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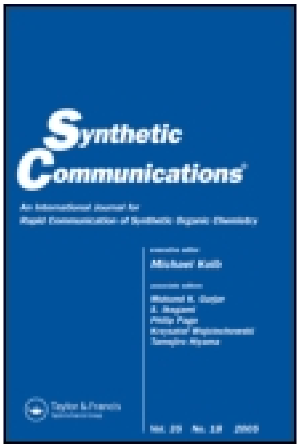

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PHOTOLYSIS OF PHENACYL ESTERS IN A TWO-PHASE SYSTEM

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PHOTOLYSIS OF PHENACYL ESTERS IN A TWO-PHASE SYSTEM

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ABSTRACT

Phenacyl esters are useful photoremovable protecting groups for carboxylic acids in organic synthesis and biochemistry. In this work, simple one-pot arrangements of the phenacyl and 2,5-dimethylphenacyl ester photolysis are proposed. The reactions were performed in both the benzene/water two-phase system and in water. Cetyltrimethylammonium bromide was found to increase substantially the efficiency of the deprotection as well as the purity of the products by lowering the interfacial tension between the phases. Utilizing water as a medium significantly reduced the necessity to use environmentally malign organic solvents. The overall yields varied from 72 to 98% depending on the reaction conditions.

Key Words: Phenacyl; Two-phase system; Photochemistry; Protecting group

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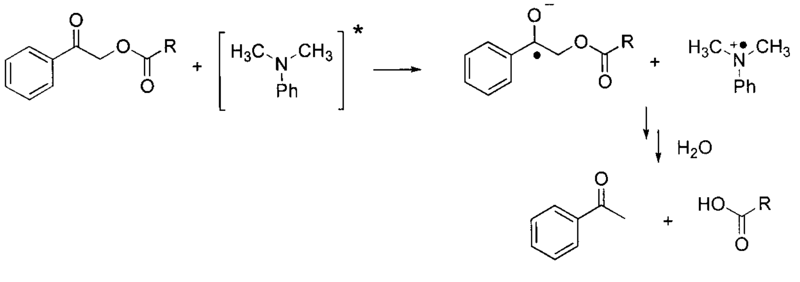
Photochemically removable protecting (PRP) groups are recognized today as a class of groups of great practical significance. They found their applications in organic synthesis as well as in biochemistry.[1–4] Phenacyl ester derivatives certainly belong among the widely used PRP groups for carboxylic acids and phosphates. The *p*-hydroxyphenacyl group received a considerable attention as quite a versatile moiety by Givens and other authors, especially in terms of oligopeptide synthesis.[5–10] Phenacyl and *p*-methoxyphenacyl groups have been reported as efficient PRP groups for photochemical release of carboxylic acids, alcohols, and phosphates.[11–17] Recently we proposed the 2,5-dimethylphenacyl chromophore as a new photoremovable protecting group for carboxylic acids.[18,19]

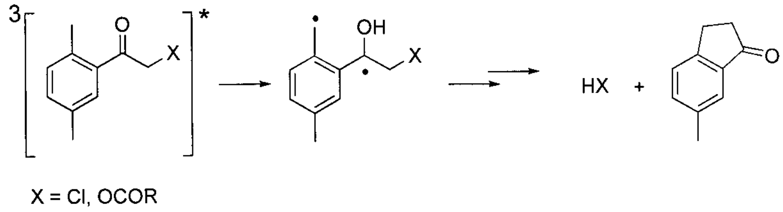
There has been long-standing interest to introduce water to the chemical processes and consequently replace environmentally malign solvents. By reducing or eliminating the application of those substances associated with a particular synthesis, chemists can greatly reduce risk to human health and the environment. Such efforts belong to a new program called *green chemistry*.[20] Now we wish to report on the photoreactions of phenacyl and 2,5-dimethylphenacyl esters in aqueous two-phase systems.

RESULTS AND DISCUSSION

The protection reactions of carboxylic acids with the phenacyl group is well-described in the literature.[11–17] The carboxylic acid usually reacts with phenacyl halide in the presence of a base to obtain the corresponding ester in a high yield. The photorelease of the acid could be affected through photosensitization using excited-state electron donors[14–16,21] or efficient hydrogen donors.[17] Falvey and Banerjee proposed a mechanism of the sensitized deprotection of the phenacyl esters which results in C–O bond scission and consequently the formation of the corresponding carboxylic acid and acetophenone (Scheme 1).[15]



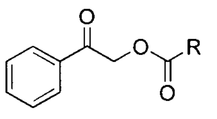
Scheme 1.



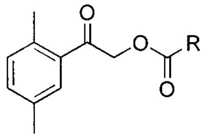
Scheme 2.

