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Metal catalysed reactions of β,β′-tricarbonyl derivatives with isocyanates

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ABSTRACT

The reactions of β,β′-tricarbonyl derivatives with isocyanates are catalysed by 2 mol % transition metal acetylacetonates (e.g., [Co(acac)$_2$] and [Zn(acac)$_2$]) at room temperature. 3-Oxo-1,5-pentanedioic acid dimethylester (**1**) reacts with RNCO (R=Et, $CH_2CH{=}CH_2$, CH_2Ph, Ph, 4-Cl–Ph) to give 1:1 adducts involving the formation of a new C–C bond between the intercarbonylic methylene and the isocyanato group. Under similar conditions 2,4,6-heptanetrione (**2**) reacts with the same isocyanates to afford pyridinone and pyranone derivatives resulting from the cyclisation of unstable 1:1 and 1:2 adducts.

1. Introduction

Polyketides represent a class of natural products, which cyclise to a great number of aromatic and heteroaromatic derivatives or are transformed in fatty acids.[1]

Tricarbonyl derivatives, such as dialkyl 3-oxopentane-dionates, have been studied as simple polyketide models. In particular the regioselective alkylation of Cu(II) and Co(II) complexes of ethyl 3,5-dioxohexanoate has been reported.[2]

It is well known that β-dicarbonyls derivatives react in the presence of metal catalysts with carbon electrophiles,[3] such as isocyanates,[4] Michael acceptors[5] and nitriles,[6] in the presence of metal catalysts to give adducts derived from the formation of new C–C bonds between the methylene group of dicarbonyls and the reactive atom of the electrophile.

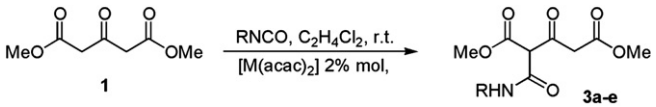
In an interesting recent extension new chiral bifunctional ruthenium-based catalysts are very efficiently used in Michael reactions involving a series of dicarbonyls and activated olefins.[7] In all cases deprotonation of 1,3-dicarbonyl compounds to give coordination to the metal of C- or O-bonded enolates is the key step of the catalytic process.

In this context, it is surprising that, to the best of our knowledge, no catalytic reactions of β,β′-tricarbonyl derivatives with electrophiles have been up to now reported. In fact, on the basis of the previously reported results on the metal catalysed reactions of β-dicarbonyls with electrophiles,[3–7] and on the alkylation of Cu(II) and Co(III) metal complexes of diethyl 3-oxopentane-dionate,[2] it is expected that also β,β′-tricarbonyl derivatives should give similar interesting C–C bond formations.

In this paper we report the reactions of 3-oxo-1,5-pentanedioic acid dimethylester (**1**) and of 2,4,6-heptanetrione (**2**), chosen as model compounds, with isocyanates in the presence of catalytic amounts of metal acetylacetonates.

2. Results and discussion

The reactions of the two tricarbonyl substrates **1** and **2** with the various isocyanates were performed in dichloroethane in the presence of 2 mol % transition metal acetylacetonates, at room temperature and times changing from 1 day for **1** to 3 days for **2**. Under these conditions 3-oxo-1,5-pentanedioic acid dimethylester (**1**) was allowed to react with ethyl isocyanate: high yields of the 1:1 adduct **3a** (Scheme 1) were obtained using as catalyst [Co(acac)$_2$] (yield 98%), [Zn(acac)$_2$] (97%), [Ni(acac)$_2$] (95%), [Cu(acac)$_2$]



M: Co(II); Zn(II); Ni(II); Cu(II); Mn(II); **a**: R= Et;
M: Co(II); **b**: R= $CH_2{=}CH{-}CH_2$-; **c**: R= Bn; **d**: R= Ph; **e**: R= 4-Cl-Ph

Scheme 1.

