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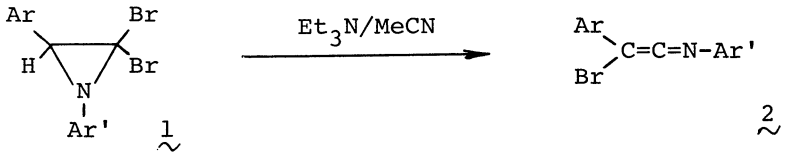
A NOVEL SYNTHESIS OF HALOKETENIMINE

Toshikazu HIRAO, Ken-ichiro HAYASHI, Jiro MOTOYOSHIYA
Yoshiki OHSHIRO,* and Toshio AGAWA
Department of Petroleum Chemistry, Faculty of Engineering, Osaka University
2-1 Yamada-oka, Suita, Osaka 565

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



1 2

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

Ar	1 Ar'	Solv.	Reaction Temp.(°C)	Time(h)	2	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]

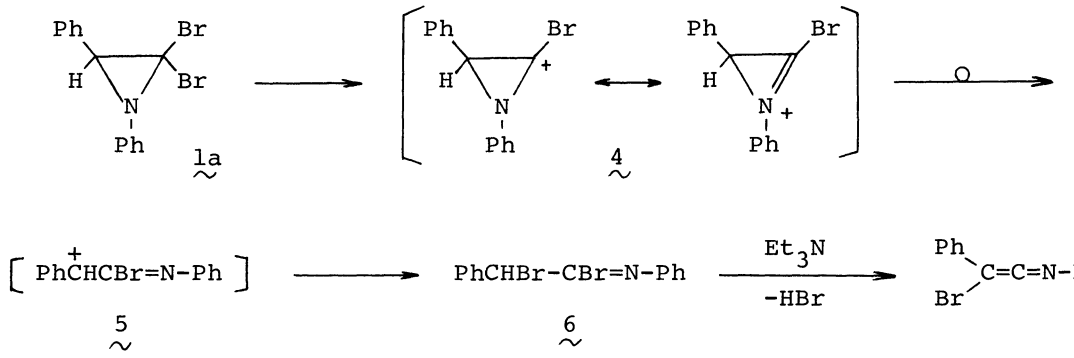
a Crystallization of 2b and 2c was difficult.

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

Scheme 1



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.

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]

Acknowledgment. This work was carried out with Grant-in-aid for Scientific Research (543025) from the Ministry of Education.

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 ν(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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