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Short communication

The synthesis of 1,5-benzodiazepines in a fluorous aqueous emulsion

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ABSTRACT

The synthesis of 1,5-benzodiazepine derivatives was smoothly carried out in a fluorous aqueous emulsion system composed of perfluorooctane (C_8F_{18}) and potassium perfluorooctanesulfonate ($C_8F_{17}SO_3K$, KFOS) at room temperature. The aqueous perfluorinated emulsion can be recovered and used again without a significant loss of efficiency.

1. Introduction

Benzodiazepines are very important compounds, widely used in the last decades as anticonvulsant, antianxiety, antitumor, psychosis, hypnotic and antipyretic agents [1]. Some benzodiazepine derivatives are also used in industry, such as light-sensitive material [2], and also as anti-inflammatory agents [3]. 1,5-Benzodiazepines are also used for preparation of some fused ring benzodiazepine derivatives, such as triazol [4], and oxadiazol [5].

Due to their wide range of pharmacological activity, industrial and synthetic applications, many methods for their preparation are reported in the literature. These include condensation reactions of *o*-phenylenediamine with α,β-unsaturated carbonyl compounds [2,6], β-haloketones [7], β-aminoketones [8], or ketones in the presence of BF_3–etherate [9], $NaBH_4$ [10], polyphosphoric acid [11], SiO_2 [11], MgO and $POCl_3$ [12], cerium (III) chloride/sodium iodide [13], zirconia [14], acetic acid [15], 12-tungstophosphoric acid [$(NH_4)H_2PW_{12}O_{40}$] [16], low-valent titanium [17], ytterbium trichloride ($YbCl_3$) [18] and ytterbium triflate [$Yb(OTf)_3$] [19]. Unfortunately, many of these processes suffer from major or minor limitations, such as drastic reaction conditions, tedious work-up procedures for reusing catalyst and co-occurrence of several side reactions.

Recently, fluorous biphasic system composed of fluorous Lewis acid ytterbium perfluorooctanesulfonate [$Yb(OPf)_3$], fluorous solvents (perfluorocarbon, PFC), and organic solvents, has been reported for the synthesis of 1,5-benzodiazepines from our group [20]. In this catalytic system, the fluorous catalyst with perfluoroalkylated "pony tails" can dissolve into the fluorous phase containing the product after the reaction. However, the requirement of heavy fluorous Lewis acid and use of fluorous solvent at high temperature brought about various issues concerning the cost for catalyst, and solvent leaching by evaporation. Therefore, the development of the strategy to eliminate the above requirement for fluorous catalysis is a topic of enormous importance.

It was known to us that fluorocarbon solvents have poor miscibility and lower solvation power than ordinary organic solvents and that these fluorinated solvents have solvophobic properties that are similar to those observed in water [21–24]. It was expected that the exclusive property shown by fluorous solvents and water might cause the organic substrates to remain in the interfacial area between a fluorous phase and aqueous media, resulting in the acceleration of their intermolecular reactions due to repulsion from the both sides (fluorous and aqueous phase) [21–24]. In 2006, Chiba group reported a successful example of the Diels–Alder reaction in an aqueous micellar system composed of perfluorohexane (C_6F_{14}) and lithium perfluorooctanesulfonate ($C_8F_{17}SO_3Li$, LiFOS) [25]. In continuation of our interest in fluorous technique [26], we have developed a practical protocol for the synthesis of 1,5-benzodiazepine derivatives in a fluorous aqueous emulsion system composed of perfluorooctane (C_8F_{18}) and potassium perfluorooctanesulfonate ($C_8F_{17}SO_3K$, KFOS) under aerobic conditions at room temperature.

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2. Experimental

2.1. General remarks

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were taken with a Bruker Advance RX300 spectrometer. GC–MS analyse was performed on a Saturn 2000GC/MS instrument. Particle size distribution was measured on a Mastersize2000 laser granularity testing apparatus. IR spectra were recorded on a Bomen MB154S infrared analyzer. Perfluorooctane and potassium perfluorooctanesulfonate were commercially obtained from DeiFu Chemical Co. of Wuhan. Other fluorous solvents were commercially obtained from ARCOS Co. Commercially available reagents were used without further purification.