It is known that aryl ketones with *o*-alkyl groups undergo an efficient photoinduced intramolecular photoenolization.[22–24] 2,5-Dimethylphenacyl (DMP) group is released in the reaction starting with triplet excitation of the ketone and followed by *intramolecular* hydrogen abstraction (Scheme 2). Chloride[25,26] and carboxylates[18,19] are the only leaving groups (X) so far described.

In this work, the esters **1–5** were synthesized from the phenacyl halide derivatives and the sodium salt of the corresponding acid in high yields (67–95%).



R = Ph (**1**)
CH_2Ph (**2**)
$(CH_2)_6CH_3$ (**3**)



R = Ph (**4**)
$(CH_2)_{14}CH_3$ (**5**)

Phenacyl esters were irradiated in the presence of electron or hydrogen donors; DMP esters released the carboxylic acid upon a direct irradiation. The starting compound was photolyzed either in a two-phase (benzene/aqueous Na_2CO_3 solution) system or in the aqueous Na_2CO_3 solution only. Since phenacyl and DMP esters are insoluble in the latter system they remained in the crystalline state during the irradiation until they reacted off. We have not found any significant solid-state photoreactivity of any ester derivative, thus photoreactions had to occur in the liquid phase. Cetyltrimethylammonium bromide (CTAB) as a surfactant was added in some experiments to increase the reaction efficiency. The experiments were performed in a sealed flask equipped with a stir bar at 20°C. The wavelength used (>280 nm) guaranteed an efficient photochemical transformation. The reaction mixtures were vigorously stirred and irradiated until the ester was completely consumed. The acids were obtained as the corresponding sodium salt solutions in water. The following acidification and purification gave the desired products.

The following tables compare the results from the experiments in two-phase systems: Table 1 shows the photolysis with the presence and Table 2 without the presence of a surfactant (CTAB).

The phenacyl ester in the water/benzene system was dissolved in the organic layer while the resulting acid was transferred into an alkaline aqueous solution. When the phenacyl esters were used diethylamine (DEA) and triethylamine (TEA) served as the electron donors to afford the reaction, benzylalcohol (BzOH) was used as a hydrogen donor. While DEA is almost completely miscible with water but partially soluble in benzene, TEA and BzOH are poorly soluble in water but well soluble in the organic layer.

Photochemistry occurred with or without the presence of a surfactant, however, the chemical yields and the purity of the acids, as well as the photochemical reaction efficiencies, were considerably higher in the former experiments. Time necessary for the reactions without CTAB was approximately 2-times longer. Furthermore, the products were contaminated

Table 1. Photolysis of Phenacyl Esters in a Two-Phase System with CTAB[a]

	Reaction Mixture	Hydrogen or Electron Donor	Photolysis Time [h]	Yield [%][b]
1	Phenacyl benzoate (water)	BzOH	16	98
2	Phenacyl benzoate (water/benzene)	BzOH	16	94
3	Phenacyl phenylacetate (water)	TEA	12	93
4	Phenacyl phenylacetate (water/benzene)	TEA	14	93
5	Phenacyl phenylacetate (water)	DEA	24	88[c]
6	Phenacyl phenylacetate (water/benzene)	DEA	24	92[c]
7	Phenacyl octanoate (water)	TEA	19	86
8	Phenacyl octanoate (water/benzene)	TEA	19	82
9	2,5-dimethylphenacyl benzoate (water)	–	12	0[d]
10	2,5-dimethylphenacyl benzoate (water/benzene)	–	14	82
11	2,5-dimethylphenacyl palmitate (water/benzene)	–	12	86

[a]Irradiated at > 280 nm at 20°C. No ground state deprotection reaction was observed at given reaction conditions; [b]Isolated chemical yields of the crude acids (> 95% purity); [c]The GC purity ~ 88%; [d]The ester remained in the solid state during the experiment.

Table 2. Photolysis of Phenacyl Esters in a Two-Phase System without CTAB[a]

	Reaction Mixture	Hydrogen or Electron Donor	Photolysis Time [h]	Yield (Purity) [%]
1	Phenacyl benzoate (water)	BzOH	24	72 (74)
2	Phenacyl benzoate (water/benzene)	BzOH	24	64 (88)
3	Phenacyl phenylacetate (water)	TEA	24	83 (91)
4	Phenacyl phenylacetate (water/benzene)	TEA	24	81 (95)
5	Phenacyl phenylacetate (water)	DEA	24	72 (86)
6	Phenacyl phenylacetate (water/benzene)	DEA	24	76 (82)

[a] Irradiated at >280 nm at 20°C. No ground state deprotection reaction was observed at given reaction conditions.

by additional unwanted byproducts, thus photoproduct purification was more difficult (the overall loss was almost 50% in comparison to the experiments from Table 1). The surfactant apparently lowered the interfacial tension, thus increased the emulsification of the reaction mixture. This facilitated the transport of a water soluble material out of the organic phase.

