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A Study on the Mechanism and Scope of the Radical-mediated Oxidation of Arylacetoacetates

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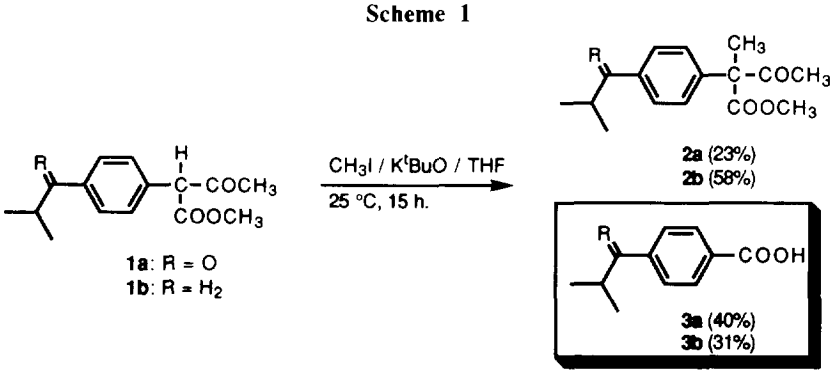
Abstract: Arylacetoacetate **1a** undergoes an oxidative degradation in the presence of K^{t}BuO, THF, catalytic I_2 and O_2, to give keto ester **4** as major compound. Hydrolysis and decarboxylation of this intermediate led to the corresponding arylcarboxylic acid **3a** in satisfactory overall yields. By experiments conducted in the presence of $^{18}O_2$, incorporation of atmosphere oxygen into the benzylic position of **4** was evidenced. Furthermore, spin-trap experiments showed that benzyl radical **7** was generated in the reaction medium, which supports its role as intermediate in the pathway leading to the observed oxidation products. A plausible mechanism for this process is presented. On the other hand, appropriate conditions for achieving the alkylation of these arylacetoacetates with no concomitant formation of oxidation side-products are reported. Finally, arylacetates suffer also this degradative oxidation process leading to the corresponding arylcarboxylic acids without isolation of the intermediate keto ester derivative.

Recently we reported a study on the arylation of ß-dicarbonyl compounds (methyl acetoacetate and dimethyl malonate) as an extension of the photochemical decomposition reaction of arylazosulfides developed by Erba et al. [1] Our objective was the preparation of 2-arylpropionic acid isotopomers of pharmaceutical interest. For this purpose, the arylated ß-dicarbonyl compound obtained was subjected to methylation and further hydrolytic cleavage to give, for the case of the malonate derived adducts, the expected 2-arylpropionic acids in good overall yields. [2] However, different results were obtained when the methylation, which was usually performed using a mixture of CH_3I and K^{t}BuO in THF, was assayed on arylacetoacetates **1**. Reaction rates were slow, the conversions into the methylated compounds **2** were not satisfactory and the formation of unexpected products was observed. Thus, the analysis of the crude reaction mixture obtained after an aqueous acid workup treatment, showed the presence of arylcarboxylic acids **3** in moderate yields (Scheme 1).

Scheme 1



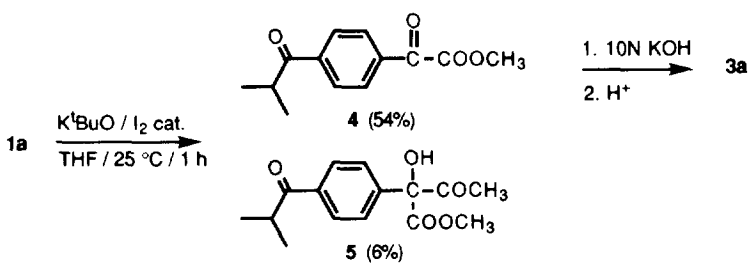
Formation of these acids, which could be envisaged as a formal degradative oxidation of arylacetoacetate **1**, called our attention. Up to our present knowledge, no references related to this conversion had been reported heretofore, although the mixture K^{t}BuO-THF-O_2 has been involved in the oxidation of different substrates, such as tocopherol derivatives. [3] Moreover, DiBiase et al. reported that treatment of arylalkylnitriles under the above conditions led to the isolation of arylcarboxylic acids. [4] This paper constitutes the closest example to our observations found in the literature, although mechanistic studies were not carried out and its extension to other substrates was not further explored.

The present paper reports our results on the formal oxidative degradation suffered by model arylacetoacetates under basic conditions and in the presence of oxygen. From the experiments carried out by using labelled reagents and ESR techniques a suitable pathway for this process is proposed. Finally, its synthetic scope is also explored.

Results and Discussion

Study of the Oxidation. Initially, it was anticipated that oxygen gas was required for this oxidation to proceed and that the overall process might involve the intervention of radical intermediates. If this was the case, the free iodine present in the methyl iodide used for the methylation assays described above might had been operating as radical initiator. To corroborate this hypothesis, acetoacetate **1a** was treated with K^{t}BuO (one molar equivalent) in THF in the presence of 10% molar equivalents of iodine for 1 h at 25 °C in an oxygen atmosphere. A rapid reaction occurred but no arylcarboxylic acid **3a** was detected; instead, keto ester **4** and alcohol **5** were obtained in 54 and 6% yield, respectively (Scheme 2). These compounds did not exhibit interconversion under the above reaction conditions, which indicated that they were formed by independent pathways. On the other hand, further treatment of keto ester **4** with aqueous base followed by acidification led to the isolation of acid **3a** in 78% yield, which suggested the participation of **4** as intermediate in the oxidation pathway. The lability exhibited by keto ester **4** towards hydrolytic conditions might explain that long reaction times such as those employed in the methylation reaction had caused its final conversion into **3a**, which was the product isolated in that case.

Scheme 2



Once the intervention of keto ester **4** in the oxidation reaction was evidenced, our efforts were directed towards rationalizing its formation. To this aim, several assays were carried out and initial results obtained are shown in Table 1. As seen, when iodine was absent (entry 1) or base/solvent combinations different from K^{t}BuO/THF were used (entries 4-6), the starting acetoacetate remained essentially unaltered and only minor

amounts of methyl 4-isobutyrylphenylacetate (**6**), the product originated from an expected evolution of **1a** under basic conditions, were detected. Use of diethyl ether as solvent required the addition of an equimolecular amount of iodine for obtaining the oxidized products (entry 7). These results suggested the participation of anionic species in the oxidation process, which might be stabilized by highly polar solvents such as THF. It is worth of noting that treatment of phenylacetate **6** under the conditions depicted in Scheme 2 did not afford keto ester **4**; instead, the direct formation of acid **3a** was observed. Finally, complementary assays performed by using the K^{t}BuO/DME system afforded the expected oxidation products working at 25 °C, but the reaction was completely inhibited at 0 °C. The potential synthetic implications of these findings are discussed below.

