7.88 (ms, 4 H); IR (mull) 1790, 1780, 1720, 1515, 1460, 1380, 1345, 1270 cm^{-1}; ^{13}C NMR (Me_2SO-d_6, ref Me_4Si) δ 17.8, 19.0 (2-CH_3), 72.1 (C-2), 65.9 (C-3), 72.7 (C-5), 56.1 (C-6).[23]

In the combined solution of the toluene filtrate and acetone rinse, a 2–3% solid was recovered, which was identical to an authentic sample of the *p*-nitrobenzyl ester of 3-hydroxyl-3-methyl-7β-phthalimidocephalosporin.

Acknowledgments. We thank the National Science Foundation and the National Institutes of Health for financial support.

Registry No.—**10** (R^1 = phthalimido; R^2 = *p*-nitrobenzyl, 35160-70-4; **14a,** 65102-78-5; **14b,** 65102-79-6; **15,** 65102-80-9; **16b,** 65102-81-0; **17,** 65102-82-1; **18,** 65102-83-2; **19,** 65102-84-3; **20,** 65102-85-4; **21,** 65102-86-5; **22,** 65102-87-6; **23,** 65102-88-7; **24,** 65165-49-3; benzyl 6β-aminopenam-3α-carboxylate β-oxide, 65165-50-6; phthalic anhydride, 85-44-9; benzyl 6β-aminopenam-3α-carboxylate, 3956-31-8; benzyl 6β-amino-6α-methylpenicillinate, 36273-78-6; 2-mercaptobenzthiazole, 149-30-4.

Supplementary Material Available. Tables of atomic coordinates, temperature factors, bond angles, and bond distances (3 pages). Ordering information is given on any current masthead page.

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Haloaziridines. 2. Synthesis and Pyrolysis of Some *gem*-Dichloroaziridines[1,2]

Marcus K. Meilahn,* David K. Olsen,[3a] William J. Brittain,[3b] and Ralph T. Anders[3b]

Department of Chemistry, University of Northern Colorado, Greeley, Colorado 80639

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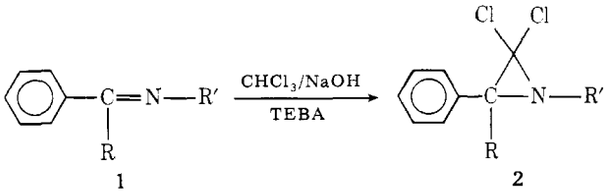
An improved synthesis of *gem*-dichloroaziridines from imines and dichlorocarbene is reported using chloroform, sodium hydroxide, and triethylbenzylammonium chloride to generate the dichlorocarbene. The preparation of some *gem*-dichloroaziridines from phenyl(trihalomethyl)mercury reagents is reported and the previous reports are examined. The *gem*-dichloroaziridines prepared under these latter conditions are subject to a phenylmercuric halide catalyzed ring-opening reaction. A pyrolysis study delineated the factors controlling the ring-opening reaction and demonstrated the synthetic utility of this reaction.

The preparation of *gem*-dichloroaziridines has been accomplished by the addition of dichlorocarbene to the carbon–nitrogen double bond of an imine. The dichlorocarbene in this reaction has been generated from the reaction of chloroform, hexachloroacetone, or ethyl trichloroacetate with the appropriate base.[4] Recently, Seyferth has reported the preparation of 1,3-diphenyl-2,2-dichloroaziridine in low yield using $PhHgCBrCl_2$ to generate the dichlorocarbene.[5] Makosza has reported the generation of dichlorocarbene from chloroform and aqueous sodium hydroxide using a phase-transfer agent.[6] These phase-transfer catalyzed two-phase reactions have been used in a variety of reactions in addition to generating dichlorocarbene. The chemistry of these types of reactions has been recently reviewed.[7]

Phase-Transfer Preparations. We have examined the preparation of *gem*-dichloroaziridines from imines (1) using



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aqueous sodium hydroxide, chloroform, and triethylbenzylammonium chloride (TEBA) as the phase-transfer agent. The isolated yields for this catalytic method are contrasted to the best yield obtained from the other reported methods

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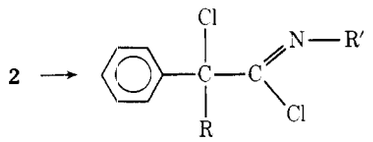
Table I. Preparation of *gem*-Dichloroaziridines

