2,2′-Dicyano-3,3′-bis[indole] (10). A solution of 2-cyanoindole (825 mg, 0.0023 mol) and finely cut potassium (86 mg, 0.0022 mol) in xylene (10 mL) was heated at 140 °C in an oil bath for 6 h. The solution was cooled and iodine (280 mg, 0.0011 mol) in xylene (15 mL) was added. After being stirred for 10 h, the solution was filtered and the filtrate evaporated in vacuo to give a residue which was chromatographed on neutral alumina (Camag, Brockmann activity 1, 50 g, 2 × 20 cm). Elution with benzene gave 2-cyano-3-iodoindole: 18 mg (2.6%); mp 170 °C dec; IR (KBr) 3350 (NH), 2230 cm^{-1} (C≡N); mass spectrum (70 eV), *m/e* (relative intensity), 268 (M^{+}·, 71), 141 (M^{+}· − I, 100), 115 (27), 114 (48), 76 (27), 52 (21). Elution with chloroform gave 2,2′-dicyano-3,3′-bis[indole]: 57 mg (22%); mp 184 °C dec; identical with the material obtained from the thermolysis of 2-azidoquinoline 1-oxide (**5**).

2-Azidoquinoxaline 1-Oxide and Its Decomposition to 26. A solution of 2-chloroquinoxaline 1-oxide (0.5 g, 0.0028 mol), NaN_3 (0.5 g, 0.008 mol) and concentrated HCl (0.5 mL) in acetone (35 mL) and water (35 mL) was stirred at room temperature for 72 h. Extraction with $CHCl_3$ gave an oil (0.5 g) which was chromatographed on basic alumina (50 g, 60–200 mesh, 4 × 10 cm). Elution with CH_2Cl_2 gave 2-chloroquinoxaline 1-oxide: 386 mg (77%); mp 114–116 °C. Elution with $CHCl_3$ gave 2-azidoquinoxaline 1-oxide (**25**): 85 mg (68% based on chloride consumed); mp 101–104 °C dec; IR (KBr) 2170, 2130 (N_3), 1260 cm^{-1} (N^{+}–O^{-}). Attempts to recrystallize this compound led to its decomposition and the formation of 2-cyano-1-hydroxybenzimidazole (**26**): 73 mg (87%); mp 236–238 °C dec (lit.[14] mp 236 °C); identical (IR, NMR, mass spectrum) with an authentic sample.[14]

2-Cyano-1-(*p*-toluenesulfonyloxy)benzimidazole. A solution of **25** (1.10 g) and *p*-toluenesulfonyl chloride (1.90 g) in CH_2Cl_2 (75 mL) and pyridine (1 mL) was boiled under reflux for 5 h and then kept at room temperature overnight. The solution was washed with 10% aqueous K_2CO_3 and the organic layer separated, dried ($MgSO_4$), and evaporated in vacuo to give the tosylate: 1.40 g (65%); mp 112–114 °C (EtOH); IR (KBr) 2250 (C≡N), 1400, 1182, 1090 cm^{-1}; NMR ($CDCl_3$) δ 7.90 (d, 2 H, J_o = 8 Hz, toluene protons), 7.50 (m, 4 H, benzimidazole protons), 7.48 (d, 2 H, J_o = 8 Hz, toluene protons). Anal. Calcd for $C_{15}H_{11}N_3O_3S$: C, 57.50; H, 3.52; N, 13.42. Found: C, 57.45; H, 3.67; N, 13.63.

Attempted Thermal Disproportionation of 1-Hydroxy-2-phenylindole at 100 °C. A solution of 1-hydroxy-2-phenylindole[18] (0.5 g) in toluene (21 mL) was heated at 100 °C for 2 h. Evaporation of the solvent gave unchanged starting material: 485 mg (97%); mp 170–172 °C.

Acknowledgment. This work was supported by grants from the NSF (GP-33361X), from the National Institutes of Health (GM 16626) and from Mead Johnson Research Center.

Registry No. **5**, 51796-60-2; **7**, 30958-68-0; **8**, 2423-68-9; **9**, 51796-61-3; **10**, 51796-62-4; **11**, 75548-90-2; **12**, 51796-64-6; **13**, 51991-49-2; **14**, 36193-65-4; **15**, 51796-68-0; **16**, 634-47-9; **17**, 10286-18-7; **18**, 51796-66-8; **25**, 51796-69-1; **26**, 40159-90-8; (cyanomethyl)-triphenylphosphonium chloride, 4336-70-3; triethyl phosphite, 554-70-1; mesitylene, 25551-13-7; 2-chloroquinoxaline 1-oxide, 5227-57-6; 2-cyano-1-(*p*-toluenesulfonyloxy)benzimidazole, 75558-42-8; 1-hydroxy-2-phenylindole, 1859-39-8.

Stereospecific Synthesis of N-Substituted *cis*-2-Aryl-3-alkylaziridines

Norbert De Kimpe,*[1] Roland Verhé, Laurent De Buyck, and Niceas Schamp

Laboratory of Organic Chemistry, Faculty of Agricultural Sciences, State University of Gent, Coupure 533, B-9000 Gent, Belgium

Received August 13, 1980

A convenient stereospecific synthesis of N-substituted *cis*-2-aryl-3-alkylaziridines is reported, by reaction of *N*-alkyl or *N*-aryl α,α-dichloroalkyl aryl ketimines with lithium aluminum hydride in ethereal medium. The mechanism involves the addition of hydride at the carbon–nitrogen double bond followed by intramolecular chloride displacement and loss of chloride anion from the intermediate α-chloroaziridine to generate an azirinium chloride, which is stereospecifically attacked by hydride to afford the title compounds. The formation of some side reactions in the case of *N*-aryl derivatives is discussed.

Introduction

Several methods have been described in the literature for the stereospecific synthesis of *cis*-aziridines.[2] Practically all of them suffer from the use of difficultly accessible starting materials or are less convenient because of the formation of various side products, which make the purification of the desired products difficult and laborious. N-Substituted *cis*-aziridines have been prepared from *threo*-β-amino alcohols by means of the Wenker procedure, i.e., conversion into the sulfate ester and base-induced intramolecular nucleophilic substitution,[3,4] or by means of triphenylphosphine dihalide and base treatment.[5–7] An analogous method involved the transformation of *erythro*-β-amino alcohols into *threo*-β-chloro amines (using PCl_5, $SOCl_2$, ...) with subsequent base-induced ring closure.[8,9] In one single case, (dimethylamino)-(*p*-tolyloxo)sulfonium ethylide was reported to condense stereospecifically with benzylideneaniline to produce the *cis*-aziridine.[10] A more general stereospecific synthesis of *cis*-aziridines entailed the reaction of *threo*-β-iodoalkyl azides with aryl- and alkyldichloroboranes to give the corresponding β-iodo

(1) N. De Kimpe, "Bevoegdverklaard Navorser" of the Belgian "Nationaal Fonds voor Wetenschappelijk Onderzoek". This paper was presented at the Third IUPAC Symposium on Organic Synthesis, Madison, WI, June 1980, Abstracts p 42. This is part 22 of our series dealing with the chemistry of α-halogenated imino compounds.

