# Reactions of Group IV Organometallic Compounds. III. Addition of Trimethylsilyldialkylamine to Epoxide

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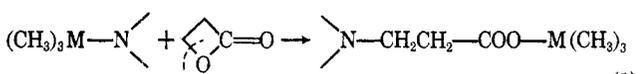
The addition reaction of trimethylsilyldialkylamine to γ,γ,γ-trichloropropylene oxide at 80° proceeds through the normal fission of the epoxide ring, giving α-trichloromethyl-β-dialkylaminoethoxytrimethylsilane IIIa–c. Treatment of IIIa–c with protic reagents caused desilylation, giving α-trichloromethyl-β-dialkylaminoethanol IVa–c. Nmr spectra of IIIa–c and IVa–c were typical ABX. The conformation of IIIa–c estimated from their vicinal coupling constants is ascribed as mainly VII, in which the trichloromethyl and dialkylamino groups are situated *trans* to each other; however, that of IVa–c is twisted slightly from *staggared* to *eclipsed* form because of hydrogen bonding, N···H—O. Although the reactivity of epichlorohydrin was lower than that of γ,γ,γ-trichloropropylene oxide, the mode of the ring opening was common.

Addition reactions of organosilylamines with a variety of polar double bonds have been reported in the case of carbon dioxide,[2] carbon disulfide,[3] isocyanate,[4-7] isothiocyanate,[5] ketene,[8] di-*p*-tolylcarbodiimide,[4] and chloral.[4] Also it has been shown that β-propiolactone was cleaved selectively with alkyl oxygen bond fission by trimethylsilyl- and trimethylgermyldialkylamine, giving, respectively, the trimethylsilyl and trimethylgermyl ester of N,N-dialkyl-β-alanine.[1,9]



M = Si and Ge (1)

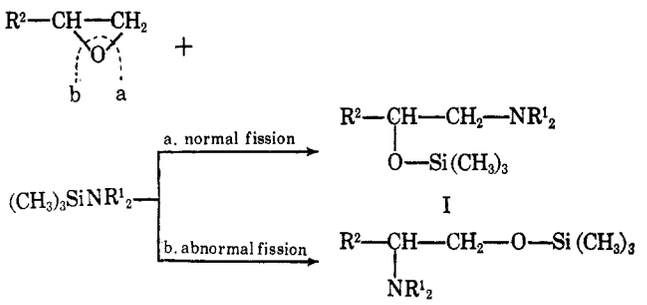
The mode of the ring fission and the acceleration of rate by higher basicity of reagent and in polar media predict that trimethylsilyl- and trimethylgermylamine behave as a nucleophilic reagent on β-propiolactone.[10]

In this paper, the ring-opening reaction between epoxide and trimethylsilyldialkylamine is studied, and the structures of the adducts, as well as those of β-dialkylamino alcohols derived from them, are elucidated.

## Results and Discussion

Two possible β-dialkylaminosiloxanes I and II, may be obtained from the ring opening reaction of epoxide $R^2$—CH(—O—)—$CH_2$, with trimethylsilyldialkylamine $(CH_3)_3SiNR^1_2$, as visualized in eq 2.

The reaction was carried out by heating the mixture of trimethylsilyldialkylamine and γ,γ,γ-trichloropropylene oxide or epichlorohydrin at 80°. Adducts α-trichloromethyl- or α-chloromethyl-β-dialkylaminoethoxytrimethylsilane IIIa–d, obtained by distilling the product under reduced pressure, are shown in Table I.



(2)

The adduct with γ,γ,γ-trichloropropylene oxide ($R^2$ = $Cl_3C$) showed the methine proton signal at extremely low field, that is, τ 5.93–5.99 at room temperature, as shown in Table II.

According to Silverstein and Bassler,[11] the chemical shift of methylene proton adjacent to both $CF_3$ and RO or HO groups appeared at τ 6.07 or 6.27, respectively. However, the methylene proton adjacent to $CF_3$ and $R_2N$ groups shows the signal at considerably higher field, that is, τ 7.06. Therefore, it may be presumed that the methine proton of the adducts IIIa–c is that of normal product I.

