Registry No.—**2b** HCl, 50599-89-8; **3**, 50599-78-5; **4**, 50599-79-6; **5**, 50599-80-9; **6**, 50679-04-4; **7** isomer A, 50599-87-6; **7** isomer B, 50599-88-7; **8**, 50599-86-5; **9**, 50599-84-3; **9** HBr, 50599-85-4; **10** HBr, 50599-83-2; **11** HBr, 50599-81-0; phenylacetonitrile, 140-29-4; 2-dimethylaminoethyl chloride, 107-99-3; 2,9β-dimethyl-8-oxo-6,7-benzomorphan, 51096-41-4; 2,9β-dimethyl-8-oxo-6,7-benzomorphan hydrochloride, 50599-82-1.

References and Notes

(1) (a) Chemical Abstracts name: 3,11β-dimethyl-1,2,3,4,5,6-hexahydro-2,6-methano-3-benzazocine. (b) The β designation relates to the hydroaromatic ring.
(2) Visiting Associate of Tanabe Laboratories, Tokyo, Japan.
(3) K. Kanematsu, M. Takeda, A. E. Jacobson, and E. L. May, *J. Med. Chem.*, **12**, 405 (1969).
(4) E. L. May and M. Takeda, *J. Med. Chem.*, **13**, 805 (1970). We have learned (personal communication) from M. Takeda, Tanabe Laboratories, Tokyo, that powerful antagonists can be made from **1**.
(5) J. H. Ager, S. E. Fullerton, and E. L. May, *J. Med. Chem.*, **6**, 322 (1963).
(6) Many variations of the procedures reported by J. H. Ager, S. E. Fullerton, E. M. Fry, and E. L. May, *J. Org. Chem.*, **28**, 2470 (1963), were tried. See ref 3.
(7) G. Thyagarajan and E. L. May, *J. Heterocycl. Chem.*, **8**, 465 (1971).
(8) S. E. Fullerton, E. L. May, and E. D. Becker, *J. Org. Chem.*, **27**, 2144 (1962).
(9) R. S. Wilson, H. J. C. Yeh, T. Oh-ishi, and A. E. Jacobson, unpublished results.
(10) Over Na_2SO_4.
(11) E. Tagman, E. Sury, and K. Hoffmann, *Helv. Chim. Acta*, **35**, 1235 (1952).
(12) W. Wilson, *J. Chem. Soc.*, 6 (1952), prepared **4** in 57% yield from $PhCH_2COMe$, $NaNH_2$, and $Me_2NCH_2CH_2Cl$.

Structure and Chemistry of the Aldehyde Ammonias. II. Phenylacetaldimines, Styrylamines, and 2,4,6-Tribenzyl-1,3,5-hexahydrotriazines

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Reaction of phenylacetaldehyde, hydratropaldehyde, and diphenylacetaldehyde with ammonia in methanol or ether at −15° leads to 2,4,6-tribenzyl-1,3,5-hexahydrotriazines **2a–c**. Two of these products had been described by others as hydratropaldimine and diphenylacetaldimine. The platinum-catalyzed hydrogenation of 2,2-diphenyl-1-nitroethene gave 2,2-diphenylethenamine, not diphenylacetaldimine as previously reported. Oxidation of triazines **2a** and **2b** with *tert*-butyl hypochlorite gave 2,4,6-tribenzyl-1,3,5-triazabicyclo[3.1.0]hexanes **3a** and **3b**. The stereochemistry of triazines **2a–c** and oxidation products **3a** and **3b** was established from ^1H and ^{13}C nmr spectra. Thermolysis of triazines **2a–c** in aprotic solvents was followed by nmr spectroscopy; the principal initial products are ammonia and *N,N'*-distyryl-1,1-diamino-2-phenylethanes (**5a–c**). Prolonged heating of triazine **2c** or 2,2-diphenylethenamine gave bis(2,2-diphenylethen)amine (**6c**). 5,5-Diphenyl-2-(diphenylmethyl)-3-oxazoline (**14**) was isolated as a minor product of the reaction of diphenylacetaldehyde with methanolic ammonia.

Accounts of the synthesis of unsubstituted aldimines, RCH=NH, from aldehydes and ammonia are found in the literature.[2-13] However, recent reexamination of some of these reports has established that unsubstituted aldimines of this type cannot be isolated as stable free bases.[14-16] Rather, their self-reaction occurs extremely rapidly, leading to other products such as 2,4,6-trisubstituted 1,3,5-hexahydrotriazines and diimines, $(RCH{=}N)_2CHR$.[7,14-19] Unsubstituted aldimines often are described as reaction intermediates, *e.g.*, in photolysis of azides and primary aliphatic amines, and in reduction of oximes.[20-23]

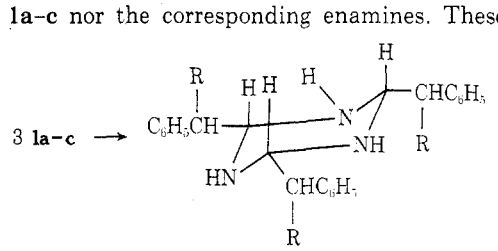
Reactions of hydratropaldehyde and diphenylacetaldehyde with ammonia have been reported by several workers to produce white crystalline solids described as monomeric aldimines **1b** and **1c**, respectively.[6,10,12,13]

$$C_6H_5CH(R)CHO + NH_3 \longrightarrow C_6H_5CH(R)CH{=}NH + H_2O$$

1a, R = H
b, R = CH_3
c, R = C_6H_5

Aldimine **1c** has erroneously been described as a product of hydrogenation of 2,2-diphenyl-1-nitroethene.[9] An unstable solid ammonia derivative of phenylacetaldehyde has been reported, but it could not be purified and its molecular formula was not established.[24] Enamine 2-phenyl-2-methylethenamine has been described as the product of reaction of hydratropaldehyde with ammonia in ethyl acetate solvent;[25] Witkop describes it as imine **1b**.[12]

In the present work the reactions of phenylacetaldehyde, hydratropaldehyde, and diphenylacetaldehyde with ammonia at low temperature were found to produce 2,4,6-tribenzyl-1,3,5-hexahydrotriazines **2a–c**, not aldimines **1a–c** nor the corresponding enamines. These reactions were usually conducted in methanol or ether solvent with a slight excess of ammonia at *ca.* −15° for a few days. Isolated products are white, crystalline solids obtained in variable yields (Table I). Only **2a**, derived from phenylacetaldehyde, forms a stable hydrate ($3H_2O$). Anhydrous **2a** was prepared and its trihydrate formation is reversible. These results agree with previous findings that 2,4,6-tris(*n*-alkyl)-1,3,5-hexahydrotriazines derived from *n*-alkanals form stable trihydrates whereas a 2,4,6-triisopropyl derivative obtained from the α-substituted isobutyraldehyde does not.[14] Repetition of earlier work said to produce **1b** and **1c** or the corresponding enamines gave



