

## Synthesis of bicyclic lactams using novel Schmidt reactions

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**Dedicated to Professor Tony McKervey on the occasion of his retirement from Queen's University, Belfast**

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### Abstract

Several  $\gamma,\delta$ -unsaturated  $\beta$ -diketones were prepared by acylation of the lithium enolates of cyclic ketones by cinnamoyl chlorides. Reaction of the cinnamoylcyclohexanones with 2 equivalents of hydrazoic acid in sulfuric acid gave bicyclic lactams in good yields. The mechanism of this process involves a Schmidt reaction, followed by addition of  $\text{HN}_3$  to the enone, migration of the aryl group onto nitrogen, and a cyclisation in which the arylamino group is displaced by the amide nitrogen. The scope of the reaction is limited to the preparation of 7-5 bicyclic systems from enoyl cyclohexanones, other precursors gave dihydropyrones or complex mixtures.

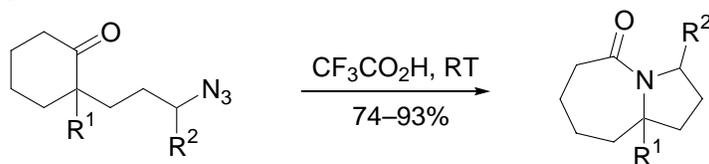
**Keywords:** Acylation, diketones, enones, Schmidt, lactams, alkaloids

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### Introduction

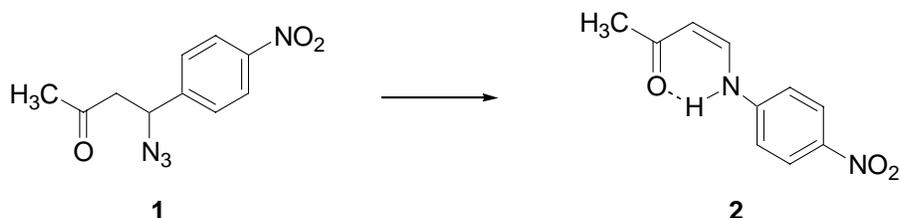
The reaction of carbonyl compounds with hydrazoic acid, known as the Schmidt reaction, is a convenient method for the synthesis of a wide variety of nitrogen containing materials.<sup>1</sup> It has the advantages of simplicity, ready availability of reactants, mild reaction conditions, and good functional group tolerance. The reaction of cyclic ketones to give lactams is a particularly useful application, and many examples are known. In recent times, this method has been extended to provide access to some *N*-substituted lactams by replacing hydrazoic acid with organic azides.<sup>2</sup> A notable development, that greatly extends the power of the reaction, has been the discovery that the intramolecular Schmidt reaction of organic azides with ketones (Scheme 1),<sup>3</sup> or with carbocations derived from alkenes or alcohols,<sup>4</sup> can give a wide range of bicyclic products bearing nitrogen at one of the ring fusion positions. Such ring systems are core structures in a wide variety of alkaloids. The work of Aubé provides an impressive demonstration of the synthetic utility of this intramolecular variant.<sup>5</sup>

<sup>§</sup> Deceased 27<sup>th</sup> June 1991.



**Scheme 1**

The acid-catalysed reaction of hydrazoic acid with  $\alpha,\beta$ -unsaturated ketones is less widely used. A systematic investigation by Boyer established that alkenes with conjugated electron-withdrawing groups readily undergo addition reactions with hydrazoic acid.<sup>6</sup> It is noteworthy that cinnamoyl derivatives, in which the conjugation is extended into a benzene ring, do not generally react with hydrazoic acid.<sup>6,7</sup> However, the presence of a strongly electron-withdrawing substituent, *e.g.* 4-nitro, on the aryl group restores the reactivity. In these reactions the use of strongly acidic conditions is unsuitable if the azide adduct is to be isolated. The azide may decompose by a Schmidt-type reaction with loss of nitrogen, *e.g.* the sulfuric acid catalysed decomposition of 4-azido-4-*p*-nitrophenylbutan-2-one **1** to give enamino **2** (Scheme 2).<sup>8</sup>



**Scheme 2**

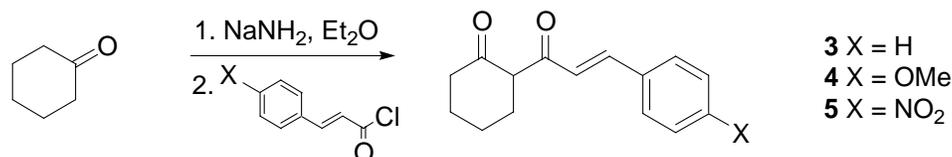
As a continuation of the investigation into the chemistry of the  $\alpha,\beta$ -unsaturated 1,3-diketone moiety undertaken in this laboratory,<sup>9</sup> it was decided to study the Schmidt reaction of cinnamoyl cyclohexanone **3**. It was thought incorporation of a nitrogen atom into the saturated ring or the side chain, followed by cyclisations, might constitute an entry into oxygen and nitrogen heterobicyclic systems. We now report that reaction of  $\alpha,\beta$ -unsaturated 1,3-diketones, such as **3**, with hydrazoic acid produces bicyclic lactams via an unexpected sequence of reactions that includes two Schmidt processes.

## Results and Discussion

### Preparation of $\gamma,\delta$ -unsaturated $\beta$ -diketones

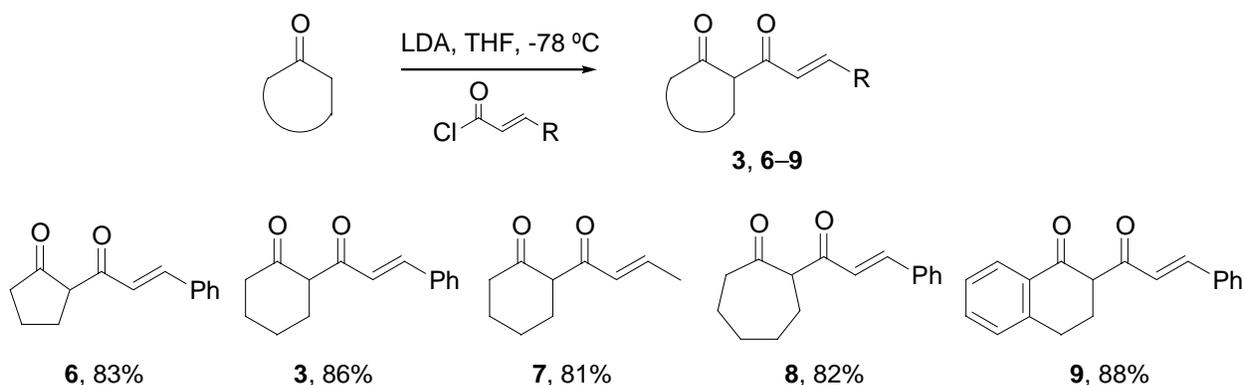
The  $\gamma,\delta$ -unsaturated  $\beta$ -diketones required for this work were prepared by reaction of ketone enolates with enoyl chlorides. The acylation of enolates is a somewhat unpredictable process, and the yield and selectivity for *C*-acylation versus *O*-acylation depend on the ketone, and on the

acylating agent used.<sup>10</sup> The synthesis of cinnamoylcyclohexanone **3** in this way was described by Linn and Hauser.<sup>11</sup> Sodium amide was prepared *in situ* by the reaction of sodium with liquid ammonia, and the excess ammonia was removed and replaced by dry diethyl ether before adding the cyclohexanone. Reaction of the enolate (3 molar equivalents were used to prevent diacylation) with cinnamoyl chloride at 0 °C gave the cinnamoylcyclohexanone **3** in 40% yield. Subsequently, Sheehy used commercial NaNH<sub>2</sub>, in ether,<sup>9</sup> and removed the ammonia generated in the formation of the enolate by passing a stream of nitrogen through the reaction mixture, thus reducing the possibility of cinnamide formation. Difficulties in isolating product **3** were eased by removing the excess cyclohexanone with aqueous sodium metabisulfite. These measures increased the yield to 60%. In the present work the method of Sheehy was employed, but the reaction temperature was reduced from 0 °C to -78 °C, and it was found that the yield of cinnamoylcyclohexanone **3** increased to 75%, and the 4-methoxy and 4-nitro analogues **4** and **5** were obtained in 60% and 15% yields, respectively (Scheme 3).



