recrystallized from benzene to give 3.17 g (70%) of **1d**: mp 128–130°; uv max (95% ethanol) 244 m μ (ϵ 2.56 \times 10⁴); uv shoulder 215 m μ (ϵ 1.60 \times 10⁴), 280 (2.64 \times 10³), and 290 (1.12 \times 10³); ir (neat) 3440 (NH), 1650 (C=O), and 1640 cm⁻¹ (C=N); nmr (CDCl₃) δ 8.34 (s, 1, CH=N), 7.86–7.15 (m, 10, ArH), 6.80 (broad, 1, CONH), and 3.80 ppm (m, 4, CH₂-CH₂); mass spectrum (70 eV) m/e (rel intensity) 252 (41, molecular ion), 131 (43), 118 (58), 105 (83), 91 (49), 78 (100), 77 (66).

Anal. Calcd for C₁₆H₁₈N₂O: C, 76.16; H, 6.39; N, 11.10. Found: C, 76.04; H, 6.46; N, 10.96.

2-Hydroxy-2-phenylethylamine-N-benzylidene (1e).—Benzaldehyde, 3.1 g (0.029 mol), and 2-hydroxy-2-phenylethylamine, 4.0 g (0.029 mol), were heated at reflux in benzene (40 ml) for 3 hr. The solution was cooled to give a white precipitate which was recrystallized from benzene to give 5.7 g (86%) of **1e**: mp 115.0–115.5°; uv max (95% ethanol) 248 m μ (ϵ 1.95 \times 10⁴); uv shoulder 280 m μ (ϵ 1.87 \times 10³) and 290 (1.46 \times 10³); ir (CHCl₃) 3500 (OH) and 1643 cm⁻¹ (C=N); nmr (CDCl₃) δ 8.24 (t, 1, J = 1 Hz, CH=N), 7.85–7.14 (m, 10, ArH), 4.97 (m, 1, CH-O), 3.76 (m, 2, CH₂-N), and 3.22 ppm (broad, 1, OH); mass spectrum (70 eV) m/e (rel intensity) 225 (1, molecular ion), 208 (1), 148 (2), 118 (100), 91 (41), 77 (15).

Anal. Calcd for C₁₅H₁₆NO: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.97; H, 6.85; N, 6.35.

5-Hexen-2-one Anil (3).—A benzene solution (40 ml) of 5-hexen-2-one, 10.0 g (0.01 mol), aniline, 9.5 g (0.01 mol), and 48% HBr, 0.1 ml, was heated at reflux for 10 hr. The solvent was removed, and the residue was vacuum distilled three times to give 6.3 g (36%) of pale yellow **3**: bp 71–72° (0.2 mm); uv max (95% ethanol) 221 m μ (ϵ 1.28 \times 10⁴) and 281 (3.58 \times 10³); ir (neat) 1670 (C=C) and 1650 cm⁻¹ (C=N); nmr (CDCl₃) δ 7.4–6.5 (m, 5, ArH), 5.7 (m, 1, =CH-), 5.0 (m, 2, CH₂), 2.6–2.1 (m, 4, CH₂-CH₂), and 1.73 ppm (s, 3, CH₃); mass spectrum (70 eV) m/e (rel intensity) 173 (35, molecular ion), 158 (28), 118 (100), 77 (84), 55 (43). The anil was stored under vacuum.

Because the anil was too unstable to be characterized by analysis, it was reduced to 5-(N-phenyl)amino-1-hexene. An ether suspension (30 ml) of 5-hexen-2-one anil, 1.6 g (0.0094 mol), and lithium aluminum hydride, 3.5 g (0.094 mol), was

heated at reflux for 12 hr. Quenching with moist sodium sulfate and filtration, concentration, and two vacuum distillations gave 1.33 g (80%) of 5-(N-phenyl)amino-1-hexene: bp 79–80° (0.2 mm); uv max (95% ethanol) 252 m μ (ϵ 1.4 \times 10⁴) and 300 (1.8 \times 10³); ir (neat) 3350 (NH) and 1640 cm⁻¹ (C=C); nmr (CDCl₃) δ 7.3–6.4 (m, 5, ArH), 5.8 (m, 1, =CH-), 5.0 (m, 2, CH₂=C-), 3.40 (m, 1, CH-N), 3.18 (broad, 1, NH), 2.14 (m, 2, CH₂), 1.56 (m, 2, CH₂), and 1.15 ppm (d, 3, J = 6 Hz, CH₃); mass spectrum (70 eV) m/e (rel intensity) 175 (6, molecular ion), 160 (30), 120 (100), 77 (51).

