remarkable retardation of the reaction. Chlorobenzene was also unsuitable for the solvent.

Among tertiary amines employed in the thermolysis, Dabco was the most effective and *N,N*-diethylaniline, which showed negative effect, was the least. With triethylamine, thermolysis gave the azirine **2a** in a high yield, but the reaction was slower than with Dabco. Hence, the order of the effectiveness is just in the order of basicity of the amines.

By measuring the rate of nitrogen evolution in the thermolyses, nitrogen release from the vinyl azide **1a** was found to obey good first-order kinetics. The rate constants are listed in Table II. The rates are equal

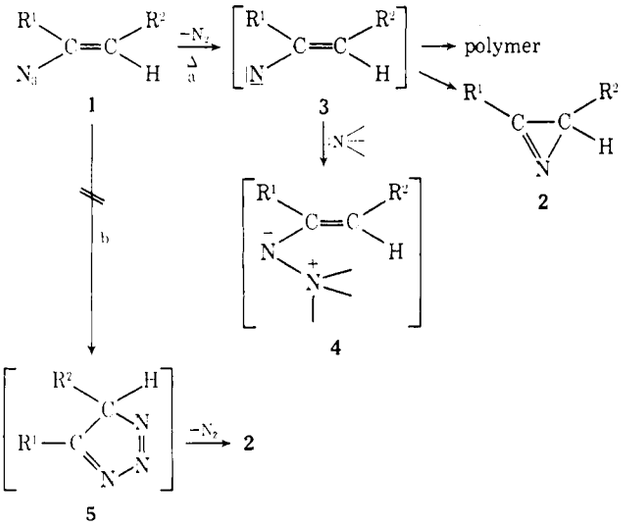
TABLE II

RATE CONSTANT FOR N_2 EVOLUTION IN THERMOLYSIS OF α-AZIDOSTYRENE (**1a**) AT 110°

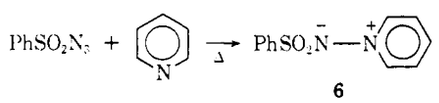
Run[a]	Solvent	Amine catalyst	$k \times 10^3$, sec^{-1}
1	Toluene		2.03
2	Toluene	NEt_3	2.03
3	Chlorobenzene	NEt_3	1.04
4	Toluene	$PhNEt_2$	1.92
5	Toluene	Dabco	2.15

[a] Run numbers correspond to those in Table I.

within an experimental error when toluene was employed as a solvent, showing that these amines do not participate in the step of nitrogen release from the azide. The low rate in chlorobenzene is due to the increase in solvent polarity, since the highly polarized vinyl azide should be more stabilized than the intermediate or the product by a polar solvent. Consequently, it is reasonable to postulate a nitrene intermediate **3** which is formed with the release of nitrogen from the azide **1** in the initial step. The intermediate **3** will convert into



an azirine **2** by intramolecular cyclization or into polymers. However, in the presence of a tertiary amine, the formation of a 1:1 adduct **4** is expected and this intermediate will give an azirine exclusively. Postulation of the adduct **4** is supported by the fact that a relatively stable adduct **6** is obtained in decomposition



6

of benzenesulfonyl azide in refluxing pyridine.[10] Such a coordination is sterically hindered in the case of *N,N*-diethylaniline, which has poor coordinating ability because of its lower basicity. In this case, the presence of the amine instead promotes the polymerization reaction.

Our runs were not successful in capturing the nitrene **3**. Similar failures in detecting nitrenes are reported in some pyrolyses and photolyses of vinyl azides.[1,11,12] However, these failures to detect any of the nitrenes do not necessarily exclude the formation of a nitrene intermediate.

As an alternative mechanism, Smolinsky proposed a triazole intermediate **5** formed by an initial cyclization.[1] This cyclization does occur in a strong basic medium, but does not take place in neutral or protic solvents, as loss of nitrogen molecule occurs much faster.[6,13] If path b to a triazole **5** in neutral solvents is promoted by an amine as a base, the rate of nitrogen evolution of the thermolysis with amines should be greater than that without amines. However, the rates are equal and, therefore, path b may be excluded.