Table 1: Oxidation Assays of Arylacetoacetate **1a**.

Entry	Base[a]	Iodine[b]	Solvent	Products (%)[d]
1	K^{t}BuO	-	THF	**1a** + **6** (90:10)
2	K^{t}BuO	+	THF	**1a** + **4** + **5** (9:82:9)
3	$NaOCH_3$	+	THF	**1a**
4	NaH	+	THF	**1a** + **6** (92:8)
5	K^{t}BuO	+	hexane	**1a** + **6** (98:2)
6	K^{t}BuO	+	EtOEt	**1a** + **6** (98:2)
7	K^{t}BuO	+[c]	EtOEt	**1a** + **4** + **5** (7:67:26)
8	K^{t}BuO	+	THF	**1a** + **4** + **5** (10:76:14)[e]

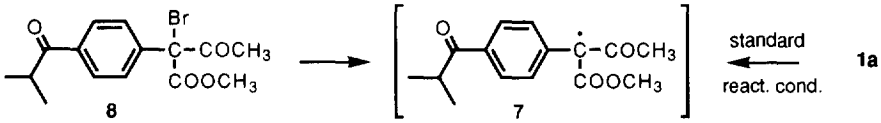
[a] 1.2 Molar equivalents of base were used and assays were carried out in oxygen atmosphere at 25 °C. [b] Unless indicated otherwise 0.015 equivalents of a 3.9 10^{-2} M iodine solution were used. [c] 1 Molar equivalent. [d] Product percentages were calculated by GC analysis of an aliquote after 1h reaction and are shown in parentheses. [e] Assay performed in the dark.

To verify the intervention of oxygen gas in the oxidation reaction, acetoacetate **1a** was treated with the K^{t}BuO/THF mixture and a catalytic amount of iodine under argon atmosphere. Once it was confirmed that **1a** remained unaltered after 1 h at 25 °C, an $^{18}O_2$ atmosphere was introduced into the reaction vessel. The analysis by mass spectrometry of an aliquote after 1 h at the same temperature, which was poured into the minimum amount of water to avoid solvent exchange, [5] revealed the presence of compounds **4** and **5** labelled with ^{18}O. Thus, mass spectrum of **4** showed additional peaks at m/z 236, 193 and 177, which corresponded to the ^{18}O enriched peaks for the molecular peak M^+, and for the fragments $[M - 42]^+$ and $[M - 59]^+$ (base peak). Likewise, mass spectrum of alcohol **5** showed the isotopic characteristic peaks at m/z 280, 237 and 205 (cf. Experimental section). On the other hand, the fact that neither keto ester **4** nor alcohol **5** were detected when the reaction was assayed by using equimolecular amounts of *tert*-butyl or tetrahydrofuran-2-yl hydroperoxide under argon atmosphere discarded the intervention of ^{t}BuOH or THF in the oxygen activation process.

Concerning the participation of a radical species derived from acetoacetate **1a** in the oxidative process, we deemed that benzyl radical **7** might be a feasible candidate (Scheme 3). This intermediate could be generated under the reaction conditions, *i.e.*, by oxidation of the carbanion derived from **1a**, and it should be stable enough to react with oxygen leading to the formation of compounds **4** and **5**. In order to corroborate this hypothesis we devised a strategy involving the independent preparation of radical **7** from a suitable precursor, such as bromoacetoacetate **8**, and its detection by ESR by using a spin trap agent. The comparison of the spectroscopic

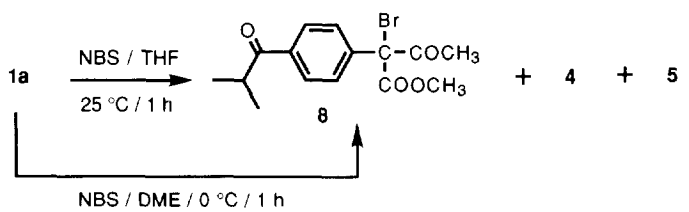
features exhibited by **7** with those eventually obtained from the treatment of **1a** under the oxidation conditions in the ESR probe would permit to confirm the intervention of the postulated benzyl radical in the oxidative process (Scheme 3).

Scheme 3

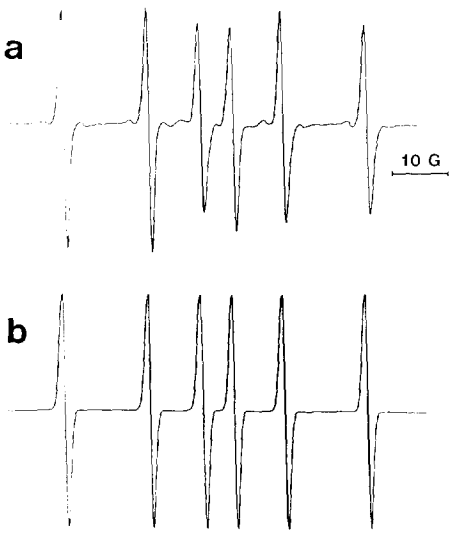


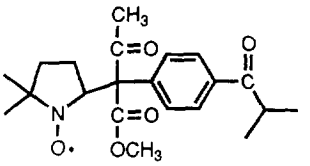
Accordingly, preparation of bromoacetoacetate **8** was attempted. Treatment of **1a** with NBS in THF for 1 h at 25 °C led to the formation of the expected bromoderivative **8** but accompanied by compounds **4** and **5** in a 46:41:13 ratio (GC). This result indicated that formation of **4** and **5** must involve radical intermediates, since under the above reaction conditions the intervention of anionic species was hardly conceivable. On the other hand, as anticipated, the oxidative processes were inhibited by performing the bromination at 0 °C in DME, which enabled the preparation of the desired bromoderivative **8** in satisfactory yields (Scheme 4).

Scheme 4



Irradiation of a benzene solution of bromoderivative **8** did not show detectable signals by ESR. However, when the experiment was performed in the presence of DMPO as spin trap, a spectrum consistent with the formation of the expected nitroxide adduct **9** was observed (Figure 1). As shown, a doublet of triplets (g = 2.0057, and peak to peak linewidth, ΔH_{pp} = 0.96G) with the expected coupling constant values (a_N = 14.38 G, $a_{H\beta}$ = 23.31 G) for the capture of a tertiary carbon centered radical were obtained. The high value for the coupling constant with H_β suggests that this hydrogen atom is eclipsed with respect to the *p* nitrogen orbital ($\phi \approx 0$). [6] Furthermore, when a mixture of arylacetoacetate **1a**, K^{t}BuO, iodine and DMPO in THF (in the molar ratios used for the oxidation experiments) was monitored by ESR at 25 °C, a weak absorption corresponding to the nitroxide adduct **9** was observed; this absorption increased considerably after UV irradiation. The detection of **9** indicated that radical species **7** was an intermediate generated during the oxidation process.





