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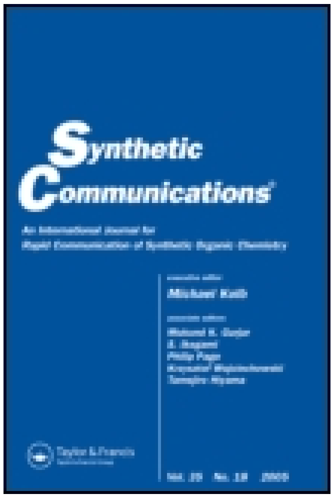

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A Convenient and Inexpensive Method for Conversion of Thiocarbonyl Compounds to Their Oxo Derivatives Using Oxone Under Solvent-Free Conditions

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A Convenient and Inexpensive Method for Conversion of Thiocarbonyl Compounds to Their Oxo Derivatives Using Oxone Under Solvent-Free Conditions

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ABSTRACT

A series of thioamides, thioureas and thioesters are transformed to their corresponding carbonyl compounds in good to excellent yields with oxone under solid phase conditions, while thioketones remained unchanged under these conditions.

The transformation of thioamides to their corresponding amides is an important reaction in synthetic organic chemistry. Amides are valuable chemical intermediates in some organic reactions; they can be

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hydrolyzed to carboxylic acids, dehydrated to nitriles and degraded to amines in Hofmann rearrangement. Many methods and reagents such as *t*-butyl hypochlorite,[1] diaryl selenoxide,[2] dimethyl selenoxide,[3] diaryl telluroxide,[4] benzeneseleninic anhydride,[5] singlet-oxygen,[6] thiophosgene,[7] sodium peroxide,[8] dimethyl sulfoxide/iodine,[9] *m*-chloroperbenzoic acid,[10] $NOBF_4$,[11] *N*-nitrosamines,[12] soft NO^+ species,[13] trifluoroacetic anhydride,[14] clayfen,[15] *p*-nitrobenzaldehyde/TMSOTf,[16] 2-nitrobenzenesulfonyl chloride/potassium superoxide,[17] manganese dioxide,[18] clayfen or clayan/MW[19] and caro's acid supported on silica gel,[20] have been reported for the conversion of thiocarbonyl compounds to their parent carbonyl compounds. However, some of these methods have certain limitations such as long reaction times, toxic or expensive reagents and tedious procedures.

Oxone is a cheap, easily handled and stable ternary composite of $KHSO_5$, $KHSO_4$, and K_2SO_4 in a 2:1:1 molar ratio. Recently we have introduced oxone as an efficient reagent for deprotection of trimethylsily and tetrahydropyranyl ethers, ethylene acetals and ketals.[21] We now report a convenient method for the conversion of thioamides, thioureas and thioesters to their oxo derivatives with oxone under solid phase conditions.

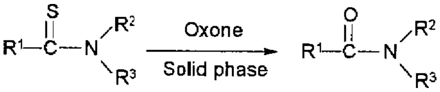
As shown in Table 1, a variety of thioamides and thioureas were treated with oxone under solid phase conditions afforded the corresponding carbonyl compounds in good to excellent yields (Entries 1–31). Thioesters were also transformed to esters in good yields (Entries 32–35). However, thioketones are resistant towards this reagent and remained intact in the reaction mixture (Entries 36–39). Deprotection of larger amounts (8–10 mmol) of some thioamides to their corresponding amides was also investigated. The results were comparable to those of small scale experiments, therefore, it seems that the methodology is also applicable for operation on molar scale. It was found that in these reactions sulfur is converted to sulfate and replaced by oxygen.

In conclusion, we have developed a mild and convenient procedure for the conversion of thioamides, thioureas and thioesters to their carbonyl compounds using oxone as a commercial available, nontoxic and inexpensive reagent under solvent-free conditions.

EXPERIMENTAL

All of the products were identified by comparison of their physical and spectral data with those of authentic samples. The starting thiocarbonyl compounds are either commercially available or were prepared according to described procedures.[22–25]

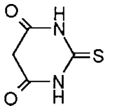
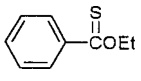
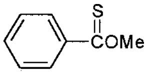
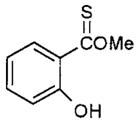
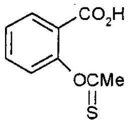
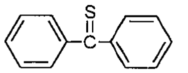
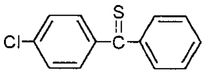
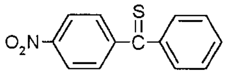
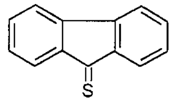
Table 1. Transformation of thiocarbonlyl compounds to carbonyl compounds with oxone.



