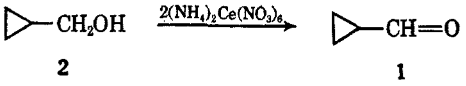

one-step preparation of **1** from commercially available starting materials.

Several other methods are known for the preparation of **1**. Of the few known oxidative routes to **1**,[2–5] only the copper-catalyzed air oxidation of cyclopropanemethylamine gives **1** in greater than 50% yield.[5] However, this method is experimentally more complex than the cerium(IV) oxidation. Good yields of **1** are obtained by several reductive methods.[6–10] A summary of the known routes to **1** is presented in Table I. It is apparent from inspection of the table that the yield of **1** obtained by the cerium(IV) oxidation is as high as that obtained by any other method. Although the starting materials for the other methods may be less expensive than those for the cerium(IV) oxidation, the extremely simple procedure for the isolation of **1** from the cerium(IV) oxidation of **2** makes this method attractive.

TABLE I

METHODS OF PREPARATION OF CYCLOPROPANECARBALDEHYDE

Substrate[a]	Reagent	Yield of aldehyde, %	Ref
RCH_2OH	$(NH_4)_2Ce(NO_3)_6$	64[b]	*c*
RCH_2OH	CrO_3	30[b]	2
RCH_2OH	H_2O_2, Fe(II)	30–37[d]	3
RCH_2OH	Al(O-*i*-Pr)$_3$	20[d]	4
RCH_2NH_2	O_2, Cu	54–57[b]	5
RCN	$LiAlH_4$	48[b]	6
RCN	$LiAlH(OEt)_3$	69[e]	7
RCN	LiAlH(O-*n*-Bu)$_3$	66,[b] 89[e]	7
RCOCl	LiAlH(O-*t*-Bu)$_3$	42[e]	8
$RCONC_2H_4$	$LiAlH_4$	60,[b] 67[e]	9
$RCON(CH_3)_2$	$LiAlH_2(OEt)_2$	78[e]	10
$RCON(CH_3)_2$	$LiAlH(OEt)_3$	67[e]	10
$RCONC_5H_{10}$	$LiAlH_4$	20[b]	6
$RCONHNHSO_2Ph$	Na_2CO_3	16[e]	*f*

[a] R = cyclopropyl. [b] Isolated yield. [c] This work. [d] Yield by glpc. [e] Yield from 2,4-dinitrophenylhydrazone derivative. [f] J. D. Roberts, *J. Am. Chem. Soc.*, **73**, 2959 (1951).

Experimental Section

To 8.07 g (0.112 mole) of cyclopropanemethanol (**2**) (Aldrich Chemical Co.) was added a solution of 136.5 g (0.241 mole) of ceric ammonium nitrate (G. F. Smith Chemical Co.) in 250 ml of water. The cloudy, deep red solution was heated on a steam bath until it was colorless (5–15 min). (The cloudiness can be avoided by filtering the ceric ammonium nitrate solution through a sintered-glass funnel prior to its addition to **2**.) The solution was cooled, saturated with sodium chloride, and transferred to a separatory funnel. Water (400 ml) was added[11] and the solution was extracted four times with 50-ml portions of methylene chloride.[12] The combined methylene chloride layers were dried over a mixture of magnesium sulfate and sodium bicarbonate. The volume of the methylene chloride solution was reduced to 50–60 ml by distillation through a 30-cm Vigreux column at atmospheric pressure. A quantity of 4 ml of bromobenzene was added to the residue and the residue was distilled through a 20-cm vacuum-jacketed column packed with glass helices into a receiver flask cooled in an ice–acetone bath. A quantity of 6.1 g of material was isolated, bp 97–99° (760 mm) [lit.[9] bp 97–100° (740 mm)], which was 82.6% (by weight) **1** (0.027 mole) and 17.4% methylene chloride as shown by nmr. The yield of **1** was 64%. In a similar experiment, 4.85 g of a mixture composed of 93% (by weight) **1** and 7% methylene chloride was isolated. The yield of **1** was 57%.[13] Glpc determination of the amount of **1** in the methylene chloride layer showed that little product was lost in the distillation.

