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New Strong Base Synthesis of Symmetrical 1,5-Diaryl-1,3,5-pentanetriones from Acetone and Benzoate Esters

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Abstract: Lithium hexamethyldisilazide (LiHMDS) was used to condense substituted benzoate esters with acetone to afford symmetrical 1,5-diaryl-1,3,5-pentanetriones that were isolated, characterized (including a representative X-ray crystallographic analysis), and acid cyclized to the respective 2,6-diaryl-4*H*-pyran-4-ones.

Keywords: Acetone; benzoate esters; diarylpentanetriones; lithium hexamethyldisilazide

INTRODUCTION

One of the earliest methods for the preparation of 1,5-diaryl-1,3,5-pentanetriones, developed by Hauser et al. involved the condensation of 1-benzoylacetone with ethyl benzoate employing potassium amide in liquid ammonia[1] or sodium hydride in monoglyme.[2] They also reported sodium hydride initiated condensations of acetone **1** with several benzoate esters **2** to afford symmetrical 1,5-diaryl-1,3,5-pentanetriones **3**. Also, diphenyl triketone **3a** has been prepared by hydrolysis opening of 2,6-diphenylpyran-4-one with either potassium hydroxide or potassium methoxide.[3]

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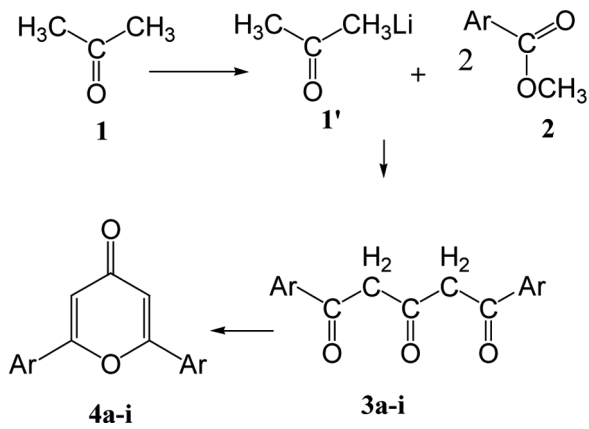
A few symmetrical 1,5-diaryl-1,3,5-pentanetriones have been reported since the initial reports,[4] indicating the potential for them to be used in the preparation of useful heterocyclic compounds,[5] chelates,[6] and other compounds,[7] many of which have biological potential.[8] Also, 1,3-diaryl-1,3,5-pentanetriones have been involved in spectral, theoretical, and X-ray studies.[9]

Our initial focus was on the possible substitution of lithium hexamethyldisilazide (LiHMDS) or lithium diisopropylamide (LDA) in tetrahydrofuran (THF) for sodium hydride in the preparation of substituted 1-aroylacetones and 1,5-diarylpentanetriones. Syntheses of these di- and triketones by an alternative new method offer an expanded potential for some of the various studies cited.

RESULTS AND DISCUSSION

During the current investigation, monolithiated acetone **1′** was prepared from acetone **1** by deprotonation with either excess LiHMDS or LDA and was condensed with a variety of substituted benzoate esters **2** (Scheme 1). Initially, LiHMDS was used for lithiation of **1** followed by condensation with methyl 3,4,5-trimethoxybenzoate, and this resulted in 1,3-diacylation of **1** to afford symmetrical 1,5-bis(3,4,5-trimethoxyphenyl)-1,3,5-pentanetrione **3d** (1:2 condensation acetone–ester) in 68% yield. The general ratio of reactants was determined for this reaction and the other reaction products (acetone–LiHMDS–ester 1:3:2); see Table 1.



Scheme 1. 1,5-Diaryl-1,3,5-pentanetriones **3a–i** and 2,6-diaryl-4*H*-pyran-4-ones **4a–i**.

