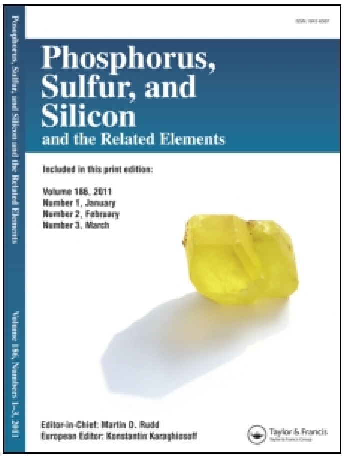


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Reaction in Dry Media: Silica Gel Supported Ferric Chloride Catalyzed Synthesis of 1,8-Dioxo-octahydroxanthene Derivatives

Hamid Reza Shaterian[a]; Asghar Hosseinian[a]; Majid Ghashang[a]
[a] Department of Chemistry, Faculty of Sciences, University of Sistan and Baluchestan, Zahedan, Iran

To cite this Article Shaterian, Hamid Reza , Hosseinian, Asghar and Ghashang, Majid(2008) 'Reaction in Dry Media: Silica Gel Supported Ferric Chloride Catalyzed Synthesis of 1,8-Dioxo-octahydroxanthene Derivatives', Phosphorus, Sulfur, and Silicon and the Related Elements, 183: 12, 3136 — 3144

To link to this Article: DOI: 10.1080/10426500802066096

URL: http://dx.doi.org/10.1080/10426500802066096

Phosphorus, Sulfur, and Silicon, 183:3136–3144, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500802066096

Reaction in Dry Media: Silica Gel Supported Ferric Chloride Catalyzed Synthesis of 1,8-Dioxo-octahydroxanthene Derivatives

**Hamid Reza Shaterian, Asghar Hosseinian,
and Majid Ghashang**
Department of Chemistry, Faculty of Sciences, University of Sistan
and Baluchestan, Zahedan, Iran

Herein, we describe a green procedure for the one-pot preparation of 1,8-dioxo-octahydroxanthene derivatives by condensation of dimedone and substituted benzaldehydes in the presence of $FeCl_3$-SiO_2 *as an efficient and heterogeneous catalyst under microwave irradiation and thermal conditions. This method has the advantages of high yields, cleaner reactions, efficient and cost-effective method, simple methodology, short reaction times, easy workup, and greener conditions.*

Keywords Aldehyde; dimedone; 1,8-dioxo-octahydroxanthene; $FeCl_3$-SiO_2; heterogeneous catalyst

INTRODUCTION

Avoiding organic solvents during the reactions in organic synthesis leads to a clean, efficient, and economical technology (green chemistry); safety is largely increased, work-up is considerably simplified, cost is reduced, increased amounts of reactants can be used in the some equipment, and the reactivities, and sometimes selectivities, are enhanced without dilution.[1–3] Due to all these advantages there is an increasing interest in the use of environmentally benign reagents and procedures.[3] Or, in other words, the absence of solvents coupled with the high yields and short reaction times often associated with reactions of this type make these procedures very attractive for synthesis.[3,4] In the present discussion, we describe the advantages of dry reaction

Received 25 February 2008; accepted 19 March 2008.

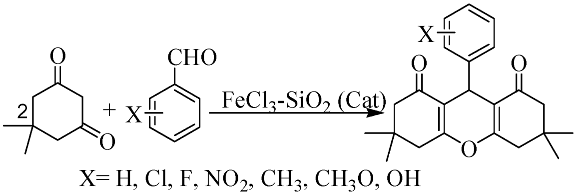
We are thankful to the Sistan and Baluchestan University Research Council for the partial support of this research.

Address correspondence to Hamid Reza Shaterian, Department of Chemistry, Faculty of Sciences, University of Sistan and Baluchestan, P.O. Box 98135-674, Zahedan, Iran. E-mail: hrshaterian@hamoon.usb.ac.ir

techniques coupled with microwave activation and their applications to organic synthesis using solid supports.