Anal. Calcd for C₁₂H₁₇N: C, 82.23; H, 9.78; N, 7.99. Found: C, 82.22; H, 9.90; N, 8.07.

Ethylenediamine-N,N'-dibenzylidene,¹⁷ N-methylbenziminomethyl ether,¹⁸ N-methylbenziminomethyl ether,¹⁹ N-phenylacetiminomethyl ether,²⁰ and N-phenylbenziliminomethyl ether²¹ were prepared by standard procedures.

meso-1,2-Diamino-1,2-diphenylethane was synthesized by the method of Staab and Vogtle:²² mp 117–118° (lit.²² mp 118°); uv max (ethanol) 259 m μ (ϵ 428); ir (CHCl₃) 3330 cm⁻¹ (NH); nmr (CDCl₃) δ 7.27 (s, 10, ArH), 3.94 (s, 2, CH), and 1.23 ppm (s, 4, NH₂).

meso-N,N'-Bis(2-cyanoethyl)-1,2-diamino-1,2-diphenylethane (2a).—Acrylonitrile, 8.1 g (0.15 mol), and meso-1,2-diamino-1,2-diphenylethane, 1.5 g (0.007 mol), and 40% potassium hydroxide, 0.5 ml, were heated at reflux for 60 hr. The mixture was made strongly basic with 40% sodium hydroxide (20 ml) and was extracted with chloroform. The extract was dried (MgSO₄) and concentrated to give a viscous oil which was crystallized from 95% ethanol to give 0.2 g (10%) of **2a**: mp 106–107°; mmp (with **2a** from photolysis) 106–107°; ir (Nujol) 3310 (NH) and 2250 cm⁻¹ (C=N); nmr (CDCl₃) δ 7.52–7.15 (m, ArH), 3.85 (s, Ph-CH), 2.65 (t, J = 6 Hz, CH₂), 2.28 (t, J = 6 Hz, CH₂), and 1.65 ppm (s, NH, exchanges in D₂O); mass spectrum (70 eV) m/e (rel intensity) 318 (0.03, molecular ion), 159 (100), 118 (17), 91 (1), 77 (4).

Anal. Calcd for C₂₀H₂₂N₄: C, 75.45; H, 6.96; N, 17.59. Found: C, 75.74; H, 7.01; N, 17.52.

meso-N,N'-Bis(3-aminopropyl)-1,2-diamino-1,2-diphenylethane.—An ether suspension (40 ml) of lithium aluminum hydride, 3 g (0.08 mol), and meso-N,N'-bis(2-cyanoethyl)-1,2-diamino-1,2-diphenylethane, 0.279 g (0.0018 mol), was heated at reflux for 16 hr. The reaction was quenched with moist sodium sulfate to give, after evaporation of solvent, 0.116 g (41%) of a pale yellow oil: uv max (95% ethanol) 249 m μ (ϵ 8.4 \times 10³); ir (CHCl₃) 3450, 3380, 3300 cm⁻¹ (NH); nmr (CDCl₃) δ 7.35 (s, 10, ArH), 3.72 (s, 2, benzyl), 2.4 (m, 8, N-CH₂), 1.36 (broad, 6, NH; exchanges in D₂O), and 1.41 ppm (m, 4, C-CH₂-C); mass spectrum (70 eV) m/e (rel intensity) 327 (3, M⁺ + 1), 163 (54), 120 (67), 105 (7), 91 (52), 77 (11), 58 (35), 43 (100).

A picrate was made in 95% ethanol and recrystallized from methanol: mp 228–230°; mmp (with picrate of the tetraamine from hydrolysis of **2c**) 228–230°; the ir spectrum was identical with that of tetraamine, obtained from hydrolysis of the photodimer **2c**.

The tetrabenzamide was made by the Schotten-Baumann²³ method and was recrystallized from methanol to give pure material: mp 262–263°; mmp (with tetraamide derived from the photodimer **2c**) 262–263°; ir (KBr) 3350, 3260 (NH) and 1635, 1620 (sh) cm⁻¹ (C=O); mass spectrum (70 eV) m/e (rel intensity) 742 (0.05, molecular ion), 637 (0.1), 460 (5), 371 (16), 267 (2), 249 (24), 146 (37), 105 (100), 91 (5), 77 (31).

Anal. Calcd for C₄₈H₄₆N₄O₄: C, 77.60; H, 6.24; N, 7.54. Found: C, 77.32; H, 6.20; N, 7.75.