(2) O. C. Dermer and G. E. Ham, "Ethylenimine and other Aziridines", Academic Press, New York and London, 1969.

(3) S. J. Brois and G. P. Beardsley, *Tetrahedron Lett.*, 5113 (1966).

(4) R. Ghirardelli and H. J. Lucas, *J. Am. Chem. Soc.*, **79**, 734 (1957).

(5) I. Okada, K. Ichimura, and R. Sudo, *Bull. Chem. Soc. Jpn.*, **43**, 1185 (1970).

(6) (a) J. C. Pommelet and J. Chuche, *Tetrahedron Lett.*, 3897 (1974); (b) *Can. J. Chem.*, **54**, 1571 (1976).

(7) N. Manisse and J. Chuche, *J. Am. Chem. Soc.*, **99**, 1272 (1977).

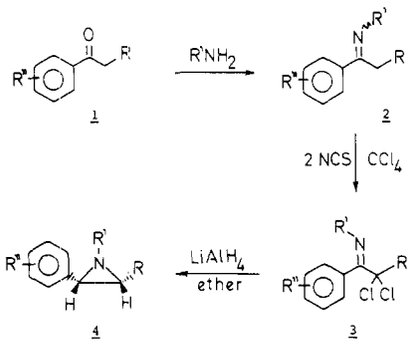
(8) R. N. Loeppky and D. H. Smith, *J. Org. Chem.*, **41**, 1578 (1976).

(9) R. Bartnik, G. Mloston, and S. Lesniak, *Pol. J. Chem.*, **53**, 537 (1979).

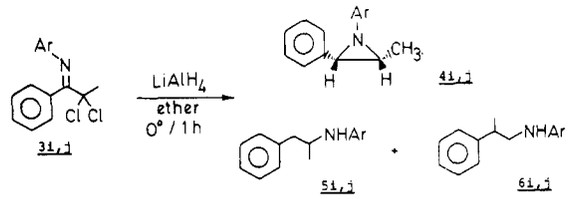
(10) C. R. Johnson and E. R. Janiga, *J. Am. Chem. Soc.* **95**, 7692 (1973).

0022-3263/80/1945-5319$01.00/0

Scheme I



Scheme II



secondary amines, which underwent ring closure with base.[11] N-Unsubstituted *cis*-aziridines have been synthesized from the reaction of ketoximes with mixed metal hydrides[12-14] or Grignard reagents (i.e., the so-called Hoch–Campbell reaction)[15] and from the reaction of α,β-unsaturated ketoximes,[16-18] trimethylhydrazonium halides,[13] or *threo*-β-iodo azides[19] with mixed metal hydrides. Finally, N-unsubstituted *cis*-aziridines have been obtained by the addition of pseudohalogens, e.g., iodine isocyanate, to (*Z*)-olefins,[19,20] the reaction of lithium aluminum hydride with azirines,[21] and the triphenylphosphine-induced ring closure of *threo*-β-azido alcohols.[22]

We report here the stereospecific synthesis of N-substituted *cis*-aziridines **4**, which were obtained, free of side products, in high yields by starting from alkyl aryl ketones **1** through a three-step sequence via α,α-dichloroalkyl aryl ketimines **3**.

Results and Discussion

In continuation of synthetic and mechanistic work in the field of α-halogenated imino compounds, we explored the reactivity of N-substituted α,α-dichloroalkyl aryl ketimines **6**.[23] As a result of previous investigations in this area, the α-haloimino system was developed as a convenient synthetic tool for the synthesis of aziridines,[24,25] originating from nucleophilic attack of mixed metal hydrides at the imino function and subsequent intramolecular halide displacement. It was found that α,α-dichloroimino compounds also furnished the same aziridines[24a,b] and the mechanism was explained via the intermediacy of a highly reactive α-chloroaziridine, which was rapidly transformed into the final aziridines by hydride substitution of the chloro atom. There was no indication as to whether the substitution of the α-chloroaziridine was a result of a first-order or second-order reaction.

It was reasoned that appropriate substitution of the α,α-dihaloimino system would permit mechanistic conclusions to be drawn from the stereochemistry of the final products. For this purpose, *N*-alkyl and *N*-aryl α,α-dichloroalkyl aryl ketimines **3** were chosen as target molecules. They were prepared in high yields (85–96%) from the condensation of alkyl aryl ketones **1** with primary amines, using titanium tetrachloride in ethereal medium as an effective drying agent (for aliphatic amines) or by means of the Dean–Stark procedure in toluene (for anilines), followed by chlorination of the resulting alkyl aryl ketimine **2** with *N*-chlorosuccinimide in carbon tetrachloride (Scheme I). α,α-Dichloro ketimines **3** occurred exclusively as the *E* isomer in CCl_4 solution (NMR). The synthesis and spectroscopic data of compounds **3** are compiled in a table in the supplementary material.

The reaction of *N*-alkyl α,α-dichloroalkyl aryl ketimines **3a–g** with excess (8 equiv) lithium aluminum hydride in ether under reflux resulted in the formation of exclusively *cis*-1,2-dialkyl-3-arylaziridines **4a–g** (isolated yield, 71–84%) (Scheme I). The stereochemistry of the *cis*-aziridines **4** was determined by the coupling constant (NMR, CCl_4) of the vicinal ring protons. Vicinal coupling constants of ring protons in aziridines are usually about 6–6.5 Hz for the cis hydrogens and about 2.5–3.5 Hz for the trans hydrogens.[3,26,27] The coupling constant of *cis*-aziridines **4** ranged from 6.2 to 6.5 Hz, clearly indicating the cis stereochemistry. The spectrometric properties (NMR, IR, mass spectrum) of *cis*-aziridines **4** are compiled in Table I.

Besides the spectrometric analysis, *cis*-1,2-dimethyl-3-phenylaziridine (**4a**), obtained by our method, was proven to be identical in all aspects with the known **4a** obtained by independent synthesis from *threo*-ephedrine.[3] It may be mentioned that attempts to synthesize *trans*-1,2-dimethyl-3-phenylaziridine from *erythro*-ephedrine failed, despite its reported successful isolation and characterization.[3] In our hands, the *trans*-aziridine polymerized on standing, a phenomenon which was also observed by others.[5,28]