Registry no.	Compd	R	R′	Catalytic[a]	Other	Time[b]	Solvent[c]	Lit.[d]
3543-98-4	**2a**	Hydrogen	Phenyl	74	80[e]	40	Hexane	*f*
31528-97-9	**2b**	Ethyl	Phenyl	76	56	30	Hexane	1
972-14-5	**2c**	Phenyl	Phenyl	72[g]	63	40	Hexane–EtOAc	*h*
31528-96-8	**2d**	Phenyl	Benzyl	72	65[i]	40	EtOAc	1
31528-95-7	**2e**	Hydrogen	1-Naphthyl	72	44	40	Hexane–EtOAc	1
65016-16-2	**2f**	Methyl	1-Naphthyl	74	45	50	EtOAc	*a*
25252-58-8	**9**			88	53[j]	180	Hexane[a]	5

[a] See Experimental Section. [b] Reaction time in minutes. [c] Solvent for crystallization. [d] Literature reference for the best reported preparation of the aziridine by other methods. [e] Normal yields are ~50–60%; see ref 1. [f] R. E. Brooks, J. O. Edwards, G. Levey, and F. Smyth, *Tetrahedron*, **22,** 1279 (1966). [g] Yield of the α-chloroimidoyl chloride **3c**. [h] K. Ichimura and M. Ohta, *Bull. Chem. Soc. Jpn.*, **40,** 1933 (1967). [i] Normal yields are ~4%; see ref 1. [j] This yield is based on the carbene.

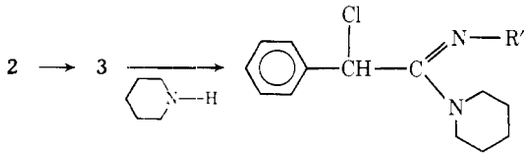
for the preparation of *gem*-dichloroaziridines in Table I. In all cases the yields are about equal to or superior to the best previously reported preparations of *gem*-dichloroaziridines. In addition, the catalytic method has the advantage of being quick, convenient, and inexpensive. The reaction is exothermic and precautions should be taken to maintain the temperature at 40 °C in large-scale preparations.[6] Graefe has reported high yields of phenyl substituted 1,3-diphenyl-2,2-dichloroaziridines (**2a**) using the catalytic method at temperatures between 0 and 20 °C.[8]

Longer reaction times failed to significantly improve the yields reported in Table I and resulted in lower isolated yields of **2b** and **2f** due to the instability of these aziridines to longer reaction times. Aziridine **2c** was not stable to the reaction conditions and rearranged to the α-chloroimidoyl chloride **3c** which was isolated in 72% yield. This aziridine could be prepared in 71% yield via the catalytic method using lower temperatures and a longer reaction period.



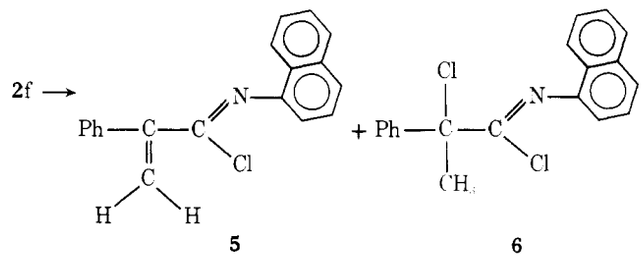
3

Pyrolysis Studies. In our investigations of the synthetic utility of *gem*-dichloroaziridines, it was necessary to determine the thermal stability of some of these compounds. There were two isolated reports of pyrolysis reactions in the literature; aziridine **2a** afforded **3a** in hot toluene (no reported yield)[9] and **2c** was converted to **3c** (71% yield) after 1 h in hot xylene.[10] Of the aziridines in Table I, the pyrolysis of **2a** and **2e** were conveniently monitored via NMR spectrometry by following the loss of the aziridinyl proton at δ 3.6 and the appearence of the benyzlic proton of **3** near δ 5.8. Aziridine **2e** was quantitatively converted in 4 h while **2a** was 83% rearranged after 24 h.[11] Longer reaction times in the latter reaction resulted in significant decomposition. These pyrolysis reactions have synthetic utility since quenching the reaction with piperidine afforded high yields of the α-chloroamidines **4a** and **4e.**