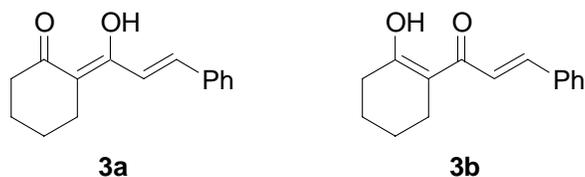
Scheme 3

As expected,<sup>12</sup> attempted synthesis of cinnamoylcyclopentanone by the above method failed. However, deprotonation of cyclopentanone using LDA in THF at -78 °C, and reaction with cinnamoyl chloride (0.3 eq. to prevent diacylation) at -78 °C gave cinnamoylcyclopentanone **6** in 83% yield. A number of other  $\alpha,\beta$ -unsaturated 1,3-diketones were prepared in good yields (based on acyl chloride) by this method (Scheme 4). Clean C-acylation was observed in all cases. The reaction of lithium enolates with acyl chlorides has been found to give C-acylation in most, but not all, cases.<sup>13</sup> Improvements in acylation methodology have been reported since the completion of this work,<sup>14</sup> so it is likely that our procedure could be improved upon.



**Scheme 4**

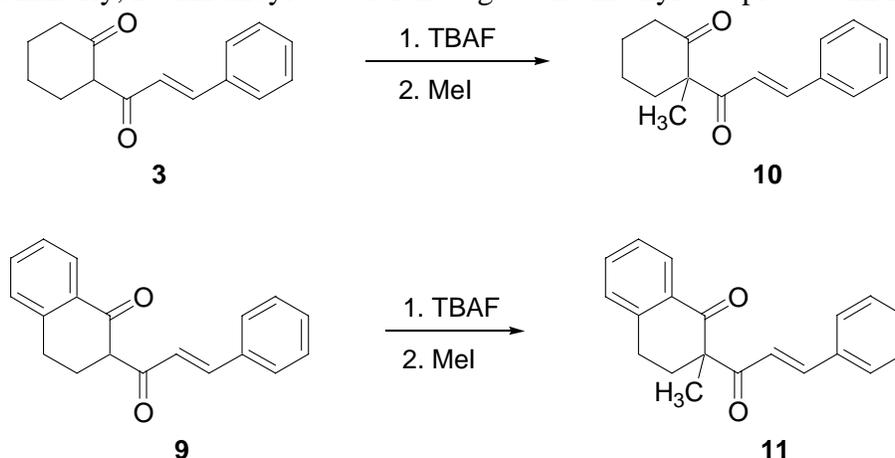
The  $^1\text{H}$  NMR spectrum of **3** contained a one-proton singlet, exchangeable with  $\text{D}_2\text{O}$ , at  $\delta$  16.83, a position typical of the hydroxy group in a keto-enol system that is stabilised by intramolecular hydrogen bonding. Clearly it existed in one of the two possible enol forms **3a** and **3b** (Figure 1).

**Figure 1**

The observed  $^{13}\text{C}$  NMR chemical shifts were  $\delta$  193.4 for the carbonyl carbon and  $\delta$  180.1 for the enolic carbon. The predicted values, using the method of additive shift parameters, for enol **3a** were 196 and 177 ppm, respectively, whereas the values for enol **3b** were predicted to be 180 and 163 ppm, respectively. The observed chemical shifts were much closer to those predicted for isomer **3a**, suggesting that this is the predominant enol form. More conclusive proof was obtained from a carbon-hydrogen correlation spectrum, optimised for long range coupling (COLOC), which showed strong cross peaks between (i) the carbonyl carbon at  $\delta$  193.4 and the 8H multiplet at  $\delta$  1.74-2.60 ( $\text{CH}_2 \times 4$ ), (ii) the 2'-olefinic carbon at  $\delta$  107.3 and the enolic OH singlet at  $\delta$  16.8, and (iii) the enolic carbon at  $\delta$  180.1 and the 2'-olefinic hydrogen doublet at  $\delta$  7.0. As the  $^{13}\text{C}$  peaks at  $\delta$  193.4 and  $\delta$  180.1 can be unambiguously assigned to the keto and enol carbons, respectively, the COLOC correlations are then consistent with the structure possessing the exocyclic double bond **3a** and not the alternative enol **3b**. In these  $\alpha,\beta$ -unsaturated 1,3-diketo systems the exocyclic enol form is considerably stabilised by the extended conjugation. The same tautomer probably predominates in the case of the cyclopentanone and cycloheptanone derivatives **6** and **8** also, judging by the observation of long-range coupling between the 2'-olefinic hydrogen and the enolic OH proton in both cases.

During the course of the study of the reactions of some of the  $\alpha,\beta$ -unsaturated-1,3-diketones prepared in the previous sections, it was found necessary to block the enolisation by the incorporation of an alkyl group between the two keto functions. The major difficulty in alkylating 1,3-dicarbonyl compounds is that both *C*- and *O*-alkylation can occur. When the equilibrium concentration of the enol tautomer is high, such as in 1,3-diketones, predominant *O*-alkylation is observed.<sup>15</sup> Clarke and Miller reported a very useful method for selective mono-*C*-alkylation of a number of 1,3-dicarbonyl compounds, using alkyl iodides and tetraalkylammonium fluorides, under mild conditions.<sup>16</sup> In a simple adaptation of Miller's method, three molar equivalents of tetrabutylammonium fluoride (as a solution in THF) were added to cinnamoylcyclohexanone **3** at 0 °C and the solvent was removed under reduced pressure, yielding an orange solid which was dissolved in dry dichloromethane before addition of

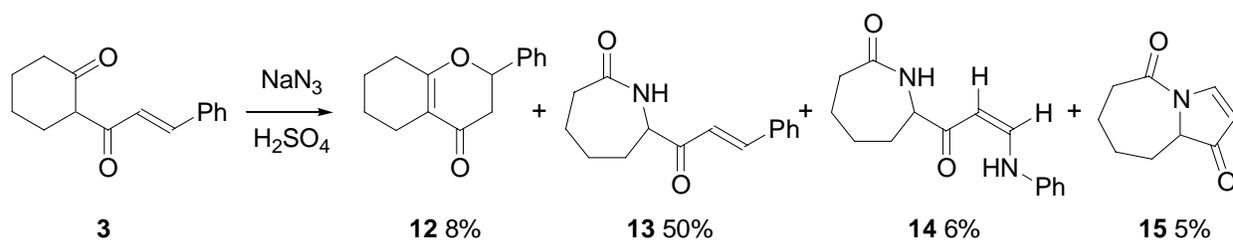
four molar equivalents of iodomethane. The C-alkylated product **10** was obtained in 87% yield (Scheme 5). Similarly, 2-cinnamoyl- $\alpha$ -tetralone **9** gave the methylated product **11** in 80% yield.



