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ORIGINAL PAPER

Interaction of push–pull *tert*-enamines with phenylglyoxal

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Abstract The reaction of push–pull enamines with 1,2-biselectrophilic phenylglyoxal was investigated. Phenylglyoxal was found to react depending on the structure of the push–pull enamine, affording either a hydroxyalkylation product at the methyl group or the cyclic product via participation of the methyl group and the β-carbon of the enamine.

Keywords Cyclizations · Electrophilic additions · Ene reactions · Alcohols · Ketones

Introduction

Until now the main object of our study has been the reaction with electrophilic reagents of tertiary push–pull enamines bearing a methyl group at the α-position. We have shown that these enamines, depending on their structure, react readily with monoelectrophilic reagents either at the methyl group or at the β-carbon of the enamines [1–3]. The enamines thus functionalized at the methyl group have a β-carbon capable of further acting as a C-nucleophile. Indeed, it has been found that the tertiary push–pull enamines react both at the methyl group and at the β-carbon with 1,3-biselectrophilic reagents affording six-membered cyclic products, thus providing a convenient synthetic approach to polyfunctionalized cyclohexanes and benzene derivatives [4–6]. One can assume that tertiary push–pull enamines in reactions with 1,2-biselectrophilic reagents can also behave analogously, affording cyclopentenone derivatives. Thus, 1,3-bis(silyl)enol ethers and 1,3-dicarbonyl dianions have been shown to react with 1,2-diketones affording functionalized 4-hydroxycycloprop–2-en-1-ones. Although reaction with phenylglyoxal itself proved unsuccessful, its ketal, 2,2-dimethoxy-2-phenylacetaldehyde, afforded cyclopentenone derivatives in moderate yields [7]. It is worth noting that primary and secondary push–pull enamines have been shown to react with 1,2-biselectrophilic reagents as CCN binucleophiles, affording five-membered heterocyclic derivatives [8–10]. The main object of our study was the reaction of tertiary push–pull enamines with 1,2-biselectrophilic reagents with the objective of synthesizing cyclopentane derivatives.

Results and discussion

For this study a set of tertiary push–pull enamines with dialkylamino substituents of different basicity—pyrrolidine and morpholine—and electron-withdrawing groups (EWG) were chosen as model compounds (Fig. 1). Phenylglyoxal (**1**) was used as the 1,2-biselectrophilic reagent.

We found that enamines **3a** and **3b**, derivatives of β-aminocrotonic acid, depending on the structure of the dialkylamino group, gave different products. Enamine **3a** in the reaction with phenylglyoxal gave the product resulting from hydroxyalkylation at the methyl group, **6a**. In a few hours the reaction comes to completion in dry ether at room temperature in high yield. By increasing the reaction time and temperature γ-functionalized enamine **6a** gave cyclic product **7**. In contrast, the enamine derived from the less basic morpholine **6b** does not cyclize, but is

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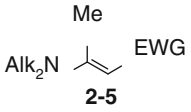

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Alk_2N = **a:** $N(CH_2)_4$, **b:** $N(CH_2CH_2)_2O$
EWG = **2:** CN; **3:** CO_2Et; **4:** COMe; **5:** COPh

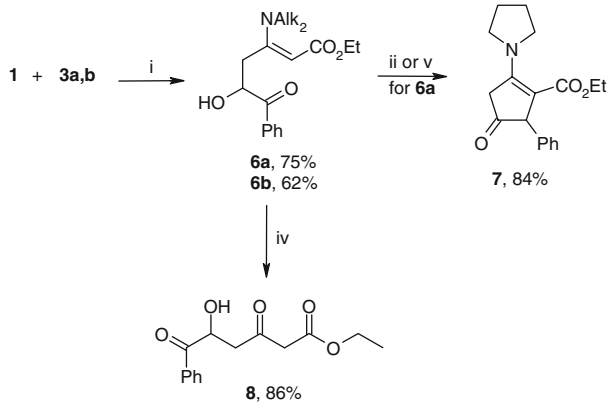
Fig. 1 The structures of the starting 'push–pull' enamines

easily hydrolysed to its ketone derivative **8** instead. Recently [7], it was demonstrated that such compounds are key intermediates in the synthesis of functionalized 4-hydroxy-2-penten-1-ones, which are present in a number of natural products, for example prostaglandins [11, 12] (Scheme 1).

