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REACTIONS OF COPPER(II) β-DIKETONATES UNDER FREE RADICAL CONDITIONS. PREPARATION OF HIGHLY CONGESTED β-DIKETONES.[1]

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Abstract.- Copper(II) β-diketonates react with alkyl bromides under free radical conditions to give highly congested β-diketones such as 3-(1-adamantyl)-3-alkylpentane-2,4-diones. Another typical free radical reagent: benzoyl peroxide, reacts also functionalizing the intercarbonyl positions.

INTRODUCTION

The use of β-diketones in the form of their nickel(II),[2] cobalt(III),[3] zinc(II),[3] and mainly cobalt(II) complexes has broadened the scope of their C-alkylations. Thus, Co(II) complexes of β-dicarbonyl compounds have been used in alkylations with easily dehydrohalogenable alkyl halides,[4a,b] non-active halides such as 1-bromoadamantane[4c] and 2-bromoadamantane,[4b] and other special alkyl halides such as 9-bromofluorene.[4d] These procedures have been particularly useful in the regioselective alkylation of methyl 3,5-dioxohexanoate, a β,δ-diketoester considered as a polyketide model.[5]

Mechanistic studies on the Co(II) mediated alkylations showed that two different mechanisms operate. One of them (Scheme 1) is a chain mechanism containing oxidative addition to Co(I) and reductive elimination from Co(III) steps, initiated by an inner-sphere electron transfer induced by Co(II). This mechanism operates at high concentration (> 0.73M in Co) producing high reaction rates.[6] The fact that Co is a d^9 transition metal, possesing radicaloid properties, makes the participation of electron-transfer mechanisms possible (2nd initiation step). Cu(II) Diketonates are more stable and more readily prepared than their Co(II) congeners. Therefore, we considered the possibility of using Cu(II) complexes of β-diketones. Copper, being a d^{11} transition metal, could behave similarly to cobalt.

Cobalt(III) species are present in the mechanism of cobalt mediated alkylations.[6] Copper(III) species are also known.[7] Thus, the oxidative addition of benzoyl peroxide to copper(I) chloride to afford $[Cu^{III}Cl(OCOPh)_2(py)_2]_2$ is worth of mention.[8]

However, use of Cu(II) complexes in C-alkylation has been quite unsuccessful[9] and, in fact, these complexes have been rather used to protect intercarbonyl positions.[5,10]

However, a few examples of successful alkylations of β-dicarbonyl compounds through their Cu(II) complexes have been reported. One of them requires thiouronium salts as alkylating agents and the involved mechanisms are, therefore, probably ionic.[11] Also, copper(II) bis(pentane-2,4-dionato), as well as copper(II) complexes of methyl 3,5-dioxohexanoate and related diketoesters react with benzhydryl bromide to give C-alkylation products.[5]

SCHEME 1

Initiation:

$M^{II}(acac)_2 + 2\ R\text{-}X \longrightarrow 2\ R(acac) + M^{II}X_2$ (Slow process)

$M^{II}X_2 + R\text{-}X \longrightarrow R\cdot + M^{III}X_3$

$R\cdot + M^{II}(acac)_2 \longrightarrow (acac)_2M^{III}R$ (15)

Propagation:

$(acac)_2M^{III}R$ (15) $\longrightarrow (acac)M^{I} + R(acac)$

$(acac)M^{I} + R\text{-}X \longrightarrow (acac)M^{III}XR$

$(acac)M^{III}XR \longrightarrow R(acac) + M^{I}X$

$M^{I}X + R\text{-}X \longrightarrow M^{III}X_2R$

$M^{III}X_2 + M^{II}(acac)_2 \longrightarrow M^{II}X_2 + (acac)_2M^{III}R$

RESULTS

Preparation of highly congested β-diketones

Copper(II) bis(3-methylpentane-2,4-dionato), **1**, reacts with alkyl bromides in concentrated chloroform solutions (> 0.6M) under the conditions specified in Table I, to give disubstituted pentane-2,4-diones **2a-e** (Scheme 2). Diketones **2** are, in general, formed in good yields. Compound **2e** is remarkable in that it has two vicinal quaternary centers. Its conformational analysis has been described elsewhere.[4b] Some side products have been identified. Thus, 3-bromo-3-methylpentane-2,4-dione, **5**, has been isolated in run 3. Copper(II) bromide, a reaction product in the alkylation procedure, has brominating properties on activated positions. Run 5 was performed with 8.6 mmole of **1**. A decrease in yield, down to 5%, was observed when the reaction was scaled up to 34.4 mmole of **1**.

