A Synthetic Route to 3,3-Diphenyl-2-indolinone Derivatives

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N-Aryl-α-chloro-α,α-diphenylacetimidoyl chlorides were prepared from Schiff bases and dichlorocarbene generated by use of the phase transfer catalyst. Treatment in sulfuric acid gave 3,3-diphenyl-2-indolinone derivatives. The synthetic route to 2-indolinone was found to give a higher overall yield than that by other methods. 2,2-Dichloro-1,3-diphenylaziridine gives α-chloro, α-acetoxy or α-hydroxy-α,α-diphenylacetanilide on treatment with sulfuric acid. Comparison of 2,2-dichloro-1,3-diphenylaziridine, 2,2-dichloro-1,3,3-triphenylaziridine and *N*-aryl-α-chloro-α,α-diphenylacetimidoyl chloride in their reactivities with sulfuric acid shows that the pathway of the reaction is governed by the character and number of substituents at the reaction center where carbonium ions are developed.

3,3-Diaryl-2-indolinone derivatives have pharmaceutical properties such as mothproofing,[1] laxative,[2] antibacterial and antiprotozoal[3] activities. Isacene (3,3-bis(*p*-acetoxy-phenyl)-2-indolinone) is used as a purgative. Copolymer of 3,3-bis(*p*-aminophenyl)-2-indolinone and benzophenone-tetracarboxylic dianhydride is useful as adhesive laminating resin for instrument boards, fiber and coating.[4] 3,3-Diaryl-2-indolinone derivatives were synthesized in various ways: from 2,3-indolinedione by the Grignard reaction,[5,6] from 2,3-indolinedione and diphenylurea with aluminium chloride,[8] form 3,3-dihalo-2-indolinone[5,7] or trichloroacetanilide[5] by the Friedel-Crafts reaction with benzene, by the reaction of *N'*-phenyldiphenylacetohydrazide with sodium,[9] α-acetoxy-α,α-diphenylacetyl chloride with aniline,[5] α-chloro-α,α-diphenylacetanilide with sodium hydride[10] or boron trifluoride etherate,[3] and by the treatment of α-hydroxy-α,α-diphenylacetanilide with sulfuric acid.[5,11–14] In a previous paper, we reported a synthetic route to various lactams from *gem*-dichloroaziridines or α-chloro-α,α-diphenylacetimidoyl chloride.[15] *gem*-Dichloroaziridines were prepared by the reaction of Schiff bases with dichlorocarbene. Makosza showed that the phase-transfer catalyst provides an excellent method for generation of dichlorocarbene.[16] Applying this method to the synthesis of 1-aryl-2,2-dichloro-3,3-diphenylaziridines, we obtained not 1-aryl-2,2-dichloro-3,3-diphenylaziridines but their isomerization products, *N*-aryl-α-chloro-α,α-diphenylacetimidoyl chlorides, in good yields. From these various 2-indolinone derivatives were obtained in good yields.

Results and Discussion

N-Benzhydrylideneanilines were prepared from benzhydrylidene dichloride and the corresponding aromatic amines in 40—60% yields(Table 1). The method[17] seems to give higher yields under moderate reaction conditions as compared with the other methods.[18,19] The *N*-benzhydrylideneanilines(**1a**—**e**) were allowed to react with dichlorocarbene generated by the method using phase-transfer catalyst. A chloroform solution of **1a**—**e** and an aqueous solution of 33.3 wt% NaOH

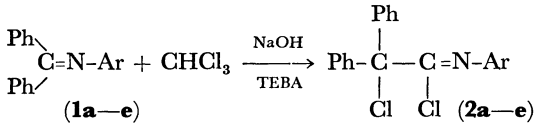
Table 1. *N*-Benzhydrylideneanilines

Compd No.	Ar	Yield, %	Mp, °C (lit)	IR, $\nu_{C=N}$, cm^{-1} (KBr disk)
1a	C_6H_5	60	112(113)[19]	1614
1b	*o*-CH_3-C_6H_4	63	50—51(51—52)[20]	1622
1c	*p*-CH_3-C_6H_4	53	48—49(48)[29]	1615
1d	*p*-Cl-C_6H_4	41	94—94.5(92—93)[21]	1612
1e	α-naphtyl	49	139—140(137.5)[29]	1601