2.2. Preparation of fluorous aqueous emulsion

Potassium perfluorooctanesulfonate (2.94 g, 5 mmol) was added to a mixture of perfluorooctane (4.38 g, 10 mmol) and deionized water (10 ml). The mixture was stirred for 2 h and then surged with sonication for 2 h at ambient temperature. After the completion of the emulsion formation, the dispersion was partially applied for the measurement of the particle size distributions at 25 °C.

2.3. Typical procedure for the synthesis of 1,5-benzodiazepine in fluorous aqueous emulsion

o-Phenylenediamine (0.22 g, 2 mmol) was added to the above emulsion in a glass flask under vigorous stirring. After *ca.* 5 min, acetophenone (0.72 g, 6 mmol) was introduced into the glass flask. After being stirred at room temperature for 72 h, the mixture was transferred to an extraction and separation funnel. Ether/hexane (1:1, 10 ml × 3 ml) was added to the funnel to extract organic substrates. The recovered emulsion was ready for further runs. The organic extraction was washed with water (10 ml), 10% $NaHCO_3$ solution (10 ml) and water (10 ml × 2 ml), and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: CH_2Cl_2/MeOH = 90/10) to give the condensation product 2,4-diphenyl-2-methyl-2,3-dihydro-1*H*-1,5-benzodiazepine **1** (0.44 g, 71%). All the condensation products are known compounds and adequately characterized by IR, ^{1}H NMR, ^{13}C NMR and GC–MS.

Diphenyl-2-methyl-2,3-dihydro-1*H*-1,5-benzodiazepine **1**: yellow solid; m.p. 150–152 °C (Lit. [12] 151–152 °C); IR (KBr): ν 3342 (NH), 1635 (C=N), 1588 (Ar) cm^{-1}; ^{1}H NMR (300 MHz, TMS, $CDCl_3$) δ 1.76 (s, 3H, CH_3), 2.93 (d, 2H, $-CH_2$, J = 0.17 Hz), 3.10 (d, 2H, $-CH_2$, J = 0.17 Hz), 3.36 (br, 1H, –NH), 6.80–7.71 (m, 14H, Ar); ^{13}C NMR (50 MHz, TMS, $CDCl_3$) δ 167.4, 146.6, 140.2, 139.5, 138.2, 129.9, 128.6, 128.4, 128.1, 127.2, 127.2, 126.4, 125.7, 121.7, 121.6, 74.1, 43.0, 29.9; MS(EI) *m*/*z*: 312 (10), 310 (14), 295 (100), 132 (65), 92 (12), 65 (8).

2,2,4-Trimethyl-2,3-dihydro-1*H*-1,5-benzodiazepine **2**: white solid; m.p. 125–126 °C (Lit. [8] 126 °C); IR (KBr): ν 3295 (NH), 1640 (C=N), 1592 (Ar) cm^{-1}; ^{1}H NMR (300 MHz, TMS, $CDCl_3$) δ 1.34 (s, 6H, 2-CH_3), 2.20 (s, 2H, $-CH_2$), 2.36 (s, 3H, $-CH_3$), 3.45 (br, 1H, –NH), 6.62–7.21 (m, 4H, Ar); ^{13}C NMR (50 MHz, TMS, $CDCl_3$) δ 171.6, 140.4, 138.0, 126.9, 125.3, 121.8, 121.6, 68.1, 45.4, 30.6, 29.5, 29.5; MS(EI) *m*/*z*: 188 (40), 173 (100), 132 (64), 131 (22), 92 (10).

2,2,4-Triethyl-3-methyl-2,3-dihydro-1*H*-1,5-benzodiazepine **3**: yellow solid; m.p. 143 °C (Lit. [12] 144–145 °C); IR (KBr): ν 3328 (NH), 1645 (C=N), 1588 (Ar) cm^{-1}; ^{1}H NMR (300 MHz, TMS, $CDCl_3$) δ 0.80–1.52 (m, 14H), 2.32 (m, 2H, CH_2), 2.91 (q, 1H, CH, J = 7.0 Hz), 3.69 (br, 1H, –NH), 6.66–7.38 (m, 4H, Ar); ^{13}C NMR (50 MHz, TMS, $CDCl_3$) δ 173.8, 142.0, 139.6, 132.7, 126.8, 118.0, 117.4, 68.3, 46.2, 35.4, 28.3, 28.0, 12.2, 11.6, 7.8, 7.3; MS(EI) *m*/*z*: 244 (12), 201 (100), 161 (13), 132 (25), 131 (6), 87 (3).

