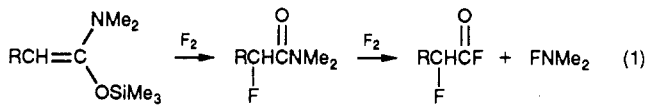
Table I

product	yield (%) (purified)	^{19}F NMR	$^2J_{HF}$	$^3J_{HF}$	lit. ref
1. $CH_3(CH_2)_5CHFCO_2Et$	69	-194.0 (m)	48.0	24.0	11
2. $CH_3CH_2CHFCO_2Et$	57	-194.4 (m)	49.1	24.4	12
3. $C_6H_5CHFCO_2CH_3$	53	-174.4 (d)	48.0		13
4. $(CH_3)_2iCFCO_2CH_3$	76	-146.5 (m)		21.1	14
5. $CHF(CO_2Et)_2$	59	-196.3 (d)	48.0		15
6. $CH_3CF(CO_2Et)_2$	68	-158.0 (q)		24.4	15
7. $C_6H_5CF(CO_2Et)_2$	73	-162.4 (s)			15
8. $CH_3CH_2CHFCON(CH_3)_2$	44[a]	-187.3 (m)	48.8	24.4	*b*
9. $C_6H_5CHFCON(CH_3)_2$	53[c]	-174.6 (d)	49.5		16
10. $CH_3CH_2CHFCO_2H$	83	-194.4 (m)	48.5	24.4	16
11. $C_6H_5CHFCO_2H$	82	-180.5 (d)	48.0		16
12. $O{=}\overline{COCH_2CH_2}CHF$	31	-162.7 (m)			17

[a] $CH_3CH_2CHFCO_2H$ (35%) also obtained. [b] Anal. Calcd for $C_6H_{12}FNO$: C, 52.53; H, 8.83; N, 10.21. Found: C, 52.27; H, 9.19; N, 9.96. [c] $C_6H_5CHFCO_2H$ (31%) also obtained.

acid was prepared in 86% yield from the diethyl phenylfluoromalonate (entry 7).

Fluorination of the ketene silyl amides (entries 8 and 9) led to rather unusual results. The product consisted of a mixture of fluorinated amide and carboxylic acid. Direct fluorination of amides is known to lead to cleavage of the C-N bond.[18] We propose that after formation of the α-fluoro amide, fluorine-promoted cleavage of the dimethylamino group results in *N*-fluorodimethylamine and the acid fluoride (eq 1). A ^{19}F NMR spectrum of the crude reaction mixture showed a multiplet at +24.5; the signal of $FNMe_2$ is reported to be at +24.5.[19] The signal for acyl fluorides is also in this range. On aqueous workup, the acid fluoride hydrolyzes to the observed α-fluoro carboxylic acid.



(1)

The low yield obtained from the lactone (entry 12) is attributed to difficulty in purifying the fluoro derivative. In conclusion, direct fluorination of silyl derivatives of carboxylic acids, other than amides, provides a convenient route to their α-fluoro counterparts.

Experimental Section

The ^1H NMR (90 MHz) and ^{19}F NMR (90 MHz) spectra were obtained on a Varian EM-390 NMR spectrometer. Chemical shifts are reported in ppm downfield relative to external Me_4Si for ^1H NMR and internal $CFCl_3$ for ^{19}F NMR, with $CDCl_3$ as the solvent in both cases. The microanalysis was performed by Atlantic Microlab, Inc., Norcross, GA. The 5% F_2 in N_2 was supplied by Air Products. Solvents used (DMF and THF) were distilled from sodium benzophenone ketyl prior to use. Chlorotrimethylsilane, diisopropylamine, and hexamethyldisilazane were distilled from CaH_2 under N_2 prior to use. The esters, malonates, amides, carboxylic acids, and lactone were distilled under pressure prior to use. Their ketene silyl acetals were prepared by standard procedures.[7-9] All glassware was oven dried and flame dried.

