



NOTE

Silica Sulfuric Acid as Heterogeneous and Recoverable Catalysts for the Synthesis of Dithienylmethanes under Solvent-Free Conditions

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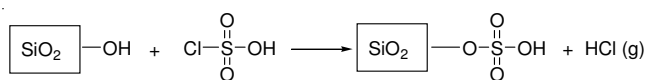
An efficient synthesis of dithienylmethanes from the reaction of thiophene and aromatic aldehydes under solvent-free conditions in good to excellent yields and short reaction times using reusable silica sulfuric acid as heterogeneous acid catalyst has been investigated.

Key Words: Dithienylmethanes, Thiophene, Silica sulfuric acid, Solvent-free.

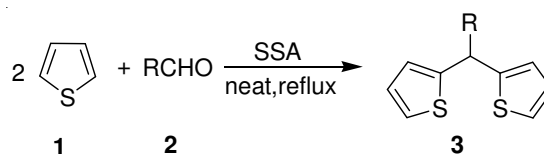
Reusable heterogeneous catalysts have attracted a great deal of interest in recent years¹. Since most of the catalysts are expensive and contaminate the environment, the development of efficient methods for recovery and reuse of the catalysts is a very important aspect. An easy solution to this problem is to heterogenize the homogeneous catalysts by supporting them on solid materials. The major advantages of solid-supported catalysts are the facile recovery from the reaction mixture and the possibility of reusing them. Furthermore, supporting of the catalysts efficiently increases the surface area and subsequently the reactivity of the catalysts.

Dithienylmethanes are widely being used as important building blocks for the synthesis of a variety of functional porphyrins and porphyrin analogues², which can be of wide interest in materials science³. Recently the synthesis of dithienylmethanes has been reported using trifluoroacetic acid^{2a}, BF₃·O(Et)₂^{2a}, TiCl₄^{2b}, NaHSO₄-SiO₂⁴ as catalysts. Silica sulfuric acid (SSA) has been used as efficient heterogeneous catalysts for many organic transformations because of their low cost, ease of preparation (**Scheme-I**), catalyst recycling and ease of handling⁵. Now we reported an efficient method for the preparation of dithienylmethane derivatives using silica sulfuric acid as recyclable solid acid catalyst under solvent-free conditions (**Scheme-II**).

NMR spectra were determined on Bruker AV-400 spectrometer at room temperature using TMS as internal standard, coupling constants (*J*) were measured in Hz; elemental analysis were performed by a Vario-III elemental analyzer; melting points were determined on a XT-4 binocular microscope and were uncorrected; SSA was prepared according to literature^{5a};



Scheme-I



Scheme-II

commercially available reagents were used throughout without further purification unless otherwise stated.

General procedure for the preparation of 3: The aldehyde (1 mmol), thiophene (10 mmol) and silica sulfuric acid (SSA) (100 mg) were mixed together in a 10 mL round-bottomed flask equipped with a magnetic stir bar at reflux temperature for the given time (Table-3). After completion of the reaction, as indicated by TLC, the reaction mixture was diluted with ethyl acetate (2 × 5 mL). The liquid was filtered off, the catalyst washed with acetone (5 mL). Then the organic layer was concentrated under reduced pressure to afford crude product which was then purified by column chromatography eluted with ethyl acetate and petroleum ether mixture.

To choose optimum conditions, first we tried to prepare 2,2'-(phenylmethylene)dithiophene from the reaction of benzaldehyde (1 mmol) and thiophene (10 mmol) as a model in the absence and presence of SSA under thermal solvent-free conditions (Table-1). As shown from Table-1, this transformation requires a catalyst and also 100 mg silica sulfuric acid at reflux

TABLE-1

OPTIMUM CONDITIONS FOR THE PREPARATION OF 2,2'-(PHENYLMETHYLENE)DITHIOPHENE UNDER SOLVENT-FREE THERMAL CONDITIONS AT REFLUX TEMPERATURE^a

Entry	Catalyst	Time (min)	Yield (%) ^b
1	–	120	0
2	SiO ₂ (200 mg)	120	0
3	H ₂ SO ₄ (0.1 mmol)	60	54
4	SSA (100 mg)	30	86

^aReaction conditions: benzaldehyde (1 mmol); thiophene (10 mmol); reflux; neat. ^bIsolated yield.

temperature can be chosen for the preparation of dithienylmethane derivatives.