A 0.5-g-scale reaction was carried out as before except that sodium chloride and the addition of extra water were omitted in the isolation procedure. Glpc analysis of the methylene chloride layer indicated that the yield of **1** was comparable with that obtained in the original procedure.

We have found that aqueous acetic acid[1c] and aqueous acetonitrile are useful solvents for cerium(IV) oxidations of water-insoluble compounds.

Registry No.—**1**, 1489-69-6; **2**, 2516-33-8.

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(2) E. D. Venus-Danilova and V. F. Kazimirova, *Zh. Obshch. Khim.*, **8**, 1438 (1938); *Chem. Abstr.*, **33**, 4204 (1939).

(3) C. C. Lee, A. J. Cessna, and M. K. Frost, *Can. J. Chem.*, **43**, 2924 (1965).

(4) C. C. Lee and I. S. Bhardwaj, *ibid.*, **41**, 1031 (1963).

(5) Z. I. Shuikina, *Zh. Obshch. Khim.*, **7**, 983 (1937); *Chem. Abstr.*, **31**, 5332 (1937).

(6) L. I. Smith and E. R. Rogier, *J. Am. Chem. Soc.*, **73**, 4047 (1951).

(7) H. C. Brown and C. P. Garg, *ibid.*, **86**, 1085 (1964).

(8) H. C. Brown and B. C. Subba Rao, *ibid.*, **80**, 5377 (1958).

(9) H. C. Brown and A. Tsukamoto, *ibid.*, **83**, 4549 (1961).

(10) H. C. Brown and A. Tsukamoto, *ibid.*, **86**, 1089 (1964).

(11) Water was added to facilitate the separation of the organic and aqueous layers.

(12) The use of ether as extractant led to lower yields.

(13) Attempts to isolate **1** by preparative glpc on a Carbowax 20 M/Chromosorb P column resulted in only 30–40% yields of **1**.

Structure of the Product of Condensation of Aromatic 1,2-Diamines with Aromatic 1,2-Dicarboxaldehydes[1]

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Ried and co-workers have reported[2] structures **1b**–**4b** as products of the condensations of *o*-phenylenediamine (**5**), 2,3-naphthylenediamine (**6**), and 1,2-naphthylenediamine (**7**), with *o*-phthalaldehyde (**8**) and 2,3-naphthalenedicarboxaldehyde (**9**). (see Chart I).

The postulation of these structures appears in doubt, in view of the chemical[3] and recent spectroscopic[4] confirmation of ·*o*-benzylene-2,1-benzimidazole (**10**) as the product obtained by the condensation of Thiele and Falk[5] of **5**·2HCl with **8**. Also, structure **1b** has recently been questioned[3c] on the basis of analogy with the assignment[3c] of structure **10** to the compound of Thiele and Falk. However, even if **10** is correct, it should not be concluded that the reactions involving *free* amines **5**, **6**, and **7** give **1a**–**4a** and not **1b**–**4b**. Whereas condensation of **5**·2HCl with 2 moles of benzaldehyde has been shown to give 1-benzyl-2-phenylbenzimidazole (**11**),[4,6] N,N′-dibenzylidene-*o*-phenylene-

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(1) Grateful acknowledgment is made to the Foundation for the Advancement of Graduate Study in Engineering of Newark College of Engineering for support of this work.

(2) W. Ried and H. Bodem, *Chem. Ber.*, **89**, 708 (1956); W. Ried and E. Torinus, *ibid.*, **92**, 2902 (1959).

(3) (a) F. M. Rowe, W. C. Dovey, B. Garforth, E. Levin, J. D. Pask, and A. T. Peters, *J. Chem. Soc.*, 1796 (1935); (b) A. Bistrzycki and W. Schmutz, *Ann.*, **415**, 1 (1918); (c) F. Sparatore and G. Bignardi, *Gazz. Chim. Ital.*, [7] **92**, 606 (1962).