**Scheme 5**

### The reaction of cinnamoyl cyclohexanones with hydrazoic acid

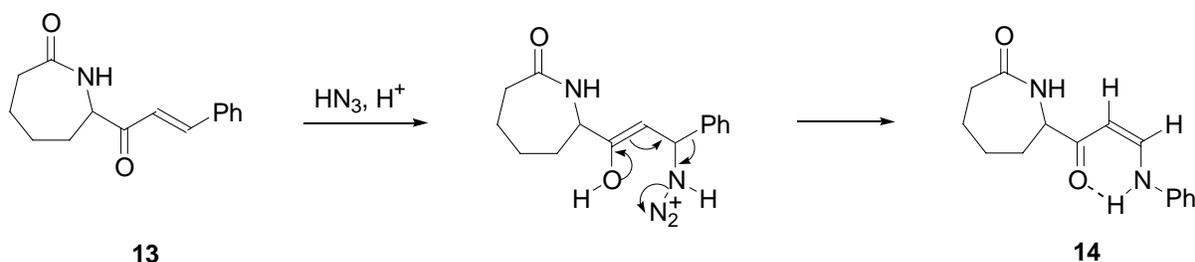
The Schmidt reaction may be catalysed by a variety of protic and aprotic acids, of which sulfuric acid is the most extensively used. The room temperature reaction of cinnamoyl cyclohexanone with one equivalent of sodium azide, using concentrated sulfuric acid as the catalyst and reaction medium, resulted in a mixture of products (Scheme 6).



**Scheme 6**

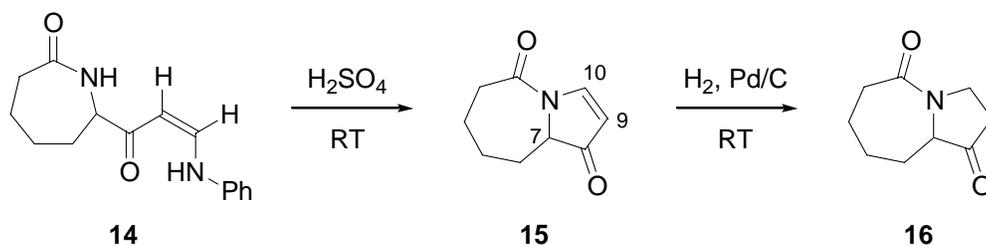
The dihydropyranone **12**, resulting from the acid catalysed cyclisation of the starting ketone, was isolated in 8% yield. Cyclisations of  $\alpha,\beta$ -unsaturated 1,3-diketones under acidic conditions have been reported previously.<sup>17</sup> Indeed, the dihydropyranone **12** can be obtained in 80% yield by heating cinnamoylcyclohexanone in acetic acid for 8 h. The major product (50% yield) was identified as 7-(3-phenylprop-2-enoyl)hexahydro-2-azepinone **13** resulting from attack of the hydrazoic acid on the ring ketone followed by migration of the more substituted bond. The cyclohexanone carbonyl is expected to be more reactive than the side-chain carbonyl whose reactivity is diminished by conjugation. It was evident from the spectroscopic data that the product was the  $\alpha$ -amido ketone **13** and not the isomer resulting from migration of the less substituted bond, in agreement with the results reported for other 2-substituted cyclohexanones.<sup>18</sup>

A third product, isolated in 6% yield, was shown to have molecular formula  $C_{15}H_{18}N_2O_2$ , corresponding to the addition of another NH group to the lactam **13**. The  $^1H$  NMR spectrum showed a doublet for an alkene hydrogen at  $\delta$  5.27 with a coupling constant of 8.2 Hz. The second alkene proton appeared as a double doublet at  $\delta$  7.40, coupled both with the  $\alpha$ -H and a second proton which appeared as a broad doublet at  $\delta$  11.30 with a coupling constant of 12.9 Hz. The IR spectrum showed two carbonyl bands, one at  $1649\text{ cm}^{-1}$ , the other at the exceptionally low value of  $1606\text{ cm}^{-1}$ . On this basis, the structure was assigned as the enaminone **14**, resulting from the addition of hydrazoic acid to the  $\beta$ -position of the  $\alpha,\beta$ -unsaturated system followed by migration of the phenyl group (Scheme 7). Migration of the aryl group on treatment of benzyl azides with acids is well precedented (e.g. Scheme 2).<sup>8,19</sup> The enaminone derivative **14** has a *cis*-configuration due to intramolecular hydrogen bonding between the NH and the carbonyl. This accounts for the low  $J_{2,3}$  coupling constant, and the low carbonyl stretching frequency. As pointed out earlier, addition of hydrazoic acid to the aryl enone was not expected. The unexpected reactivity may be a result of the inductive effect of the ring amide, which may be protonated under the strongly acidic reaction conditions.



Scheme 7

The final product, isolated in 5% yield, was identified as lactam **15**. The  $^1H$  NMR spectrum contained a pair of doublets at  $\delta$  5.72 and  $\delta$  8.71, assigned to H-9 and H-10, respectively, with H-7 observed as double doublet at  $\delta$  3.92. The unusually high chemical shift of the H-10 signal is attributed to its proximity to the amide carbonyl. The other spectroscopic and analytical data were fully in accord with this structure. The bicyclic lactam **15** results from acid catalysed cyclisation of lactam **14** with elimination of aniline (Scheme 8).

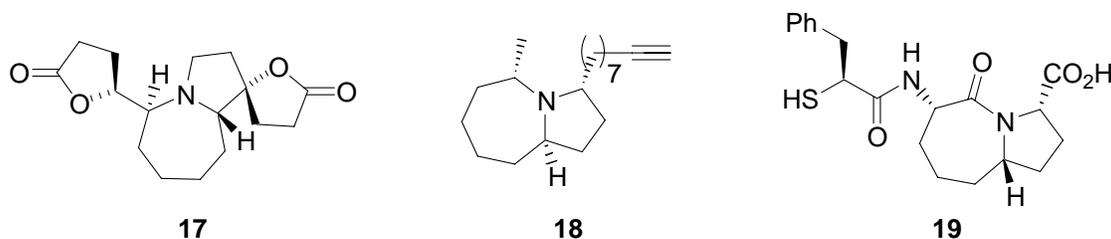


Scheme 8

In support of this proposal, treatment of compound **14** with concentrated sulfuric acid resulted in a quantitative conversion into the bicyclic compound **15**. Thus, the series of products include two of the intermediates formed *en route* to the ultimate product **15** and they provide clear evidence for the mechanism of formation of **15**. Hydrogenation of lactam **15** gave the known saturated bicyclic compound **16**<sup>20</sup> in quantitative yield (Scheme 8).

No products arising from further reactions of the dihydropyrone **12** or the bicyclic compound **15** with hydrazoic acid were isolated. Moreover, treatment of both these compounds with hydrazoic acid resulted in the complete recovery of starting material. It is not surprising that the lactam did not react as its two carbonyl groups have diminished reactivity, being an amide and a vinylogous amide. However, the carbonyl of the dihydropyrone **12** is very similar to that of the enolised diketone **3a**, so it might have been expected to react further. This could be interpreted as an indication that the Schmidt reaction of diketone **3** proceeds via a small amount of the diketo form, present at equilibrium with the dominant keto enol tautomer.

