Sunlight-induced functionalisation reactions of heteroaromatic bases with aldehydes in the presence of TiO$_2$: A hypothesis on the mechanism

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Abstract

In previous studies we reported a new photocatalytic system involving polycrystalline TiO$_2$ for the selective functionalisation of heteroaromatic bases with ethers and amides. In order to extend the applications of this new reaction and to better understand the mechanism involved, we have examined aromatic and aliphatic aldehydes as acyl radical sources for the nucleophilic addition to protonated N-heteroarenes in acetonitrile as the solvent and TiO$_2$/H$_2$O$_2$ as the photocatalytic system. Acyl radicals may undergo decarbonylation to yield the corresponding alkyl radicals. Acyl/alkyl derivative ratios depend on the nature of the aldehydes, and present a different distribution from that obtained in corresponding redox reactions. Indeed, decarbonylation of primary aldehydes occurs in our system in significant amounts. For instance, the acyl/alkyl ratio in the case of the pivaloyl radical is 0.03 versus 1.2 for the redox reaction carried out under otherwise identical conditions of temperature and base concentration. Different polycrystalline TiO$_2$ samples were used and some differences in yields and product distribution were found. A mechanism is proposed on the basis of results obtained for which oxidation of the intermediate adducts is considered to occur on the surface of the photocatalyst TiO$_2$ either via direct involvement of valence band holes or indirectly via photogenerated $^\bullet$OH radicals, whereas the additional oxidants H$_2$O$_2$ and O$_2$ (air) scavenge the photoelectrons produced.
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1. Introduction

The inexpensive and non-toxic polycrystalline TiO$_2$ photocatalyst has been used widely both in gas–solid and liquid–solid systems for its effectiveness in oxidation reactions of a large number of molecules to their complete mineralization [1–8]. In previous papers [9,10] we pointed out that TiO$_2$ can be used not only for the degradation of organic substances, but also in the sunlight-induced functionalisation of heteroaromatic bases. Note that no reaction occurred in the dark. However, small amounts of products were observed under sunlight in the absence of TiO$_2$. This likely occurred by the direct photo-excitation of the N-heteroarenes. The protonated heteroaromatic bases were functionalised with amides and ethereal groups via a radical

mechanism, as demonstrated by the selective substitution in the α or γ positions to the heterocyclic nitrogen. This addition is typical of nucleophilic radicals as pointed out by Minisci and coworkers [11]. A crucial step of this reaction is the oxidation of the intermediate radical adduct following addition of the radical to the heteroaromatic bases (reaction (1)):

$$R = CONH_2, CH_2N(CH_3)COH, R\text{-}CH\text{-}O\text{-}R' \qquad (1)$$
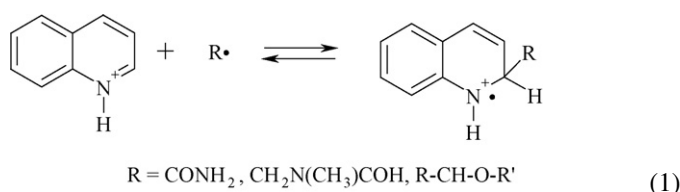
The nature of the products and the regioselectivity depend on the oxidative strength of the solution because addition of the radical to the protonated base is a reversible process. In fact, when two different agents were used for the oxidation, namely air

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Table 1
Sunlight-induced acylation and alkylation of heteroaromatic bases by means of the TiO$_2$/H$_2$O$_2$ system in the presence of aldehydes

| Entry	Base (1.0 mmol)	Aldehyde (5.0 mmol)	Irradiation time (h)	Yield (%)[a]	Selectivity (%)	
					Acyl derivative	Alkyl derivative
1	Lepidine	Acetaldehyde	15	15	(**7**) 100	0
2	Lepidine	Hexanal	10	54	(**8**) 45	(**9**) 55
3	Quinoxaline	Hexanal	10	15	(**16**) 60	(**17**) 40
4	Lepidine	Ethylbutyraldehyde	10	72	(**10**) 27	(**11**) 73
5	Quinoxaline	Ethylbutyraldehyde	10	72	(**18**) 29	(**19**) 71
6	Quinaldine	Ethylbutyraldehyde	10	14	(**14**) 46	(**15**) 54
7	Quinaldine	Ethylbutyraldehyde	15	27	(**14**) 46	(**15**) 54
8	6-NO$_2$ quinoline	Ethylbutyraldehyde	10	14	(**24**) 16	(**25**) 84
9	6-NO$_2$ quinoline	Ethylbutyraldehyde	15	17	(**24**) 18	(**25**) 82
10	*iso*-Quinoline	Ethylbutyraldehyde	10	70	(**22**) 34	(**23**) 66
11	Lepidine	Pivalaldehyde	10	37	0	(**12**) 100
12	Lepidine	Pivalaldehyde	15	67	0	(**12**) 100
13	Quinoxaline	Pivalaldehyde	10	34	(**20**) 3	(**21**) 97
14	4-CN-Pyridine	Pivalaldehyde	10	88	0	(**26**) 75
						(**27**) 1
						(**28**) 22
						(**29**) 2
15	Lepidine	Benzaldehyde	10	22	(**13**) 100	0