2,3,4-Trimethyl-2-ethyl-2,3-dihydro-1*H*-1,5-benzodiazepine **4**: yellow solid; m.p. 136–137 °C (Lit. [12] 137–138 °C); IR (KBr): ν 3340 (NH), 1643 (C=N), 1593 (Ar) cm^{-1}; ^{1}H NMR (300 MHz, TMS, $CDCl_3$) δ 0.98 (t, 3H, CH_3, J = 7.0 Hz), 1.25 (t, 3H, CH_3, J = 7.1 Hz), 1.71 (q, 2H, CH_2, J = 7.0 Hz), 2.16 (m, 2H, $-CH_2$), 2.35 (s, 3H, $-CH_3$), 2.69 (q, 2H, $-CH_2$, J = 7.1 Hz), 3.29 (br, 1H, –NH), 6.80–7.31 (m, 4H, Ar); ^{13}C NMR (50 MHz, TMS, $CDCl_3$) δ 175.6, 140.6, 138.1, 127.0, 126.2, 125.3, 121.6, 70.8, 42.1, 35.6, 35.6, 26.8, 10.6, 8.4; MS(EI) *m*/*z*: 216 (7), 214 (32), 207 (93), 199 (100), 133 (20), 132 (75), 96 (27), 65 (8).

2,4-Dimethyl-3-ethyl-2-(n-propyl)-2,3-dihydro-1*H*-1,5-benzodiazepine **5**: yellow solid; m.p. 138–141 °C (Lit. [20] 139–140 °C); IR (KBr): ν 3342 (NH), 1640 (C=N), 1589 (Ar) cm^{-1}; ^{1}H NMR (300 MHz, TMS, $CDCl_3$) δ 0.76–1.48 (m, 13H), 2.39 (s, 3H, CH_3), 2.89 (q, 1H, CH, J = 7.0 Hz), 3.70 (br, 1H, –NH), 6.67–7.44 (m, 4H, Ar); ^{13}C NMR (50 MHz, TMS, $CDCl_3$) δ 173.8, 142.2, 139.6, 132.7, 126.8, 118.1, 117.3, 68.2, 45.9, 30.4, 28.3, 28.0, 12.2, 11.6, 7.8, 7.3; MS(EI) *m*/*z*: 244 (11), 202 (13), 201 (100), 161 (13), 133 (16), 132 (25), 87 (3).

10-Spirocyclopentan-1,2,3,9,10,10a-hexahydrobenzo[b]-cyclopenta[e][1,4]diazepine **6**: yellow solid; m.p. 134–136 °C (Lit. [8] 134 °C); IR (KBr): ν 3338 (NH), 1658 (C=N), 1610 (Ar) cm^{-1}; ^{1}H NMR (300 MHz, TMS, $CDCl_3$) δ 1.01–2.24 (m, 13H), 3.26 (m, 2H, CH_2), 3.72 (br, 1H, –NH), 6.58–7.23 (m, 4H, Ar); ^{13}C NMR (50 MHz, TMS, $CDCl_3$) δ 178.0, 143.2, 139.6, 132.2, 126.8, 119.1, 118.6, 68.0, 54.3, 39.2, 38.4, 33.3, 28.9, 24.2, 24.0, 23.6; MS(EI) *m*/*z*: 240 (6), 236 (16), 207 (24), 187 (98), 145 (63), 132 (100), 92 (12), 55(6).

10-Spirocyclohexan-2,3,4,10,11,11a-hexahydro-1H-dibenzo[-b,e][1,4]diazepine **7**: yellow solid; m.p. 138–139 °C (Lit. [12] 137–139 °C); IR (KBr): ν 3310 (NH), 1645 (C=N), 1600 (Ar) cm^{-1}; ^{1}H NMR (300 MHz, TMS, $CDCl_3$) δ 0.96–2.35 (m, 17H), 3.25 (m, 2H, CH_2), 3.70 (br, 1H, –NH), 6.57–7.18 (m, 4H, Ar); ^{13}C NMR (50 MHz, TMS, $CDCl_3$) δ 178.4, 142.7, 138.0, 129.4, 126.5, 121.4, 121.2, 63.0, 52.8, 40.6, 39.2, 34.3, 33.3, 25.4, 24.3, 23.2, 21.7, 21.7; MS(EI) *m*/*z*: 268 (3), 188 (24), 145 (100), 132 (43), 92 (8), 65 (8).