The structures of products **6a**, **6b**, and **7** were confirmed by use of physicochemical methods. ^{1}H NMR spectra of compounds **6a** and **6b** are unequivocally indicative of an acyclic structure. The signal of the methylene group is indicative of an ABX-system, and the signal of the α-carbonyl proton is indicative of an AB-system. Furthermore, the doublet of *ortho*-phenyl protons is shifted downfield to ~8.2 ppm because of conjugation with the carbonyl group. At the same time the ^{1}H NMR spectrum of compound **7** shows the methylene group as an AB-system, whereas the signal of the α-carbonyl proton is absent. Furthermore, *ortho*-phenyl protons shifted upfield compared with acyclic products confirm the absence of conjugation between the phenyl ring and the carbonyl group. Unlike enamines **3**, enaminonitriles **2** and enaminones **4** react with phenylglyoxal at room temperature in ether with low selectivity affording a mixture of hardly separable products. An attempt to run the reaction at −20 °C gave the same result. This can be explained by assuming that the EWG function is reactive toward phenylglyoxal. This is probably typical behaviour of enaminones bearing an acyl group in reactions with strongly electrophilic reagents [1]. In going to enaminones **5a** and **5b** (EWG = COPh), the reaction with phenylglyoxal runs analogously to those with enamines **3**. Thus, in ether at room temperature phenylglyoxal readily reacts with enamines **5a** and **5b** giving hydroxyalkylation products **9a** and **9b** which, in acidic media, cyclize into the corresponding cyclopentenones **10a** and **10b**. It should be noted that heating the reactants in benzene results in complex mixtures of unidentifiable products. Unfortunately, our attempts to prepare cyclopentanediones by hydrolysis of compounds **10** failed. Thus, under mild conditions (two-phase CH_2Cl_2–5% aqueous HCl or in MeOH–5% aqueous HCl mixture) the starting material was recovered intact. In contrast with that, under more drastic conditions (dissolution in 5% aqueous HCl) compounds **10** decompose. Numerous attempts at hydrolysis of compounds **9** also failed. Thus, under mild conditions (two-phase CH_2Cl_2–5% aqueous HCl) the acidic cleavage product of **9**—benzoyl acetone **12**—was separated (Scheme 2).

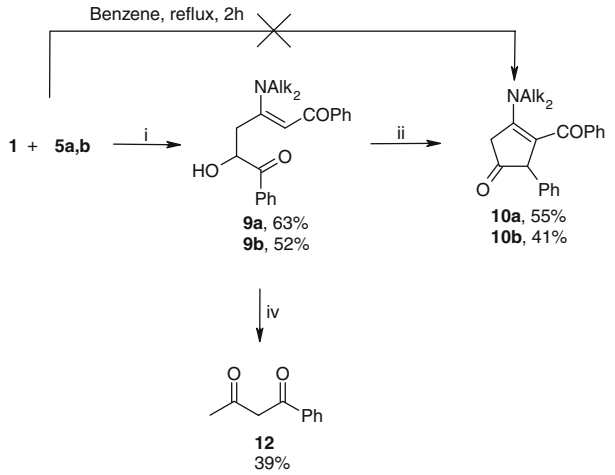
With other 1,2-biselectrophilic reagents we failed to achieve reaction. Thus, in the reaction of enamines **2–5** with 1,2-biselectrophilic butan-2,3-dione (**13**) at room temperature the starting materials were recovered. Our attempts at running the reaction at 80 °C resulted in a complex mixture of unidentifiable products. To promote the reaction we used lithiated enamine **3a**. It was found that the reaction leads to formation of bicyclic product **17** (Scheme 3).