[a] No other products were detected except the unreacted base.

oxygen (from purging the reaction mixture with air) or H$_2$O$_2$ added to the solution, different product ratios were obtained for attack of the amido radical to the two reactive positions of quinoline. Interestingly, on the basis of the regioselectivity, the TiO$_2$/air system was more efficient than TiO$_2$/H$_2$O$_2$ in the oxidation of the intermediate [12]. No heteroaromatic products were detected when ethers and *N*-alkyl amides were used in the presence of either air or oxygen. This behaviour was explained by considering that the oxygen present in solution was more efficient in quenching the corresponding carbon-centred radicals.

On the basis of these preliminary results, we applied this system to aldehydes both to enlarge the synthetic scope of the reaction giving a "greener" route for the synthesis of acyl and/or alkyl derivatives of the heteroaromatic bases, and to elucidate some elusive aspects of the mechanism of the heterogeneous photocatalytic process.

2. Results and discussion

Nucleophilic acyl radicals can either attack protonated heteroaromatic bases or can undergo decarbonylation reactions [13,14] to yield carbon monoxide and nucleophilic alkyl radicals able to attack in turn a protonated heteroaromatic base [15], as for reaction (2):

$$R-C\overset{O}{\underset{\bullet}{\bigg\Vert}} \longrightarrow R\bullet \; + \; CO$$
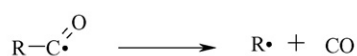
R = CH$_3$, n-C$_5$H$_{11}$, (CH$_3$CH$_2$)$_2$CH, (CH$_3$)$_3$C, Ph   (2)

The relevant results are reported in Table 1, whereas Scheme 1 illustrates the products obtained in the presence of this catalytic system.

A wide range of aldehydes was employed, including primary aldehydes (acetaldehyde, R = CH$_3$, and hexanal, R = *n*-C$_5$H$_{11}$), a secondary aldehyde (ethylbutyraldehyde, R = (CH$_3$CH$_2$)$_2$CH) and a tertiary one (pivalaldehyde, R = (CH$_3$)$_3$C). As reported in literature [14,16], the rate of decarbonylation depends on the nature of the group bonded to CO. No decarbonylation occurred when R was an aromatic group, whereas in the presence of aliphatic aldehydes, the decarbonylation rate increased on increasing the complexity of the alkyl group. As expected [16,17], the rate is even faster with secondary and tertiary substituents.

Table 2 reports a few selected results for reactions involving lepidine and ethylbutyraldehyde in the presence of three commercial photocatalysts, namely Merck TiO$_2$ (anatase, BET specific surface area: 10 m^2 g^{-1}), Tioxide TiO$_2$ (rutile, specific surface area: 10 m^2 g^{-1}) and Degussa P25 TiO$_2$ (ca. 80% rutile, 20% anatase, BET surface area: ca. 50 m^2 g^{-1}).

As pointed out earlier, the rate of decarbonylation for benzoyl and acetyl radicals is extremely slow [14] so that only the acyl derivative is recovered (the decarbonylation rate for the acetyl radical in gas phase is ca. 100 times slower compared with CH$_3$CH$_2\overset{\bullet}{C}$=O radical [14]). For all the other aldehydes the rates of decarbonylation of the corresponding acyl radicals are known from the literature. The reported rates of

Table 2
Distribution of acyl and alkyl derivatives depending on different TiO$_2$ polymorphs for the reaction between lepidine and ethylbutyraldehyde