Similar reactions were performed with copper(II) bis(2-methyl-1-phenylbutane-1,3-dionato), **3**, and the results are gathered in Table II. Again, good C-alkylation yields were obtained for several alkyl bromides to afford compounds **4a-d**. Diketone **4e**, bearing an 1-adamantyl radical at the activated intercarbonyl position, could be isolated only in trace amount. The free starting diketone, 2-methyl-1-phenylbutane-1,3-dione, **10**, was, instead, isolated.

Diketone **4c** has slow rotation around sigma bonds as evidenced by the presence of two set of singlets in the PMR spectrum at δ 2.44 and 2.17 and at 2.07 and 1.67. Upon standing, the oily **4c** solidifies and the PMR of the freshly dissolved solid sample presents signals only at δ 2.07 and 1.67.

Bromination of the starting complex ocurred again as shown by the isolation of **6** in runs 1, 2 and 4. The isolation of the demethylated diketones **9c-d** was surprising. They come from demethylation of **4c-d** during the isolation procedure which includes column chromatography through silica gel. This was shown by careful examination (PMR monitoring) of the reaction crudes and by an independent experiment in which a mixture of **4c**, silica gel (Chromagel 60 A CC from "SDS" company) and hexane-dichloromethane (1:1) was left one week at room temperature to afford, after filtration and evaporation, a mixture of **4c** (67%) and **9c** (33%). The steric congestion present in these molecules is probably the reason of this unexpected reactivity.

Further examples of the usefulness of copper(II) complexes of diketones in alkylations leading to sterically congested compounds are exemplified in Scheme 3. Thus, copper(II) bis(3-ethylpentane-2,4-dionato), **11**, (0.8M in chloroform) reacts with 1-bromoadamantane at 100ºC to give 3-(1-adamantyl)-3-ethylpentane-2,4-dione, **12**, in 31% yield. No other products, apart from the starting bromide, were identified. Also, the copper(II) complex of 2,2,6,6-tetramethyl-3,5-heptanedione, **13**, (0.8M in chloroform) reacts with 1-bromoadamantane to give 4-(1-adamantyl)-2,2,6,6-tetramethylheptane-3,5-dione, **14**, in 31% yield. This yield is similar to that obtained in a similar reaction with the cobalt(II) complex in refluxing chlorobenzene.[4c] Other isolated products were 1-adamantanol and the free starting diketone.

<u>Reactions of copper(II) diketonates with benzoyl peroxide</u>

The propagation steps proposed for cobalt(II) mediated alkylations[6] require species of type **15** (M = Co, Cu) (Scheme 1), formed in the last initiation step by radical collapse between the β-diketonate and a carbon free radical. We decided to use oxygen-based radicals speculating with the possibility of isolating **15** (R = oxygen-based radical). It is known that benzoyl peroxide, **17**, adds to metallic copper(0) to give copper(II) benzoate[12] and to copper(I) chloride in the presence of pyridine[8] to give a dinuclear complex of Cu(III) formulated as $[Cu^{III}Cl(OCOPh)_2(Py)_2]_2$. Reactions of $Cu^{I}Cl$ with oxygen radicals to give Cu(II) species have also been reported.[13]

Other precedents of coordination to the copper atom of diketonates, pertinent to our discussion can be found in the reactions of copper β-diketonates with ethyl diazoacetate[14] and with benzaldehyde bis(ethylthio)acetal.[15]

First, we studied the behaviour of $Co(acac)_2$ towards benzoyl peroxide. Isolation of **15** (R = OCOPh) was not possible since reductive elimination was too fast. Similar reactions with copper complex **16** gave better results in terms of final products yields. Therefore, the discussion will deal with the interaction of **16** with **17** (Scheme 4).

The reaction between **16** and **17** was already reported, in conexion with an alternative preparation of caprolactam, to give 3,3-bis(benzoyloxy)pentane-2,4-dione, **19**

TABLE I.- Preparation of products **2** from complex **1** and alkyl bromides.

Run	R	[1][a]	Time	2(%)	Other products (%)
1	$PhCH_2$-	2.15M	50 min	**2a** (80)	-----
2	CH_2=CH-CH_2-	0.86M	2h 15min	**2b** (88)	-----
3	Ph_2CH-	0.86M	2h	**2c** (44)	**5** (18), **7** (17)
4	9-Fluorenyl	0.86M	5h	**2d** (65)	-----
5	1-Adamantyl	0.86M	48h	**2e** (25)	**8** (20)

[a]In terms of solvent volume. No correction has been made for R-Br volume.