Most probably its formation proceeds in a stepwise manner as presented in Scheme 4. An excess of lithiated enamine in the reaction mixture is the main cause of the



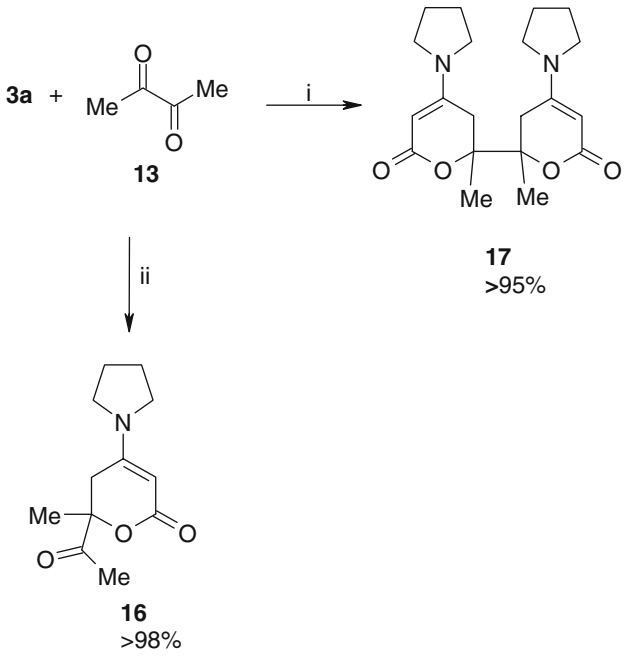
(i) diethyl ether, rt, 6–8 h; (ii) diethyl ether, rt, 48 h; (v) diethyl ether, reflux, 5 h; (iv) CH_2Cl_2, 5% aq HCl, rt, 48 h

Scheme 1



(i) diethyl ether, rt, 6–8 h; (ii) benzene, aq. HCl, rt, 12 h; (iv) CH_2Cl_2, 5% aq HCl, rt, 48 h

Scheme 2

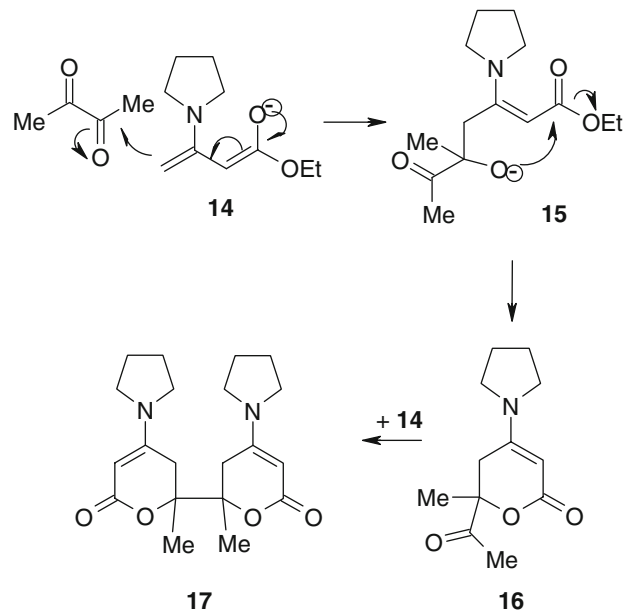


(i) diisopropylamine, *n*-BuLi, THF, -78 °C, 10–20 min; (ii) diisopropylamine, *n*-BuLi, THF, -78 °C, 30 min (reverse addition of reagents)

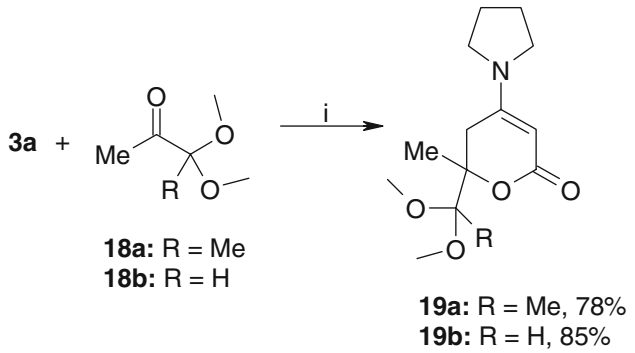
Scheme 3

formation of compound **17**. Indeed, changing the order of addition of the reagents enables isolation of monocyclic compound **16** in good preparative yield.

