

sharply defined structure, to permit an accurate determination of the interval between the zero-point levels⁷ of the electronic states. Furthermore, a low relative quantum yield of phosphorescence (α plus β), compared with fluorescence, indicating a high point of crossing, should correspond to a large discrepancy of the two energy values as shown in the figure. The luminescence properties of such molecules as porphyrin, phthalocyanine and chlorophyll makes them especially suited for use in experiments to test these ideas.

In the case of acid fluorescein dye, aside from uncertainties in determining the spectroscopic energy value due to diffuseness of the emission bands, the high relative quantum yield of phosphorescence probably favored the correlation between the spectroscopic and thermal values.

A recent paper on the luminescence of inorganic crystalline impurity "phosphors" by Williams and Eyring⁸ proposes an energy-coordinate diagram somewhat similar to the one discussed here. However, it will be noted that the physical systems and some aspects of the phenomena differ considerably in the two cases. Thus, in the present case the system consists of dilute solutions of the complex molecule in a homogeneous rigid glassy medium. Furthermore, the process of luminescence consists of transition between electronic levels of the complex molecule itself, with no electron transfer to the medium. In the phenomena treated by Williams and Eyring, energy levels of the crystal lattice are involved, with electron transfer from the absorbing center.

Although Williams and Eyring studied thermal properties of the inorganic phosphors, no spectroscopic data such as required for the correlation described above were included, although it is possible that an analogous relationship of spectroscopic and thermal energies may exist for inorganic luminescent materials.

(7) The frequency of maximum intensity of a diffuse emission band (such as is obtained for an ionic dye) does not, of course, give the fundamental energy of the excited state, but merely the frequency of most probable emission, according to the Franck-Condon principle.

(8) F. E. Williams and H. Eyring, *J. Chem. Phys.*, **15**, 289 (1947).

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One-Step Synthesis of 1,2,3,4-Tetrahydrocarbazole and 1,2-Benzo-3,4-dihydrocarbazole

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1,2,3,4-Tetrahydrocarbazole has previously been synthesized in two steps— isolation of cyclohexanone phenylhydrazone followed by ring closure.¹ We have found that certain hydrocarbazoles, such as 1,2,3,4-tetrahydrocarbazole and

(1) Drechsel, *J. prakt. Chem.*, **38**, 69 (1888); Baeyer and Tutein, *Ber.*, **23**, 2178 (1889); Baeyer, *Ann.*, **278**, 88 (1893); Borsche, *ibid.*, **359**, 49 (1908); Perkins and Plant, *J. Chem. Soc.*, **119**, 1825 (1921); Ghigi, *Gazz. chim. ital.*, **60**, 194 (1930).

1,2-benzo-3,4-dihydrocarbazole, can be prepared by a one-step process which by-passes the isolation of the intermediate phenylhydrazones. There is considerable merit in this abbreviation of the synthesis because these phenylhydrazones are not stable. For example, cyclohexanone phenylhydrazone, although a clean, crystalline compound when first prepared, decomposes in a few days to a sticky, brown mass. An organic acid such as formic, acetic, or propionic can be used as combination solvent and catalyst, or the reaction medium can be water or aqueous alcohol with hydrochloric, phosphoric or sulfuric acid as catalyst.

Experimental

Organic Acid Method.—Phenylhydrazine (108 g., 1 mole) was added during one hour to a stirred, refluxing solution of 98 g. (1 mole) of cyclohexanone in 360 g. of glacial acetic acid. After refluxing and stirring an additional hour, the mixture was cooled to 5° and filtered. The crude solid was washed with water, 75% methyl alcohol, and air dried (yield, 150 g., 88%). Crystallization from methyl alcohol gave a first crop of 120 g. and a second crop of 24 g. The reaction goes equally well if acetic acid is replaced by formic or propionic acid. The solubilities of 1,2,3,4-tetrahydrocarbazole in 10 cc. of various solvents are: methyl alcohol, 0.5, 1.2, 1.8 g. at 10, 35, 55°, respectively; acetic acid, 0.5, 1.1, 2.0, 3.0 g. at 20, 39, 58, 68°, respectively; cyclohexane, 0.1, 0.5, 0.9, 1.5 g. at 1, 54, 69, 77°, respectively.

