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Enamides as Nucleophilic Reagents. Reactions with Cyclic *N*-Formylimmonium and Acylium Ions

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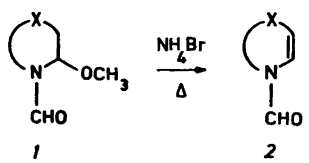
Stabilized cations, formed from cyclic *N*-formyl-*α*-methoxyamines or their corresponding enamides by treatment with an acidic catalyst, have been shown to react with substitution at the *β*-vinylic carbon of cyclic enamides (2,3-dihydro-1*H*-pyrrole-1-carboxaldehyde, 3,4-dihydro-1(2*H*)-pyridinecarboxaldehyde, 2,3,4,5-tetrahydro-1*H*-azepine-1-carboxaldehyde, and 2,3-dihydro-4*H*-1,4-oxazine-4-carboxaldehyde). The same type of reactions could be carried out with acylium ions (from acyl halides and aluminium chloride) to give vinylogous amides. With a suitable acyl group these compounds can undergo further intramolecular amidoalkylation, in the particular case of 3,4-dihydro-5-phenylacetyl-1(2*H*)-pyridinecarboxaldehyde giving an easy access to the benzo[*h*]quinoline ring system.

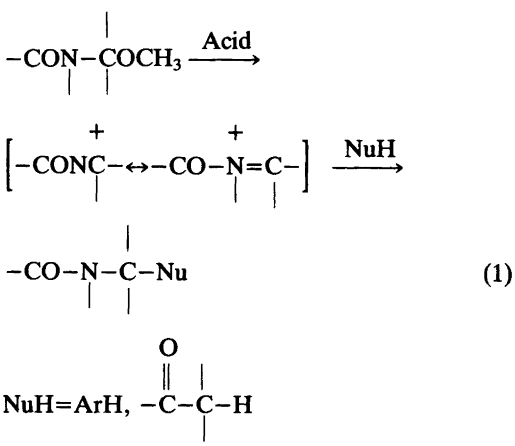
Cyclic *N*-formyl-*α*-methoxyamines (*1*), available in excellent yields and large quantities from the anodic methoxylation of cyclic *N*-formylamines,[1–4] act as amidoalkylating agents toward aromatic compounds and enolisable carbonyl compounds in the presence of suitable acidic catalysts[5–7] (eqn. 1). In the course of these reactions it was frequently noted that the intermediate cation can lose a proton to give an enamide (*2*, in eqn. 2), in itself a powerful amidoalkylating agent (the enamides are separately available by NH_4Br catalyzed elimination of methanol from *N*-formyl-*α*-methoxyamides[8] or, more laboriously, by a rhodium-catalyzed rearrangement of allylic *N*-acylamides[9]). As a consequence, side-reactions were sometimes observed in which the enamide was substituted at the vinylic *β*-carbon by the intermediate *N*-formylimmonium ion to give the biheterocycle *3* (*e.g.* *3b* from *2b*[7,10]). Analogous products have been prepared from cyclic enamines[11,12] and amines,[13] the latter *via* mercury(II) acetate oxidation.



1 *2*

1a, *2a* X=$-(CH_2)_2-$
1b, *2b* X=$-(CH_2)_3-$
1c, *2c* X=$-(CH_2)_4-$
1d, *3d* X=$-(CH_2)_2O-$

This paper describes some of the synthetic scope of this side-reaction, showing that cyclic enamides indeed can be substituted in reasonable yield by stabilized carbocations (*N*-formylimmonium ions or acylium ions) at the *β*-vinylic carbon atom.