Fluorinations. Fluorinations were done following standard procedure reported earlier.[6] All fluorinations in $FCCl_3$ were done at -78 °C. The fluorine was passed through a NaF trap to remove HF. The reaction vessel was purged with nitrogen for 10 min prior to addition of 5% fluorine in nitrogen and after addition was completed. Potassium iodide traps (0.5 g/200 mL) were used to destroy any unreacted fluorine eluting from the reaction vessel and to determine when the reaction was completed.

Silyl compound (1-2 g) was diluted in approximately 25 mL of $FCCl_3$. The dilute fluorine was bubbled through the reaction vessel at a rate of 2 bubbles per second for 1.5-3.0 h. The addition of fluorine was stopped when the second potassium iodide trap began to change color. After fluorination, the solvent was removed by rotary evaporation, leaving the crude α-fluoro products. After obtaining a crude NMR spectrum, the sample was washed with water dried over $MgSO_4$ and chromatographed. The pure mono-α-fluoro carbonyl products were obtained by eluting the concentrated reaction mixtures over silica gel using various organic solvents. The α-fluoro carboxylic acids could be purified by acid-base extraction.

Synthesis of α-Fluorobenzeneacetic Acid. This compound was prepared by minor modification of standard procedures reported earlier.[10] Diethyl fluorophenylmalonate (0.50 g, 1.97 mmol) was added to a 50-mL round-bottom flask equipped with a cold water condenser and magnetic stirrer. A solution of glacial acetic acid (5 mL), concentrated sulfuric acid (0.63 mL), and water (3.3 mL) was added and the mixture was refluxed for 18 h. The cooled solution was made basic with 20% NaOH. The aqueous layer was made acidic with 10% sulfuric acid and extracted with ether. The combined ether extracts were dried with $MgSO_4$. The ether was removed by rotary evaporation, leaving the product (0.26 g) 86% yield. ^{19}F NMR -181.0 (d) (lit.[16] -181.4 (d)).

(17) Shian-Jan, S.; Partridge, J. J.; Uskokovic, M. R. *J. Org. Chem.* **1988**, *53*, 1040.
(18) Grakauskas, V.; Baum, K. *J. Org. Chem.* **1970**, *35*, 1545.
(19) Williamson, S. M.; Gupta, O. D.; Shreeve, J. M. *Inorg. Synth.* **1986**, *24*, 64.

Synthesis and Properties of Aryl-1,3-dioxo Carboxylic Acids

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Received January 5, 1990

Aryl 1,3-diketones have been used extensively as intermediates in organic synthesis. A number of methods for the preparation of aryl 1,3-dione alkanoic acids and their equivalents have been reported. The most common method employs the Knoevenagel condensation[1] of a benzoate and a substituted malonate. Following the condensation, an additional decarboxylation step is necessary. Another well-investigated method involves benzoylation of acetoacetate dianions;[2-5] however, this method limits the side-chain length of the resultant dione acid to a single methylene unit. A more versatile approach involves the reaction of mono acid chloride esters with the enolates of aryl ketones which allows for more variations in the dione side chain.[6] A related synthesis prepares 6-hydroxyl-1,3-hexanediones by sodium hydride catalyzed condensation of methyl ketones with lactones.[7]

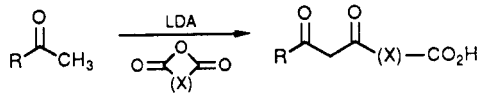
In our synthetic efforts toward a number of heterocyclic systems we required a more versatile method for the synthesis of a wide variety of aryl 1,3-dione alkanoic and benzoic acids. Dibasic anhydrides, i.e. succinic, maleic, glutaric, etc. serve as a good pool for the keto acid portion of the molecule. Aryl methyl ketones serve as a source for the remainder of the molecule.

We found that by forming the anion of an arylmethyl ketone with LDA at -78 °C in THF, and quenching it with

(1) Jones, G. *Organic Reactions*; John Wiley & Sons, Inc.: New York, 1969; Vol. 15, Chapter 2.
(2) Wolfe, J. F.; Harris, T. M.; Hauser, C. R. *J. Org. Chem.* **1964**, *29*, 3249.
(3) Hucklin, S. N.; Weiler, L. *Tetrahedron Lett.* **1972**, *23*, 2405.
(4) Hucklin, S. N.; Weiler, L. *Can. J. Chem.* **1974**, *52*, 1343.
(5) Narasimhan, N. S.; Ammanamanchi, R. *J. Org. Chem.* **1983**, *48*, 3945.
(6) Hauser, C. R.; Linn, O. *J. Am. Chem. Soc.* **1957**, *79*, 731.
(7) Detty, M. R. *J. Org. Chem.* **1979**, *44*, 2073.