The formation of the 1-azabicyclic compound **15** was noteworthy since it contains an important substructure found in many alkaloids, including the *Stemona* alkaloids,<sup>21</sup> such as croomine **17**, and the lehmizidines,<sup>22</sup> such as alkaloid 275A **18** (Figure 2). Synthetic derivatives of this ring system,<sup>23</sup> such as the angiotensin-converting enzyme inhibitor **19**,<sup>24</sup> have also attracted attention from medicinal chemists.



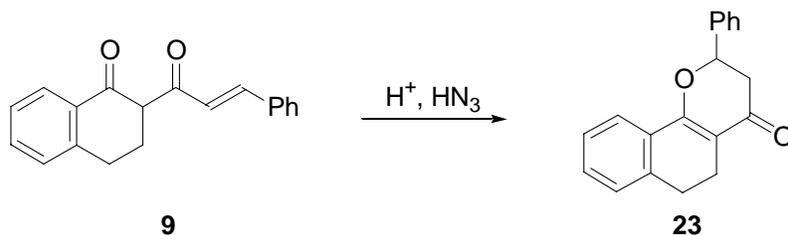
**Figure 2**

The formation of **15** was also of mechanistic interest, since it involved the unexpected addition of hydrazoic acid to a  $\beta$ -phenyl  $\alpha,\beta$ -unsaturated ketone. With these factors in mind, it was decided to optimize the reaction conditions for the formation of the 7-5 bicyclic compound **15** and also study the effect of the substituent in the  $\beta$ -position on the course of the reaction. Clearly, compound **15** arose from reaction of lactam **14** with a second molecule of hydrazoic acid. Therefore, cinnamoylcyclohexanone was treated with two equivalents of sodium azide using sulfuric acid as solvent. Using a reaction time of 8 h, bicyclic lactam **15** was obtained in only 9% yield, the major product being its precursor **14** (65% yield). Using a longer reaction time (24 h) the desired product was obtained in a yield of 76%. This yield was very gratifying considering the complexity of the reaction sequence involved. Changing the order of addition or increasing the quantity of sodium azide to four equivalents made no difference to the overall

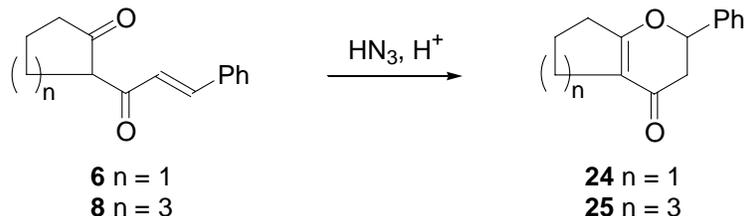


**Scheme 10**

Reaction of 2-cinnamoyl- $\alpha$ -tetralone **9** with 1 equiv. of sodium azide using conc. sulfuric acid as catalyst gave the dihydropyrone **23** in 85% yield (Scheme 11). It would appear that because this aryl ketone is less electrophilic, and more nucleophilic, the acid-catalysed cyclisation is faster than the addition of hydrazoic acid. The Schmidt reaction of compound **11**, for which cyclisation is impossible, gave a complex mixture and no pure product could be isolated. It is evident that some variation in the structure of the cinnamoylcyclohexanone is tolerated, but dihydropyrone formation may intervene when the Schmidt reaction is disfavoured. Further exploration of the scope of this route to 7-5 systems has not yet been carried out.

**Scheme 11**

It was also hoped to apply the Schmidt reaction of  $\alpha,\beta$ -unsaturated-1,3-diketones to the synthesis of some other 1-azabicyclic systems. Reaction of cinnamoylcyclopentanone **6** and cinnamoylcycloheptanone **8** with two equivalents of hydrazoic acid gave mixtures of products. The pyrones resulting from acid-catalysed cyclisation, **24** and **25**, were isolated in low yields (8% and 9%, respectively) (Scheme 12), along with traces of cinnamic acid, possibly formed by hydrolytic cleavage of the 1,3-diketones. For cinnamoylcyclopentanone various experimental conditions were investigated but a complex mixture of products was obtained in every case.

**Scheme 12**

The decreased reactivity of these cycloalkanones relative to the cyclohexanone **3** is in accord with relative rates of addition to the carbonyl group in 5-, 6-, and 7-membered cyclic ketones. Indeed, it has been reported that the rate of the Schmidt reaction and the yields of lactams are greater with 2-alkylcyclohexanones than with 2-alkylcyclopentanones.<sup>18</sup> The failure to isolate any Schmidt products may be a consequence of the further reduced reactivity of these ketones,

relative to simple cyclopentanones and cycloheptanones, due to their highly conjugated keto enol structures, or to the very small amounts of diketo tautomers present (see above).

## Conclusions

The reaction of hydrazoic acid with 2-(prop-2-enoyl)cyclohexanones provides a novel route to 1-azabicyclic compounds in good yields, via a sequence involving two Schmidt type reactions. The nature of the substituent in the 3'- position, or the presence of a substituent in the 2-position, do not affect the course of the reaction. Attempted application to the synthesis of other 1-azabicyclic systems failed. Although this new route to bicyclic lactams process is much more limited in scope, at present, than the intramolecular Schmidt reactions of organic azides,<sup>3,4</sup> it does possess some advantageous features. It uses readily accessible starting materials, it does not require the handling of organic azides, and it gives more heavily functionalised products, which will facilitate further synthetic manipulation. It is deserving of consideration as a simple and efficient method for the preparation of 7-5 bicyclic lactams.

## Experimental Section

**General Procedures.** Melting points were determined on a Gallenkamp melting point block or a Büchi 530 capillary melting point apparatus and are uncorrected. <sup>1</sup>H NMR spectra were recorded at 270 MHz on a JEOL JNM-GX 270 FT spectrometer. <sup>13</sup>C NMR were recorded at 67.80 MHz on the same instrument. Tetramethylsilane was used as internal reference in all cases. IR spectra were recorded on a Perkin Elmer 1710 FT spectrometer and a Galaxy series FTIR 3000 spectrometer from Mattson instruments. A VG Analytical 7070 mass spectrometer with attached INCOS 8700 data system in the E1 mode was used for recording mass spectra. Thin layer chromatography was performed on Merck precoated kieselgel 60F<sub>254</sub> slides. Merck silica 9385, particle size 0.04-0.063 (230-400) mesh was used for flash chromatographic separations. Tetrahydrofuran was distilled from sodium/benzophenone. Dichloromethane and diisopropylamine were distilled from calcium hydride. Combustion analyses were carried out by the Microanalytical Laboratory, University College Dublin.

### General procedure for the preparation of $\alpha,\beta$ -unsaturated 1,3-diketones using sodium amide

Cyclohexanone (11.30 g,  $1.2 \times 10^{-1}$  mol) was added dropwise to a stirred suspension of sodium amide (4.58 g,  $1.2 \times 10^{-1}$  mol) in dry ether (100 mL) and the mixture was stirred for 3 h under a constant stream of dry nitrogen. The mixture was then cooled to  $-78$  °C and the acid chloride ( $4.0 \times 10^{-2}$  mol) in dry diethyl ether (50 mL) was added dropwise over 1 h. The reaction mixture was stirred at  $-78$  °C for 1.5 h and then the temperature was allowed to increase slowly to 0 °C.