Table 1. Pentanetriones 3 and pyranones 4: percentage yield and melting point data

Ar	Compound no. trione	Mp (°C) (recryst. solv.)	Yield (%)	Compound no. pyranone	Mp (°C) (recryst. EtOH)	Yield (%)
C_6H_5	**3a**	105–107, lit. 106–110 (EtOH)	63	**4a**	139–140, lit.[2] 140	80
4-$CH_3OC_6H_4$	**3b**	123–125, lit. 126–129 (EtOH)	78	**4b**	189–191, lit.[2] 190	83
3,4-$(CH_3O)_2C_6H_3$	**3c**	114–116, (EtOH)	59	**4c**	215–217[11]	81
3,4,5-$(CH_3O)_3C_6H_2$	**3d**	137–139 (benz./EtOH)	69	**4d**	212–213	81
3,5-$(CH_3O)_2C_6H_3$	**3e**	149–151 (benz./EtOH)	61	**4e**	193–196	83
4-FC_6H_4	**3f**	115–116 (EtOH)	69	**4f**	167–170	78
4-ClC_6H_4	**3g**	156–157, lit. 156–158 (benz./EtOH)	60	**4g**	234–235[a]	84
4-BrC_6H_4	**3h**	175–177 (benz./EtOH)	63	**4h**	245 d, 250[12]	75
4-$(CH_3)_3CC_6H_4$	**3i**	105–106 (hexanes)	41	**4i**	192–194[13]	71

[a]This pyranone was originally recrystallized from benzene, mp 274–275 °C; see Ref. 2. This investigation used recryst. ethanol/water, mp 232–235 °C, incorporated water in pure crystal; see data for **4d–f** in this report.

Triones **3a**, **3b**, and **3h** from this group of symmetrical triones **3a–i**, reported here have been cited previously.[1,2] In this study, **3a–i** were isolated in 41–78% yield, with an average 62% yield. Each of these triones was acid cyclized to the targeted pyranone **4a–i** in 71–84% yield, with an average yield of 80%; pyranones **4d–f** are new.

The 1:1 condensation of lithiated acetone **1′**, from LDA deprotonation of **1**, with methyl 3,4,5-trimethoxybenzoate occurred [acetone–LDA–ester 1:3:1] to afford 1-(3,4,5-trimethoxyphenyl)-1,3-butanedione in 65% yield[10]; however, this is a limited synthesis currently under separate investigation.

All compounds were characterized by absorption spectra with support from combustion analysis when applicable. IR spectra displayed carbonyl and other absorptions for triones **3**, 1568–1600 $cm^{-1}$and 1635–1669 cm^{-1} for pyranones **4**; ^{13}C and ^{1}H NMR spectra for **3a–i** displayed numerous additional absorptions that indicated the presence of several tautomers in solution. Although this has resulted in complex absorption spectra,[4d,7c,9] ^{1}H NMR of each product **3a–i**, displayed two separate methylene proton absorptions and two separate methyne proton absorptions. The range for the two methylene protons was δ 3.99–4.51 ppm with an average of δ 4.22 ppm, and the second methylene was δ 4.15–4.65 ppm with an average of δ 4.39 ppm. Methyne protons were noted from δ 5.99 to 6.65 ppm, average of δ 6.27 ppm. The second methyne proton was δ 6.23–6.86 ppm, with an average of δ 6.52 ppm. NMR spectra for **4a–i** were straightforward, with characteristic ^{1}H NMR for C_3-H δ 6.70–6.99 ppm and ^{13}C NMR for carbonyl carbons from δ 178.2–180.8 ppm.

As a result of obtaining good quality crystals for **3d**, an X-ray single-crystal analysis of trione **3d** was completed. Analysis of the data indicated a single tautomer in the crystal. The molecular structure is shown in Figures 1 and 2 and selected bond distances and angles are listed in Table 2. Atomic positional parameters and all bond distances and angles

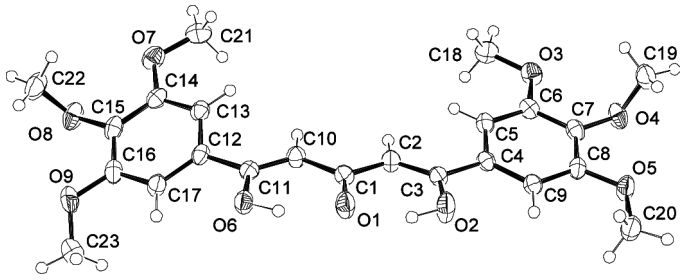


Figure 1. ORTEP[14] diagram (50% ellipsoid for non hydrogen atoms) for **3d**, $C_{23}H_{26}O_9$.