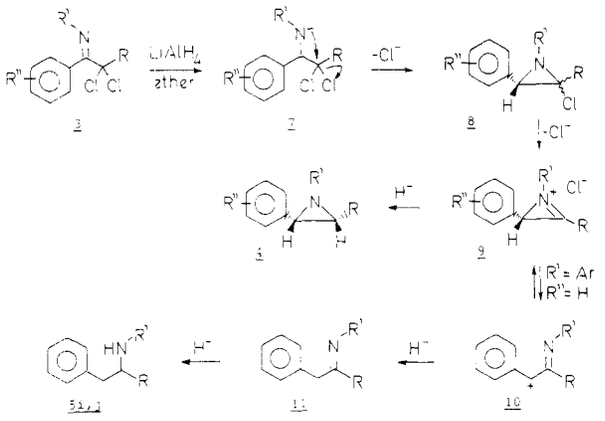
(11) A. B. Levy and H. C. Brown, *J. Am. Chem. Soc.*, **95**, 4067 (1973).
(12) (a) K. Kitahonoki, K. Kotera, Y. Matsukawa, S. Miyazaki, T. Okada, H. Takahashi, Y. Takano, *Tetrahedron Lett.*, 1059 (1965); (b) Shionogi & Co, Ltd, Neth. Appl., 6,515,376 (Cl.C07a), May 27, 1966; Japan Appl., Nov. 26, 1964, and Aug. 13, 1956; *Chem. Abstr.*, **65**, 15324 (1966); (c) K. Kotera, Y. Matsukawa, H. Takahashi, T. Okada, and K. Kitahonoki, *Tetrahedron*, **24**, 6177 (1968); (d) K. Kotera and K. Kitahoniki, *Org. Synth.*, **48**, 20 (1968); (e) K. Kotera, S. Miyazaki, H. Takahashi, T. Okada, and K. Kitahonoki, *Tetrahedron*, **24**, 3681 (1968); (f) K. Kotera and K. Kitahonoki, *Org. Prep. Proced.*, **1**, 305 (1969).
(13) Y. Girault, M. Decouzon, and M. Azzaro, *Tetrahedron Lett.*, 1175 (1976).
(14) S. R. Landor, O. O. Sonola, and A. R. Tatchell, *J. Chem. Soc., Perkin Trans. 1*, 1294 (1974).
(15) (a) A. Laurent and A. Muller, *Tetrahedron Lett.*, 759 (1969); (b) G. Alvernhe and A. Laurent, *Bull. Soc. Chim.* Fr., 3003 (1970); (c) Y. Diab, A. Laurent, and P. Mison, *Tetrahedron Lett.*, 1605 (1974).
(16) M. Y. Shandala, M. D. Solomon, and E. S. Waight, *J. Chem. Soc.*, 892 (1965).
(17) J. Dimmock, P. Smith, L. Noble, and W. Pannekoek, *J. Pharm. Sci.*, **67**, 1536 (1978).
(18) M. Y. Shandala and R. G. Salik, *Egypt. J. Chem.*, **19**, 881 (1978).
(19) A. Hassner, R. P. Hoblitt, C. Heathcock, S. E. Kropp, and M. Lorber, *J. Am. Chem. Soc.*, **92**, 1326 (1970).
(20) A. Hassner, G. J. Matthews, and F. W. Fowler, *J. Am. Chem. Soc.*, **91**, 5046 (1969).
(21) A. Hassner and F. W. Fowler, *Tetrahedron* Lett., 1545 (1967).
(22) Y. Ittah, Y. Sasson, I. Shahak, S. Tsaroom, and J. Blum, *J. Org. Chem.*, **43**, 4271 (1978).
(23) N. De Kimpe, R. Verhé, L. De Buyck, S. Tukiman, and N. Schamp, *Tetrahedron*, **35**, 789 (1979).
(24) (a) N. De Kimpe, R. Verhé, L. De Buyck, and N. Schamp, *Synth. Commun.*, **5**, 269 (1975); (b) N. De Kimpe, N. Schamp and R. Verhé, *ibid.*, **5**, 403 (1975); (c) N. De Kimpe, R. Verhé, L. De Buyck, W. Dejonghe, and N. Schamp, *Bull. Soc. Chim. Belg.*, **85**, 763 (1976); (d) N. De Kimpe, R. Verhé, L. De Buyck, and N. Schamp, *Recl. Trav. Chim. Pays-Bas*, **96**, 242 (1977).
(25) See also the following literature citations: L. Duhamel and J. Y. Valnot, *Tetrahedron Lett.*, 3167 (1974); A. Picot and X. Lusinchi, *ibid.*, 679 (1974); A. Hassner and A. B. Levy, *J. Am. Chem. Soc.*, **93**, 5469 (1971).
(26) (a) S. J. Brois, *Tetrahedron*, **26**, 227 (1970); (b) S. J. Brois, *J. Org. Chem.*, **27**, 3532 (1962).
(27) P. Scheiner, *J. Am. Chem. Soc.*, **90**, 988 (1968).