Table 2. *N*-Aryl-α-chloro-α,α-diphenylacetimidoyl chlorides

Compd No.	Yield %	Mp, °C (lit)	IR, $\nu_{C=N}$, cm^{-1} (KBr disk)	NMR, ppm in $CDCl_3$	Formula	Found (Calcd), % C	H	N
2a	78	68.0—69.0 (70—71)[22]	1680	7.30(m)	$C_{20}H_{15}NCl_2$	70.54 (70.60)	4.40 (4.44)	3.94 (4.12)
2b	81	114.5—111.5	1672	7.30(m, 14) 2.10(s, 3)	$C_{21}H_{17}NCl_2$	71.45 (71.20)	4.87 (4.84)	4.03 (3.95)
2c	83	97.5—98.0 (92.5—94.0)[22]	1680	7.30(m, 14) 2.32(s, 3)	$C_{21}H_{17}NCl_2$	71.42 (71.20)	4.86 (4.84)	4.08 (3.95)
2d	75	109.0—110.0 (106.0—107.0)[22]	1655	7.30(m)	$C_{20}H_{14}NCl_3$	64.82 (64.11)	3.77 (3.77)	3.66 (3.74)
2e	71	106.0—107.0	1682	7.50(m)	$C_{24}H_{17}NCl_2$	74.21 (73.85)	4.48 (4.39)	3.64 (3.59)

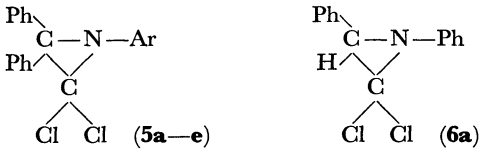
and triethylbenzylammonium chloride(TEBA) were mixed and strirred at room temperature for 2 h to give the corresponding *N*-aryl-α-chloro-α,α-diphenylacetimidoyl chloride(**2a**—**e**) in quantitative yield. IR spectra of these compounds showed the characteristic strong absorption in the region 1650—1690cm^{-1}. The results are shown in Table 2.



(**1a**—**e**) (**2a**—**e**)

In this formula, Ar stands for phenyl(**a**), *o*-tolyl(**b**), *p*-tolyl(**c**), *p*-chlorophenyl(**d**) and α-naphtyl(**e**).

The reaction would proceed *via* the formation of 1-aryl-2,2-dichloro-3,3-diphenylaziridines(**5a**—**e**) followed by its isomerization.



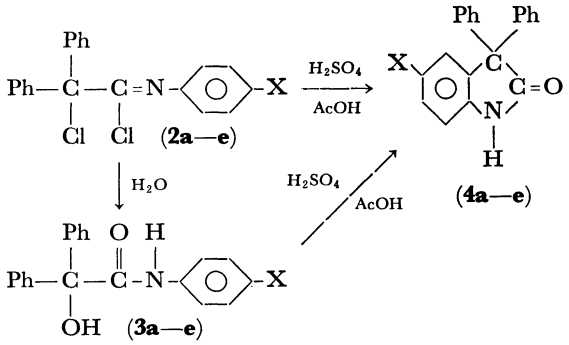
(**5a**—**e**) (**6a**)

Under the present reaction conditions, however, the aziridines(**5a**—**e**) were not isolated. Dichlorocarbenes generated in the phase-transfer catalytic system are known to be rich in reactivity.[23] The reactions take place at 5 °C or higher, since the reaction mixture becomes semi-solid at lower temperatures. Thus, the aziridines are not stabilized and isomerize into the corresponding *N*-aryl-α-chloro-α,α-diphenylacetimidoyl chloride.