(1)

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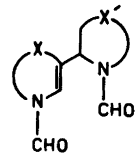
RESULTS

Compounds *3* were formed from either α-methoxylated amide (*1*) or enamide (*2*) upon treatment with neat formic acid or a mild Lewis



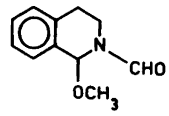
3

3a, X=X′=$-(CH_2)_2-$
3b, X=X′=$-(CH_2)_3-$
3c, X=X′=$-(CH_2)_4-$
3d, X=X′=$-(CH_2)_2O-$
3e, X=$-(CH_2)_3-$, X′=$-(CH_2)_2-$
3f, X=$-(CH_2)_3-$, X′=$-(CH_2)_4-$
3g, X=$-(CH_2)_2-$, X′=$-(CH_2)_3-$
3h, X=$-(CH_2)_4-$, X′=$-(CH_2)_3-$

acid catalyst (BF_3 or $ZnCl_2$) in dichloromethane. More potent catalysts (methanesulfonic acid or $AlCl_3$) gave lower yields, and in general the enamide (*2*) gave slightly better yields. Table 1 shows examples of reactions of *1* or *2* under what are presently deemed to be the best possible conditions.

The major problem in obtaining a good yield of *3* is the propensity of *3* to react further with the ultimate formation of polymeric material. In this respect only the doubly six-membered system (*3b*) was reasonably stable under the reaction conditions applied, while *3a*, *3c* and *3d* readily reacted further. This is in agreement with previous observations on the reactivity patterns of *1* and *2* toward Lewis of Brønsted acids, *1b* (*2b*) being generally the least reactive in the series.[6,7]

Thus we can surmise that optimal stability of *3* should be associated with the unsaturated ring being six-membered. Therefore, mixed couplings between *2b* and other enamides to form products *3* in which the six-membered enamide ring is preserved should be feasible. Table 1 shows that this is indeed the case, in that *2b* reacts with *1a* or *1c* to give *3e* and *3f* (as deduced mainly from the MS fragmentation pattern[14]) together with *3b*, whereas none of the other self-condensation products with a 5- or 7-membered enamide moiety (*3a* or *3c*) were detectable.



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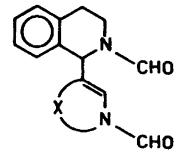


5

5a, X=$-(CH_2)_2-$
5b, X=$-(CH_2)_3-$
5c, X=$-(CH_2)_4-$

Also the isoquinoline derivative *4*, which cannot give rise to a self-condensation product, readily engaged in mixed reactions with *2b* and *2c* to give *5b* and *5c* in 97 and 55 % yield, respectively.

Table 1. Yields of *3* from reactions of *1* or *2*.

Starting material(s)	Reaction conditions	Product (yield/%)
1a or *2a*	HCOOH/25 °C/170 h or CH_2Cl_2-BF_3/reflux/170 h	*3a* (≤15)
1b	HCOOH/25 °C/170 h	*3b* (56)
	CH_2Cl_2-BF_3/reflux/140 h	*3b* (35)
1c	HCOOH/reflux/40 min	*3c* (45[a])
1d	HCOOH/25 °C/170 h or $CH_2Cl_2-BF_3$/reflux/140 h	[b]
1a+*2b*	HCOOH/25 °C/48 h	*3e* (40), *3b* (?)
1c+*2b*	HCOOH/25 °C/48 h	*3f* (80), *3b* (12)
1d or *2d*+ *1b* or *2b*	HCOOH/25 °C/48 h	*3b* (?)
2b+*4*	HCOOH/80 °C/3 h	*5b* (97)
2c+*4*	HCOOH/80 °C/3 h	*5c* (55)

[a] 85 % purity. [b] Only polymeric material was formed.

Table 2. Yields (%) of *6* from reaction between *2a-d* and acyl halides, RCOCl.

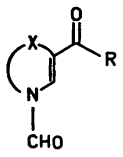
R	*2a*	*2b*	*2c*	*2d*
$-CH_3$	28	61	51	11
$-C_6H_5$		56		
$-CH_2-C_6H_5$[a]		69		

[a] This product cyclized to give compound *7* during the reaction.

Speckamp *et al.*[15] observed concomitant attack on solvent when carrying out intramolecular *N*-acylimmonium mediated cyclizations of olefins in formic acid; this was not observed in the reactions reported in Table 1. Bipiperidyl alkaloids related to *3* have previously been studied by others.[14,16]

Acylium ions, generated from acyl halides by treatment with a two-fold excess of aluminium chloride in dichloromethane, readily substituted the hydrogen at the β-carbon of *2* with formation of *6* (see Table 2). Again it was noticed that the six-membered enamide system (*6*, $X=-(CH_2)_3-$) is less prone to undergo side-reactions than the others; however, due to the deactivation of the C=C bond in *6* by the acyl group even the morpholine derivative (*6d*, $R=CH_3$) can be isolated, although in low yield.