2a, R = H
b, R = CH_3
c, R = C_6H_5

Table I
2,4,6-Tribenzyl-1,3,5-hexahydrotriazines

Compd	R	Yield, %[a]	Mp, °C[b]	Molecular formula
2a	H		62–69	$C_{24}H_{27}N_3$
2a·$3H_2O$	H	9.6[c]	60–64	$C_{24}H_{27}N_3 \cdot 3H_2O$
2b	CH_3	79	111–112[d]	$C_{27}H_{33}N_3$
2b′	CH_3		144–150[e]	$C_{27}H_{33}N_3$
2c	C_6H_5	34	82–88[f]	$C_{42}H_{39}N_3$
2c′	C_6H_5		105–110[e]	$C_{42}H_{39}N_3$

[a] Yield of isolated form having melting point listed. [b] Capillary melting points of analytical samples; melting occurs with decomposition and depends on the method of determination (Kofler or capillary) and on the rate of heating.[6] [c] An additional 90% yield of crude product was isolated, mp 45–60°. [d] Lit. mp 114° for sample recrystallized from ethanol (rapid heating); mp 104–105° (slow heating rate);[5] mp 110–112° (crude product), 114–115° after recrystallization from ethanol;[10] mp 98–105°, 95–112°, 96–102° on crude samples prepared in different solvents;[12] mp 100–105° on sample recrystallized from ethanol.[12] [e] Polymorph obtained by heating **2b** or **2c** in methanolic potassium hydroxide; for **2b′** lit. mp 143–145°, 143–147°,[10] 135–137°.[12] [f] Lit. mp 75–82°, 88–89°, 89°, 91° on samples prepared in different solvents.[12,13]

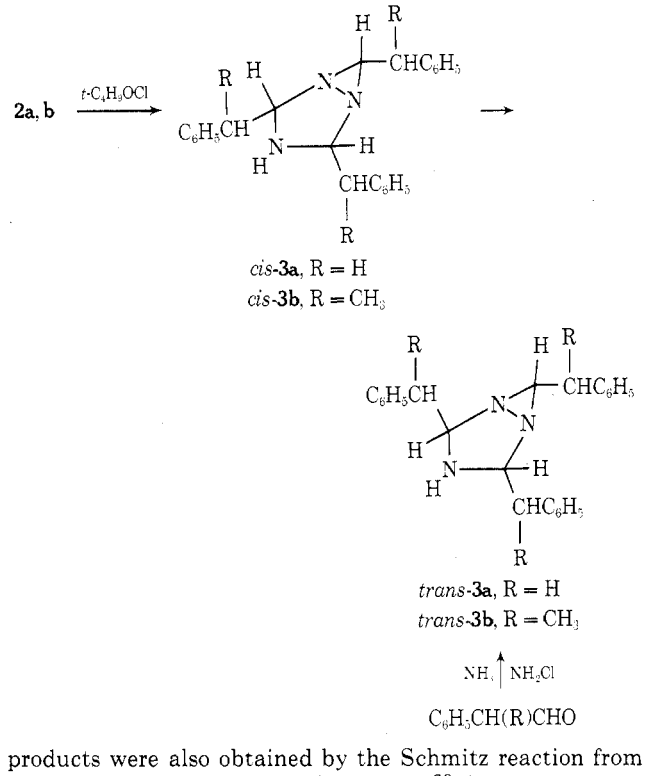
products identical with those described in Table I.[6,10,12,13,25,26]

Structures **2a–c** are supported by the following: molecular formula, spectral data, and chemical behavior. Molecular weights determined by vapor phase osmometry on chloroform or benzene solutions of anhydrous samples indicate a trimeric aldimine structure. Surprisingly, previous workers[6,10,12,13] did not report molecular weight determinations for their products of reaction of aldehydes with ammonia—with the exception of 2-phenyl-2-methylethenamine.[25,26] The infrared spectra determined on pure samples of **2a–c** in Nujol mulls or freshly prepared carbon tetrachloride or chloroform solutions reveal strong NH bands (3270 cm^{-1}) but no C=N bands. However, solutions of **2c** are unstable and in chloroform a C=N band (1670 cm^{-1}) appears rapidly on standing at room temperature; after *ca.* 15 min the 1670-cm^{-1} band is replaced by an enamine C=CN band at 1640 cm^{-1}. The presence of C=N bands at 1661, 1664, and 1668 cm^{-1} in chloroform solutions of diphenylacetaldehyde and hydratropaldehyde ammonias was used by Witkop as evidence to support aldimine structures **1b** and **1c**.[12]

The ^1H and ^{13}C nmr spectra of **2a–c** in various solvents support the assigned structures, including stereochemistry. A broad NH signal is observed which is shifted to the HOD region by addition of D_2O (three protons). The simple proton spectra of **2a** and **2c**, revealing a single ring CH signal, indicate an all-equatorial configuration of the 2,4,6 substituents in agreement with previous results for 2,4,6-trialkyl-1,3,5-hexahydrotriazines.[14] The ^{13}C nmr spectra of **2a** and **2c** are in agreement with this assignment, revealing single peaks for ring and benzyl carbons. Although compound **2b** would also be expected to have all-equatorial 2,4,6-ring substituents, the multiplicity of the observed ^1H and ^{13}C nmr peaks shows the sample to be a mixture of three, possibly four epimers. It is the first reported 1,3,5-hexahydrotriazine having chiral ring substituents. Several all-equatorial **2b** diastereoisomers having similar properties are possible, since epimerization in the ring substituent cannot occur under the reaction conditions. Even more vigorous reaction conditions fail to effect epimerization (*vide infra*).

Interesting and unique behavior is exhibited by triazines **2b** and **2c** in refluxing methanolic potassium hydroxide. A higher melting form **2b′** is produced, mp 144–150°, in agreement with previous findings (Table I).[10,12] Its properties, except for melting point, appear indistinguishable from those of the lower melting form. Interconversion of the two forms occurs readily. Dissolving it in chloroform, followed by solvent removal, leads to recovered low-melting **2b**. Triazine **2c** in refluxing methanolic potassium hydroxide produces a higher melting isomer **2c′**, mp 105–110°. Triazine **2a** is decomposed rapidly by this treatment. It is suggested that forms **2b,b′** and **2c,c′** are polymorph pairs, distinguished possibly by configurations of one or more NH groups in the crystal.[27] The polymorph pairs **2b,b′** appear not to differ in epimer composition. Isomerization by epimerization at the benzyl carbon cannot be involved in the interconversion **2b** ⇌ **2b′** since heating **2b** in methanol-*O*-*d*-KOD produced **2b′** (after washing with water) having no CD bonds (ir and ^1H nmr spectra). The thermal stability order in hot methanolic potassium hydroxide is **2b** > **2c** > **2a** (in contrast to the stability order in aprotic solvents, where **2a** is more stable than **2c**). The stability of **2b** and **2c** in hot methanolic potassium hydroxide contrasts with the instability of these substances in hot neutral solvents. This result suggests that the facile thermolysis of **2a–c** in solutions containing no added base is autocatalytic and/or catalyzed by solvent (alcohol) acting as an acid; this catalysis would be repressed in strongly basic media.

