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THE SELECTIVE REDUCTION OF αβ-OLEFINIC AMIDES

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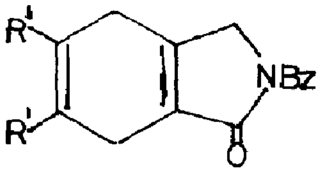
ABSTRACT. The carbon-carbon double bond in αβ-olefinic amides can be selectively reduced by magnesium and methanol; other olefinic bonds, including those of the stilbene type are unaffected.

We have been interested in developing a method for the selective reduction of a conjugated olefinic lactam grouping in the presence of an isolated double bond. No general method for the monomolecular reduction of the carbon-carbon double bond in simple αβ-olefinic amides, apart from catalytic hydrogenation, has so far been established, although several reagents have been used in individual cases[1]. We now report that magnesium and methanol[2] reduces a range of αβ-olefinic amides (1) to the corresponding saturated amides (2).

$$\underset{(1)}{R^1R^2C{=}CR^3CONR^4R^5} \rightarrow \underset{(2)}{R^1R^2CH{-}CHR^3CONR^4R^5}$$

The results are shown in the Table. Amides in which the double bond is mono-, di-, tri- and tetrasubstituted have all been successfully reduced, and the reaction works for aryl- and alkyl-substituted systems equally well, and for all substitution patterns at the nitrogen atom which we have so far investigated.

Selective reduction in the presence of an isolated double bond was indeed achieved in the lactams (3; R^1 = H or Me)[3,4] which gave a mixture of the cis- and trans- forms[4] of the lactams (4; R^1 = H or Me). It has recently been reported that stilbenes are reduced to



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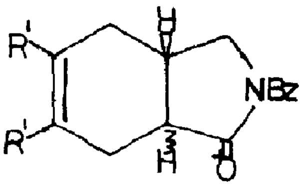

(4)

1,2-diphenylethanes by magnesium and methanol[2c]. Nevertheless reduction of (3; R^1 = Ph) also gives a mixture of the cis- and trans- forms[4] of (4; R^1 = Ph) in which the stilbene system has not been reduced.

An important feature of this reaction is that it is remarkably simple to perform; there is an induction period before the vigorous exothermic reaction sets in, at which point the reaction must be controlled by efficient external cooling.

We thank Miss S. Lee for some preliminary experiments.

TABLE

Reductions with Magnesium and Methanol

Compound Reduced						Isolated Yield of Pure Product, %	Cis/trans ratio[5]
	R^1	R^2	R^3	R^4	R^5		
1	H	H	H	H	Ph	54	-
1	Me	H	H	H	Ph	77	-
1	Me	Me	H	H	Ph	71	-
1	H	H	Me	H	Ph	84	-
1	Ph	H	H	H	H	50	-
1	Ph	H	H	Et	Et	83	-
1	Ph	H	H	H	Ph	72	-
1	Ph	Me	H	H	Ph	74	-
3	H	-	-	-	-	15 (71% recovered starting material)	2.8 : 1
3	Me	-	-	-	-	61 (22% recovered starting material)	4.0 : 1
3	Ph	-	-	-	-	83 (14% recovered starting material)	4.7 : 1

References and Notes

1. TiCl$_3$; P. Karrer, Y. Yen and I. Reichstein, Helv. Chim. Acta, 1930, 13, 1308. NaHTe; K. Ramasamy, S.K. Kalyanasundaram and P. Shanmugam, Synthesis, 1978, 545. Cob(I)alamin/Zn/CH$_3$CO$_2$H; A. Fischli and D. Süss, Helv. Chim. Acta, 1979, 62, 2361. NaHFe$_2$(CO)$_8$; J.P. Collman, R.G. Finke, P.L. Matlock, R. Wahren, R.G. Komoto and J.I. Brauman, J. Amer. Chem. Soc., 1978, 100, 1119. Co/H$_2$O/Rh$_6$(CO)$_{16}$; T. Kitamura, N. Sakamoto and T. Joh, Chem. Letters, 1973, 379; T. Kitamura, T. Joh and N. Nagihara, Chem. Letters, 1975, 203.
2. a) L. Zechmeister and P. Rom, Annalen, 1929, 468, 117 b) J.A. Profitt, D.S. Watt and and E.J. Corey, J. Org. Chem., 1975, 40, 127 c) J.A. Profitt and H.H. Ong, J. Org. Chem. 1979, 44, 3972.
3. The synthesis of these compounds will be described elsewhere.
4. All known compounds had physical properties in agreement with reported values. All new compounds ran as single materials on analytical t.l.c. and gave satisfactory microanalytical results; the ^{1}H, ^{13}C nmr and mass spectra were in accord with the structures and stereochemistries given.
5. Cis/trans ratios were estimated from the peak areas of traces obtained from analytical h.p.l.c. Pure samples of both forms were separated by preparative t.l.c. in each case.

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