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(91%) and [Mn(acac)$_2$] (95%). No product was obtained in a test reaction of **1** with ethyl isocyanate in the absence of catalyst.

The formation of compound **3a** clearly indicates that the presence of a metal catalyst is able to promote C–C bond formation between one intercarbonylic and one isocyanato carbon atom, thus closely resembling the behaviour observed with β-dicarbonyls substrates.

[Co(acac)$_2$] was employed in the reactions of β,β′-ketodiester **1** with different R substituted isocyanates. The results were very similar: higher yields (ca. 90%) were obtained in the reactions with R=ethyl, vinyl and benzyl, whereas with aryl isocyanates (R=Ph, 4-Cl–Ph) (Scheme 1) yields dropped to ca. 65%.

Although compound **3** series could present more than one species in solution, the ^{1}H NMR spectra in $CDCl_3$ show the presence of only one tautomer characterised by two resonances at ca. 9.0 and ca. 18.5 ppm, attributable, respectively, to an NH and an OH involved in hydrogen bonds. Moreover the ^{13}C NMR spectrum shows an absorption at 186.9 ppm attributable to the enolic carbon atom.

On the basis of these data the more probable species present in solution is the enolic tautomer depicted in Figure 1.

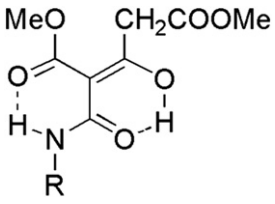


Figure 1.

X-ray diffraction analysis of the crystalline compound **3e** derived from the reaction of **1** with 4-chlorophenylisocyanate demonstrated that in the solid-state this compound has the structure depicted in Figure 2. The presence of two strong hydrogen bonds explains the ^{1}H NMR absorptions of OH and of NH hydrogens at very high frequency.

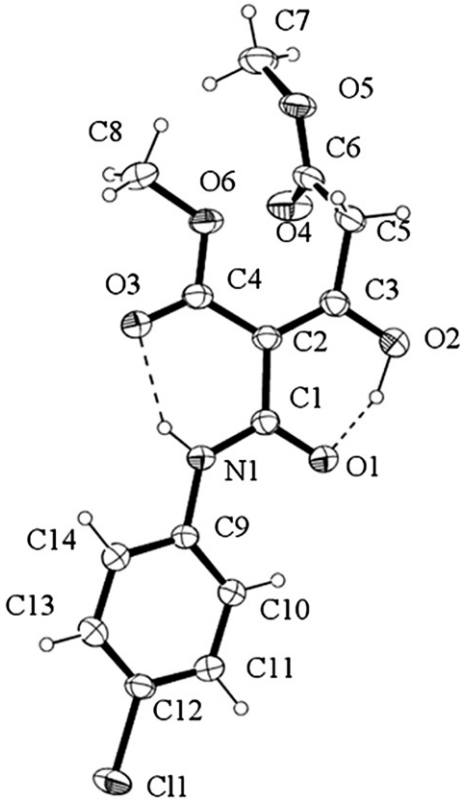
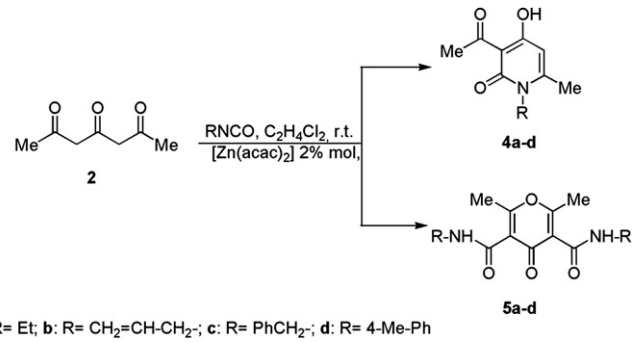


Figure 2. An ORTEP view of compound **3e** displaying the thermal ellipsoids at 30% probability.