Additional evidence supporting the structure of triazines **2a** and **2b** was obtained by *tert*-butyl hypochlorite oxidation to 2,4,6-tribenzyl-1,3,5-triazabicyclo[3.1.0]hexanes **3a** and **3b** with C-2, C-4 trans stereochemistry. These

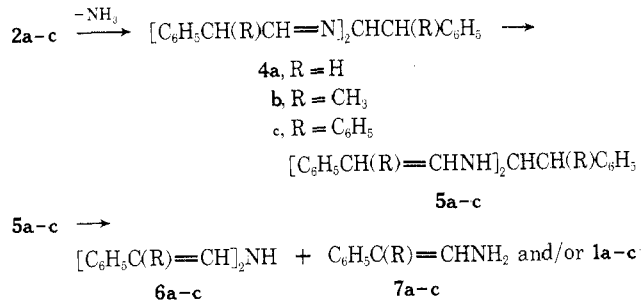


products were also obtained by the Schmitz reaction from the required aldehyde and chloramine.[28] Attempts to prepare 2,4,6-tris(diphenylmethyl)-1,3,5-triazabicyclo-[3.1.0]hexane (**3c**, R = C_6H_5) from **2c** by oxidation or from diphenylacetaldehyde by the Schmitz reaction were unsuccessful. The C-2, C-4 groups in **3a** and **3b** were observed to have trans stereochemistry; this fact is evident from the ^1H and ^{13}C nmr spectra of these compounds, which reveal separate signals for the C-2,4,6 carbons and their attached protons. Cis isomers **3a** and **3b** are the expected initial products from all-equatorial **2a** and **2b**. These are unstable intermediates, however, since it has been established that the cis → trans epimerization of

2,4,6-trialkyl-1,3,5-triazabicyclo[3.1.0]hexanes occurs rapidly and completely in the reaction medium in those examples where the 2,4,6 substituents are large.[14,29] The ^1H and ^{13}C spectra of *trans*-**3b** indicate that it, like its precursor **2b**, is a mixture of three or four epimers owing to the chiral ring substituents.

Triazines **2a–c** are relatively unstable materials with properties similar to those of known 2,4,6-trialkyl-1,3,5-hexahydrotriazines.[14] They may be stored at −15° for extended periods, but at room temperature they evolve ammonia to produce brown, amorphous solids.[6] The thermal stability order of the anhydrous compounds or their solutions is **2b** > **2a** > **2c**.

Heating **2a–c** under reflux in aprotic solvents such as chloroform, benzene, or toluene produces ammonia (1 molar equivalent in *ca.* 1–1.5 hr); removal of the solvent after this period of heating yields oils believed to contain principally bis enamines **5a–c** (tautomers of diimines **4a–c**) and polymers thereof. Prolonged heating of **2c** gave

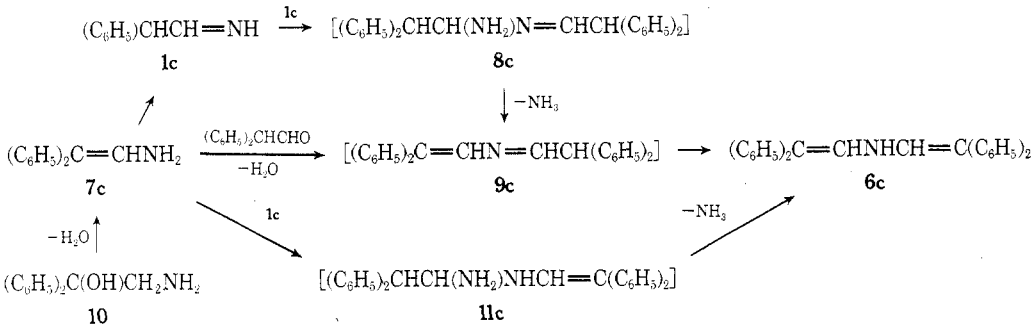


bis(2,2-diphenylethen)amine (**6c**, R = C_6H_5) by cleavage of **5c**. (This result was interpreted by Witkop as a dimerization reaction of imine **1c**.[12]) 2,2-Diphenylethenamine **7c** and/or imine **1c** would be expected as the other products of **5c** cleavage, but **7c** should readily tautomerize to the corresponding imine (**1c**) and ultimately be consumed in a repeating chain sequence: **7** → **1** → **2** → **4** → **5** → **6** + **7**. Bis(2-methyl-3-phenylethen)amine (**6b**, R = CH_3, mp 120°) has been reported to form from **2b** (our assignment) in methanolic formic acid;[25] we have been unable to repeat this experiment, however. Behavior contrasting to that of **2a–c** is observed with 2,4,6-trialkyl-1,3,5-hexahydrotriazines during thermolysis in refluxing cyclohexane; the products are not enamines but diimines (high yields of **4**; C_6H_5 = alkyl; R = H or alkyl).[14] Phenyl conjugation favors enamine tautomers **5**, **6**, and **7** over imine tautomers **4** and **1**.

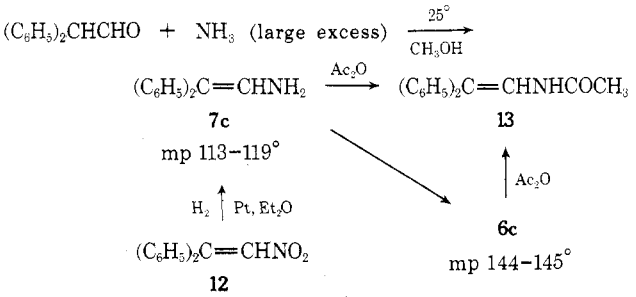
Evidence for intermediates **4a–c** and **5a–c** was obtained by following changes in the proton nmr spectra.[30] Transient formation of diimines **4a–c** occurs on heating dilute chloroform, benzene, or toluene solutions of **2a–c** at 60–70° for short periods (10–30 min). Weak signals appear at *ca.* δ 4.4, 5.3, and 5.4 assigned to =NCHN= protons in **4a**, **4b**, and **4c**, respectively, by analogy with the nmr spectra of known diimines [$(RCH{=}N)_2CHR$, R = alkyl].[14] These signals disappear during longer periods of heating (1–3 hr at 60–70°) with formation of relatively high concentrations of new products believed to be **5a–c** [strong signals near δ 6.5–6.7 (=CH) and 4.2–5.0 (HNCHNH)]. Removal of solvent from the solution containing principally **5c** gave an oil [λ_{max} 285 nm (ε 20,800) in methylcyclohexane; a band near 360 nm is absent; 2,2-diphenylethenamine (**7c**) has λ_{max} 283 nm (ε 15,000) and **6c** has λ_{max} 362 nm (ε 30,000)]. Formation of acetophenone on ozonolysis of cyclohexane solutions of **2b** (our assignment) agrees with structures **5b**, **6b**, or **7b** and suggests decomposition of **2b** into one or more of these products during the reaction.[25] Prolonged heating of **2a–c** yields products in which nonvinylic benzylic protons are absent and only phenyl and vinyl =CH signals are present in their nmr spectra (principally **6a–c**, **7a–c**, and polymers).

