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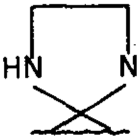
SOME DIAZASPIRANES FROM THE REACTION OF KETONES WITH ETHYLENEDIAMINE AND 1,3-DIAMINOPROPANE

John W. ApSimon*
Department of Chemistry, Carleton University, Ottawa K1S 5B6
Canada
and
R. Wayne Thompson, John C.S. Wong and William G. Craig
Department of Chemistry, University of Prince Edward Island
Charlottetown, P.E.I. Canada

Abstract

The reaction of a variety of ketones with ethylenediamine and 1,3-diaminopropane has been found to provide the expected 2,2 substituted diazaspiranes.

In our studies of the magnetic anisotropic effects of ethyleneketal and thioketal groups, (1), we wished to extend our studies to the nitrogen analogs, the imidazolidines i.e. 1. The literature concerning imidazolidine syntheses (2,3,4) is scant. Thus, the preparation of an N,N-unsubstituted imidazolidine was first reported by Bergmann who carried out the condensation between cyclohexanone and ethylenediamine by azeotropic removal of water to yield 1,4-diazaspiro [4,5] decane 2 (5,6).



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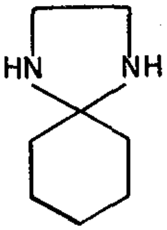

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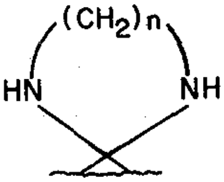

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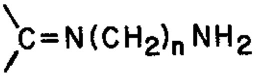

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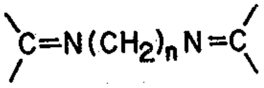

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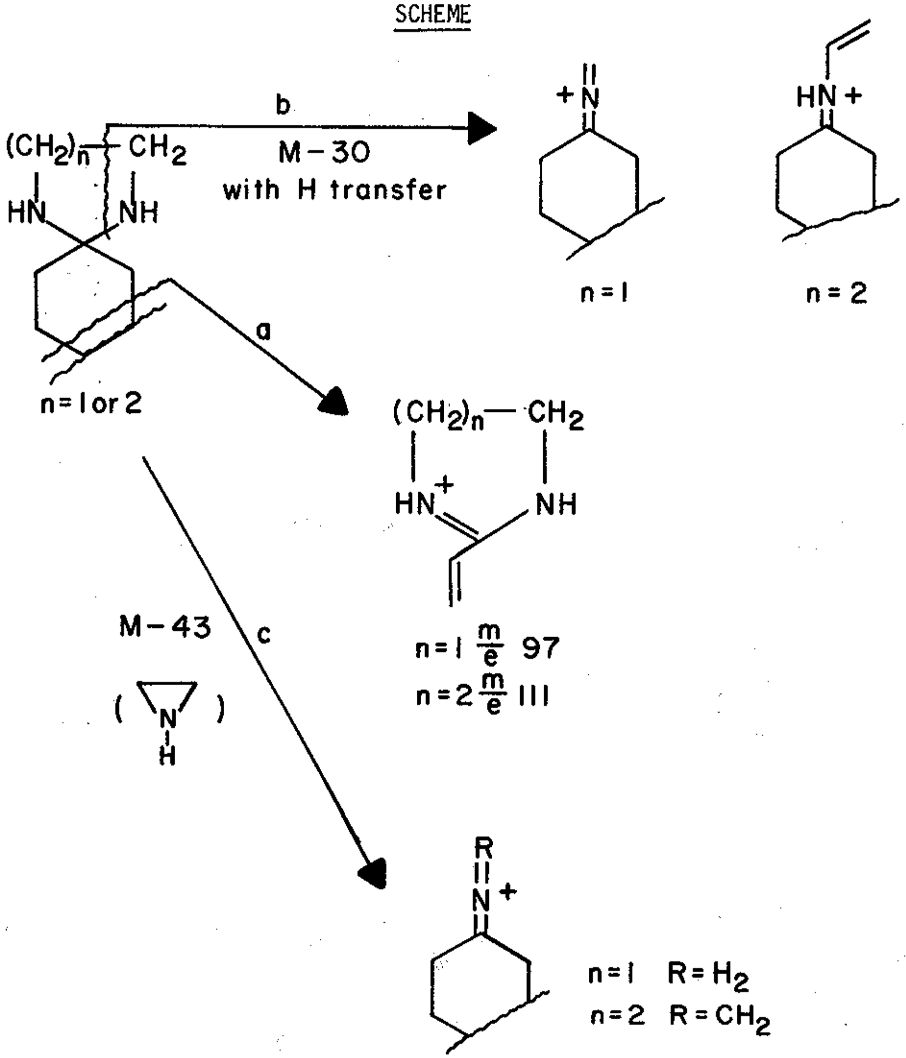
We have reacted a number of aldehydes and ketones with ethylenediamine, 1,3-diaminopropane and 1,4-diaminobutane. Three types of compounds were isolated; diazaspiranes 3, mono-Schiff bases 4 and bis-Schiff bases 5; the ratios depending on the nature of the carbonyl constituent and the diamine used. We describe here the isolation and characterisation of a number of diazaspiranes 3, observed with ketones and either ethylenediamine or 1,3-diaminopropane. Azeotropic removal of water from a boiling benzene solution of the diamine and the ketone followed by drying and evaporation of solvent was the method of preparation of these compounds which are described in the table.