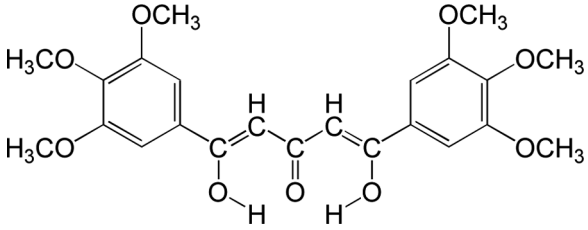


Figure 2. Conventional illustration of **3d**.

are listed in the supplementary material. CCDC 657942 contains the supplemental crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The molecule exhibits both intramolecular and intermolecular hydrogen bonding. The O1 atom is bonded to the H atoms bonded to O2 and O6 within the same molecule, and the O1 atom is bonded to the H atom bonded to O2 in another molecule.

When other bases such as LDA, lithium 2,6-dimethylpiperidide, or lithium diethylamide were used, diaryl triones **3a–i** did not result, and this indicates that the reaction itself is dependent on the overall properties of LiHMDS as a base. The ratio of acetone and LiHMDS is important.[15]. Optimum yields were obtained when the ratio was 1:3:2 (acetone–LiHMDS–ester), and essentially no product was obtained with a ratio of 1:2:2 (acetone–LiHMDS–ester). This is compared to ratios used with sodium hydride–activated synthesis: 1:5:3 (acetone–NaH–ester).[2]

Although this is a synthesis report, it opens the possibility of further studies. One of three intermediates may be involved: the 1,3-dianion of acetone **1″**; the 1,3-dianion of 1-aroylacetone **5″**; and a monoanion of 1-aroylacetone **5′**. The participation of **1″** in this reaction is improbable, because its preparation requires the sequential reactions of two stronger bases under different reaction conditions.[16] Arguments can be made for and against **5″** or **5′** based on the strength of base, coordination ability, and size of LiHMDS. Additional mechanistic studies would be required to confirm or deny either of these intermediates. See Fig. 3.

CONCLUSIONS

A new synthesis of 1,5-diaryl-1,3,5-pentanetriones **3a–i** and their acid cyclization to 1,6-diarylpyranones **4a–i** has resulted in an experimental sequence for the preparation of multigram quantities of targeted

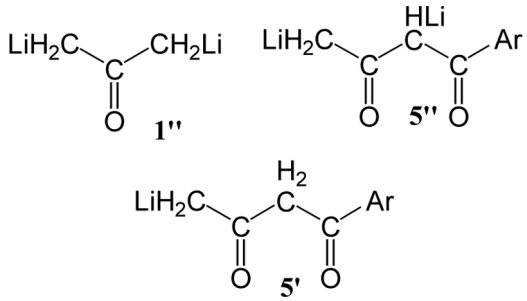


Figure 3. Reaction intermediates.

products that can easily be purified by recrystallization from common solvents. Because all procedures are general, the yield of a particular product may not be optimal, and the preparation of individual compounds has potential for being scaled up. The synthetic processes are practical in terms of the availability of acetone, benzoate esters, and reagents. Our explanation for the exclusivity of LiHMDS over other lithium bases is incomplete based on this initial investigation, but strength and size of base in comparison to other lithium bases, along with the lithium nitrogen coordination ability of hexamethyldisilazine, need to be taken into account. The project data has also provided results for spectral, X-ray, and theoretical studies.

EXPERIMENTAL

Melting points were obtained with a Mel-Temp II melting-point apparatus in open capillary tubes and are uncorrected. Fourier Transform infrared spectra were obtained with a Nicolet Impact 410 FT-IR and a Mattson Genesis II FT-IR with Specac Golden Gate Accessory. Nuclear magnetic resonance (NMR) spectra were obtained with a Varian Mercury-Vx spectrometer in an Oxford 300/54 magnet. Chemical shifts are recorded in δ parts per million (ppm) downfield from internal tetramethylsilane (TMS) reference. Combustion analyses were performed by Quantitative Technologies, Inc., Whitehouse, N.J.