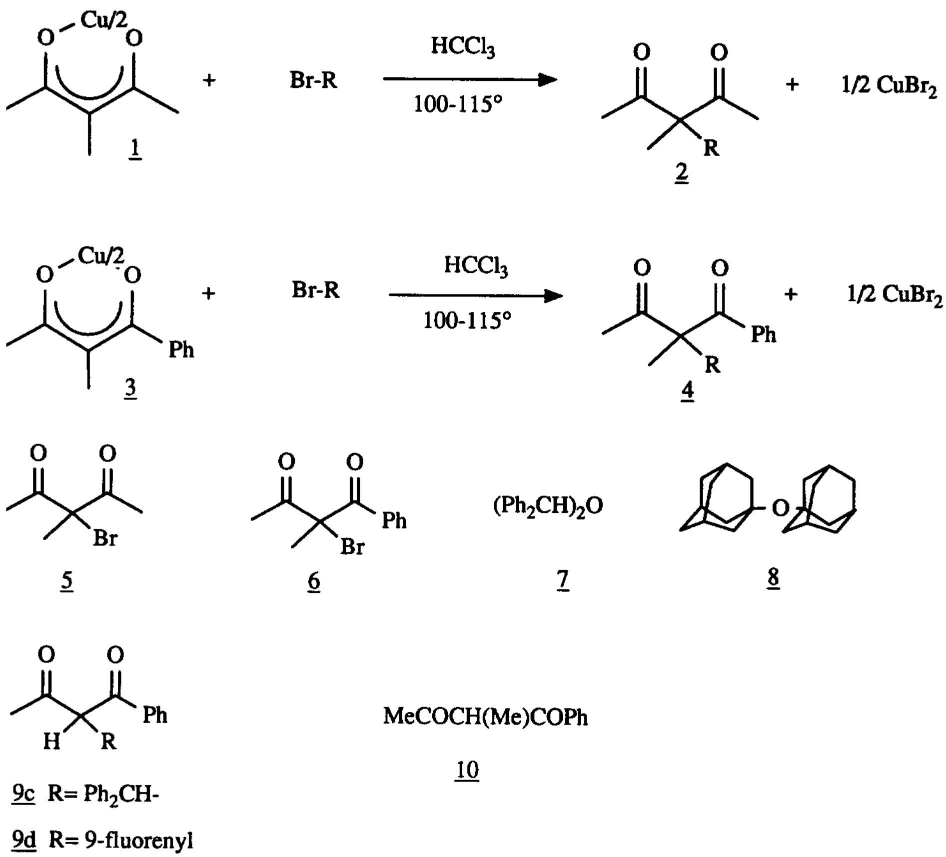
TABLE II.- Preparation of products **4** from complex **3** and alkyl bromides.

Run	R	[3][a]	Time	4(%)	Other products (%)
1	$PhCH_2$-	0.60M	5h	**4a** (43)	**6** (12)
2	CH_2=CH-CH_2-	0.60M	5h	**4b** (30)	**6** (10)
3	Ph_2CH-	0.60M	2h	**4c** (76)	**9c** (11)
4	9-Fluorenyl	0.60M	3h 30min	**4d** (30)	**6** (12), **9d** (3)
5	1-Adamantyl	0.60M	48h	**4e** (1)	**10** (59)

[a]In terms of solvent volume. No correction has been made for R-Br volume.

Table III.- Reactions of copper complexes with **17** in refluxing chloroform.

Run	[Cu(II) complex]	[$(PhCOO)_2$]	18 (%)	19(%)
1	**16** 0.063M	0.126M	(35)	(13)
2	**16** 0.047M	0.188M	(18)	(45)
3	**21** 0.055M	0.110M	----	(76)


Cu/2
O
O
1
+
Br-R
HCCl3
100-115°
O
O
R
2
+
1/2 CuBr2
Cu/2
O
O
Ph
3
+
Br-R
HCCl3
100-115°
O
O
Ph
R
4
+
1/2 CuBr2
O
O
Br
5
O
O
Ph
Br
6
(Ph2CH)2O
7
O
8
O
O
Ph
H
R
9c R= Ph2CH-
9d R= 9-fluorenyl
MeCOCH(Me)COPh
10