TiO$_2$	Irradiation time (h)	Yield (mol%)	Acyl derivative	Alkyl derivative
Merck anatase	10	25	14	86
Tioxide rutile	10	21	13	87
Degussa P25	10	72	27	73
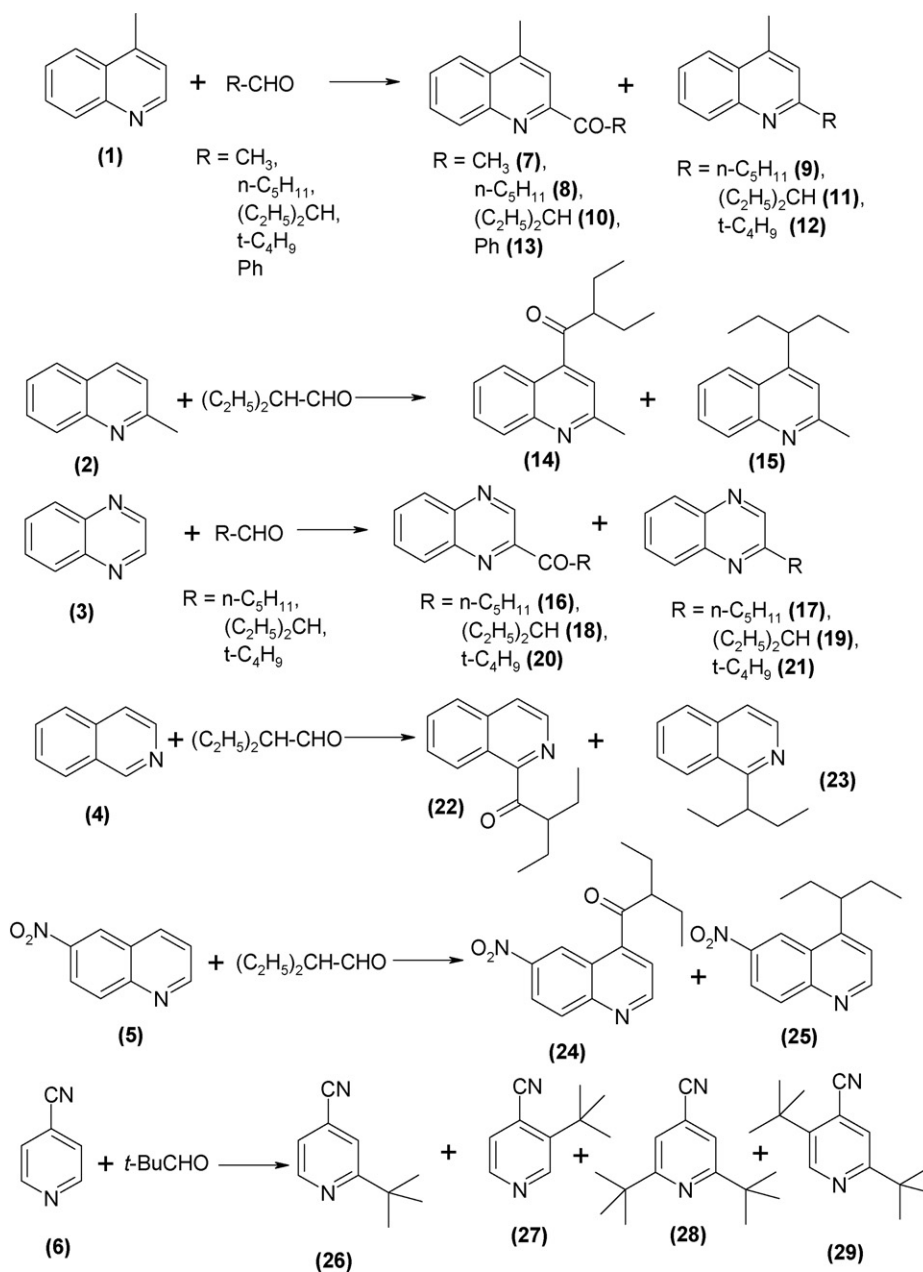
Scheme 1. Products obtained in the presence of the sunlight-activated TiO_2/H_2O_2 catalytic system.

decarbonylation for the acyl radicals substituted with primary, secondary and tertiary alkyl groups, are 1.9×10^4, 3.9×10^5, and $1.0 \times 10^7 \, s^{-1}$ at 80 °C, respectively [18]. Furthermore, the rate of decarbonylation depends strongly on the temperature [17]; for example, in the case of the pivaloyl radical (the more prone to undergo decarbonylation), the following dependence was reported: $\log k_d = 11.9 - 9.3/2.3RT$ [19]. While it is obvious that the rate of decarbonylation increases for entropic reasons on increasing the temperature, a strong influence of the polarity of the solvent has also been observed. In particular, the rate of decarbonylation of the pivaloyl radical increases on going from polar acetonitrile ($1.9 \times 10^5 \, s^{-1}$) to non-polar hexane ($8.3 \times 10^5 \, s^{-1}$) [20]. As reported for the generation of the acyl radicals via redox methods in the presence of pro-

tonated heteroaromatic bases, in the case of pivalaldehyde a substantial amount of the acyl derivative was observed together with the *tert*-butyl adduct, depending on the base concentration (acyl/alkyl = 1.2 at 25 °C with quinoxaline = 0.025 M) [21].