X-ray Determination

Single-crystal X-ray measurements for crystals of **3d** $C_{23}H_{26}O_9$ recrystallized from benzene were collected on a Mercury CCD area detector

coupled with a Rigaku AFC8 diffractometer with graphite monochromated Mo-Kα ($\lambda = 0.71073$Å) radiation. The data were collected at a temperature of 163(2) K to a maximum θ value of 25.14°. Data were collected in 0.50°oscillations in ω (two identical scans were performed at each position to identify detector anomalies). A sweep of data was done using ω oscillations from -90.0 to 90.0° at $\chi = 45.0°$ and $\phi = 0.0°$; a second sweep was performed using ω oscillations from -30.0 to 30.0°at $\chi = 45.0°$ and $\phi = 90.0°$. Data were collected, processed, and corrected for Lorentz polarization and for absorption using CrystalClear (Rigaku).[17] Cell parameters and additional details of the data collection are reported in Table 3 and in the supplementary material.

The structure was solved by direct methods and expanded using Fourier techniques. Structure solution, refinement, and the calculation of derived results were performed using the SHELX-97[18] package of computer programs. Neutral atom scattering factors were those of Cromer and Waber,[19] and the real and imaginary anomalous dispersion corrections were those of Cromer.[20]

The nonhydrogen atoms were refined anisotropically. Ideal hydrogen atom coordinates were calculated, and the hydrogen atoms were allowed to ride on their respective carbons atoms. The hydrogen atoms on O2 and O6 were located from a difference Fourier and the coordinates were fixed. The temperature factors of all hydrogen atoms were varied isotropically. The final cycle of full-matrix least-squares refinement were performed on F^2.

Table 2. Selected bond distances (Å) and angles (°)

Parameter	Value
C1–C2	1.429(3)
C1–C10	1.437(3)
C2–C3	1.354(3)
C10–C11	1.357(3)
C3–C4	1.475(3)
C11–C12	1.478(3)
C1–O1	1.277(2)
C3–O2	1.335(2)
C11–O6	1.338(2)
C4–C5	1.402(3)
C5–C6	1.385(3)

(*Continued*)

Table 2. Continued

Parameter	Value
C6–C7	1.404(3)
C7–C8	1.389(3)
C8–C9	1.388(3)
C9–C4	1.396(3)
C12–C13	1.395(3)
C13–C14	1.389(3)
C14–C15	1.400(3)
C15–C16	1.389(3)
C16–C17	1.391(3)
C17–C12	1.397(3)
C6–O3	1.368(2)
C7–O4	1.379(2)
C8–O5	1.368(2)
C14–O7	1.365(2)
C15–O8	1.378(2)
C16–O9	1.365(3)
O3–C18	1.435(3)
O4–C19	1.425(3)
O5–C20	1.424(3)
O7–C21	1.428(3)
O8–C22	1.421(3)
O9–C23	1.396(3)
C10–C1–C2	119.3(2)
C1–C2–C3	123.1(2)
C1–C10–C11	122.9(2)
C2–C3–C4	125.0(2)
C10–C11–C12	123.2(2)
C3–C4–C5	120.4(2)
C11–C12–C13	119.5(2)
C6–O3–C18	117.2(2)
C14–O7–C21	116.1(2)
C7–O4–C19	114.0(2)
C15–O8–C22	114.0(2)
C8–O5–C20	117.5(2)
C16–O9–C23	118.4(2)
O1–C1–C2	120.6(2)
O1–C1–C10	120.1(2)
O2–C3–C2	121.1(2)
O6–C11–C10	121.8(2)
O2–C3–C4	113.9(2)
O6–C11–C12	114.9(2)

Table 3. Selected crystallographic data, **3d**, $C_{23}H_{26}O_9$, CCDC 657942

Parameter	Value
Crystal dimensions (mm)	$0.65 \times 0.46 \times 0.24$
Space group	P2(1)/n
a (Å)	8.188 (2)
b (Å)	26.706 (5)
c (Å)	10.184 (2)
α	90°
β	100.75 (3)°
γ	90°
Limiting indices	$-9 \leq h \leq 9$ $-25 \leq k \leq 31$ $-12 \leq l \leq 12$
V (Å^3)	2188.0 (7)
fw	446.44
Z	4
d_{calc} (g/cm^3)	1.355
μ (mm^{-1})	0.105
Exposure time (s)	15
Crystal-to-detector distance (mm)	37.95
Number of reflections	12514
Unique reflections	3811
R_{int}	0.0301
R_1 ($I > (2.00)\sigma(I)$)[a]	0.0514
wR_2 (all data)[b]	0.1283
Goodness of fit	1.078
Highest difference peak (e Å^{-3})	0.167
Deepest hole (e Å^{-3})	− 0.278