On the other hand, the reaction of *N*-benzylideneaniline with chloroform in the presence of phase-transfer catalyst affords 2,2-dichloro-1,3-diphenylaziridine (**6a**) in a good yield, which dose not isomerize in this reaction system.[24] The difference in reactivity of aziridines 5 and 6 was revealed by DSC analyses. The DSC measurement of 2,2-dichloro-1-(*p*-chlorophenyl)-3,3-diphenylaziridine(**5d**), prepared by the reaction of **1d** with dichlorocarbene generated from *t*-BuOK–$CHCl_3$ in hexane at −5 °C, shows an exothermic peak at 362 K. It was confirmed from IR spectra before and after this peak that this transition is due to isomerization. Isomerization is accompanied by melting of the isomerized product **2d**, as revealed by observation under a microscope. The heat of transition combined with the heat of melting was determined to be −38.1 kJ mol^{-1}.

On the other hand, a separate run of **2d** showed an exothermic peak due to melting at 380 K, the heat of melting being 30.5 kJ mol^{-1}. Because of the melting point depression of the mixture, melting would be observed at the temperature of isomerization. By subtracting the heat of melting the heat of isomerization of **5d** into **2d** was determined to be −68.6 kJ mol^{-1}. On the other hand, aziridine **6a** was stable up to 404 K, where it was decomposed into several fragments. The difference in thermal behavior between **5d** and **6a** should be ascribed to the existence of two phenyl substituents at 3-position of **5d**. The substituents greatly affect the reactivity of aziridines.

N-aryl-α-chloro-α,α-diphenylacetimidoyl chlorides (**2a**—**e**) derived from **1a**—**e** were treated with sulfuric acid in acetic acid at room temperature for 2 h to give 3,3-diphenyl-2-indolinone derivatives(**4a**—**e**) in good yields. The formation of 3,3-diphenyl-2-indolinones proceeded also *via* *N*-aryl-α-hydroxy-α,α-diphenylacetamide(**3a**—**e**) obtained from hydrolysis of the corresponding *N*-aryl-α-chloro-α,α-diphenylacetimidoyl chlorides. The results are given in Tables 3 and 4.



(**2a**—**e**) (**4a**—**e**) (**3a**—**e**)

In the above formula, X denotes H(**a**), *o*-CH_3(**b**), *p*-CH_3(**c**), *p*-Cl(**d**) and 5,6-benzo(**e**).

Table 3. α-Hydroxy-α,α-diphenylacetanilides

Compd No.	Yield %	Mp, °C (lit)	IR, cm^{-1} (KBr disk)	NMR, ppm in $CDCl_3$	Formula	Found (Calcd), % C	H	N
3a	98	173.0—174.0 (174—175)[14]	3400 (ν_{OH}) 3330 (ν_{NH}) 1672 (ν_{CO})	7.40 (m, aromatic, 15) 3.57 (s, OH, 1)	$C_{20}H_{17}NO_2$	83.67 (84.19)	6.22 (6.01)	4.83 (4.91)
3b	98.4	149.0—149.8	3400 (ν_{OH}) 3355 (ν_{NH}) 1672 (ν_{CO})	7.30 (m, aromatic, 14) 3.98 (s, OH, 1) 2.00 (s, methyl, 3)	$C_{21}H_{19}NO_2$	78.69 (79.47)	6.10 (6.03)	4.38 (4·41)
3c	99.2	189.0—189.8 (190)[11]	3400 (ν_{OH}) 3300 (ν_{NH}) 1655 (ν_{CO})	7.30 (m, aromatic, 14) 3.65 (s, OH, 1) 2.35 (s, methyl, 3)	$C_{21}H_{19}NO_2$	78.81 (79.47)	6.16 (6.03)	4.36 (4.41)
3d	94.9	213.0—214.0 (210—212)[12]	3400 (ν_{OH}) 3340 (ν_{NH}) 1660 (ν_{CO})	7.25 (m, aromatic, 14) 3.30 (s, OH, 1)	$C_{20}H_{16}NO_2Cl$	70.04 (71.11)	4.82 (4.77)	4.11 (4.15)
3e	98.2	194.7—195.0 (195)[13]	3340 (ν_{NH}) 1668 (ν_{CO})	7.45 (m, aromatic, 17) 3.75 (s, OH, 1)	$C_{24}H_{19}NO_2$	81.23 (81.56)	5.51 (5.42)	3.90 (3.96)

