Azetidine Enamines

By Teng-Yueh CHEN, Hiroshi KATO[1] and Masaki OHTA

Laboratory of Organic Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo

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The increasing interest in the chemistry of azetidines and recent reports[2a-d] on the addition reactions of aziridines to dimethyl acetylenedicarboxylate prompt us to report some similar results with azetidines.

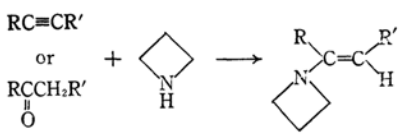
Azetidine was added exothermally to dimethyl acetylenedicarboxylate and to methyl propiolate in ether to give dimethyl 1-azetidinylmaleate and methyl β-(1-azetidinyl)-*trans*-acrylate respectively. Similar enamine-type azetidinyl derivatives were readily prepared by the concondensation of azetidine with suitable ketones at room temperature; ethyl acetoacetate gave β-(1-azetidinyl)-crotonate, while cyclopentanone and cyclohexanone gave 1-(1-azetidinyl)cyclopentene and 1-(1-azetidinyl)cyclohexene respectively. With the more acidic ketones, such as ethyl benzoylacetate, dibenzoylmethane and acetylacetone, however, the rapid separation of a precipitate (presumably the azetidinium salts) was observed, while the expected condensation products could not be isolated. The results, as well as the characteristic spectral data, are summarized in Table I.

All the compounds show a strong infrared absorption of the enamine double bond in the 1500—1660 cm^{-1} region while a typical triplet-quintet NMR pattern of an azetidinyl group is present at 6.20—6.70 and 7.75—7.81 τ. An NMR peak of a vinylic hydrogen at quite a high resonance field is relevant to the cis addition of azetidine to the triple bond; this idea is further supported by the large coupling constant ($J=15$ c.p.s.) of the two trans vinylic protons of azetidinyl-acrylate. This is in contrast to the behavior of aziridine, where the trans addition competes to some degree with the cis addition.

The appearence of the vinylic proton chemical shifts in such a high field is remarkable. Indeed, it is probably the highest among all the chemical shifts of this type so far reported.

The exclusive formation of (*cis*)-crotonate by the reaction with acetoacetate may be explained by the initial attack of azetidine from the less crowded site.

TABLE I



R	R′	Constants	IR (cm^{-1})[c]	NMR (τ)[d]	Anal. Found/Calcd. C	H	N
COOMe	COOMe	66.5—67[a]	1740, 1680 1570	5.90 (singlet)	54.35 54.27	6.85 6.53	7.04 7.03
H	COOMe	46.5—47[a]	1680 1590	2.93 (doublet) 5.91 (doublet)	59.95 59.55	8.06 7.85	10.33 9.92
Me	COOEt	110—113/2 mmHg[b] n_D^{25} 1.5068	1680 1585	6.05 (singlet)	63.58 63.88	9.23 8.94	8.59 8.28
$(CH_2)_3$		60—66/15 mmHg[b] n_D^{25} 1.4835	1630	Not measured	76.00 77.99	10.62 10.64	11.12[e] 11.37
$(CH_2)_4$		51—53/4 mmHg[b] n_D^{25} 1.4840	1660	6.08 (triplet)	78.67 78.77	11.35 11.02	10.63 10.21

a) M.p.; b) B.p.; c) Ester carbonyl and double bond; d) Vinylic proton only; e) Unstable

1) To whom inquiries should be addressed.

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