The reactions in the aqueous Na_2CO_3 solution can be classified as a solid/liquid phase system because the esters are practically insoluble in water. Surprisingly, the presence of the surfactant was not obligatory for the reaction to take place, however, the yields as well as the purity was considerably higher when CTAB was added. The reaction between the ester and an electron/hydrogen donor probably occurred in a quasi-liquid layer at the surface of the crystalline material (the organic donor molecules dissolve the esters). This procedure requires removing the unwanted reaction material from the resulting acid salt solution by washing with an organic solvent (dichloromethane, petroleum ether, ethyl acetate etc.). Moreover, the sodium salt is a practical form of the acid for a further purification. Photolysis of DMP esters was successful only in the benzene/water system. No reaction was observed in the aqueous environment where the ester remains in the solid state.

In conclusion, we propose simple reaction conditions for phenacyl and 2,5-dimethylphenacyl ester photolysis with the emphasis to environmentally friendly reactions in water. Application of a surfactant increased the overall reaction efficiency—the products were obtained in very high chemical yields (82–98%) as well as purity. Moreover, all reactions have an ‘‘one-pot’’ arrangement which might be beneficial in organic synthesis when the phenacyl is used as a protecting group.

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EXPERIMENTAL

Materials and Methods

Benzene and methanol were purified by distillation through a vacuum-sealed column (70 cm) packed with glass detritus. Phenacyl bromide and α-chloro-2′,5′-dimethylacetophenone were prepared according to the standard procedure described elsewhere.[15,25,26]

NMR spectra were recorded on a Bruker 300 MHz spectrometer. ^{1}H and ^{13}C NMR data were measured in the indicated solvent with tetramethylsilane as an internal standard. Mass spectra were obtained using EI (30 eV). Gas chromatography was performed on a Shimadzu GC 17A gas chromatograph equipped with a DB1 column. Melting points were determined on a Kofler hot-stage Rapido 79–2106 and were not corrected.

Preparation of Phenacyl Esters: A Typical Procedure

α-Chloro-2′,5′-dimethylacetophenone (32 mmol) in acetone (25 mL) was added to a stirred mixture of the acid (1.3–2 equiv.) or its sodium salt (1.2 equiv.), sodium iodide (1.2 equiv.) and triethylamine (1.1 equiv.) in 250 mL of acetone. The mixture was stirred and heated under reflux for ~8 h. The product formation was monitored by TLC. The solids were removed, the solvent was distilled off, and the residue was extracted with benzene. The benzene layer was washed three times with 10% HCl (50 mL), 1 M aqueous sodium hydroxide (50 mL), and water. The organic layer was dried over $MgSO_4$ and the solvent was removed to obtain the crude product. The crude products were purified by crystallization or by flash chromatography (petroleum ether–diethyl ether mixture, 4 : 1).

2-Oxo-2-phenyl-ethyl Ester of Benzoic Acid (Phenacyl Benzoate, 1): Synthesized from phenacyl bromide with 71% yield; white solid; m.p. 123–125°C (from diethyl ether); IR (KBr) 3058, 2944, 1721, 1699, 1597, 1449, 1283, 1229, 1122, 959 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.58 (s, 2H), 7.46–7.65 (m, 6H), 7.98 (d, $J = 7.2$ Hz, 2H), 8.16 (d, $J = 7.2$ Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 66.7, 128.1, 128.7, 129.1, 130.2, 133.5, 134.1, 134.6, 166.3, 192.3.

2-Oxo-2-phenyl-ethyl Ester of Phenylacetic Acid (Phenacyl Phenylacetate, 2): Synthesized from phenacyl bromide with 93% yield; yellowish solid; m.p. 48–50°C (from ethanol); IR (KBr) 3060, 2939, 1731, 1702, 1596, 1450, 1282, 1225, 1142, 971 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.84 (s, 2 H), 5.37 (s, 2H), 7.37 (d, $J = 4.3$ Hz, 5H), 7.49 (t, $J = 7.2$ Hz, 2H), 7.62 (d, $J = 7.2$ Hz, 1H), 7.91 (d, $J = 7.9$ Hz, 2H); ^{13}C NMR (75.5 MHz,

$CDCl_3$) δ 41.0, 66.4, 127.3, 127.9, 128.7, 128.9, 129.5, 133.7, 133.9, 134.4, 171.1, 192.1.