Table I. Physical and Spectrometric Properties of *cis*-Aziridines 4

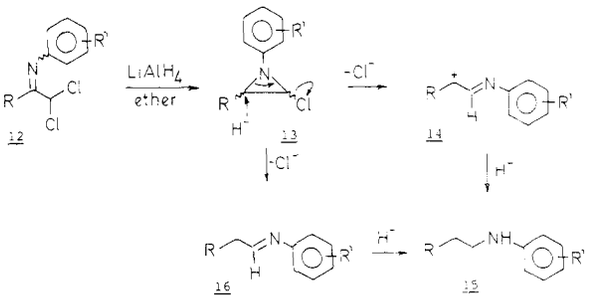
compd	R	R′	R″	% yield[a]	bp, °C (mmHg)	NMR (CCl_4), δ	mass spectrum, *m/e* (relative abundance)
4a	Me	Me	H	84	79–82 (12)[b]	0.83 (3 H, d, J = 5.5 Hz, CH_3C), 2.28 (1 H, d, J = 6.4 Hz, CHPh), 2.41 (3 H, s, NCH_3), 1.55 (1 H, q + d, J = 5.5, 6.4 Hz, CHMe), 7.15 (5 H, s, C_6H_5)[3,5]	147 (M^+, 28), 146 (100), 132 (28), 118 (10), 117 (14), 105 (22), 91 (16), 89 (6), 77 (8), 55 (9), 51 (6), 42 (21)
4b	Me	Et	H	74	32–34 (0.7)	0.87 (3 H, d, J = 5 Hz, CH_3C), 1.18 (3 H, t, J = 7 Hz, NCMe), 2.2–2.7 (2 H, m, NCH_2), 2.35 (1 H, d, J = 6.5 Hz, CHPh), 1.7 (1 H, m, CHMe), 7.26 (5 H, s, C_6H_5)	161 (M^+, 26), 160 (56), 132 (100), 105 (73), 91 (46), 77 (30)
4c	Me	*i*-Pr	H	78	35–36 (0.02)	0.85 (3 H, d, J = 5.4 Hz, CH_3C), 1.11 and 1.15 (2 × 3 H, 2 × d, J = 5.6 Hz each, $(CH_3)_2$), 7.16 (5 H, s, C_6H_5), 1.4–1.9 (2 H, overlap, NCH and CHMe), 2.35 (1 H, d, J = 6.3 Hz, CHPh)	175 (M^+, 18), 174 (16), 132 (100), 117 (6), 105 (19), 91 (7), 90 (3), 89 (3), 79 (2), 77 (4), 65 (2), 63 (1), 54 (1), 51 (1), 43 (11), 42 (2), 41 (2), 39 (2)
4d	Me	*i*-Pr	*p*-Cl	76	51–54 (0.1)	0.87 (3 H, d, J = 5.5 Hz, CH_3), 2.37 (1 H, d, J = 6.3 Hz, CHAr), 7.24 (4 H, s, C_6H_4), 1.4–1.9 (2 H, m, Me_2CH and MeCH), 1.12 and 1.18 (2 × 3 H, 2 × d, J = 6 Hz, $(CH_3)_2$)	209/211 (M^+, 18), 208/210 (9), 166/168 (100), 149/151 (15), 125/127 (8), 103 (12), 89 (8), 43 (4), 42 (4), 41 (4)
4e	Me	*t*-Bu	H	71[c]		0.80 (2 H, d, J = 5.8 Hz, CH_3C), 1.00 (9 H, s, *t*-Bu), 2.65 (1 H, d, J = 6.5 Hz, CHPh), 6.9–7.3 (5 H, m, C_6H_5), 1.80 (1 H, m, CHMe)	189 (M^+, 5), 174 (2), 162 (6), 132 (100), 117 (3), 106 (9), 91 (5), 77 (2), 58 (2), 57 (3), 41 (3)
4f	Me	cyclohexyl	H	71	77–81 (0.02)	0.86 (3 H, d, J = 5 Hz, CH_3), 2.36 (1 H, d, J = 6.2 Hz, CHPh), 1–2 (12 H, m, cyclohexyl + CHMe), 7.17 (5 H, 1, C_6H_5)	215 (M^+, 4), 214 (3), 132 (100), 118 (5), 117 (8), 105 (36), 91 (30), 79 (10), 77 (9), 65 (9), 55 (18), 54 (9), 41 (18)
4g	Et	Et	H	75	48–58 (0.01)	1.14 (3 H, t, J = 7 Hz, CH_3CN), 2.43 (2 H, q, J = 7 Hz, CH_2N), 2.40 (1 H, d, J = 6.5 Hz, CHPh), 1–1.6 (3 H, overlap, m, CHEt and CCH_2Me), 7.21 (5 H, s, C_6H_5), ~1 (3 H, overlap, CH_3CC)	175 (M^+, 52), 174 (57), 160 (12), 146 (100), 118 (7), 117 (10), 104 (10), 91 (57), 84 (15), 77 (9), 56 (19), 41 (15)
4i	Me	C_6H_5	H	61	95–100 (0.08)[d]	1.10 (3 H, d, J = 5.6 Hz, CH_3C), 3.17 (1 H, d, J = 6.4 Hz, CHPh), 2.43 (1 H, quintet, J = 6 Hz, CHMe), 6.7–7.5 (10 H, m, $(C_6H_5)_2$)	209 (M^+, 67), 208 (100), 194 (10), 193 (6), 181 (32), 180 (32), 167 (15), 118 (20), 105 (50), 104 (22), 91 (22), 77 (60), 51 (17)
4j	Me	*p*-$MeOC_6H_4$	H	61	127–131 (0.025)	1.08 (3 H, d, J = 5.7 Hz, CH_3), 2.35 (1 H, m, CHMe), 3.11 (1 H, d, J = 6.6 Hz, CHAr), 7.1–7.5 (5 H, m, C_6H_5), 6–6.7 (2 H, d, AB, J = 9 Hz, 2 × CH=, ortho with respect to N), 6.88 (2 H, d, AB, J = 9 Hz, 2 × CH=, meta with respect to N), 3.68 (3 H, s, OCH_3)	239 (M^+, 90), 238 (100), 197 (24), 148 (80), 135 (82), 134 (40), 92 (14), 91 (24), 77 (28)

[a] Isolated yields by distillation except as otherwise stated (compounds 4 gave satisfactory elemental analyses). [b] Lit.[5] bp 82 °C (14 mmHg). [c] Measured by GLC of the reaction mixture (20 equiv of $LiAlH_4$/THF/Δ, 3 days). [d] Known compound,[10,27] but no boiling point reported.

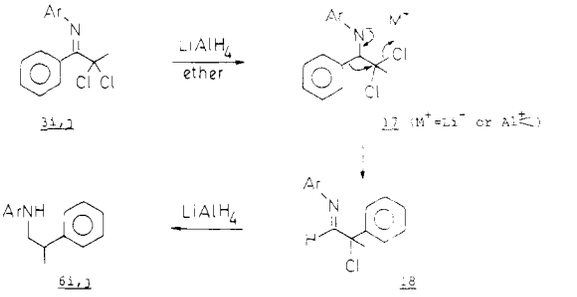
Scheme III



Scheme IV



Scheme V



N-Aryl α,α-dichloroalkyl aryl ketimines **3i,j** (R′ = Ph, *p*-$CH_3OC_6H_4$), under similar conditions used for the *N*-alkyl analogues **3a–g** (R′ = alkyl), gave lower yields of *cis*-aziridines **4i,j** due to the formation of the rearranged secondary amines **5i,j** and **6i,j** (Scheme II). Formation of these byproducts could be reduced by working at 0 °C for 1 h. Compounds **4i,j**, **5i,j**, and **6i,j** were separated by careful rectification or by thick-layer chromatography on silica gel (2-mm thickness) with CCl_4/hexane/EtOH 49:49:2 as eluant. Compounds **4i,j** gave an R_f value of about 0.55–0.65 while anilines **5i,j** and **6i,j** had an R_f value of 0.3–0.45.

From the mechanistic point of view, the formation of *cis*-aziridines **4** from α,α-dichloroalkyl aryl ketimines **3** can be explained by initial hydride attack at the carbon–nitrogen double bond followed by intramolecular nucleophilic substitution to give intermediate α-chloroaziridines **8**. These initial reactions have been exemplified already several times in reactions of α-halo imines with hydrides.[24,25] The chemistry of α-chloroaziridines is not well documented in the literature because of their difficult accessibility, but their reactive behavior contains remarkable synthetic aspects.[29] α-Chloroaziridines, like **8**, and α,α-dichloroaziridines (**8**, R = Cl) have the tendency to expel chloride anion to give an azirinium chloride (see **9**) or its isomeric ring opened form, i.e., an α-imino carbenium ion **10**.[29,30] Hydride attack at the cyclic iminium derivative from the less hindered side (most remote from the aryl substituent) furnishes *cis*-aziridines **4** (Scheme III). This route clearly established the stereospecific conversion of **3** into **4**. This mechanistic proposal is supported by the fact that azirines are known to add hydrides in a stereospecific manner, giving rise to N-unsubstituted *cis*-aziridines.[21] It has to be stressed here that the stereospecific conversion of oximes to N-unsubstituted *cis*-aziridines with lithium aluminum hydride[12–14] or Grignard reagents[15] was explained in terms of the intermediacy of azirines, to which the reagents added from the less hindered side. The rearrangement of α,α-dichloroalkyl aryl ketimines **3i,j** into anilines **5i,j** can be explained by α-chloroaziridine formation (**8**, R′ = aryl; R = Me; R″ = H) and expelling of a chloride anion to give the azirinium chloride (**9**, R′ = aryl; R = Me; R″ = H). Isomerization to the ring-opened isomer, i.e., α-imino carbenium ion **10** (R′ = aryl) and consecutive attack of hydride at the carbenium ion and the imino function finally afforded the rearranged secondary amines **5i,j** (Scheme III). These anilines (**5i,j**) do not originate from opening of aziridines **4i,j** by hydride attack. Even under reflux for a long period with lithium aluminum hydride in ether, compounds **4i,j** are recovered unchanged, as evidenced by a control experiment.

