

Transformation of Thiocarbonyls to Their Corresponding Carbonyl Compounds Using *n*-Butyltriphenylphosphonium Dichromate $(\text{Bu}^n\text{PPh}_3)_2\text{Cr}_2\text{O}_7$ in Solution and under Microwave Irradiation

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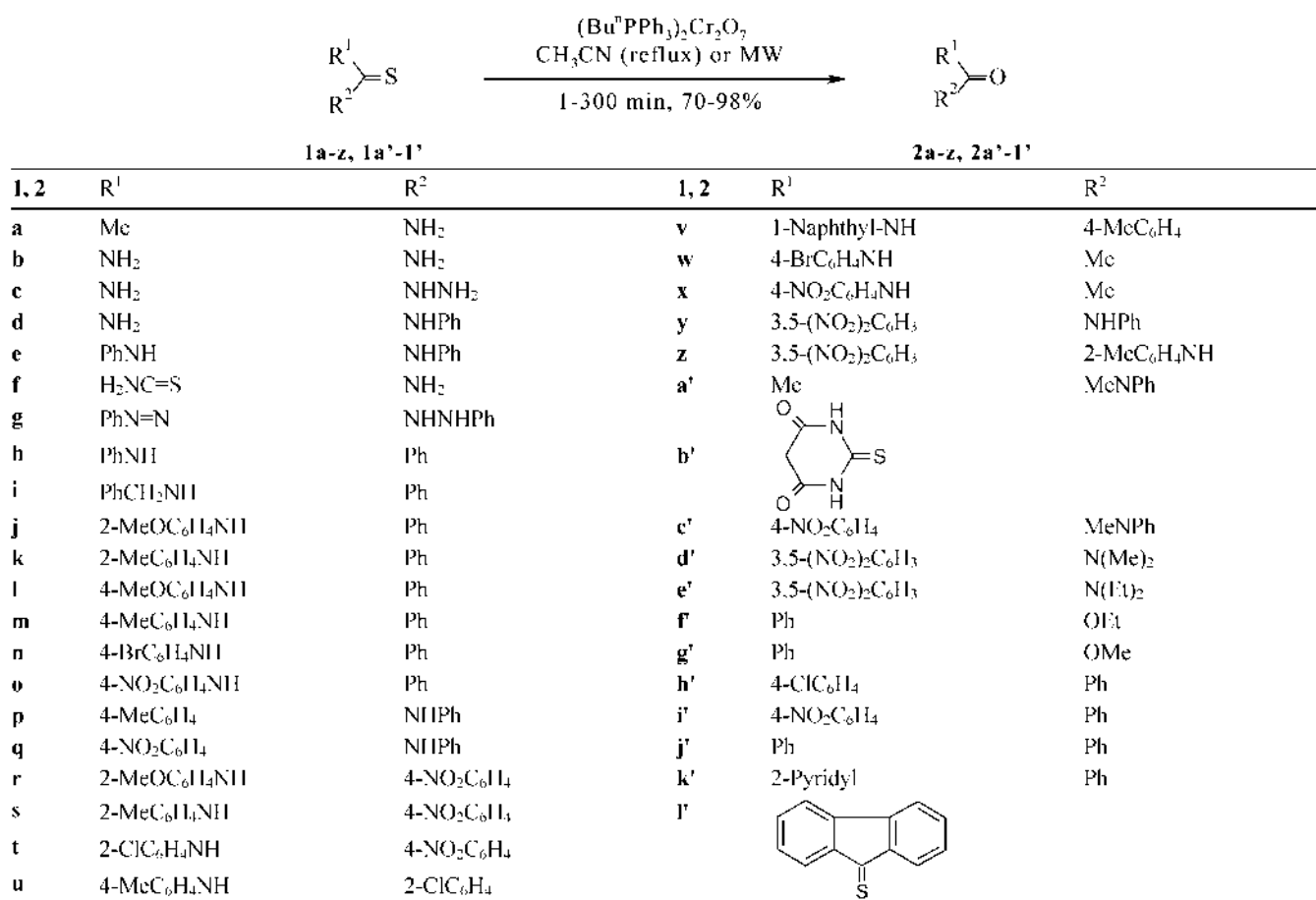
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The introduction and removal of functional groups is of great importance in the synthesis of polyfunctional organic molecules. The conversion of thiocarbonyls to their corresponding carbonyl compounds is an important chemical transformation. Various methods and reagents have been reported for the deprotection of thiocarbonyl compounds to their oxygen analogues.¹⁻²¹ However, some of these methods are not suitable for deprotection of primary thioamides, and some of the others also show limitations such as long reaction times, low yields of the products, use of expensive reagents and tedious work-up.