Aluminum Amalgam Reduction of 2-Cyanoethylamine-N-benzylidene.—An ether suspension (80 ml) of the cyanoimine, 2.5 g (0.016 mol), and aluminum amalgam,²⁴ 3 g (0.01 mol),

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was allowed to stand for 16 hr. The amalgam residue was removed and triturated with boiling methanol, which was combined with the original solution and condensed to give 2.12 g of yellow oil. The nmr spectrum (CDCl_3) of the crude product showed some impurities (δ 7.1 and 3.1 ppm) and possibly 5% *dl* isomer. Part of the product was crystallized to give 0.5 g (20%) of *meso*-*N,N'*-bis(2-cyanoethyl)-1,2-diamino-1,2-diphenylethane **2a**: mp 106–107°; mmp (with **2a** from photolysis) 106–107°; the ir and nmr spectra were identical with those of **2a** from photolysis.

Aluminum Amalgam Reduction of B-Benzoyl-*N'*-benzylidene-1,2-ethanediamine (1d).—An ether-tetrahydrofuran suspension (250 ml, 2:1, v:v) of *N*-benzoyl-*N'*-benzylidene-1,2-ethanediamine, 0.54 g (0.002 mol), and aluminum amalgam,²⁴ 5.0 g (0.017 mol), was allowed to stand for 8 hr. The amalgam residue was collected by vacuum filtration and triturated three times with boiling methanol. The filtrates were combined, refiltered, and condensed to give 0.52 g (96%) pale yellow solid which was recrystallized from methanol to give 0.38 g (70%) of **2d**: mp 207–208°; mmp (with **2d** isolated from the photolysis) 207–208°; uv max (95% ethanol) 220 μ (ϵ 2.06×10^4); ir (KBr) 3420 (NH) and 1635 cm^{-1} (C=O); nmr (CDCl_3) δ 7.7–7.2 (m, 20, ArH), 6.36 (broad, 2, CONH), 3.83 (s, 2, benzyl), 3.36 (m, 4, N-CH₂), 2.60 (m, 4, N-CH₂), and 1.7 ppm (broad, 2, NH); mass spectrum (70 eV) *m/e* (rel intensity) 507 (1, M⁺ + 1), 253 (51), 148 (76), 118 (52), 105 (71), 91 (51), 77 (100).

General Photolysis Procedure.—Most irradiations were done in a Pyrex vessel containing a water-cooled, quartz immersion well into which were placed the high-pressure lamp and the filter. Before irradiation the solution was degassed with dry, oxygen-free nitrogen for a minimum of 30 min. Nitrogen was also bubbled through the reaction solution during the irradiation. All photolyses in hexane and alcoholic solvents were monitored by the disappearance of the ultraviolet absorption of the imine chromophore.

Photolyses of 2-Cyanoethylamine-*N*-benzylidene.—A 95% ethanol solution (425 ml) of the benzylidene **1a**, 0.131 g (0.00083 mol), was irradiated for 6 hr. The solution was concentrated to a volume of 5 ml and cooled to give 63% white solid which was recrystallized from methanol and was shown to be *meso*-*N,N'*-bis(2-cyanoethyl)-1,2-diamino-1,2-diphenylethane (**2d**): mp 106–106.5°; uv max (ethanol) 259 μ (ϵ 470); ir (Nujol) 3310 (NH) and 2250 cm^{-1} (C≡N); nmr (CDCl_3) δ 7.50–7.10 (m, 10, ArH), 3.82 (s, 2, benzyl), 2.64 (t, 4, $J = 6$ Hz, CH₂), 2.28 (t, 4, $J = 6$ Hz, CH₂), and 1.65 ppm (s, 2, NH; exchanges in D₂O); mass spectrum (70 eV) *m/e* (rel intensity) 318 (0.4, molecular ion), 159 (100), 118 (16), 91 (9), 77 (2); metastables *m/e* (fragmentation) 87.6 (159–118) and 69.6 (118–91).

Anal. Calcd for C₂₀H₂₆N₄: C, 75.45; H, 6.96; N, 17.59. Found: C, 75.60; H, 6.89; N, 17.36.

To determine the yield of **2a**, 0.130 g of crude photoproduct was developed (CHCl₃) on a preparative tlc plate. Elution of the bands with methanol-chloroform gave 0.098 g (76%) of a viscous oil whose ir spectrum (CHCl₃) was identical with that (CHCl₃) of **2a**. Addition of ethanol gave a solid (mp 102–105°).