SCHEME 2

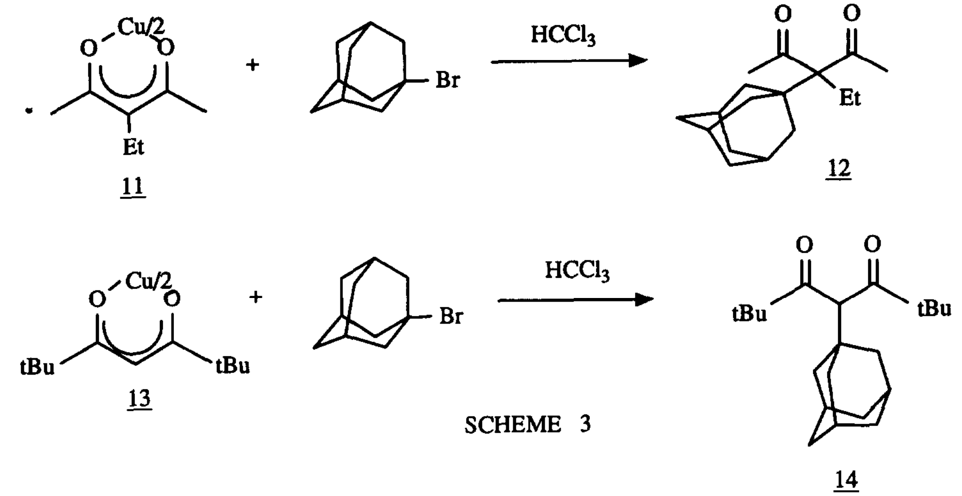
as the only product.[16] We have studied this reaction in more detail and our results are collected in Table III and Scheme 4. Since the presence of free radicals should be facilitated by the nature and the thermal behaviour of **17**, all experiments in Table III were performed at low concentration of reagents. As indicated in run 1, the product of monoreaction, 3-benzoyloxypentane-2,4-dione, **18**, could be isolated in reasonable yields, although product **19** was also formed. Products of double reaction at the activated central position are uncommon in the cobalt(II) and copper(II) mediated C-alkylation chemistry, although not without precedent.[4a] The question raises of the origin of **19**. Free β-dicarbonyl compounds[17], their sodium salts,[18] and their enamines[19] react with peroxides at the activated intercarbonyl positions. This could be the origin of **19**. An alternative explanation is the in situ formation of complex **21** which would react with more **17**. Complex **21** is prepared from diketone **18** and it reacts with **17** in an independent experiment to give **19** in 76% yield (run 3, Table III). Another compound routinely isolated in these reactions is benzoic acid.

Diketone **18** reacts with exccess hydrazine to afford the fully enolic 4-hydroxy-3,5-dimethylpyrazole, **20**.

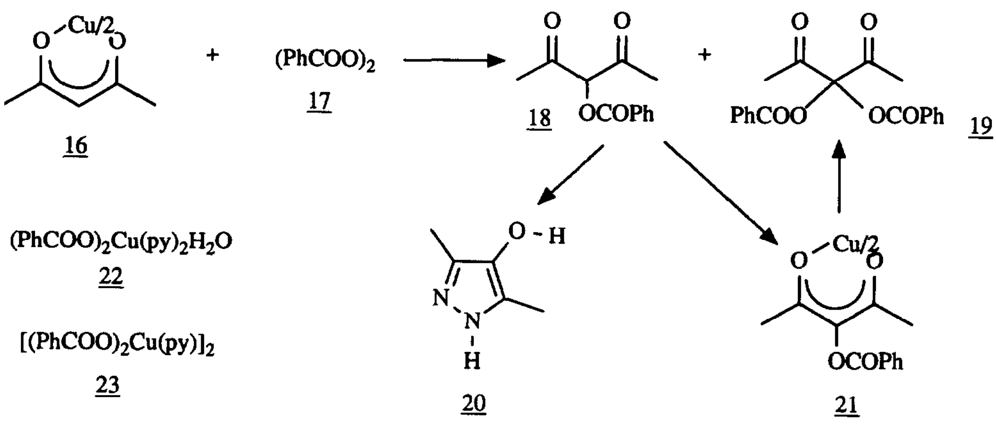
Attempts were made to identify the fate of the copper atom. Thus, in one reaction between **16** and **17**, the final reaction mixture was not partitioned between dichloromethane and aqueous HCl. Instead, the formed precipitate was filtered off and treated with pyridine to give a complex (mp 305-8ºC) whose elemental analysis fits in with molecular formula $C_{24}H_{22}CuN_2O_5$. This corresponds to structure **22**, a copper(II) benzoate complex. A complex of structure **23**, having the same melting point is the product from the reaction of **17** with metallic copper in pyridine.[12] Thus, although structures of type **15**, possessing Cu^{III} atoms have not been isolated, the formation of **22** indicates that free radicals attack to the metal atom in one step of the mechanism.