Xanthenes are an important class of organic compounds that have attracted strong interest due to their useful biological and pharmacological properties, such as antibacterial,[5] antiviral,[6] anti-inflammatory activities,[7] as well as efficiency in photodynamic therapy[8] and antagonist for the paralyzing action of zoxazolamine.[9] In addition, they also constitute a structural unit of a series of natural products and because of the inherent reactivity of the inbuilt pyran ring are versatile synthesis.[10] Furthermore, these compounds can be employed as cosmetics, pigments[11] and utilized as potential biodegradable agrochemicals.[12] The synthesis of xanthenediones usually condenses appropriate active methylene carbonyl compounds with aldehydes catalyzed by sulfuric acid or hydrochloric acid.[13] Recently, many procedures have been reported to synthesis 1,8-dioxo-octahydroxanthene derivatives by condensation of dimedone and aldehydes using silica sulfuric acid,[14] Dowex-50W,[15] $HClO_4$-SiO_2 and PPA-SiO_2,[16] silica chloride and $NaHSO_4$-SiO_2,[17] *p*-dodecylbenzenesulfonic acid,[18] Fe^{3+}-montmorillonite,[19] amberlyst-15,[20] diammonium hydrogen phosphate,[21] TMSCl,[22] tetrabutylammonium hydrogen sulphate[23] and [Hmim]TFA[24] as catalyst. However, some of the reported methods suffer from drawbacks such as long reaction time,[17,20,24] and toxic reagents and by-products.[22] Therefore, a great need still exists for versatile, simple and environmentally friendly processes.

Herein, we report an efficient one-pot synthesis of 1,8-dioxo-octahydroxanthene derivatives by the condensation reaction of various aromatic aldehydes with dimedone under thermal solvent-free and microwave conditions in the presence of $FeCl_3$-SiO_2 (Scheme 1).



SCHEME 1

RESULTS AND DISCUSSION

For choice optimum conditions, we tried to minimizing the time, temperature, and amount of the catalyst. Thus, the reaction of 2,5-dimethoxybenzaldehyde and dimedone was selected as model to

TABLE I $FeCl_3$-SiO_2 **Catalyzed Multicomponent Synthesis of 9-(2,5-Dimethoxyphenyl)-3,3,6,6-tetramethyl-3,4,6,7-tetrahydro-2H-xanthene-1,8(5H,9H)-dione**

Entry	Catalyst (g)	Temperature (°C)	Microwave power (W)	Method A[a] time (min)/ yield(%)[b]	Method B[a] time (min)/ yield (%)[b]
1	0.01	120	—	30/75	—
2	0.02	120	—	19/83	—
3	0.03	120	—	8/91	—
4	0.04	120	—	7/91	—
5	0.03	90	—	36/74	—
6	0.03	60	—	50/60	—
7	0.03	—	180	—	11/67
8	0.03	—	300	—	9/72
9	0.03	—	450	—	5/84

[a]Molar ratio: benzaldehyde (1 mmol), dimedone (2 mmol); and [b]isolated yield.

investigate the effects of the catalyst at different reaction temperatures (60, 90, and 120°C) and the different amount of catalyst (0.01, 0.02, 0.03, and 0.04 g) for method A and the different power of microwave irradiation (180, 300 and 450 W) for method B. The best result was obtained by carrying out the reaction with 1:2 molar ratios of aldehyde/dimedone and SiO_2-$FeCl_3$ (0.03 g) at 120°C (Table I, Method A) or 450 W microwave power (Table I, Method B) in solvent-free conditions.

Thus, we prepared a range of aryl 1,8-dioxo-octahydroxanthenes under the optimized reaction conditions: aryl aldehyde (1 equiv), dimedone (2 equiv) in the presence of $FeCl_3$-SiO_2 (0.03 g) (Table II).

As summarized in Table II, several different aromatic aldehydes and dimedone were reacted in the presences $FeCl_3$-SiO_2 as catalyst under thermal solvent-free and microwave conditions resulting corresponding aryl 1,8-dioxo-octahydroxanthene in good to excellent yields (Scheme 1, Table II). The reaction was performed with benzaldehyde containing withdrawing as well as electron donating groups, but benzaldehyde with electron donating groups are generally more reactive than their corresponding benzaldehyde with electron withdrawing groups and give the desired product at short reaction time with excellent yield (Table II).

