

THE REACTIONS OF ORGANOLITHIUM COMPOUNDS WITH  $\alpha,\alpha$ -DIBROMOALDIMINES  
 AND OF LITHIUM AMIDE WITH  $\alpha$ -BROMINATED ALDIMINES

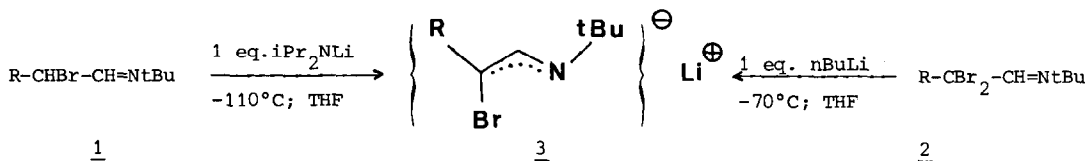
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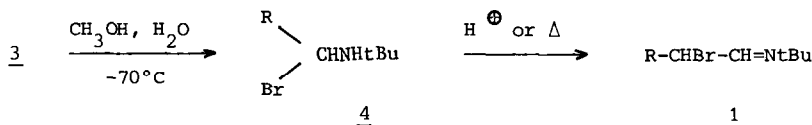
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**Abstract** :  $\beta$ -Bromo enamines 4 and  $\alpha$ -bromoaldehydes 6 are synthesised from the ambident anions 3 generated from either  $\alpha$ -bromoaldimines 1 or  $\alpha,\alpha$ -dibromoaldimines 2.

Although ambident anions derived from imines have been extensively studied (1,2,3), derivatives with an  $\alpha$ -halogen substituent were previously unknown. We now describe two independent routes (4) to these anions (i) by metalation of  $\alpha$ -bromoaldimines 1 (5) and (ii) by halogen-metal exchange from  $\alpha,\alpha$ -dibromoaldimines 2 (6).  $\alpha$ -Bromoimine anions 3 are stable to an excess of n-butyllithium.



Although the  $\alpha$ -bromoimine anions 3 are ambident, protonation with methanol at  $-70^\circ\text{C}$  led only to the N-protonated products, the  $\beta$ -bromo enamines 4 (4,7) in 79-87 % yield.

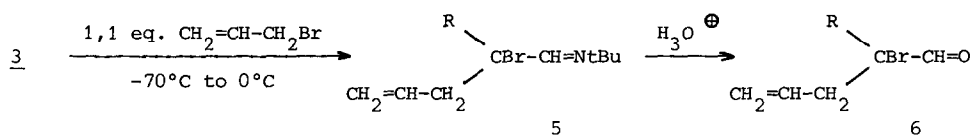


Secondary  $\beta$ -haloenamines were previously unknown except when further conjugated (8,4). The secondary enamines 4 were stable for several days at  $-30^\circ\text{C}$ ; their transformation to the tautomeric  $\alpha$ -bromoimines 1 occurred on distillation and was accelerated by traces of acid. The

$\beta$ -bromo enamines 4 were characterized by their spectral data : I R : 3350-3370,  $1660 \text{ cm}^{-1}$ ; N M R ( $\delta$ ,  $\text{CDCl}_3$ , TMS) : =CH 5,9 to 6,1 ppm; U V  $\lambda_{\text{max}} \sim 224 \text{ nm}$  ( $11000 \text{ l.mol}^{-1}.\text{cm}^{-1}$ ) in cyclohexane (compare with the values for the corresponding imines 1 (4,5); I R :  $1670 \text{ cm}^{-1}$ ; N M R :

7,3 ppm; U V : 217 nm (110 l.mol<sup>-1</sup>.cm<sup>-1</sup>).

Alkylation of the  $\alpha$ -bromoimine anions 3 with allyl bromide gave only C-alkylated products. The intermediate imine 5 was hydrolyzed without isolation into the corresponding  $\alpha$ -bromoaldehyde 6 (9) in 50-60 % yield. This provides an alternative and useful synthetic route to such compounds (10).



Unoptimised yield of aldehydes 6

Yield % \ R	H	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	nC <sub>5</sub> H <sub>11</sub>
from <u>1</u>	-	-	51	48
from <u>2</u>	60 (11)	51 (11)	55	55

#### REFERENCES AND NOTES

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- G. STORK, S. DOWD, *J.Amer.Chem.Soc.* 1968, 90, 2179.
- T. CUVIGNY, H. NORMANT, *Bull.Soc.Chim.Fr.* 1970, 3976.
- J.Y. VALNOT, Thèse Doctorat ès Sciences, Rouen Juin 1977.
- Imines 1 were prepared according to P. DUHAMEL, L. DUHAMEL, J.Y. VALNOT, *C.R.Acad.Sci.* 1970, 271C, 1471.
- Imines 2 were prepared according to N. de KIMPE, R. VERHE, L. de BUYCK, N. SCHAMP, *Synth.Comm.* 1975, 5(4), 269.
- Enamines R-CBr=CHNtBu 4 were isolated as crude products (purity > 90 %) :  
R = CH<sub>3</sub> : yield 79 %; C<sub>2</sub>H<sub>5</sub> : 87 %; nC<sub>5</sub>H<sub>11</sub> : 83 %. For results concerning secondary non halogenated enamines see : B. de JESO, J.C. POMMIER, *Chem.Comm.* 1977, 565.
- H. ALBRECHT, M.T. REINER, *Tetrahedron Letters* 1971, 4901.
- Spectral data are in good agreement with the proposed structure : I R 3080, 1730, 1645 cm<sup>-1</sup>; N M R ( $\delta$ , TMS in CDCl<sub>3</sub>); CHO 9,3-9,5 ppm; CH<sub>2</sub>Br 2,7-2,8 ppm.
- For results concerning the selective bromination of carbonyl compounds see :  
V.W. ARMSTRONG, N.H. CHISTE, R. RAMAGE, *Tetrahedron Letters* 1973, 373 and references cited.
- Crude product; purity > 95 % by G L C.

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