After 0.5 h at 0 °C, the slurry was poured onto ice (100 g) and concentrated hydrochloric acid (25 mL). The ether layer was separated, washed with aqueous sodium bicarbonate and water, and then left stirring overnight with an aqueous (20%, 100 mL) solution of sodium metabisulfite (to remove the excess cyclohexanone). The organic layer was separated, washed with water and dried (MgSO<sub>4</sub>). Removal of the solvent afforded a solid which was recrystallised from industrial methylated spirits (IMS).

**(2Z,2'E)-2-(1-Hydroxy-3-phenylprop-2-enylidene)cyclohexanone (3).** Prepared from cyclohexanone (11.30 g, 1.2 x 10<sup>-1</sup> mol) and cinnamoyl chloride (6.47 g, 4.0 x 10<sup>-2</sup> mol) according to the general procedure. Cinnamoyl cyclohexanone **3** was obtained as a yellow solid (6.64 g, 75%), mp 92–93 °C, (Lit. 92.5–93.5 °C).<sup>11</sup> <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 1.74–1.76 (4H, m), 2.38–2.48 (2H, m), 2.52–2.60 (2H, m), 6.97 (1H, d, *J* = 15.8 Hz), 7.26–7.58 (5H, m), 7.70 (1H, d, *J* = 15.8 Hz), 16.83 (1H, s). <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>): δ 21.75, 23.00, 23.87, 34.20, 107.31, 119.66, 128.12, 128.87, 129.98, 135.35, 141.22, 180.39, 193.56.

**(2Z,2'E)-2-[1-Hydroxy-3-(4-methoxyphenyl)prop-2-enylidene]cyclohexanone (4).** Prepared from cyclohexanone (11.30 g, 1.2 x 10<sup>-1</sup> mol) and *p*-methoxycinnamoyl chloride (7.86 g, 4.0 x 10<sup>-2</sup> mol) according to the general procedure. The *p*-methoxycinnamoyl cyclohexanone **4** was obtained as a yellow solid (5.98 g, 58%), mp 113–115 °C. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 1.74–1.75 (4H, m), 2.38–2.47 (2H, m), 2.53–2.59 (2H, m), 3.84 (3H, s), 6.83 (1H, d, *J* = 15.8 Hz), 6.90 (2H, d, *J* = 8.8 Hz), 7.51 (2H, d, *J* = 8.8 Hz), 7.67 (1H, d, *J* = 15.8 Hz), 16.92 (1H, s). <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>): δ 21.80, 23.05, 23.87, 33.90, 55.39, 106.931, 114.35, 117.34, 128.12, 129.85, 141.19, 161.26, 181.64, 192.14. Anal. Calcd. for C<sub>16</sub>H<sub>18</sub>O<sub>3</sub>: C, 74.40; H, 7.02. Found: C, 74.66; H, 6.86.

**(2Z,2'E)-2-[1-Hydroxy-3-(4-nitrophenyl)prop-2-enylidene]cyclohexanone (5).** Prepared from cyclohexanone (11.30 g, 1.2 x 10<sup>-1</sup> mol) and *p*-nitrocinnamoyl chloride (8.46 g, 4.0 x 10<sup>-2</sup> mol) according to the general procedure. The *p*-nitrocinnamoyl cyclohexanone **5** was obtained as a yellow solid (3.26 g, 30%), mp 167–169 °C. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 1.72–2.06 (4H, m), 2.48–2.50 (2H, m), 2.54–2.68 (2H, m), 7.06 (1H, d, *J* = 15.8 Hz), 7.40–7.88 (4H, m), 8.34 (1H, d, *J* = 15.8 Hz), 16.50 (1H, s). Anal. Calcd. for C<sub>15</sub>H<sub>15</sub>NO<sub>4</sub>: C, 65.93; H, 5.53; N, 5.13. Found: C, 65.91; H, 5.50; N, 4.84.

#### General procedure for the preparation of α,β-unsaturated 1,3-diketones using LDA

A solution of the ketone (3 molar equiv.) in dry THF was added dropwise to LDA (3 molar equiv.), in dry THF (50 mL), at -78 °C. The acid chloride (1 molar equiv.) in dry THF was then added dropwise over 1 h and the reaction mixture was stirred at -78 °C for 1 h. The temperature was then allowed to rise slowly to 0 °C and the mixture was stirred at this temperature for a further hour. The reaction was then worked up as described for the sodium amide procedure.

**(2Z,2'E)-2-(1-Hydroxy-3-phenylprop-2-enylidene)cyclopentanone (6).** Prepared from LDA (0.1189 mol), cyclopentanone (10.0 g, 0.1189 mol) in dry THF (80 mL) and cinnamoyl chloride (6.61 g, 4.0 x 10<sup>-2</sup> mol) in dry THF (60 mL), cinnamoylcyclopentanone **25** was obtained as a yellow solid (7.10 g, 83%), mp 76–77 °C. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 1.80–1.95 (2H, m),

2.36–2.42 (2H, m), 2.65–2.70 (2H, m), 6.51 (1H, dd,  $J = 2.4, 15.7$  Hz), 7.31–7.49 (5H, m), 7.54 (1H, d,  $J = 15.7$  Hz), 12.92 (1H, br s).  $^{13}\text{C}$  NMR (68 MHz,  $\text{CDCl}_3$ ):  $\delta$  20.52, 25.48, 37.99, 111.14, 119.76, 127.76, 128.86, 129.68, 135.46, 138.97, 163.81, 210.54.  $\nu_{\text{max}}$  (KBr): 1619, 1652  $\text{cm}^{-1}$ .  $m/z$  (EI): 214 ( $\text{M}^+$ , 47%), 196 (34), 157 (51), 131 (100), 104 (72). Anal. Calcd. for  $\text{C}_{14}\text{H}_{14}\text{O}_2$ : C, 78.48; H, 6.59. Found: C, 78.39; H, 6.35.

**(2Z,2'E)-2-(1-Hydroxy-3-phenylprop-2-enylidene)cyclohexanone (3)**. Prepared from LDA ( $1.02 \times 10^{-1}$  mol), cyclohexanone (10.0 g,  $1.02 \times 10^{-1}$  mol) in dry THF (80 mL) and cinnamoyl chloride (5.66 g,  $3.4 \times 10^{-2}$  mol) in dry THF (60 mL), cinnamoyl cyclohexanone **3** was obtained as a yellow solid (6.67 g, 86%). The spectroscopic data matched those previously reported.

**(2Z,2'E)-2-(1-Hydroxybut-2-enylidene)cyclohexanone (7)**. Prepared from LDA ( $1.02 \times 10^{-1}$  mol), cyclohexanone (10.0 g,  $1.02 \times 10^{-1}$  mol) in dry THF (80 mL) and 2-butenoyl chloride ( $3.52 \text{ g}, 3.4 \times 10^{-2}$  mol) in dry THF (50 mL), the diketone **7** was obtained as a pale yellow solid (4.57 g, 81%) mp 46–48 °C (Lit., 46–48 °C).  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.67–1.78 (4H, m), 1.94 (3H, dd,  $J = 1.3, 6.7$  Hz), 2.34–2.47 (4H, m), 6.34 (1H, dd,  $J = 1.3, 14.7$  Hz), 6.98 (1H, dq,  $J = 6.7, 14.7$  Hz), 16.72 (1H, br s).  $^{13}\text{C}$  NMR (68 MHz,  $\text{CDCl}_3$ ):  $\delta$  18.47 (CH<sub>3</sub>), 21.73, 22.99, 23.71, 33.66, 106.06, 124.47, 141.60, 182.14, 191.76.  $\nu_{\text{max}}$  ( $\text{CHCl}_3$ ): 1602, 1651  $\text{cm}^{-1}$ .  $m/z$  (EI): 166 ( $\text{M}^+$ , 9%), 151 (63), 138 (5), 123 (15), 95 (52), 69 (100). Anal. Calcd. for  $\text{C}_{10}\text{H}_{14}\text{O}_2$ : C, 72.26; H, 8.49. Found: C, 71.99; H, 8.38.