$FeCl_3$-SiO_2 can act as Brønsted and Lewis acid catalysts,[26] as illustrated in Scheme 2.

The effect of catalyst and their abilities to acts as a Brønsted or Lewis acid (empty π orbital of Fe in $FeCl_3$-SiO_2) in this reactions is unknown. But, in this suggested mechanism, we have proposed, that an acid-base

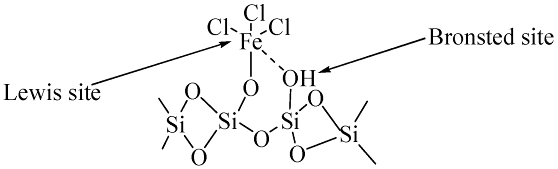
TABLE II Preparation of 1,8-Dioxo-octahydroxanthene Derivatives

Entry	Aldehyde	Method A time (min)/ yield (%)[a]	Method B time (min)/ yield (%)[a]
1	Benzaldehyde	7/90	5/79
2	2-Chlorobenzaldehyde	8/89	9/78
3	3-Chlorobenzaldehyde	8/85	6/76
4	4-Chlorobenzaldehyde	10/92	7/80
5	2,4-Dichlorobenzaldehyde	11/90	8/85
6	3-Nitrobenzaldehyde	14/84	11/75
7	4-Nitrobenzaldehyde	10/87	9/78
8	4-Methylbenzaldehyde	10/93	8/81
9	4-Methoxybenzaldehyde	6/88	4/79
11	4-Hydroxybenzaldehyde	8/91	6/78
12	4-Hydroxy-3-methoxybenzaldehyde	7/94	7/80
13	2-Pyridinecarbaldehyde	50/76	17/60
14	Cinnamaldehyde	13/86	10/73
15	4-Fluorobenzaldehyde	9/91	6/82
16	3-Fluorobenzaldehyde	7/89	6/83
17	2-Hydroxybenzaldehyde	8/93	5/85
18	2,5-Dimethoxybenzaldehyde	8/91	5/80
19	1-Naphthaldehyde	20/95	10/89

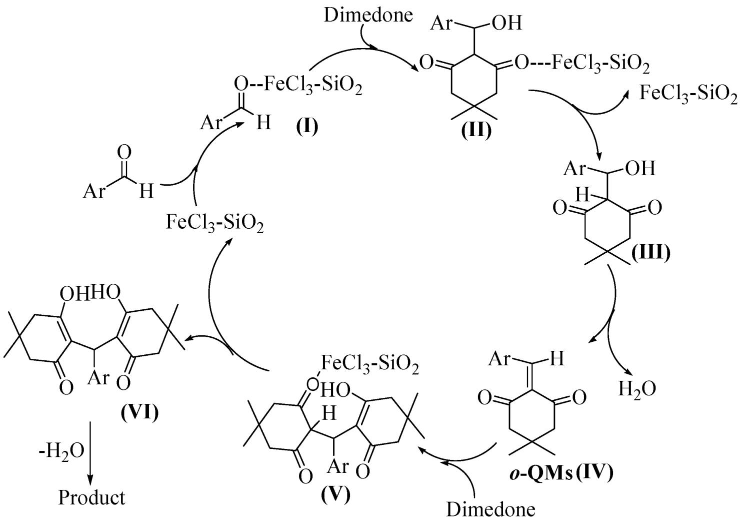
[a] Yields refer to the pure isolated products. All known products have been reported previously in the literature and were characterized by comparison of IR and NMR spectra with authentic samples.[14–24]

interaction between $FeCl_3$-SiO_2 and loan pair of oxygen polarizes C=O bond of aldehyde.