The acyl/alkyl ratios were greater for the other aldehydes, considering that the rate of decarbonylation for hexanoyl radical is more than 500 times smaller than that observed with the pivaloyl radical. For this reason, it is worth noting that practically no competing alkylation reaction has been reported with the redox system in the presence of primary aldehydes. In the present instance, besides the fact that the photoreactions were carried out at a lower temperature and in a polar solvent, decarbonylation seemed to be the favoured reaction in most cases. Moreover, the acyl/alkyl ratios and the product yields changed, when using
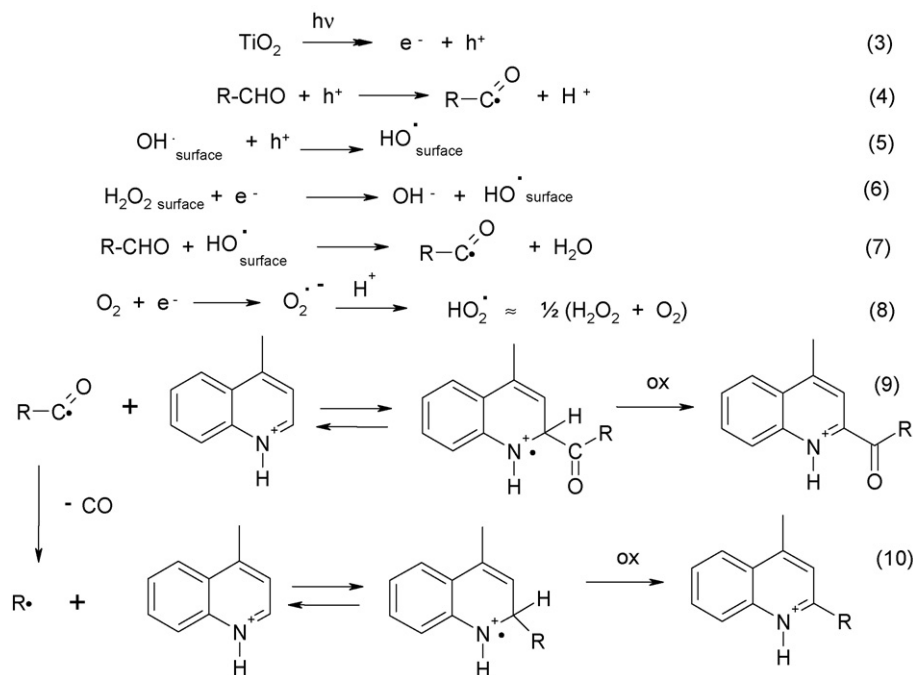
Scheme 2. Proposed reaction mechanism.

different photocatalysts (see Table 2). In particular, the Degussa P25 TiO$_2$ consisting of anatase and rutile particles appeared significantly different from either of the two single phase Merck anatase and Tioxide rutile samples. Evidently, many factors can influence the mechanism (Scheme 2), and several steps need to be taken into consideration to explain the experimental data.

As depicted in Scheme 2, the crucial step concerns the formation of the acyl radical, and sunlight excited TiO$_2$ should play a fundamental role in this contest. The protonated base may be attacked by the acyl radical or, after its decarbonylation, by the corresponding alkyl radical. Therefore, each of the intermediates needs to be oxidised or it reverts back to the starting base and radical. In principle, this oxidation may be in charge of the oxidative reagent in solution (namely H$_2$O$_2$) or of the TiO$_2$ on its surface. If the oxidation occurred involving H$_2$O$_2$, we could expect a closer acyl/alkyl derivatives ratio with respect to those obtained in the redox process. Moreover, if the role of the photocatalyst was only to produce radicals from aldehydes and H$_2$O$_2$ was the species responsible for the oxidation step, we would not observe a different products' distribution using different TiO$_2$ samples and the ratio between acyl and alkyl adducts would be the same with the three catalytic systems. Nevertheless, this is not the case (see Table 2). A plausible hypothesis logically explaining the reported results is that the intermediates are oxidised onto the TiO$_2$ surface and in turn the oxidant, i.e. H$_2$O$_2$, restores Ti^{III} to Ti^{IV}. On the other hand, it cannot be excluded, although the presence of water is very low, that a fraction of the used H$_2$O$_2$ is also restored because it could be produced under irradiation onto the TiO$_2$ surface.