0022-3263/90/1955-3424$02.50/0

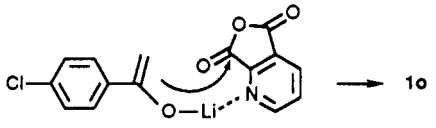
Table I. Reactions of Aryl Ketone Enolates with Cyclic Anhydrides



product[a]	R	X	yield, %
1a	4-chlorophenyl	$(CH_2)_2$	75
1b	4-chlorophenyl	CH=CH (*Z*)	56
1c[b]	4-chlorophenyl	phenyl	96
1d	*N*-methylpyrrol-2-yl	$(CH_2)_2$	88
1e	3-thienyl	$(CH_2)_2$	64
1f[b]	4-chlorophenyl	*cis*-3-cyclohexenyl	66
1g[b]	4-chlorophenyl	*cis*-cyclohexyl	81
1h[b]	4-chlorophenyl	*trans*-cyclohexyl	65
1i	phenyl	$(CH_2)_2$	68
1j	4-chlorophenyl	$(CH_2)_3$	65
1k[b]	4-chlorophenyl	7-oxabicyclo [2.2.1]hept-2-ene	70
1l	2-thienyl	$(CH_2)_2$	60
1m[c]	4-chlorophenyl	$-CH(CH_3)CH_2-$	65
1n[d]	4-chlorophenyl	$-CH_2C(CH_3)_2-$	66 (25)
1o[e]	4-chlorophenyl	2-pyridyl	68

[a] Satisfactory analytical data (±0.4%) were reported for all compounds in this table. [b] The aryl diketo and carboxylic acid side chains on all rings are on consecutive carbons. [c] A 50:50 mixture of isomers was inseparable. [d] 25% of the major isomer, 4,6-diketo-2,2-dimethyl-6-phenylhexanoic acid, was isolated by crystallization; a total yield of 66% was noted as a 3:1 mixture of the 2,2-dimethyl to the 3,3-dimethyl compound. [e] The dioxoaryl is bound to the 2-carbon of the pyridine ring while the carboxylic acid is bound to the 3-carbon.

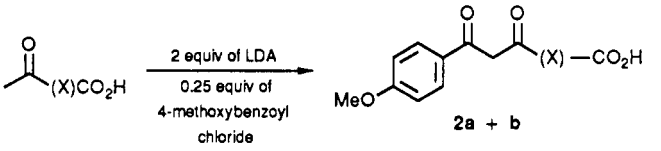
0.4–0.5 equiv of the desired cyclic anhydride, we can generate the desired diketones in 50–96% yield (Table I). Symmetrical cyclic anhydrides afford good yields of the desired aryl-1,3-dioxo carboxylic acids (**1a**–**l**). Unsymmetrical cyclic anhydrides such as 2-methylsuccinic anhydride and 2,2-dimethylsuccinic anhydride afford similar yields of the isomeric mixtures **1m** and **1n**. We see some regioselectivity in the case of the pivalate like 2,2-dimethylsuccinic anhydride **1n** where the more hindered carbonyl is apparently less active toward the aryl ketone enolate. In the case where 2,3-pyridinedicarboxylic anhydride is used as the acylating agent, we see only acylation at the 2-carbonyl. We believe this is due to a chelation-controlled delivery of the enolate to the 2-carbonyl.[8]



The keto acids generated by this procedure can also be isolated by acid/base extraction, avoiding the problems of chromatography. This procedure is amenable to scale up to the multikilo range. This method gives us versatility because of the large number of anhydrides which can be prepared by Diels–Alder reactions of maleic anhydride or DMAD with suitable dienes.