Experimental Section

Infrared spectra of the products were obtained on a JASCO IR-E spectrophotometer and showed good agreements with those of authentic samples. Gas–liquid phase chromatographic analyses were performed on a Ohkura MS-1100 instrument using the following column: 4 mm × 2 m, 3% silicon gum SE-52 on 80–100 mesh Chromosorb W.

Materials.—α-Azidostyrene (**1a**) was prepared by Smolinsky's procedure[1] and 1-azido-1-phenylpropene (**1b**) and 2-azido-1-octene (**1c**) were obtained by the method of Fowler.[4] Authentic azirines **2a–c** were prepared by photolysis of the corresponding vinyl azides:[2] **2a**, bp 76° (10 mm), ir 1745 cm^{-1} (C=N); **2b**, bp 78° (10 mm), ir 1740 cm^{-1} (C=N); **2c**, bp 87° (40 mm), ir 1765 cm^{-1} (C=N).

Thermolysis of Vinyl Azides.—The general procedure for the thermolysis was as follows. In a 50-ml three-necked flask fitted with a dropping funnel, a magnetic stirrer, a thermometer, and a condenser whose top was connected with a gas buret, a solution of a tertiary amine was heated to the reaction temperature under nitrogen atmosphere. Then a vinyl azide was added through the funnel all at once and the rate of nitrogen evolution was measured. On a parallel run performed under the same conditions, the yield of a produced azirine was estimated by glpc.

Registry No.—**1a**, 16717-64-9; **1b**, 28022-21-1; **1c**, 42393-62-4; **2a**, 7654-06-0; **2b**, 16205-14-4; **2c**, 42393-63-5.

(10) T. Curtious and J. Rissom, *J. Prakt. Chem.*, **125**, 311 (1930).
(11) W. Lwowski, A. Hartenstein, C. de Vita, and R. L. Smick, *Tetrahedron Lett.*, 2497 (1961); W. Lwowski and T. W. Mattingly, Jr., *J. Amer. Chem. Soc.*, **87**, 1947 (1965).
(12) G. R. Harvey and K. W. Ratts, *J. Org. Chem.*, **31**, 3907 (1966).
(13) H. Reimlinger, *Chem. Ber.*, **103**, 1900 (1970).

One-Step Synthesis of 1,1-Dimethyl- and 1-Spirocycloalkano-1,2,3,4-tetrahydro-β-carbolines

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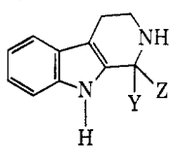
Received July 23, 1973

The condensation of tryptamine and substituted tryptamines with aldehydes and with α-keto acids in aqueous solution to yield 1-alkyl- and 1-alkyl-1-carboxy-

1,2,3,4-tetrahydro-β-carbolines, respectively, is a well-documented reaction.[1] 6-Hydroxy- and alkoxytryptamine derivatives also react quite readily with acetone in aqueous solution, affording the expected 1,1-dimethyl-1,2,3,4-tetrahydro-β-carboline derivatives.[2] Tryptamine and 5-methoxytryptamine, on the other hand, do not react with simple ketones to any appreciable extent under the same conditions, and the corresponding carbolines have been prepared by cyclization of the Schiff bases using dilute sulfuric acid[3] or phosphorus oxychloride[2] as catalysts. A previous report of the cyclodehydration of tryptamine and acetone under rather unusual circumstances lacks adequate proof of the structure of the product.[4]

Using acetone as solvent, and with ethyl polyphosphate[5] as catalyst, we were able to prepare 1,1-dimethyl-1,2,3,4-tetrahydro-β-carboline (I) in one step in



I, Y = Z = Me
II, Y, Z = $(CH_2)_4$
III, Y, Z = $(CH_2)_5$

66% yield. The melting point of our product (140–141°) is practically the same as that reported by Vanderwerff,[3] and quite different from that of Hester's compound (111.5–115.5°).[2] The uv spectra, however, are similar, and our structural assignment is supported by ir and nmr spectral evidence. Also, the *N*(2)-benzoyl derivative, judging from its melting point, is the same as that described by Manske over 40 years ago.[4]