9

Figure 1. a) ESR spectrum of spin adduct **9** in THF solution at 20 °C, and b) its computer simulation using the splitting constants given in the text. For ESR registering and computer simulation conditions, see Esperimental part.

All these results led to postulate a plausible pathway for the conversion of arylacetoacetate **1a** into keto ester **4** and alcohol **5** (Scheme 5). Thus, K^{t}BuO would generate the anionic intermediate **I**. Oxidation of this intermediate by the iodine present in the reaction medium (or eventually by oxygen itself) would lead to the formation of radical species **II** (i.e., **7** for the case of arylacetoacetate **1a**). The formation of this intermediate has been supported by the ESR experiments described above. Reaction of **II** with molecular oxygen would afford peroxyl radical **III**, which could react with hydrogen atom to give hydroperoxide **IV**. Homolysis of this intermediate would give alcohol **5**. On the other hand, peroxyl radical **III** could undergo a monoelectron transfer with anion **I** (a species prone to be oxidized) to afford the peroxyl anionic species **V**, which could generate keto ester **4** through the oxetane intermediate **VI**. An alternative to the formation of anion **V** could be the deprotonation of hydroperoxide **IV**. However, the sole intervention of this process would demand a second equivalent of base, which is not required. Moreover, the participation of anionic species **I** in the electron transfer with **III** would account for the catalytic role of iodine, since once the reaction has been initiated, benzyl intermediate **II** would be generated from the interaction of **I** with **III**.

Scope of the Oxidation. We were also interested in studying the scope of this oxidative process. As mentioned in the introduction, the formation of an arylcarboxylic acid was observed during the methylation attempted on arylacetate **1b**, which presents an isobutyl substituent in the *para* position. This result suggested that the oxidative degradation could also take place in arylacetoacetates lacking of electron withdrawal substituents in the aromatic ring. On the other hand, this study was completed by employing two additional arylacetoacetates, *i.e.*, **10p** and **10m**, which contain an aromatic ring bearing an acetyl group in the *para* and *meta* positions, respectively, with respect to the acetoacetate moiety. In addition, alkylacetoacetate **11** was also assayed. Results obtained on the oxidative degradation of these acetoacetates by using the standard procedure are shown in Table 2.

Scheme 5

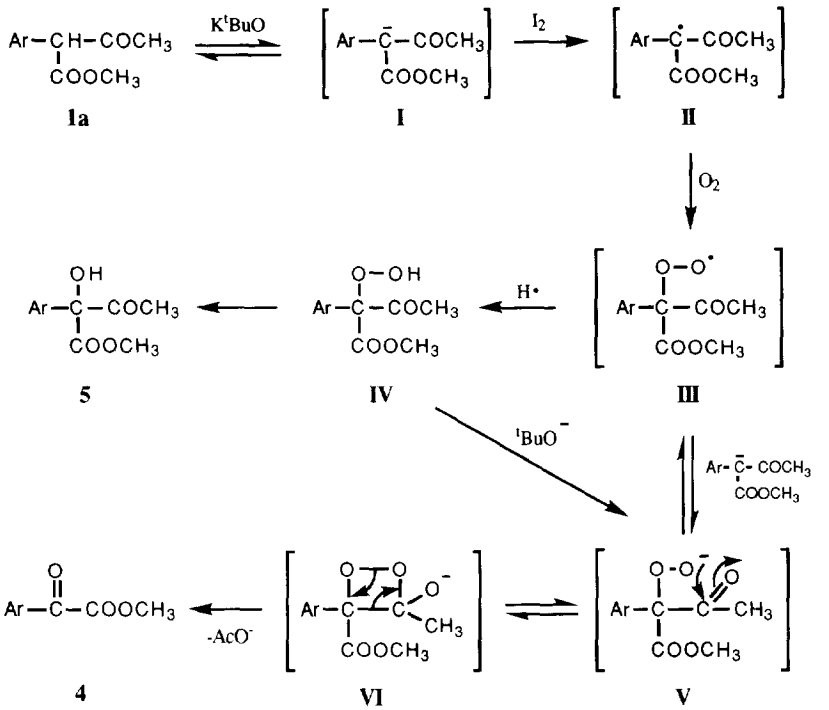


Table 2: Oxidation Assays on Arylacetoacetates **10p** and **10m**, Alkylacetoacetate **11** and Arylacetates **6** and **15** [a].

Substrate	Products	
	Keto ester	Other
*p*AcArCH(COMe)CO_2Me (**10p**)	*p*AcArCOCO$_2$Me (**12p**) (47%)	*p*AcArCOH(COMe)CO_2Me (**13p**) (8%)
*m*AcArCH(COMe)CO_2Me (**10m**)	*m*AcArCOCO$_2$Me (**12m**) (52%)	*m*AcArCOH(COMe)CO_2Me (**13m**) (10%)
C_7H_{15}CH(COMe)CO_2Me (**11**)	C_7H_{15}COCO$_2$Me (**14**) (23%) [b]	$C_7H_{15}CO_2H$ (18%) [a]
p(Me$_2$CHCO)ArCH$_2$CO$_2$Me (**6**)		*p*(Me$_2$CHCO)ArCO$_2$H (**3a**) (75%)
ArCH$_2$CO$_2$Me (**15**)		ArCO$_2$H (85%)

[a] Reaction conditions for oxidation of **10p**, **10m** or **11**: 1:1.2:0.001 ester:K^{t}BuO:iodine molar ratio in THF in an oxygen atmosphere for 1 h at 25 °C. For arylacetates **6** and **15** similar conditions were used, with the exception of iodine addition; reaction times were also shortened to 15 min. [b] Conversion yields determined by GC. A 54% of starting compound **11** remained unaltered.

As seen, arylacetoacetates **10p** and **10m** gave similar results in terms of conversion yields and products to those obtained for arylacetoacetate **1a**. Thus, the corresponding keto ester was the major compound obtained from the oxidation reaction and a small amount of the respective hydroxyester was also isolated. It is noteworthy that this route might constitute a useful synthetic procedure for the preparation of 3-acylbenzoic acids, which are not easily available compounds. [7] Conversely, the oxidation assay on alkylacetoacetate **11** was far from being completed under the standard reaction conditions assayed; however, a mixture of the corresponding keto ester and the carboxylic acid resulting from the oxidative degradation was present in an overall 40% conversion yield.