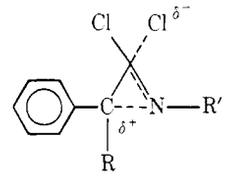
4a and 4e

The toluene pyrolysis of **2c** for 1 h afforded a 78% yield of **3c.** The pyrolysis of **2d** and **2f** was monitored via NMR spectrometry by following the loss of the aziridinyl methylene and methyl signals, respectively. Aziridine **2d** was quantatively converted in 8 h while **2f** required 3 h and afforded a 1:3 mixture of **5** and **6.**[11] In pyridine, a more polar solvent, the pyrolysis of **2f** required 1 h and a 45:55 mixture of **5** to **6** was observed while a 2:3 mixture of the amides corresponding to the hydrolysis of **5** and **6** was obtained in water after 15 min.[11]



5 **6**

The order of decreasing pyrolysis rates for the 1-aryl substituted *gem*-dichloroaziridines is **2c** > **2f** > **2e** > **2a** and roughly correlates with decreasing strain and decreasing carbonium ion stability. The difference in reactivity between **2a** and **2e** is attributed to the greater electron-donating ability of naphthyl in stabilizing the transition state since both aziridines give rise to the same carbonium ion. These data are consistent with transition state **7** which is also supported by recently reported observations.[12]



7

Phenyl(trihalomethyl)mercury Preparations. We have also examined the synthetic utility of some phenyl(trihalomethyl)mercury reagents as the carbene source in the preparation of *gem*-dichloroaziridines. These thoroughly studied Seyferth reagents undergo pyrolysis to yield dihalocarbene and the phenylmercuric halide.

$$PhHgCX_3 \rightarrow PhHgX + X\ddot{C}X$$

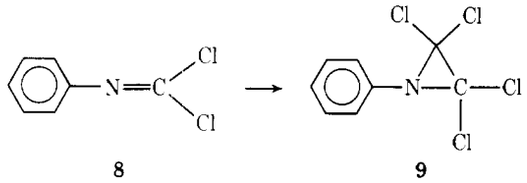
They have been used to prepare *gem*-dihalocyclopropanes and have the advantage of not requiring basic reaction conditions.[13] Recently, Seyferth et al. have reported the use of these reagents for the addition of dichlorocarbene to the C=N, C=S, C=O, and N=N.[14] Seyferth reported the reaction of benzylideneaniline (**1a**) with phenyl(bromodichloromethyl)-mercury lead to tar formation in benzene[15] and a trace of **2a** and tar in carbon tetrachloride.[5] The inability of this reagent to convert the imine to the *gem*-dichloroaziridine was attributed by Seyferth to nucleophilic attack of the imine ni-

Table II. Stability Studies of 1,3-Diphenyl-2,2-dichloroaziridine (2a)

Reactant(s)	Conditions	Time[a]	NMR analysis	
			% aziridine	% imidoyl chloride
Benzene[b]	Reflux	48	100[c]	*d*
CCl_4/PhHgCl[e,f]	r.t.[g]	48	100[c]	*d*
Benzene/PhHgCl	Reflux	24	36	64
DME/PhHgCl	r.t.[g]	48	98[c]	2
Benzene/PhHgBr	Reflux	2	100	*d*
DME/NaI	r.t.[g]	48	100	*d*

[a] Reaction time in hours. [b] Similar results were obtained for CCl_4 (48 h) and DME (18 h). [c] Recovered >85%. [d] The imidoyl chloride could not be detected. [e] A saturated solution. [f] Comparable results were obtained for PhHgBr. [g] Room temperature.

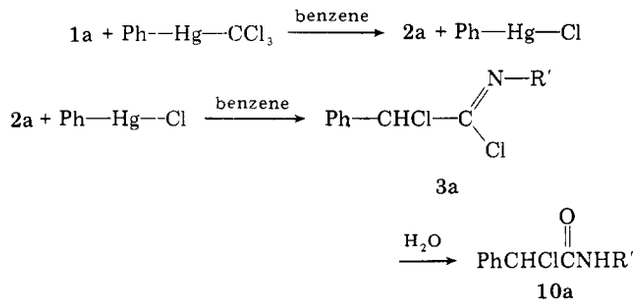
trogen at mercury giving rise to tar formation. Using a less nucleophilic imine such as phenylcarbonimidoyl dichloride (**8**), Seyferth obtained the tetrachloroaziridine **9** in 53% yield