1-Spirocyclopentano- (II) and 1-spirocyclohexano-1,2,3,4-tetrahydro-β-carboline (III) were obtained similarly by cyclodehydration of tryptamine and cyclopentanone or cyclohexanone, respectively. The low solubilities of the hydrochlorides in dilute acid made their isolation and purification as such particularly easy. The uv spectra of all three compounds show that the indole chromophore is intact. The absence of ir absorption around 1665 cm^{-1} excludes the possibility of their being Schiff bases, and the absence of C(2)-H signals in the aromatic region of the nmr spectra shows that cyclization did indeed take place.

Experimental Section

Ir spectra were recorded with Perkin-Elmer 337 and 621 spectrophotometers, uv spectra with a Zeiss DMR-21, and nmr spectra with a Varian A-60 spectrometer using TMS as internal reference. Elementary analyses were performed by F. and E. Pascher, Bonn. Tlc was carried out on Merck silica gel chromatofoils, using cyclohexane–$CHCl_3$–Et_2NH (5:4:1). Melting points were determined in open capillaries, and are uncorrected.

1,1-Dimethyl-1,2,3,4-tetrahydro-β-carboline (I).—A solution of tryptamine (0.66 g) and ethyl polyphosphate (3.0 g) in acetone (80 ml) was refluxed during 36 hr. The solvent was then removed under vacuum, and the residue was diluted with water and neutralized with 4 *N* NaOH to yield a precipitate (0.54 g) which, recrystallized from cyclohexane, melted at 140–141°. The R_f values of tryptamine and of the product were 0.11 and 0.24, respectively: λ_{max}^{EtOH} (log ε) 225 (4.55), 274 (3.78), 279 (3.80), 289 nm (3.71); $\bar{\nu}_{max}^{KBr}$ 1145 (C–N), 1450 cm^{-1}(*gem*-dimethyl); δ^{CDCl_3} 1.46 (s, 6 H, *gem*-dimethyl), 2.15 (s, 1 H, 2-H), 2.71 and 3.21 (2 t, J = 5.8 Hz, 4 H, CH_2CH_2), 7.0–7.5 (m, 4 H, 5-, 6-, 7-, and 8-H), 8.0 (br s, 1 H, 9-H); the signals at δ 2.15 and 8.0 disappear upon exchange with D_2O. *Anal.* Calcd for $C_{13}H_{16}N_2$: C, 77.96; H, 8.05; N, 13.99. Found: C, 77.80; H, 8.25; N, 13.70.

Benzoylation of I yielded a compound which after recrystallization from acetone melted at 280–282°: λ_{max}^{EtOH} (log ε) 225 (4.60), 273 (3.72), 279 (3.69), 289 nm (3.61); $\bar{\nu}_{max}^{KBr}$ 1630 cm^{-1} ($PhCONR_2$). *Anal.* Calcd for $C_{29}H_{20}N_2O \cdot {}^1/_4H_2O$: C, 77.74; H, 6.70; N, 9.07. Found: C, 77.64; H, 6.61; N, 9.13.

I, heated with an excess of methyl iodide in acetone, afforded the methiodide, which decomposed without melting at 200°: λ_{max}^{EtOH} (log ε) 225 (4.81), 272 (3.88), 278 (3.84), 288 nm (3.76). *Anal.* Calcd for $C_{15}H_{22}N_2I$: C, 50.57; H, 5.94; N, 7.86; I, 53.62. Found: C, 50.77; H, 5.89; N, 7.77; I, 35.71.