Table 4. 3,3-Diphenyl-2-indolinones

Compd No.	Yield, % (a)	Yield, % (b)	Mp, °C (lit)	IR, cm^{-1} (KBr disk)	NMR, ppm in $CDCl_3$	Mass, *m/e*	Found (Calcd), % C	H	N
4a	96.0	79.7	222—225 (225—226)[14]	3300 (ν_{NH}) 1670 (ν_{CO})	7.30 (m)	285 (M^+), 257, 256 254, 208, 180	84.10 (84.19)	5.18 (5.30)	4.99 (4.91)
4b	86.0	87.8	256.5—257.5 (254—255)[12]	3160 (ν_{NH}) 1705 (ν_{CO})	7.30 (m)[c] 2.29 (s)	299 (M^+), 271, 270, 254, 222, 194	83.85 (84.25)	5.68 (5.72)	4.99 (4.68)
4c	70.0	57.2	284—285 (283—283.5)[25]	3260 (ν_{NH}) 1715 (ν_{CO}) 1672 (ν_{CO})	7.30 (m) 2.28 (s)	299 (M^+), 271, 270, 254, 222, 194	83.66 (84.25)	5.70 (5.72)	4.71 (4.68)
4d	65.5	56.5	266.0—266.5 (263—265)[12]	3250 (ν_{NH}) 1728 (ν_{CO}) 1681 (ν_{CO})	7.30 (m)	319 (M^+), 291, 290, 284, 254, 242, 214	75.01 (75.12)	4.52 (4.41)	4.31 (4.38)
4e	73.1	69.6	253.0—254.0 (254)[12]	3160 (ν_{NH}) 1702 (ν_{CO})	7.40 (m)	335 (M^+), 307, 306, 258, 230	84.60 (85.95)	5.07 (5.11)	4.11 (4.18)

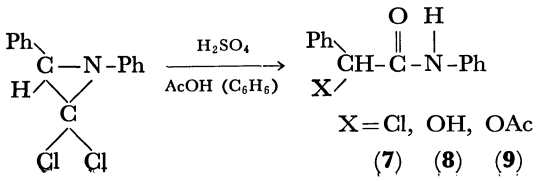
a) Produced from the corresponding *N*-aryl-α,α-diphenylacetimidoyl chloride. b) Produced from the corresponding α-hydroxy-α,α-diphenylacetanilides. c) In DMSO-d_6.

Table 5. α,α-Diphenylacetanilide derivatives

Compd No.	Ar_1	Ar_2	Yield %	Mp, °C (lit)	IR, cm^{-1} (KBr disk)	NMR ppm in $CDCl_3$	Mass, *m/e*	Found (Calcd), % C	H	N
10a	C_6H_5	C_6H_5	48	179—180 (180)[26]	3310 (ν_{NH}) 1655 (ν_{CO})	7.3 (m) 5.1 (s)	287 (M^+), 194, 169 168, 167, 166, 165 153, 152, 120, 115	82.68 (83.68)	5.87 (5.96)	4.89 (4.87)
10b	C_6H_5	*p*-ClC_6H_4	25	205—206	3300 (ν_{NH}) 1655 (ν_{CO})	7.21 (m) 4.97 (s)	323, 321 (M^+), 169, 168, 167, 165, 152	73.95 (74.65)	5.03 (5.01)	4.42 (4.35)
10c	*p*-ClC_6H_4	C_6H_5	47	185—186 (182)[27]	3300 (ν_{NH}) 1660 (ν_{CO})	7.25 (m) 4.97 (s)	323, 321 (M^+), 204, 203, 202, 201, 169 166, 165, 120	75.59 (74.65)	5.08 (5.01)	4.32 (4.35)