8 **9**

based on the mercurial.[5] We obtained the same aziridine in 88% yield using the phase-transfer reaction.[11]

Our initial attempts to prepare *gem*-dichloroaziridines from the Seyferth reagents involved the pyrolysis of a 1:1 mixture of **1a** and phenyl(trichloromethyl)mercury in benzene for 48 h. The product was a red oil which was identified as the imidoyl chloride **3a** by its NMR spectrum and by conversion to the amide **10a** in 22% yield. Using a fourfold excess of the mercurial afforded the amide in 68% yield. The isolation of the amide strongly suggested the intermediacy of **2a** since the pyrolysis of **2a** to **3a** has been established. In hot benzene, **2a** was stable for 48 h; however, in the presence of phenylmercuric chloride, **2a** was quantitatively converted to **3a** (via NMR) establishing the phenylmercuric chloride catalyzed ring opening reaction. Consequently, the use of phenyl(trihalomethyl)mercury reagents should be limited by the thermal stability of the *gem*-dichloroaziridine and its stability toward the phenylmercuric halide produced in the reaction and/or the phenyl(trihalomethyl)mercury reagent. The results of some stability studies with the rather stable aziridine **2a** are presented in Table II. These results tend to rule out the pyrolysis of phenyl(trichloromethyl)mercury for the preparation of these *gem*-dichloroaziridines.



3a

10a

Treatment of phenyl(trichloromethyl)mercury with sodium iodide and dry dimethoxyethane (DME) at room temperature affords dichlorocarbene[16] and circumvents the pyrolytic ring opening reaction. Under these conditions, **1d** was converted to **2d** in 98% yield, the highest yield ever reported for a *gem*-dichloroaziridine preparation. Application of this reaction to **1a** and **1e** failed to yield the aziridine; however, NMR analysis established the presence of the rearrangement products **3a** and **3e**. Chromatography over alumina afforded the amide **10a** in 59% yield. Aziridines **2a** and **2e** were stable to phenylmercuric chloride under these conditions; however, it was established that the phenylmercuric iodide formed in the reaction catalyzed the ring opening.

Seyferth's attempted preparation of *gem*-dichloroaziridines using phenyl(bromodichloromethyl)mercury required even milder conditions than those for phenyl(trichloromethyl)-mercury, albeit he reported tar formation and only a trace of **2a**.[5] Based on our high percent conversions of imines **1a, 1d,** and **1e** to the corresponding aziridine or their rearrangement products with phenyl(trichloromethyl)mercury and the stability studies (Table II), we felt that these earlier reports should be examined. Duplicating this experimental by pyrolysis of a 1:1 mixture of phenyl(bromodichloromethyl)-mercury and **1a** in benzene for 2 h afforded phenylmercuric bromide (87%) and a dark oil. NMR analysis of this oil detected a strong aziridinyl proton signal at δ 3.58 and the impure aziridine was isolated in 40% yield after several recrystallizations from hexane.[17] Doubling the concentration of the mercurial failed to increase the aziridine yield. Using phenyl(bromodichloromethyl)mercury and NaI at 0 to −10 °C in DME also afforded **2a** in low yield. Consequently, phenyl-(bromodichloromethyl)mercury can be used to prepare *gem*-dichloroaziridines from imines, although the yields are relatively low and the isolation and purification of the aziridine is considerably more difficult than the conventional methods.

Experimental Section

All melting points are uncorrected and were determined on a Mel-Temp melting point apparatus. The nuclear magnetic resonance spectra were recorded on a Varian Associates A-60A or T-60A spectrometer using tetramethylsilane as an internal standard. Infrared spectra were determined in potassium bromide on a Perkin-Elmer 137 spectrophotometer. The microanalyses were performed by Midwest Microlab, Ltd., Indianapolis, Ind. Toluene, *p*-xylene, and DME were purified by distillation from $LiAlH_4$, while pyridine and piperidine were distilled from potassium hydroxide pellets prior to use.

Preparation of *gem*-Dichloroaziridines. General Procedure. The basic procedure of Makosza and Wawrzyniewicz was used.[6] To a mixture of imine (0.01 mol), chloroform[18] (8 mL, 0.10 mol) and triethylbenzylammonium chloride (0.1 g) is added a 50% solution of sodium hydroxide (20 mL). The mixture is vigorously stirred via a magnetic stirrer for ~30 to 60 min at 40 °C. The mixture is extracted with 3 × 20 mL portions of methylene chloride; the combined extracts are washed once with water (20 mL) and dried ($MgSO_4$). The mixture is filtered and the solvent removed in vacuo to afford the crude aziridine. The aziridines are purified by crystallization and the reaction times, yields, and solvents for crystallization are summarized in Table I.