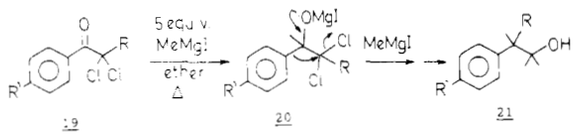
For comparative reasons, the previously found rearrangement of *N*-aryl dichloromethyl ketimines **12** into anilines **15** is mentioned here and can likewise be explained by a mechanism involving a transient α-imino carbenium ion **14**[31] (Scheme IV).

Previously, an alternative explanation was put forward in which a nucleophilic attack of hydride at the nonhalogenated ring carbon took place with concomitant expulsion of a chloride anion.[31] The latter mechanism was supported by the absence of rearrangement with *tert*-butyl derivative **22** (R = *t*-Bu; R′ = H), which was explained in terms of steric hindrance of the nucleophilic attack at the *tert*-butyl substituted carbon. Accordingly, 2-*tert*-butyl-1-phenylaziridine was the major compound resulting from the reaction via the corresponding azirinium chloride and subsequent hydride addition. The above-mentioned isomerization of the azirinium chloride into the α-imino carbenium ion **14** can be ruled out as the mode of rearrangement of α,α-dichloro ketimines **12** (R $\neq$ *t*-Bu) into anilines **15** because the α-imino carbenium ion **14** would be the most favorable one for the *tert*-butyl derivative. However, as mentioned before, such rearrangement was not observed in the latter case.

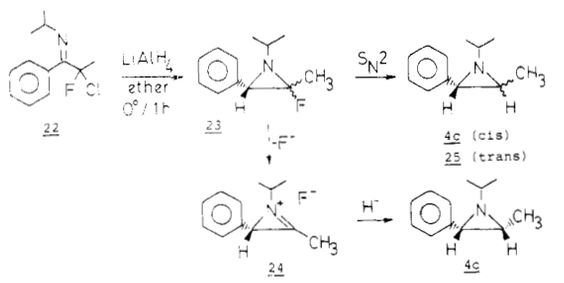
N-Aryl α,α-dichloroalkyl aryl ketimines **3i,j** are further distinguished from their *N*-alkyl analogues by the rearrangement into the branched anilines **6i,j**, resulting from rearrangement in the carbon skeleton. The identity of rearranged anilines **6i,j** was established by spectrometric methods and by synthesis of authentic material by condensation of 2-phenylpropanal with the aniline and subsequent reduction with mixed metal hydrides. The unexpected rearrangement is explained by addition of hydride at the carbon–nitrogen double bond of the *N*-aryl α,α-dichloro ketimine, but the resulting β,β-dichloro amine

(28) T. Taguchi and M. Kojima, *Chem. Pharm. Bull. (Tokyo)*, **7**, 103 (1959).
(29) J. A. Deyrup and R. B. Greenwald, *J. Am. Chem. Soc.*, **87**, 4538 (1965).
(30) R. E. Brooks, J. O. Edwards, G. Levey, and F. Smyth, *Tetrahedron*, **22**, 1279 (1966).
(31) N. De Kimpe, R. Verhé, and N. Schamp, *Bull. Soc. Chim. Belg.*, **84**, 701 (1975).

Scheme VI



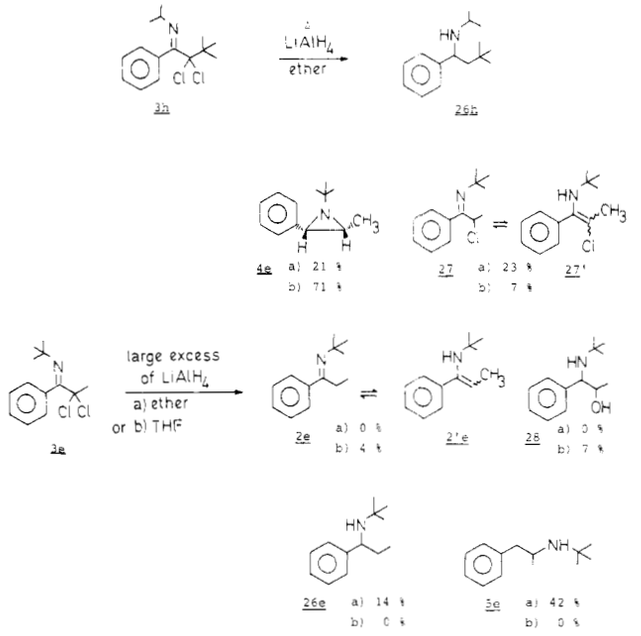
Scheme VII



anion **17** does not give rise to ring closure. Instead, phenyl migration to the halogenated carbon atom takes place according to a semi(aza)pinacol rearrangement. The α-chloro aldimine **18** thus formed undergoes addition of hydride at the imino function and substitution of the chlorinated carbon atom (Scheme V). Another possibility would be that initial α-substitution of the dichloro ketimine **3i,j** occurred to form a monochloro ketimine and that an analogous rearrangement as given in Scheme V would result. This mechanism is the aza analogue of the semipinacol rearrangement encountered with α,α-dichloroalkyl aryl ketones **19** or the corresponding β,β-dichloro alcohols and Grignard reagents, affording highly branched alcohols **21**[32] (Scheme VI). It is by now well recognized that such pinacol-type rearrangements occur preferentially when the halide is secondary or tertiary, when the migrating group can participate in the transition state, and when the halide and the Z–M moiety (e.g., OMgX, NLi) can come into a cis alignment.[33] When *N*-(2-chloro-2-fluoro-1-phenyl-1-propylidene)isopropylamine (**22**) was subjected to reaction with lithium aluminum hydride in ether (0 °C, 1 h), the reaction proceeded smoothly to afford a 3:1 mixture of *cis*- and *trans*-1-isopropyl-2-methyl-3-phenylaziridine, **4c** and **25**, respectively (Scheme VII). It is reasonable to suppose that the nucleophilic addition of hydride at the carbon–nitrogen double bond is followed by intramolecular chloride displacement. If the corresponding α-chloroaziridine were formed, it would result in exclusively *cis*-aziridine **4c** as discussed before. The more plausible α-fluoroaziridine **23** can behave analogously which results in an azirinium fluoride **24**. This intermediate has to suffer stereospecific hydride addition to yield the *cis*-aziridine **4c** as there is no doubt why it should behave in a different manner. The only remaining possibility of obtaining *trans*-aziridine **25** is an S_N2 substitution of the ring fluoride, which produces a mixture of *cis*- and *trans*-aziridines **4c** and **25**. Most probably, both routes, i.e., nucleophilic ring substitution (S_N2) and the addition of hydride at the azirinium halide, take place in this reaction. The S_N2 displacement of **23** seems to be another example of the scarcely reported substitution of α-haloaziridines.[29]

Only *tert*-butyl-substituted derivatives **4** are not accessible in a synthetically useful manner. *N*-(2,2-Dichloro-3,3-dimethyl-1-phenyl-1-butylidene)isopropylamine

Scheme VIII



(**3h**, R = *t*-Bu; R′ = *i*-Pr; R″ = H) reacted with lithium aluminum hydride (8 equiv, Δ, 24 h) in ether to afford *N*-(3,3-dimethyl-1-phenylbutyl)isopropylamine (**26h**) as the sole product (70% isolated yield by distillation) (scheme VIII).