Since both free β-dicarbonyl compounds[17] and complex **16** react with peroxides, we studied the reaction of **17** with complex **24** which bears both a free activated position and a copper complexed diketone moiety. Complex **24** has been used for regioselective alkylation at position C2 under ionic conditions.[5,10] This means that copper complexation is a good protection technique for the intercarbonyl position in typical ionic reactions. However, **24** also reacts with benzhydryl bromide at C4 in a reaction assumed to take place by our proposed chain mechanism.[5]

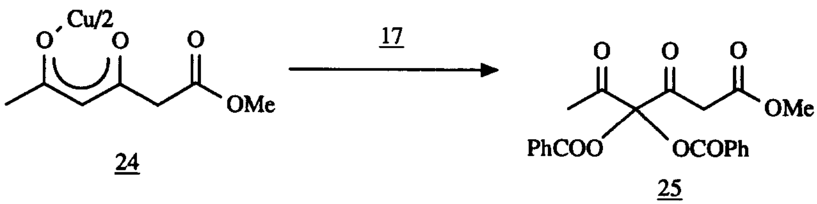
The reaction between complex **24** and peroxide **17** (Scheme 5) produced 20% yield of a single compound: methyl 4,4-bis(benzoyloxy)-3,5-dioxohexanoate, **25**. The proton coupled CMR spectrum permits unambiguous assignment of structure **25** (Table IV). Thus, both ketone carbon atoms give signals at 198.28 (quartet) and 193.94 (triplet), indicating double substitution at C4. The signal of C1 appears as a triplet at 163.88, indicating that C2 is unsubstituted.



SCHEME 3



SCHEME 4



SCHEME 5

TABLE IV.- CMR Spectrum of **25** (δ values).

C1	163.88 (t, J = 4.1Hz with H_2 at C2)
C2	45.77 (t, J = 131.7Hz with H_2 at C2)
C3	193.94 (t, J = 7.6Hz with H_2 at C2)
C4	97.88 (s)
C5	198.28 (q, J = 6.4Hz with H_3 at C6)
C6	26.58 (q, J = 128.7Hz with H_3 at C6)
MeO	52.35 (q, J = 146.5Hz)
PhCO	166.07 (m)

CONCLUSION

Copper(II) complexes of β-dicarbonyl compounds react through radical initiated reactions at the intercarbonyl position. However, copper(II) complexes are quite inert under standard ionic conditions and useful, in such cases, to protect the intercarbonyl position.

EXPERIMENTAL

PMR and CMR spectra were registered at 80 and 20Mz, respectively. Mass spectra were recorded at 70eV. Bp's refer to oven temperatures. Mp's are uncorrected.

2-methyl-1-phenylbutane-1,3-dione

This diketone is prepared by reaction of 1-phenylbutane-1,3-dione with methyl iodide in refluxing acetone and in the presence of potassium carbonate, according to a described procedure.[20]

Copper(II) bis(3-methylpentane-2,4-dionato), **1.**

A solution of 3-methylpentane-2,4-dione (5.00 g, 44 mmole) in methanol (5 ml) is slowly added upon a stirred, ice-cooled, solution of copper(II) acetate monohydrate (4.37 g, 22 mmole) in water (70 ml) and methanol (7 ml). A precipitate is immediately formed. The mixture is stirred for 3 h at room temperature and filtered. The precipitate is washed with water and dried at 80ºC to afford 3.70 g (60%) of **1**; mp 180ºC; IR(KBr): 1576 cm^{-1}.

Copper(II) bis(2-methyl-1-phenylbutane-1,3-dionato), **3.**

Complex **3** is prepared in 72% yield from 2-methyl-1-phenylbutane-1,3-dione by the same procedure as **1**. Compound **3** has mp 192-4ºC; IR(KBr): 1580 cm^{-1}.

Copper(II) bis(3-ethylpentane-2,4-dionato), 11.
3-Ethylpentane-2,4-dione is prepared by reaction of pentane-2,4-dione with ethyl bromide in refluxing acetone and in the presence of potassium carbonate. The resulting mixture contains 3,3-diethylpentane-2,4-dione and is treated directly with copper(II) acetate monohydrate as for preparation of 1. Complex 11 has mp 189-191ºC (Lit.[21] mp 190ºC); IR(KBr): 1571, 1525 cm^{-1}.
Copper(II) bis(2,2,6,6-tetramethylheptane-3,5-dionato), 13.
Complex 13 is prepared in 67% yield from 2,2,6,6-tetramethylheptane-3,5-dione by the same procedure as 1. Compound 13 has mp 198º (Lit.[22] mp 198ºC); IR(KBr): 1594, 1567 cm^{-1}.
3-Benzyl-3-methylpentane-2,4-dione, 2a.
A mixture of complex 1 (2.50 g, 8.6 mmole), benzyl bromide (2.94 g, 17.2 mmole) and ethanol-free chloroform (4 ml) is introduced in a 25 ml closed reactor and heated at 115ºC for 50 min. The solution changes from green to yellowish and a white precipitate appears. After cooling, the mixture is diluted with dichloromethane (250 ml). The organic layer is washed with 1N HCl (3 x 100 ml), dried with sodium sulphate and evaporated. The residue is distilled to afford 2a (2.81 g, 80%). Bp 94-6ºC/0.05mmHg (Lit.[23] bp 125-132ºC/3mmHg); IR(film): 1718, 1697 cm^{-1}; PMR($CDCl_3$): δ 1.2 (s, 3H), 2.0 (s, 6H), 3.1 (s, 2H), 7.1 (m, 5H); CMR($CDCl_3$): δ 17.6, 26.4, 39.6, 66.5, 126.1, 127.6, 129.5, 136.0, 206.0.