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$
[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

General Procedure for Preparation of 1,5-Diaryl-1,3,5-pentanetriones (3a–i)

[Ratio of reagents acetone–LiHMDS–ester 1:3:2]. A 20.0 mL sample of 1.6 *M* *n*-butyllithium (0.0315 mol) in hexanes (0 °C) under N_2 was added to a three-necked round-bottomed flask (e.g., 500 mL), equipped with a nitrogen inlet tube, a side-arm addition funnel (e.g., 125 mL), and a magnetic stir bar. The flask was cooled in an ice-water bath, and 5.24 g (0.0315 mol) of hexamethyldisilazine (97%, Aldrich Chem. Co.) dissolved in 25–30 mL of dry THF (freshly distilled from sodium) was added from

the addition funnel at a fast drop rate during a 5-min (0°, N_2) period. The solution was stirred for an additional 15–20 min and then treated via the addition funnel, during 5 min, with 0.581 g (0.0100 mol) of distilled acetone dissolved in 30 mL of THF. After 10–15 min, 2 equivalents (0.0210 mol + 5% excess) of an aromatic ester dissolved in 25 mL of THF were added, and the solution was allowed to stir overnight under N_2 atmosphere and at room temperature. Finally, 100 mL of 3 *M* hydrochloric acid was added all at once. The two-phase mixture was well stirred for 5 min. It was then poured into a large flask (ca. 1 or 2 L) containing ice (ca. 100 g), followed by the addition of 100 mL of solvent-grade ether. The mixture was then neutralized with solid sodium bicarbonate, and the layers were separated. The aqueous layer was extracted with ether (2 × 50 mL), and the organic fractions were combined, not dried, and evaporated. Most products crystallized upon removal of the organic solvents. Recrystallization was achieved using common solvents such as ethanol, benzene/ethanol, benzene/hexanes, or hexanes.

Data

1,5-Diphenyl-1,3,5-pentanetrione (3a)

Acetone was condensed with methyl benzoate (1:2) using the general procedure to afford 1.68 g of **3a**, dark gold-colored crystals. IR: 1586 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.29 (s), 4.44 (s), 6.34 (s), 6.61 (s), 7.47–7.65 (m), and 7.87–8.04 (m). ^{13}C NMR ($CDCl_3$): δ 50.2, 54.0, 97.6, 98.4, 126.8, 127.5, 129.0, 129.3, 132.5, 133.3, 133.6, 134.3, 136.7, 173.4, 182.0, 192.5, 194.6, and 194.7.

1,5-bis(4-Methoxyphenyl)-1,3,5-pentanetrione (3b)

Acetone was condensed with methyl 4-methoxybenzoate (1:2) using the general procedure to afford 2.55 g of **3b**, yellow crystals. IR: 1584 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.83–3.84 (m), 4.14 (s), 4.30 (s), 6.24 (s), 6.48 (s), 7.00–7.04 (m), and 7.81–7.98 (m). ^{13}C NMR ($CDCl_3$): δ 49.2, 53.9, 56.2, 56.3, 96.3, 97.8, 114.6, 114.7, 115.0, 125.7, 126.8, 128.9, 129.8, 129.9, 131.6, 163.1, 163.8, 164.2, 173.0, 183.3, 190.5, 193.5, 193.8, and 194.0.

1,5-bis(3,4-Dimethoxyphenyl)-1,3,5-pentanetrione (3c)

Acetone was condensed with methyl 3,4-dimethoxybenzoate (1:2) using the general procedure to afford 2.27 g of **3c**, bright yellow crystals. IR:

1584 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.93–3.95 (m), 4.04 (s), 4.28 (s), 5.94 (s), 6.26 (s), 6.86–6.92 (m), and 7.36–7.71 (m). ^{13}C NMR ($CDCl_3$) δ (ppm): 50.3, 56.2, 56.3, 95.9, 96.5, 109.2, 109.8, 110.3, 110.4, 110.7, 112.2, 120.4, 121.6, 124.4, 126.6, 127.1, 129.7, 149.1, 149.2, 152.3, 153.2, 154.1, 173.5, 183.4, 188.8, 192.7, and 193.3. Anal. calcd. for $C_{21}H_{22}O_7 \cdot 1/2\ H_2O$: C, 63.79; H, 5.86. Found: C, 63.74; H, 5.86.