Table 2 shows also the results obtained from the oxidation assays performed on two arylacetates, namely **6** and **15**. As seen, good yields of the respective arylcarboxylic acids, *i.e.*, *p*-isobutyrylbenzoic acid and benzoic acid, were obtained. In these cases, however, no intermediate keto esters were detected. Furthermore, preliminary assays on the oxidative degradation of arylacetate **6** carried out in the ESR probe in the presence of DMPO as spin-trap showed the formation of spin-adducts of the nitroxide type, although the spectra obtained were not so clean as in the case of arylacetoacetate **1a** (*vide supra*). The fact that the oxidation of the benzylic carbon atom of **6** requires the elimination of two hydrogen atoms probably results in a more complicated reaction pathway, which could give rise to more than one radical species prone to be captured by the spin-trap. In any case, these results suggest that the oxidative degradation of arylacetates in the presence of K^{t}BuO, THF and O_2 occurs also by intervention of radical intermediates.

A final remark. It is unquestionable that acetoacetates have demonstrated to be very useful synthetic tools for organic chemists. Under the classical approach, they are susceptible of alkylation [8] and arylation [2] at the methylene carbon atom and the C-substituted acetoacetates obtained may afford methyl ketones or carboxylic acids, depending upon the final treatment of the crude reaction mixture. The results reported herein extend the potential application of these versatile intermediates, particularly for the case of arylacetoacetates, by opening the possibility of performing an oxidation reaction that leads to α-keto esters or arylcarboxylic acids. Moreover, it appears that by controlling the reaction conditions, alkylation of arylacetoacetates can be chemoselectively favoured due to the observed inhibition of the oxidation reaction working at low temperatures. For instance, methylation of arylacetoacetates **10p** or **10m** (K^{t}BuO, DME, CH_3I, 0 °C), afforded exclusively the methylated compound, **16p** or **16m**, respectively, in good reproducible yields.

Experimental Section

Melting points were obtained with a Koffler apparatus and are uncorrected. The IR spectra were recorded in film layer with a Bomen model MB120 apparatus and absorptions are given in cm^{-1}. The NMR spectra (^1H, ^{13}C) were recorded on a Varian Gemini 200 or a Varian Unity 300 spectrometer. All NMR spectra were performed in neutralized $CDCl_3$ solutions; chemical shifts are given in ppm using tetramethylsilane and deuterated chloroform as internal references for ^1H and ^{13}C NMR, respectively. The ESR spectra were recorded with a Varian E-109 spectrometer working in the X band, and the ESR simulation was carried out with a Hewlett-Packard 9835-B computer using a modified version of the software package from a Varian E-935 data Acquisition System. For the recording of the spectra, solutions were carefully degassed by the freeze-pump-thaw-technique. The GC-MS-EI spectra (70 eV) were obtained using a Fisons model MD 800 mass spectrometer coupled to a Fisons GC 8000 apparatus, which was equipped with a 25 m HP-5 capillary column. Elemental analyses were performed on a Carlo Erba 1108 instrument (Microanalysis Service, CID).

Reagents were used as received from commercial sources. Tetrahydrofuran-2-yl hydroperoxide was prepared according to reported procedures. [9] The photochemical reactions were performed with a Heraeus apparatus provided by an immersion mercury lamp TQ-150 and a Pyrex filter. Unless otherwise stated, organic extracts coming from crude reaction mixtures were routinely washed with water, brine and dried over $MgSO_4$, and silica gel was used for the flash chromatography purifications.

Preparation of arylacetoacetates. These compounds were synthesized according to Tona et al.. [2]

Methyl 3-oxo-2-(4'-isobutyryl)phenylbutanoate (1a). This compound was obtained in 47% yield.[2]

Methyl 3-oxo-2-(4'-isobutyl)phenylbutanoate (1b). A soln. of acetoacetate **1a** (0.07 g, 0.26 mmol) in EtOH (1 ml) was hydrogenated under pressure (4 atm) at 25 °C, using Pd/C (10%) (0.014 g) as catalyst. After reaction was completed (9 h, GC monitoring), the solvent was eliminated, the residue was redissolved in ^{t}BuOMe, filtered through Celite® and dried. Elimination of solvent led a residue which was purified by flash chromatography (40:1 hexane:^{t}BuOMe) to give **1b** (0.055 g, 82% yield) as a pale yellow oil. **1b**: IR: 2954, 1751, 1737, 1718, 1647, 1267, 1228. ^{1}H NMR (60:40 keto:enol mixture): 13.02 (s, 1 H, OH, *enol*), 7.00-7.31 (4 H, H_{Ar}), 4.67 (s, 1 H, H-2, *keto*), 3.74 (s, 3 H, OCH_3, *keto*), 3.68 (s, 3 H, OCH_3, *enol*), 2.48 (d, 2 H, J = 7.0, CH_2, *keto*), 2.47 (d, 2 H, J = 7.0, CH_2, *enol*), 2.16 (s, 3 H, $COCH_3$, *keto*), 1.79-1.98 (1 H, H-2", *keto* +*enol*), 1.84 (s, 3 H, $COCH_3$, *enol*), 0.92 (d, 3 H, J = 7.0, H-3", *keto*), 0.90 (d, 3 H, J = 7.0, H-3", *enol*).^{13}C NMR keto form: 201.6 ($\underline{C}OCH_3$), 173.9 (COO), 141.0 (C-4'), 132.2 (C-1'), 130.7, 128.9 (C-2', C-6', C-3', C-5'), 65.2 (C-2), 52.4 (OCH_3), 45.1 (CH_2), 28.6 ($CO\underline{C}H_3$), 22.4 (C-3"). Enol form: 173.1 (COO), 169.1 ($\underline{C}OCH_3$), 140.4 (C-4'), 129.7 (C-1'), 129.6, 128.8 (C-2', C-6', C-3', C-5'), 103.8 (C-2), 51.7 (OCH_3), 45.0 (CH_2), 30.1 (C-2"), 22.3 (C-3"), 19.7 ($CO\underline{C}H_3$). MS: 190 (37), 148 (400, 147 (98), 105 (100), 91 (55). Anal calcd. for $C_{15}H_{20}O_3$: C, 72.6; H 8.1. Found: C, 72.6; H, 8.2.

Methylation of arylacetoacetates 1. A soln. of **1a** (0.12 g, 0.45 mmol) in THF (1.2 ml) was added to a suspension of K^{t}BuO (0.061 g, 0.54 mmol) in the same solvent (0.5 ml) and the mixture was stirred for 30 min at room temperature. Then, CH_3I (34 µl, 0.54 mmol) was then added to the reaction mixture and stirring was prolonged for 15 h. The crude reaction mixture was poured into 1 N HCl and extracted with ^{t}BuOMe. Purification of the residue obtained after solvent elimination afforded: 5 mg of unreacted **1a**, 35 mg (40% yield) of 4-isobutyrylbenzoic acid (**3a**) [10] and 27 mg (23% yield) of the methylated derivated **2a** [2]. Acid **3a** was identified as methyl ester. IR: 2954, 2927, 1726, 1687, 1278. ^{1}H NMR: 8.11 (d, 2H, J = 8.5, H-2', H-6'), 7.99 (d, 2H, J = 8.5, H-3', H-5'), 3.95 (s, 3H, OCH_3), 3.56 (hp, 1H, J = 7.0, CH), 1.23 (d, 6H, J = 7.0, CH_3). ^{13}C NMR: 203.9 (CO), 166.3 (COO), 139.5 (C-4'), 133.5 (C-1'), 129.8, 128.1 (C-2', C-6', C-3', C-5'), 52.4 (OCH_3), 35.8 (CH), 18.9 (CH_3). MS: 206 (M^+, 3), 175 (6), 163 (100), 135 (28), 103 (15).

