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# A NOVEL SYNTHESIS OF HALOKETENIMINE

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Haloketenimines are prepared by treatment of 2,2-dihaloaziridines with triethylamine in acetonitrile.

In spite of versatility of functionalized heterocumulenes in the field of heterocyclic syntheses, there are few investigations on a preparation of functionalized ketenimines. From this point of view, we wish to report a novel synthesis of haloketenimines from 2,2-dihaloaziridines. Transformation of 1,3,3-triaryl-2,2-dichloroaziridines to ketenimines by treatment with sodium iodide in acetone has been reported,[1] but the products are only N-aryl-diarylketenimines.

Treatment of 1,3-diaryl-2,2-dibromoaziridines[2] with triethylamine in acetonitrile gave N-aryl-arylbromoketenimines in good yields. A typical experimental procedure is as follows. To a suspension of 1,3-diphenyl-2,2-dibromoaziridine (1a; 11.9 g, 33.7 mmol) in 40 ml of acetonitrile was added triethylamine (3.40 g, 33.7 mmol), and the mixture was stirred under nitrogen atmosphere at room temperature for 7h. After separation of the precipitate, $Et_3N{\cdot}HBr$, the solution was concentrated and extracted with hexane to give N-phenyl-phenylbromoketenimine (2a), which was recrystallized from hexane. The structure of the ketenimine 2a was identified by IR, NMR, MS, and elemental analysis.[3] The results are shown in Table 1.

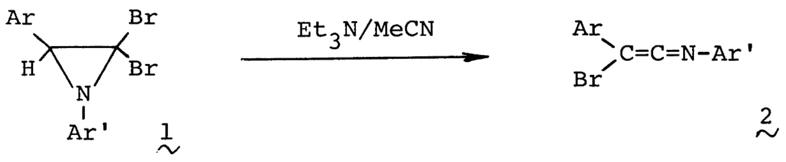


Table 1. Synthesis of Bromoketenimines

| 1 |  |  | Reaction |  | 2 |  |  |
|---|---|---|---|---|---|---|---|
| Ar | Ar' | Solv. | Temp.(°C) | Time(h) |  | Yield(%) | mp(°C) |
| Ph | Ph | MeCN | rt | 7 | 2a | 86 | 70-70.5 |
| Ph | Ph | PhH | 45 | 22 | 2a | 71 |  |
| p-Cl-$C_6H_4$ | Ph | MeCN | rt | 9 | 2b | 81 | —[a] |
| Ph | p-Cl-$C_6H_4$ | MeCN | rt | 6 | 2c | 65 | —[a] |

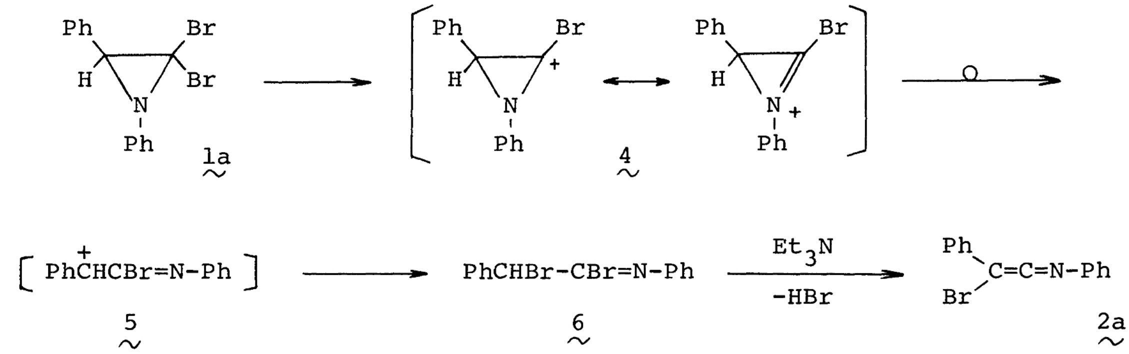
a Crystallization of 2b and 2c was difficult.

Transformation of the aziridine 1 to the ketenimine 2 was smoothly accomplished by use of acetonitrile as a solvent though 1 is not sufficiently soluble. On the contrary, the reaction in benzene, a good solvent for 1a, was very slow unless the reaction temperature was raised to 45°C.

The reaction of 1a in the presence of 5 molar excess of lithium chloride at room temperature for 11.5h gave the mixture of the ketenimine 2a and N-phenylphenylchloroketenimine (3).[3] The mass spectrum of the mixture showed the parent peaks in the ratio ~10:1.

The probable reaction course is shown in Scheme 1. The aziridine 1a is converted into α-bromo-α-phenyl-N-phenylacetimidoylbromide (6), followed by elimination of hydrogen bromide with triethylamine to give the ketenimine 2a. In the absence of triethylamine, the aziridine 1a was subjected to solvolysis in acetonitrile at room temperature to form the imidoylbromide 6, the presence of which was confirmed by the IR spectrum.[4] The imidoylbromide 6 was converted into the ketenimine 2a quantitatively by the addition of triethylamine to the solution. The chlorine atom of the ketenimine 3 is assumed to be introduced by the attack of the chloride ion to the intermediate, 4 or 5.

Scheme 1



The chloroketenimine 3 was also obtained in 88% yield by the two-step treatment of 1,3-diphenyl-2,2-dichloroaziridine as shown in above.

The present method provides a versatile synthetic method for haloketenimines which are easily obtainable by other methods.[5]

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## References

1) K. Ichimura and M. Ohta, Bull. Chem. Soc. Jpn., 40, 1933 (1967). 2) H. Yamanaka, J. Kikui, K. Teramura, and T. Ando, J. Org. Chem., 41, 3794 (1976). 3) 2a: IR (KBr) 1990 $cm^{-1}$; NMR ($CDCl_3$ with TMS) δ7.03-7.56 (m, 10H); MS m/e 271 ($M^+$). Anal. Calcd. for $C_{14}H_{10}NBr$: C, 61.79; H, 3.70; N, 5.15; Br, 29.36. Found: C, 61.64; H, 3.67; N, 5.12; Br, 29.45. The other ketenimines (2b, 2c, and 3) were similarly identified. For example, the IR spectra of these compounds exhibited strong bands assigned to $\nu$(C=C=N); 2b: 1995 $cm^{-1}$(neat), 2c: 1990 $cm^{-1}$(neat), 3: 2000 $cm^{-1}$(KBr). 4) IR (MeCN) 1690, 1590, 1490, and 1450 $cm^{-1}$. 5) G. R. Krow, Angew. Chem., Int. Ed. Engl., 10, 435 (1971).

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