Run	R^1	R^2	R^3	Oxone/ subs.	Time (min.)	Yield (%)[a]
1	Me	H	H	1	5	95
2	NH_2	H	H	1	5	96
3	NH_2	NH_2	H	1	5	81
4	NH_2	Ph	H	1.5	10	85
5	PhNH	Ph	H	1.5	20	82
6	$H_2NC{=}S$[b]	H	H	2	10	85
7	PhN=N	PhNH	H	1.5	20	99
8	Ph	Ph	H	3	15	90
9	Ph	$PhCH_2$	H	3	25	98
10	Ph	$2\text{-}MeOC_6H_4$	H	3	10	95
11	Ph	$2\text{-}MeC_6H_4$	H	3	15	92
12	Ph	$4\text{-}MeOC_6H_4$	H	3	30	90
13	Ph	$4\text{-}MeC_6H_4$	H	3	35	90
14	Ph	$4\text{-}BrC_6H_4$	H	3	20	75
15	Ph	$4\text{-}NO_2C_6H_4$	H	3	25	77
16	$4\text{-}MeC_6H_4$	Ph	H	3	25	88
17	$4\text{-}NO_2C_6H_4$	Ph	H	3	30	90
18	$4\text{-}NO_2C_6H_4$	$2\text{-}MeOC_6H_4$	H	3	20	85
19	$4\text{-}NO_2C_6H_4$	$2\text{-}MeC_6H_4$	H	3	25	78
20	$4\text{-}NO_2C_6H_4$	$2\text{-}ClC_6H_4$	H	3	25	86
21	$2\text{-}ClC_6H_4$	$4\text{-}MeC_6H_4$	H	3	20	82
22	$4\text{-}MeC_6H_4$	1-Naphthyl	H	3	30	90
23	Me	$4\text{-}BrC_6H_4$	H	3	15	99
24	Me	$4\text{-}NO_2C_6H_4$	H	3	20	95
25	$3,5\text{-}(NO_2)_2C_6H_3$	Ph	H	3	25	73
26	$3,5\text{-}(NO_2)_2C_6H_3$	$2\text{-}MeC_6H_4$	H	3	25	75
27	Me	Ph	Me	3	10	95
28	$4\text{-}NO_2C_6H_4$	Ph	Me	3	25	90
29	$3,5\text{-}(NO_2)_2C_6H_3$	Me	Me	3	30	96
30	$3,5\text{-}(NO_2)_2C_6H_3$	Et	Et	3	20	85

(*continued*)

Table 1. Continued.

Run	R^1	R^2	R^3	Oxone/ subs.	Time (min.)	Yield (%)[a]
31	—		—	1.5	20	90
32	—		—	3	20	80
33	—		—	3	25	75
34	—		—	3	30	60
35	—		—	3	35	58
36	—		—	3	60	0
37	—		—	3	60	0
38	—			3	60	0
39	—		—	3	60	0

[a] Isolated yields.

[b] Oxamide was obtained from the reaction mixture.

General Procedure for the Conversion of Thiocarbonyl Compounds to Their Corresponding Carbonyl Compounds

A mixture of substrate (1 mmol) and oxone (1–3 mmol) in a mortar was prepared. The mixture was ground with a pestle for the length of time according to Table 1. The progress of the reaction was monitored by TLC. The mixture was extracted with CH_2Cl_2. The solvent was evaporated and the crude product was either recrystallized from ethanol or subjected to column chromatography using silica gel.

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REFERENCES

1. El-Wassimy, M.T.M.; Jorgensen, K.A.; Lawesson, S.-O. The reaction of *t*-butyl hypochlorite with thiocarbonyl compound- A convenient method for the $>C{=}S \rightarrow >C{=}O$ transformation. Tetrahedron **1983**, *39* (10), 1729–1734.
2. Tamagaki, S.; Hatanaka, I.; Kozuka, S. Reduction of selenoxide with thione reagents. Bull. Chem. Soc. Jpn. **1977**, *50* (12), 3421–3422.
3. Mikolajczyk, M.; Luczak, J. Dimethyl selenoxide oxidation of trivalent phosphorus compounds, thio- and selenophosphoryl compounds, and thiocarbonyl compounds. Stereochemical studies and selective modification of the thiocarbonyl-containing nucleic acid components. J. Org. Chem. **1978**, *43* (11), 2132–2138.
4. Ley, S.V.; Meerholz, C.A.; Barton, D.H.R. Catalytic oxidation of thiocarbonyl compounds involving the use of 1,2-dibromotetrachloroethane as a brominating reagent for diaryl Te^{II} species. Tetrahedron Lett. **1980**, *21*, 1785–1788.
5. Cussans, N.J.; Ley, S.V.; Barton, D.H.R. Conversion of thiocarbonyl compounds into their corresponding oxo-derivatives using benzeneselenic anhydride. J. Chem. Soc. Perkin Trans. 1 **1980**, 1650–1653.
6. Gano, J.E.; Atik, S. Photodesulfurization of O-alkyl thioesters. Tetrahedron Lett. **1979**, 4635–4636.
7. Abuzar, S.; Sharma, S.; Iyer, R.N. A new convenient method of desulfurization of thioureas and thioamides. Indian J. Chem. **1980**, *19 B*(3), 211–212.
8. Kalm, M. J. Peroxide desulfurization of thioureas. J. Org. Chem. **1961**, *26*, 2925–2929.
9. Mikolajczyk, M.; Luczak, J. Dimethyl sulfoxide oxidations. Iodine-catalyzed conversion of thio- or selenophosphoryl and thiocarbonyl compounds into their oxygen analogs. Synthesis **1975**, 114–115.