Likewise, methylation of **1b** (45 mg, 0.18 mmol) under the above conditions afforded: 4 mg of unreacted **1b**, 10 mg (31% yield) of 4-isobutylbenzoic acid (**3b**) [11] and 27 mg (58% yield) of the methylated derivative **2b**. **2b**: IR: 2954, 1743, 1716, 1251. ^{1}H NMR: 7.10-7.22 (4H, H_{Ar}), 3.78 (s, 3H, OCH_3), 2.46 (d, 2H, J = 7.0, CH_2), 2.09 (s, 3H, $COCH_3$), 1.85 (n, 1H, J = 7.0, CH), 1.76 (s, 3H, C-$\underline{C}H_3$), 0.90 (d, 6H, J = 7.0, CH_3). ^{13}C NMR: 205.1 ($\underline{C}OCH_3$), 172.6 (COO), 141.2 (C-4'), 135.5 (C-1'), 129.3, 127.5 (C-2', C-6', C-3', C-5'), 64.3 (C-CH_3), 52.5 (OCH_3), 44.8 (CH_2), 30.1 (CH), 27.1 ($CO\underline{C}H_3$), 22.3 (C-3"), 21.1 (C-$\underline{C}H_3$). MS: 262 (M^+, 0.4), 220 (90), 188 (99), 159 (55), 145 (100), 117 (52). Anal. calcd. for $C_{16}H_{22}O_3$: C, 73.3; H, 8.5. Found: C, 73.4; H, 8.6.

Oxidation of 1a. A soln. of **1a** (0.15 g, 0.6 mmol) in THF (7 ml) and of iodine (0.2 ml of a 40 mM soln., 8.6 μmol) in the same solvent were added to a suspension of K^{t}BuO (0.076 g, 0.7 mmol) in THF (8 ml), and the mixture was sitrred for 1 h at 25 °C. The crude reaction mixture was poured into 1 N HCl and extracted with ^{t}BuOMe. Purification of the residue obtained after solvent elimination (10:1 hexane:EtOAc) afforded: 0.070 g of keto ester **4** (54% yield) and 0.010 g of hydroxyester **5** (6% yield). **4**: IR: 2972, 2931, 1739, 1687, 1207. ^{1}H NMR: 8.07 (d, 2H, J = 9.0, H-2', H-6'), 7.98 (d, 2H, J = 9.0, H-3', H-5'), 3.93 (s, 3H, OCH_3), 3.48 (hp, 1H, J = 7.0, CH), 1.16 (d, 6H, J = 7.0, CH_3). ^{13}C NMR: 203.6 (C-1''), 185.1 (C-2), 163.3 (COO), 140.8 (C-4'), 135.2 (C-1'), 130.3, 128.5 (C-2', C-6', C-3', C-5'), 53.0 (OCH_3), 36.0 (CH), 18.8 (CH_3). MS: 234 (M^+, 3), 191 (44), 175 (100), 163 (10), 147 (15), 132 (9), 104 (56). Anal. calcd. for $C_{13}H_{14}O_4$: C, 66.6; H, 6.0. Found: C, 66.9; H, 6.2.

5: IR: 3450-3500, 2958, 2931, 1747, 1725, 1685, 1373. ^{1}H NMR: 7.97 (d, 2H, J = 8.5, H-3', H-5'), 7.57 (d, 2H, J = 8.5, H-2', H-6'), 5.99 (s, 1H, OH), 3.74 (s, 3H. OCH_3), 3.53 (hp, 1H, J = 7.0, CH), 2.22 (s, 3H, CH_3CO), 1.22 (d, 6H, J = 7.0, H-3''). ^{13}C NMR: 203.7 (COAr), 170.1, 168.7 ($CH_3\underline{C}O$, COO), 138.1 (C-1'), 136.7 (C-4'), 128.7, 127.7 (C-2', C-6', C-3', C-5'), 73.8 (C-OH), 52.8 (OCH_3), 35.5 (CH), 29.6 ($\underline{C}H_3CO$), 19.0 (C-3''). MS: 278 (M^+, 2), 235 (72), 203 (100), 177 (18), 161 (20), 133 (21), 105 (17).

Hydrolysis and decarboxylation of keto ester 4. A soln. of **4** (0.018 g, 0.076 mmol) in THF (25 μl) was treated with 10 N KOH (0.7 ml) for 15 h at 25 °C. The crude reaction mixture was acidified with 9 N H_2SO_4, diluted with H_2O and extracted with EtAcO, to give acid **3a** (0.011 g, 78% yield).

Methyl 4-isobutyrylphenylacetate (6). A mixture of arylacetoacetate **1a** (0.080 g, 0.3 mmol) 2:1 hexane:benzene (1 ml) and H_2O (100 ml), was added to a suspension of KtBuO (0.044 g, 0.4 mmol) in hexane (5 ml) and the mixture was stirred for 2 h at 25 °C. The crude reaction mixture was poured into 1 N HCl and extracted with ^{t}BuOMe. Chromatography purification of the residue obtained after solvent elimination afforded phenylacetate **6** (0.046 g mg, 70% yield). **6**: IR: 2964, 2929, 1739, 1681, 1278. ^{1}H NMR: 7.85 (d, 2H, J = 8.5, H-3', H-5'), 7.30 (d, 2H, J = 8.5, H-2', H-6'), 3.63 (s, 3H, OCH_3), 3.61 (s, 2H, CH_2), 3.46 (hp, 1H, J = 7.0, CH), 1.14 (d, 6H, J = 7.0, CH_3). ^{13}C NMR: 203.9 (CO), 171.2 (COO), 138.8 (C-1'), 135.1 (C-4'), 129.5, 128.6 (C-2', C-6', C-3', C-5'), 52.1 (OCH_3), 41.0 (CH_2), 35.3 (CH), 19.1 (CH_3). MS: 220 (M^+, 2), 177 (100), 161 (4), 149 (9), 89 (16). Anal. calcd. for $C_{13}H_{16}O_3$: C, 70.9; H, 7.3. Found: C, 70.8; H, 7.3.