Experiments were run to determine the effect of sensitizing and inhibiting agents on the irradiation of 2-cyanoethylamine-*N*-benzylidene (**1a**); the data obtained are summarized in Table I. A 95% ethanol solution (625 ml) of benzylidene **1a** and the appropriate compound was stirred and degassed for 30 min before irradiation. A 100-ml portion was then removed, and the remaining 525 ml was irradiated for the indicated time. The solutions were concentrated and their nmr spectra were recorded. The amount of **1a** remaining was determined from the relative areas of the benzylidene proton (δ 8.17 ppm) and the aromatic protons (δ 7.79–7.15 ppm) in the nmr spectrum.

In one experiment a 95% ethanol solution (525 ml) of 2-cyanoethylamine-*N*-benzylidene (**1a**) 0.541 g (0.00342 mol), and 2-mercaptomesitylene, 0.568 g (0.00376 mol), was irradiated for 36 hr; the nmr spectrum showed that 46% of the imine **1a** remained. Tlc and the nmr spectrum of the product indicated that the imine **1a**, the mercaptan, hydrobenzoin, 1-phenyl-1,2-propanediol, and the photodimer **2a** were present. The product was then extracted with 8% hydrochloric acid and water. The extract was 0.075 g yellow oil whose nmr spectrum (CDCl_3) indicated the presence of the photodimer **2a** (50%) and a mixture of hydrobenzoin (25%) and 1-phenyl-1,2-propanediol (25%). The nonbasic material was then extracted with 40% potassium hydroxide and water to remove as much 2-mercaptomesitylene as possible. The remaining chloroform solution yielded 0.376 g

of brown tar whose nmr spectrum (CDCl_3) indicated the presence of hydrobenzoin (25%) and 2-mercaptomesitylene (75%). A control extraction showed that the imine hydrolyzed under the extraction conditions. No new photoproducts were found.

Photolyses of **1a** in benzene and hexane led only to recovered **1a**. Photolyses with a low-pressure mercury lamp gave only unidentified products.

Photolysis of Acetophenone-*N*-(2-Cyano)ethylimine (1f).—A 95% ethanol solution (525 ml) of the azomethine, 0.530 g (0.0032 mol), was irradiated for 35 hr. The ethanol was concentrated to give 0.318 g (60%) of a white solid which was recrystallized from methanol to give pure **2f**: mp 131–133°; uv max (95% ethanol) 259 μ (ϵ 457); ir (Nujol) 3280 (NH) and 2210 cm^{-1} (C≡N); nmr (CDCl_3) δ 7.45–7.95 (m, 10, ArH), 2.80–2.35 (m, 8, CH₂-CH₂), 2.10 (s, 2, NH; exchanges in D₂O), 1.58 (s, 3, CH₃), and 1.49 ppm (s, 3, CH₃); nmr (DMSO-*d*₆, 90°) no change in position or relative intensity of δ 1.58 and 1.49 ppm signals; mass spectrum (70 eV) *m/e* (rel intensity) 346 (0.2, molecular ion), 173 (100), 132 (16), 91 (17), 77 (8); metastables *m/e* (fragmentation) 100.7 (173–132) and 62.7 (132–91).

Anal. Calcd for C₂₂H₂₆N₄: C, 76.27; H, 7.56; N, 16.17. Found: C, 76.36; H, 7.56; N, 16.39.

Photolyses of 3-Butenylamine-*N*-benzylidene.—The imine **1b**, 0.51 g (0.0032 mol), was irradiated in 95% ethanol (425 ml) for 10 hr. The ethanol was removed, leaving 0.50 g (98%) yellow oil whose nmr spectrum (CDCl_3) showed two benzyl peaks at δ 3.76 and 3.68 ppm (area ratio, 1:1). The crude product was chromatographed on a silica gel column.

From a benzene-2% ether elutant was isolated 0.21 g (42%) pale yellow oil which was crystallized from pentane to give 0.14 g (28%) of *meso*-*N,N'*-bis(3-butenyl)-1,2-diamino-1,2-diphenylethane (**2b**): mp 40–41°; uv max (95% ethanol) 259 μ (ϵ 5.1×10^2); ir (CCl₄) 3420 (NH) and 1640 cm^{-1} (C=C); nmr (CDCl_3) δ 7.36 (s, 10, ArH), 5.50 (m, 2, =C-H), 4.80 (m, 4, CH₂=), 3.78 (s, 2, benzyl), 2.34 (m, 4, CH₂), 2.17 (m, 4, CH₂), and 1.49 ppm (broad, 2, NH, exchanges in D₂O); mass spectrum (70 eV) *m/e* (rel intensity) 320 (1, molecular ion), 160 (100), 131 (175), 118 (74), 104 (22), 91 (85), 77 (30).