Aqueous Mineral Acid Method.—To a stirred, refluxing mixture of 500 cc. of water and 172 cc. (2 moles) of concentrated hydrochloric acid (d. 1.18) was added 108 g. of phenylhydrazine during five minutes. α -Tetralone² (145 g., 1 mole) was added during one hour, and the mixture was stirred and refluxed for an additional four hours. Worked up as above, the first crop was 123 g. and the second crop was 74 g.; 90% total yield. The solubility of 1,2-benzo-3,4-dihydrocarbazole in 10 cc. of methyl alcohol is 0.2, 0.5 and 0.8 g. at 0, 30 and 50°, respectively.

Aqueous Alcohol-Mineral Acid Method.—A mixture of 108 g. of phenylhydrazine, 920 cc. of 75% ethyl alcohol and 1.5 moles of hydrochloric acid was stirred and refluxed while 98 g. of cyclohexanone was added during one hour. The yield of air-dried 1,2,3,4-tetrahydrocarbazole was about 95%.

Where phosphoric acid was substituted for hydrochloric acid, the usual yield of tetrahydrocarbazole was obtained, but the product was contaminated by ammonium phosphate, although it was readily purified by crystallization from methyl alcohol. Where formic acid was employed in the aqueous alcohol-mineral acid method, the product was β -formylphenylhydrazine.³ The latter was converted to tetrahydrocarbazole by boiling with an acetic acid or formic acid solution of cyclohexanone. β -Acetylphenylhydrazine remained unchanged upon similar treatment.

Inapplicability of Acetic Acid and Mineral Acid Methods for Synthesis of 6-Nitro-1,2,3,4-Tetrahydrocarbazole.—Refluxing a glacial acetic acid solution containing equivalent amounts of *p*-nitrophenylhydrazine and cyclohexanone produced an 80% yield of β -acetyl-*p*-nitrophenylhydrazine melting at 211–212°. The previously reported melting point of this compound was 205–206°. ⁴

Anal. Calcd. for C₈H₉N₃O₃: C, 49.2; H, 4.7; N, 21.5. Found: C, 48.9; H, 4.8; N, 21.5.

(2) Where the α -tetralone was not pure, owing to contamination with 5–10% of α -tetralol, the appropriate excess was added to compensate for the lack of purity. The ketone-alcohol mixture was analyzed according to Bryant and Smith, *This Journal*, **57**, 57 (1935).

(3) Hirst and Cohen, *J. Chem. Soc.*, **67**, 829 (1895).

(4) Freund and Haase, *Ber.*, **26**, 1316 (1893); Hyde, *ibid.*, **32**, 1811 (1899).

TABLE I
YIELDS AND CONSTANTS OF HYDROCARBAZOLES

Carbazoles	% Yield, crude	M. p., °C. (cor.)	Analyses, %							
			Calculated			Found				
			C	H	N	Mol. wt.	C	H	N	Mol. wt.
1,2,3,4-Tetrahydro. ^a	88 ^d -95 ^e	117-118	84.2	7.7	8.2	171	84.2	8.0	8.5	170
2-Methyl-1,2,3,4-tetrahydro. ^b	65 ^d	98-100 ^e	84.3	8.2	7.6	185	84.2	8.6	7.2	190
3-Methyl-1,2,3,4-tetrahydro. ^b	70 ^d	108-111 ^h	84.3	8.2	7.6	185	84.3	8.0	7.5	184
2,4-Dimethyl-1,2,3,4-tetrahydro. ^a	60 ^d	103-106 ⁱ	84.4	8.6	7.0	199	84.2	8.6	7.0	202
1,2-Benzo-3,4-dihydro. ^a	80 ^d	163-164 ^j	87.6	6.0	6.4	219	87.7	5.8	6.8	217
6-Nitro-1,2,3,4-tetrahydro. ^c	60 ^f	169-172 ^k	66.7	5.6	13.0	216	66.7	5.2	12.8	221

^a From methyl alcohol. ^b From methyl alcohol or cyclohexane. ^c Red-brown crystals from 95% ethyl alcohol. ^d Acetic acid method. ^e Alcohol-hydrochloric acid method. ^f Aqueous mineral acid method; contaminated by *p*-nitrophenylhydrazine. ^g Borsche, *Ann.*, **359**, 62 (1908), reported 94° as m. p.; Plancher and Carrasco, *Atti. accad. Lincei*, [5] **13**, I, 632 (1904), reported 98-99°. ^h Plant and Rosser, *J. Chem. Soc.*, 2454 (1928). ⁱ Braun and Haensel (*Ber.*, **59**, 1999 (1926)) reported m. p. to be 96-99°; their product was red, ours was faintly yellow. ^j Ghigi, *Gazz. chim. ital.*, **60**, 194 (1930). ^k Borsche, *Ann.*, **359**, 49 (1908).