By contrast with the reactions of the β,β′-ketodiester **1**, the triketone 2,4,6-heptanetrione (**2**) reacts with isocyanates (R=Et, CH_2=CH–CH_2, $PhCH_2$, 4-Me–Ph) in the presence of [Zn(acac)$_2$] (2 mol %) to give two types of products, the pyridinones **4** and the 4-pyranones **5** (Scheme 2).



a: R= Et; **b**: R= CH_2=CH-CH_2-; **c**: R= $PhCH_2$-; **d**: R= 4-Me-Ph

Scheme 2.

The pyridinone **4** can simply be derived from an 1:1 adduct analogous to compound **3**, which cyclises to give **4** with elimination of a molecule of water, whereas the formation of the 4-pyranone **5** requires the addition/insertion of two molecules of isocyanate to triketone **2**. One can envisage the formation of an unstable 1:2 adduct followed by its cyclisation involving also in this case elimination of a water molecule. As expected the reactions carried out with a higher RNCO/(**2**) molar ratio (Table 1) afford the double insertion product **5** in higher yields.

Table 1
Reaction of 2,4,6-heptanetrione (**2**) with isocyanates catalysed by [Zn(acac)$_2$] with varying reagents ratios

R	RNCO/(**2**) molar ratio	Yield (%)	
Et	1.1/1	35 (**4a**)	8 (**5a**)
Et	4/1	6 (**4a**)	41 (**5a**)
CH_2=$CHCH_2$	1.1/1	45 (**4b**)	14 (**5b**)
CH_2=$CHCH_2$	4/1	20 (**4b**)	40 (**5b**)
$PhCH_2$	1.1/1	35 (**4c**)	15 (**5c**)
$PhCH_2$	4/1	10 (**4c**)	65 (**5c**)
4-MeC_6H_5	1.1/1	35 (**4d**)	14 (**5d**)
4-MeC_6H_5	4/1	10 (**4d**)	42 (**5d**)

The different behaviour exhibited by the two types of tricarbonyls requires a few comments. The reaction mechanism implies the formation of the real catalyst via ligand exchange of the tricarbonyl substrate with the acetylacetonato metal complex. This reaction involves the deprotonation of the intercarbonylic methylene group. Metal(II) complexes of this type (M=Mg,[8] Ca,[8] Mn,[9] Co,[9] Ni,[9] Cu,[8,9] Zn[8,9]) are well known, and this exchange reaction represents a reported synthetic procedure to give triketonato complexes.[10] With β,β′-ketodiesters only one of the methylene groups can be deprotonated, giving a monoanionic ligand coordinated to only one metal center (Fig. 3, form A). The situation drastically changes with the 1,3,5-triketones, in fact here deprotonation of one or both methylene groups can occur, giving rise to coordination of one or two metal centers for each triketonato ligand (Fig. 3, forms A and B).[11–13]

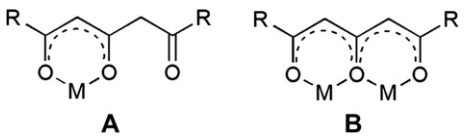


Figure 3. Possible coordination modes of tricarbonyl compounds.

Electrophilic addition by the isocyanate can occur only to the CH moiety of the coordinated carbonyl enolato fragment. This interpretation fits well with the observed behaviour of β,β′-ketodiester **1**, which gives only one type of C–C bond product. This catalysis closely resembles that observed with β-dicarbonyl compounds.[3,5,6]

Along these lines the results obtained with 1,3,5-triketone **2** can be easily interpreted. In fact, one or two methine groups can undergo electrophilic addition, giving rise to the two observed type of products.

3. Conclusion

The results detailed in this paper demonstrate that metal acetylacetonates are catalysts for the reactions of β,β′-tricarbonyl derivatives **1** and **2** with isocyanates. A new C–C bond between the methylene carbon and the isocyanate carbon atoms is formed at room temperature and neutral pH giving 1:1 or 1:2 adducts.