Oxidation of 1a in the presence of $^{18}O_2$. K^{t}BuO (0.010 g, 0.09 mmol, maintained and manipulated under Ar atmosphere) and degassed THF (1 ml) were introduced into a three-necked flask which was connected to the $^{18}O_2$ cylinder and to the Argon flow. Then a soln. of **1a** (0.020 g, 0.075 mmol) in THF (1 ml) and 30 μl of a soln. of iodine (3.9 10^{-2} M) in the same solvent were added to the reaction flask. The reaction mixture was purged with Ar, the Ar was eliminated under vacuum and labeled oxygen was introduced into the flask. After stirring for 1 h at 25 °C, an aliquote was treated with 3 μl H_2O to afford mixtures of compounds **4** and **5** which exhibited partial incorporation of ^{18}O as shown by GC/MS analysis. **4**: MS: 193 (M^+-43, 4), 191 (M^+-43, 40), 177 (10), 175 (100). **5**: MS: 237 (M^+-43, 62), 235 (M^+-43, 56), 205 (100), 203 (91), 179 (19), 177 (2).

Bromination of 1a. A soln. of **1a** (0.080 g, 0.3 mmol) in DME (7.5 ml) and H_2O (0.5 ml) was treated with NBS (65 mg, 0.36 mmol) and the mixture was stirred under an inert atmosphere for 1 h at 0 °C. The crude reaction mixture was diluted with hexane and washed with water and brine. Purification of the residue obtained after solvent elimination by flash chromatography (12:1 hexane:^{t}BuOMe) afforded a yellow oil identified as bromoester **8** (0.060 g, 60% yield). **Methyl 2-bromo-2(4-isobutyrylphenyl)-3-oxobutanoate (8)**: IR:

2970, 2933, 1739, 1728, 1685, 1247, 1226. ^{1}H NMR: 7.96 (d, 2H, J = 8.5, H-3', H-5'), 7.60 (d, 2H, J = 8.5, H-2', H-6'), 3.88 (s, 3H, OCH_3), 3.53 (hp, 1H, J = 7.0, CH), 2.44 (s, 3H, CH_3CO), 1.22 (d, 6H, J = 7.0, H-3''). ^{13}C NMR: 203.5 (COAr), 196.2 ($CH_3\underline{C}O$), 167.3 (COO), 138.4 (C-1'), 136.4 (C-4'), 129.1, 128.3 (C-2', C-6', C-3', C-5'), 69.8 (C-Br), 54.2 (OCH_3), 35.5 (CH), 26.3 ($\underline{C}H_3CO$), 19.0 (C-3''). MS: 343 (M^+, 0.8), 341 (M^+, 0.9), 300 (93), 298 (82), 257 (100), 255 (92), 225 (21), 223 (22), 187 (99).

Preparation of arylazosulfides 17p-17m. These compounds were prepared following a general procedure reported elsewhere.[2] Thus, the diazonium salt from 4-aminobenzophenone (3.37 g, 0.025 mol), maintained at -5 °C was added to a soln. of 2-methylpropan-2-thiol (3.1 ml, 0.027 mol) in 10% NaOH (250 ml). Treatment and further purification by flash chromatography of the crude reaction mixture afforded pure diazosulfide **17p** (5.2 g, 88% yield) as a yellow solid. **Methyl 4-[(*tert*-butylthio)diazenylphenyl ketone (17p)**: mp 47-48 °C (lit. [1] 47.4-47.8). IR: 2962, 2921, 1685, 1485, 1263. ^{1}H NMR: 8.07 (d, 2H, J = 8.5, H-3, H-5), 7.11 (d, 2H, J = 8.5, H-2, H-6), 2.62 (s, 3H, CH_3), 1.60 (s, 9H, ^{t}Bu). ^{13}C NMR: 196.6 (CO), 159.1 (C-1), 135.9 (C-4), 129.6 (C-3, C-5), 117.8 (C-2, C-6), 49.4 (C, ^{t}Bu), 29.9 (CH_3, ^{t}Bu), 26.4 (CH_3). Likewise, starting from the diazonium salt of 3-aminobenzophenone (3.37 g, 0.025 mol), reaction with the sodium salt of 2-methylpropan-2-thiol (0.027 mol) afforded pure diazosulfide **17m** (5.4 g, 92% yield). **Methyl 3-[(*tert*-butylthio)diazenylphenyl ketone (17m)**: IR: 2962, 2921, 1689, 1479, 1361. ^{1}H NMR: 7.93 (dt, 1H, J_1 = 8.0, J_2 = 1.5, H-2), 7.65 (t, 1H, J = 2.0, H-6), 7.58 (t, 1H, J = 8.0, H-4), 7.23-7.30 (1H, H-5), 2.63 (s, 3H, CH_3), 1.60 (s, 9H, ^{t}Bu). ^{13}C NMR: 196.9 (CO), 156.0 (C-1), 137.9 (C-3), 129.5 (C-4), 127.5 (C-5), 122.5 (C-6), 117.8 (C-2), 49.4 (C, ^{t}Bu), 30.0 (CH_3, ^{t}Bu), 26.6 (CH_3). Anal calcd. for $C_{12}H_{16}N_2OS$: C, 61.0; H, 6.8; N, 11.9; S; 13.6. Found: C, 61.0; H, 6.9; N, 11.8; S, 13.3.