1-Phenyl-2,2,3,3-tetrachloroaziridine (9). The above catalytic procedure was adapted for larger scale preparations by replacing the magnetic stirrer with a high speed mechanical stirrer and the temperature was maintained at 30 °C by external cooling. To a mixture of 10.24 g (0.0588 mol) of phenylcarbonimidoyl dichloride, chloroform (100 mL), and ~0.1 g of TEBA was added a 50% solution of sodium hydroxide (200 mL). The reaction was vigorously stirred and the

temperature maintained at 30 °C for 3 h. The mixture was extracted with 4 × 30 mL of methylene chloride; the combined extracts were washed with water (3 × 30 mL) and dried ($MgSO_4$). The mixture was filtered and the solvent removed in vacuo. 1-Phenyl-2,2,3,3-tetrachloroaziridine crystallized on standing overnight to afford 13.25 g (87%), mp 37–40 °C. Recrystallization from hexane afforded the pure aziridine, mp 39–40 °C (lit.[5] 38–40 °C).

1-(1-Naphthyl)-3-methyl-3-phenyl-2,2-dichloroaziridine (2f). Using the above general procedure, **2f** was obtained in 74% yield, while the yield from the sodium methoxide–chloroform method[1] was 45%: mp 109–110 °C; NMR ($DCCl_3$) δ 8.3–7.1 (m, 12, aromatic) and 1.8 (s, 3, CH_3).

Anal. Calcd for $C_{19}H_{15}Cl_2N$: C, 69.52; H, 4.62; N, 4.27. Found: C, 69.57; H, 4.69; N, 4.19.

Pyrolysis Reactions. General Procedure. The aziridines (0.1–0.5 g) were placed in a two-necked flask fitted with condenser and septum or stopper. The condenser was connected to a nitrogen-vacuum double manifold and a nitrogen atmosphere was introduced by the standard method.[19] The solvent was introduced via syringe through the septum or by removing the stopper while maintaining a positive nitrogen pressure. The magnetically stirred solution was heated at the reflux temperature of the solvent and samples were removed for analysis by syringe. The solvent was removed from the reaction mixture via the vacuum manifold to obtain the products. The imidoyl chlorides exhibited the C=N (neat) stretch near 1670 cm^{-1} in the infrared spectrum.

2-Chloro-*N*,2,2-triphenylacetimidoyl Chloride (3c). Using the above procedure, 271 mg (0.797 mmol) of **2c** was pyrolyzed for 1 h in toluene. The solvent was removed in vacuo and crystallization of the residue from hexane afforded 211 mg (78%) of the crude product, mp 68–71 °C. Recrystallization gave 201 mg (74%) of the pure imidoyl chloride: mp 69.5–71 °C (lit.[10] 67–70 °C); NMR ($CDCl_3$) δ 7.3 (m, aromatic); IR (KBr) 1660 cm^{-1} (C=N).

1-(*N*,2-Diphenyl-2-chloroacetimidoyl)piperidine (4a). Pyrolysis of 0.503 g (0.0019 mol) of **2a** in hot toluene for 24 h followed by a piperidine (2 mL) quench afforded the crude product. The reaction mixture was poured into a 10% potassium hydroxide solution (20 mL) and extracted once with ether (20 mL). The ether extract was dried ($MgSO_4$) and filtered and the solvent removed in vacuo. Chromatography of the residue over alumina (2% EtOAc–hexane) afforded 0.365 g (61%) of the amidine **4a** (via NMR). Crystallization from hexane afforded 0.205 g (34%) of the crystalline amidine: mp 93.5–95 °C; IR (KBr) 1600 cm^{-1} (C=N); NMR (CCl_4) δ 7.4–6.5 (m, 10, aromatic), 6.04 (s, 1, PhCH), 3.3 (m, 4, CH_2N), and 1.4 (m, 6, CH_2).

Anal. Calcd for $C_{19}H_{21}N_2Cl$: C, 72.93; H, 6.78; N, 8.96. Found: C, 72.88; H, 6.69; N, 8.74.