Bis(2,2-diphenylethen)amine (**6c**), a thermolysis product of **2c**, is encountered as a product of several other reactions. For example, reaction of diphenylacetaldehyde with aqueous or methanolic ammonia (slight excess) at *ca.* 25° deposits crystals of **6c** (mp 144–145°) in 18–50% yield;[10,13,31] however, at −15° triazine **2c** is formed. The formation of **6c** at the higher reaction temperature could be interpreted as a decomposition reaction of initially formed **2c** (**2c** → **4c** → **5c** → **6c**). Alternatively, it could involve dimerization of **1c** to diamine **8c**, followed by deamination of the latter. Reaction of diphenylacetaldehyde with 2,2-diphenylethenamine (**7c**) yields **6c**; however, this result is obscured by the fact that **7c** alone also forms **6c** under similar conditions. Enamine imine **9c** could be an intermediate in these transformations.

2,2-Diphenylethenamine (**7c**), by heating in ethanol or without solvent, or by treatment with ethereal hydrogen bromide at 25°, yields ammonia and **6c**.[12,13,30] Heating 2,2-diphenyl-2-hydroxy-1-aminoethane (**10**, a **7c** precursor) in refluxing benzene with phosphorus pentoxide leads to **6c** in 76% yield.[32] These reactions are believed to involve the tautomeric imine **1c**, either by its dimerization to **8c**, or reaction with **7c** to yield diamine **11c**. Bis enamine **6c** was discovered by Lipp, who obtained it as a product of aluminum amalgam reduction of 1,1-diphenyl-2-nitroethane (**12**).[33]



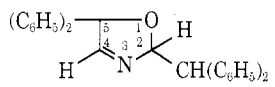
2,2-Diphenylethenamine (**7c**, mp 113–119°) was prepared by passing a large excess of ammonia gas into methanolic diphenylacetaldehyde solution at 25° for 12 hr.[13] Its molecular formula and spectra support the struc-



ture assignment. Earlier claims of preparation of **7c** appear to be erroneous. A compound described by Krabbe as **7c** has a reported melting point much higher than that of authentic **7c**.[10,26] Its reaction with acetic anhydride gave *N*-acetyl-2,2-diphenylethenamine (**13**), which result was taken as evidence of precursor structure **7c**.[26] However, we have found that bis enamine **6c** reacts with acetic anhydride (as does authentic **7c**) to produce **13**. It is concluded that Krabbe's compound is **6c** not **7c**.

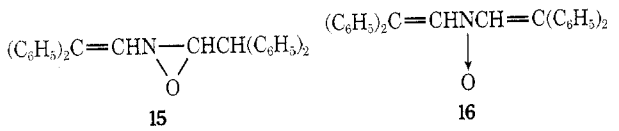
Hydrogenation of 2,2-diphenyl-1-nitroethene (**12**) in ether solvent with platinum catalyst has been reported to yield diphenylacetaldimine (**1c**).[9] We have repeated this experiment and find this product to be enamine **7c**, formed in nearly quantitative yield. A report of the preparation of 2-phenyl-2-methylethenamine [$C_6H_5C(CH_3)$=$CHNH_2$, **7b**] by reaction of hydratropaldehyde with ammonia is also believed to be erroneous.[25] The product is triazine **2b**.

A new product of reaction of diphenylacetaldehyde with ammonia was encountered in the present study. Reaction with methanolic ammonia by the procedure of Curtin[13] gave, in addition to 2,2-diphenylethenamine (**7c**, 69% yield), a white, crystalline material, $C_{28}H_{23}NO$, mp 125–127°, in *ca.* 5% yield. Spectral data and chemical behavior support the assigned structure, 5,5-diphenyl-2-(diphenylmethyl)-3-oxazoline (**14**), a new derivative of the rarely encountered 3-oxazoline ring system.[34-36] The infrared

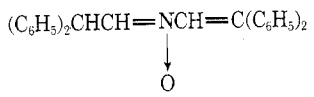


14

spectrum reveals absence of NH and C=O bands; a weak C=N band appears at 1630 cm^{-1} (Nujol). Styrene-derived structures **15–17** cannot be considered, since strong ultraviolet absorption near 300 nm is absent. The ^1H nmr



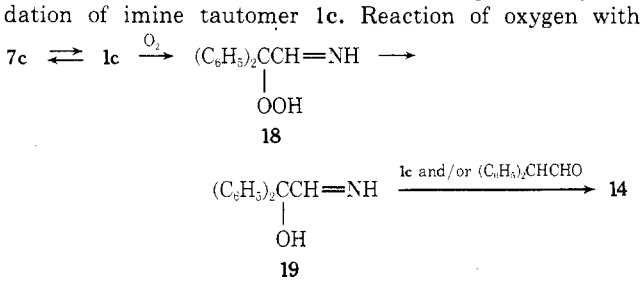
15 **16**



17

spectrum is in agreement with a CH=NCHCH grouping; the C-2 ring proton signal appears as a split doublet (δ 6.44, J = 5 Hz) owing to additional long-range coupling with the C-4 vinyl proton (δ 7.78, d, J = 2.5 Hz); the exocyclic benzyl proton appears as a doublet at δ 4.48 (J = 5 Hz). The proton-coupled and decoupled ^{13}C nmr spectra also support structure **14**. In the proton-coupled spectrum the C-4 vinyl ring carbon (δ 163.5) appears as a doublet, the C-2 ring carbon (δ 107.4) appears as a singlet with weak splitting indicating a quaternary carbon with adjacent CH, and the C-5 ring carbon appears as a singlet (δ 95.3). The exocyclic benzyl carbon appears as a doublet (δ 56.1). Acid hydrolysis of **14** gave diphenylacetaldehyde.