This conclusion is also supported by the appearance of a sharp singlet for the trimethylsiloxy group at τ 9.82. Trimethylsiloxy protons show a sharp singlet around τ 10.0 for most trimethylalkoxysilanes; however, in this case the peak shifts to considerably lower field because of the existence of the strongly electronegative trichloromethyl group at the α-carbon atom.

Treatment of IIIa–c with a protic reagent such as methanol or acetic acid caused desilylation, giving α-trichloromethyl-β-dialkylaminoethanols IVa–c as well as trimethoxysilane or trimethylsilyl acetate, respectively. Addition of excess amounts of hydrochloric acid to IIIb in dry ether gave the hydrochloride of IVb. Their melting points, analytical data, and $\nu_{C-O}$ are shown in Table III.

The existence of $\nu_{C-O}$ around 1110 $cm^{-1}$ for IVa–c also indicates that the β-aminoethanols obtained are secondary alcohols.[12]

Appearance of methylene multiplets above τ 6.9, whose position was almost the same as that of dialkylamino protons, and the absence of signal between τ

(1) Part II: K. Itoh, S. Sakai, and Y. Ishii, *Tetrahedron Letters*, 4941 (1966).
(2) H. Breederveld, *Rec. Trav. Chim.*, **81**, 276 (1962).
(3) H. Breederveld, *ibid.*, **79**, 1126 (1960).
(4) A. G. Davies and Y. Ishii, unpublished result.
(5) J. F. Klebe, J. B. Bush, Jr., and J. E. Lyons, *J. Am. Chem. Soc.*, **86**, 4400 (1964).
(6) W. Fink, *Chem. Ber.*, **97**, 1433 (1964).
(7) D. Y. Zhinkin, M. M. Morgunova, K. K. Popkov, and K. A. Andrianov, *Dokl. Akad. Nauk SSSR*, **158**, 641 (1964).
(8) W. W. Limburg and H. W. Post, *Rec. Trav. Chim.*, **81**, 430 (1962).
(9) K. Itoh, S. Sakai, and Y. Ishii, *J. Org. Chem.*, **31**, 3948 (1966).
(10) K. Itoh, Y. Kato, S. Sakai, and Y. Ishii, *J. Chem. Soc. Japan, Ind. Sect.*, in press; *Chem. Commun*, 36 (1967).
(11) R. M. Silverstein and G. C. Bassler, "Spectromeric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 88.
(12) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, Methuen & Co., Ltd., London, 1958, p 108.

TABLE I

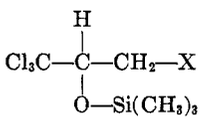
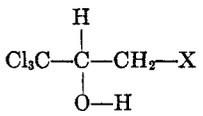
PRODUCT FROM THE REACTION OF TRIMETHYLSILYLDIALKYLAMINE, $(CH_3)_3SiX$, WITH EPOXIDE[a] $R^2—CH—CH_2$ (O)

| Compd | $R^2$ | X | Bp, °C (mm) | Time, hr | Yield, % | Cl, % Found | Cl, % Calcd |
|---|---|---|---|---|---|---|---|
| | | | | 1.3 | 40 | | |
| IIIa | $Cl_3C$ | $N(CH_3)_3$ | 79.5–80.2 (2.9) | 5.0 | 45 | 38.23 | 38.16 |
| | | | | 19.0 | 91 | | |
| | | | | 1.3 | 65 | | |
| IIIb | $Cl_3C$ | $N(C_2H_5)_2$ | 103.4–104.0 (3.2) | 3.0 | 72 | 34.47 | 34.67 |
| | | | | 22.0 | 87 | | |
| IIIc | $Cl_3C$ |  | 103.0–104.0 (1.0) | 1.3 | 89 | 32.89 | 33.35 |
| IIId | $ClCH_2$ |  | 85.0–87.0 (1.0) | 22.0 | 45 | 14.22 | 14.18 |

[a] Ten-millimole scale, without solvent at 80°.