Monoelectrophilic derivatives of methylglyoxal dimethylacetal **18a** and butan-2,3-dione **18b** behave analogously with lithiated enamine **14** yielding cyclic products **19a** and



Scheme 4



(i) diisopropylamine, *n*-BuLi, THF, -78 °C, 30 min

Scheme 5

19b (Scheme 5). Hydroxyalkylation products of type **6** were never observed. Thus, we have shown that phenylglyoxal reacts with push–pull enamines affording γ-functionalized enamines which could then be cyclized into cyclopentenone derivatives. The enamines bearing a nitrile or acyl group react with phenylglyoxal non-selectively affording a complex mixture. Cyclic enamines **7** and **10** were shown to be stable to hydrolysis.

Thus, it was demonstrated that phenylglyoxal in the presence of triethylamine in the reaction with push–pull enamines uniquely behaves as 1,2-biselectrophilic reagent affording cyclopentanone derivatives.

Experimental

All solvents were purified and dried by standard methods. ^{1}H NMR spectra were recorded on a Varian VXR-300 spectrometer and ^{13}C NMR spectra were recorded on a Varian Mercury-400 spectrometer. ^{1}H and ^{13}C NMR spectra were measured at 300 and 100 MHz, respectively, with TMS as internal standard. IR spectra of samples as KBr discs were recorded on a Nexus-470 spectrometer. Mass spectra were obtained on a MX-1321 instrument (EI 70 eV) by direct inlet or on VG 70-70EQ, VG Analytical (FAB). Microanalyses were performed in the Microanalytical Laboratory of the Institute of Organic Chemistry, National Academy of Sciences of Ukraine, and their results agreed favourably with calculated values. Starting enamines were prepared in accordance with Refs. [13] and [14].

General procedure for reaction of enamines with phenylglyoxal

To a solution of 0.5 g phenylglyoxal (3.73 mmol) in 5 cm^3 dry diethyl ether was added a solution of 3.73 mmol enamine in 10 cm^3 dry diethyl ether. The resulting mixture

was maintained at rt for 6–8 h. The ether was decanted from the precipitate, which was crystallized from *n*-hexane.

Ethyl 5-hydroxy-3-pyrrolidin-1-yl-6-oxo-6-phenylhex-2-enoate (**6a**, $C_{18}H_{23}NO_4$)
Yellow solid; mp = 85 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.28 (3H, t, $^3J_{HH}$ = 7.2, CH_3), 1.88 (4H, br s, CH_2), 2.97 (1H, dd, $^2J_{HH}$ = 11.7 Hz, CH_2), 3.26 (4H, m, NCH_2), 3.52 (1H, m, CH_2), 4.14 (2H, q, $^3J_{HH}$ = 7.2 Hz, OCH_2), 4.6 (2H, br s, CH and OH), 5.39 (1H, dd, $^3J_{HH}$ = 11.7 Hz, CH), 7.52 (3H, m, CH), 8.26 (2H, d, $^3J_{HH}$ = 7.1 Hz, CH) ppm; ^{13}C NMR (125 MHz, C_6D_6): δ = 14.8, 24.7, 36.1, 48.1, 58.5, 73.4, 84.9, 128.6, 129.9, 133.6, 134.3, 159.0, 169.7, 201.7 ppm.

Ethyl 5-hydroxy-3-morpholin-4-yl-6-oxo-6-phenylhex-2-enoate (**6b**, $C_{18}H_{23}NO_5$)
Yellow solid; mp = 95–97 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.27 (3H, t, $^3J_{HH}$ = 7.2 Hz, CH_3), 2.95 (1H, dd, $^2J_{HH}$ = 14.1 Hz, $^3J_{HH}$ = 9.9 Hz, CH_2), 3.24 (4H, m, NCH_2), 3.66 (5H, m), 4.14 (2H, q, $^3J_{HH}$ = 7.2 Hz, OCH_2), 4.89 (1H, s, CH), 5.35 (1H, dd, $^3J_{HH}$ = 9.9 Hz, $^3J_{HH}$ = 4.5 Hz, CH), 7.55 (3H, m, CH), 8.21 (2H, d, $^3J_{HH}$ = 7.2 Hz, CH) ppm; ^{13}C NMR (125 MHz, C_6D_6): δ = 14.6, 37.5, 49.6, 58.7, 66.3, 74.1, 82.1, 128.5, 130.1, 132.5, 133.7, 160.1, 168.6, 200.8 ppm; MS (EI 70 eV): *m/z* (%) = 333 (6) [M^+], 315 (38), 242 (100), 172 (11), 128 (15), 77 (10).