3. Results and discussion

Initially, effect of the media on the condensation of *o*-phenylenediamine with acetophenone was investigated (Table 1). Potassium perfluorooctanesulfonate was selected as an emulsifier because it was cheap and easily obtained from industrial production. The control experiment showed that only trace amount of condensation product could be obtained in water, fluorous solvent and ordinary organic solvents. Even in the presence of aliphatic-chain surfactants such as potassium octyl sulfate (POS) and sodium dodecyl sulfate (SDS) at higher temperature, no remarkable acceleration was observed. The reaction did not improve by addition of potassium perfluorooctanesulfonate, indicating that potassium perfluorooctanesulfonate itself has almost no catalytic activity for the condensation.

Table 1
Media effect for the condensation of *o*-phenylenediamine with acetophenone[a].

Condition	Yield (%)[b]	Condition	Yield (%)[b]
H_2O[c]	2	SDS/H_2O[c,d]	11–17
C_2H_5OH	<1	C_8F_{18}/H_2O/KFOS[e]	37
C_8F_{18}[c]	<1	C_8F_{18}/H_2O/KFOS[f]	71, 68, 69
n-Octane[c]	<1	C_6F_{14}/H_2O/KFOS[f]	75
Toluene[c]	<1	C_7F_{14}/H_2O/KFOS[f]	54
C_8F_{18}/H_2O (1:1)[c]	6	C_7F_8/H_2O/KFOS[f]	49
POS/H_2O[c,d]	8–15	$C_{10}F_{18}$/H_2O/KFOS[f]	58

[a] The reaction condition: phenylenediamine, 2 mmol; acetophenone, 6 mmol; reaction over 72 h at RT.
[b] Isolated yields based on the phenylenediamine.
[c] 10 ml of each reaction medium.
[d] Surfactants, 10 mmol, 25–60 °C.
[e] PFC (10 mmol), H_2O (10 ml) and KFOS (2 mmol).
[f] PFC (10 mmol), H_2O (10 ml) and KFOS (5 mmol).

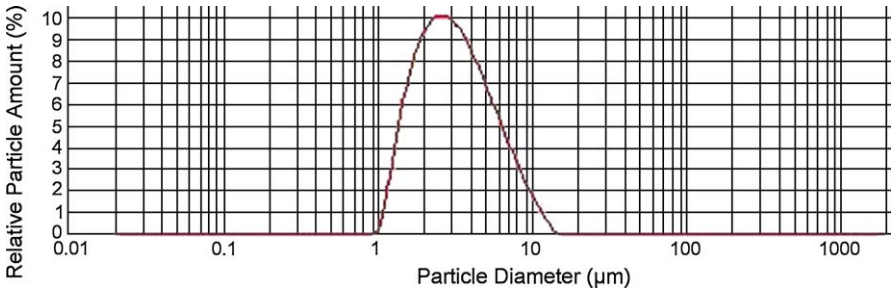


Fig. 1. Particle size distributions of C_8F_{18}/H_2O/KFOS emulsion.

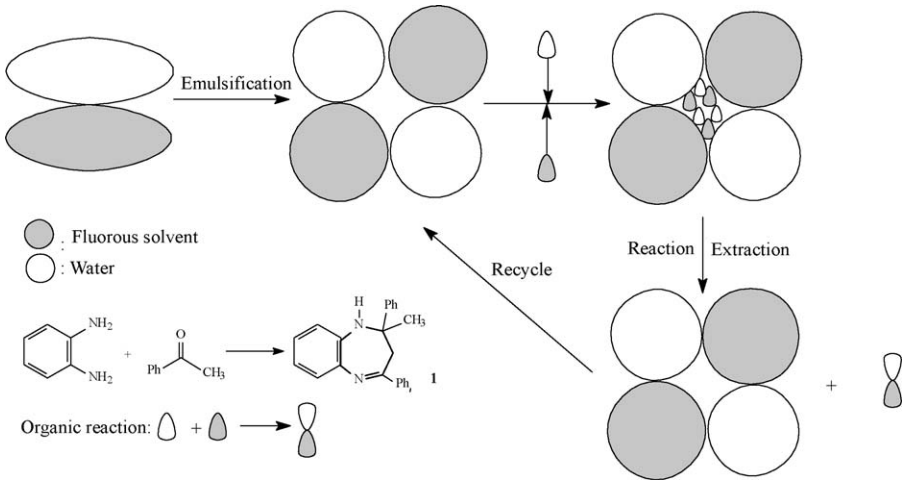


Fig. 2. The proposed organic synthesis of 1,5-benzodiazepine in the fluorous aqueous emulsion.