By scrutinizing the results reported in Table 2 it can be noticed that TiO$_2$ Degussa P25 is the most efficient photocatalyst as the yields and the selectivity are concerned. The good photo-

oxidant properties of this photocatalyst in liquid–solid and in gas–solid systems have been widely reported in the literature. They have been explained invoking both intrinsic electronic, as the presence of a juxtaposition of the anatase and rutile phases [22], and surface physico-chemical properties as the acid–base properties [23] and the higher specific surface area (50 m^2 g^{-1} versus 10 m^2 g^{-1} in this case with respect to the other two samples), although it is well known that the extent of the surface area does not guarantee a more significant photoreactivity in heterogeneous photocatalysis. It can be hypothesized that the significantly higher yield (see Table 2) found in the presence of TiO$_2$ Degussa P25 with respect to the other two commercial samples, are due to a facility in the oxidation of the intermediate adduct produced after the attack by the radicals. This reaction, moreover, could be a kinetically favoured step addressing the process towards the final products in the case of both acyl and alkyl derivatives.

The idea that the role of the TiO$_2$ surface is mainly to oxidize the intermediate adduct is supported by the finding that the ratios acyl/alkyl derivatives are different between the first two employed photocatalysts and the third one. This could reflect different interactions between the surface and the reacting species. Another point to discuss is the similar behaviour observed for anatase and rutile TiO$_2$ Tioxide samples. Although at first it could appear surprising because anatase TiO$_2$ has been often reported to be more photoactive than rutile for photodegradation reaction in aqueous systems [24,25], the finding that rutile TiO$_2$ Tioxide works in a similar way can be explained by taking into account that: (i) the amount of H$_2$O in the reacting ambient (acetonitrile as the solvent) in which the photoreactions were carried out is very low; (ii) it has been reported that rutile works similarly to anatase in the presence of H$_2$O$_2$ as electron scavenger [26]; (iii) the photo-processes

here reported do not involve a complete photo-oxidation of the substrates, but only their functionalization that implies a partial photo-oxidation. Only in an aqueous system will full mineralization occur, as in non-aqueous systems once OH radicals have been consumed it may be difficult to regenerate others.

Many (photo)oxidation steps, indeed, are needed to achieve a complete mineralization and the presence of water as the solvent gives rise to the formation of a significant amount of $^\bullet$OH radicals that attach (along with other oxidant radicals, as for instance $^\bullet$OOH) the substrate and the various intermediates until their disappearance. Moreover, the hydroxylation of the photocatalyst surface can be restored in the case of commercial anatase TiO_2 that often appears to be more photoactive than rutile TiO_2. For the latter, instead, not only the surface areas could decrease (in our case we tested a rutile sample with the same area of the anatase sample) due to thermal aggregation of the particles and to formation of bigger crystals, but also some Ti–O–Ti bridges can irreversibly be produced from adjacent Ti–OH sites due to the higher temperature to which rutile is usually prepared. The presence of these surface bridges onto the rutile surface does not allow a complete restoration of the surface hydroxylation in water and this fact could be responsible for the observed low photoactivity of rutile in photodegradation reactions performed in water, along with the reported lower adsorption of O_2 and the higher electron–hole recombination rate [27,28].

The results obtained in this work indicate that rutile TiO_2 works satisfactorily for this kind of photoreactions for which only a partial oxidation is required and water is present in very small amounts. It appears that the surface of rutile TiO_2 can successfully lead to the occurrence of the photoreactions because it possesses the essential electronic and physico-chemical characteristics (e.g. the presence of Ti–O–Ti bridges, which do not play any relevant role) needed to produce a moderate quantity of oxidant species able to oxidize the intermediate radical adducts.