TABLE II

NMR SPECTRA OF α-TRICHLOROMETHYL-β-DIALKYLAMINOETHOXYTRIMETHYLSILANES IIIa–c, α-TRICHLOROMETHYL-β-DIALKYLAMINOETHANOLS IVa–c, HYDROCHLORIDE OF IVb, V, AND α-TRICHLOROMETHYL-β-BROMOETHANOL (VI)[a]

| Compd | X | Compd no. | Temp, °C | Vicinal coupling constant, cps $J_{AX}$ | Vicinal coupling constant, cps $J_{BX}$ | Chemical shift of methine proton ($\tau$), ppm | Population of VII |
|---|---|---|---|---|---|---|---|
|  | $N(CH_3)_2$ | IIIa | 71 | 2.4 | 8.1 | 5.91 | 0.89 |
| | | | 21 | 2.2 | 8.3 | 5.93 | 0.92 |
| | | | −26 | 2.1 | 8.3 | 6.07 | 0.93 |
| | $N(C_2H_5)_2$ | IIIb | 21 | 2.1 | 8.7 | 5.96 | 0.94 |
| |  | IIIc | 21 | 2.4 | 8.4 | 5.99 | 0.90 |
|  | $N(CH_3)_2$ | IVa | 21 | 4.3 | 8.4 | 5.80 | ...[b] |
| | $N(C_2H_5)_2$ | IVb | 21 | 4.6 | 8.7 | 5.83 | ...[b] |
| |  | IVc | 21 | 4.5 | 8.7 | 5.86 | ...[b] |
| | $N(C_2H_5)_2 \cdot HCl$ | V | 21 | 1.8 | 8.8 | 5.78 | 0.97 |
| | Br | VI | 21 | 2.1 | 8.8 | 5.69 | 0.96 |

[a] Fifteen per cent solution in chloroform; tetramethylsilane as internal standard. [b] See text.

TABLE III

α-TRICHLOROMETHYL-β-DIALKYLAMINOETHANOL IV AND THE HYDROCHLORIDE OF IVb

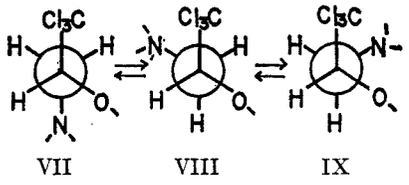
| Compd | X | Mp, °C | Found, % C | Found, % H | Found, % N | Calcd, % C | Calcd, % H | Calcd, % N | $\nu_{C-O}$, $cm^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| IVa | $N(CH_3)_2$ | 117.0–119.0 | 28.71 | 5.11 | 6.80 | 29.05 | 4.89 | 6.78 | 1113 |
| IVb | $N(C_2H_5)_2$ | 68.2–68.6 | 35.68 | 6.16 | 5.95 | 35.84 | 6.03 | 5.97 | 1112 |
| IVc |  | 100.3–101.0 | 38.44 | 5.71 | 5.68 | 38.97 | 5.73 | 5.68 | 1112 |
| V | $N(C_2H_5)_2 \cdot HCl$ | 104.0–104.8 | 30.93 | 6.09 | 4.85 | 31.02 | 5.59 | 5.17 | 1101 |

6.0 and 6.8 for IVa–c exclude the possibility of eq 2b. Since methine and methylene proton signals in $Cl_3C$-$CH(OH)CH_2OH$, prepared by the acid-catalyzed hydrolysis of γ,γ,γ-trichloropropylene oxide, appeared at $\tau$ 5.77 and 5.85 as well as 6.18 and, if β-amino alcohols derived from II are present, eight methylene signals should be found around $\tau$ 6.0. Therefore, the mother compound is the normal addition product I.