Anal. Calcd for C₂₂H₂₈N₂: C, 82.45; H, 8.81; N, 8.74. Found: C, 82.55; H, 8.89; N, 8.82.

Eluted from benzene-2% ether was 0.17 g (34%) of pale yellow oil which could not be crystallized. It was assigned the structure of *dl*-*N,N'*-bis(3-butenyl)-1,2-diamino-1,2-diphenylethane (**2b**) on the basis of the following evidence: uv max (95% EtOH) 249 μ (ϵ 7.5×10^2); ir (CCl₄) 3300 (NH) and 1640 cm^{-1} (C=C); nmr (CDCl_3) δ 7.14 (s, 10, ArH), 5.8 (m, 2, =C-H), 5.1 (m, 4, CH₂=C-), 3.66 (s, 2, benzyl), and 2.7–2.0 ppm (m, 10, CH₂ and NH); mass spectrum (70 eV) *m/e* (rel intensity) 320 (0.4, molecular ion), 160 (100), 131 (35), 118 (9), 104 (5), 91 (16), 77 (5). A bis benzamide was made of this photodimer: mp 248–249°; ir (KBr) 1640 (C=C) and 1630 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* (rel intensity) 528 (0.3, molecular ion), 264 (69), 105 (100), 91 (10), 77 (41).

Photolyses of *N*-Acetyl-*N'*-benzylidene-1,3-propanediamine (1c).—A 95% ethanol solution (525 ml) of the imine **2c**, 2.0 g (0.0098 mol), was irradiated for 12 hr. The ethanol was removed and the residue was dissolved in chloroform, dried (Na₂SO₄), and concentrated to give 2 g (100%) of a pale yellow oil whose nmr spectrum (CDCl_3) contained 2 singlets at δ 3.82 and 3.68 ppm (relative area 1:1, benzyl) and 2 singlets at δ 1.92 and 1.88 ppm (relative area 1:1, CH₃). The crude product was chromatographed on a silica gel column.

From the chloroform-5% methanol elutant was isolated 0.76 g (33%) of a yellow oil which was assigned the structure of *meso*-*N,N'*-bis[3-(*N*-acetyl)aminopropyl]1,2-diamino-1,2-diphenylethane **2c**: uv max (95% ethanol) 253 μ (ϵ 9.1×10^2); ir (CHCl₃) 3420, 3300 (NH) and 1653 cm^{-1} (C=O); nmr (CDCl_3) δ 7.25 (s, 10, ArH), 6.55 (broad, 2, CONH), 3.86 (s, 2, benzyl), 3.19 (m, 4, N-CH₂), 2.69 (broad, 2, NH, exchanges in D₂O), 2.44 (t, 4, $J = 6$ Hz, N-CH₂), 1.89 (s, 6, CH₃), and 1.52 ppm (m, 4, C-CH₂-C); mass spectrum (70 eV), *m/e* (rel intensity) 410 (0.2, molecular ion), 205 (48), 146 (3), 105 (8), 100 (30), 83 (22), 91 (16), 77 (6), 58 (21), 43 (100). This viscous oil appeared to be sensitive to heat and air.

A picrate of the photodimer **2c** was made in 95% ethanol and recrystallized from methanol: mp 226–227°; ir (KBr) 3400 (NH) and 1630 cm^{-1} (C=O).

Anal. Calcd for C₂₈H₄₀N₁₀O₁₆: C, 49.77; H, 4.64; N, 16.12. Found: C, 49.72; H, 4.59; N, 15.94.

From the chloroform-10% methanol elutant was isolated 0.41 g (21%) pale yellow oil which was assigned the structure of *dl*-N,N'-bis[3-(N-acetyl)aminopropyl]-1,2-diamino-1,2-diphenylethane (**2c**): uv max 253 m μ (ϵ 8.1 \times 10³); ir (CHCl₃) 3420, 3295 (NH) and 1653 cm⁻¹ (C=O); nmr (CDCl₃) δ 7.16 (s, 10, ArH), 7.00 (broad, 2, CONH), 3.69 (s, 2, benzyl), 3.34 (m, 4, N-CH₂), 2.98 (s, 2, NH, exchanges in D₂O), 2.50 (m, 4, N-CH₂), 1.93 (s, 6, CH₃), and 1.64 ppm (m, 4, C-CH₂-C); mass spectrum (70 eV) *m/e* (rel intensity) 410 (0.4, molecular ion), 205 (85), 146 (2), 105 (2), 100 (30), 91 (8), 83 (100), 77 (1), 43 (23). Attempts to make a picrate of **2c** were unsuccessful.