However, in the presence of potassium perfluorooctanesulfonate and fluorous solvents, the aqueous condensation was obviously accelerated. It was suggested that micelles in fluorous aqueous emulsion should be effective for the reaction. Stirring and then sonication of the mixture of PFC (10 mmol), H_2O (10 ml) and KFOS (5 mmol) resulted in the formation of a white, stable emulsion having an average diameter of 3.02 μm (Fig. 1). The organic substrates showed low miscibility with PFC and water; the exclusive property of the fluorous/aqueous interface accelerated the reaction (Fig. 2). The condensation of *o*-phenylenediamine with acetophenone gave the product 2,4-diphenyl-2-methyl-2,3-dihydro-1*H*-1,5-benzodiazepine (**1**) in 71% yield after 72 h in the fluorous aqueous emulsion system C_8F_{18}/H_2O/KFOS. Although the yield is lower than that in FBS case (99% yield at 60 °C for 2 h) and rather longer reaction time is needed in the present protocol, the fluorous aqueous emulsion strategy eliminates heating and the use of Lewis acids.

When the reaction was finished, ether/hexane was added to the reaction mixture to extract the organic compounds. Based on the ^{19}F NMR and UV–vis spectroscopic data and GC–MS, no loss of fluorous surfactant or fluorous solvent to the organic extraction could be detected. The use of the fluorous aqueous emulsion recycled without purification was equally effective. For example, the yields of condensation in C_8F_{18}/H_2O/KFOS emulsion from the first run to the third run were 71, 68, and 69%, respectively.

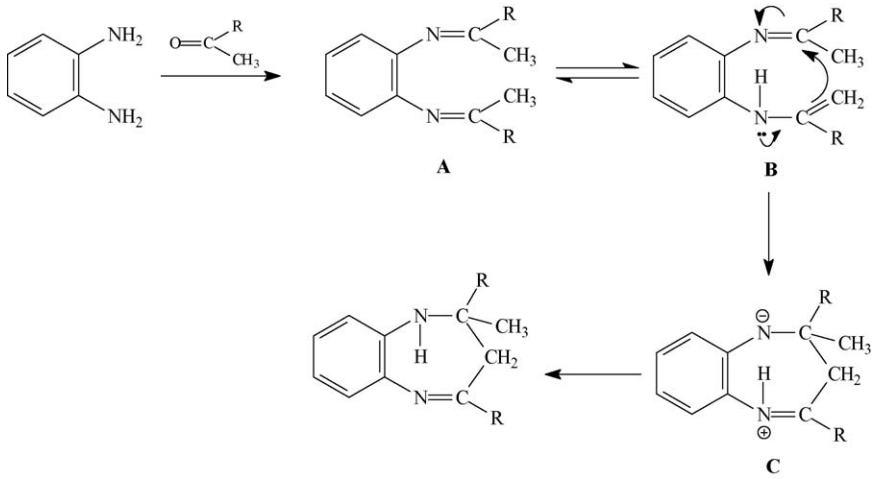
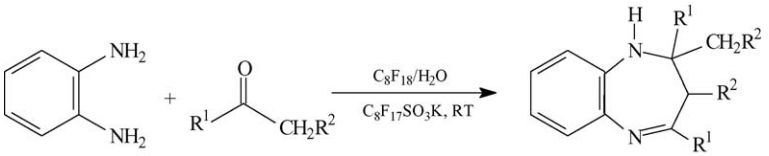


Fig. 3. The possible mechanism for the formation of 1,5-benzodiazepins.

Table 2
The synthesis of 2,3-dihydro-1*H*-1,5-benzodiazepines in the fluorous/aqueous emulsion[a].