The assigned structure of *6d*, $R=CH_3$ to the product of reaction between *2d* and acetyl chlor-



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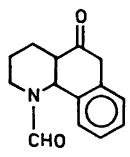

7

ide is presently tentative since it has separately been shown[17] that the amidoalkylation of aromatic compounds by *2d* takes place predominantly at the position α to nitrogen. An indication that this also has occurred in the acylation of *2d* is an unexpected fragment in the mass spectrum of the product, showing M^+-CO is one of the most intense peaks. This is in contrast to the behaviour of *6a-c* for which the normal loss of CHO from M^+ was observed.

With a properly substituted acyl halide, further intramolecular amidoalkylation of *6* should be feasible. Thus *6*, $R=PhCH_2$ underwent this reaction to give the tricyclic benzo[*h*]quinoline system *7*; a moderate yield of *6*, $R=PhCH_2$ could be obtained under slightly modified reaction conditions.

Attempts to extend the reaction to other electrophiles, such as alkyl halides or α,β-unsaturated carbonyl compounds, have so far been unsuccessful. An analogous reaction, β-acylation of cyclic α,β-unsaturated carbamates (*i.e.*, *2* with N–COOR instead of N–CHO), was recently reported.[18] Although sometimes useful alternatives to the use of cyclic enamides or α-methoxyamides, the carbamates suffer from the disadvantage of not giving easy possibilities to extend the carbon chain of the *N*-endocyclic substituent. This is important for the facile construction of ring systems, *e.g.*, of the pyrrolizidine and quinolizidine type.[19,20]

EXPERIMENTAL

GLC analyses were performed using a Hewlett-Packard HP-5830 instrument equipped with a 3 m×3 mm OV 17 on Chromosorb W column. ^1H NMR spectra were recorded on a Jeol 100 MHz instrument using $CDCl_3$ as solvent. MS analyses were performed on a Finnigan 4021 spectrometer using GLC inlet unless otherwise indicated.

The methoxyamides[1–4,10] and the enamides[8] were prepared according to published methods. The methoxyamides are commercially available from SynthElec AB, P.O. Box 1128, S-221 04 Lund, Sweden (see also *J. Org. Chem. 48* (1983) No. 2, p. 7A).

5-(1-Formyl-2-piperidyl)-3,4-dihydro-1(2H)-pyridinecarboxaldehyde (*3b*). Compound *1b* (0.1 mol) was dissolved in CH_2Cl_2 (50 ml) and boron trifluoride diethyl etherate (0.2 mol) was added. The mixture was refluxed, the course of reaction being monitored by GLC analysis. After 140 h most of the starting material and enamide, formed during the reaction, had been consumed and sodium hydroxide solution (50 ml, 2.5 M) was added. The mixture was shaken and the phases were separated; the aqueous layer was

extracted twice with CH_2Cl_2 (2×50 ml). The combined extracts were washed with water, dried over $MgSO_4$ and evaporated *in vacuo*. The crude product was recrystallized from ethyl acetate, yield 3.9 g (35 %), m.p. 82–87 °C. MS *m/e* (% rel. int.): 222 (24, M), 205 (21, M–OH), 204 (100, M–H_2O), 197 (19), 193 (30, M–CHO), 175 (24), 150 (40), 137 (20), 136 (25), 135 (19), 117 (21), 103 (24), 101 (32), 87 (42), 73 (36). ^1H NMR: δ 1.33–2.21 (10 H, m), 2.81–3.90 (4 H, m), 3.92–4.13 and 4.98–5.13 (1 H, m), 6.35, 6.44, 6.96 and 7.08 (1 H, 4 indistinct d, J 1 Hz approx.), 8.03, 8.08, 8.15 and 8.23 (1 H, 4 br s).

The same product was obtained in 56 % yield when compound *1b* (0.1 mol) was dissolved in formic acid (1.0 mol) and allowed to stand at room temperature for 170 h.