3. Experimental

3.1. Reagents and characterization

Lepidine (**1**), quinaldine (**2**), quinoxaline (**3**), isoquinoline (**4**), 6-nitroquinoline (**5**) and Pyridine-4-carbonitrile (**6**) are commercial products. Acetyllepidine (**7**) [29], *n*-pentyllepidine (**10**) [30], *tert*-butyllepidine (**12**) [31], benzoyllepidine (**13**) [32], pivaloyl (**20**) and *tert*-butylquinoxaline (**21**) [33], 2-*tert*-butyl-Pyridine-4-carbonitrile (**26**), 3-*tert*-butyl-Pyridine-4-carbonitrile (**27**), 2,6-di-*tert*-butyl-Pyridine-4-carbonitrile (**28**) and 2,5-di-*tert*-butyl-Pyridine-4-carbonitrile (**29**) [34] were reported earlier in the literature and were identified by comparison with authentic samples. Mass spectra were obtained on a GC–MS (Hewlett Packard GC 5890 series II equipped with 5972 series mass selective detector) instrument, using a gas chromatograph equipped with SBP-1 fused silica column (30 m × 0.2 mm i.d.; 0.2 mm film thickness) and helium as carrier gas. NMR spectra were recorded on a Bruker Advance spectrometer operating at 400 MHz (^{1}H). Proton chemical shifts are referred to internal TMS. Product yields are reported in Table 1.

3.2. General procedure

A Pyrex tube containing a solution of the aldehyde (5.0 mmol) in acetonitrile (40 mL) and 10 mg of polycrystalline anatase TiO_2 (Degussa P25, specific surface area: $50 \, m^2 \, g^{-1}$) was sonicated for 1 min to obtain a milky suspension. The heteroaromatic base (1.0 mmol), CF_3COOH (1.1 mmol) and H_2O_2 (5.0 mmol) were added to the suspension and the resulting mixture was exposed to the sunlight (mean total irradiation in Milan during the period December–February was $200 \, W \, m^{-2}$) with mechanical stirring (1000 rpm) for the reported time behind the window inside the laboratory, where the temperature was $20 \, ^\circ C$. The solution temperature was 32–$35 \, ^\circ C$, due to the sunlight warming. The tube was closed with a stopper, with no degassing (with degassing no differences were observed). Irradiation was carried out between 10 a.m. and 3 p.m. and storing the reactor in the dark till the following day when the procedure was repeated. The reaction was checked after the irradiation and before the following irradiation to control that no change in yield or products distribution occurred after storing in the dark. At the end of the irradiation, the solution was alkalinised with a saturated aqueous solution of $NaHCO_3$, extracted with CH_2Cl_2 and dried on solid Na_2SO_4. After removal of the solvent under vacuum, the resulting mixture was analysed via GC–MS and separated via flash-chromatography (silica gel; solvent ethyl acetate:hexane = 7:3). Selectivity was determined by GC–MS with the use of an internal standard. Yields were referred to the isolated products. No products were detected in addition to the described acyl and alkyl derivatives along with the unreacted base. The experiments were duplicated and no significant differences were found. Compounds (**8**), (**16**), (**17**), (**23**), (**24**) were identified only via GC–MS analysis of the reaction mixture due to the low reaction conversions.

(**8**) oil: *m/z* 241 (M$^+$, 10%), 213 (13), 198 (32), 184 (22), 170 (26), 157 (12), 143 (100), 115 (43), 89 (7), 77 (4).

(**10**) oil: (found C% 79.55, H% 7.91, N% 5.82. Calc. for $C_{16}H_{19}NO$ C% 79.63, H% 7.94, N% 5.80). δ_H(400 MHz; CDCl$_3$; Me$_4$Si) 8.20 (1 H, d, *J* 7.8, CH), 8.03 (1 H, *J* 8.4, CH), 7.96 (1 H, s, CH), 7.76 (1 H, dt, *J* 6.9 and 7.8, CH), 7.55 (1 H, dt, *J* 8.4 and 6.9, CH), 4.24 (1 H, m, *J* 7.6, (CH$_3$CH$_2$)$_2$C*H*), 2.76 (3 H, s, CH$_3$), 1.82 (2 H, m, *J* 7.7 and 7.6, 2 × (CH$_3$CH*H*)$_2$CH), 1.65 (2 H, m, *J* 7.7 and 7.6, 2 × (CH$_3$CH*H*)$_2$CH), 0.91 (6 H, t, *J* 7.7, 2 × (C*H$_3$*CH$_2$)$_2$CH). *m/z* 241 (M$^+$, 25%), 226 (55), 212 (15), 198 (16), 184 (37), 157 (8), 143 (100), 115 (36), 89 (6).