One possible route to oxazoline **14** could proceed by oxidation of imine tautomer **1c**. Reaction of oxygen with

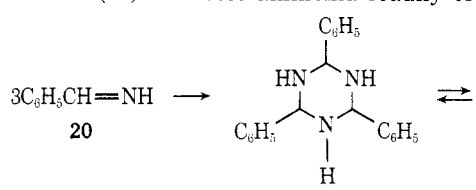


18

19

phenylacetaldehyde-derived Schiff bases occurs rapidly in solution without added catalyst to produce C-2 hydroperoxy derivatives.[12] Decomposition of hydroperoxide **18** could yield hydroxyimine **19**, a reaction facilitated in alcohol solvents;[37] a covalent hydrate or amminate of **19** [$(C_6H_5)_2C(OH)CH(OH)NH_2$ or $(C_6H_5)_2C(OH)CH(NH_2)_2$] could also be an intermediate. The reaction of β-amino alcohols with aldehydes or of α-hydroxy ketones with ammonia yields 3-oxazolines.[34-36]

A product obtained by ammonolysis of hydrobenzamide (**22**) in liquid ammonia which has been described as benzaldimine (**20**) is possibly 2,4,6-triphenyl-1,3,5-hexahydrotriazine (**21**).[7] It loses ammonia readily to regenerate hydrobenzamide, as does **21**, a very unstable substance said to form from benzaldehyde in methanolic ammonia at −10°.[38] Owing to their instabilities, these materials have been poorly characterized and their molecular weights could not be accurately determined.[7,38] Attempts to prepare benzaldimine from its salts gave hydrobenzamide.[17]



20 **21**

$(C_6H_5CH{=}N)_2CHC_6H_5 + NH_3$

22

It is concluded from our studies of the aldehyde ammonias that unsubstituted aldimines (RCH=NH; R = alkyl, aryl), although able to exist at low concentrations in solution or the vapor phase, are too reactive to permit isolation of the pure free bases. We have examined the reaction of three phenylacetaldehydes with ammonia and isolated several products; none have the aldimine structures previously reported.

Experimental Section[39]

Aldehydes. Phenylacetaldehyde, hydratropaldehyde, and diphenylacetaldehyde were commercial samples, reagent grade, distilled immediately before use.

2,4,6-Tribenzyl-1,3,5-hexahydrotriazine Trihydrate (2a-3H$_2$O). Phenylacetaldehyde (50.0 g, 0.416 mol) was added dropwise with stirring to 50 ml of 9 *M* methanolic ammonia during 15 min (reaction temperature of 2–5° maintained during addition by ice-bath cooling). The clear solution was stored at −15° for 4 days, then treated with 1.5 ml of water and 5 ml of ether. After storage at −15° for 3 weeks, crystals were removed by filtration and washed successively with cold aqueous methanol and isopentane to yield 4.8 g (9.6%) of **2a** trihydrate as chunky, white prisms: mp 60–64° dec; ir (Nujol) 3250 cm^{-1} (broad) OH and NH, C=O and C=N bands absent; ^1H nmr (C_5D_5N) δ 7.00 (15, m, C_6H_5), 3.67 (3, t, J = 6 Hz, CH), 2.55 (6, d, J = 6 Hz, CH_2), 3.0–4.0 [9, broad s, NH and H_2O, disappeared on addition of D_2O to produce a signal at δ 5.17 (9, s, OH)]. Elemental analysis for nitrogen was determined by dissolving a rapidly weighed sample in a mixture of 1 *N* hydrochloric acid (excess) and ethanol and titrating with 1 *N* sodium hydroxide.

Anal. Calcd for $C_{24}H_{27}N_3{\cdot}3H_2O$: N, 10.21. Found: N, 10.0.

The filtrate remaining from removal of the first crop (excluding washings) was diluted with 250 ml of cold 15 *M* aqueous ammonia. After storage at 0° for 3 months there was obtained 45 g (90%) of crude **2a** trihydrate as slightly gummy, chunky, white crystals, mp 40–65° dec, which could not be recrystallized without decomposition. In another procedure anhydrous ammonia was bubbled into a solution of phenylacetaldehyde (**2g**) in 20 ml of ether for 1 hr at 0°. After storage at −15° for 2 months there was obtained 0.54 g (27%) of crude **2a** trihydrate, mp 45–65° dec.

2,4,6-Tribenzyl-1,3,5-hexahydrotriazine (2a). Triazine **2a** trihydrate (2.0 g) was added to 10 ml of benzene at room temperature. Water which separated (0.25 ml) was removed and the benzene solution was dried briefly with Drierite. Filtration, followed by rapid removal of solvent under reduced pressure at 25°, gave

1.6 g (90%) of anhydrous **2a**, mp 61–67° dec. Recrystallization from hexane gave prisms (50% recovery): mp 62–69° dec; ir (Nujol) 3200 cm^{-1} (sharp, NH), C=O and C=N bands absent; ^1H nmr ($CDCl_3$) δ 7.10 (15, s, C_6H_5), 3.72 (3, t, J = 6 Hz, CH), 2.67 (6, d, J = 6 Hz, CH_2), 1.20 (3, s, broad, NH); ^{13}C nmr ($CDCl_3$) δ 136.1 (C-1, C_6H_5), 128.8 (C-2, C_6H_5), 127.8 (C-3, C_6H_5), 125.9 (C-4, C_6H_5), 70.2 (CH), 42.1 (CH_2).

Anal. Calcd for $C_{24}H_{27}N_3$: N, 11.76; mol wt, 357.5. Found: N, 11.2 (titration); mol wt, 380.

2,4,6-Tris(1-phenylethyl)-1,3,5-hexahydrotriazine (Low-Melting Form 2b). Hydratropaldehyde (20 g, 0.149 mol) was added during 15 min to 20 ml (0.18 mol) of 9 *M* methanolic ammonia keeping the temperature at 5–7° by ice-bath cooling. Storage at −15° for 3 days gave white crystals, removed by filtration and washed with cold methanol to yield **2b**: 15.7 g (79%); mp 114–120° (capillary), 111–112° (Kofler); melting occurs with decomposition (gas evolution); *cf.* Table I for literature melting point; ir (Nujol) 3280 cm^{-1} (NH), C=N and C=O bands absent; ir (CCl_4 solution) 3270 cm^{-1} (NH, sharp), C=N and C=O absent; ^1H nmr (C_6D_6) δ 7.15 (15, m, C_6H_5), 3.77, 3.75, 3.70 (3, three doublets, NCHN, $J \simeq 7$ Hz), 2.4–3.0 (3, m, $CH_3CHC_6H_5$), 1.62, 1.55, 1.40, 1.35 (9, four doublets, $J \sim 7$ Hz, CH_3CH), 0.82 (3, broad s, NH); ^{13}C nmr ($CDCl_3$) δ 141.9 (C-1, C_6H_5), 127.6 (C-2, C_6H_5), 127.3, 126.9, 125.7, 125.3 (C-3 and C-4 C_6H_5), 74.8, 74.6, 73.9 (more intense, CH), 43.7, 43.6, 43.1 (CH_2), 16.6, 16.0, 15.7 (CH_3).

Anal. Calcd for $C_{27}H_{33}N_3$: C, 81.16; H, 8.33; N, 10.52, mol wt, 399.56. Found: C, 81.42; H, 8.35; N, 10.52; mol wt, 390.

A 1.0-g (2.5 mmol) sample of **2b** in 100 ml of dry benzene was heated under reflux for 1 hr with a stream of nitrogen passing through the liquid. The exit gas, having a strong ammonia odor, was bubbled through 1 *N* hydrochloric acid solution; titration with 1 *N* sodium hydroxide indicated that 2.5 mmol of ammonia had evolved. Concentration under reduced pressure to remove solvent gave 0.95 g of a yellow oil; crystallization from heptane gave 0.02 g of recovered **2b**, but no other crystalline product could be isolated; ir (neat film) 3250 (NH, sharp, weak), 1640 cm^{-1} (C=CN); ^1H nmr ($CDCl_3$) δ 7.15 (m, C_6H_5), 4.46 (d, $J \cong 7$ Hz, HNCHNH), 3.4–3.9 (m, $C_6H_5CHCH_3$), 2.47 (s, CH_3C=, weak), 1.1–1.4 (several doublets, J = 7 Hz, CH_3CH).