2-Oxo-2-phenyl-ethyl Ester of Octanoic Acid (Phenacyl Octanoate, 3): Synthesized from phenacyl bromide with 71% yield; yellowish liquid; IR (NaCl) 2953, 2928, 2856, 1746, 1705, 1597, 1450, 1375, 1222, 1161, 967 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.81 (s, 3H), 1.21 (bs, 8H), 1.63 (d, $J = 6.6$ Hz, 2H), 2.40 (t, $J = 7.3$ Hz, 2H), 5.24 (s, 2H), 7.39 (t, $J = 7.0$ Hz, 2H), 7.50 (t, $J = 7.0$ Hz, 1H), 7.82 (d, $J = 7.0$ Hz, 2 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.2, 22.7, 25.1, 29.1, 29.2, 31.8, 34.1, 66.0, 127.9, 129.0, 133.9, 134.6, 173.3, 192.5.

2-(2,5-Dimethyl-phenyl)-2-oxo-ethyl Ester of Benzoic Acid (2,5-Dimethylphenacyl Benzoate, 4): Synthesized from α-chloro-2′,5′-dimethylacetophenone with 95% yield; white solid; mp. 90–91°C (from diethyl ether); IR (KBr) 2944, 1720, 1700, 1597, 1450, 1372, 1283, 1229, 1122, 1019, 958 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 3H), 2.48 (s, 3H), 5.40 (s, 2H), 7.15–7.25 (m, 2H), 7.43–7.48 (m, 3H), 7.58 (t, $J = 7.6$ Hz, 1H), 8.11–8.14 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 20.8, 21.1, 67.9, 128.6, 128.9, 129.7, 130.1, 132.3, 133.1, 133.5, 134.7, 135.6, 136.1, 166.3, 196.0; MS (EI) m/z 268 (M^+), 147, 133, 105, 77. Anal. calcd. for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 76.53; H, 6.11.

2-(2,5-Dimethyl-phenyl)-2-oxo-ethyl Ester of Palmitoic Acid (2,5-Dimethylphenacyl Palmitate, 5): Synthesized from α-chloro-2′,5′-dimethylacetophenone with 67% yield; white solid; mp. 38–39°C (from aqueous ethanol); IR (KBr) 2916, 2851, 1746, 1701, 1572, 1467, 1420, 1282, 967, 818 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, $J = 6.2$ Hz, 3H), 1.26 (s, 26H), 1.67 (k, $J = 7.3$ Hz, 2H), 2.36 (s, 3H), 2.45 (s, 3H), 5.14 (s, 2H), 7.15 (d, $J = 7.8$ Hz, 1H), 7.21 (d, $J = 7.8$ Hz, 1H), 7.39 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.3, 20.7, 21.1, 22.9, 25.1, 29.3, 29.5, 29.6, 29.7, 29.8, 29.9, 32.1, 34.1, 67.4, 128.8, 132.2, 132.9, 134.9, 135.5, 135.9, 173.5, 196.5; MS (EI) m/z 402 (M^+), 239, 133, 105, 77. Anal. calcd. for $C_{26}H_{42}O_3$: C, 77.56; H, 10.51. Found: C, 77.22; H, 10.76.

Photolysis of Phenacyl Esters: The reaction mixture consisted either of ~0.2-M ester solution in benzene (5 mL) mixed with a 2-M Na_2CO_3 aqueous solution (5 mL) or the ester (1 mmol) added to a 2-M Na_2CO_3 aqueous solution (5 mL). A hydrogen donor (benzylalcohol) or an electron donor (triethylamine or diethylamine) (10 equiv.), respectively, were added in case of phenacyl esters. In some experiments, a small amount (1–3%, w/w) of cetyltrimethylammonium bromide was added. The reaction mixtures, placed into a Simax vessel sealed with a septum and equipped with a stir bar, were degassed by bubbling the solution with argon for 5 min. The Simax (Pyrex equivalent) glass was used in all cases to filter off UV radiation below 280 nm. The well-stirred mixture was irradiated using a 125-W medium-pressure mercury lamp (Teslamp) at the ambient temperature for 12–24 h. The reaction conversion was monitored by GC. The main by-product from the phenacyl ester photolysis was identified as acetophenone which confirms that the reaction is a photochemical process as described elsewere.[11–17] No deprotection reaction was observed in dark at given reaction conditions.

The benzene/water system. When the photolysis reached a maximal concentration of the photoproduct (the carboxylic acid) the aqueous layer was separated, acidified with HCl, and the acid was extracted into dichloromethane. The organic layer was dried over $MgSO_4$ and the solvent was evaporated to yield the crude product. The isolated acid was analyzed by ^{1}H NMR and GC methods and compared to the authentic samples obtained from commercial sources.

The water/solid ester system. The water layer was washed with a small amount of an organic solvent (e.g., dichloromethane), acidified with HCl, and the acid was extracted into dichloromethane. The organic layer was worked up in the same way as described above.

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