10. Kochhar, K.S.; Cottrell, D.A.; Pinnick, H.W. Facile conversion of thioamides into amides. Tetrahedron Lett. **1983**, *24* (13), 1323–1326.
11. Olah, G.A.; Arvanaghi, M.; Ohannesian, L.; Surya Prakash, G.K. Thiocarbonyl to carbonyl group transformation with nitrosonium tetrafluroborate. Synthesis **1984**, 785–786.
12. Jorgensen, K.A.; El-Wassimy, M.T.M.; Lawesson, S.-O. *N*-Nitrosamines as reagents for the >C=S → >C=O transformation. Tetrahedron **1983**, *39* (3), 469–474.
13. Jorgensen, K.A.; Ghattas, A.-B.A.G.; Lawesson, S.-O. The >C=S → >C=O transformation using the soft NO^+ -species. Tetrahedron **1982**, *38* (9), 1163–1168.
14. Masuda, R.; Hojo, M.; Ichi, T.; Sasano, S.; Kobayashi, T.; Kuroda, C. An alternative efficient method for transformation of thiocarbonyl to carbonyl group using trifluroacetic anhydride. Tetrahedron Lett. **1991**, *32* (9), 1195–1198.
15. Chalais, S.; Cornelis, A.; Laszlo, P.; Mathy, A. Thiocarbonyl into carbonyls: Efficient conversion by clay-supported ferric nitrate. Tetrahedron Lett. **1985**, *26* (19), 2327–2328.
16. Ravindranathan, T.; Chavan, S.P.; Awachat, M.M.; Kelkar, S.V.A facile and efficient method for deprotection of thioketones. Tetrahedron Lett. **1995**, *36* (13), 2277–2280.
17. Kim, Y.H.; Chung, B.C.; Chang, H.S. Novel desulforization of thiocarbonyl compounds into their corresponding oxo-derivatives using a peroxy-sulfur intermediate generated from 2-nitrobenzenesulfonyl chloride and superoxide anion. Tetrahedron Lett. **1985**, *26* (8), 1079–1082.
18. Radha Rani, R.; Rahman, M.F.; Bhalerao, U.T. Manganese dioxide in a new role of sulfur extrusion in thioamides. Tetrahedron **1992**, *48* (10), 1953–1958.
19. Varma, R.S.; Kumar, D. Solventless regeneration of ketones from thioketones using clay supported nitrate salts and microwave irradiation. Synth. Commun. **1999**, *29* (8), 1333–1340.
20. Movassagh, B.; Lakouraj, M.M.; Ghodrati, K. Caro's Acid Supported on Silica Gel. Part 2: Conversion of thioamides into amides. Synth. Commum. **2000**, *30* (13), 2353–2358.
21. Mohammadpoor-Baltork, I.; Amini, M.K.; Farshidipoor, S. Selective, convenient and efficient deprotection of trimethylsilyl and tetrahydropyranyl ethers, ethylene acetals and ketals with oxone under non-aqueous conditions. Bull. Chem. Soc. Jpn. **2000**, *73* (12), 2775–2778.

22. Scheeren, J.W.; Ooms, P.H.J.; Nivard, R.J.F. General procedure for the conversion of a carbonyl group into a thione group with tetraphosphorus decasulfide. Synthesis **1973**, 149–151.
23. Fieser, L.F.; Fieser, M. *Reagents for Organic Synthesis*; Vol. 1, Wiley: New York, 1967, p. 333.
24. Pedersen, B.S.; Scheibye, S.; Nilsson, N.H.; Lawesson, S.-O. Studies on organophosphorus compounds. XX. Syntheses of thioketones. Bull. Soc. Chim. Belg. **1978**, *87* (3), 223–228.
25. Pedersen, B.S.; Scheibye, S.; Clausen, K.; Lawesson, S.-O. Studies on organophosphorus compounds. XXII. The dimer of *p*-methoxyphenyl-thionophosphine sulfide as thiation reagent. A new route to *o*-substituted thioesters and dithioesters. Bull. Soc. Chim. Belg. **1978**, *87* (4), 293–297.

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