IR spectra of these 2-indolinones show strong bands at 3160—3250cm^{-1} and 1670—1720cm^{-1}, assigned to cis bonded NH stretching and amide I, respectively. Compounds **4c** and **4d** show two bands ascribed to amide 1, which seem to be due to free amide and dimer, since dilute solutions of **4c** and **4d** in chloroform show only a single band at 1721cm^{-1} and 1726cm^{-1}, respectively.

The reaction of **6a** with sulfuric acid gave α-chloro-α-phenylacetanilide(**7**) in 60% yield[15] Reexamination of this reaction confirmed that no intramolecular condensation of **6a** into 3-phenyl-2-indolinone occurs in H_2SO_4–AcOH mixture. The crude reaction product was carefully examined by silicagel column chromatography and α-hydroxy-α-phenylacetanilide(8) and α-acetoxy-α-phenylacetanilide(**9**) were isolated together with **7**. When **7** separated from the other products was treated with H_2SO_4–AcOH under similar conditions to those above, it remained unchanged. A similar treatment of **8** or **9** showed that they could be converted into each other.



The results show that ring-opening of **6a** proceeds *via* an ion pair which can exchange its counter ions to some extent. However, **7** dose not undergo nucleophilic substitution. This would reflect lack in its ability of carbonium ion formation in H_2SO_4–AcOH.

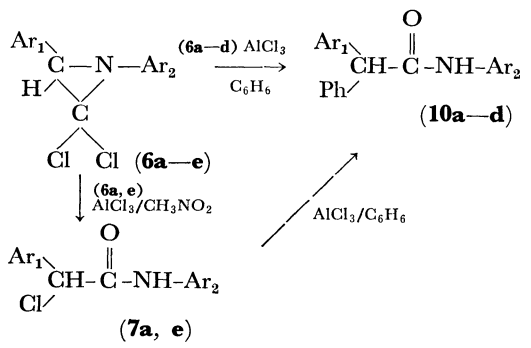
To compare the catalytic ability of sulfuric acid with that of Lewis acid, some *gem*-dichloroaziridines were treated with aluminium chloride in benzene.* The reaction gave tarry products, from which Friedel-Crafts reaction products were isolated. From spectroscopic and elemental analyses these compounds were identified to be α,α-diphenylacetanilide derivatives(**10a—c**). The results are given in Table 5.

When **6a** was treated with sulfuric acid in the presence of benzene, the resulting products were **7**, **8** and **9**, **10a** not being obtained.

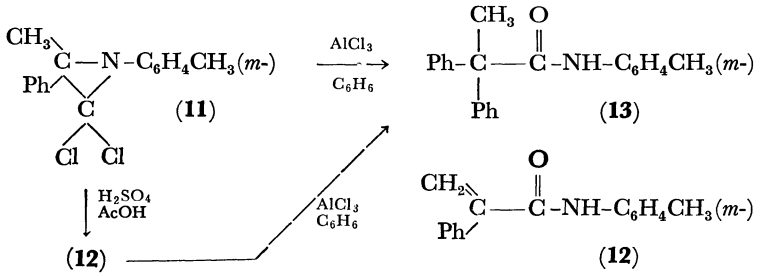
Treatment of **7a** with aluminium chloride in benzene afforded **10a**. This suggests that, if the reactions were carried out without addition of benzene, 3-phenyl-2-indolinone would be formed by intramolecular condensation. The reaction of *gem*-dichloroaziridines(**6a**,**6e**) with aluminium chloride was conducted in nitromethane, which dissolves aluminium chloride to form complexes. Compound **6d** stands for 2,2-dich-

* *gem*-Dichloroaziridines used were **6a**, 2,2-dichloro-1-(*p*-chlorophenyl)-3-phenylaziridine(**6b**), and 2,2-dichloro-3-(*p*-chlorophenyl)-1-phenylaziridine(**6c**).

loro-3-phenyl-1-(*m*-tolyl)aziridine. The reaction was carried out at various ratios of aluminium chloride to substrate, but the isolated products were acetanilide derivatives(**7a**,**7e**) in 30-60% yields.