Preparation of arylacetoacetates 10p and 10m. These compounds were prepared following the general procedure described elsewhere. [2] Thus, a soln. of diazosulfide **17p** (1.18 g, 5 mmol) in DMSO (24 ml) was added to a soln. of the potassium salt of methyl acetoacetate (5.4 ml, 50 mmol) in the same solvent (36 ml), and the mixture was irradiated for 10 h. Treatment and chromatography purification of the crude reaction mixture afforded pure arylacetoacetate **10p** (0.54 g, 50% yield). **Methyl 3-oxo-2-(4'-acetyl)phenylbutanoate (10p)**: mp 55-56 °C. IR: 3004, 2954, 1747, 1735, 1722, 1681, 1647. ^{1}H NMR (65:35 keto:enol mixture): 13.08 (s, 1H, OH, *enol*), 7.96 (t, 2H, J = 8.5, H-3', H-5', *keto* + *enol*), 7.46 (d, 1H, J = 8.5, H-2', H-6', *keto*), 7.28 (d, 1H, J = 8.5, H-2', H-6', *enol*), 4.81 (s, 1H, CH, *keto*), 3.77 (s, 3H, OCH_3, *keto*), 3.70 (s, 3H, OCH_3, *enol*), 2.62 (s, 3H, CH_3COAr, *enol*), 2.61 (s, 3H, CH_3COAr, *keto*), 2.22 (s, 3H, CH_3, keto), 1.87 (s, 3H, CH_3CO, *enol*). ^{13}C NMR: ketone form: 200.3 ($\underline{C}OCH_3$), 197.6 (COAr), 174.2 (COO), 140.2 (C-1'), 136.8 (C-4'), 131.4, 128.7 (C-2', C-6', C-3', C-5'), 65.1 (CH), 52.7 (OCH_3), 28.9 ($CO\underline{C}H_3$), 26.5 ($\underline{C}H_3$COAr). Enol form: 197.4 (COAr), 172.2 (COO), 168.2 ($\underline{C}OCH_3$), 137.3 (C-1'), 135.7 (C-4'), 129.6, 128.1 (C-2', C-6', C-3', C-5'), 103.3 (C-OH), 51.8 (OCH_3), 26.5 ($\underline{C}H_3$COAr), 19.8 ($CO\underline{C}H_3$). MS: 176 (M^+-58, 6), 161 (10), 134 (100), 105 (17). Anal. calcd. for $C_{13}H_{14}O_4$: C, 66.6; H, 6.0. Found: C, 66.7; H, 6.1. Likewise, photochemical decomposition of diazosulfide **17m** (1.18 g, 5 mmol) under the same conditions described above, gave pure arylacetoacetate **10m** (0.45 g, 39% yield). **Methyl 3-oxo-2-(3'-acetyl)phenylbutanoate (10m)**: IR: 3002, 2954, 1747, 1732, 1720, 1685, 1650. ^{1}H NMR (60:40 keto:enol mixture): 13.05 (s, 1H, OH, *enol*), 7.34-8.00 (4H, H_{Ar}), 4.83 (s, 1H, CH, *keto*), 3.77 (s, 3H, OCH_3, *keto*), 3.68 (s, 3H, OCH_3, *enol*), 2.61 (s, 3H, CH_3COAr, *keto* + *enol*), 2.23 (s, 3H, CH_3CO, *keto*), 1.85 (s, 3H, CH_3CO, *enol*). ^{13}C NMR: 200.5 ($\underline{C}OCH_3$, *keto*), 197.8 (COAr, *enol*), 197.4 (COAr, *keto*), 174.3 (COO, *enol*), 172.4 (COO, *keto*), 168.4 ($\underline{C}OCH_3$, *enol*), 137.5 (C-3', *keto*), 137.0 (C-3', *enol*), 135.5

(C-1', *keto*), 133.0 (C-1', *enol*), 135.8, 133.8, 130.9, 129.2, 129.1, 128.3, 128.2, 127.1 (C_{Ar}, *keto + enol*), 103.2 (CH, *enol*), 64.9 (CH, *keto*), 52.6 (OCH_3, *keto*), 51.8 (OCH_3, *enol*), 29.0 ($CO\underline{C}H_3$, *keto*), 26.5 (CH_3COAr, *keto + enol*), 19.7 ($CO\underline{C}H_3$, *enol*). MS: 176 (M^+-58, 5), 161 (5), 134 (100), 118 (11), 105 (5). Anal. calcd. for $C_{13}H_{14}O_4$: C, 66.7; H, 6.0. Found: C, 66.7; H, 6.1.

Methyl 2-acetylnonanoate (11). A soln. of methyl acetoacetate (1.85 ml, 17.2 mmol) in DME (15 ml) was added dropwise to a suspension of K^{t}BuO (1.9 g, 17.2 mmol) in DME (20 ml) and the mixture was stirred for 1 at 25 °C. Then, heptyl bromide (3 ml, 18.9 mmol) was added to the reaction flask and stirring was pursued under gentle reflux for 8 h. Treatment of the crude reaction mixture and further Kugelrohr distillation of the residue obtained after solvent elimination afforded pure acetoacetate **11** (2.9 g, 80% yield). **11**: IR: 2954, 2925, 2856, 1745, 1718. ^{1}H NMR: 3.73 (s, 3H, OCH_3), 3.43 (t, 2H, J = 7.5, CH), 2.22 (s, 3H, CH_3CO), 1.55-1.59 (2H, $C\underline{H}_2$-CH), 1.27 (sa, 10H, CH_2), 0.87 (t, 3H, J = 6.5, CH_3). ^{13}C NMR: 203.1 ($CH_3\underline{C}O$), 170.2 (COO), 59.5 (CH), 52.1 (OCH_3), 31.5 (C-5'), 29.1, 28.8, 28.1 (C-2', C-3', C-4'), 28.6 ($\underline{C}H_3CO$), 27.3 (C-1'), 22.4 (C-6'), 13.9 (C-7'). MS: 214 (M^+, 6), 172 (20), 143 (24), 129 (44), 116 (84), 87 (100). Anal. calcd. for $C_{12}H_{22}O_3$: C, 67.2; H, 10.4. Found: C, 67.3; H, 10.4.

Oxidation of arylacetoacetates 10p and 10m. The oxidation of these compounds was carried out as described above for the case of **1a**. Thus, reaction of **10p** (0.11 g, 0.5 mmol), afforded keto ester **12p** (0.045 g, 47% yield) and hydroxyester **13p** (0.009 g, 8% yield) as pure compounds. **Methyl 2-oxo-2-(4'-acetyl)phenylacetate (12p)**: mp 67-8 °C. IR: 1729, 1691. ^{1}H NMR: 8.13 (d, 2H, J = 8.5, H-2', H-6'), 8.06 (d, 2H, J = 8.5, H-3', H-5'), 4.01 (s, 3H, OCH_3), 2.67 (s, 3H, CH_3CO). ^{13}C NMR: 197.2 ($CH_3\underline{C}O$), 185.1 (CO), 163.2 (COO), 141.2 (C-4'), 135.4 (C-1'), 130.2, 128.4 (C-2', C-6', C-3', C-5'), 53.0 (OCH_3), 26.9 ($\underline{C}H_3CO$). MS: 206 (M^+, 1), 191 (21), 163 (31), 147 (100). Anal. calcd. for $C_{11}H_{10}O_4$: C, 64.1; H, 4.9. Found: C, 64.1; H, 4.8. **Methyl 2-hydroxy-3-oxo-2-(4'-acetyl)phenylbutanoate (13p)**: IR: 3370-3490, 1749, 1730, 1689. ^{1}H NMR: 7.98 (d, 2H, J = 8.5, H-3', H-5'), 7.58 (d, 2H, J = 8.5, H-2', H-6'), 6.0 (s, 1H, OH), 3.73 (s, 3H, OCH_3), 2.61 (s, 3H, CH_3COAr), 2.22 (s, 3H, CH_3CO). ^{13}C NMR: 197.1 (COAr), 170.2, 168.5 ($CH_3\underline{C}O$, COO), 138.2 (C-1'), 136.8 (C-4'), 128.6, 127.6 (C-2', C-6', C-3', C-5'), 73.7 (C-OH), 52.7 (OCH_3), 26.6 ($\underline{C}H_3CO$), 20.5 ($\underline{C}H_3COAr$). MS: 208 (M^+-42, 37), 191 (14), 149 (100).