(4) D. Amos and R. G. Gillis, *Australian J. Chem.*, **17**, 1440 (1964). A referee has called this paper to the author's attention.

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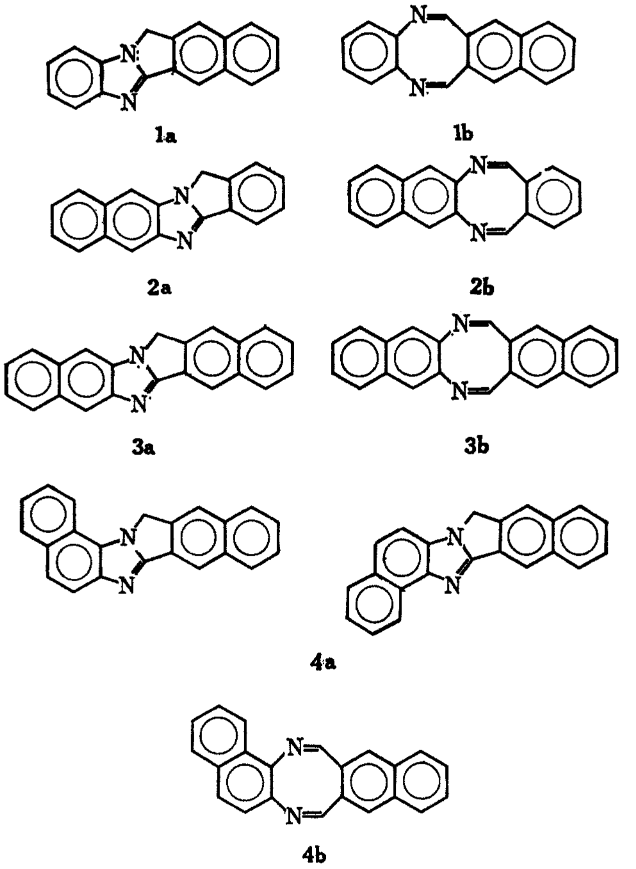
(6) K. Hofmann, "Imidazole and Derivatives," Part I, Interscience Publishers, Inc., New York, N. Y., 1953, pp 266, 267, and references cited therein.

CHART I



diamine (12) was reported as the product using free amine **5** in cold ethanol, although **12** was unstable, rearranging readily to **13**.[6]

In view of this reservation, the condensations of Ried and co-workers were repeated. Free amines were used in all cases, and in addition, **5**·2HCl was used. The nmr spectra of the products were similar to those obtained by Amos and Gillis[4] for **10** and by Hawthorne and coworkers[7] for a similar adduct. Each compound evinced an aromatic multiplet centered at *ca.* τ 2.3 and a singlet at *ca.* 4.5. (Relative areas corresponded to theory.) The latter chemical shift contrasts with the value of τ 1.5 for the aldimine proton of benzylideneaniline. The aforementioned results certainly rule out diimine structures **1b**–**4b** and support the formation of **1a**–**4a**[8] under either acidic or nonacidic[9] conditions.

Experimental Section[10]

Chemicals.—*o*-Phenylenediamine was Eastman Yellow Label material. *o*-Phthalaldehyde was from L. Light and Co., Ltd., England. 2,3-Naphthylenediamine was from Columbia Organic Chemicals, Columbia, S. C. 1,2-Naphthylenediamine was obtained from Aldrich Chemical Co. All the above materials were either sublimed or recrystallized and stored under nitrogen before use. *o*-Phenylenediamine dihydrochloride was Eastman White Label material and was used without further purification. 2,3-Naphthalenedicarboxaldehyde was prepared by the method of Ried and Bodem,[2] and was stored under nitrogen before use.

Amine Hydrochloride–Aldehyde Condensation. General Method.[5]—The stoichiometric amount of *o*-phenylenediaminedihydrochloride was dissolved in water and added to a solution of either *o*-phthalaldehyde in water or 2,3-naphthalenedicarboxaldehyde in water–ethanol. The solution was made neutral with alkali and the resulting solid was either recrystallized from the appropriate solvent or sublimed.