(**11**) oil: (found C% 84.53, H% 9.00, N% 6.59. Calc. for $C_{15}H_{19}N$, C% 84.46, H% 8.98, N% 6.57). δ_H(400 MHz; CDCl$_3$; Me$_4$Si) 8.09 (1 H, d, *J* 8.2, CH), 7.91 (1 H, d, *J* 8.5, CH), 7.64 (1 H, m, 1 H, d, *J* 8.2 and 6.9, CH), 7.46 (1 H, m, 1 H, d, *J* 8.5 and 6.9, CH), 7.08 (1 H, s, CH), 2.75 (1 H, septuplet, *J* 7.2, (CH$_3$CH$_2$)$_2$C*H*), 2.65 (3 H, s, CH$_3$), 1.79 (4 H, m, *J* 7.6 and 7.2, 2 × (CH$_3$C*H$_2$*)$_2$CH), 0.84 (6 H, t, *J* 7.6, 2 × (C*H$_3$*CH$_2$)$_2$CH). *m/z* 213 (M$^+$, 2%), 198 (17), 184 (63), 170 (100), 157 (14), 143 (5), 115 (12), 89 (3);

(**14**) oil: (Found C% 79.89, H% 7.96, N% 5.81. Calc. for $C_{16}H_{19}NO$, C% 79.63, H% 7.94, N% 5.80). δ_H(400 MHz;

CDCl$_3$; Me$_4$Si) 8.11 (1 H, d, *J* 8.5, CH) 8.04 (1 H, d, *J* 8.5, CH), 7.69 (1 H, m, *J* 8.5 and 6.9, CH), 7.50 (1 H, m, *J* 8.5 and 6.9, CH), 7.34 (1 H, s, CH), 2.77 (s, 3H, CH$_3$), 3.13 (1 H, m, *J* 7.2, (CH$_3$CH$_2$)$_2$C*H*), 1.81 (2 H, m, *J* 7.6 and 7.2, 2 × (CH$_3$CH*H*)$_2$CH)), 1.73 (2 H, m, *J* 7.6 and 7.2, 2 × (CH$_3$CH*H*)$_2$CH), 0.93 (6 H, t, *J* 7.6, 2 × (C*H*$_3$CH$_2$)$_2$CH). *m/z* 241 (M$^+$, 21%), 170 (100), 142 (65), 115 (21), 101 (29), 75 (21).

(**15**) oil: (Found C% 81.23, H% 8.94, N% 6.58. Calc. for C$_{15}$H$_{19}$N, C% 84.46, H% 8.98, N% 6.57. δ$_H$(400 MHz; CDCl$_3$; Me$_4$Si) 8.03 (2 H, d, *J* 8.5, 2 × CH), 7.63 (1 H, m, *J* 8.5 and 6.9, CH), 7.44 (1 H, m, *J* 8.5 and 6.9, CH), 7.11 (1 H, s, CH), 2.71 (s, 3H, CH$_3$), 3.27 (1 H, m, *J* 7.2, (CH$_3$CH$_2$)$_2$C*H*), 1.73 (2 H, m, *J* 7.6 and 7.2, 2 × (CH$_3$CH*H*)$_2$CH)), 1.56 (2 H, m, *J* 7.6 and 7.2, 2 × (CH$_3$CH*H*)$_2$CH)), 0.80 (6 H, t, *J* 7.6, 2 × (C*H*$_3$CH$_2$)$_2$CH). *m/z* 213 (M$^+$, 48%), 198 (5), 184 (100), 168 (37), 156 (9), 141 (4), 128 (11), 115 (13), 101 (4), 89 (3), 77 (5).

(**16**) oil: *m/z* 228 (M$^+$, 7%), 200 (33), 185 (13), 171 (25), 157 (43), 144 (40), 130 (100), 102 (62), 75 (25).

(**17**) oil: *m/z* 200 (M$^+$, 7%), 171 (6), 157 (17), 144 (100), 129 (5), 117 (6), 102 (12), 89 (5), 76 (10).

(**18**) oil: (Found C% 73.94, H% 7.06, N% 12.27. Calc. for C$_{14}$H$_{16}$N$_2$O C% 73.66, H% 7.07, N% 12.27). δ$_H$(400 MHz; CDCl$_3$; Me$_4$Si) 8.73 (1 H, s, CH), 8.11 (2 H, m, *J* 7.4, 2 × CH), 7.74 (2 H, m, *J* 7.4, 2 × CH), 2.89 (1 H, quintuplet, *J* 7.5, (CH$_3$CH$_2$)$_2$C*H*), 1.88 (2 H, m, *J* 7.5 and 7.4, 2 × (CH$_3$C*H*$_2$)$_2$CH), 0.85 (6 H, t, *J* 7.4, 2 × (C*H*$_3$CH$_2$)$_2$CH).