Ethyl 4-oxo-5-phenyl-2-(pyrrolidin-1-yl)cyclopent-1-enoate (**7**, $C_{18}H_{21}NO_3$)
The general procedure was applied. The resulting reaction mixture was maintained at rt for 48 h (or heated under reflux for 5 h). The ether was decanted from the precipitate, which was crystallized from *n*-pentane. Colourless solid; mp = 112 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.33 (3H, t, $^3J_{HH}$ = 7.5 Hz, CH_3), 2.03 (4H, t, $^3J_{HH}$ = 5.4 Hz, CH_2), 3.45 (4H, t, $^3J_{HH}$ = 5.4 Hz, NCH_2), 3.63 and 4.04 (1H, 2H, AB-syst., $^2J_{HH}$ = 3.4 Hz), 4.31 (2 h, q, $^3J_{HH}$ = 7.5 Hz, CH_2), 5.05 (1H, s, CH), 7.3 (2H, d, $^3J_{HH}$ = 8.9 Hz, CH), 7.38 (1H, d, $^3J_{HH}$ = 8.9 Hz, CH), 7.45 (2H, t, $^3J_{HH}$ = 8.9 Hz, CH) ppm; ^{13}C NMR (125 MHz, C_6D_6): δ = 14.2, 25.2, 46.3, 52.3, 54.7, 59.4, 92.3, 126.5, 129.3, 131.5, 167.4, 209.4 ppm; MS (EI 70 eV): *m/z* (%) = 299 (37) [M^+], 226 (100), 128 (10), 70 (21).

Ethyl 5-hydroxy-4,6-dioxo-6-phenylhexanoate (**8**, $C_{14}H_{16}O_5$)
Functionalized enamine **6b** (1 g, 3 mmol) was dissolved in 15 cm^3 dichloromethane and 15 cm^3 5% aq. HCl were added. The resulting two-phase system was stirred at rt for 48 h. The organic layer was dried over sodium sulfate, filtered, and evaporated. Light yellow solid; mp = 73 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26 (3H, t, $^3J_{HH}$ = 7.2 Hz, CH_3), 2.86 (1H, dd, $^3J_{HH}$ = 16.8 Hz, $^3J_{HH}$ = 8.1 Hz, CH_2), 3.03 (1H, dd, $^3J_{HH}$ = 16.8 Hz, $^3J_{HH}$ = 3.3 Hz, CH_2), 3.54 (2H, s, CH_3), 4.17 (2H, q, $^3J_{HH}$ = 7.2 Hz, OCH_2), 5.48 (1H, dd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 3.3 Hz, CH), 7.48–7.66 (3H, m, CH), 7.93 (2H, d, $^3J_{HH}$ = 7.2 Hz, CH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1, 47.7, 50.1, 61.6, 69.8, 128.7, 129.0, 133.2, 134.2, 166.8, 199.9, 200.3 ppm.

5-Hydroxy-1,6-diphenyl-3-(pyrrolidin-1-yl)-hex-2-en-1,6-dione (**9a**, $C_{22}H_{23}NO_3$)
Colourless solid; mp = 132 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.88 (4H, br s, CH_2), 3.09 (1H, m, CH_2), 3.48 and 3.54 (4H, m, NCH_2), 3.79 (1H, m, CH_2), 5.39 (1H, m, CH), 5.67 (1H, s, CH), 6.05 (1H, d, $^3J_{HH}$ = 6.9 Hz, OH), 7.44–7.65 (6H, m, CH), 7.86 (2H, d, $^3J_{HH}$ = 7.1 Hz, CH), 8.14 (2H, d, $^3J_{HH}$ = 7.1 Hz, CH) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ = 26.7, 51.1, 69.4, 87.1, 126.4, 127.5, 128.4, 129.1, 138.6, 163.4, 197.5, 199.6 ppm; MS (EI 70 eV): *m/z* (%) = 349 (11) [M^+], 331 (17) [$M^+ - H_2O$], 244 (16) [M^+ − PhCO], 226 (100) [M^+ − PhCO − H_2O], 105 (92) [$PhCO^+$], 77 (61) [Ph^+], 70 (50).