The alcohol-mineral acid method produced the *p*-nitrophenylhydrazone of cyclohexanone (m. p. 144-145°), which was converted to 6-nitro-1,2,3,4-tetrahydrocarbazole by boiling with 10% sulfuric acid according to the directions of Borsche.^g

Purification of Hydrocarbazoles.—It has been reported that tetrahydrocarbazole quickly turns yellow-brown in the air and that it has a fecal odor.^g We fractionally crystallized tetrahydrocarbazole from methyl alcohol and obtained a colorless, odorless product which was unchanged on standing three months in air and light. 1,2-Benzo-3,4-dihydrocarbazole was also easily purified, but the methyl-substituted tetrahydrocarbazoles became yellowish upon removal from the solvent, although the analytical values were satisfactory.

Freezing and Melting Points of 1,2,3,4-Tetrahydrocarbazole.—Four successive cooling curve determinations were made on a sample of highly purified tetrahydrocarbazole. The slope of the first plateau was zero within the accuracy of the determination, but the slopes of the subsequent plateaus became successively greater. The extrapolated freezing points were 118.4, 117.2, 115.4 and 111.7°, respectively. Purified tetrahydrocarbazole showed a capillary melting point (cor.) of 117-118° with the usual rate of heating; but with slow heating (1° per min.), the melting point was 113-114°, and the sample started to soften at 109°.

(5) Borsche, *Ann.*, **359**, 52 (1908).

(6) Zanetti, *Ber.*, **26**, 2006 (1893).

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The Preparation of 4-Thiazolidones by the Reaction of Thioglycolic Acid with Schiff Bases

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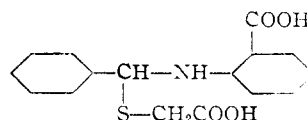
The appearance of a paper by Erlenmyer and Oberlin¹ on the reaction of Schiff bases with thioglycolic acid prompts the writer to report on similar work in this field carried out in this Laboratory.

We have found that in many instances 4-thiazolidones (Table I) can be prepared conveniently by the reaction of thioglycolic acid with Schiff bases in refluxing benzene. By removing the water continuously as it forms, it was possible to follow the condensation and determine the re-

action time. In some cases the Schiff base was prepared in the same solvent. When the calculated amount of water had separated, the thioglycolic acid was added and refluxing was continued. The initial step, the addition of the thiol group to the anil, was usually accompanied with the evolution of heat. Where the Schiff base was only slightly soluble in benzene, vigorous mechanical stirring was employed.

Several other procedures were tried in the preparation of 2,3-diphenyl-4-thiazolidone. At room temperature, in the absence of solvent a 35% yield of the product was obtained; in alcohol or glacial acetic acid, the yield was 12%. The reaction of ethyl thioglycolate with benzylideneaniline in refluxing Skellysolve E for sixteen hours gave an 8% yield of the thiazolidone.

When thioglycolic acid was added to a stirred suspension of benzylidene-2-carboxyaniline in benzene an exothermic reaction occurred and a clear solution resulted. In a short time, a solid which proved to be the addition compound, separated from the benzene solution. When the



reaction was run in refluxing benzene for twenty-four hours, approximately 75% of the calculated amount of water was collected. Although thiazolidone formation is indicated, the product has not yet been isolated from the reaction mixture.

Experimental Part²

General Procedure for the Preparation of the 4-Thiazolidones.—The following general directions for the preparation of the thiazolidones (Table I) includes the procedure for the preparation of the Schiff base in the same solvent. A mixture of 0.2 mole of benzaldehyde and 0.2 mole of aniline in 100 cc. of dry benzene was refluxed with a water separator connected to the apparatus. After about 3.5 cc. of water had been collected, 20 g. of thioglycolic acid was added and refluxing continued until an additional 3.5 cc. of water had separated. The amount of water collected

(1) Erlenmyer and Oberlin, *Helv. Chim. Acta*, **30**, 1329 (1947).

(2) All melting points are uncorrected unless otherwise indicated.