Treatment of 3-methyl-3-phenyl-1-(*m*-tolyl)-2,2-dichloro-aziridine(**11**) with H_2SO_4–AcOH gave *N*-(*m*-tolyl)-2-phenylpropene-amide(12). On the other hand, treatment of compound(**11**) with aluminium chloride in benzene gave *N*-(*m*-tolyl)-α-methyl-α,α-diphenylacetamide(**13**) and **12** in 41% and 6.3% yields, respectively. Treatment of **12** with aluminium chloride in benzene also gave **13**, probably owing to the presence of a small amount of water;2-indolinone derivative could not be obtained from 1-aryl-2,2-dichloro-3-methyl-3-phenylaziridine.



From a comparison of reactivities of these compounds, we see that intramolecular condensation into 2-indolinone occurs effectively only when stable carbonium ions are formed and the reaction pathway of dichloroaziridines is strongly governed by the character and number of substituents at the reaction center where carbonium ion is generated.

Experimental

*Preparation of Schiff Bases(**1a**—**e**).* A mixture of 0.3 mol of aromatic amine and 0.1 mol benzhydrylidene dichloride in 200 ml of benzene was heated to reflux with stirring for 2 h. The mixture was cooled and shaken with water to remove the amine hydrochloride. The organic layer was dried over anhydrous sodium sulfate and evaporated. Recrystalization of the residue from ethanol gave the corresponding Schiff base. The results are summarized in Table 1.

Syntheses of N-*Aryl-α-chloro-α,α-diphenylacetimidoyl Chlorides (**2a**—**e**) by Using Phase Transfer Catalyst.* A solution of 0.03 mol of *N*-benzhydrylideneaniline and 1 mmol of triethylbenzylammonium chloride in 50 ml of chloroform, and 75 g of an aqueous solution of 33.3 wt % sodium hydroxide were mixed and stirred at 5 °C for 30 min and then at room temperature for 2 h. The chloroform layer was separated and washed with dil. hydrochloric acid and then water. It was dried over sodium sulfate and evaporated. Recrystalization of the residue from hexane gave the corresponding *N*-aryl-α-chloro-α,α-diphenylacetimidoyl chloride. The results are summarized in Table 2.

*Syntheses of 2-Indolinones(**4a**—**e**).* 20 ml of concd H_2SO_4 was slowly added dropwise to a solution of *N*-aryl-α-chloro-α,α-diphenylacetimidoyl chloride(6 mmol) in 20 ml of glacial acetic acid. The mixture was then poured into 80 ml of water to form precipitates, which were collected by filtration. The crystals were dissolved in chloroform and washed with 0.5 M sodium hydrogencarbonate solution and then water. The chloroform solution was dried over anhydrous sodium sulfate. Evaporation of the solvent and recrystalization of the residue from an appropriate solvent gave a pure product. The results are summarized in Table 4.

Hydrolysis of N-*Aryl-α-chloro-α,α-diphenylacetimidoyl Chloride (**2a**—**e**).* A solution of 0.01 mol of *N*-aryl-α-chloro-α,α-diphenylacetimidoyl chloride in 50 ml of 33.3% aqueous dioxane was heated to reflux for 2 h. Evaporation of the solvent and recrystalization of the residue from ethanol gave *N*-aryl-α-hydroxy-α,α-diphenylacetamide(**3a**—**e**) quantitatively. The results are summarized in Table 3.