For find optimize amount of SSA, the reaction was carried out by varying amount of the catalyst (Table-2). Maximum yield was obtained with 100 mg of catalyst. Further increase in amount of SSA in mentioned reaction did not have any significant effect on the product yield.

TABLE-2

AMOUNTS OF CATALYST OPTIMIZATION FOR THE SYNTHESIS OF 2,2'-(PHENYLMETHYLENE)DITHIOPHENE^a

Entry	SSA (mg/mmol)	Time (min)	Yield (%) ^b
1	0	90	0
2	20	60	40
3	40	45	61
4	60	45	68
5	80	30	79
6	100	30	86
7	120	30	86
8	140	30	85
9	160	30	86

^aReaction conditions: benzaldehyde (1 mmol); thiophene (10 mmol); reflux; neat. ^bIsolated yield.

The generality of this reaction was examined using several types of aldehydes. In all cases, the reactions gave the corresponding products in good to excellent yield (Table-3).

TABLE-3

SYNTHESIS OF DITHIENYLMETHANES CATALYZED BY SSA^a

R	Time (min)	Products ^b	Yield (%) ^c	m.p. (lit.) (°C)
C ₆ H ₅	30	3a	86	70-72 (73-74) ^d
4-Br-C ₆ H ₄	25	3b	82	64-65 (62-64) ^d
4-NO ₂ -C ₆ H ₄	40	3c	87	85-86 (87-89) ^d
3-NO ₂ -C ₆ H ₄	25	3d	83	70-73 (72-74) ^d
4-MeO-C ₆ H ₄	45	3e	75	89-91 (88-90) ^d
3-OH-C ₆ H ₄	70	3f	74	Oil (oil) ^d
3,4-(OCH ₂ O)-C ₆ H ₃	80	3g	66	92-94 (94-96) ^d
2-Thienyl	80	3h	72	48-49 (50-51) ^d

^aReaction conditions: aldehyde (1 mmol); thiophene (10 mmol); SSA (100 mg); neat; reflux. ^bAll products were identified by comparing their physical and spectral data with those of the authentic samples (see references 4). ^cIsolated yield.

The reusability of the catalyst was tested in the synthesis of 2,2'-(phenylmethylene)dithiophene, as shown in Table-4. The catalyst was recovered after each run, washed 3 times with acetone, dried in an oven at 100 °C for 0.5 h prior to use and tested for its activity in the subsequent run and fresh catalyst was not added. The catalyst was tested for 4 runs. It was seen that the catalyst displayed very good reusability.

TABLE-4

EFFECT OF REUSABILITY OF SSA CATALYST ON 2,2'-(PHENYLMETHYLENE)DITHIOPHENE SYNTHESIS^a

Run	Cycle	Yield (%) ^b
1	0	86
2	1	85
3	2	82
4	3	79

^aReaction conditions: benzaldehyde (1 mmol); thiophene (10 mmol); SSA (100 mg); reflux; neat. ^bIsolated yield.

Present findings reflect the wide applicability and usefulness of the method. Some previously reported data on reaction conditions and the yield of product were compared with our results (Table-5). As one can see our results show good comparability with previously reported data in respect to reaction time although the yield was not always the best.

TABLE-5

SSA CATALYZED SYNTHESIS OF 2,2'-(PHENYLMETHYLENE)DITHIOPHENE IN COMPARISON WITH OTHER LITERATURES

Entry	Reaction conditions	Time (min)	Yield (%) ^a	Ref.
1	Benzaldehyde;; thiophene: SSA = 1:10:0.25, reflux, neat	30	86	Present method
2	Benzaldehyde;; thiophene: BF ₃ ·O(Et) ₂ = 1:37:1, r.t., neat	30	62	[2a]
3	Benzaldehyde;; thiophene: CF ₃ COOH = 1:37:10, r.t., neat	22	60	[2a]
4	Benzaldehyde;; thiophene: NaHSO ₄ -SiO ₂ = 1:37:0.5, reflux, neat	150	82	[4]

Conclusion

For the first time, a novel, eco-friendly and simple protocol for the synthesis of dithienylmethanes using inexpensive silica sulfuric acid is established. The short reaction procedure and reusability of the catalyst make this method one of the most efficient methods for the synthesis of this class of compounds.

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