As reported in the literature, the reaction of dimedone with aldehydes in the presence of acid catalyst is known to give *ortho*-quinone methides (*o*-QMs). The same *o*-QMs, generated in situ, have been reacted with another dimedone to form **V** intermediate. A possible reasonable explanation for this result can be given by considering the Michael addition of dimedone as CH acid to *o*-QMs intermediate is favorable via conjugate addi-



SCHEME 2 Brønsted acidity arising from inductive effect of Lewis acid center coordinated to a silicasupport.[26]



SCHEME 3

TABLE III Comparison Results of $FeCl_3$-SiO_2 with Other Catalysts Reported in the Literature[a]

Entry	Catalyst	Conditions	Time/yield (%)
1	Silica sulfuric acid	Solvent-free; 80°C; catalyst (0.2 g)	1 h/97
2	$NaHSO_4.SiO_2$	CH_3CN; under reflux; catalyst (0.1 g)	6.5 h/90
3	Tetrabutylammonium hydrogen sulfate	1,4-dioxane/water: 1/4; r.t.; catalyst (10 mol%)	3.5 h/88
4	TMSCl	CH_3CN; under reflux; catalyst (1 mmol)	8 h/84.1
5	Amberlyst-15	CH_3CN; under reflux; catalyst (0.2 g)	5 h/92
6	Fe^{3+}-Montmorillonite	ethanol; under reflux; catalyst (0.05 g)	6 h/94
7	[Hmim]TFA	Solvent-free; 80°C; catalyst (0.1 g)	3 h/86
8	Dowex-50W	Solvent-free; 100°C; catalyst (0.4 g)	3 h/87
9	*p*-Dodecylbenzenesulfonic acid	H_2O; ultrasonic; 25–30°C; catalyst (10 mol%)	1 h/89
10	PPA-SiO_2	Solvent-free; 140°C; catalyst (10 mol%)	0.5 h/92.8
11	$FeCl_3$-SiO_2	Solvent-free; 120°C; catalyst (0.03 g)	7 min/90

[a] Based on dimedone (2 equiv.), benzaldehyde (1 equiv.)

tion on α,β-unsaturated carbonyl group. Cyclodehydration of **VI** intermediate afford 1,8-dioxo-octahydroxanthene (Scheme 3). To show the merit of the present work in comparison with reported results in the literature, we compared results of $FeCl_3$-SiO_2 with silica sulfuric acid,[14] Dowex-50W,[15] PPA-SiO_2,[16]$NaHSO_4$-SiO_2,[17] p-dodecylbenzenesulfonic acid,[18] Fe^{3+}-montmorillonite,[19] amberlyst-15,[20] TMSCl,[22] tetrabutylammonium hydrogen sulphate,[23] and [Hmim]TFA[24] in the synthesis of 1,8-dioxo-octahydroxanthene derivatives. As shown in Table III, $FeCl_3$-SiO_2 can act as effective catalyst with respect to reaction times, yields and the obtained products.

CONCLUSION

In summary, an efficient method for the one-pot preparation of 1,8-dioxo-octahydroxanthene derivatives by the condensation of an aromatic aldehydes and dimedone using $FeCl_3$-SiO_2 as a heterogeneous catalyst under solvent-free, thermal and microwave conditions with short reaction times was developed.

EXPERIMENTAL

All reagents were purchased from Merck and Aldrich and used without further purification. All yields refer to isolated products after purification. Products were characterized by comparison with authentic samples and by spectroscopy data (IR, ^1H NMR, and ^{13}C NMR spectra) and melting point. The NMR spectra were recorded on a Bruker Avance DPX 500 and 300 MHz instrument. The spectra were measured in $CDCl_3$ relative to TMS (0.00 ppm). Mass spectra were recorded on an Agilent Technologies 5973 Network Mass Selective Detector (MSD) operating at an ionization potential of 70 eV. IR spectra were recorded on a JASCO FT-IR 460 plus spectrophotometer. All of the compounds were solid and solid-state IR spectra were recorded using the KBr disk technique. Melting points were determined in open capillaries with a BUCHI 510 melting point apparatus and are uncorrected. TLC was performed on Silica-gel polygram SIL G/UV 254 plates.