Stoichiometric additions or addition/insertions of electrophiles to coordinated β,β′-ketodiesters were known but, to our knowledge, these ones are the first examples of a metal-catalysed process.[8]

The reactivity of the 1,3,5-triketones towards electrophiles appears rather unexplored and the catalytic formation of compounds **4** and **5** is particularly interesting. In fact, cyclic compounds similar to **4** are well known and used, for example, in the gene transcription therapy.[14] The success for this catalytic procedure opens the way to a variety of C–C bond forming reactions between tricarbonyl substrates and different electrophiles.

4. Experimental

4.1. General remarks

The reagents and the solvents were high purity products and generally used as received. 2,4,6-Heptanetrione (**2**) was synthesised according to literature procedures.[15] The solution ^{1}H- and ^{13}C{^{1}H}-NMR spectra were recorded on a Bruker Avance 300 (300.1 MHz for ^{1}H and 75.5 MHz for ^{13}C); chemical shifts (δ) are reported in units of parts per million relative to the residual solvent signals, using tetramethylsilane as an internal standard. The FT IR spectra were recorded on a Bruker Tensor 27 spectrophotometer at 2 cm^{-1} resolution.

4.2. Reaction of 3-oxo-1,5-pentanedioic acid dimethylester (1) with isocyanates

General procedure: To a solution of 3-oxo-1,5-pentanedioic acid dimethylester (**1**) (0.87 g, 5.0 mmol) in anhydrous dichloroethane (2 mL), isocyanate (6.0 mmol) and [Co(acac)$_2$] (0.1 mmol) were added. The reaction mixture was stirred at room temperature for 24 h and diluted with diethyl ether. The resulting suspension was filtered on Celite™ and the obtained solution was concentrated under reduced pressure to give compound **3**.

*4.2.1. Reaction with ethyl isocyanate: 2-ethylcarbamoyl-3-oxo-pentanedioic acid dimethylester (**3a**).* Yield 98%, colourless crystals, mp 50–52 °C. Anal. Calcd for $C_{10}H_{15}NO_6$ (245.23): C, 48.98; H, 6.17; N, 5.71%. Found: C, 48.74; H, 6.15; N, 5.55%. IR (KBr): 3300 (br), 1740, 1670, 1560 cm^{-1}. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 1.21 (t, J=7.3 Hz, 3H, Me), 3.3–3.5 (m, 2H, CH_2), 3.72 (s, 5H, OMe+CH_2), 3.75 (s, 3H, OMe), 9.20 (br, 1H, NH), 18.80 (s, 1H, OH). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 14.2, 34.3, 45.5, 51.0, 52.0, 93.6, 168.1, 168.6, 171.9, 186.9. Quite similar yields were obtained with different metal acetylacetonates: [Zn(acac)$_2$] (97%), [Ni(acac)$_2$] (95%), [Cu(acac)$_2$] (91%) and [Mn(acac)$_2$] (95%).

*4.2.2. Reaction with allyl isocyanate: 2-allylcarbamoyl-3-oxo-pentanedioic acid dimethylester (**3b**).* Yield 92%, yellow oil. Anal. Calcd for $C_{11}H_{15}NO_6$ (257.24): C, 51.36; H, 5.88; N, 5.45%. Found: C, 50.78; H, 6.14; N, 5.17%. IR (oil): 3450 (br), 1750 (br), 1570 (br) cm^{-1}. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.69 (s, 3H, OMe), 3.72 (s, 3H, OMe), 3.74 (s, 2H, CH_2), 3.96 (m, 2H, CH_2N), 5.1–5.3 (m, 2H, CH_2=), 5.7–5.9 (m, 1H, CH), 9.2 (br, 1H, NH), 18.68 (s, 1H, OH). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 41.1, 44.8, 50.7, 51.6, 92.7, 115.9, 132.6, 167.5, 168.1, 171.6, 186.3.