2,4,6-Tris(1-phenylethyl)-1,3,5-hexahydrotriazine (High-Melting Form 2b′). A 2.5-g sample of low-melting **2b** was heated with stirring under reflux with 100 ml of 20% methanolic potassium hydroxide for 2 hr. The mixture was chilled at 0°, filtered, and washed with hot ethanol to yield 1.7 g (68%) of **2b′**, rectangular prisms, mp 136–144° dec; *cf.* Table I for literature melting point. The infrared, ^1H nmr, and ^{13}C nmr spectra of the product were virtually identical with spectra of low-melting **2b**.

Anal. Calcd for $C_{27}H_{33}N_3$: C, 81.16; H, 8.33; N, 10.52; mol wt, 399.56. Found: C, 81.27; H, 8.30; N, 10.49; mol wt, 378.

A 0.50-g sample of **2b** was heated under reflux with stirring for 2 hr with 20 ml of methanol-*O-d* (99% assay) containing 6.0 g of potassium hydroxide-*O-d*. The solution was chilled and filtered and the product was washed with water and methanol to yield 0.43 g (86%) of **2b′**, mp 144–150°; the infrared, ^1H nmr, and ^{13}C nmr spectra of the product were virtually identical with those of low-melting **2b**. Evaporation of a chloroform solution of **2b′** gave **2b** in quantitative recovery, mp 109–116° dec.

2,4,6-Tris(diphenylmethyl)-1,3,5-hexahydrotriazine (2c). Diphenylacetaldehyde (4.0 g, 0.0207 mol) was added during 8 min to 40 ml of a saturated solution of ammonia in ether (temperature maintained at 0–2°). After storage at −15° for 2 days white crystals were removed by filtration and washed with ether, 1.36 g (34%), mp 82–88° dec (A second crop precipitated from the filtrate after storage at −15° for 4 additional days, 0.45 g, mp 68–70° dec.): ir (Nujol) 3270 cm^{-1} (NH), C=O and C=N bands absent; ir ($CHCl_3$) 3350 (NH), 1670 cm^{-1} (C=N), band forms very rapidly (A = 0.10 after 0.5 min, 0.25 after 3 min); after 15 min the 1670-cm^{-1} band had virtually disappeared with the formation of a strong C=CN band at 1640 cm^{-1} (A = 0.44) which was virtually absent initially; nmr spectra were determined rapidly; ^1H nmr ($CDCl_3$) δ 7.58 (30, s, C_6H_5), 4.62, 4.18 [6, AB q, J = 6 Hz, ring CH at δ 4.62 (slight broadening), $(C_6H_5)_2CH$ at δ 4.18], 1.4 (3, broad s, NH; signal disappears on addition of D_2O); ^{13}C nmr ($CDCl_3$) δ 140.7 (C-1, C_6H_5), 128.4 (C-2, C_6H_5), 127.9 (C-3, C_6H_5), 126.1 (C-4, C_6H_5), 72.9 (NCN), 56.1 (CHC_6H_5).

Anal. Calcd for $C_{42}H_{39}N_3$: N, 7.17; mol wt, 585.8. Found: N, 7.03 (titration); mol wt, 553 (osmometry, C_6H_6).

In an alternate procedure 10 g of diphenylacetaldehyde was added to 20 ml of 9 *M* methanolic ammonia (temperature at 0–5° during the addition). After storage at −15° for 1 day a few drops of water was added to the clear solution and storage at −15° was continued for 2 weeks. A precipitate which formed was filtered off and washed with cold methanol to yield 8.64 g (87%) of crude **2c**, mp 63–78° dec; the material decomposed on attempted recrystallization. The filtrate after standing at room temperature for 2 weeks deposited crystals of oxazoline 14, 0.20 g, mp 123–125° (*vide infra*).

A 0.10-g sample of triazine **2c** was heated under reflux with 20% methanolic potassium hydroxide for 2 hr. Chilling at 0°, followed by filtration and washing of the precipitate with methanol, gave 0.80 g (80%) of crystalline isomer **2c′**, mp 105–110° dec; its infrared and nmr spectra were virtually identical with those of **2c**.

2,4,6-Tribenzyl-1,3,5-triazabicyclo[3.1.0]hexane (*trans*-3a). Procedure A. Phenylacetaldehyde (6.0 g, 0.050 mol) was added dropwise, with stirring during 5 min, to a methanolic solution of chloramine (prepared by addition, during 10 min, of 3.0 ml of *tert*-butyl hypochlorite to 25 ml of 9 *M* methanolic ammonia containing 3 ml of *tert*-butyl alcohol keeping the reaction temperature at −35°); a reaction temperature of −35 to −37° was maintained by an ethylene dichloride–Dry Ice bath. Stirring magnetically was continued (flask capped with a calcium chloride tube) maintaining the temperature at −30 to −37° for 2.25 hr and at ambient temperature for 3 hr. The mixture, which contained a voluminous precipitate, was concentrated *in vacuo* to near dryness and the residue was extracted three times with hot chloroform. The cooled extracts were filtered and the filtrate was concentrated to dryness; the pale yellow solid residue was crystallized from 1:1 benzene–hexane to yield 2.9 g (49%) of *trans*-**3a**, mp 163–168°; a second crop of crude material was recovered from the filtrate, 1.0 g, mp 130–155°. Several recrystallizations from cyclohexane gave long needles: mp 172–175°; ir (KBr) 3130 cm^{-1} (NH); ^1H nmr ($CDCl_3$) δ 7.42 (15, s, C_6H_5), 4.46, 4.37 (2, apparent triplets, $J \cong 5$ Hz, ring CH at C-4 and C-6), 2.9 (6, two nearly superimposed apparent triplets, $J \cong 5$ and 5.5 Hz, CH_2), 2.22 (1, apparent triplet, $J \cong 5.5$ Hz, ring CH at C-2); ^{13}C nmr ($CDCl_3$, the multiplicities of the proton-coupled spectra are given in parentheses) δ 138.8, 137.8, 136.9 (s, C-1 C_6H_5), 129.8, 129.1, 128.3, 128.2, 126.8, 128.4 (d, C-2,3,4 C_6H_5), 80.8, 76.9 (d, ring C-2,4), 52.5 (d, ring C-6), 41.1, 37.6, 36.0 (t, CH_2).