From the chloroform-5% methanol elutant was also isolated 0.27 g of a yellow oil whose nmr spectrum (CDCl₃) was compatible with a mixture of the *meso* and *dl* photodimers: nmr δ 1.93 and 1.89 ppm (relative area 61.6%:38.4%). From these data total spectroscopic yields of 42% *meso* and 29% *dl* **2c**, respectively, were calculated.

To obtain the *meso*-tetraamine, the 1,2-diamine **2c** (0.106 g, 0.00026 mol) was heated at reflux in 8% hydrochloric acid (25 ml) for 8 hr. The solution was extracted with chloroform, made basic, and again extracted with chloroform, dried (Na₂SO₄), and concentrated to give 0.057 g (68%) of *meso*-N,N'-bis(3-aminopropyl)-1,2-diamino-1,2-diphenylethane: uv max (95% ethanol) 249 m μ (ϵ 6.9 \times 10³); ir (CHCl₃) 3450, 3380, and 3300 cm⁻¹ (NH); nmr (CDCl₃) δ 7.30 (s, 10, ArH), 3.83 (s, 2, benzyl), 2.4 (m, 8, N-CH₂), 1.44 (m, 4, C-CH₂-C), and 1.21 ppm (broad, 6, NH, exchanges in D₂O); mass spectrum (70 eV) *m/e* (rel intensity) 326 (0.2, molecular ion), 163 (13), 120 (10), 91 (6), 77 (2), 43 (100).

A picrate was made in 95% ethanol and recrystallized from methanol: mp 228-229°; mmp (with picrate of authentic **2c**) 228-230°. A tetrabenzamide was made by the Schotten-Baumann²³ method: mp 261-263°; mmp (with benzamide from authentic tetraamine) 261-263°; ir (KBr) 3350, 3260 (NH) and 1635, 1620 cm⁻¹ (C=O); mass spectrum (70 eV) *m/e* (rel intensity) 742 (0.01, molecular ion), 460 (5), 371 (5), 276 (1), 249 (5), 146 (9), 105 (100), 91 (9), 77 (42).

Anal. Calcd for C₄₈H₄₈N₄O₄: C, 77.60; H, 6.24; N, 7.54. Found: C, 77.32; H, 6.20; N, 7.75.

Photolysis of N-Benzoyl-N'-benzylidene-1,2-ethanediamine (1d).—A 95% ethanol solution (525 ml) of the imine **1a**, 1.1 g (0.0044 mol), was irradiated for 26 hr. The ethanol was removed to give an off-white solid whose nmr spectrum (CDCl₃) exhibited only one benzyl peak (δ 3.83 ppm). The crude product was chromatographed on silica gel.

From chloroform-2% methanol was eluted 0.55 g (50%) of off-white solid whose nmr spectrum (CDCl₃) was identical with that of the *meso*-1,2-diamine (**2d**) produced by aluminum amalgam reduction. This photoproduct was recrystallized from methanol to give 0.48 g (44%) of pure *meso*-N,N'-bis[2-(N-benzoyl)aminoethyl]-1,2-diamino-1,2-diphenylethane (**2d**): mp 201-203°; uv max (95% ethanol) 220 m μ (ϵ 3.36 \times 10⁴); ir (Nujol) 3390 (NH) and 1630 cm⁻¹ (C=O); nmr (CDCl₃) δ 7.8-7.2 (m, 20, ArH), 6.7 (broad, 2, CONH), 3.87 (s, 2, benzyl), 3.44 (m, 4, CH₂), and 2.67 ppm (m, 6, CH₂ and NH); mass spectrum (70 eV) *m/e* (rel intensity) 506 (0.005, molecular ion), 253 (100), 180 (14), 179 (15), 178 (12), 148 (53), 133 (6), 132 (3), 119 (3), 118 (8), 106 (10), 105 (42), 91 (8), 77 (17); metastables (fragmentation) 86.57 (253-148), 74.49 (148-105), 44.41 (253-106), 56.46 (105-77).

Anal. Calcd for C₃₂H₃₄N₄O₂: C, 75.86; H, 6.76; N, 11.06. Found: C, 75.69; H, 6.63; N, 11.11.

Photolyses of 2-Hydroxy-2-phenylethylamine-N-benzylidene (1e).—A 95% ethanol solution (525 ml) of the imine (**1e**), 1.5 g (0.0067 mol), was irradiated for 10 hr. The ethanol was removed to give a pale yellow solid which was chromatographed on silica gel.