**(2Z,2'E)-2-(1-Hydroxy-3-phenylprop-2-enylidene)cycloheptanone (8)**. Prepared from LDA ( $5.35 \times 10^{-2}$  mol), cycloheptanone (6.0 g,  $5.35 \times 10^{-2}$  mol) in dry THF (50 mL) and cinnamoyl chloride (2.97 g,  $1.78 \times 10^{-2}$  mol) in dry THF (40 mL). Cinnamoyl cycloheptanone **8** was obtained as a yellow solid (3.5 g, 83%), mp 94–95 °C.  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.61–1.80 (6H, m), 2.53–2.66 (4H, m), 6.95 (1H, dd,  $J = 1.1, 16.5$  Hz), 7.29–7.58 (5H, m), 7.65 (1H, d,  $J = 16.5$  Hz), 16.10 (1H, d,  $J = 1.1$  Hz).  $^{13}\text{C}$  NMR (68 MHz,  $\text{CDCl}_3$ ):  $\delta$  24.96, 26.26, 29.53, 31.40, 42.50, 112.72, 119.16, 129.50, 128.82, 127.77, 135.75, 139.42, 170.53, 207.47.  $\nu_{\text{max}}$  (KBr): 1583, 1632  $\text{cm}^{-1}$ .  $m/z$  (EI): 242 ( $\text{M}^+$ , 14%), 224 (12), 165 (22), 131 (100), 103 (57). Anal. Calcd. for  $\text{C}_{16}\text{H}_{18}\text{O}_2$ : C, 79.31; H, 7.49. Found: C, 79.26; H, 7.51.

**2-Cinnamoyl  $\alpha$ -tetralone (9)**. Prepared from LDA ( $4.1 \times 10^{-2}$  mol),  $\alpha$ -tetralone (6.0 g,  $4.1 \times 10^{-2}$  mol) in the dry THF (60 mL) and cinnamoyl chloride (2.28 g,  $1.37 \times 10^{-2}$  mol) in dry THF (30 mL). 2-Cinnamoyl  $\alpha$ -tetralone **9** was obtained as a yellow solid (3.25 g, 88%), mp 104–106 °C.  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.79–2.98 (4H, m), 7.05 (1H, d,  $J = 15.7$  Hz), 7.19–7.60 (8H, m), 7.72 (1H, d,  $J = 15.7$  Hz), 8.01 (1H, dd,  $J = 1.5, 7.7$  Hz), 16.76 (1H, s, br).  $^{13}\text{C}$  NMR (68 MHz,  $\text{CDCl}_3$ ):  $\delta$  22.57, 28.29, 107.12, 119.01, 126.53, 126.87, 127.62, 127.93, 128.82, 129.78, 132.52, 132.65, 135.43, 140.24, 141.82, 174.96.  $\nu_{\text{max}}$  (KBr): 1626, 1640  $\text{cm}^{-1}$ .  $m/z$  (EI): 276 ( $\text{M}^+$ , 72%), 258 (53), 199 (54), 144(48), 131 (100), 115 (85). Anal. Calcd. for  $\text{C}_{19}\text{H}_{16}\text{O}_2$ : C, 82.58; H, 5.84. Found: C, 82.49; H, 5.86.

### General procedure for the $\alpha$ -methylation of $\alpha,\beta$ -unsaturated 1,3-diketones

Tetrabutylammonium fluoride (3 molar equiv 1.6 M solution in THF) was added to the diketone at 0 °C and the solvent was removed under reduced pressure. The resulting orange solid was dissolved in dry dichloromethane (25 mL), iodomethane (4 molar equiv.) was added, and the

mixture was stirred at 40 °C for 1 h. The solvent was removed, diethyl ether added and the precipitated tetrabutylammonium iodide was filtered off. The filtrate was concentrated affording a white solid which was recrystallised from IMS.

**(E)-2-Methyl-2-(3-phenylprop-2-enoyl)cyclohexanone (10).** Prepared from tetrabutylammonium fluoride (9.0 mL, 1.6 mol solution in THF), 2-cinnamoyl cyclohexanone (1.0 g, 4.4 x 10<sup>-3</sup> mol) and iodomethane (2.5 g, 1.76 x 10<sup>-2</sup> mol). 2-Methyl-2-cinnamoylcyclohexanone **10** was obtained as a white solid (0.92 g, 87%), mp 65–66 °C. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 1.31 (3H, s), 1.47–2.65 (8H, m), 6.80 (1H, d, *J* = 15.6 Hz), 7.35–7.40 (3H, m), 7.52–7.56 (2H, m), 7.73 (1H, d, *J* = 15.6 Hz). <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>): δ 21.07, 22.43, 27.76, 36.90, 42.03, 63.15, 120.47, 128.63, 128.95, 130.85, 134.25, 144.72, 197.14, 211.04. *v*<sub>max</sub> (CHCl<sub>3</sub>): 1608, 1678, 1715 cm<sup>-1</sup>. Anal. Calcd. for C<sub>16</sub>H<sub>18</sub>O<sub>2</sub>: C, 79.31; H, 7.49. Found: C, 79.15; H, 7.49.

**(E)-2-Methyl-2-cinnamoyl-α-tetralone (11).** Prepared from tetrabutylammonium fluoride (8 mL, 1.6 M solution in THF), 2-cinnamoyl-α-tetralone (1.0 g, 3.6 x 10<sup>-3</sup> mol) and iodomethane (2.1 g, 1.4 x 10<sup>-2</sup> mol). 2-Methyl-2-cinnamoyl-α-tetralone **11** was obtained as a white solid (0.84 g, 80%), mp 73–75 °C. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 1.41 (3H, s), 1.75–3.20 (4H, m), 6.90 (1H, d, *J* = 15.5 Hz), 7.15–7.52 (8H, m), 7.65 (1H, d, *J* = 15.5 Hz), 8.00 (1H, dd, *J* = 1.5, 7.5 Hz). <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>): δ 21.28, 25.96, 32.57, 59.16, 120.94, 126.70, 127.86, 128.63, 128.84, 128.92, 130.66, 133.77, 132.11, 134.39, 143.85, 144.15, 196.81, 198.59. *v*<sub>max</sub> (KBr): 1615, 1680, 1705 cm<sup>-1</sup>. *m/z* (EI): 290 (M<sup>+</sup>, 6%), 272 (6), 131 (100), 121 (25), 103 (21). Anal. Calcd. for C<sub>20</sub>H<sub>18</sub>O<sub>2</sub>: C, 82.73; H, 6.25. Found: C, 82.58; H, 6.19.