1,5-bis(3,4,5-Trimethoxyphenyl)-1,3,5-pentanetrione (3d)

Acetone was condensed with methyl 3,4,5-trimethoxybenzoate (1:2) using the general procedure to afford 3.08 g of **3d**, golden crystals. IR: 1589 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.90 (s), 3.91–3.93 (m), 4.08 (s), 5.96 (s), 6.23 (s), 7.08 (s), 7.10 (s), and 7.32 (s). ^{13}C NMR ($CDCl_3$): δ 50.5, 55.9, 56.0, 60.7, 96.1, 96.5, 103.4, 104.2, 128.6, 128.9, 131.0, 141.0, 142.0, 152.8, 152.9, 173.1, 189.2, 192.2, and 193.0. Anal. calcd. for $C_{23}H_{26}O_9$: C, 61.88; H, 5.87. Found: C, 61.90; H, 5.88.

1,5-bis(3,5-Dimethoxyphenyl)-1,3,5-pentanetrione (3e)

Acetone was condensed with methyl 3,5-dimethoxybenzoate (1:2) using the general procedure to afford 2.35 g of **3e**, bright yellow crystals. IR: 1568 cm^{-1}. ^1H NMR (DMSO-d_6): δ 3.80–3.81 (m), 4.31 (s), 4.43 (s), 6.50 (s), 6.71–6.80 (m), and 7.00–7.13 (m). ^{13}C NMR (DMSO-d_6): δ 49.6, 55.5, 55.6, 97.7, 98.5, 104.1, 104.2, 104.7, 104.9, 105.5, 106.3, 135.0, 135.8, 138.1, 160.7, 160.7, 172.3, 181.2, 191.9, 193.9, and 194.1. Anal. calcd. for $C_{21}H_{22}O_7$: C, 65.28; H, 5.74. Found: C, 65.12; H, 5.65.

1,5-bis(4-Fluorophenyl)-1,3,5-pentanetrione (3f)

Acetone was condensed with methyl 4-fluorobenzoate (1:2) using the general procedure to afford 1.78 g of **3f**, faint yellow crystals. IR: 1589 cm^{-1}. ^1H NMR (DMSO-d_6): δ 4.32 (s), 4.46 (s), 6.41 (s), 6.70 (s), 7.31–7.40 (m), and 7.90–8.12 (m). ^{13}C NMR (DMSO-d_6): δ 49.2, 53.4, 97.0, 98.0, 115.7, 115.8, 115.9, 116.1, 116.2, 128.9, 129.0, 129.4, 129.8, 129.9, 130.3, 131.5, 131.6, 132.9, 162.8, 163.3, 163.7, 166.1, 166.6, 167.1, 171.6, 180.9, 191.3, 193.1, 193.7, 193.8, and 201.4. ^{19}F NMR (DMSO-d_6): δ −107.77-(−)107.68(m), −106.66-(−)106.56(m), −105.63-(−)105.53(m), and −105.50-(−)105.40 (m). Anal. calcd. for $C_{17}H_{12}F_2O_7$: C, 67.55; H, 4.00. Found: C, 67.23; H, 3.85.

1,5-bis(4-Chlorophenyl)-1,3,5-pentanetrione (3g)

Acetone was condensed with methyl 4-chlorobenzoate (1:2) using the general procedure to afford 2.01 g of **3g**, light yellow crystals. IR: 1588 cm^{-1}. ^1H NMR (DMSO-d_6 at 90 °C): δ 4.30 (s), 4.40 (s), 6.41 (s), 6.61 (s), 7.55–7.58 (m), and 7.87–8.01 (m). ^{13}C NMR (DMSO-d_6 at 90 °C): δ 50.2, 54.1, 98.3, 98.9, 128.8, 129.4, 129.6, 129.7, 130.9, 132.8, 133.5, 135.9, 137.6, 139.4, 172.5, 193.8, and 193.9.