1-[*N*-(1-Naphthyl)-2-chloro-2-phenylacetimidoyl]piperidine (4e). Pyrolysis of **2e** in hot toluene (4 h) with piperidine quench afforded the crude amidine in 63% yield (via NMR) via the above procedure. Crystallization of the amidine from hexane afforded the pure product in 39% yield: mp 106–107.5 °C; IR (KBr) 1600 cm^{-1} (C=N); NMR ($CDCl_3$) δ 8.7–7.2 (m, 12, aromatic), 6.16 (s, 1, PhCH), 3.5 (m, 4, CH_2N), and 1.5 (m, 6, CH_2).

Anal. Calcd for $C_{23}H_{23}N_2Cl$: C, 76.11; H. 6.40; N, 7.72. Found: C, 76.04; H, 6.57; N, 7.40.

Pyrolysis of 2f. Pyrolysis of 0.487 g (0.0015 mol) of **2f** in hot toluene for 4 h followed by a water quench afforded 0.457 g of the crude amides corresponding to the hydrolysis of **5** and **6**. Chromatography of this material over alumina afforded 0.319 g (69%) of the α-chloroamide (via NMR) in the fractions eluted with hexane and 10% EtOAc–hexane. The unsaturated amide, 0.102 g (25%), was obtained in the EtOAc fractions. Crystallization of the appropriate fractions from hexane–EtOAc afforded 0.055 g (14%) of the crude unsaturated amide and 0.172 g (37%) of the crude α-chloroamide. Recrystallization afforded the following analytically pure samples.

***N*-(1-Naphthyl)-2-chloro-2-phenylpropanamide:** mp 131–131.5 °C; IR (KBr) 3300 (N—H) and 1650 cm^{-1} (C=O); NMR (CCl_4) δ 8.2–7.2 (m, 12, aromatic), 8.8 (m, 1, NH), and 2.2 (s, 3, CH_3).

Anal. Calcd for $C_{19}H_{16}ClNO$: C, 73.67; H, 5.21; N, 4.52. Found: C, 73.79; H, 5.21; N, 4.46.

***N*-(1-Naphthyl)-2-phenylpropenamide:** mp 145–146 °C; IR (KBr) 3300 (N—H), 1650 (C=O), and 1600 cm^{-1} (C=C); NMR ($CCl_4/CDCl_3$) δ 8.3–7.2 (m, 13, aromatic and N—H), 5.70 and 6.38 (2, d, CH_2=, J = 1 Hz).

Anal. Calcd for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.12. Found: C, 83.20; H, 5.36; N, 5.01.

Hydrolysis of 2f. The aziridine and water (10 mL) were heated on a steam bath for 15 min and cooled and the mixture was extracted with ether. The ether was dried ($MgSO_4$) and filtered and the solvent was removed in vacuo to afford the NMR sample.

Reaction of 1a with Phenyl(trichloromethyl)mercury. A magnetically stirred solution of 1.0 g (0.00552 mol) of **1a**, 2.41 g (0.00608 mol) of phenyl(trichloromethyl)mercury, and dry benzene (35 mL) was heated at the reflux temperature for 48 h under a nitrogen atmosphere. Filtration of the cooled solution through a medium porous sintered-glass funnel afforded 1.66 g (87%) of phenylmercuric chloride, mp 237–246 °C. The solvent was removed in vacuo to yield a red oil; the NMR spectrum of the oil exhibited a peak at δ 5.8 assigned to **3a** (PhCH). Several drops of water were added to the red oil and the resulting material was chromatographed over alumina. Elution with 2–10% EtOAc–hexane afforded 0.302 g (22%) of the crude amide. Crystallization from ethanol after several treatments with decolorizing carbon afforded 0.286 g (21%) of the amide **10a**, mp 147–150 °C (lit.[20] mp 146–148 °C).

Using the above procedure, 0.183 g (1.01 mmol) of **1a**, 1.58 g (3.99 mmol) of phenyl(trichloromethyl)mercury, and dry benzene (7 mL) afforded 0.167 g (62%) of the crude amide (via NMR) and 0.131 g (53%) of pure amide, mp 148–150 °C.