### The reaction of cinnamoyl cyclohexanone with one equivalent of hydrazoic acid

Sodium azide (0.29 g, 4.39 x 10<sup>-3</sup> mol) was added in portions to a solution of cinnamoyl cyclohexanone in concentrated sulfuric acid (10 mL) at 0 °C and the mixture was stirred for 8 h. The mixture was poured onto ice (100 g) and extracted with chloroform (4 x 100 mL). The aqueous layer was neutralised with aqueous sodium hydroxide (20%) and further extracted with chloroform (2 x 100 mL). The combined chloroform extracts were washed with water, dried (MgSO<sub>4</sub>) and evaporated to dryness. The resulting yellow oil was fractionated by preparative thin layer chromatography (PLC) using chloroform-methanol (95:5) as eluant. Four compounds were isolated, in order of elution as follows:

**2-Phenyl-2,3,5,6,7,8-hexahydro-4H-1-benzopyran-4-one (12).** mp 43–45 °C (Lit. 56–57 °C).<sup>25</sup> <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 1.51–1.85 (4H, m), 2.20–2.43 (4H, m), 2.63 (1H, dd, *J* = 3.5, 16.8 Hz), 2.88 (1H, dd, *J* = 14.5, 16.8 Hz), 5.34 (1H, dd, *J* = 3.5, 14.5 Hz), 7.40 (5H, s). Anal. Calcd. for C<sub>15</sub>H<sub>16</sub>O<sub>2</sub>: C, 78.92; H, 7.06. Found: C, 78.65; H, 7.00.

**(E)-7-(3-Phenylprop-2-enoyl)hexahydro-2-azepinone (13).** mp 107–108 °C. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 1.30–2.54 (8H, m), 4.36 (1H, dd, *J* = 4.0, 9.1 Hz), 6.82 (1H, d, *J* = 15.9 Hz), 6.90 (1H, s, br), 7.30–7.61 (5H, m), 7.75 (1H, d, *J* = 15.9 Hz). <sup>13</sup>C NMR (68 MHz, CDCl<sub>3</sub>): δ 22.94, 30.19, 33.20, 37.13, 61.26, 121.10, 128.65, 129.11, 131.29, 133.79, 145.41, 175.54, 194.62. *v*<sub>max</sub> (KBr): 1613, 1655, 1695 cm<sup>-1</sup>. *m/z* (EI): 243 (M<sup>+</sup>, 3%), 146 (12), 131 (22), 112 (100), 103 (23). Anal. Calcd. for C<sub>15</sub>H<sub>17</sub>NO<sub>2</sub>: C, 74.05; H, 7.04; N, 5.76. Found: C, 73.82; H, 6.91, N, 5.92.

**(Z)-7-[3-(Phenylamino)prop-2-enoyl]hexahydro-2-azepinone (14).** mp 171–173 °C.  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.40–2.55 (8H, m), 4.10 (1H, dd,  $J = 4.5, 9.1$  Hz), 5.27 (1H, d,  $J = 8.2$  Hz), 6.90 (1H, s, br), 7.01–7.35 (5H, m), 7.40 (1H, dd,  $J = 8.2, 12.9$  Hz), 11.30 (1H, d,  $J = 12.9$  Hz).  $^{13}\text{C}$  NMR (68 MHz,  $\text{CDCl}_3$ ):  $\delta$  23.03, 30.17, 34.91, 37.17, 60.36, 93.44, 116.37, 124.15, 129.63, 139.72, 145.51, 176.23, 195.05.  $\nu_{\text{max}}$  (KBr): 1582, 1606, 1649  $\text{cm}^{-1}$ .  $m/z$  (EI): 258 ( $\text{M}^+$ , 7%), 146 (100), 112 (6). Anal. Calcd. for  $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_2$ : C, 69.74; H, 7.02; N, 10.84. Found: C, 69.68; H, 7.02; N, 10.78.

**1-Azabicyclo[5.3.0]dec-9-ene-2,8-dione (15).** mp 75–76 °C.  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.23–2.81 (8H, m), 3.92 (1H, dd,  $J = 1.7, 11.7$  Hz), 5.72 (1H, d,  $J = 4.2$  Hz), 8.71 (1H, d,  $J = 4.2$  Hz).  $^{13}\text{C}$  NMR (68 MHz,  $\text{CDCl}_3$ ):  $\delta$  24.15, 29.26, 32.36, 37.62, 64.92, 109.38, 155.51, 169.92, 201.49.  $\nu_{\text{max}}$  (KBr): 1675–1690  $\text{cm}^{-1}$ .  $m/z$  (EI): 165 ( $\text{M}^+$ , 95%), 147 (5), 137 (12), 122 (10), 109 (100), 96 (88), 80 (71), 70 (81). Anal. Calcd. for  $\text{C}_9\text{H}_{11}\text{NO}_2$ : C, 65.44; H, 6.71; N, 8.48. Found: C, 65.27; H, 6.81; N, 8.52.

### 1-Azabicyclo[5.3.0]dec-9-ene-2,8-dione (15)

The reaction was repeated as previously, but using sodium azide (0.58 g,  $8.7 \times 10^{-3}$  mol, 2 equiv.). The crude product was purified by PLC using chloroform-methanol (95:5) as eluant, affording compounds **14** and **15** in yields of 65% and 9% respectively. The reaction was also repeated as previously but using sodium azide (0.58 g,  $8.7 \times 10^{-3}$  mol, 2 equiv.), concentrated sulfuric acid (25ml) and a reaction time of 24 h. After work up, the crude product was purified by flash column chromatography using chloroform as eluant affording the bicyclic compound **15** in 76% yield.

### Acid-catalysed cyclisation of enaminone (14)

A solution of lactam **14** (0.40 g,  $1.5 \times 10^{-3}$  mol) in concentrated sulfuric acid (20 mL) was stirred at room temperature for 24 h. The reaction was worked up as in the previous experiment, and the product was purified by flash column chromatography using chloroform as eluant to give the bicyclic compound **15** (0.26 g, 96%).

### Hydrogenation of 1-azabicyclo[5.3.0]dec-9-ene-2,8-dione

Hydrogen gas was bubbled through a stirred mixture of Pd/C (0.04 g), unsaturated lactam **15** (0.40 g,  $2.4 \times 10^{-3}$  mol) and ethanol (40 mL) for 4 h. The mixture was filtered and the Pd/C washed with ethanol ( $2 \times 10$  mL). Removal of the solvent gave a colourless oil which was purified by flash column chromatography using chloroform as eluant to give 1-azabicyclo[5.3.0]dec-2,8-dione **16** (0.40 g, 100%).  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.10–2.82 (10H, m), 3.58–4.06 (3H, m).  $^{13}\text{C}$  NMR (68 MHz,  $\text{CDCl}_3$ ):  $\delta$  22.99, 29.45, 31.73, 34.75, 37.87, 40.65, 63.53, 174.66, 212.08.  $\nu_{\text{max}}$  (KBr): 1640, 1760  $\text{cm}^{-1}$ .  $m/z$  (EI): 167 ( $\text{M}^+$ , 51%), 149 (6), 139 (100), 124 (31), 111 (44), 83 (67). Anal. Calcd. for  $\text{C}_9\text{H}_{13}\text{NO}_2$ : C, 64.65; H, 7.84; N, 8.38. Found: C, 64.51; H, 7.59; N, 8.26.