Preparation of $FeCl_3$-SiO_2

Acetone solution (600 ml) of $FeCl_3.6H_2O$ (50 g, or anhydrous $FeCl_3$, 30 g) and chromatographic grade silica gel (500 g, Merck Kieselgel 60, 70–230 Mesh ASTM) were stirred at room temperature in a rotary evaporator until dry and then in high vacuum (0.1 torr) for 3 h, resulting in the "inactive" $FeCl_3$-SiO_2 reagent (yellow powder). This powder was heated for 1 h at 100°C in a rotary evaporator to give a brownish powder ("active" $FeCl_3$-SiO_2 reagent).[25a]

General Procedure for Preparation of 1,8-dioxo-octahydrxanthene Derivatives by Using $FeCl_3$-SiO_2 as Catalyst

Solvent-Free Thermal (Method A)

To a mixture of aldehyde (10 mmol), dimedone (20 mmol), $FeCl_3$-SiO_2 (0.3 g) was added and the mixture was inserted in an oil bath and heated at 120 °C for the appropriate time (Table II); completion of the reaction was indicated by TLC. After completion, the reaction mass was cooled to 25°C. Then CH_2Cl_2 was added and the mixture stirred, until solid crude product was dissolved and filtered; the filtrate solution was concentrated. The solid product was purified by recrystallization procedure in aqueous EtOH (30%).

Solvent-Free Microwave Irradiation (Method B)

To a mixture of aldehyde (10 mmol), dimedone (20 mmol), $FeCl_3$-SiO_2 (0.3 g) was added. The mixture was inserted in a microwave oven (Samsung, model KE300R) and irradiated at 450 W for the appropriate time (Table II); completion of the reaction was indicated by TLC. After completion, the reaction mass was cooled to 25°C. Then CH_2Cl_2 was added and the mixture stirred until solid crude product was dissolved and filtered; the filtrate solution was concentrated. The solid product was purified by recrystallization procedure in aqueous EtOH (30%).

The desired pure products were characterized by comparison of their physical data with those of known 1,8-dioxo-octahydrxanthene. The spectral data of some representative 1,8-dioxo-octahydroxanthenes are given as follows.

9-(3-fluorophenyl)-3,3,6,6-tetramethyl-3,4,6,7-tetrahydro-2H-xanthene-1,8(5H,9H)-dione (Table II, Entry 16). [m.p.: 178–179°C]; ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 0.99$ (s, 6H), 1.10 (s, 6H), 2.20 (q, $J = 16.3$ Hz, 4H), 2.46 (s, 4H), 4.75 (s, 1H), 6.76–6.80 (m, 1H), 6.97–6.93 (m, 1H), 7.10 (d, $J = 7.6$ Hz, 1H), 7.14–7.18 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 27.30$, 29.30, 29.35, 31.66, 31.67, 32.12, 40.83, 50.70, 113.18, 113.35, 115.05, 115.18, 115.23, 124.20, 129.24, 129.31, 146.60, 146.64, 161.78, 162.46, 163.73, 196.14 ppm; IR (KBr, cm^{-1}) 2961, 2873, 1660, 1624, 1590, 1485, 1450, 1361, 1241, 1201, 1165, 1140, 1003, 930, 769, 696, 575; Mass(m/z (%)): 368.1 (M^+, 56), 274.1 (21), 273.1 (100), 231.1 (24), 217.1 (16), 161.1 (9), 55.2 (5).

9-(2-hydroxyphenyl)-3,3,6,6-tetramethyl-3,4,6,7-tetrahydro-2H-xanthene-1,8(5H,9H)-dione (Table II, Entry 17). [m.p.: 206–208°C]; ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 0.98$ (d, $J = 2.5$ Hz, 6H), 1.01 (s, 3H), 1.11 (s, 3H), 1.96 (q, $J = 16.5$ Hz, 2H), 2.27–2.58 (m, 6H), 4.68 (s, 1H), 6.98 (d, $J = 4.9$ Hz, 3H), 7.11–7.15 (m, 1H), 10.44 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 26.60$, 27.11, 27.66, 29.17, 29.68, 30.97, 32.20, 41.53, 43.19, 49.96, 50.59, 111.04, 115.69, 118.28, 124.39, 124.48, 127.42, 128.00, 150.97, 168.84, 170.66, 196.50, 200.55 ppm; IR (KBr, cm^{-1}) 3148, 2961, 2884, 1628, 1578, 1489, 1457, 1377, 1313, 1233, 1186, 1151, 1134, 1079, 1023, 872, 763, 656, 584, 474; Mass(m/z (%)): 366.1 (M^+, 45), 283.1 (21), 282.1 (100), 281.1 (50), 267.1 (10), 227.1 (73), 171.1 (23), 115.1 (13), 83.2 (6), 55.2 (5).