Procedure B. To 2,4,6-tribenzyl-1,3,5-hexahydrotriazine (**2a**, 0.715 g, 2 mmol), 0.11 g of sodium carbonate, and 30 ml of methanol at −35° (Dry Ice–ethylene dichloride bath) was added, with stirring, *tert*-butyl hypochlorite (0.22 g, 2 mmol). The mixture was stirred at −35° for 1.8 hr and at ambient temperature for 2 hr. The mixture was concentrated to dryness under reduced pressure and the residue was extracted with hot benzene. The extract was filtered and concentrated to dryness and the residue was crystallized from hexane to yield 0.14 g of crystals, mp 75–141°; recrystallizations from cyclohexane gave needles, 30 mg, mp 172–175°. This material was identical with the product obtained by procedure A, above (mixture melting point, ir, nmr).

Anal. Calcd for $C_{24}H_{25}N_3$: C, 81.09; H, 7.09; N, 11.82; mol wt, 355.46. Found: 81.04; H, 6.92; N, 11.63; mol wt, 356.

2,4,6-Tris(1-phenylethyl)-1,3,5-triazabicyclo[3.1.0]hexane (*trans*-3b). Procedure A. Hydratropaldehyde (6.71 g, 0.05 mol) was treated with chloramine using the procedure described for preparation of *trans*-**3a** to yield 0.35 g of crude product, mp 110–130°. Recrystallization from hexane gave 0.17 g, mp 148–154°. Further recrystallization gave prisms: mp 161–164°; ir (KBr) 3150 cm^{-1} (NH); ^1H nmr ($CDCl_3$) δ 7.26 (15, broad m, C_6H_5), 3.9–4.4 (2, m, C-4,6 ring CH), 2.0–3.0 (4, m, C-2 ring CH and CH_3CH), 1.0–1.6 (9, nine major doublets, $J \cong 7$ Hz, CH_3); ^{13}C nmr ($CDCl_3$) δ 144.0, 143.2, 142.9 (C-1, C_6H_5), 128.3, 128.2, 128.1, 128.0, 127.9, 127.4, 127.3, 127.1, 126.5, 126.4, 126.2, 126.1 (C-2,3,4 C_6H_5, 85.1, 84.2, 82.8, 82.6, 82.3, 81.2 (ring C-2,4), 58.4, 58.1 (ring C-6), 45.0, 44.7, 44.2, 43.2, 42.7, 41.8, 41.4, 41.1, 40.8 (CH_3CH), 21.2, 20.8, 20.3, 19.9, 19.5, 17.8, 17.5, 16.6, 15.8 (CH_3).

Procedure B. 2,4,6-Tris(1-phenylethyl)-1,3,5-hexahydrotriazine (**2b**, 0.80 g) was oxidized with *tert*-butyl hypochlorite by the procedure employed with **2a** to yield 14 mg of crude product, mp 115–144°. Recrystallizations from hexane gave *trans*-**3b**, mp 161–165°, identical with the product obtained by procedure A (ir, nmr, mixture melting point).

Anal. Calcd for $C_{27}H_{31}N_3$: C, 81.57; H, 7.86; N, 10.57; mol wt, 397.54. Found: C, 81.61; H, 7.80; N, 10.46; mol wt, 394.

Attempts to prepare 2,4,6-tris(diphenylmethyl)-1,3,5-triazabicyclo[3.1.0]hexane (**3c**) from diphenylacetaldehyde by the procedures employed for preparing **3a** and **3b** were unsuccessful. Procedures A and B both gave small amounts (2–5%) of diphenylacetamide, mp 167–169° (prisms from cyclohexane), as the only isolated crystalline product (lit.[40] mp 167.5–169°), ir (Nujol) 1630 cm^{-1}

(C=O, strong, amide); elemental analyses and molecular weight data agree with the molecular formula $C_{14}H_{13}NO$.

Bis(2,2-diphenylethen)amine (6c). Procedure A. 2,4,6-Tris(diphenylmethyl)-1,3,5-hexahydrotriazine (**2c**, 0.50 g, 0.854 mmol) in 50 ml of benzene was heated under reflux for 1.3 hr while nitrogen was passed through the solution. The exit gas containing ammonia was passed through 1 *N* hydrochloric acid solution to yield 1.0 mequiv of ammonia (0.72 mequiv formed in 45 min); assay determined by titration with 1 *N* sodium hydroxide. The solution was concentrated to dryness to yield pale yellow crystals, mp 100–135° dec. Recrystallization from methanol gave 0.14 g (44%) of **6c**: mp 143–144° (lit.[33] mp 142–146°); ir (Nujol) 3300 (NH), 1625 cm^{-1} (C=CN); ^1H nmr ($CDCl_3$) δ 7.32 (20, m, C_6H_5), 6.90 (2, s, CH=); ^{13}C nmr ($CDCl_3$) δ 141.2 (C-1, C_6H_5), 138.1 (C-1, C_6H_5), 129.8, 128.9, 128.3 (C-2,3 C_6H_5), 128.0, 126.8, 125.1 (C-4, C_6H_5 and CH=), 116.0 [quaternary C, $(C_6H_5)_2C$=]; ^{13}C assignments were based on peak intensities, multiplicities observed in the proton-coupled spectra, and/or relaxation times; uv (ethanol) λ_{max} 362 nm (ϵ_{max} 30,000).

Procedure B. 2,2-Diphenylethenamine[13] (0.20 g, 1 mmol) and diphenylacetaldehyde (0.20 g, 1 mmol) were dissolved in 10 ml of methanol by warming on the steam bath. The cooled solution was diluted with water until turbid. Chilling at 0° gave 15 mg of **6c**, mp 140–144°.

Procedure C. 2,2-Diphenylethenamine (0.10 g) in 10 ml of 95% ethanol was warmed on the steam bath until a clear solution was obtained. After standing at room temperature for 40 hr and at 0° for 6 hr there was obtained 10 mg of **6c**, mp 145–147°.

Procedure D. 2,2-Diphenylethenamine (0.10 g) was heated, without solvent, on the steam bath for 1 hr. Ammonia was evolved vigorously during the heating. Recrystallization of the product from methanol gave 35 mg of **6c**, mp 144–149°. After **6c** itself was heated for 1 hr the compound was unchanged.

Procedure E. Phenylacetaldehyde (5 g) and 9 *M* methanolic ammonia (10 ml) were added to 400 ml of methanol. After standing at room temperature for 1 week the solution was concentrated to dryness and the residue was recrystallized from ethanol to yield 0.85 g (18%) of **6c**, mp 145–148°.

Anal. Calcd for $C_{28}H_{23}N$: C, 90.04; H, 6.21; N, 3.75; mol wt, 373.47. Found: C, 90.07; H, 6.10; N, 3.70; mol wt, 375.

2,2-Diphenyl-1-nitroethene (12) was prepared from 1,1-diphenylethene (Aldrich) by the procedure of Bordwell and Garbisch[41] as crystals from hexane, mp 85–87° (lit.[41] mp 85–86°).