(**19**) oil: *m/z* 200 (M$^+$, 22%), 185 (10), 171 (46), 157 (100), 144 (38), 129 (15), 102 (19), 76 (16); δ$_H$(400 MHz; CDCl$_3$; Me$_4$Si) 9.50 (1 H, s, CH), 8.21 (1 H, d, *J* 7.8, CH), 8.19 (1 H, d, *J* 7.9, CH), 7.86 (2 H, m, *J* 7.8 and 7.9, 2 × CH), 4.10 (1 H, m, *J* 6.6, (CH$_3$CH$_2$)$_2$C*H*), 1.86 (2 H, m, *J* 7.6 and 6.6, 2 × (CH$_3$CH*H*)$_2$CH), 1.66 (2 H, m, *J* 7.6 and 6.6, 2 × (CH$_3$CH*H*)$_2$CH), 0.92 (6 H, t, *J* 7.6, 2 × (C*H*$_3$CH$_2$)$_2$CH). *m/z* 228 (M$^+$, 4%), 213 (8), 200 (21), 185 (14), 171 (48), 158 (15), 130 (100), 102 (39), 76 (19).

(**22**) oil: (Calcd. C$_{15}$H$_{17}$NO C% 79.26, H% 7.54, N% 6.16: found C% 79.11, H% 7.53, N% 6.14). δ$_H$(400 MHz; CDCl$_3$; Me$_4$Si) 8.13 (1 H, d, *J* 7.0, CH), 7.82 (1 H, m, CH), 7.72 (1 H, d, *J* 7.0, CH), 7.67 (1 H, m, CH), 7.62 (2 H, m, 2 × CH), 3.89 (1 H, quintuplet, *J* 6.2, (CH$_3$CH$_2$)$_2$C*H*), 1.85 (2 H, m, *J* 7.1 and 6.2, 2 × (CH$_3$CH*H*)$_2$CH), 1.62 (2 H, m, *J* 7.1 and 6.2, 2 × (CH$_3$CH*H*)$_2$CH), 0.99 (6 H, t, *J* 7.1, 2 × (C*H*$_3$CH$_2$)$_2$CH). *m/z* 227 (M$^+$, 17%), 212 (26), 198 (10), 184 (12), 170 (30), 129 (100), 101 (27), 77 (17).

(**23**) oil: *m/z* 199 (M$^+$, 10%), 184 (18), 170 (75), 156 (100), 143 (18), 128 (22), 115 (14), 101 (9), 77 (12).

(**24**) oil: *m/z* 272 (M$^+$, 39%), 244 (29), 201 (81), 185 (100), 174 (96), 155 (28), 127 (94), 115 (22), 100 (80), 74 (64).

(**25**) oil: (Found C% 69.04, H% 6.62, N% 11.50. Calc. for C$_{14}$H$_{16}$N$_2$O$_2$, C% 68.83, H% 6.60, N% 11.47. δ$_H$(400 MHz; CDCl$_3$; Me$_4$Si) 9.13 (1 H, d, *J* 2.4, CH), 9.03 (1 H, d, *J* 4.5, CH), 8.49 (1 H, dd, *J* 9.3 and 2.4, CH), 8.34 (1 H, d, *J* 9.3, CH), 7.45, (1 H, d, *J* 4.5, CH), 3.41 (1 H, m, *J* 5.8, (CH$_3$CH$_2$)$_2$C*H*), 1.94 (2 H, m, *J* 7.6 and 5.8, 2 × (CH$_3$CH*H*)$_2$CH) 1.79 (2 H, m, *J* 7.6 and 5.8, 2 × (CH$_3$CH*H*)$_2$CH), 0.85 (6 H, t, *J* 7.6, 2 × (C*H*$_3$CH$_2$)$_2$CH). *m/z* 244 (M$^+$, 49%), 229 (16), 216 (56), 201 (73), 188 (20), 169 (100), 154 (66), 141 (9), 127 (16), 115 (11), 101 (5), 89 (4), 77 (5).

4. Conclusions

In the framework of our studies on the realisation of environmentally friendly chemical reactions, we have herein reported the acylation/alkylation reactions of *N*-heterocyclic bases with the use of sunlight in the presence of TiO$_2$ as the photocatalyst and the aldehydes as the source of free radicals. The products are formed in good to fair yields, and the ratios of the products obtained are different from those obtained from the corresponding redox reactions. The results obtained have provided an opportunity to propose a plausible mechanism that involves TiO$_2$ and additional oxidants (air and hydrogen peroxide).

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