On the other hand, when the N atom is carrying the *tert*-butyl substituent, i.e., *N*-(2,2-dichloro-1-phenyl-1-propylidene)-*tert*-butylamine (**3e**, R = CH_3; R′ = *t*-Bu; R″ = H), the starting material is extremely slowly consumed, even by a 20-fold excess of lithium aluminum hydride in ether under reflux during about 3 days. A very complex reaction mixture was formed, which was analyzed by preparative gas chromatography. This indicated the presence of 21% *cis*-aziridine **4e**, 23% α-chloro ketimine **27** (in equilibrium with its enamino form **27′**), 42% rearranged secondary amine **5e**, and 14% nonrearranged secondary amine **26e**. The reaction of **3e** with $LiAlH_4$ in tetrahydrofuran under similar reaction conditions afforded mainly (71%) *cis*-aziridine **4e**, with small amounts of imines **27** and **2e** (7% and 4%, respectively, each occurring in equilibrium with their enamino form) and 7% β-hydroxy amine **28** (Scheme VIII).

The deviating results obtained in these cases have to originate from steric congestion. A competitive S_N2 displacement of the chlorides in **6h** at the expense of addition at the imino function seems unlikely and therefore reduction of the imino functions and subsequent halide displacements are apparently the reactions involved. The occurrence of ketimine **2e** and α-chloro ketimine **27** in the reaction mixture starting from **3e** points to the possibility of initial S_N2 displacement of the chlorides. The lack of reactivity of **2e** and **27** is undoubtedly due to their propensity to form enamine salts, a proposition which was verified by independent experiments.

β-Hydroxy amine **28** must originate from the workup procedure in which the aziridines are in contact with a strongly alkaline medium (despite the temperature of 0 °C). The occurrence of rearranged secondary amine **5e** can be explained via azirinium chloride formation (**9**, R = CH_3; R′ = *t*-Bu; R″ = H) and isomerization to α-imino carbenium ion **10** (R = CH_3; R′ = *t*-Bu; R″ = H).

In conclusion, *cis*-aziridines **4** are now available from very easily accessible starting materials, i.e., alkyl aryl ketones, via a high-yield three-step sequence. The ac-

(32) N. De Kimpe, R. Verhé, L. De Buyck, and N. Schamp, *Tetrahedron Lett.*, 955 (1979).
(33) T. A. Geissman and A. I. Akawie, *J. Am. Chem. Soc.*, **73**, 1993 (1951).

cessibility of *cis*-aziridines opens new possibilities in the study of their metabolic processes in view of the different behavior of stereoisomeric aziridines in biological systems.[34]

Experimental Section

IR spectra were measured with a Perkin-Elmer Model 256 spectrophotometer, while NMR spectra were recorded with a Varian T-60 NMR spectrometer. Mass spectra were obtained from a AEI MS 20 mass spectrometer coupled with a Pye Unicam gas chromatograph (Model 104; 1.5% SE-30; 1.5 m; He carrier gas). GLC analyses were performed with a Varian Model 920 gas chromatograph (5% SE-30; 3 m; H_2 carrier gas).

Starting Materials. *N*-(1-Aryl-1-alkylidene)anilines **2i,j** were prepared by condensation of the appropriate aromatic ketones **1** with anilines in toluene under catalytic influence of *p*-toluenesulfonic acid (using a Dean–Stark apparatus).[23,25] *N*-(1-Aryl-1-alkyliden)amines **2a–h** were synthesized according to the method using $TiCl_4$ as effective drying agent.[36] *N*-(1-Aryl-2,2-dichloro-1-alkyliden)amines **6a–j** were prepared by our previously reported method[23,37] involving chlorination of ketimines **2** with *N*-chlorosuccinimide in carbon tetrachloride at room temperature. However, in some cases, e.g., **3h**, it was necessary to heat the reaction mixtue for a while in order to start the reaction. In general, α,α-dichloro ketimines **3** were obtained in very pure state and distillation was not required. *N*-Aryl α,α-dichloro ketimines **3i,j** were always used without distillation in these experiments.

General Procedure for Synthesis of *cis*-Aziridines 4. A cooled (ice bath) and vigorously stirred suspension of 3.8 g (0.10 mol) of lithium aluminum hydride in 100 mL of freshly distilled dry diethyl ether was treated dropwise with a solution of 0.05 mol of α,α-dichloro ketimine **3** in 100 mL of dry diethyl ether. The reaction mixture was then refluxed overnight (~16 h) in the case of the *N*-alkyl derivatives, except for *cis*-1,2-dimethyl-3-phenylaziridine (**4a**) which was obtained after a reflux period of 2.5 h. *N*-Aryl derivatives **4i,j** were synthesized from **3i,j** under less drastic reaction conditions, i.e., 0 °C, 1 h. *N*-(2,2-Dichloro-1-phenyl-1-propylidene)-*tert*-butylamine (**3e**) was converted into a complex reaction mixture. After α,α-dichloro ketimines **3** were reacted with lithium aluminum hydride for the time and at the temperature indicated above, the cooled reaction mixture was slowly and cautiously added to a mixture of ice, water, and diethyl ether. The organic layer was isolated and the aqueous layer twice extracted with ether. The combined ethereal extracts were dried ($MgSO_4$) and distilled to give *cis*-aziridines **4** (Table I). Short-path distillation was used in the case of **4a–d,f,g**, while rectification over a 20-cm Vigreux column was executed for **4i,j**. In general, it has to be reported here that it is advisable to follow the course of the reaction by sampling (GC–MS coupling being the preferable technique). Deviations in reaction time were noticed in a few cases and were ascribed to the reactivity of commercial lithium aluminum hydride used (Aldrich, UCB-Belgium, Merck).

Compounds **4e**, **2e** (and **2'e**), **27** (and **27'**), **28**, **26e**, and **5e**, resulting from the reaction of α,α-dichloro ketimine **3e** with lithium aluminum hydride, were identified by spectrometric methods (NMR, IR, and mass spectra) and/or by comparison with samples obtained by independent syntheses.

***cis*-1-*tert*-Butyl-2-methyl-3-phenylaziridine (4e)**: see Table I.

***N*-(1-Phenyl-1-propylidene)-*tert*-butylamine (2e)** (and its enamine form **2'e**) were compared with a sample of the starting material, described above.

***N*-(1-Phenyl-1-propyl)-*tert*-butylamine (26e)** was identical with a sample obtained from reduction of ketimine **2e** with lithium aluminum hydride.