Likewise, oxidation of arylacetoacetate **10m** (0.11 g, 0.47 mmol) afforded keto ester **12m** (0.050 g, 52% yield) and hydroxyester **13m** (0.011 g, 10% yield) as pure compounds. **Methyl 2-oxo-2-(3'-acetyl)phenylacetate (12m)**: IR: 3006, 2956, 1739, 1689. ^{1}H NMR: 8.59 (t, 1H, J = 2.0, H-2'), 8.26 (dt, 2H, J_1 = 2.0, J_2 = 7.5, H-4', H-6'), 7.65 (t, 1H, J = 8.0, H-5'), 4.02 (s, 3H, OCH_3), 2.67 (s, 3H, CH_3CO). ^{13}C NMR: 196.7 (($CH_3\underline{C}O$), 184.9 (CO), 163.2 (COO), 137.5 (C-3'), 134.2, 134.0 (C-4', C-6'), 132.8 (C-1'), 129.7, 129.3 (C-2', C-5'), 53.0 (OCH_3), 26.6 (CH_3CO). MS: 206 (M^+, 0.5), 191 (32), 163 (29), 147 (100), 105 (5). Anal. calcd. for $C_{11}H_{10}O_4$: C, 64.1; H, 4.9. Found: C, 63.4; H, 5.0. **Methyl 2-hydroxy-3-oxo-2-(3'-acetyl)phenylbutanoate (13m)**: IR: 3384-3450, 2958, 2927, 1749, 1735, 1689, 1228. ^{1}H NMR: 8.06 (t, 1H, J = 2.0, H-2'), 7.97 (dt, 1H, J_1 = 8.0, J_2 = 2.0, H-4'), 7.68 (d, 1H, J = 8.0, H-6'), 7.51 (t, 1H, J = 8.0, H-5'), 6.00 (s, 1H, OH), 3.73 (s, 3H, OCH_3), 2.63 (s, 3H, CH_3COAr), 2.22 (s, 3H, CH_3CO). ^{13}C NMR: 197.4 (COAr), 170.1, 168.9 ($CH_3\underline{C}O$, COO), 137.5 (C-3'), 134.4 (C-1'), 132.1, 129.1, 129.0, 127.3 (C-2', C-4', C-5', C-6'), 127.3 (C-4'), 73.9 (C-OH), 52.8 (OCH_3), 26.7 ($\underline{C}H_3CO$), 20.6 (CH_3COAr). MS: 208 (M^+-42, 32), 191 (15), 149 (100), 105 (10).

Oxidation of acetoacetate 11. The oxidation of this substrate was carried out as described above. Thus, reaction of **11** (0.032 g, 0.28 mmol) for 1 h at 25 °C afforded a mixture of unreacted **11**, methyl 2-oxononanoate (**14**) and octanoic acid in a 59:23:18 ratio (GC). **14**: MS: 186 (M^+, 9), 127 (55), 57 (100).

Methylation of arylacetoacetates 10p and 10m. By using a procedure similar to that described above for the methylation of **1a**, a soln. of arylacetoacetate **10p** (0.125 g, 0.53 mmol) in DME (5 ml) was added to a suspension of K^{t}BuO (0.072 g, 0.65 mmol) in the same solvent (6 ml), maintained at 0 °C. After 30 min, CH_3I (185 µl, 3 mmol) was added to the reaction flask and the mixture was stirred for 3 h at the same temperature. Treatment and further chromatography purification of the crude reaction mixture afforded the methylated product **16p** as pure compound (0.091 g, 70% yield). **Methyl 2-methyl-3-oxo-2-(4'-acetyl)phenylbutanoate (16p)**: IR: 2999, 2952, 1741, 1716, 1685, 1257. ^{1}H NMR: 7.96 (d, 2H, J = 8.5, H-3', H-5'), 7.40 (d, 2H, J = 8.5, H-2', H-6'), 3.80 (s, 3H, OCH_3), 2.61 (s, 3H, CH_3COAr), 2.13 (s, 3H, CH_3CO), 1.81 (s, 3H, C-$\underline{C}H_3$). ^{13}C NMR: 203.7 ($\underline{C}OCH_3$), 197.3 (COAr), 171.7 (COO), 143.2 (C-1'), 136.2 (C-4'), 128.4, 127.6 (C-2', C-6', C-3', C-5'), 64.6 ($\underline{C}$-CH_3), 52.7 (OCH_3), 26.9 (CO$\underline{C}H_3$), 26.5 ($\underline{C}H_3COAr$), 21.0 (C-$\underline{C}H_3$). MS: 206 (M^+-42, 100), 174 (37), 159 (35), 131 (33), 105 (15), 77 (56). Anal. calcd. for $C_{14}H_{16}O_4$: C, 67.7; H, 6.5. Found: C, 67.8; H, 6.6.

Likewise, methylation of arylacetoacetate **10m** (0.125 g, 0.53 mmol) under the same conditions described for **10p** afforded the methylated arylacetoacetate **16m** as pure compound (0.088 g, 68% yield). **Methyl 2-methyl-3-oxo-2-(3'-acetyl)phenylbutanoate (16m)**: IR:2999, 2952, 1739, 1716, 1685, 1251. ^{1}H NMR: 7.45-8.00 (4H, H_{Ar}), 3.80 (s, 3H, OCH_3), 2.61 (s, 3H, CH_3COAr), 2.13 (s, 3H, CH_3CO), 1.84 (s, 3H, C-$\underline{C}H_3$). ^{13}C NMR: 204.1 ($\underline{C}OCH_3$), 197.5 (COAr), 171.8 (COO), 138.6 (C-1'), 137.2 (C-3'), 132.3, 128.7, 127.8, 126.8 (C-2', C-4', C-5', C-6'), 64.4 ($\underline{C}$-CH_3), 52.7 (OCH_3), 26.9 (CO$\underline{C}H_3$), 26.5 ($\underline{C}H_3COAr$), 20.9 (C-$\underline{C}H_3$). MS: 206 (M^+-42, 55), 174 (100), 159 (5), 131 (54), 105 (4). Anal. calcd. for $C_{14}H_{16}O_4$: C, 67.7; H, 6.5. Found: C, 67.8; H, 6.6.

Oxidation of phenylacetate 6. A soln. of **6** (0.010 g, 0.04 mmol) in THF (0.5 ml) was added, under oxygen atmosphere, to a suspension of K^{t}BuO (0.006 g, 0.05 mmol) in the same solvent (0.5 ml), and the mixture was vigorously stirred for 15 min at 25 °C. Treatment and further purification of the crude reaction mixture gave 4-isobutyrylbenzoic acid (**3a**, 0.006 g, 75% yield).

Oxidation of methyl phenylacetate (15). By using a similar procedure, **15** (0.025 g, 0.16 mmol) was subjected to the above treatment to give pure benzoic acid (0.017 g, 85 % yield). [12]

Notes and References

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