One problem with this method involves 4-alkoxyacetophenones which are poorly acylated on carbon. In the case of 4-methoxyacetophenone, the enolate acylates exclusively on oxygen, and the resulting product is hydrolyzed to the starting ketone on workup. We addressed this problem by using a different reaction scheme (Table II). In this scheme a keto acid, i.e. levulinic acid, is converted to its dianion with 2 equiv of LDA. The dianion is then acylated

Table II. Reactions of Keto Acid Dianions with 4-Methoxybenzoyl Chloride

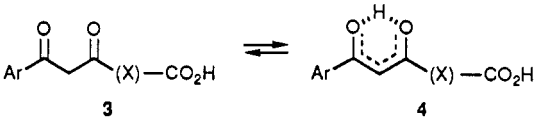


product[a]	X	yield, %
2a	$(CH_2)_2$	26
2b	$(CH_2)_3$	22

[a] Both products in this table had satisfactory combustion analysis (±0.4%).

with 4-anisoyl chloride. We have observed acylation only at the terminal methyl group with no evidence of acylation at the methylene adjacent to the ketone. When the reaction was quenched we recovered only desired product **2** and starting material. The yields are low due principally to the insolubility of the dianion. We have, however, been unsuccessful in increasing the yields of this reaction by use of various cosolvents.

In most cases compounds **1** and **2** exist as the proton/chelate form **4** in the solid state. This is evident by observing the IR spectrum (KBr). In $CDCl_3$ solution compounds **1** and **2** are predominantly in the proton chelate form **4**. The ratios between **3** and **4** can be easily obtained from the proton NMR analysis.[9] The methylene protons in **3** resonate between δ 4.0 and 5.2, and those for **4** resonate between δ 6.0 and 7.0. In all cases the compounds were more enolized in $CDCl_3$ than in DMSO-d_6.



In conclusion we feel we have a straightfoward, versatile approach to the synthesis of aryl-1,3-dioxo carboxylic acids. These reactions are amenable to scale up to produce large quantities of these versatile intermediates.

Experimental Section

Melting points are uncorrected. NMR spectra were recorded on an IBM WP 100 spectrometer and referenced (δ) to TMS. IR spectra were recorded on a Perkin-Elmer 1420 ratio recording IR spectrometer as cm^{-1}. Mass spectra were recorded on a Finnegan MAT 8230 spectrometer as DCI spectra. Elemental analyses were carried out on a Perkin-Elmer 240C elemental analyzer.

THF was dried over 4A molecular sieves and freshly distilled from sodium. Diisopropylamine was distilled from potassium hydroxide. Butyllithium was 1.6 M in hexane (Aldrich). Silica gel for flash chromatography was EM Kieselgel 60, 230–240 mesh. Unless stated otherwise NMR data is of the enol form of the dione.

General Procedures for Aryl 1,3-Dione Alkanoic Acids. Procedure A. To a reaction vessel containing 250 mL of dry THF and diisopropylamine (14 mL, 0.1 mol) stirring under nitrogen at 0 °C was added by syringe, *n*-butyllithium, 1.6 M (62.5 mL, 0.1 mol). The vessel was then chilled to −78 °C. The methyl ketone (0.1 mol) in 50 mL of dry THF was added. The solution was allowed to stir for 30 min at −78 °C. At this time the anhydride (0.04 mol) in 100 mL of THF was added by syringe. The solution was allowed to stir for 1 h at −78 °C and then warmed to room temperature. After being stirred for 1 h the reaction mixture was poured into 250 mL of 5% HCl. The mixture was extracted with 2 × 300-mL portions of ether. The combined ether

(8) Gribble, G. W.; Fletcher, G. L.; Ketcha, D. M.; Rajopadhye, M. *J. Org. Chem.* **1989**, *54*, 3264.

(9) Yoshida, Z.; Ogoshi, H.; Tokumitsu, T. *Tetrahedron* **1970**, *26*, 5691.

(10) The same conditions, substituting 5-ketohexanoic acid for 4-ketopentanoic acid were used to generate **2b**.