*4.2.3. Reaction with benzyl isocyanate: 2-benzylcarbamoyl-3-oxo-pentanedioic acid dimethylester (**3c**).* Yield 86%, colourless crystals, mp 165–167 °C (ethanol). Anal. Calcd for $C_{15}H_{17}NO_6$ (307.30): C, 58.63; H, 5.58; N, 4.56%. Found: C, 59.02; H, 5.70; N, 4.72%. IR (KBr): 3320 (br), 1760, 1690, 1580 cm^{-1}. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.71 (s, 3H, OMe), 3.73 (s, 3H, OMe), 3.75 (s, 2H, CH_2), 4.53 (d, J=5.8 Hz, 2H, CH_2), 7.2–7.4 (m, 5H, Ph), 9.60 (br, 1H, NH), 18.73 (s, 1H, OH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 43.6, 45.6, 51.5, 52.5, 95.0, 128.1, 128.3, 129.5, 137.9, 169.2, 169.6, 173.2, 187.9.

*4.2.4. Reaction with phenyl isocyanate: 3-oxo-2-phenylcarbamoyl-pentanedioic acid dimethylester (**3d**).* Yield 60%, colourless crystals, mp 58–61 °C. Anal. Calcd for $C_{14}H_{15}NO_6$ (293.27): C, 57.34; H, 5.16; N, 4.78%. Found: C, 57.10; H, 5.19; N, 4.74%. IR (KBr): 3000 (br), 1740, 1670, 1600, 1540 cm^{-1}. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.75 (s, 5H, OMe+CH_2), 3.80 (s, 3H, OMe), 7.1–7.6 (m, 5H, Ph), 11.30 (br, 1H, NH), 18.56 (s, 1H, OH). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 45.5, 51.6, 52.3, 95.3, 121.5, 125.2, 129.0, 136.4, 168.4, 170.6, 186.8.

*4.2.5. Reaction with 4-chlorophenyl isocyanate: 2-(4-chloro-phenylcarbamoyl)-3-oxo-pentanedioic acid dimethylester (**3e**).* Yield 65%, colourless crystals, mp 118–119 °C. Anal. Calcd for $C_{14}H_{14}ClNO_6$ (327.71): C, 51.31; H, 4.31; N, 4.27%. Found: C, 51.40; H, 3.77; N, 4.91%. IR (KBr): 3100 (br), 1730, 1670, 1540 cm^{-1}. ^{1}H NMR (300.1 MHz, DMSO-d_6): δ 3.62 (s, 3H, OMe), 3.71 (s, 5H, OMe+CH_2), 7.40–7.60 (m, 4H, Ph), 10.54 (br, 1H, NH), 16.81 (br, 1H, OH). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 45.3, 51.8, 52.4, 95.6, 121.3, 122.7, 129.1, 135.1, 168.3, 168.5, 170.5, 186.7.

4.3. X-ray crystal structure analysis of 3e

$C_{14}H_{14}ClNO_6$, M_r=327.71, triclinic, space group *P-1* (no. 2) with a=5.7960(2), b=9.0652(4), c=15.0964(7) Å, α=100.898(2), β=95.957(3), γ=108.220(3) , V=728.47(5) Å^3, Z=2, D_c=1.494 g cm^{-3}, 8883 reflections measured, 3320 independent, R_{int}=0.031, (3<θ<27.7°, T=295 K, Mo Kα radiation, λ=0.71073 Å) on a Nonius Kappa CCD diffractometer. The structure was solved by direct methods (SIR97)[16] and refined on F^2 (SHELXL-97)[17]. Refinement converged at a final $wR2$ value of 0.1141 (all reflections), $R1$=0.0426 (for 2629 reflections with $I>2\sigma(I)$), S=1.045. All non-H atoms were refined anisotropically and the hydrogens isotropically. The compound displays two strong intramolecular hydrogen bonds: N1–H···O3 [N1···O3=2.636(2) Å, N1-H···O3=143(2)°] and O2–H···O1 [O2···O1=2.430(2) Å, O2–H···O1=157(2)°]. Complete crystallographic data (excluding structural factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 212155. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0) 1223 336033 or e-mail: deposit@ccdc.com.ac.uk].

