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SYNTHESIS AND REACTIVITY OF DIENAMINES (1)

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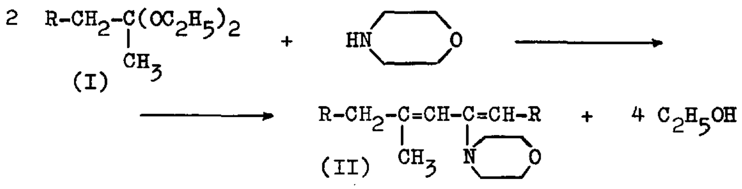
It is known that enamines can be easily obtained by heating secondary amines with ketals (2, 3, 4, 5).

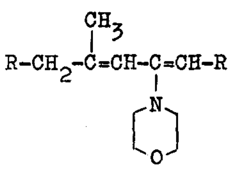
We now wish to report the synthesis of 1,3-diene-2-amines (II) by heating morpholine with ketal derivatives of methyl-n-alkyl-ketones (I) (R = $-CH_3$; $-C_2H_5$; $-C_3H_7$-n; $-C_4H_9$-n):



Some physical-chemical data of the new dienamines (II) are reported in the table. (Reported yields are obtained by heating an equimolecular mixture of ketal and amine to the boiling point until the theoretical amount of ethanol is distilled (36-48 hours)).

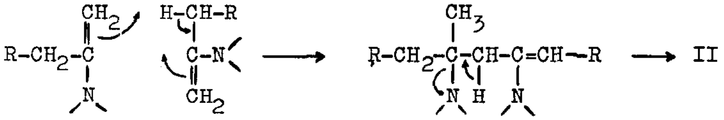
Chemical and spectroscopic evidence of the correctness of structure (II) are given. Acidic hydrolysis of compounds (II) yields the α-unsaturated ketones (III), which with H_2/Pd give the corresponding saturated ketones (IV), some of which were known. The same ketones (III) by ozonolysis gave the known methyl-ketones (V) and carboxylic acids (VI). The observed maxima (216-220 mμ) in the U. V. spectra of dienamines (II) clearly support the conjugation of the two double bonds.

TABLE



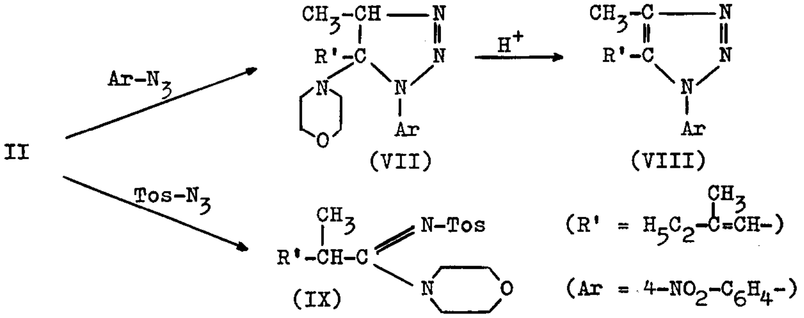
R	Yield	b.p., °C	n_D^{20}	λ_{max}, mμ
$-CH_3$	80%	$87\text{-}90_{\ 0.2}$	1.4962	216
$-C_2H_5$	75%	$86\text{-}90_{\ 0.05}$	1.4865	220
$-C_3H_7\text{-n}$	55%	$98\text{-}99_{\ 0.1}$	1.4906	216
$-C_4H_9\text{-n}$	65%	$120\text{-}21_{\ 0.1}$	1.4882	218

It seems likely that dienamines (II) derive from a bimolecular condensation of the intermediate enamines, perhaps through the following schema:



This view is indirectly supported by the fact that ketals (I) do not react with tertiary amines under the reaction conditions employed in the dienamine synthesis.

The reactivity of the above dienamines has been tested with reference to the reactions with arylazides and with tosylazide, which are known to react easily with simple enamines (3, 5, 6, 7, 8). For instance 3-N-morpholino-5-methyl-epta-2,4-diene (II: R = $-CH_3$) (obtained from the ketal of 2-butanone) reacts with 4-nitrophenylazide yielding the corresponding morpholino-triazoline (VII, m.p. 115°C) which by acidic treatment gave the triazole (VIII, m.p. 57°C). On the other side the reaction of the above dienamine (II: R = $-CH_3$) with tosylazide yielded the expected amidine (IX, m.p. 116°C):



$(R' = H_5C_2\text{-}\overset{CH_3}{C}\text{=}CH\text{-})$

$(Ar = 4\text{-}NO_2\text{-}C_6H_4\text{-})$

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