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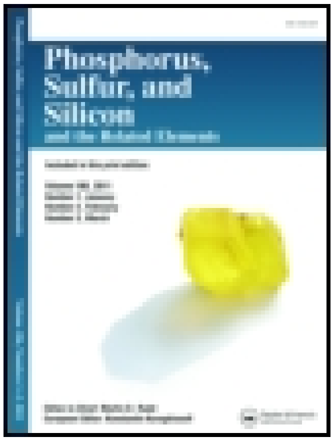

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Conversion of Thioamides into Their Corresponding Oxygen Analogues Using Silver Carbonate Supported on Celite

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CONVERSION OF THIOAMIDES INTO THEIR CORRESPONDING OXYGEN ANALOGUES USING SILVER CARBONATE SUPPORTED ON CELITE

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Silver carbonate supported on celite (Ag_2CO_3/Celite) is used as a mild heterogeneous reagent for conversion of a variety of thioamides into their corresponding amides in acetonitrile at room temperature.

Keywords: Amides; celite; silver carbonate; thioamides

Amides are important chemical intermediates since they can be hydrolyzed to acids, dehydrated to nitriles, and degraded to amines containing one less carbon atom by the Hofmann reaction. They constitute a group of substances of increasing interest and applications in pharmacology and industry. These compounds are very prevalent in nature, since all peptides and proteins are polymers of the natural α-amino acids. Several general methods are available for the preparation of amides.[1] Among them, the chemical transformation of thioamides into their corresponding oxo-derivatives, i.e., amides, is highly valuable for the preparation of nucleic thiobases and thionucleosides.[2] Reported reagents used for the conversion of thiocarbonyl into carbonyl compounds include iodate or bromate in alkaline solutions,[3] sodium peroxide,[4] dimethyl sulfoxide-acids,[5,6] thiophosgene,[7] diaryl telluroxide,[8] dimethyl selenoxide,[9] dimethyl sulfoxide-iodine,[10] benzeneseleninic acid,[11] singlet oxygen,[12] nitric acid,[13] selenium dioxide,[14] soft NO^+ species,[15] clayfen,[16] mercuric acetate,[17] and trifluroacetic anhydride.[18] Very recently, a convenient and mild procedure was introduced for conversion of secondary and tertiary thioamides into the corresponding amides using Caro's acid supported on silica gel.[19] Oxidation of thioamides can take several courses,

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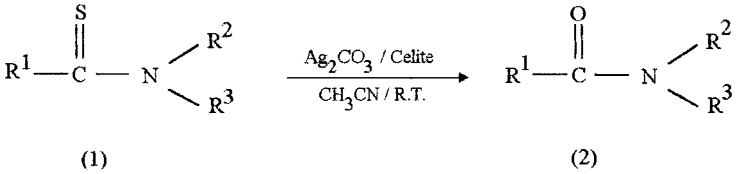
but all involve the sulfur atom; sulfur is removed as sulfate and replaced by oxygen when an oxidant (e.g. iodine or hydrogen peroxide) is used in basic solution.[20]

RESULTS AND DISCUSSION

Oxidations by Ag_2CO_3/Celite are heterogeneous reactions which take place under essentially neutral conditions. This reagent is used for oxidation of different functionalities.[21] Here we report the use of silver carbonate supported on celite, Ag_2CO_3/celite, as a viable new method for effecting this transformation. This supported reagent can be used for the generation of a variety of amides from their corresponding thioamides in acetonitrile at room temperature under air atmosphere in high to excellent yields (Table I). Isolation of the product from this oxidation is remarkably simple and consists merely in filteration to remove the spent reagent system, followed by evaporation of the solvent.



SCHEME 1

This procedure is applicable to a variety of thioamides including N,N-disubstituted-, N-substituted-, and unsubstituted thioamides, thiobenzamides, and thioureas by reaction with one molar equivalent of the reagent, except for 1,4-dithiobenzoyl piperazine (entry 13, Table I) for which two molar equivalents of the reagent is used. The highest yield is obtained with N,N-diethyl-4-(N,N-dimethylamino)benzamide (98%, entry 12, Table I), and the lowest with thioacetamide (77%, entry 1, Table I).

From the results above, it can be concluded that by using silver carbonate supported on Celite, different types of thioamides are smoothly converted to amides in high to excellent yields.

EXPERIMENTAL

General

All yields refer to pure isolated products. The amides were characterized by comparison of their spectral (IR, ^{1}H-NMR) and physical data (melting point) with those of authentic samples.[10,11,19,22] The starting

TABLE I Reaction of Thioamides with Ag_2CO_3/Celite in Acetonitrile

Entry	R^1	R^2	R^3	Ref. for educt	Reaction time (h)	Yield[a] (%)	m.p. of product (°C)	Ref. for product
1	Me	H	H	25	7.5	77	80	25
2	NH_2	H	H	25	3	85	133	25
3	Ph	H	H	22	2.5	83	126	25
4	Me	H	Ph	26	4.5	83	114	26
5	Ph	H	4-ClC_6H_4	19	5.5	84	193	19,25
6	4-$NO_2C_6H_4$	H	$PhCH_2$	19	18.5	83	142	19
7	PhNH	H	Ph	25	3	96	240	25
8	Ph	—$CH_2CH_2CH_2CH_2CH_2$—		19	6.5	97	47	19,25
9	4-ClC_6H_4	—$CH_2CH_2CH_2CH_2CH_2$—		19	2	85	76	19
10	4-$NO_2C_6H_4$	Me	Ph	19	3	90	108	19,27
11	4-$NO_2C_6H_4$	Et	Et	19	4	78	68	19,28
12	4-$Me_2NC_6H_4$	Et	Et	29	5	98	65	30
13	1,4-dithiobenzoyl piperazine			31	2.5	84[b]	196	32

[a] Isolated yields.

[b] Thioamide: reagent system ratio is 1:2.

thioamides were either prepared from the corresponding amides using tetraphosphorous decasulfide (P_4S_{10})[23] or the modified Willgerodt-Kindler reaction.[24] ^{1}H-NMR spectra were recorded at 60 MHz in CCl_4 and $CDCI_3$ using tetramethylsilane (TMS) as internal standard.

Preparation of Silver Carbonate Supported on Celite[21]

The celite was purified by washing it successively with methanol containing 10% concentrated hydrochloric acid and then with distilled water until neutral; it was dried at 120°C. Purified celite (3 g) was added to a stirred solution of silver nitrate (3.4 g, 20 mmol) in distilled water (20 ml). A solution of sodium carbonate (1.1 g, 10.4 mmol) in distilled water (30 ml) was then added slowly to the homogeneous suspension and stirring was continued for a further 15 min. The yellow-green precipitate which was formed was collected by filtration and dried in a vacuum oven for 3 h. The reagent system thus prepared contained about 0.35 g (1.3 mmol) of Ag_2CO_3 per gram.

General Procedure for Conversion of Thioamides into Amides

A mixture of the thioamide (1 mmol) and Ag_2CO_3/celite (1 or 2 mmol) in acetonitrile (15 ml) was stirred at room temperature for the period indicated (Table I). Progress of the reaction was followed by TLC (eluent: Et_2O/CCI_4, 3/1). After completion of the reaction the solids were collected by filtration, washed with excess acetonitrile, and the combined filtrates evaporated. The crude amide was either recrystallized from n-heptane, $EtOH/H_2O$, or subjected to column chromatography using silica gel (n-heptane/Et_2O).

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