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A NEW PREPARATION OF ENAMIDES AND DIENAMIDES.

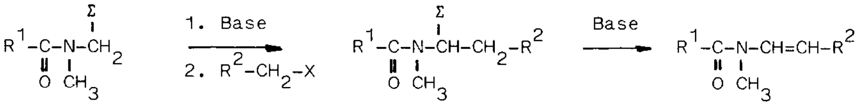
L. BERTHON and D. UGUEN *

Laboratoire de Chimie, Ecole Normale Supérieure,
24, rue Lhomond, 75231 Paris Cedex 05 - FRANCE.

SUMMARY : *α-Carbamido sulphones were anionized and alkylated ; basic elimination of the sulphonyl residue then led to enamides.*

Enamides and dienamides have proved to be valuable reagents, especially for the synthesis of alkaloids (1,2). The main methods for their preparation involve acylation of enamines (2a), thermal rearrangement of propargylic trichloroacetimidates or Curtius rearrangement of dienyl azides (2b).

The well documented feature of sulphone chemistry (3), i.e., 1-enhanced acidity of the methylene closed to the sulphonyl group, 2-leaving group ability of a sulphinate anion, led us to examine the efficiency of the following pathway :



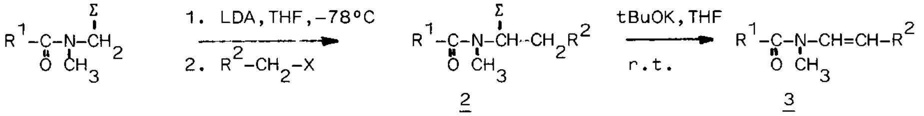
$$R^1\text{-}\underset{O}{\underset{\|}{C}}\text{-}\underset{CH_3}{\underset{|}{N}}\text{-}\overset{\Sigma}{\overset{|}{CH_2}} \xrightarrow[2.\ R^2\text{-}CH_2\text{-}X]{1.\ Base} R^1\text{-}\underset{O}{\underset{\|}{C}}\text{-}\underset{CH_3}{\underset{|}{N}}\text{-}\overset{\Sigma}{\overset{|}{CH}}\text{-}CH_2\text{-}R^2 \xrightarrow{Base} R^1\text{-}\underset{O}{\underset{\|}{C}}\text{-}\underset{CH_3}{\underset{|}{N}}\text{-}CH\text{=}CH\text{-}R^2$$

1 2 3

The starting α-carbamido sulphones 1 ($\Sigma=SO_2$-Ph, R^1=Ph or OEt), easily prepared from formaldehyde and phenylsulphinic acid (4), were treated with one molar-equivalent of L.D.A. in THF at -78°. After a few minutes the halide was added and the mixture stirred overnight at that temperature. Partition between water and methylene chloride followed by flash-chromatography on silica gel (hexane, ethyle acetate) of the organic extract afforded the homologated sulphones 2 (5), which were then stirred (4 to 16hrs) in THF with one molar-equivalent of potassium t-butoxide (6) at room temperature to give the unsaturated amides 3 (7) (Table).

Since both the halides and the starting amides are readily available, this procedure nicely complements the previous ones. Further applications of this methodology are under investigation.

TABLE :



R^1	R^2-CH_2-X	2, yield* (m.p.)	3, overall yield* (ν max, EtOH)
Ph	CH_3-i	53(69-71°)[1]	
"	CH_2=CH-CH_2-Br	83.5(93-94°)	61(265)**
"	CH_2=CHBr-CH_2-Br	63(103-105°)	
"	Ph-CH_2-Br	84(114-116°)	34(287)
"	CH_3-C(Me)=CH-CH_2Br		33
OEt	CH_2=CH-CH_2-Br	73(oil)	
"	CH_2=CMe-CH_2Br	60(45-47°)	56(254.5)
"	CH_2=CHBr-CH_2Br	85(56°)	28(261)
"	Ph-CH_2-Br	81(66°)	68(273)

* Yields in analytically pure products.
** Adduct with maleic anhydride, m.p. 140-142°.

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(7) All compounds described in this paper have given satisfactory NMR (H^1, C^{13}) Mass and I.R. spectra.

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