***N*-(2-Chloro-1-phenyl-1-propylidene)-*tert*-butylamine (27)** (and its enamine form **27'**): NMR (CCl_4), ketimine/enamine ratio 28:72. Ketimine **27**: NMR (CCl_4) δ 1.02 (s, *t*-Bu), 1.53 (d, J = 7 Hz, CH_3), 4.55 (q, J = 7 Hz, CHCl), 7.1–7.4 (m, C_6H_5). Enamine **27'** (one isomer, undetermined configuration): NMR (CCl_4) δ 0.92 (s, *t*-Bu), 1.96 (s, CH_3C=), 3.8 (br s, NH), 7.1–7.4 (m, C_6H_5); IR (NaCl; mixture of **27** and **27'**) 3440 cm^{-1} (ν_{NH}), 1645 and 1625 cm^{-1} (overlap; $\nu_{C=N}$ and $\nu_{C=C}$); mass spectrum, m/e (%) 223/225 (M^+, 36), 208/210 (16), 167/9 (100), 160 (18), 132 (54), 115 (17), 104 (48), 77 (11), 57 (68), 41 (24).

***N*-(1-Phenyl-2-propyl)-*tert*-butylamine (5e)**: NMR (CCl_4) δ 0.94 (9 H, s, *t*-Bu), 1.00 (3 H, d, covered, CH_3), 2.4–3.1 (3 H, m, CHN and CH_2), 0.5 (1 H, br s, NH), 7.13 (5 H, s, C_6H_5); IR (NaCl) 3310 cm^{-1} (ν_{NH}); mass spectrum, m/e (%) no M^+, 176 (4), 132 (2), 120 (3), 119 (2), 104 (3), 100 (51, *t*-BuN^+H=CHMe), 91 (13), 84 (2), 77 (2), 65 (2), 58 (8), 57 (13), 44 (100, CH_3CH=NH_2^+), 42 (3), 41 (8), 39 (3).

1-(*tert*-Butylamino)-1-phenyl-2-propanol (28): NMR (CCl_4) δ 1.01 (9 H, br s, *t*-Bu), 0.86 (3 H, d, J = 6 Hz, CH_3), 2.15 (2 H, br s, NH and OH), 3.3 (1 H, m, CH–O), 3.73 (1 H, d, J = 4 Hz, CH–N), 7.23 (5 H, s, C_6H_5); IR (NaCl) 3500–3100 cm^{-1} (ν_{NH}); mass spectrum, m/e (%) no M^+, 162 (45), 146 (10), 132 (2), 117 (4), 106 (100), 105 (6), 104 (6), 103 (4), 91 (6), 79 (8), 77 (6), 58 (17), 57 (17), 44 (4), 43 (8), 42 (4), 41 (12), 39 (4).

Reaction of *N*-(2-Chloro-2-fluoro-1-phenyl-1-propylidene)isopropylamine (22) with Lithium Aluminum Hydride. An ethereal solution of 1.4 g (6.2 mmol) of α-chloro-α-fluoro ketimine **22** was reacted with 0.46 g (12.4 mmol) of lithium aluminum hydride at 0 °C during 1 h, essentially as indicated in the general procedure given above. After workup, the reaction mixture was distilled to give 0.8 g (74%) of a 3:1 mixture of *cis*- and *trans*-1-isopropyl-2-methyl-3-phenylaziridines, **4c** and **25**, respectively, bp 35–36 °C (0.02 mmHg). Both products were separated by preparative GLC (peak 1 = **4c** and peak 2 = **25**). Compounds **4c** and **25** (3:1 ratio) were already present in the reaction mixture before distillation. *trans*-1-Isopropyl-2-methyl-3-phenylaziridine (**25**): NMR (CCl_4) δ 1.08 (3 H, d, J = 6 Hz, CH_3), 1.08 and 1.33 (2 × 3 H, 2 × d, br, J = 6 Hz, $(CH_3)_2$), 1.6–2.7 (3 H, m, NCH and CHCH), 7.14 (5 H, s, C_6H_5); IR (NaCl) 1602–1498 cm^{-1} ($\nu_{aromatic}$); mass spectrum, m/e (relative abundance) 175 (M^+, 17), 174 (15), 132 (100), 117 (8), 105 (26), 91 (13), 77 (6), 70 (6), 51 (3), 43 (8), 42 (4), 41 (4), 39 (4).

Synthesis of *cis*-1,2-Dimethyl-3-phenylaziridine (4a) by an Independent Route. Compound **4a** was prepared according to a modified procedure of Brois.[3,26b] Chlorosulfonic acid (9.78 g, 0.08 mol, + 5% excess) was cautiously added, drop by drop, to commercial *d*-ephedrine (6.6 g, 0.04 mol). The mixture was heated for 15 min, cooled to 0 °C, and neutralized with aqueous 2 N sodium hydroxide. An additional 4 equiv of 2 N sodium hydroxide was added after which steam distillation was applied. Extraction with ether of the distillate, drying ($MgSO_4$), and evaporation afforded, after distillation in vacuo, 1.5 g (25%) of *cis*-aziridine **4a**, bp 81–85 °C (12 mmHg) (95% pure).

Reaction of *N*-(2,2-Dichloro-3,3-dimethyl-1-butylidene)-isopropylamine (3h) with Lithium Aluminum Hydride. According to the general procedure described above, α,α-dichloro ketimine **3h** (0.03-mol scale) was converted into *N*-(3,3-dimethyl-1-phenylbutyl)isopropylamine (**26h**) by reaction with $LiAlH_4$ (8 equiv) under reflux for 24 h. Usual workup furnished 70% of **26h**: bp 54–57 °C (0.02 mmHg); NMR (CCl_4) δ 0.90 (9 H, s, *t*-Bu), 3.73 (1 H, t, J = 5.8 Hz, PhCHN), 1.50 (2 H, d, J = 5.8 Hz, CH_2), 2.40 (1 H, m, $NCHMe_2$), 0.89 and 0.95 (6 H, 2 × d covered by *t*-Bu signal, $(CH_3)_2$), 7.16 (5 H, s, C_6H_5); IR (NaCl) 3300 cm^{-1} (ν_{NH}); mass spectrum, 219 (M^+, 0.1), 218 (0.3), 217 (0.2), 204 (0.5), 202 (0.7), 161 (3), 160 (4), 148 (100), 132 (1), 120 (1.5), 117 (0.8), 106 (18), 105 (3), 104 (6), 103 (1), 91 (4), 79 (3), 77 (2), 57 (16), 44 (6), 43 (4), 42 (1), 41 (6).

Acknowledgment. We are indebted to the Belgian "Nationaal Fonds voor Wetenschappelijk Onderzoek" for financial support to our laboratory.

Registry No. 1 (R = Me; R'' = H), 93-55-0; 1 (R = Me; R'' = Cl), 6285-05-8; 1 (R = Et; R'' = H), 495-40-9; 1 (R = *t*-Bu; R'' = H), 31366-07-1; **2a**, 29640-04-8; **2b**, 75458-22-9; **2c**, 28916-25-8; **2d**, 75458-23-0; **2e**, 75458-24-1; **2f**, 6125-76-4; **2g**, 75458-26-3; **2h**, 75458-27-4; **2i**, 14752-72-8; **2j**, 29640-03-7; **3a**, 75458-28-5; **3b**, 75458-29-6; **3c**, 75458-30-9; **3d**, 75458-31-0; **3e**, 75458-32-1; **3f**, 75458-33-2; **3g**, 75458-34-3; **3h**, 75458-35-4; **3i**, 72374-71-1; **3j**, 72374-74-4; **4a**, 936-42-5; **4b**, 75458-36-5; **4c**, 75458-37-6; **4d**, 75458-38-7; **4e**, 75458-39-8;

(34) Y. Hata, M. Watanabe, T. Matsubara, and A. Touchi, *J. Am. Chem. Soc.*, **98**, 6033 (1976).
(35) H. Ahlbrecht and S. Fischer, *Tetrahedron*, **26**, 2837 (1970).
(36) H. Weingarten, J. P. Chupp, and W. A. White, *J. Org. Chem.*, **32**, 3246 (1967).
(37) N. De Kimpe, R. Verhé, L. De Buyck, and N. Schamp, *Synth. Commun.*, **8**, 75 (1978).