4.4. Reaction of 2,4,6-heptanetrione (2) with isocyanates

General procedure: To a solution of 2,4,6-heptanetrione (**2**) (0.142 g, 1.0 mmol) in anhydrous dichloroethane (1 mL), isocyanate

(1.1 mmol or 4.0 mmol) and [Zn(acac)$_2$] (5 mg, 0.02 mmol) were added. The reaction mixture was stirred at room temperature under argon atmosphere for 3 days. The reaction mixture was concentrated under reduced pressure and the residue was purified by column chromatography (SiO_2, eluent: ethyl acetate/light petroleum 1:1).

*4.4.1. Reaction with ethyl isocyanate to give 3-Acetyl-1-ethyl-4-hydroxy-6-methyl-1H-pyridin-2-one (**4a**) and 2,6-Dimethyl-4-oxo-4H-pyran-3,5-dicarboxylic acid bis-ethylamide (**5a**).* (**4a**).[18] Yellow crystals, mp 116-118 °C. IR (KBr): 1654, 1610, 1427, 1361 cm^{-1}. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 1.28 (t, *J*=7.1 Hz, 3H, CH_2CH_3), 2.37 (s, 3H, Me), 2.71 (s, 3H, MeCO), 4.01 (q, *J*=7.0 Hz, 2H, CH_2CH_3), 5.80 (s, 1H, CH), 15.48 (s, 1H, OH). (**5a**). Yellow crystals, mp 86-88 °C. Anal. Calcd for $C_{13}H_{18}N_2O_4$ (266.29): C, 58.63; H, 6.81; N, 10.52%. Found: C, 58.51; H, 6.86; N, 10.37%. IR (KBr): 3273 (br), 1676 (br), 1541, 1408 (br), 1261, 1097 (br) cm^{-1}. ^{1}H NMR (300.1 MHz, CDCl3): δ 1.23 (t, *J*=7.1 Hz, 6H, 2 CH_2CH_3), 2.78 (s, 6H, 2Me), 3.43 (q, *J*=7.2 Hz, 4H, $2CH_2CH_3$), 9.05 (br, 2H, 2 NH). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 14.6, 20.9, 34.2, 118.0, 163.0, 171.9, 178.4.

*4.4.2. Reaction with allyl isocyanate to give 3-Acetyl-1-allyl-4-hydroxy-6-methyl-1H-pyridin-2-one (**4b**) and 2,6-Dimethyl-4-oxo-4H-pyran-3,5-dicarboxylic acid bis-allylamide (**5b**).* (**4b**). Colourless crystals, mp 78-80 °C. Anal. Calcd for $C_{11}H_{13}NO_3$ (207.23): C, 63.76; H, 6.32; N, 6.76%. Found: C, 63.52; H, 6.25; N, 6.59%. IR (KBr): 3435 (br), 1653 (br), 1612, 1560, 1361 cm^{-1}. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 2.35 (s, 3H, Me), 2.71 (s, 3H, COMe), 4.62 (d, *J*=4.5 Hz, 2H, CH_2), 5.02 (d, *J*=16.7 Hz, 1H, =CH_2), 5.20 (d, *J*=11.2 Hz, 1H, =CH_2), 5.83 (s, 1H, CH), 5.90-5.98 (m, 1H, CH=), 15.57 (s, 1H, OH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.0, 31.5, 45.8, 101.1, 105.6, 116.4, 132.1, 153.8, 162.6, 175.3, 205.9. (**5b**). Colourless crystals, mp 74-76 °C. Anal. Calcd for $C_{15}H_{18}N_2O_4$ (290.31): C, 62.06; H, 6.25; N, 9.65%. Found: C, 61.80; H, 6.09; N, 9.48%. IR (KBr): 3249 (br), 3086,1682, 1602, 1534 cm^{-1}. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 2.79 (s, 6H, 2 Me), 4.03 (m, 4H, 2 CH_2N), 5.17 (d, *J*=10.3 Hz, 2H, CH_2=CH), 5.20 (d, *J*=15.5 Hz, 2H, CH_2=CH), 5.85-5.99 (m, 2H, 2 CH_2=CH), 9.25 (br s, 2H, 2 NH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.6, 42.3, 116.7, 118.4, 134.5, 163.6, 172.9, 178.9.