All nmr spectra for IIIa–c, IVa–c, V, and bromohydrin VI, $Cl_3CCH(OH)CH_2Br$, prepared from the reaction between γ,γ,γ-trichloropropylene oxide and hydrogen bromide in acetic acid, showed typical ABX spectra as exemplified in Figure 1.

Their vicinal coupling constants and the chemical shifts of α-methine proton are summarized in Table II.

The following conformational equilibria are considered for IIIa–c.



VII VIII IX

Recently, Snyder[13] estimated the population of conformers for a system similar to that above. Using his equation, the population of VII relative to VIII was calculated from the two vicinal coupling constants, and the results are summarized in Table II. These results suggest that most of IIIa–c compounds have conformation VII. Temperature dependency of the population of VII for IIIa implies restricted rotation about the

(13) E. I. Snyder, *J. Am. Chem. Soc.*, **88**, 1165 (1966).

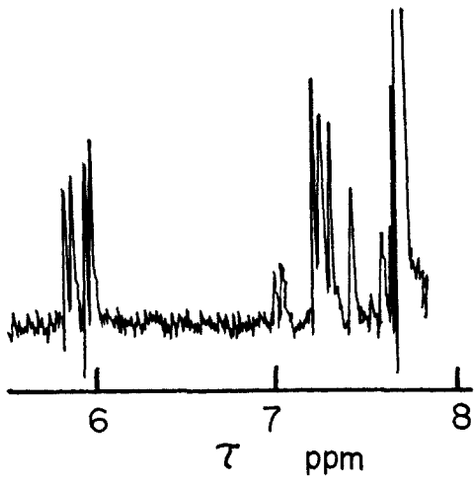
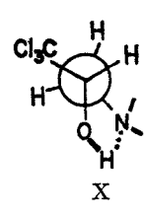



Figure 1.—Nmr spectrum of α-trichloromethyl-β-dimethylaminoethoxytrimethylsilane (IIIa), measured in 15% solution in chloroform at 71°. Strong signal at 7.73 ppm is ascribed to the methyl proton of dimethylamino group.

$C_\alpha$–$C_\beta$ bond, because the population of VII varied with temperature.

The vicinal coupling constants ($J_{AX}$) for IVa–c were found to be considerably larger than those for corresponding IIIa–c. The fact that $J_{AX}$ for V and VI showed almost the same feature as IIIa–c suggested interaction between the hydroxyl and the dialkylamino group in IVa–c. The relationship between the vicinal coupling constant and the dihedral angle proposed by Karplus[14] or Abraham, *et al.*,[15] predicted that the decrease of the dihedral angle ($\theta$) caused an increase in the vicinal coupling constant for $0° \leq \theta \leq 90°$. Therefore, the conformation of IVa–c, analogous to VII, appeared to be twisted a little from the *staggered* to the *eclipsed* form. With the Karplus equation, the dihedral angle is between 45 and 55°. The reason of this twist of conformation may be a hydrogen-bond formation as visualized in X. This kind of hydrogen bonding was already reported for several β-aminoethanols.[16]




X

When 10 mmoles of N-trimethylsilylpiperidine was treated with the same molar amount of γ,γ,γ-trichloropropylene oxide, epichlorohydrin, or propylene oxide at 80° for 1.3 hr, the reaction was completed for $R^2 = Cl_3C$, a considerable amount of unreacted epichlorohydrin was detected by gas chromatography for $R^2 = ClCH_2$, and no reaction took place for $R^2 = CH_3$. Therefore, epoxide rings having low electron density reacted more easily with trimethylsilyldialkylamine. The addition product between epichlorhydrin and N-trimethylsilylpiperidine IIId showed the α-methine proton signal as a complex multiplet because of the further coupling with methylene protons of the chloromethyl group at τ 6.22. However, the appearance of a methine proton at such low field suggests that the same mode of ring fission had taken place for epichlorohydrin as for γ,γ,γ-trichloropropylene oxide. This result is compatible with the fact that epichlorohydrin was cleaved by various nucleophiles, giving selectively normal fission as indicated in eq 2a.[17]