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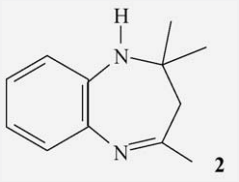
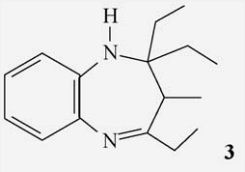
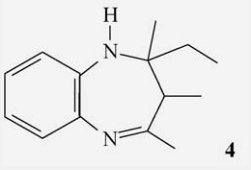
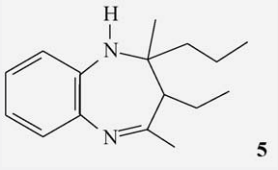
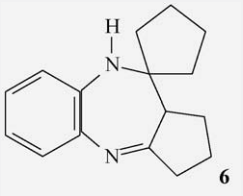
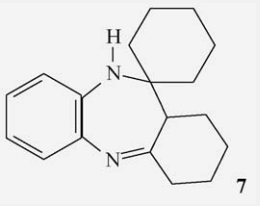
Reactant	Product	Time (h)	Yield (%)[b]	m.p. (°C)
Acetone	 **2**	72	8	125–126 (Lit. [8] 126)
3-Pentanone	 **3**	36	82	143 (Lit. [12] 144–145)
2-Butanone	 **4**	48	87	136–137 (Lit. [12] 137–138)
2-Pentanone	 **5**	48	79	138–141 (Lit. [20] 139–140)
Cyclopentanone	 **6**	72	55	134–136 (Lit. [8] 134)
Cyclohexanone	 **7**	72	58	138–139 (Lit. [12] 137–139)

[a] The reaction condition: phenylenediamine, 2 mmol; ketone, 6 mmol; C_8F_{18} (10 mmol), H_2O (10 ml) and KFOS (5 mmol); RT.
[b] Isolated yields based on the phenylenediamine.

A possible mechanism for the formation of 1,5-benzodiazepine is shown Fig. 3. Amino groups of *o*-phenylenediamine attack carbonyl group of ketone, giving the intermediate diimine **A**. Then, a 1,3-shift of the hydrogen attached methyl group occurs to afford an isomeric enamine **B**, which cyclizes to produce seven-membered ring **C** [11].

Fluorous solvents such as, perfluorohexane (C_6F_{14}), perfluoromethylcyclohexane (C_7F_{14}), perfluorotoluene (C_7F_8), and perfluorodecalin ($C_{10}F_{18}$, *cis* and *trans*-mixture) were also examined for the condensation. Perfluorohexane (C_6F_{14}) and perfluorotoluene (C_7F_8) are in fact miscible with aromatic compounds such as acetophenone at room temperature. Thus, it is impossible to separate the organic compounds from fluorous and aqueous phases by extraction. The loss of fluorous solvent was very obvious during repeated reactions when using perfluoromethylcyclohexane (C_7F_{14}) as a fluorous solvent because it is very volatile (bp 76 °C). The yield of the desired product in perfluorodecalin ($C_{10}F_{18}$) was lower than that in perfluorooctane (C_8F_{18}). Moreover, perfluorodecalin is much more expensive than perfluorooctane (C_8F_{18}). Therefore, perfluorooctane is an efficient and economical fluorous solvent for the synthesis of 1,5-benzodiazepine in fluorous aqueous emulsion.

Next, we applied the fluorous aqueous system to the synthesis of various 1,5-benzodiazepine derivatives. The results are summarized in Table 2. The reaction products were isolated and identified as 1,5-benzodiazepines, and no side reactions were observed. The reaction of acetone gave a poor yield of (8%, 2,2,4-trimethyl-2,3-dihydro-1*H*-1,5-benzodiazepine, **2**) after 72 h, due to it's miscibility with water. 3-Pentanone produced 2,2,4-triethyl-3-methyl-2,3-dihydro-1*H*-1,5-benzodiazepine (**3**) in 82% yield within in a shorter reaction time. It is interesting to note that, when using unsymmetrical ketones such as 2-butanone or 2-pentanone as substrates, the ring closure occurs selectively only from one side of the carbon skeleton giving a single product (**4** and **5**). Cyclic ketones such as cyclopentanone and cyclohexanone reacted to give the corresponding 2,3-dihydro-1*H*-1,5-benzodiazepines **6** and **7** in 55% and 58% yield, respectively.

In conclusion, a fluorous aqueous system composed of perfluorooctane and potassium perfluorooctanesulfonate was shown to effectively accelerate the synthesis of 1,5-benzodiazepines. This fluorous aqueous system will receive considerable attention in the future because it is possible to carry out the reactions without heating or the use of Lewis acids.

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