4f, 75458-40-1; **4g**, 75458-41-2; **4i**, 3683-70-3; **4j**, 75458-42-3; **5e**, 75458-43-4; **22**, 75458-44-5; **25**, 75458-45-6; **26e**, 75458-46-7; **26h**, 75458-47-8; **27**, 75458-48-9; **27′**, 75458-49-0; **28**, 75458-50-3; methanamine, 74-89-5; ethanamine, 75-04-7; 2-propanamine, 75-31-0; 2-methyl-2-propanamine, 75-64-9; cyclohexanamine, 108-91-8; benzenamine, 62-53-3; 4-methoxybenzenamine, 104-94-9; *d*-ephedrine, 321-98-2.

Supplementary Material Available: Table II describing the synthesis and spectrometric properties of N-substituted α,α-dichloroalkyl aryl ketimines (2 pages). Ordering information is given on any current masthead page.

Anti-Bredt Molecules. 3.[1a] 3-Oxa-1-azabicyclo[3.3.1]nonan-2-one and 6-Oxa-1-azabicyclo[3.2.1]octan-7-one, Two Atom-Bridged Bicyclic Urethanes Possessing Bridgehead Nitrogen

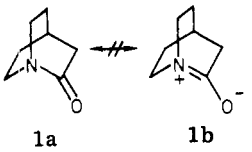
H. K. Hall, Jr.,* and Ali El-Shekeil[1b]

Chemistry Department, University of Arizona, Tucson, Arizona 85721

Received July 8, 1980

The first atom-bridged bicyclic urethanes possessing bridgehead nitrogen have been synthesized and their properties examined briefly. 3-Oxa-1-azabicyclo[3.3.1]nonan-2-one was synthesized from 3-(hydroxymethyl)-piperidine and phosgene by using two alternate reaction schemes. 6-Oxa-1-azabicyclo[3.2.1]octan-7-one was synthesized similarly from 3-hydroxypiperidine. Both compounds were stable, white, crystalline solids with normal infrared spectra. They were rather stable to acids and bases, but phosphoric acid initiated ring-opening polymerization demonstrated strain in the system. A novel O → N rearrangement of two aminochloroformates to hydroxy *N*-carbamoyl chlorides was demonstrated.

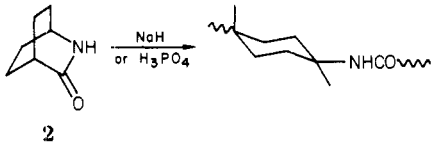
Anti-Bredt Lactams. Bicyclic lactams with a bridgehead nitrogen (1), according to Bredt's rule,[2] should be very unstable because resonance form **1b** would be prohibited.[3]



1a **1b**

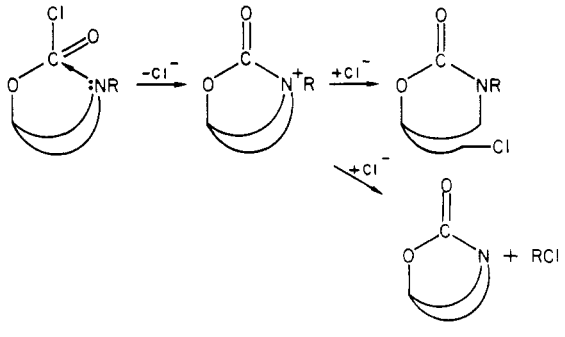
However, Yakhontov[4] and Pracejus[5–7] synthesized 1-azabicyclo[2.2.2]octan-2-one (1) itself and its 2,2-dimethyl and 2,2,6-trimethyl derivatives. These lactams showed unusual properties. Their carbonyl infrared absorptions were found at anomalously high frequencies, they hydrolyzed readily in water, and they polymerized.

However, lactam 1 and its derivatives are also destabilized by their possession of a boat six-membered ring. That this could contribute to destabilizing structure 1 was shown by Hall,[8] who showed that the analogous lactam 2-azabicyclo[2.2.2]octan-3-one (**2**) smoothly polymerized to the open-chain polyamide.

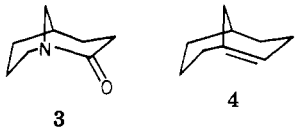


2

Scheme I



In an attempt to separate the effect of NCO resonance inhibition from conformational strains, Hall, Shaw, and Deutschmann[1a] synthesized 1-azabicyclo[3.3.1]nonan-2-one (**3**). Although **3** could adopt a two-chair form, the NMR



3 **4**

spectrum showed that a chair–boat form was preferred, in keeping with Wiseman's rule.[9–12] Lactam **3** was not very reactive, but it polymerized to the corresponding polyamide under the influence of phosphoric acid. This degree of stability for **3** corresponds well to that of the homomorphic olefin **4**, which is isolable yet reactive.[9–12]

Anti-Bredt Urea. Hall and Johnson[13] synthesized the urea 3-isopropyl-1,3-diazabicyclo[3.3.1]nonan-2-one (**5**).

(1) (a) Paper 2: Hall, H. K., Jr.; Shaw, R. G., Jr.; Deutschmann, A. *J. Org. Chem.* **1980**, *45*, 3722. (b) On leave from the University of Sanaa, Yemen.
(2) Bredt, J.; Thouet, H.; Schmitz, J. *Justus Liebigs Ann. Chem.* **1924**, *437*, 1.
(3) Lukes, R. *Collect Czech. Chem. Commun.* **1939**, *10*, 148.
(4) Yakhontov, L. N. *Usp. Khim.* **1969**, *38*(6), 1038.
(5) Pracejus, H. *Chem. Ber.* **1959**, *92*, 988.
(6) Pracejus, H. *Chem. Ber.* **1965**, *98*, 2897.
(7) Pracejus, H.; Kehlen, M.; Matschiner, M. *Tetrahedron* **1965**, *21*, 2257.
(8) Hall, H. K., Jr. *J. Am. Chem. Soc.* **1958**, *80*, 6412.
(9) Wiseman, J. R.; Pletcher, W. A. *J. Am. Chem. Soc.* **1970**, *92*, 956.
(10) Marshall, J. A.; Faubl, H. *J. Am. Chem. Soc.* **1970**, *92*, 948.
(11) Becker, K. B. *Helv. Chim. Acta* **1977**, *60*(1), 81.
(12) Greenberg, A.; Liebman, J. F. *Chem. Rev.* **1976**, *76*(3), 311.
(13) Hall, Jr., H.K.; Johnson, R. C. *J. Org. Chem.* **1972**, *37*, 697.

0022-3263/80/1945-5325$01.00/0