2,2-Diphenylethenamine (7c). Procedure A. 2,2-Diphenyl-1-nitroethene (**12**, 1.0 g, 4.45 mmol) in 50 ml of ether was shaken with platinum oxide catalyst (0.37 g) and hydrogen in a Parr apparatus (33 psi, 25°) for 45 min (3 molar equiv of hydrogen absorbed). Filtration of the catalyst followed by concentration of the filtrate gave 0.70 g of white solid which was triturated with cold ether and isopentane to yield 0.42 g (48%) of **7c** as white prisms, mp 122–129° (Kofl), identical with that prepared by procedure B (ir, nmr, mixture melting point) (lit.[13] mp 116–125° dec).

Procedure B. The procedure of Curtin was employed with modifications.[13] Diphenylacetaldehyde (19.6 g, 0.1 mol) was added to 9 *M* methanolic ammonia (150 ml) during 20 min with ice-bath cooling (reaction temperature below 5°). Ammonia was bubbled into the solution for 12 hr (20–22°). Chilling at 0° deposited crystals which were removed by filtration and washed with cold methanol, 13.5 g (69%) of **7c**, mp 100–128°. Recrystallization from ethanol gave long prisms: mp 119–127°; ir (KBr) 3270, 3350 (NH), 1630 cm^{-1} (C=CN); ^1H nmr ($CDCl_3$) δ 7.38, 7.18 (10, two singlets, C_6H_5), 6.70 (1, broad m, =CH, sharpens to singlet on addition of D_2O), 3.44 (2, broad m, NH_2, disappears on addition of D_2O).

Anal. Calcd for $C_{14}H_{13}N$: C, 86.11; H, 6.71; N, 7.17; mol wt, 195.25. Found: C, 85.90; H, 6.69; N, 7.00; mol wt, 201.

***N*-Acetyl-2,2-diphenylethenamine (13).** Bis(2,2-diphenylethen)amine (**6c**, 0.20 g) in 20 ml of acetic anhydride was heated on the steam bath for 16 hr. Concentration to dryness gave an oil which was recrystallized from benzene–heptane to yield 35 mg (28%) of **13**, prisms, mp 158–163° (Kofl) (lit. mp 162–163°,[26] 162–164°,[13] 166°[32]).

Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90; mol wt, 237.29. Found: C, 80.79; H, 6.17; N, 5.99; mol wt, 226.

5,5-Diphenyl-2-(diphenylmethyl)-3-oxazoline (14). The filtrate remaining after removal of the first crop of 2,2-diphenylethenamine (**7c**) (from reaction of diphenylacetaldehyde with ammonia, procedure B, above) was concentrated to a small volume to yield a gummy solid, which on standing overnight produced 0.72 g of prisms, mp 125–128°; additional material was obtained in a similar manner from the mother liquors remaining from recrystallization of **7c**, 0.34 g, mp 124–127°; total yield of high-purity **14**, 1.04 g (5.4%). Recrystallization from ethanol gave needles: mp 125–127°; ir (Nujol) 1630 cm^{-1} (C=N, weak), NH band absent; uv (methylcyclohexane) λ_{max} 218 nm (ϵ 23,900), 260 (5050); ^1H nmr ($CDCl_3$) δ 7.78 (1, d, $J \cong 2.5$ Hz, CH= at C-4), 6.7–7.5 (20, m, C_6H_5), 6.44 (1, dd, $J \cong 5$ and 2.5 Hz, CH at C-2), 4.48 [1, d, $J \cong 5$ Hz, $CHCH(C_6H_5)_2$]; ^{13}C nmr ($CDCl_3$) δ 163.5 (C-4 oxazoline ring), 141.2, 140.8, 140.6, 140.3 (C-1, C_6H_5), 129.4, 128.5, 128.2, 128.0, 127.8, 127.6, 127.0, 126.5, 126.2 (C-2,3,4, C_6H_5), 107.4 (C-2 oxazoline ring), 95.3 (C-5 oxazoline ring), 56.1 (C_6H_5CH).

Anal. Calcd for $C_{28}H_{23}NO$: C, 86.34; H, 5.95; N, 3.60; mol wt, 389.47. Found: 86.38; H, 5.97; N, 3.58; mol wt, 389 (mass spectrum), 380 (osmometry).

A sample of **14** dissolved in hot methanol was treated with 1 *N* hydrochloric acid to adjust the pH of the solution to 4.0. After standing at 25° for 24 hr the solution was made slightly alkaline by addition of 1 *N* sodium hydroxide solution. Concentration gave an oil (wet), which was dissolved in benzene and treated with Drierite. Filtration, followed by concentration to dryness, gave a pale yellow oil: ir 1700 cm^{-1} (C=O, aldehyde); ^1H nmr ($CDCl_3$) δ 9.77 (s, CHO aldehyde); diphenylacetaldehyde spectra reveal the same aldehyde peaks (ir and ^1H nmr).

Registry No.—**2a**, 51003-90-8; **2b**, 51003-91-9; **2c**, 51003-92-0; *trans*-**3a**, 51003-11-3; *trans*-**3b**, 51003-93-1; **6c**, 985-09-1; **7c**, 947-90-0; **12**, 5670-69-9; **13**, 1722-89-0; **14**, 51002-92-7; phenylacetaldehyde, 122-78-1; hydratropaldehyde, 93-53-8; diphenylacetaldehyde, 947-91-1.

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Bicyclic Enamines. VIII. Mechanistic Studies of Rearrangements in a Quinuclidine System[1]

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When an unsaturated quaternary quinuclidine-3-carboxylic acid ester of type **1** (X = I^-) is heated to about 150° for 1 min or less, it rearranges in very good yield to a lactone of type **7**. The same lactone is formed from the corresponding base **4**, although prolonged heating at higher temperature is required (200° for 30 min). We have shown that these conversions are multistep reactions initiated by the attack of a nucleophile, which can either be the counterion of the quaternary salts **1–3** or another base molecule in the rearrangement of the bases **4–6**.

Recently we reported[3,4] that the unsaturated quinuclidine-3-carboxylic acid esters **1** and **2**, when heated, were converted into tetrahydronicotinic acid lactones. We have now extended this work to all the esters **1–6** and studied the mechanism for their conversion into lactones **7–10**.

In a preliminary report[3] several mechanisms were considered for the thermal conversions of Scheme I, and it was concluded that the intermediate **11** (Scheme II) was formed by successive sigmatropic rearrangements. Further studies have shown that this proposal was in error, and evidence now indicates that, contrary to the preliminary report, the rearrangements probably occur by attack of the counterion of the quaternary salt. Rearrangement of the tertiary bases probably occurs *via* a related mechanism.

In our early studies on this problem we observed that bases **4** and **5** gave lactones in a manner similar to that of quaternary salts **1** and **2** (Scheme I). This indicated to us that the bases and the quaternary salts were converted *via* the same mechanism, and in a preliminary report[3] we proposed that the lactone **7** was formed *via* sigmatropic rearrangements. However, we later found that the nitrogen substituent of compounds of type **1** influenced the ease of rearrangement to lactones. We could thus demonstrate that *N*-allyl- and *N*-propargylquinuclidine-3-carboxylic acid esters gave the corresponding lactones when

Scheme I