The rest of compounds 2 and 4 are prepared by the same procedure as 2a under the conditions specified in Tables I and II. Runs 3, 4 and 5 of Table I and all runs of Table II require column chromatography on silica gel.
3-Allyl-3-methylpentane-2,4-dione, 2b.
This compound is known.[23] PMR($CDCl_3$): δ 1.4 (s, 3H), 2.1 (s, 6H), 2.6 (d, J = 8.0Hz, 2H), 4.9-5.3 (m, 2H), 5.4-5.8 (m, 1H).
Bis(2,4-dinitrophenylhydrazone) of 2b: mp 228-230ºC; IR(KBr):3328, 1618, 1590, 1511, 1336 cm^{-1}; PMR($CDCl_3$): δ 1.53 (s, 3H), 2.06 (s, 6H), 2.85 (d, J = 8.0Hz, 2H), 5.0-5.4 (m, 2H), 5.5-6.0 (m, 1H), 8.00 (d, J = 10Hz, 2H), 8.40 (dd, J = 10 and 3Hz, 2H), 9.18 (d, J = 3Hz, 2H), 11.1 (broad s, 2H).
Calculated for $C_{21}H_{22}N_8O_8$: C, 49.03; H, 4.31; N, 21.78. Found: C, 48.57; H, 4.17; N, 21.69.
3-Benzhydryl-3-methylpentane-2,4-dione, 2c.
Mp 81-82ºC; IR(KBr): 1695 cm^{-1}; PMR($CDCl_3$): δ 1.6 (s, 3H), 2.0 (s, 6H), 5.8 (s, 1H), 7.2 (m, 10H); CMR($CDCl_3$): δ 16.8, 26.8, 52.4, 72.8, 126.6, 128.3, 129.7, 141.1, 205.9.
Calculated for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.05; H, 7.30.
3-(9-Fluorenyl)-3-methylpentane-2,4-dione, 2d.
Mp 64-66ºC; IR(KBr): 1723, 1691 cm^{-1}; PMR($CDCl_3$): δ 0.79 (s, 3H), 2.36 (s, 6H), 5.30 (s, 1H), 7.33 (m, 6H), 7.76 (m, 2H); CMR($CDCl_3$): δ 12.8, 27.7, 50.9, 71.3, 119.7, 125.0, 127.0, 127.6, 141.7, 143.0, 206.2.
Calculated for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 81.56; H, 6.73.
3-(1-Adamantyl)-3-methylpentane-2,4-dione, 2e.
Mp 88-90ºC; IR(KBr): 1714, 1689 cm^{-1}; PMR($CDCl_3$): δ 1.43 (s, 3H), 1.59-2.07 (m, 15H), 2.14 (s, 6H); CMR($CDCl_3$): δ 16.4, 28.8, 30.6, 36.8, 36.9, 39.7, 70.3, 208.4.
Calculated for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.17; H, 10.05.
2-Benzyl-2-methyl-1-phenylbutane-1,3-dione, 4a.
Mp 103-104ºC (Lit.[24] mp 96.5-97ºC); IR(KBr): 1708, 1667 cm^{-1}; PMR($CDCl_3$): δ 1.4 (s, 3H), 2.1 (s, 3H), 3.4 (center of an AB system, 2H), 6.9 (m, 2H), 7.2 (m, 3H), 7.5 (m, 3H), 7.8 (m, 2H); CMR($CDCl_3$): δ 20.2, 27.4, 41.1, 65.7, 126.6, 127.9, 128.6, 128.8, 130.2, 132.8, 136.1, 136.2, 198.5, 207.3.
3-Benzoyl-3-methyl-5-hexen-2-one, 4b.
Bp 220-225ºC/15mmHg (Lit.[24] bp 95-105ºC/0.5-0.6mmHg); IR(film): 1713, 1675 cm^{-1}; PMR($CDCl_3$): δ 1.49 (s, 3H), 2.09 (s, 3H), 2.79 (d, J = 7.0Hz, 2H), 4.85-5.15 (m, 2H), 5.25-5.91 (m, 1H), 7.49 (m, 3H), 7.82 (m, 2H).
2-Benzhydryl-2-methyl-1-phenyl-1,3-butanedione, 4c.
Low melting solid; IR(KBr): 1713, 1660 cm^{-1}. See Results section for a discussion of the PMR of 4c.
Calculated for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48. Found: C, 83.79; H, 6.56.
2-(9-Fluorenyl)-2-methyl-1-phenylbutane-1,3-dione, 4d.
Mp 136-138ºC; IR(KBr): 1716, 1667 cm^{-1}; PMR($CDCl_3$): δ 0.76 (s, 3H), 2.31 (s, 3H), 5.46 (s, 1H), 7.05-7.88 (m, 13H); CMR($CDCl_3$): δ 15.2, 28.0, 51.2, 70.3, 119.6, 125.7, 126.0,