6-(1-Formyl-hexahydro-1H-azepin-2-yl)-2,3,4,-5-tetrahydro-1H-azepine-1-carboxaldehyde (*3c*). Compound *1c* (0.106 mol) was refluxed in formic acid (1.0 mol) for 40 min and then kept at room temperature for 20 h. Formic acid was removed by evaporation *in vacuo* and the product was distilled in a Kugelrohr apparatus.

The main fraction was collected at 160–210 °C/0.2 mmHg and was found to be 85 % pure according to GLC analysis, yield 5.95 g (45 %).

MS *m/e* (% rel. int.): 250 (7,m), 232 (49, M–H_2O), 221 (16, M–CHO), 204 (18), 178 (19), 164 (63), 150 (23), 136 (23), 122 (23), 108 (23), 96 (43), 55 (100).

^1H NMR analysis indicated the presence of polymeric material and the spectrum was poorly resolved. However, the vinylic proton was easily identified by four singlets at δ 6.28, 6.33, 6.53 and 6.61 and the formyl hydrogens appeared as two singlets at δ 7.91 and 8.25.

2-(1-Formyl-1,2,3,4-tetrahydro-5-pyridinyl)-hexahydro-1H-azepine-1-carboxaldehyde. Compound *2b* (0.11 mol) and *1c* (0.11 mol) were dissolved in formic acid (2 mol) and the solution allowed to stand for 48 h. Formic acid was removed by evaporation *in vacuo* and the resulting oil dissolved in water (50 ml). The solution was made alkaline with sodium hydroxide solution (5 M) and was extracted with dichloromethane (3×50 ml). The combined extracts were washed with water, dried over magnesium sulfate and evaporated *in vacuo*. GLC analysis of the crude product indicated the presence of about 5 % of starting material together with the products a mixture of *3f* and *3b* in a ratio of 6.7:1, yield 80 and 12 %, respectively. The products were not separated and only identified by MS analysis.

MS *m/e* (% rel. int.): 237 (5, M+1), 236 (29, M), 219 (20, M–OH), 218 (100, M–H_2O), 217 (14), 207 (24, M–CHO), 190 (15), 189 (18), 179 (8), 178 (10), 165 (19), 164 (43), 151 (16), 150 (34), 137 (14), 124 (12), 122 (22), 96 (22), 87 (10). MS analysis of *3a* is listed above.

1-(1-Formyl-1,2,3,4-tetrahydro-5-pyridinyl)-3,4-dihydro-2(1H)-isoquinolinecarboxaldehyde (*5b*). Compound *4* (0.05 mol) and compound *2b* (0.05 mol) were dissolved in formic acid (0.5 mol) and the solution kept at 80 °C for 3 h. GLC analysis indicated complete reaction. The formic acid was evaporated *in vacuo* and dichloromethane (100 ml) was added. The resulting solution was washed with water and saturated sodium hydrogen carbonate solution, dried over magnesium sulfate and the solvent evaporated *in vacuo*. GLC and NMR spectral analysis showed the crude product (a viscous oil) to be of high purity. Yield 13.07 g (97 %).

MS *m/e* (% rel. int.): 270 (16, M), 253 (21, M–OH), 252 (100, M–H_2O), 241 (19, M–CHO), 223 (32), 198 (48), 184 (27), 170 (35), 160 (32, $C_{10}H_{10}NO$), 141 (27), 132 (65, $C_9H_{10}N$), 130 (67), 117 (46), 115 (55), 105 (38), 77 (58).

^1H NMR: δ 1.66–1.98 (2 H, m), 1.98–2.33 (2 H,m), 2.62–3.05 (2 Hm), 3.05–4.39 (4 H, m), 4.51, 4.64, 5.07, 5.89, 6.05, 6.13, 6.22, and 6.75 (2 H, 4+4 s), 6.98–7.28 (4 H, m), 7.91, 7.95, 8.00, 8.19 and 8.27 (2 H, 5 s).