1,5-bis(4-Bromophenyl)-1,3,5-pentanetrione (3h)

Acetone was condensed with methyl 4-bromobenzoate (1:2) using the general procedure to afford 2.54 g of **3h**, light yellow crystals. IR: 1589 cm^{-1}. ^1H NMR (DMF-d_7 at 85 °C): δ 2.91 (s), 3.05 (s), 4.51 (s), 4.65 (s), 6.63 (s), 6.86 (s), 7.88–7.94 (m), and 8.03–8.18 (m). ^{13}C NMR (DMF-d_7 at 85 °C): δ 50.1, 54.0, 98.1, 98.6, 126.4, 128.6, 128.8, 129.4, 130.9, 132.5, 133.3, 138.5, 172.9, 193.8, and 194.0. Anal. calcd. for $C_{17}H_{12}Br_2O_7$: C, 48.15; H, 2.85. Found: C, 47.75; H, 2.60.

1,5-bis(4′-(1,1-Dimethylethyl)phenyl)-1,3,5-pentanetrione (3i)

Acetone was condensed with methyl 4-(1,1-dimethylethyl)benzoate (1:2) using the general procedure to afford 1.56 g of **3h**, yellow crystals. IR: 1600 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.32–1.34 (m), 4.08 (s), 4.15 (s), 5.99 (s), 6.29 (s), 7.43–7.51 (m), 7.78–7.81 (app. d, $J = 8.7$ Hz), and 7.96–7.99 (app. d, $J = 8.7$ Hz). ^{13}C NMR ($CDCl_3$): δ 31.3, 31.4, 51.1, 53.9, 96.6, 96.7, 125.8, 125.9, 126.1, 126.6, 127.3, 127.5, 129.1, 131.2, 131.4, 134.0, 155.6, 156.7, 157.9, 173.9, 182.3, 190.9, 193.8, and 194.8. Anal. calcd. for $C_{25}H_{30}O_3 \cdot 5/9\ H_2O$: C, 77.29; H, 8.07. Found: C, 77.08; H, 7.93.

Preparation of 2,6 Diaryl-4*H*-pyran-4-ones (4a-i)

A 10 to 15 mL sample of conc. sulfuric acid was slowly stirred and cooled to 0 °C, and 1.00 g of dry solid 1,5-diaryl-1,3,5-pentanetrione was slowly added during 5–10 min. When complete solution had occurred, it was poured into a beaker containing 50–75 g of ice. The mixture containing precipitated product was filtered, washed with water, partially dried by suction after filtration, and recrystallized with ethanol or ethanol/water.

Data

2,6-Diphenyl-4*H*-pyran-4-one (4a)

This compound was prepared with **3a** using the acid cyclization procedure. IR: 1660 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.84 (s, 2H), 7.53–7.56 (m, 6H), and 7.86–7.89 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 111.0, 125.8, 129.0, 131.1, 131.4, 163.4, and 180.1.

2,6-bis(4-Methoxyphenyl)-4*H*-pyran-4-one (4b)

This compound was prepared with **3b** using the acid cyclization procedure. IR: 1635 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.91 (s, 6H), 6.90 (s, 2H), 7.07–7.10 (m, 4H), and 7.92–7.95 (m, 4H). ^{13}C NMR (DMSO-d_6/$CDCl_3$): δ 55.2, 107.2, 114.5, 122.1, 127.9, 162.5, 164.9, and 179.1.

2,6-bis(3,4-Dimethoxyphenyl)-4*H*-pyran-4-one (4c)

This compound was prepared with **3c** using the acid cyclization procedure. IR: 1643 cm^{-1}. ^1H NMR ($CDCl_3$/DMSO-d_6 at 90 °C): δ 3.06 (s, H_2O), 3.85 (s, 6H), 3.89 (s, 6H), 6.79 (s, 2H), 7.10–7.13 (d, 2H, $J = 8.7$ Hz), 7.47 (s, 2H, ArH), and 7.53–7.56 (d, 2H, $J = 8.4$ Hz). ^{13}C NMR (DMSO-d_6/$CDCl_3$): δ 56.7, 56.8, 110.3, 110.7, 113.4, 120.1, 124.6, 150.2, 152.6, 163.0, and 179.4.

2,6-bis(3,4,5-Trimethoxyphenyl)-4*H*-pyran-4-one (4d)

This compound was prepared with **3d** using the acid cyclization procedure. IR: 1654 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.93 (s, 6H), 3.95 (s, 12H), 6.76 (s, 2H), and 7.07 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 56.7, 61.6, 103.7, 111.5, 127.2, 141.5, 154.2, 163.7, and 180.8. Anal. calcd. for $C_{23}H_{24}O_8 \cdot 2\ H_2O$: C, 59.48; H, 6.08. Found: C, 59.11; H, 6.12.