From chloroform-2% methanol was eluted 0.86 g (58%) of an off-white solid **2e**: mp 138-155° dec; ir (KBr) 3400 cm⁻¹ (NHOH). The solid was recrystallized from chloroform to give 0.08 g (6%) of **2e**: mp 199-201° dec; uv max (95% ethanol) 259 m μ (ϵ 2.4 \times 10³); ir (KBr) 3400 cm⁻¹ (NH); nmr (CDCl₃) δ 7.3 (m, 20, ArH), 4.5 (m, 2, Ph-CH-OH), 3.9 (m, 2, PhCH-NH), 3.6 (m, 8, CH₂, OH, NH); mass spectrum (70 eV) *m/e* (rel intensity) 452 (1, molecular ion), 345 (11), 226 (100), 209 (17), 208 (80), 121 (2), 120 (19), 119 (3), 118 (16), 117 (30), 106 (8), 105 (11), 104 (4), 103 (10), 91 (45), 77 (10). The following metastables (fragmentation) were found: 193.28 (226-209), 191.43 (226-208); 70.39 (208-121), 65.81 (208-117), 54.02 (208-106), 39.81 (208-91).

Attempts to purify or derivatize **2e** failed.

Photolyses of ethylene-N,N'-dibenzylidene, propylene-N,N'-dibenzylidene, N-methyl-O-methyl benzimidate, N-phenyl-O-methyl acetimidate, and N-phenyl-O-methyl benzimidate gave starting materials or polymers which were not characterized. Attempted sensitization of reactions of the imidates with benzaldehyde in ethanol solutions gave recovery of starting materials, hydrobenzoin, and 1-phenyl-1,2-propanediol.

Results and Discussion

The apparently diverse photoreactions of a variety of imines may be rationalized by the intermediacy of an α -amino radical formed by hydrogen atom transfer from an α -hydroxy radical to the imine.^{2,3,25,26} Such a rationale is applicable to many of the photoreactions of nitrogen hetero aromatics²⁷ as well as to simple and substituted imines. Although mechanistic work clearly needs to be done, it is interesting that almost all of the presently known imine photochemistry may be rationalized either by the ground-state process of an imine forming an α -amino radical or by excited-state processes which find formal analogy in systems having carbon-carbon double bonds.^{25e}

The nature of the excited species which could be formed on irradiation of the imines **1a-f** is not entirely clear. Although strict analogy with the carbonyl group would suggest n, π^* excitation²⁸ under our conditions, we do not observe the expected solvent shift of the shoulders of the absorption bands at 280-290 m μ for **1a** on changing the solvent from 95% ethanol to hexane.^{4a} Detailed curve analysis of the uv spectrum of the anil of benzaldehyde has been taken to indicate²⁹ that the n, π^* absorption appears at 360 m μ and the corresponding absorption in benzophenone imine is reported at 345 m μ .^{25d} We were unable to detect any absorption maxima with $\epsilon > 25$ in the 300-400-m μ region for compounds **1a-f**. By analogy with benzaldehyde anil²⁹ it appears possible that the maxima observed as shoulders for imines in the region 280-290 m μ include absorptions which do not have appreciable contributions from the lone pair on nitrogen. If this is the case,

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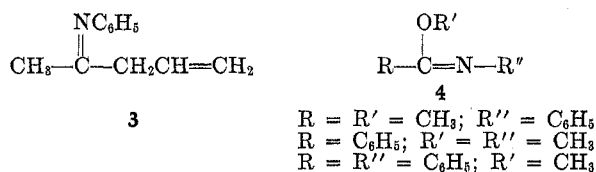
(28) W. Meister, R. D. Guthrie, J. L. Maxwell, D. A. Jaeger, and D. J. Cram, *ibid.*, **91**, 4452 (1969).

(29) H. H. Jaffe, S. Yeh, and R. W. Gardner, *J. Mol. Spectrosc.*, **2**, 120 (1958).

the limited and formal analogy between imine and carbon-carbon double-bond photochemistry, for those cases which involve a chromophore which contains the excited imine, is not so unreasonable as it might appear.

The *meso* isomers of **2a** and **2c** are unambiguously assigned on the basis of the above chemical conversions. Assignments of *meso* and *dl* stereochemistries for **2b** rest on the assumption that the resonances of the benzyl proton in the *meso* isomer will appear downfield from those of the *dl* isomer. Such a difference is observed in the mixture from **2c** and in analogous glycols.³⁰ The *meso* structure of **2d** is provisional and follows from its preparation by aluminum reduction of the imine, a reaction which appears to give *meso* products.^{3,8} Small energy differences due to steric effects and hydrogen bonding in the transition states for radical coupling leading to the *meso* and *dl* products could account for the different stereochemistries,³¹ but a contribution from photochemical equilibration has not been ruled out.