1-(1-Formyl-2,3,4,5-tetrahydro-1H-azepin-6-yl)-3,4-dihydro-2(1H)-isoquinolinecarboxaldehyde (*5c*). Compound *4* (0.05 mol) and *2c* (0.05 mol) were dissolved in formic acid (0.5 mol) and the solution kept at 80 °C for 3 h. Formic acid was removed by evaporation *in vacuo* and the product was distilled with slight decomposition in a Kugelrohr apparatus at 200–250 °C/0.2 mmHg, yield 7.75 g (55 %).

MS *m/e* (% rel. int.): 284 (6, M), 267 (22, M–OH, 266 (100, M–H_2O), 255 (15, M–CHO), 240 (12), 210 (26), 198 (38), 184 (18), 170 (24), 160 (51, $C_{10}H_{10}NO$), 141 (24), 132 (81, $C_9H_{10}N$), 130 (48), 117 (50), 115 (45), 105 (40), 77 (53).

^1H NMR δ 1.20–1.94 (4 H, m), 2.05–2.52 (2 H, m), 2.63–3.03 (2 H, m), 3.12–4.38 (4 H, m), 5.04, 5.07, 5.86, 5.91, 6.07, 6.12, 6.29, and 6.52 (2 H, 4+4 s), 6.96–7.29 (4 H, m), 7.93, 7.99, 8.05, 8.19 and 8.30 (2 H, 5s).

Acylations of enamides. General procedure. The enamide and the acyl halide (0.1 mol of each) were dissolved in CH_2Cl_2 (20 ml) and the solution added slowly to a stirred mixture of $AlCl_3$ (0.2 mol) in CH_2Cl_2 (80 ml). After complete reaction at reflux temperature (GLC analysis), the reaction mixture was hydrolyzed with water (100 ml) and the layers were separated. The aqueous phase was extracted twice with CH_2Cl_2 (2×50 ml) and the combined extracts were washed with water, sodium hydrogen

carbonate solution and water and finally dried over magnesium sulfate. The solvent was evaporated *in vacuo* and the product was purified by recrystallization or distillation at reduced pressure.

4-Acetyl-2,3-dihydro-1H-pyrrole-1-carboxaldehyde. The reaction with *2a* was carried out as above except for the amount of acetyl chloride used (0.2 mol). The reflux period was 3 h, and the reaction mixture was then left an additional 24 h at room temperature. The product was recrystallized from ethanol, yield 3.9 g (28 %)., m.p. 117–118 °C. MS *m/e* (% rel. int.): 139 (63, M), 124 (38, M–CH_3), 110 (8, M–CHO), 96 (100, M–$COCH_3$), 68 (62, C_4H_6N).

^{1}H NMR: δ 2.31 (3 H, s), 2.86 (2 H, t, *J* 9 Hz), 3.96 (2 H, t, *J* 9 Hz), 7.57 and 7.73 (small) (1 H, 2 t, *J* 1.3 Hz), 8.33 (small) and 8.63 (1 H, 2 s).

5-Acetyl-3,4-dihydro-1(2H)-pyridinecarboxaldehyde. Reflux period 5 h.

The product was recrystallized from ether (10 ml), yield 9.28 g (61 %), m.p. 45–48 °C.

MS *m/e* (% rel. int., direct inlet): 153 (53, M), 138 (100, M–CH_3), 124 (2, M–CHO), 110 (68, M–$COCH_3$), 82 (38, C_5H_8N).

^{1}H NMR: δ 1.70–2.03 (2 H, 2 p, *J* 6 Hz), 2.30 and 2.32 (3 H, 2s), 2.41 (2 H, t, *J* 6 Hz), 3.64 (2 H, t, *J* 6 Hz), 7.71 and 8.09 (1 H, 2 t, *J* 1.2 Hz), 8.25 and 8.50 (1 H, 2 s).

6-Acetyl-2,3,4,5-tetrahydro-1H-azepine-1-carboxaldehyde. Compound *2c* (0.1 mol) was reacted with acetyl chloride (0.2 mol), the reaction mixture being refluxed for 4.5 h and kept at room temperature for 24 h before work-up, yield 8.5 g (51 %), b.p. 134–137 °C/1.0 mmHg.