Preparation of 1-Benzyl-2,2-dichloro-3,3-diphenylaziridine (2d) from Phenyl(trichloromethyl)mercury and Sodium Iodide. To 0.200 g (0.738 mmol) of **1d**, 1.164 g (2.94 mmol) of phenyl(trichloromethyl)mercury, and 0.488 g (2.29 mmol) of sodium iodide in a two-necked flask fitted with condenser, septum, and a maintained nitrogen atmosphere was added freshly distilled DME (7 mL) via syringe. The solution was stirred for 8 h at room temperature. The DME was removed in vacuo, benzene (20 mL) was added, and the mixture was filtered through a sintered-glass funnel to remove the inorganic products (1.274 g). The filtrate was concentrated in vacuo to ~5 mL and filtered to remove the last traces of the inorganic products. Crystallization from hexane–ethyl acetate afforded 0.256 g (98%) of the aziridine, mp 118–134 °C. Recrystallization afforded 0.241 g (92%) of the aziridine, mp 135–137 °C (lit.[1] mp 136–137 °C).

Reaction of 1a with Phenyl(trichloromethyl)mercury and Sodium Iodide. A solution of 133 mg (0.735 mmol) of **1a**, 1.165 g (2.94 mmol) of phenyl(trichloromethyl)mercury, 0.458 (3.06 mmol) of sodium iodide, and dry DME (7 mL) was magnetically stirred under a nitrogen atmosphere for 48 h. Using the above procedure 1.06 g (89%) of phenylmercuric iodide, mp 260–280 °C, was obtained. NMR analysis of the filterate ($CDCl_3$) failed to detected the aziridine; however, the presence of the imidoyl chloride was established. Addition of moist benzene and chromatography of the residue over alumina afforded 115 mg (64%) **10a** via NMR. Crystallization from ethanol afforded 41 mg (23%) of the pure amide, mp 148–150 °C (lit.[20] mp 146–148 °C).

Preparation of 1,3-Diphenyl-2,2-dichloroaziridine (1a) from Phenyl(bromodichloromethyl)mercury. A magnetically stirred solution of 0.424 g (2.34 mmol) of **1a**, 1.283 g (2.91 mmol) of phenyl(bromodichloromethyl)mercury, and dry benzene (5 mL) was heated at the reflux temperature for 2 h under a nitrogen atmosphere. The cooled reaction mixture was filtered to remove the crude phenylmercuric bromide (0.925 g, 89%, mp 274–282 °C). The filtrate was treated with decolorizing carbon and filtered and the solvent was removed in vacuo to afford 0.598 g of a dark oil. This material was triturated with several small portions of chloroform leaving a residue of 0.106 g. The chloroform was removed in vacuo and the residue triturated with 3 × 10 mL portions of hot hexane leaving a residue of 0.125 g. The combined hexane fractions were treated with decolorizing carbon and filtered and crystallization afforded 0.247 g (40%) of the crude aziridine **2a**, mp 87–96 °C. Recrystallization from hexane afforded 0.193 g (31%) of the purified aziridine, mp 98–100 °C (lit.[20] mp 99–100 °C). Several additional recrystallizations were needed to remove the light yellow color from this material.

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Registry No.—**1a,** 538-51-2; **1b,** 14752-72-8; **1c,** 574-45-8; **1d,** 7699-79-8; **1e,** 890-51-7; **1f,** 5307-40-4; **3a,** 10295-39-3; **1c,** 17205-55-9; **4a,** 65016-17-3; **4d,** 65016-18-4; **8,** 622-44-6; **10a,** 5110-77-0; chloroform, 67-66-3; *N*-(1-naphthyl)-2-chloro-2-phenylpropanamide, 65036-36-4; *N*-(1-naphthyl)-2-phenylpropenamide, 65016-19-5; $PhHgCCl_3$, 3294-57-3; PhHgCl, 100-56-1.

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Carbon-13 Nuclear Magnetic Resonance Study of Representative *trans*- and *cis*-1-Alkyl-2-aryl(alkyl)-3-aroylaziridines

Philip Tarburton, Charles A. Kingsbury,[1] Alan E. Sopchik, and Norman H. Cromwell*[1]

Department of Chemistry, University of Nebraska—Lincoln, Lincoln, Nebraska 68588

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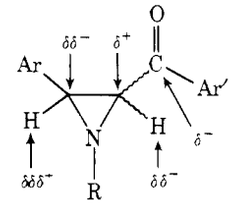
Twenty-two *trans*- and *cis*-1-alkyl-2-aryl(alkyl)-3-aroylaziridines have been studied by use of ^1H and ^{13}C NMR. The ^{13}C chemical shifts of the ring carbons have been tabulated, as well as those for the α-*N*-alkyl carbons (see Table I). Selected coupling constants are reported. The chemical shifts of the ring carbons are correlated with the phenomenon of three-ring to carbonyl hyperconjugation.[2] In addition, the effect of the nitrogen lone pair upon ^1J (^{13}C–H) values and the carbonyl carbon chemical shifts is discussed, while the α-*N*-alkyl carbon values are rationalized in terms of steric compression effects.