As shown in Table I, for the reaction of γ,γ,γ-trichloropropylene oxide with three trimethylsilyldialkylamines $(CH_3)_3SiX$, under the condition of 1.3 hr at 80°, the yield of the adducts decreased in the order as $X = NC_5H_{10} > NEt_2 > NMe_2$. Basicity of trimethylsilyldialkylamines is inferable from $pK_a$ values of corresponding secondary amine XH: $X = NC_5H_{10}$, 11.22;[18] $NEt_2$, 10.98;[19] and $NMe_2$, 10.64.[19] Agreement of the reactivity order with the presumed basicity order of trimethylsilyldialkylamine suggests that the nucleophilic attack of the nitrogen atom of trimethylsilyldialkylamine on epoxide plays an important role in the reaction.

## Experimental Section

All melting points were measured with the Yanagimoto MP-S1 melting point apparatus and are corrected. Nmr spectra were measured using Japan Electron Optics C-60 spectrometer. Infrared spectra were recorded with Nippon Bunko Type IR-S.

**Materials.**—Trimethylsilyldialkylamine was obtained with the same method reported in part I.[9] γ,γ,γ-Trichloropropylene oxide was prepared according to the method of Meerwein, *et al.*,[20] and purified by distillation submitting the fraction at 59.7–60.0° (23 mm). Epichlorohydrin and propylene oxide were commercial extra pure reagent grade and were purified by distillation before use.

**Reaction of Epoxide and Trimethylsilyldialkylamine.**—Ten millimoles of trimethylsilyldialkylamine was measured into a 10-ml flask filled with dry argon. The same molar amount of epoxide was added to the flask with a syringe and heated for the appropriate time at 80°. The reaction product was distilled under reduced pressure, and the colorless liquid adduct was obtained; IIIa–c from γ,γ,γ-trichloropropylene oxide and IIId from epichlorohydrin. Reaction conditions and results obtained are summarized in Table I. When a mixture of propylene oxide and N-trimethylsilylpiperidine were kept at 80° for 1.3 hr in a sealed tube, no reaction took place.

**Preparation of α-Trichloromethyl-β-dialkylaminoethanol IVa–c.**—Five millimoles of α-trichloromethyl-β-dimethylaminoethoxytrimethylsilane (IIIa) and a twofold molar amount of dry methanol were refluxed overnight, after which the methanol and trimethylsilylmethoxysilane were distilled off under reduced pressure. White crystals of α-trichloromethyl-β-dimethylaminoethanol (IVa) were obtained in 90% yield. Recrystallization was carried out with petroleum ether (bp 30–70°). α-Trichloromethyl-β-(N-piperidio)ethanol (IVc) was obtained in the same method. α-Trichloromethyl-β-diethylaminoethanol (IVb) was obtained from the reaction of IIIb (5 mmoles) and a slight excess molar amount of acetic acid dissolved in 3 ml of dry ether. The ether solution was washed with six 1-ml portions of 10% aqueous potassium carbonate and thereafter with 1 ml of water. The water layers were collected and extracted with ether (three 3-ml portions). White, hygroscopic crystals of IVb were obtained after the removal of solvent. Melting points and analytical data are summarized in Table III.

**Preparation of the Hydrochloride of IVb (V).**—To α-trichloromethyl-β-diethylaminoethoxytrimethylsilane (IIIb, 1.89 g) was added dropwise 10 ml of hydrochloric acid solution saturated

(14) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).
(15) R. J. Abraham and J. S. E. Holker, *J. Chem. Soc.*, 806 (1963).
(16) M. Kuhn, W. Lüttke, and R. Meche, *Z. Anal. Chem.*, **170**, 106 (1957).
(17) E. A. S. Cavell, R. E. Parker, and A. W. Scaplehorn, *J. Chem. Soc.*, 4780 (1965).
(18) S. Searles, M. Tamres, F. Block, and L. A. Quarterman, *J. Am. Chem. Soc.*, **78**, 4917 (1956).
(19) N. F. Hall and M. R. Sprinkle, *ibid.*, **54**, 3469 (1932).
(20) H. Meerwein, T. Bersin, and W. Buneleit, *Ber.*, **62**, 999 (1929).

in ether. White crystals of V formed and were washed with a small portion of ether and dried at 70° (0.5 mm). The product consist of extremely hygroscopic, needlelike crystals. Melting point and analytical data are included in Table III.