MS *m/e* (% rel. int.): 167 (75, M), 152 (100, M–CH_3), 138 (37, M–CHO), 124 (57, M–$COCH_3$), 110 (10), 96 (77, $C_6H_{10}N$).

^{1}H NMR: δ 2.32 (3 H, s), 2.74 (2 H, t, *J* 4.7 Hz), 4.23 (2 H, t, *J* 4.7 Hz), 7.39 (1 H, s), 8.64 (1 H, s).

5(?)-Acetyl-2,3-dihydro-4H-1,4-oxazine-4-carboxaldehyde. Reflux period 5 h. The product was recrystallized from ethyl acetate (3 ml), yield 1.82 g (11 %), m.p. 103–106 °C.

MS *m/e* (% rel. int.): 155 (8, M), 127 (80, M–CO), 112 (4, M–$COCH_3$), 84 (33, C_4H_6NO), 71 (28), 70 (24), 57 (100, CH_2NCHO):

^{1}H NMR: δ 2.32 (3 H, s), 2.74 (2 H, t, J 4.7 Hz), 4.23 (2 H, t, J 4.7 Hz), 7.39 (1 H, s), 8.64 (1 H, s).

5-Benzoyl-3,4-dihydro-1(2H)-pyridinecarboxaldehyde. Reflux period, 72 h. After evaporation of the solvent *in vacuo* the crude oil was dissolved in ether (100 ml) and chilled (−78 °C). The solid product was filtered off and washed with ether, yield 12.1 g (5), m.p. 74–77 °C.

MS *m/e* (% rel. int.): 216 (5, M+1), 215 (33, M), 197 (3), 186 (15, M–CHO), 170 (97), 169 (35), 138 (39, M–C_6H_5), 110 (45, M–COC_6H_5), 105 (67, C_6H_5CO), 77 (100, C_6H_5).

^{1}H NMR: 1.90 (2H, p, *J* 6 Hz), 2.54 (2 H, t, *J* 6 Hz), 3.53–3.74 (2 H, m), 7.28–7.34 and 7.77–7.85 (1 H, 2 narrow m), 7.37–7.63 (5 H, m), 8.15 and 8.23 (1 H, 2 s).

3,4,4a,5,6,10b-Hexahydro-5-oxo-benzo[h]quinoline-1(2H)-carboxaldehyde. Compound *2b* (0.1 mol) and phenylacetyl chloride (0.11 mol), dissolved in CH_2Cl_2 (20 ml), were added to a stirred mixture of $AlCl_3$ (0.2 mol) in CH_2Cl_2 (80 ml). After 1.5 h water (100 ml) was added and the work-up was continued as usual. The crude product was found to be of high purity (97 %) according to GLC and NMR analysis, yield 15.8 g (69 %). The product was distilled in a Kugelrohr apparatus, yield 9.3 g (41 %), b.p. 140–200 °C/0.2 mmHg.

^{1}H NMR: δ 1.15–2.17 (4 H, m), 2.17–4.35 approx. (3 H, m), 3.65 (2 H, s), 5.07 and 6.05 (1 H, 2 d, *J* 5 Hz), 6.87–7.45 (4 H, m), 8.16 and 8.37 (1 H, 2s).

MS *m/e* (% rel. int.): 230 (10, M+1), 229 (67 M), 211, (8), 201 (58, M–CO), 200 (55, M–CHO), 184 (68), 172 (43, M–C_2H_3NO), 158 (32, M–C_3H_5NO), 144 (48, M–C_4H_7NO), 128 (64), 115 (100, $CH_2C_6H_4CCH$), 91 (55), 77 (43).

This spectrum should be compared with that of 3,4-dihydro-5-phenylacetyl-1-(2*H*)-pyridinecarboxaldehyde (*6*, R=–$CH_2C_6H_5$):

MS *m/e* (% rel. int.): 229 (14, M), 201 (7), 200 (6, M–CHO), 184 (8), 139 (10), 138 (100, M–C_7H_7), 127 (8), 110 (27, M–C_8H_7O), 91 (12, C_7H_7), 82 (5), 67 (6), 65 (7).

The latter compound was obtained in moderate yield with an equimolar amount of catalyst.

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