(11) Dedicated to Professor Francis Johnson on his 60th birthday.

extracts were then extracted with 100 mL of 10% NaOH. The NaOH layer was separated and acidified with 150 mL of 4 N HCl. The cloudy aqueous mixture was then extracted with 2 × 300-mL portions of ether. The combined ether layers were dried over sodium sulfate, filtered, and concentrated in vacuo. The resultant residues were crystallized from ether, ether–hexane, acetone, or ethyl acetate.

Procedure B. To a reaction vessel containing 500 mL of dry THF and diisopropylamine (14 mL, 0.1 mol) mechanically stirring under nitrogen at 0 °C was added by syringe *n*-butyllithium 1.6 M (62.5 mL, 0.1 mol). The vessel was then cooled to −78 °C. 4-Ketopentanoic acid (6.5 g, 0.05 mol) in 50 mL of THF was added. The mixture began to cloud, and eventually a thick slurry formed. After 15 min of stirring *p*-anisoyl chloride (2.1 g, 0.0125 mol) in 50 mL of THF was added. The slurry (yellow) was stirred for 1 h at −78 °C and 24 h at room temperature. The slurry was then poured into 500 mL of 10% HCl with vigorous stirring. The mixture was then extracted with 2 × 300-mL portions of ether. The combined ether fractions were dried over sodium sulfate, filtered, and concentrated to a yellow oil. The oil was flash chromatographed on silica gel, hexane/EtOAc 20% to EtOAc. The pure compound [725 mg (22%), mp 113–115 °C] was isolated as a yellow powder.[10]

6-(4-Chlorophenyl)-4,6-dioxohexanoic acid (1a): mp 137–139 °C; IR (KBr) 1705, 1640; mass spec (*m/z*) 255 (M + H); NMR ($CDCl_3$) 2.7 (m, 4 H), 6.1 (s, 1 H), 7.55 (d, 2 H, *J* = 8 Hz), 7.9 (d, 2 H, *J* = 8 Hz). Anal. Calcd for $C_{12}H_{11}ClO_4$: C, 56.59; H, 4.50. Found: C, 56.21; H, 4.56.

(*Z*)-6-(4-Chlorophenyl)-4,6-dioxohex-2-enoic acid (1b): mp 172–174 °C; IR (KBr) 1700, 1650, 1590; mass spec (*m/z*) 253 (M + H); NMR (DMSO-d_6) 6.65 (d, 1 H, *J* = 16 Hz), 7.05 (s, 1 H), 7.2 (d, 1 H, *J* = 16 Hz), 7.6 (d, 2 H, *J* = 8 Hz), 8.1 (d, 2 H, *J* = 8 Hz). Anal. Calcd for $C_{12}H_9ClO_4$: C, 57.04; H, 3.59. Found: C, 56.84; H, 3.72.

2-[3-(4-Chlorophenyl)-1,3-dioxopropyl]benzoic acid (1c): mp 148–150 °C; IR (KBr) 1705, 1650, 1585, 1575; mass spec (*m/z*) 303 (M + H); NMR (DMSO-d_6) 6.9 (s, 1 H), 7.4–7.9 (m, 6 H), 8.0 (d, 2 H, *J* = 8 Hz). Anal. Calcd for $C_{16}H_{11}ClO_4$: C, 63.48; H, 3.66. Found: C, 63.33; H, 3.61.

6-(*N*-Methylpyrrol-2-yl)-4,6-dioxohexanoic acid (1d): mp 95–97 °C; IR (KBr) 1740, 1720, 1600; mass spec (*m/z*) 224 (M + H); NMR (DMSO-d_6) 2.4 (t, 2 H, *J* = 6 Hz), 2.8 (t, 2 H, *J* = 6 Hz), 3.8 (s, 3 H), 4.0 (s, 2 H), 6.0–6.2 (m, 1 H), 7.0–7.3 (m, 2 H), 11.8 (bs, 1 H). Anal. Calcd for $C_{11}H_{13}NO_4$: C, 59.18; H, 5.87; N, 6.27. Found: C, 59.03; H, 6.12; H, 6.07.