**Hydrolysis of γ,γ,γ-Trichloropropylene Oxide.**—γ,γ,γ-Trichloropropylene oxide (2 g) was refluxed with 15 ml of water containing 5 drops of sulfuric acid for 4 hr. The mixture turned homogeneous and was extracted continuously with ether for 3 hr. 3,3,3-Trichloropropane-1,2-diol was obtained after the removal of ether in 20%. Recrystallization was performed with carbon tetrachloride, mp 84.6–85.0°.

*Anal.* Calcd for $C_3H_5Cl_3O_2$: C, 20.08. Found: C, 20.07.

**Registry No.**—IIIa, 13144-12-2; IIIb, 13144-13-3; IIIc, 13144-14-4; IIId, 13144-15-5; IVa, 13144-16-6; IVb, 13144-17-7; IVc, 13144-18-8; V, 13144-19-9; VI, 13144-20-2; 3,3,3-trichloropropane-1,2-diol, 815-02-1.

# Synthesis of New Bicyclic Imines, Enamines, and Iminium Salts. I. The 1,4-Ethano-1,4-dihydro- and 1,2,3,4-Tetrahydroisoquinolines[1]

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Cyclization of γ-phenyl-δ-ketovaleric acids with sulfuric acid gives 4-acetyl-1-tetralones. 1-Monooximes or the dioximes of these are hydrogenated in the presence of palladium to give mixtures of diastereoisomeric 1-aminotetralins. The *cis*-amino ketones or amino oximes readily form dehydrobenzoisoquinuclideines (3,4-disubstituted 1,4-dihydro-1,4-ethanoisoquinolines). Quaternary iminium salts prepared from the bicyclic imines are converted by bases to bicyclic enamines (2,4-disubstituted 3-alkylidene-1,4-ethano-1,2,3,4-tetrahydroisoquinolines) and these are reconverted by acids to 2,3,4-trisubstituted 1,4-dihydro-1,4-ethanoisoquinolinium salts. A number of other reactions leading toward and defining the properties of 4-acetyl-4-phenyl-1-tetralone are described, including condensation with formaldehyde and secondary amine salts to give 2-(aminomethyl)-4-acetyl-1-tetralones, 2-nitrosation, selective reactions of the 1-tetralone group with hydrogen, glycol, and other reagents, and 2-bromination. 2-Bromo-4-acetyl-4-phenyl-1-tetralone undergoes a novel, base-catalyzed rearrangement, giving 2-acetyl-4-phenyl-1-naphthol.

Preceding papers[2,3] from our laboratory have dealt with syntheses of benzazepinones, benzomorphans, and oxindoles, in which the chemistry of functional groups appended to a quaternary carbon atom was investigated. Together with Schenker,[4] we have also been engaged in synthesis of quaternary carbon compounds having five- and six-membered bridged heterocyclic rings across the tetrahydronaphthalene ring system, incorporating amino groups attached to positions 1 and 2. The purpose of this paper is to describe the exploration of syntheses starting from tetralones which led to the finding of new bicyclic imines and enamines arising by the interaction of a 1-amino group with a ketone group attached at position 4.[5]