*4.4.3. Reaction with benzyl isocyanate to give 3-Acetyl-1-benzyl-4-hydroxy-6-methyl-1H-pyridin-2-one (**4c**) and 2,6-Dimethyl-4-oxo-4H-pyran-3,5-dicarboxylic acid bis-benzylamide (**5c**).* (**4c**).[18,19] Colourless crystals, mp 119-122 °C. IR (KBr): 3447 (br), 1648, 1615, 1560, 1363 cm^{-1}. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 2.29 (s, 3H, Me), 2.74 (s, 3H, COMe), 5.27 (s, 2H, CH_2), 5.86 (s, 1H, CH), 7.11-7.34 (m, 5H, Ph), 15.63 (s, 1H, OH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.5, 31.6, 46.8, 101.4, 105.7, 126.1, 127.6, 129.0, 136.2, 154.1, 175.5. (**5c**). Colourless crystals, mp 98-100 °C. Anal. Calcd for $C_{23}H_{22}N_2O_4$ (390.43): C, 70.75; H, 5.68; N, 7.17%. Found: C, 70.98; H, 5.80; N, 7.29%. IR (KBr): 3234 (br), 1680, 1654, 1543, 1403, 1165 cm^{-1}. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 2.82 (s, 6H, 2 Me), 4.58 (d, *J*=5.8 Hz, 4H, 2 CH_2N), 7.32-7.36 (m, 10H, 2 Ph), 9.53 (br, 2H, 2 NH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.1, 43.3, 117.9, 127.3, 127.6, 128.7, 138.2, 163.2, 172.4, 178.3.

*4.4.4. Reaction with p-tolyl isocyanate to give 3-Acetyl-4-hydroxy-6-methyl-1-p-tolyl-1H-pyridin-2-one (**4d**) and 2,6-Dimethyl-4-oxo-4H-pyran-3,5-dicarboxylic acid bis-p-tolylamide (**5d**).* (**4d**).[20] Yellow crystals, mp 197-200 °C. IR (KBr): 1658, 1622, 1655, 1631 cm^{-1}. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 1.90 (s, 3H, Me), 1.97 (s, 3H, Me), 2.79 (s, 3H, COMe), 5.85 (s, 1H, CH), 6.97 (A_2B_2 system, *J*=8.1 Hz, 2H, Ph), 7.24 (A_2B_2 system, *J*=8.1 Hz, 2H, Ph), 15.71 (s, 1H, OH). (**5d**). Colourless crystals, mp 138-140 °C. Anal. Calcd for $C_{23}H_{22}N_2O_4$ (390.43): C, 70.75; H, 5.68; N, 7.17%. Found: C, 70.51; H, 5.69; N, 7.23%. IR (KBr): 3055 (br), 1688, 1609, 1542, 1513, 1405, 1162 cm^{-1}. ^{1}H NMR (300.1 MHz, DMSO-d_6): δ 2.26 (s, 6H, 2 Me), 2.45 (s, 6H, 2 Me), 7.14 (A_2B_2 system, *J*=8.3 Hz, 4H, Ph), 7.54 (A_2B_2 system, *J*=8.3 Hz, 4H, Ph), 10.62 (s, 2H, 2 NH).

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