9-(2,5-dimethoxyphenyl)-3,3,6,6-tetramethyl-3,4,6,7-tetrahydro-2H-xanthene-1,8(5H,9H)-dione (Table II, Entry 18). [m.p.: 201–202°C]; ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 0.95$ (s, 6H), 1.07 (s, 6H), 2.15 (q, $J = 16.2$ Hz, 4H), 2.40 (q, $J = 17.6$ Hz, 4H), 3.73 (s, 3H), 3.74 (s, 3H), 4.82 (s, 1H), 6.62 (dd, $J = 3.0$, 8.8 Hz, 1H), 6.67 (d, $J = 8.8$ Hz, 1H), 6.95 (d, J = 3.0 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 26.81$, 29.31, 29.35, 31.97, 40.90, 50.75, 55.50, 55.76, 111.59, 112.70, 113.72, 117.38, 131.79, 152.06, 153.21, 162.68, 196.30 ppm; IR (KBr, cm^{-1}) 2962, 2872, 1675, 1655, 1617, 1502, 1463, 1350, 1247, 1226, 1165, 1136, 1045, 1004, 860, 813, 730, 686, 573; Mass(m/z (%)): 410.2 (M^+, 85), 395.1 (7), 380.1 (28), 379.1 (100), 323.1 (10), 295.1 (12), 273.1 (38), 217.1 (14), 161.1 (14), 83.2 (14), 55.2 (8).

3,3,6,6-tetramethyl-9-(naphthalen-1-yl)-3,4,6,7-tetrahydro-2H-xanthene-1,8(5H,9H)-dione (Table II, Entry 19). [m.p.: 236–238°C]; ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 0.96$ (s, 6H), 1.10 (s, 6H), 2.15 (q, $J = 16.3$ Hz, 4H), 2.53 (s, 4H), 5.57 (s, 1H), 7.24 (brs, 1H), 7.34 (t, $J = 7.4$ Hz, 1H), 7.47 (t, $J = 7.1$ Hz, 1H), 7.64 (t, $J = 8.0$ Hz, 1H), 7.77 (t, $J = 8.0$ Hz, 1H), 8.86 (brs, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 27.00$, 27.29, 29.23, 32.11, 40.91, 50.63, 116.59, 124.82, 125.20, 125.50, 125.75, 126.18, 127.32, 128.06, 131.70, 133.56, 142.38, 162.05, 196.40 ppm; IR (KBr, cm^{-1}) 3049, 2954, 2869, 1667, 1628, 1508, 1466, 1356, 1195, 1165, 1142, 1006, 767, 567, 459; Mass(m/z (%)): 400.4 (M^+, 67), 384.3 (18), 383.3 (57), 274.2 (20), 273.3 (100), 217.2 (21), 189.2 (7), 161.1 (13), 83.2 (5), 55.2 (4).

REFERENCES

[1] A. Corma and A. Garcia, *Chem. Rev.,* **103,** 4307(2003).

[2] M. Kidwai, *Pure Appl. Chem.*, **73,** 147 (2001).

[3] P. T. Anastas and J. C. Warner, *Green Chemistry: Theory and Practice* (Oxford University Press: Oxford, 1998).

[4] J. H. Clark and C. N. Rhodes, *Clean Synthesis Using Porous Inorganic Solid Catalysts and Supported Reagents* (Royal Society of Chemistry, Cambridge, 2000).

[5] T. Hideo, *Chem. Abstr.*, **95,** 80922b (1981).

[6] R. W. Lambert, J. A. Martin, J. H. Merrett, K. E. B. Parkes, and G. J. Thomas, *Chem Abstr.,* **126,** p212377y (1997).