Unlike such well-known groups of nitrogen-bridged ring compounds as the tropanes and quinuclidines, the isoquinuclidines did not receive much attention until recently. As pointed out by Schneider,[6] this probably is because isoquinuclidines are of infrequent natural occurrence. Recently, there has been much interest in this type of bridged ring, however, owing to its presence in the *Tabernanthe iboga* alkaloids[7] and in dioscorine.[8] The classical preparation of isoquinuclidones through the 1,4-lactam bridging reaction[6,9] has been supplemented by the development of newer syntheses, notably dienophile addition to 1,2-dihydropyridines[7b,10] and more recently addition of 1,4-cyclohexadienes to methyleneurethans and other imine derivatives.[11] These later methods, however, do not lend themselves readily to synthesis of isoquinuclidines having bridgehead substituents, and the literature contains only an isolated example of synthesis of an isoquinuclidone bearing a bridgehead phenyl group.[12] Also, only recently has any effort been made to synthesize isoquinuclideines[13] and similar bridged imines.[14]

We approached the synthesis of bridged bases from functionally modified tetralones containing a qua-

(1) Presented in part at the Gordon Research Conference on Heterocyclic Compounds, New Hampton, N. H., July 5, 1966.

(2) (a) G. N. Walker, D. Alkalay, and R. T. Smith, *J. Org. Chem.*, **30**, 2973 (1965); (b) G. N. Walker and D. Alkalay, *ibid.*, **31**, 1905 (1966).

(3) G. N. Walker, R. T. Smith, and B. N. Weaver, *J. Med. Chem.*, **8**, 626 (1965).

(4) K. Schenker, Belgian Patent 665,189 (1965); Netherlands Patent Application, 6,507,339; *Chem. Abstr.*, **65**, 696 (1966); G. N. Walker and K. Schenker, U. S. Patent 3,291,806 (1966).

(5) Some of this work has already been revealed in Netherlands Patent Application 6,504,323 (1965); *Chem. Abstr.*, **64**, 8155 (1966). The 1,4-ethanohydroisoquinoline nomenclature is simpler and clearer in respect to position numbering than either of two alternatively possible names, benzoisoquinuclideine or 5,6-benzo-3-azabicyclo[2.2.2]octa-2,5-diene. For further clarity in this discussion, tetralone precursors and the ethanohydroisoquinolines ultimately obtained have also been numbered in a mutually consistent way.

(6) W. Schneider and R. Dillmann, *Ber.*, **96**, 2377 (1963).

(7) (a) M. F. Bartlett, D. F. Dickel, and W. I. Taylor, *J. Am. Chem. Soc.*, **80**, 126 (1958). (b) See the elegant ibogamine synthesis of G. Büchi, D. L. Coffen, K. Kocsis, P. E. Sonnet, and F. E. Ziegler, *ibid.*, **87**, 2073 (1965); **88**, 3099 (1966), and additional references therein.

(8) W. A. M. Davies, J. G. Morris, and A. R. Pinder, *Chem. Ind.* (London), 1410 (1961).

(9) G. Wendt, *Ber.*, **75B**, 425 (1942); E. Ferber and H. Brückner, *ibid.*, **76B**, 1019 (1943); L. H. Werner and S. Ricca, *J. Am. Chem. Soc.*, **80**, 2733 (1958).

(10) O. Mumm and J. Diedrichsen, *Ann.*, **538**, 195 (1935); K. Schenker and J. Druey, *Helv. Chim. Acta*, **42**, 1960, 1971 (1959); **45**, 1344 (1962); T. Agawa and S. I. Miller, *J. Am. Chem. Soc.*, **83**, 449 (1961); M. Saunders and E. H. Gold, *J. Org. Chem.*, **27**, 1439 (1962). Cycloaddition of benzyne to a 1,2-dihydropyridine might serve as a synthesis of 5,6-benzo-3-azabicyclo[2.2.2]octa-5,7-diene-type compounds. The reaction of benzyne and pyrroles gives 7-azabenzonorbornadienes; see L. A. Carpino and D. E. Barr, *ibid.*, **31**, 764 (1966), and references therein. Reaction of N-methyl-2-pyridone and benzyne to give a benzodehydroisoquinuclideine was reported very recently by L. Bauer, C. L. Bell, and G. E. Wright, *J. Heterocyclic Chem.*, **3**, 393 (1966).

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