Intramolecular photocyclization between a carbonyl group and a carbon-carbon double bond has been observed with 5-hexen-2-ones.^{6b} The corresponding



(30) J. Wiemann, G. Dana, S. Thuan, and M. Brami, *C. R. Acad. Sci., Ser. C*, **258**, 3724 (1964).

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anil **3** was prepared and irradiated in hexane, benzene, and alcohol. In each case starting anil or polymeric products were observed. Imidates also appear to be stable to some photolyses.³² Photolyses of the imidates **4** in hexane, benzene, or ethanol give polymeric products or starting material. Attempts to sensitize the photo-reaction with benzaldehyde in ethanol give only hydrobenzoin³³ and 1-phenyl-1,2-propanediol.³⁴

Registry No.—**1a**, 25630-14-2; **1b**, 25558-09-2; **1c**, 25558-10-5; **1d**, 25558-11-6; **1e**, 25558-12-7; **1f**, 25558-13-8; **2a** (*meso*), 25558-54-7; **2b** (*dl*), 25558-39-8; **2b** (*meso*), 25558-55-8; **2c** (*dl*), 25558-57-0; **2c** (*meso*), 25558-56-9; **2c** (*meso*) (picrate), 25630-15-3; **2d** (*meso*), 25558-58-1; **2e**, 25558-14-9; **2f**, 25558-15-0; **3**, 25558-16-1; 5-(*N*-phenyl)amino-1-hexene, 25558-17-2; *meso*-1,2-diamino-1,2-diphenylethane, 951-87-1; *meso*-*N,N'*-bis(3-aminopropyl)-1,2-diamino-1,2-diphenylethane, 2558-60-5; *meso*-*N,N'*-bis(3-aminopropyl)-1,2-diamino-1,2-diphenylethane (tetrabenzamide), 25557-86-2.

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(33) G. Ciamician and P. Silber, *Chem. Ber.*, **34**, 1530 (1911).

(34) H. Göth, P. Cerutti, and H. Schmid, *Helv. Chim. Acta*, **48**, 1395 (1965).

Photocyclizations of 5-Vinylnorbornenes

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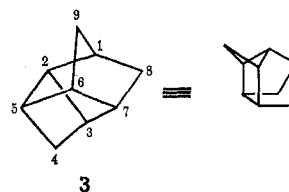
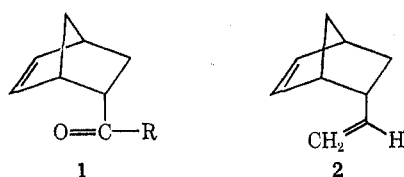
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Acetone-sensitized photocyclization of 5-vinylnorbornene (**2**) has been shown to produce tetracyclo[4.2.1.0^{2,5}.0^{3,7}]nonane (**3**). Ketone **12** has been prepared by an intramolecular thermal cycloaddition of ketene **11**. The chlorides **18c** and **18t** undergo rapid *cis-trans* interconversion in competition with cyclization to form **20**.

Concurrently with our recent studies of photocyclizations of 5-acylnorbornenes (**1**)¹ we initiated a similar investigation of the isoelectronic system 5-vinylnorbornene (**2**).² Our interest in this molecule was de-

“crossed *vs.* parallel” addition.³ By analogy with 5-acylnorbornene cyclization, the expected product should be tetracyclo[4.2.1.0^{2,5}.0^{3,7}]nonane (**3**); however, sim-



rived from the synthetic potential of the cyclization and from certain photochemical aspects in the realm of 1,5-diene systems.

The first major question we sought to answer concerned the regioselectivity of the cyclization, *i.e.*

(1) R. R. Sauer, W. Schinski, and M. M. Mason, *Tetrahedron Lett.*, 79 (1969).

(2) R. R. Sauer and W. L. Schinski, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, p 112.

ple examples of this type of behavior are absent from the literature.⁴ Furthermore, the double bonds of the constrained analog dicyclopentadiene undergo parallel cycloaddition.⁵ Although crossed addition is probably

(3) R. Srinivasan and K. H. Carlough, *J. Amer. Chem. Soc.*, **89**, 4932 (1967).

(4) Simple γ,δ -unsaturated ketones usually give mixtures of the two product types on irradiation. For a recent summary see W. L. Dilling, *Chem. Rev.*, **66**, 373 (1966). Comparable examples of simple 1,5-diene cyclizations are available only in the gas phase.³

(5) G. O. Schenck and R. Steinmetz, *Chem. Ber.*, **96**, 520 (1963).