126.8, 126.9, 127.6, 127.7, 128.6, 132.5, 137.8, 142.0, 142.8, 200.2, 206.5.
Calculated for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.22; H, 5.90.

2-(1-Adamantyl)-2-methyl-1-phenylbutane-1,3-dione, **4e**.
Mp 82-84ºC; IR(KBr): 1718, 1652 cm^{-1}; PMR($CDCl_3$): δ 1.55 (s, 3H), 1.62-2.10 (m, 15H), 2.15 (s, 3H), 7.44 (m, 3H), 7.70 (m, 2H); MS(m/e): 310(M^+, 10), 135(28), 105(39), 77(65), 43(100).

3-Bromo-3-methylpentane-2,4-dione, **5**.
Bp 80-85ºC/14mmHg (Lit.[25] bp 63-64ºC/11mmHg); PMR($CDCl_3$): δ 1.94 (s, 3H), 2.43 (s, 6H).

2-Bromo-2-methyl-1-phenylbutane-1,3-dione, **6**.
Bp 204-208ºC/15mmHg; IR(film): 1724, 1708, 1686 cm^{-1}; PMR($CDCl_3$): δ 2.15 (s, 3H), 2.44 (s, 3H), 7.49 (m, 3H), 7.97 (m, 2H); CMR($CDCl_3$): δ 26.0, 26.2, 69.0, 128.5, 129.8, 133.5, 191.7, 200.5.

Di-(1-adamantyl) ether, **8**.
Mp 177-181ºC (Lit.[26] mp 179-182ºC); MS(m/e): 286(M^+, 4), 135(100), 93(30), 79(42), 67(31), 55(23), 41(39).

2-Benzhydryl-1-phenylbutane-1,3-dione, **9c**.
Mp 148-151ºC (Lit.[27] mp 149-150ºC). Compared with an authentical sample.

2-(9-Fluorenyl)-1-phenylbutane-1,3-dione, **9d**.
Mp 104ºC (Lit.[3d] mp 97-99ºC). Compared with an authentical sample.

3-(1-Adamantyl)-3-ethylpentane-2,4-dione, **12**.
It is prepared by the same procedure as **2a** from **11** (1.5 g, 4.87 mmole), and 1-bromoadamantane (2.1 g, 9.8 mmole) in ethanol-free chloroform (6 ml) upon heating in a closed reactor at 100ºC for 18 h (PMR monitoring). Diketone **12** is isolated in 31% yield after column chromatography. Mp 76-77ºC; IR(KBr): 1714, 1680 cm^{-1}; PMR($CDCl_3$): δ 0.85 (t, J = 6.7Hz, 3H), 1.60-2.15 (m, 15H), 2.05 (q, J = 6.7Hz, 2H), 2.10 (s, 6H); CMR($CDCl_3$): δ 11.0, 23.0, 28.9, 32.7, 36.7, 37.8, 46.6, 75.5, 209.5.
Calculated for $C_{17}H_{26}O_2$: C, 77.82; H, 9.98. Found: C, 77.87; H, 10.14.

4-(1-Adamantyl)-2,2,6,6-tetramethylheptane-3,5-dione, **14**.
It is prepared by the same procedure as **2a** from **13** (3.7 g, 8.6 mmole) and 1-bromoadamantane (3.70 g, 8.6 mmole) in ethanol free chloroform (10 ml) upon heating at 100ºC for 6 days and at 160ºC for 5 more days (PMR monitoring). Diketone **14** is isolated in 31% yield after column chromatography. Mp 140-1ºC (Lit.[3c] mp 141-142ºC). It was compared with authentical sample. Other isolated compounds were 1-adamantanol and the free starting diketone.