6-(3-Thienyl)-4,6-dioxohexanoic acid (1e): mp 151–153 °C; IR (KBr) 1700, 1605; mass spec (*m/z*) 227 (M + H); NMR (DMSO-d_6) 2.3–2.8 (m, 4 H), 4.2 (s, 0.75 H, keto form), 6.4 (s, 0.5 H, enol form), 7.2–7.8 (m, 2 H), 8.2 (m, 1 H). Anal. Calcd for $C_{10}H_{10}O_4S$: C, 53.08; H, 4.48. Found: C, 53.30; H, 4.52.

***cis*-2-[3-(4-Chlorophenyl)-1,3-dioxopropyl]cyclohex-3-enoic acid (1f)**: mp 132–135 °C; IR (KBr) 1640, 1520; mass spec (*m/z*) 307 (M + H); NMR (DMSO-d_6) 2.3–2.7 (m, 4 H), 2.9–3.3 (m, 2 H), 5.6–5.8 (m, 2 H), 6.6 (s, 1 H), 7.6 (d, 2 H, *J* = 8 Hz), 8.0 (d, 2 H, *J* = 8 Hz), 12.2 (bs, 1 H). Anal. Calcd for $C_{16}H_{15}ClO_4$: C, 62.65; H, 4.92. Found: C, 62.50; H, 5.10.

***cis*-2-[3-(4-Chlorophenyl)-1,3-dioxopropyl]cyclohexanoic acid (1g)**: mp 158–160 °C; IR (KBr) 1634, 1515; mass spec (*m/z*) 309 (M + H); NMR (DMSO-d_6) 1.2–1.6 (m, 4 H), 1.6–2.2 (m, 4 H), 2.7–3.2 (m, 2 H), 4.3 (s, 0.5 H, keto form), 6.6 (s, 0.75 H, enol form), 7.5 (d, 2 H, *J* = 8 Hz), 7.9 (d, 2 H, *J* = 8 Hz), 12.2 (bs, 1 H). Anal. Calcd for $C_{16}H_{17}ClO_4$: C, 62.24; H, 5.55. Found: C, 62.06; H, 5.77.

***trans*-2-[3-(4-Chlorophenyl)-1,3-dioxopropyl]cyclohexanoic acid (1h)**: mp 177–179 °C; IR (KBr) 1703, 1596; mass spec (*m/z*) 309 (M + H); NMR (DMSO-d_6) 1.2–1.6 (m, 4 H), 1.6–2.2 (m, 4 H), 2.6–2.9 (m, 2 H), 6.7 (s, 1 H), 7.8 (d, 2 H, *J* = 8 Hz), 8.1 (d, 2 H, *J* = 8 Hz), 12.1 (bs, 1 H). Anal. Calcd for $C_{16}H_{17}ClO_4$: C, 62.24; H, 5.55. Found: C, 61.95; H, 5.84.

4,6-Dioxo-6-phenylhexanoic acid (1i): mp 103–105 °C; IR (KBr) 1704, 1606; mass spec (*m/z*) 221 (M + H); NMR ($CDCl_3$) 2.7 (s, 4 H), 6.15 (s, 1 H), 7.2–8.0 (m, 5 H). Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49. Found: C, 65.70; H, 5.55.

7-(4-Chlorophenyl)-5,7-dioxoheptanoic acid (1j): mp 127–129 °C; IR (KBr) 1705, 1640, 1600; mass spec (*m/z*) 269 (M + H); NMR (DMSO-d_6) 1.6–2.0 (m, 2 H), 2.0–2.8 (4 H, m), 4.3 (s, 0.5 H, keto form), 6.5 (s, 0.75 H, enol form), 7.6 (d, 2 H, *J* = 8 Hz), 8.0 (d, 2 H, *J* = 8 Hz), 12.1 (bs, 1 H). Anal. Calcd for: $C_{13}H_{13}ClO_4$: C, 58.11; H, 4.88. Found: C, 58.13; H, 4.85.