[7] J. P. Poupelin, G. Saint-Rut, O. Foussard-Blanpin, G. Narcisse, G. Uchida- Ernouf, and R. Lacroix, *Eur. J. Med. Chem.*, **13,** 67 (1978).

[8] (a) R. M. Ion, *Progr. Catal.* **2,** 55 (1997); (b) R. M. Ion, D. Frackowiak, A. Planner, and K. Wiktorowicz, *Acta Biochim. Pol.*, **45,** 833 (1998).

[9] (a) G. Saint-Ruf, A. De, and H. T. Hieu, *Bull. Chim. Ther.,* **7,** 83 (1972); (b) G. Saint-Ruf, H. T. Hieu, and J. P. Poupelin, *Naturwiss.,* **62,** 584 (1975).

[10] C. N. O'Callaghan and T. B. H. Mc Murry, *J. Chem. Res. (S),* 214 (1995).

[11] G. P. Ellis, A. Weissburger, and E. C. Taylor, The chemistry of heterocyclic compounds. In *Chromenes, Chromanes and Chromeones* (Wiley, New York, 1977).

[12] (a) E. A. Hafez, M. H. Elnagdi, A. A Elagamey, and F. A. M. El-Taweel, *Heterocycles.,* **26,** 903 (1987); (b) F. M. Abdel Galil, B. Y. Riad, S. M. Sherif, and M. H. Elnagdi, *Chem. Lett.,* 1123 (1982).

[13] E. C. Horning and M. G. Horning, *J. Org. Chem.,* **11,** 95 (1946).

[14] M. Seyyedhamzeh, P. Mirzaei, and A. Bazgir, *Dyes Pigm.*, **76,** 836 (2008).

[15] G. Imani-Shakibaei, P. Mirzaei, and A. Bazgir, *Appl Catal A: Gen.,***325,** 188 (2007).

[16] R. Kantevari, R. Bantu, and L. Nagarapu, *J. Mol. Catal. A: Chem.,* **269,** 53 (2007).

[17] B. Das, P. Thirupathi, K. Reddy, B. Ravikanth, and L. Nagarapu, *Catal. Commun.,* **8,** 535 (2007).

[18] T.-S. Jin, J.-S. Zhang, A.-Q. Wang, and T.-S. Li, *Ultrason Sonochem.,* **13,** 220 (2006).

[19] G. Song, B. Wang, H. Luo, and L. Yang, *Catal. Commun.,* **8,** 673 (2007).

[20] B. Das, P. Thirupathi, I. Mahender, V. -S. Reddy, and Y.-K. Rao, *J. Mol. Catal. A: Chem.,* **247,** 233 (2006).

[21] F. Darviche, S. Balalaie, F. Chadegani, and P. Salehi, *Synth. Commun.,* **37,** 1059 (2007).

[22] S. Kantevari, R. Bantu, and L. Nagarapu, *Arkivoc,* **xvi,** 136 (2006).

[23] H.-N. Karade, M. Sathe, and M. -P. Kaushik, *Arkivoc,* **xiii,** 252 (2007).

[24] M. Dabiri, M. Baghbanzadeh, and E. Arzroomchilar, *Catal. Commun.,***9,** 939 (2008).

[25] For the preparation and some application of $FiCl_3$-SiO_2: (a) D. M. Tal, E. Einan and Y. Mazur, *Tetrahedron.,* **37,** 4327 (1981); (b) A. Fadel and J. Salaüon, *Tetrahedron,* **41,** 413 (1985); (c) A. Fadel and J. Salaüon, *Tetrahedron.,* **41,** 1267 (1985); (d) K. S. Kim, Y. H. Song, B. H. Lee, and C. S. Hahn, *J. Org. Chem.,* **51,** 404 (1986); (e) H. R. Shaterian and H. Yarahmadi, *Tetrahedron Lett.,* **49,** 1297 (2008).

[26] (a) K. Wilson and J. H. Clark, *Pure Appl. Chem.,* **72,** 1313 (2000); (b) T. Cseri, S. Bekassy, F. Figeuras, E. Cseke, L. C. Demenorval and R. Dunarte, *Appl. Catal. A.,* **132,** 141 (1995).