2,6-bis(3,5-Dimethoxyphenyl)-4*H*-pyran-4-one (4e)

This compound was prepared with **3e** using the acid cyclization procedure. IR: 1645 cm^{-1}. ^1H NMR (DMSO-d_6/$CDCl_3$ at 90 °C): δ 3.07 (s, H_2O), 3.85 (s, 12H), 6.70 (s, 2H), 6.93 (s, 2H), and 7.10 (s, 4H). ^{13}C NMR (DMSO-d_6/$CDCl_3$ at 90 °C): δ 56.3, 104.4, 105.0, 112.2, 133.9, 161.9, 162.8, and 179.5. Anal. calcd. for $C_{21}H_{20}O_6 \cdot 1/4\ H_2O$: C, 67.64; H, 5.54. Found: C, 67.74; H, 5.47.

2,6-bis(4-Fluorophenyl)-4*H*-pyran-4-one (4f)

This compound was prepared with **3f** using the acid cyclization procedure. IR: 1649 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.57 (s, H_2O), 6.99 (s, 2H, CH), 7.39–7.44 (m, 4H), 8.08–8.13 (app. t, 4H). ^{13}C NMR (DMSO-d_6/$CDCl_3$): δ 110.8, 116.4–116.7 (ArC, $J_{CF} = 86.7$ Hz), 127.5 (ArC, $J_{CF} = 12.3$ Hz), 128.7–128.8 ($J_{CF} = 35.1$ Hz), 161.5–162.3 ($J_{CF} = 258$ Hz), Hz), 165.6, and 178.9. ^{19}F NMR (DMSO-d_6): δ −109.10-(−) 109.00 (m, 1 F). Anal. calcd. for $C_{17}H_{10}F_2O_2 \cdot 5/3\ H_2O$: C, 64.97; H, 4.28. Found: C, 64.90; H, 4.09.

2,6-bis(4-Chlorophenyl)-4*H*-pyran-4-one (4g)

This compound was prepared with **3g** using the acid cyclization procedure. IR: 1648 cm^{-1}. ^1H NMR ($CDCl_3$/DMSO-d_6 at 90 °C): δ 3.09 (s, H_2O), 6.91 (s, 2H, CH), 7.58–7.61 (d, 4H, ArH, $J = 8.7$ Hz), and 7.98–8.01 (d, 4H, $J = 8.7$ Hz). ^{13}C NMR (DMSO-d_6/$CDCl_3$): δ 112.1, 128.5, 129.9, 130.6, 137.0, 162.2, and 179.1.

2,6-bis(4-Bromophenyl)-4*H*-pyran-4-one (4h)

This compound was prepared with **3h** using the acid cyclization procedure. IR: 1649 cm^{-1}. ^1H NMR ($CDCl_3$/DMSO-d_6 at 90 °C): δ 2.86 (s, H_2O), 6.82 (s, 2H, CH), 7.68–7.70 (d, 4H, $J = 8.7$ Hz), and 7.80–7.83 (d, 4H, $J = 8.7$ Hz). ^{13}C NMR (DMSO-d_6/$CDCl_3$): δ 112.0, 125.9, 128.1, 130.9, 132.7, 162.4, and 179.1.

2,6-bis(4′-(1,1-Dimethylethyl)phenyl)-4*H*-pyran-4-one (4i)

This compound was prepared with **3i** using the acid cyclization procedure. IR: 1649 cm^{-1}. ^1H NMR ($CDCl_3$/DMSO-d_6 at 90 °C): δ 1.34 (s, 9H, CH_3), 3.03 (s, 2H, H_2O), 6.84 (s, 2H, CH), 7.58–7.61 (d, 2H, $J = 8.4$ Hz), and 7.91–7.94 (d, 2H, $J = 8.7$ Hz). ^{13}C NMR (DMSO-d_6/$CDCl_3$ at 90 °C): δ 30.4, 34.2, 110.0, 125.4, 125.5, 128.1, 154.1, 162.1, and 178.2. Anal. calcd. for $C_{25}H_{28}O_2 \cdot 1/8\ H_2O$: C, 82.78; H, 7.88. Found: C, 82.77; H, 7.82.

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