**Reaction 2-methylcinnamoylcyclohexanone 10 with 2 equivalents of hydrazoic acid**

Sodium azide (0.54 g,  $8.31 \times 10^{-3}$  mol) was added in portions to a solution of the diketone **10** (1.0 g,  $4.13 \times 10^{-3}$  mol) in concentrated sulfuric acid (20 mL). After 24 h, the reaction was worked up as described above. The crude product was purified by flash column chromatography using chloroform as eluant to give 3 products:

**1-Aza-7-methyl-bicyclo[5.3.0]dec-9-ene-2,8-dione (20)**. a white solid (0.55 g, 75%), mp 53–55 °C.  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.20–1.61 (2H, m), 1.44 (3H, s), 1.80–2.11 (4H, m), 2.60–2.75 (2H, m), 5.72 (1H, d,  $J = 4.4$  Hz), 8.78 (1H, d,  $J = 4.4$  Hz).  $^{13}\text{C}$  NMR (68 MHz,  $\text{CDCl}_3$ ):  $\delta$  19.35, 23.74, 24.54, 34.56, 37.36, 67.15, 106.96, 155.06, 170.07, 204.98.  $\nu_{\text{max}}$  (KBr): 1670–1690  $\text{cm}^{-1}$ .  $m/z$  (EI): 179 ( $\text{M}^+$ , 93%), 164 (7), 161 (6), 123 (100). Anal. Calcd. for  $\text{C}_{10}\text{H}_{13}\text{NO}_2$ : C, 67.02; H, 7.31; N, 7.82. Found: C, 66.89; H, 7.21; N, 7.89.

**(Z)-3-Methyl-3-[3-(phenylamino)prop-2-enoyl]cyclohexanone (22)**. a white solid (35 mg, 3%), mp 181–183 °C.  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.45 (3H, s), 1.51–1.80 (4H, m), 2.35–2.50 (4H, m), 5.66 (1H, d,  $J = 8.0$  Hz), 6.83 (1H, s, br), 7.04–7.36 (5H, m), 7.43 (1H, dd,  $J = 8.0, 12.6$  Hz), 11.90 (1H, d,  $J = 12.6$  Hz).  $^{13}\text{C}$  NMR (68 MHz,  $\text{CDCl}_3$ ):  $\delta$  29.44 (CH<sub>3</sub>), 22.88, 25.78, 37.36, 38.31, 62.54, 91.93, 115.94, 123.93, 129.62, 139.83, 149.48, 178.10, 201.33.  $\nu_{\text{max}}$  (KBr): 1606, 1650  $\text{cm}^{-1}$ .  $m/z$  (EI): 272 ( $\text{M}^+$ , 10%), 257 (4), 146 (25), 126 (100). Anal. Calcd. for  $\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_2$ : C, 70.56; H, 7.40; N, 10.29. Found: C, 70.81; H, 7.31; N, 10.11.

**(E)-3-Methyl-3-(3-phenylprop-2-enoyl)- $\epsilon$ -caprolactam (21)**. a white solid, mp 85–87 °C.  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.46 (3H, s), 1.48–2.50 (8H, m), 6.91 (1H, d,  $J = 15.8$  Hz), 6.95 (1H, s, br), 7.09–7.60 (5H, m), 7.61 (1H, d,  $J = 15.8$  Hz).  $^{13}\text{C}$  NMR (68 MHz,  $\text{CDCl}_3$ ):  $\delta$  24.26, 21.83, 25.87, 35.32, 38.14, 64.12, 119.87, 128.74, 129.22, 131.41, 133.71, 149.37, 177.08, 198.98.  $\nu_{\text{max}}$  (KBr): 1611, 1650, 1690  $\text{cm}^{-1}$ .  $m/z$  (EI): 257 ( $\text{M}^+$ , 8), 131 (31), 126 (100). Anal. Calcd. for  $\text{C}_{16}\text{H}_{19}\text{NO}_2$ : C, 74.68; H, 7.44; N, 5.44. Found: C, 74.83; H, 7.47; N, 5.39.

**Attempted Schmidt reaction of 2-cinnamoyl- $\alpha$ -tetralone (9)**. The Schmidt reaction was carried out on 2-cinnamoyl- $\alpha$ -tetralone **9** using one equivalent of sodium azide as described previously for cinnamoyl cyclohexanone. The crude product was purified by flash column chromatography using diethyl ether–light petroleum (40–60 °C) (20:80) as eluant to give 2-phenyl-5,6-dihydro-naphtho[1,2b]pyran-4-one **23** (85% yield), as a white solid, mp 71–73 °C.  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.50–2.95 (5H, m), 2.99 (1H, dd,  $J = 12.2, 16.5$  Hz), 5.42 (1H, dd,  $J = 4.6, 12.2$  Hz), 7.10–7.92 (9H, m).  $^{13}\text{C}$  NMR (68 MHz,  $\text{CDCl}_3$ ):  $\delta$  18.62, 27.46, 42.97, 80.04, 110.82, 124.33, 126.05, 126.57, 127.81, 128.62, 128.76, 131.05, 129.15, 138.72, 140.04, 164.02, 191.39.  $\nu_{\text{max}}$  (KBr): 1660  $\text{cm}^{-1}$ .  $m/z$  (EI): 276 ( $\text{M}^+$ , 11%), 258 (8), 104 (100).

**Attempted Schmidt reaction of cinnamoylcyclopentanone (6)**. The Schmidt reaction was carried out on cinnamoyl cyclopentanone using one and two equivalents of sodium azide, as described previously for cinnamoyl cyclohexanone. The crude product from each reaction was shown to contain numerous products on analysis by TLC. PLC using chloroform as eluant gave 2,3-dihydro-2-phenylcyclopenta[6]pyran-4-one **24** (8%), as a white solid, mp 41–43 °C.  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.95–2.01 (2H, m), 2.58–2.67 (5H, m), 2.83 (1H, dd,  $J = 16.9, 13.9$

Hz), 5.49 (1H, dd,  $J = 3.6, 13.9$  Hz), 7.41 (5H, s).  $\nu_{\max}$  (KBr): 1656  $\text{cm}^{-1}$ .  $m/z$  (EI): 214 ( $\text{M}^+$ , 5%), 196 (7), 104 (100), 78 (17). Anal. Calcd. for  $\text{C}_{14}\text{H}_{14}\text{O}_2$ : C, 78.48; H, 6.59. Found: C, 78.39; H, 6.42.

**Attempted Schmidt reaction of cinnamoyl cycloheptanone (8).** The Schmidt reaction was carried out on cinnamoyl cycloheptanone using one and two equivalents of sodium azide, as described previously for cinnamoyl cyclohexanone. The crude product from each reaction was shown to contain numerous components on analysis by TLC. PLC using diethyl ether–light petroleum (40–60 °C) as eluant (50:50) gave 2-phenyl-2,3-dihydrocyclohepta[b]pyran-4-one **25** (9%), as a white solid, mp 59–61 °C (Lit. 92.5–93.5 °C).  $^{25}\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.40–2.71 (11H, m), 2.81 (1H, dd,  $J = 14.4, 16.9$  Hz), 5.35 (1H, dd,  $J = 3.6, 14.4$  Hz), 7.35 (5H, s).  $^{13}\text{C}$  NMR (68 MHz,  $\text{CDCl}_3$ ):  $\delta$  22.00, 24.91, 26.95, 31.76, 34.99, 42.33, 80.09, 116.78, 126.13, 128.65, 128.74, 138.59, 177.17, 191.04.  $\nu_{\max}$  (KBr): 1659  $\text{cm}^{-1}$ .  $m/z$  (EI): 242 ( $\text{M}^+$ , 15%), 224 (6), 104 (100). Anal. Calcd. for  $\text{C}_{16}\text{H}_{18}\text{O}_2$  requires: C, 79.31; H, 7.49. Found: C, 78.99; H, 7.32.

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It is a pleasure to dedicate this paper to Professor Tony McKervey. His contributions to organic chemistry have been enormous, and he has inspired many students (MC included) to pursue careers in synthetic chemistry. We wish him well in the transition to what is sure to be an equally fruitful new phase in his life.

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