5-Hydroxy-1,6-diphenyl-3-(4-morpholinyl)hex-2-en-1,6-dione (**9b**, $C_{22}H_{23}NO_4$)
Colourless solid; mp = 121–123 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.81 (1H, m, CH_2), 3.26 (5H, m, NCH_2 and CH_2), 3.71 (4H, m, OCH_2), 5.22 (1H, m, CH), 5.53 (1H, s, CH), 7.31–7.52 (6H, m, CH), 7.91 (2H, d, $^3J_{HH}$ = 7.2 Hz, CH), 8.15 (2H, d, $^3J_{HH}$ = 7.2 Hz, CH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 37.5, 48.6, 66.8, 73.4, 89.5, 127.3, 128.0, 128.5, 130.2, 130.6, 167.4, 197.3, 200.1 ppm.

General procedure for synthesis of cyclic compounds ***10***

To a solution of 2.5 mmol acyclic compound in 10 cm^3 benzene was added 0.1 cm^3 concentrated HCl and the mixture was maintained at rt for 12 h. The benzene was decanted from the precipitated oil, and the oil was dissolved in EtOH and maintained at 0 °C for 2 h. The precipitate formed was collected by filtration.

3-Benzoyl-2-phenyl-4-(pyrrolidin-1-yl)cyclopent-3-enone (**10a**, $C_{22}H_{21}NO_2$)
Colourless solid; mp = 191 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.82 (4H, t, $^3J_{HH}$ = 6.6 Hz, CH_2), 3.45 (4H, t, $^3J_{HH}$ = 6.6 Hz), 3.69 (1H, d, $^2J_{HH}$ = 3.4 Hz), 4.02 (1H, d, $^2J_{HH}$ = 3.4 Hz), 5.2 (1H, s, CH), 7.18 (2H, m, CH), 7.31–7.45 (5H, m, CH), 7.7–7.81 (3H, m, CH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 25.8, 48.6, 53.1, 57.3, 92.7, 126.7, 127.3, 127.9, 129.8, 137.3, 154.1, 191.4, 208.4 ppm; MS (EI 70 eV): *m/z* (%) = 331 (46) [M^+], 226 (100), 105 (75), 77 (43).

3-Benzoyl-2-phenyl-4-(4-morpholinyl)cyclopent-3-enone (**10b**, $C_{22}H_{21}NO_3$)
Colourless solid; mp = 193 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.21 (4H, m, NCH_2), 3.25 and 3.43 (2H, AB-system, $^2J_{HH}$ = 13.1 Hz, CH_2), 3.63 (4H, m, OCH_2), 4.51 (1H, s, CH), 7.18 (5H, m, CH), 7.36 (2H, m, CH), 7.74 (3H, m, CH) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ = 49.1, 50.3, 57.8, 68.2, 93.0, 124.4, 125.1, 125.9, 126.7, 128.7, 135.1, 155.4, 193.4, 208.8 ppm.

2,2′-Dimethyl-4,4′-dipyrrolidin-1-yl-2,2′,3,3′-tetrahydro-6H,6′H-2,2′-bipyran-6,6′-dione (**17**, $C_{20}H_{28}N_2O_4$)
To a solution of 0.55 g diisopropylamine (5.46 mmol) in 15 cm^3 THF 2.2 cm^3 2.5 M *n*-BuLi was added at −78 °C. The reaction mixture was allowed to warm to 0 °C and at that temperature 1 g **3a** (5.46 mmol) was added. The reaction mixture was stirred for 10 min at −78 °C and then 0.47 g **13** (5.46 mmol) in 5 cm^3 THF was added. The reaction mixture was allowed to reach room temperature and was poured into 50 cm^3 water and extracted with 3 × 20 cm^3 EtOAc. The organic layer was dried and evaporated in vacuo. The residue was crystallized from ether to give **17** as a colourless solid (1.86 g, 95%). Mp > 250 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.53 and 1.54 (6H, br s, CH_3), 1.98 (8H, br s, CH_2), 2.47 and 2.88 (2H, AB-syst., $^2J_{HH}$ = 17 Hz), 2.59 and 2.89 (2H, AB-syst., $^2J_{HH}$ = 17 Hz), 3.17 and 3.25 (4H, br s, NCH_2), 3.42 (4H, br s, NCH_2), 4.59 (2H, s, CH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.0 and 20.3, 24.7 and 25.3, 31.5 and 31.7, 47.9 and 48.2, 81.2 and 81.3, 81.5 and 81.6, 157.3 and 157.6, 166.5 ppm; MS (EI 70 eV): *m/z* (%) = 360 (12) [M$^+$], 181 (17), 180 (100), 136 (14), 110 (7), 70 (14), 44 (174), 43 (14).