*Reaction of 2,2-Dichloro-1,3-diphenylaziridine(**6a**) in the Presence of Sulfuric Acid.* 50 ml of concd H_2SO_4 was slowly added dropwise to a solution of 15 mmol of 2,2-dichloro-1,3-diphenylaziridine in 50 ml of acetic acid. The mixture was heated at 60 °C for 30 min and then poured into 400 ml of water to form precipitates which were collected by filtration. The precipitates were dissolved in chloroform and the solution was washed with 0.5 M sodium hydrogencarbonate solution and then water. The combined aqueous layer was saturated with sodium chloride and shaken with chloroform. The combined chloroform solution was dried over anhydrous sodium sulfate and evaporated in vacuo. The residue was subjected to silicagel column chromatography: 9.6 mmol(64%) of α-chloro-α-phenylacetanilide(**7**) was eluted with chloroform and then 1.9 mmol(13%) of α-acetoxy-α-phenylacetanilide(**9**) and 1.5 mmol (10%) of α-hydroxy-α-phenylacetanilide(**8**) were separated with chloroform-ethyl acetate eluent in the order described. α-Chloro-α-phenylacetanilide(**7**); mp 149—150 °C (lit, 147—148 °C).[28] α-Hydroxy-α-phenylacetanilide(**8**); mp 150—151 °C (lit, 151—152 °C).[29] α-Acetoxy-α-phenylacetanilide(**9**); mp 118—119 °C(lit, 117.5 °C);[30] IR(KBr) 1738 cm^{-1}(CH_3COO, CO stretching), 1675 cm^{-1} (CONH, CO stretching); NMR($CDCl_3$), δ(ppm), 6.8—7.7 (m, aromatic, 10), 6.17(s, methyn, 1), 2.17(s, methyl, 3).

Reaction of gem-*Dichloroaziridines(**6a**—**c**) with Aluminium Chloride in Benzene.* A solution of 0.02 mol of *gem*-dichloroaziridine in 30 ml of benzene was slowly added dropwise to a solution of aluminium chloride(0.02 mol) in 10 ml of benzene. The mixture was stirred for 2 h and then poured into a hydrochloric acid solution. The organic layer separated

was washed with 0.5 M sodium hydrogencarbonate and then with water. It was dried over anhydrous sodium sulfate. After evaporation of benzene *in vacuo*, the residue was subjected to silicagel column chromatography using benzene as an eluent. The results are summarized in Table 5.

Reaction of gem-*Dichloroaziridines(**6a,d**) with Aluminium Chloride.* 0.02 mol of *gem*-dichloroaziridine in 30 ml of nitromethane was slowly added dropwise to a solution of aluminium chloride(0.02 mol) in 30 ml of nitromethane. The mixture was stirred for 2 h at room temperature. The resulting solution was treated as described in the preceding section. α-Chloro-α-phenylacetanilide(**7a**); mp 149—150 °C(lit, 147—148 °C).[28] α-Chloro-*N*-(*m*-tolyl)-α-phenylacetanilide(**7d**); mp 123.6—124.3 °C; IR(KBr) 3280 cm^{-1} (NH), 1670 cm^{-1} (CO); NMR($CDCl_3$) δ(ppm) 8.4(broad, 1, NH), 7.3(m, aromatic, 9), 5.44(s, methyn, 1), 2.29(s, methyl, 3); Found: C, 69.29; H, 5.49; N, 5.56%. Calcd for $C_{15}H_{14}NOCl$: C, 69.37; H, 5.43; N, 5.39%.

DSC Analyses. DSC analyses were performed on a Perkin-Elmer DSC-2 under the following conditions: heating rate 1.25 K/min, range 5 mcal/s, chart speed 10 mm/min. The DSC measurement of **5d** shows an exothermic peak of isomerization at 362 K, the heat of which was evaluated by comparison with a heat of fusion of indium. The heat of fusion of α-chloro-α,α-diphenylacetimidoyl chloride was determined in a similar way. DSC analysis of 2,2-dichloro-1,3-diphenylaziridine shows that it decomposes at 404 K.

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