Amine–Aldehyde Condensation. General Method.[2]—The stoichiometric amount of aldehyde dissolved in absolute ethanol was added to a solution of diamine in ethanol under nitrogen. The product was isolated either by filtering off the precipitate or by evaporating the solution to dryness. The crude product was purified by recrystallization from the appropriate solvent or by sublimation.

All products showed melting points identical with literature[2,5] values. In the case of compounds **1a**, **2a**, and **10**, melting points, mixture melting points, and infrared spectra of products obtained using either free amine or amine hydrochloride methods were identical.

Registry No.—**1a,** 10561-93-0; **1b,** 258-91-3; **2a,** 248-53-3; **2b,** 258-92-4; **3a,** 10561-96-3; **3b,** 258-95-7; 14H-benz[*f*]isoindolo[2,1-*a*]naphth[2′,1′-*d*]imidazole, 10562-17-1; 8H-benz[*f*]isoindolo[2,1-*a*]naphth[1′,2′-*d*]imidazole, 10562-18-2; **4b,** 227-06-5; **11,** 739-88-8.

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[7] J. O. Hawthorne, E. L. Mihelic, M. S. Morgan, and M. H. Wilt, *J. Org. Chem.*, **28**, 2831 (1963).

[8] Systematic names for these compounds are **1a**, 12H-benz[*f*]isoindolo[2,1-*a*]benzimidazole; **2a**, 7H-isoindolo[2,1-*a*]naphth[3′,2′-*d*]imidazole; **3a**, 14H-benz[*f*]isoindolo[2,1-*a*]naphth[3′,2′-*d*]imidazole; **4a**, 8H-benz[*f*]isoindolo[2,1-*a*]naphth[1′,2′-*d*]imidazole and 14H-benz[*f*]isoindolo[2,1-*a*]naphth[2′,1′-*d*]imidazole. *Cf.* A. M. Patterson, L. T. Cappell, and D. F. Walker, "The Ring Index," 2nd ed, American Chemical Society, Washington, D. C., 1960, RRI 2923, 4174, 5554, 5555, for model structures.

[9] Compound **10** was also formed under nonacidic conditions, using free amines **5** and **8**. See the Experimental Section.

[10] Nmr spectra were recorded on a Varian A-60A spectrometer equipped with a variable-temperature probe and a CAT (Computer of Average Transients), the latter being used for several of the spectra.

A New Synthesis of 1-Methyl-1,6-dihydro-6-oxonicotinic Acid and 1-Methyl-1,4-dihydro-4-oxonicotinic Acid Derivatives[1a]

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In connection with an interest in 1-methyl-1,4-dihydro-4-oxonicotinamide (**1a**) as a niacin metabolite,[2–4] an attempt was made to synthesize the ester (**1b**) by the self-condensation of ethyl β-methylaminoacrylate (**2**). This method has been reported[5] to furnish 1-aryl-4-pyridones from β-arylaminoacrylic esters. On heating **2** at 145°, a crystalline product was obtained in 59% yield. Hydrolysis of this ester (**3**) gave 1-methyl-1,6-dihydro-6-oxonicotinic acid (**4**), showing that the condensation of the β-alkylamino ester occurs by 1,2-carbonyl addition. This reaction represents a convenient synthesis of **4** and its derivatives. An improved synthesis of **1a** resulted from N-methylation of 4-

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[2] M. L. Wu Chang and B. C. Johnson, *J. Biol. Chem.*, **234**, 1817 (1959).

[3] M. L. Wu Chang and B. C. Johnson, *ibid.*, **236**, 2096 (1961).

[4] T. Wieland, C. Fest, and G. Pfleiderer, *Ann.*, **642**, 163 (1961).

[5] M. V. Rubtsov, *J. Gen. Chem. USSR*, **9**, 1517 (1939); *cf. Chem. Abstr.*, **34**, 2845 (1940).