6-Acetyl-6-methyl-4-pyrrolidin-1-yl-5,6-dihydro-2H-pyran-2-one (**16**, $C_{12}H_{17}NO_3$)
To a solution of 0.55 g diisopropylamine (5.46 mmol) in 15 cm^3 THF 2.2 cm^3 2.5 M *n*-BuLi was added at −78 °C. The reaction mixture was allowed to warm to 0 °C and at that temperature 1 g **3a** (5.46 mmol) was added. The reaction mixture was cooled to −78 °C and added dropwise to a solution of 0.47 g **13** (5.46 mmol) via Chem-Flex needle (system for safe transfer of air- and moisture-sensitive liquids). The reaction mixture was stirred for 10 min, and then poured into 50 cm^3 water and extracted with 3 × 20 cm^3 EtOAc. The organic layer was dried and evaporated in vacuo. The residue was crystallized from ether to give **16** as a colourless solid (1.19 g, 98%); mp = 87–89 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.47 (3H, s, CH_3), 1.97 (4H, br s, CH_2), 2.29 (3H, s, CH_3), 2.46 and 3.19 (2H, AB-syst., $^2J_{HH}$ = 15.9 Hz), 3.12 (2H, br s, NCH–), 3.41–3.52 (2H, br m, NCH_2), 4.52 (1H, s, CH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.0, 24.7, 25.1, 25.2, 33.7, 47.7, 47.9, 82.0, 83.1, 157.9, 166.9, 211.0 ppm; MS (EI 70 eV): *m/z* (%) = 223 (11) [M$^+$], 181 (14), 180 (100), 138 (22), 70 (13), 43 (22).

6-(1,1-Dimethoxyethyl)-5,6-dihydro-6-methyl-4-(1-pyrrolidinyl)-2H-pyran-2-one (**19a**, $C_{14}H_{23}NO_4$)
The procedure for compound **17** was applied. Colourless solid (1.3 g, 78%); mp = 93 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.41 (3H, s, CH_3), 1.43 (3H, s, CH_3), 1.98 (4H, br s, CH_2), 2.32 and 2.86 (2H, AB-syst., $^2J_{HH}$ = 16.8 Hz), 3.41 (4H, br s, NCH_2), 3.57 (6H, s, CH_3), 4.62 (1H, s, CH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.7, 21.3, 24.4, 30.4, 46.8, 57.3, 57.9, 81.1, 82.3, 106.7, 159.1, 165.7 ppm.

6-(Dimethoxymethyl)-6-methyl-4-pyrrolidin-1-yl-5,6-dihydro-2H-pyran-2-one (**19b**, $C_{13}H_{21}NO_4$)
The procedure for compound **17** was applied. Colourless solid (1.17 g, 85%); mp = 84–86 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.41 (3H, s, CH_3), 1.98 (4H, br s, CH_2), 2.30 and 2.88 (2H, AB-syst., $^2J_{HH}$ = 16.8 Hz), 3.22 and 3.41 (4H, br s, NCH_2), 3.54 (3H, s, CH_3), 3.57 (3H, s, CH_3), 4.25 (1H, s, CH), 4.59 (1H, s, CH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.9, 24.8, 30.1, 47.7, 57.8, 58.3, 80.7, 82.0, 108.7, 157.1, 166.7 ppm; MS (EI 70 eV): *m/z* (%) = 255 (4) [M$^+$], 194 (7), 181 (13), 180 (100), 138 (12), 75 (42), 70 (7).

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