The spectroscopic and analytical data for the compounds described were unexceptional. Previous reports of N,N'-unsubstituted species have been confined to the cyclohexane derived imidazolidine (5) and simple 1,3-diazacyclohexanes(hexahydropyrimidines) (7).

The mass spectra of the diazaspiranes showed fragmentation similar to that observed for ethyleneketals (route a in scheme) as well as two other characteristic modes of cleavage (suggested routes b and c in scheme).

SCHEME

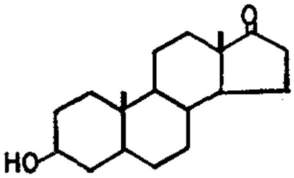
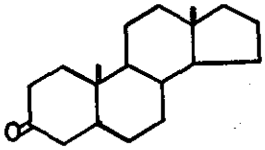


The diazaspiranes described readily regenerate the parent ketone on treatment with water.

Schiff bases (4 and 5) were observed as the major products with aldehydes, unsaturated ketones and aromatic ketones.

TABLE

SOME DIAZASPIRANES

KETONE	AMINE[1]	DIAZASPIRANE[2]	M^{+}(ms)	M.S. FRAGMENTATION
		mp°C or bp mm/Hg		% a,b,c from scheme
cyclopentanone	E	bp 47°/3 mm* (63%)	126	a(8%); b(5%)
cyclohexanone	E	mp 29.5° (71%)	140	a(100%); b(15%) c, coincides a
cyclohexanone	P	mp 45-46° (52%)	154	a(100%); c(52%)
2-methylcyclohexanone	E	bp 59/2mm (72%)	154	a(100%); b(9%); c (50%)
cyclooctanone	E	bp 65/2mm (75%)	168	a(80%); b(18%); c (12%)
cyclooctanone	P	bp 72/3mm* (60%)	182	a(100%); b(12%); c (<5%).
	E	m.p. 163° (52%)	332	a(57%); b(90%) a (30%).
	P	mp 175-180* (47%)	346	a(37%); b(31%); c(85%).
	E	mp 102-3° (50%)	316	a(100%); b(20%); c (12%).
	P	mp 115° (44%)	330	a(100%); b(4%); c (8%).

1. E, ethylenediamine; P, 1,3-diaminopropane.
2. All compounds gave the requisite C,H and N microanalysis results except those marked with an asterisk. In these cases the instability of the products prevented accurate combustion analysis, but in all cases described other spectral data including mass spectral molecular weight determination (low resolution) support the diazaspirane structures. Yields after purification are indicated in parentheses.

References and Notes

1. J.W. ApSimon, H. Beierbeck, D.K. Todd, P.V. Demarco and W.G. Craig, Can. J. Chem., 49, 9 (1971).
2. E. Bergmann, D. Herman and E. Zimkin, J. Org. Chem., 13, 353 (1948).
3. K. Hofmann, The Chemistry of Heterocyclic Compounds. Imidazole and derivatives, Part 1. Interscience, N.Y., 1953, p. 242.
4. F. Moos, Ber., 20, 732 (1887).
5. E.D. Bergmann, E. Meeron, Y. Hirschberg, and S. Pinchas, Rec. Trav. Chim., 71, 200 (1952).
6. M.M. Joullié, G.M.J. Slusarczuk, A.S. Dey, P.B. Verato and R.H. Yocum, J. Org. Chem., 32, 4103 (1967).
7. D.J. Brown, The Chemistry of Hetercyclic Compounds, The Pyrimidines. Interscience, N.Y., 1962, p. 452.
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