3-Benzoyloxypentane-2,4-dione, **18**, 3,3-bis(benzoyloxy)pentane-2,4-dione, **19** and complex **22**.
A solution of benzoyl peroxide (3.70 g, 15.2 mmole) in ethanol-free chloroform (40 ml) is added over a boiling suspension of copper(II) bis(pentane-2,4-dionato) (2.00 g, 7.6 mmole) in ethanol-free chloroform (80 ml). The solution was refluxed for 24 h. After cooling the solution was washed with 1N HCl (2 x 50 ml) and with saturated aqueous solution of sodium hydrogenocarbonate (2 x 50 ml). The organic layer was dried with sodium sulphate, filtered and evaporated. The residue was treated with carbon tetrachloride to afford a white precipitate (273 mg) of **19**. The filtrate is evaporated and the residue is chromatographed through silica gel using a mixture of hexane-dichloromethane (1:4) as eluent. Benzoic acid and diketones **19** (35% overall) and **18** (13%)are eluted in the indicated order.

Diketone **18**: bp 162ºC/0.2mmHg; IR(film): 1721 cm^{-1}; PMR($CDCl_3$): δ keto form, 2.3 (s, 6H), 5.7 (s, 1H), 7.5 (m, 3H), 8.1 (m, 2H), enol form, 2.0 (s, 6H), 7.5 (m, 3H), 8.1 (m, 2H), 14.5 (broad s, 1H); CMR($CDCl_3$): δ keto + enol forms, 20.4, 27.1, 84.9, 128.0, 128.4, 128.6, 129.7, 129.9, 133.6, 133.8, 164.6, 164.8, 184.6, 198.7; MS(m/e): 178(11), 105(100), 77(37).
Calculated for $C_{12}H_{12}O_4$: C, 65.45; H, 5.49. Found: C, 65.52; H, 5.43.

Diketone **19**: mp 143-143.5ºC; IR(KBr): 1745, 1724 cm^{-1}; PMR($CDCl_3$): δ 2.73 (s, 6H), 7.6 (m, 6H), 8.1 (m, 4H): CMR($CDCl_3$): δ 26.6, 98.2, 127.9, 128.7, 130.1, 134.2, 164.0, 199.3; MS (m/e): 269(3), 114(10), 105(100), 77(32).
Calculated for $C_{19}H_{16}O_6$: C, 67.05; H, 4.74. Found: C, 66.84; H, 4.71.

The residue (100 mg) of a reaction between **16** and **17** is taken up in dichloromethane and pyridine (2 ml) is added to that solution. A solid is formed upon evaporation, mp 305-308ºC; IR(KBr): 1605, 1599 cm^{-1}.
Calculated for $C_{24}H_{22}CuN_2O_5$: C, 59.08; H, 4.60; N, 5.81. Found: C, 59.42; H, 4.51; N, 5.73.

Copper(II) bis(3-benzoyloxypentane-2,4-dionato), **21.**
Complex **21** is prepared in 77% yield from **18** by the same procedure as **1**. Compound **21** has mp 200-210(d)ºC; IR(KBr): 1734, 1586 cm^{-1}.
Calculated for $C_{24}H_{22}CuO_8$: C, 57.43; H, 4.42. Found: C, 57.20; H, 4.35.

4-Hydroxy-3,5-dimethylpyrazole, **20.**
80% aqueous hydrazine (0.05 ml) is added to a solution of **18** (0.29 g, 1.3 mmole) in ethanol (2 ml). The solution is kept 1 h at room temperature. Upon cooling at 0ºC a solid is formed. it is filtered off to afford **20** (96 mg, 66%); mp 174-176ºC (Lit.[28] mp 173.5ºC; 3400-2300(broad with a sharp peak at 3255), 1230 cm^{-1}; PMR($CDCl_3$): δ 2.12 (s, 6H).

Methyl 4,4-Bis(benzoyloxy)-3,5-dioxohexanoate, **25.**
A solution of benzoyl peroxide (5.13 g, 21.1 mmole) in ethanol free chloroform (40 ml) is added into a suspension of copper(II) complex of methyl 3,5-dioxohexanoate (2.00 g, 5.3 mmole), prepared according to a known procedure,[5] in the same solvent (40 ml). The mixture was refluxed under argon atmosphere for 77 h. The mixture is partitioned between chloroform and 1N HCl (3 x 100 ml). The organic layer is washed with saturated solution of sodium hydrogenocarbonate, dried with anhydrous sodium sulphate and evaporated. The residue is chromatographed through a silica gel column with hexane-dichloromethane (1:4) as eluent. Compound **25** (855 mg, 20%) had mp 110-112ºC; IR(KBr): 1759, 1729 cm^{-1}; PMR($CDCl_3$): δ 2.72 (s, 3H), 3.80 (s, 3H), 4.19 (s, 2H), 7.55 (m, 6H), 8.11 (m, 4H); CMR($CDCl_3$): see Results Section for a discussion on this spectrum; MS(m/e): 172(5), 105(100), 77(27).
Calculated for $C_{21}H_{18}O_2$: C, 63.32; H, 4.55. Found: C, 62.43; H. 4.55.

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