A ^{13}C NMR study of representative *trans*- and *cis*-1-alkyl-2-aryl(alkyl)-3-aroylaziridines has been undertaken. While systematic ^{13}C NMR studies of N-unsubstituted alkyl- and phenylaziridines have appeared earlier in the literature,[3,4] no desirable ^{13}C NMR study of the title compounds has been published to date. Work pertaining to the effect of the nitrogen heteroatom in cyclic systems has appeared in the literature,[5–9] as well as that of representative 1-azirines.[10] Here we have studied the effect of three-ring to carbonyl hyperconjugation,[2] the effect of the nitrogen lone pair on selected coupling constants and the carbonyl group, and the steric compression effect (where applicable) in these systems.

The assignments made are based on chemical shift considerations; signal multiplicities from off-resonance decoupling experiments or from coupled spectra; and qualitative considerations of long-range ^{13}C–H couplings; that is to say, the C_2 line width is greater than the line width of C_3 due to three-bond coupling of the C_2 to the adjacent (ortho) protons of the C_2–H aryl substituent (see Table I and the Experimental Section for assignments).

Three-Ring to Carbonyl Hyperconjugation. As revealed in Table I, the ^{13}C NMR studies show that the trans isomers of arylaroylaziridines (except **11a** and **12a**) enjoy substantial conjugation through their three-membered rings. This is borne out by the fact that C_2 appears further downfield than C_3 for **1a–8a** and **10a** by 0.5, 1.2, 0.7, 1.3, 1.2, 1.3, 0.9, 0.9, and 1.0 ppm, respectively. The strength of this statement is not so much the ~1-ppm difference in the values of C_3 and C_2 but the fact that the trend is uniform; i.e., $\Delta\delta$ (C_2–C_3) is always greater than zero. (A similar trend is found in the IR and UV data.[2]) In marked contrast, the opposite trend is found in the ^1H NMR data (see again Table I), such that the ring proton attached to C_3 is always further downfield in both the trans and cis isomers. One plausible explanation for this trend in the trans compounds might be the greater anisotropic effect by the phenyl group upon the hydrogen cis to it.[11a–c] Of course,

Chart I. Bond Polarization along the σ Skeleton of Arylaroylaziridines Assuming Carbonyl to be the Only Electronegative Substituent



an alternating polarization effect, such as was invoked in six-membered N-heterocyclic compounds by Morishima,[11c] appears applicable here (Chart I). That is to say, Pople,[11d] using the CNDO–SCF molecular orbital calculations, suggested that the inductive effect induced by an electronegative substituent (here, carbonyl) alternates and attenuates along to σ skeleton of the arylaroylaziridine three ring. This theory appears to be well correlated with the H_2 and H_3 ring proton values in both the *trans*- and *cis*-aziridines (Table I), wherein H_3 ($\delta\delta^-$) is always further downfield than H_2 ($\delta\delta\delta^+$). Moreover, the fact that the ring hydrogens of trans are further downfield than those of the cis can clearly be attributed to the anisotropic effect of the phenyl and carbonyl groups lying cis to their hydrogens in the *trans*-aziridines.[11a] Finally, one cannot ignore the bond polarization effect of the phenyl group since the *trans*- and *cis*-1-cyclohexyl-2-methyl-3-(*p*-phenylbenzoyl)aziridines (**16a,b**) have their C_2 protons significantly upfield, i.e., ~1 ppm, from their respective trans and cis analogues, **11a,b.**[11a,d]

With respect to three-ring to carbonyl hyperconjugation, a brief explanation of the stereochemical requirements is warranted. Basically, following the established corollary[11a,13] that the *N*-alkyl group in the trans series exists preferentially syn to the carbonyl moiety, the following conformer may be drawn to represent **1a–8a, 10a,** and **11a** (see Chart II). In es-

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