***cis*-5-[3-(4-Chlorophenyl)-1,3-dioxopropyl]-4-carboxy-7-oxabicyclo[2.2.1]hept-2-ene (1k)**: mp 180–182 °C; IR (KBr) 1610, 1575, 1451; mass spec (*m/z*) 321 (M + H); NMR (DMSO-d_6) 1:1 mixture of keto to enol forms complicates the spectra; notable peaks are 5.12 (s, 1 H, keto form), 6.5 (s, 0.5 H, enol form). Anal. Calcd for $C_{16}H_{13}ClO_5$: C, 59.92; H, 4.09. Found: C, 60.12; H, 4.13.

4,6-Dioxo-6-(2-thienyl)hexanoic acid (1l): mp 100–101 °C; IR (KBr) 1700, 1580; mass spec (*m/z*) 227 (M + H); NMR ($CDCl_3$) 2.8 (s, 4 H), 4.1 (s, 0.75 H, keto form), 6.1 (s, 0.75 H, enol form), 7.0–7.4 (m, 1 H). Anal. Calcd for $C_{10}H_{10}O_4S$: C, 53.08; H, 4.46. Found: C, 52.85; H, 4.34.

6-(4-Chlorophenyl)-2-methyl-4,6-dioxohexanoic acid plus 6-(4-chlorophenyl)-3-methyl-4,6-dioxohexanoic acid (1m): IR (neat) 1705, 1600; mass spec (*m/z*) 269 (M + H); NMR ($CDCl_3$) 1.2 (superimposed doublets, 3 H), 2–3.5 (m, 3 H), 6.1 (s, 0.5 H), 6.2 (s, 0.5 H), 7.5 (d, 2 H, *J* = 8 Hz). Anal. Calcd for $C_{13}H_{13}ClO_4$: C, 58.11; H, 4.88. Found: C, 57.73; H, 5.24.

6-(4-Chlorophenyl)-2,2-dimethyl-4,6-dioxohexanoic acid (1n): mp 137–139 °C; IR (KBr) 1709, 1605; mass spec (*m/z*) 283 (M + H); NMR ($CDCl_3$) 1.4 (s, 6 H), 2.8 (s, 2 H), 6.1 (s, 1 H), 7.4 (d, 2 H, *J* = 8 Hz), 7.9 (d, 2 H, *J* = 8 Hz). Anal. Calcd for $C_{14}H_{15}ClO_4$: C, 59.47; H, 5.35. Found: C, 59.29; H, 5.21. The 3,3 isomer showed an enol vinyl resonance at 6.27.

2-[3-(4-Chlorophenyl)-1,3-dioxopropyl]pyridine-3-carboxylic acid (1o): mp 183–185 °C; IR (KBr) 1716, 1593, 1577; mass spec (*m/z*) 304 (M + H); NMR (DMSO-d_6) δ 7.24 (s, 1 H), 7.62 (d, 2 H, *J* = 8 Hz), 7.67–7.73 (m, 1 H), 8.06 (d, 2 H, *J* = 8 Hz), 8.17 (d, 1 H, *J* = 8 Hz), 8.82 (d, 1 H, *J* = 4 Hz). Anal. Calcd for $C_{15}H_{10}ClNO_4$: C, 59.32; H, 3.32; N, 4.61. Found: C, 59.00; H, 3.22; N, 4.57.

6-(4-Methoxyphenyl)-4,6-dioxohexanoic acid (2a): IR (KBr) 1704, 1604; mass spec (*m/z*) 251 (M + H); NMR ($CDCl_3$) 2.8 (s, 4 H), 3.8 (s, 3 H), 6.1 (s, 1 H), 6.9 (d, 2 H), 7.8 (d, 2 H). Anal. Calcd for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64. Found: C, 62.00; H, 5.99.

7-(4-Methoxyphenyl)-5,7-dioxoheptanoic acid (2b): mp 113–115 °C; IR (KBr) 1704, 1604; mass spec (*m/z*) 265 (M + 1); NMR (acetone-d_6) 1.8–2.2 (m, 2 H), 2.2–2.8 (m, 4 H), 3.9 (s, 3 H), 6.38 (s, 1 H), 7.0 (d, 2 H, *J* = 8 Hz), 8.0 (d, 2 H, *J* = 8 Hz). Anal. Calcd for $C_{14}H_{16}O_5$: C, 63.62; H, 6.10. Found: C, 63.53; H, 6.17.