1-Spirocyclopentano-1,2,3,4-tetrahydro-β-carboline (II) Hydrochloride.—A solution of tryptamine (0.70 g) in cyclopentanone (9.0 ml), to which ethyl polyphosphate (0.45 ml) was added, was kept at 100° during 12 hr. The reaction mixture was diluted with H_2O (40 ml) and acidified with concentrated HCl (4 ml), whereupon a crystalline precipitate (0.60 g) appeared which, recrystallized from H_2O, melted at 263–264°: λ_{max}^{EtOH} (log ε) 222 (4.68), 272 (3.94), 279 (3.92), 289 nm (3.76). *Anal.* Calcd for $C_{15}H_{19}N_2Cl$: C, 68.55; H, 7.30; N, 10.66; Cl, 13.49. Found: C, 68.59; H, 7.33; N, 10.78; Cl, 13.54.

The free base, recrystallized from cyclohexane, melted at 139–140°; δ^{CDCl_3} 1.43 (s, 1 H, 2-H), 1.88 (s, 8 H, 4 CH_2), 2.71 and 3.17 (2 t, J = 5.5 Hz, 4 H, CH_2CH_2), 7.0–7.6 (m, 4 H, 5-, 6-, 7-, and 8-H), 7.73 (br s, 1 H, 9-H); the signals at δ 1.43 and 7.73 disappear upon exchange with D_2O.

1-Spirocyclohexano-1,2,3,4-tetrahydro-β-carboline (III) Hydrochloride.—A solution of tryptamine (0.70 g) in cyclohexanone (9.0 ml), to which ethyl polyphosphate (0.45 ml) was added, was kept at 100° during 12 hr. The reaction mixture was diluted with H_2O (40 ml) and acidified with concentrated HCl (4 ml), whereupon the product (0.62 g) crystallized: recrystallized from H_2O, mp 279–280°; λ_{max}^{EtOH} (log ε) 222 (4.62), 272 (3.92), 279 (3.91), 289 nm (3.79). *Anal.* Calcd for $C_{16}H_{21}N_2Cl \cdot {}^1/_2H_2O$: C, 67.21; H, 7.74; N, 9.78; Cl, 12.40. Found: C, 66.83; H, 7.91; N, 9.89; Cl, 12.56.

The free base, recrystallized from cyclohexane, melted at 133.5–135°: δ^{CDCl_3} 1.64 (s, 11 H, 5 CH_2 and 2-H), 2.65 and 3.09 (2 t, J = 5.5 Hz, 4 H, CH_2CH_2), 6.95–7.55 (m, 4 H, 5-, 6-, 7-, and 8-H), 7.69 (br s, 1 H, 9-H); upon exchange with D_2O, the signal at δ 1.64 decreased to 10 H, and the signal at δ 7.69 disappeared.

Acknowledgments.—This work was supported by a FORGE grant. We are also grateful to Mrs. A. Bau, Mr. R. Clavijo, and Mr. J. Ferrer for spectral analyses.

Registry No.—I, 6678-85-9; I benzoyl derivative, 42282-64-4; I MeI, 42282-65-5; II, 42282-67-7; II HCl, 42282-68-8; III, 6716-66-1; III HCl, 6716-70-7; tryptamine, 61-54-1; acetone, 67-64-1; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1.

(1) W. M. Whaley and T. R. Govindachari, "Organic Reactions," Vol. VI, R. Adams, Ed., Wiley, New York, N. Y., 1951, p 151.
(2) J. B. Hester, *J. Org. Chem.*, **29**, 2864 (1964).
(3) W. D. Vanderwerff, *Diss. Abstr.*, **21**, 765 (1960).
(4) R. H. F. Manske, *Can. J. Res.*, **5**, 592 (1931).
(5) Y. Kanaoka, Y. Ban, K. Miyashita, K. Irie, and O. Yonemitsu, *Chem. Pharm. Bull.*, **14**, 934 (1966).

Stereochemistry of Reduction of Substituted Cyclohexanones with Lithium Triisobutyl-*n*-butylaluminate[1]

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Received June 12, 1973

We have recently reported the results of an investigation concerned in part with evaluation of triisobutyl-

(1) We are indebted to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work and to the Ethyl Corp. for a generous sample of triisobutylaluminum.