We have recently reported bismuth(III) nitrate pentahydrate and oxone as convenient reagents for the deprotection of thioamides and thioureas.²² Bismuth(III) nitrate pentahydrate was not effective for transformation of thiono esters and thioketones to their corresponding esters and ketones. However, with oxone thiono esters are converted to their esters while thioketones remained intact in the presence of this reagent. In continuation of our ongoing work in this area, we were interested to find an efficient method for the deprotection of all the above mentioned thiocarbonyl compounds. In this respect, we wish to report that *n*-butyltriphenylphos-

Scheme 1



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phonium dichromate is able to transform thiocarbonyls to their carbonyl compounds efficiently under different reaction conditions.

n-Butyltriphenylphosphonium dichromate is an inexpensive and easily prepared reagent and has been used for the oxidation of different organic compounds.²³ At first the deprotection of thioamides, thioureas, thiono esters and thioketones with this reagent was investigated in refluxing acetonitrile (Scheme 1). As shown in Table 1, a series of the above mentioned thiocarbonyl compounds **1a-z**, **1a'-l'** were reacted with 3 molar equivalent of the reagent to afford the corresponding carbonyl compounds **2a-z**, **2a'-l'** in 70-96% yields within 2-300 min. The transformation of

thiocarbonyls to their carbonyl compounds was also investigated under microwave irradiation. The irradiation was carried out at 900 W using a domestic microwave oven. These reactions were carried out in the presence of 2.5 molar equivalent of the reagent with reaction periods ranging between 1-30 min and the pure products were obtained in 80-98% yields. The results show that under microwave irradiation, the reaction times are shorter and the yields are higher.

In conclusion, we have described an efficient procedure for deprotection thioamides, thioureas, thiono esters and thioketones using *n*-butyltriphenylphosphonium dichromate as a stable, inexpensive and easily prepared reagent.

Table 1. Conversion of thiocarbonyls to carbonyl compounds with $(\text{Bu}^n\text{PPh}_3)_2\text{Cr}_2\text{O}_7$

Substrate	Product	Yield % ^a (Time/min)		$\nu_{\text{max}} / \text{cm}^{-1}$	Mp or bp (Lit. ²⁶)
		Solution	MW		
1a	2a	93(15)	95(2)	3340, 3168, 1680	82 (82-83 ^{26b})
1b	2b	94(15)	96(2)	3440, 3350, 1682	131-132 (132 ^{26a,b})
1c	2c	92(10)	94(3)	3415, 3245, 1685	95 (96 ^{26b})
1d	2d	95(10)	95(2)	3420, 3315, 1658	145-146 (147 ^{26a,b})
1e	2e	90(10)	92(2)	3326, 1648	238-239 (238 ^{26a})
1f	2f	93(30)	94(5)	3385, 3190, 1665	>320 (>320 ^{26b})
1g	2g	90(2)	92(1)	3312, 1662	154-156 (157 ^{26b})
1h	2h	95(30)	97(12)	3330, 1650	163 (163 ^{26a,b})
1i	2i	95(10)	98(5)	3312, 1638	105-106 (105-106 ^{26b})
1j	2j	91(20)	96(10)	3424, 1650	60-61 (60 ^{26a})
1k	2k	93(15)	94(10)	3240, 1648	143 (144 ^{26a})
1l	2l	95(20)	95(10)	3324, 1645	153 (154 ^{26a})
1m	2m	96(20)	98(8)	3310, 1647	157-158 (158 ^{26a,b})
1n	2n	94(25)	95(12)	3325, 1644	202-203 (202 ^{26b})
1o	2o	96(60)	97(15)	3330, 1657	198-199 (199-200 ^{26b})
1p	2p	95(30)	95(10)	3340, 1648	145 (146 ^{26a})
1q	2q	92(70)	94(12)	3320, 1650	211-212 (211 ^{26a,b})
1r	2r	93(60)	95(14)	3300, 1645	146-148 (148 ^{26c})
1s	2s	93(55)	91(14)	3285, 1646	153-155 (155 ^{26c})
1t	2t	94(60)	92(18)	3285, 1655	159-160 (160 ^{26c})
1u	2u	91(40)	91(10)	3376, 1658	130-131 (131 ^{26a})
1v	2v	95(20)	97(7)	3248, 1640	171-173 (173 ^{26c})
1w	2w	96(6)	95(5)	3312, 1667	168 (168 ^{26b})
1x	2x	94(10)	95(7)	3405, 1680	215-216 (215-216 ^{26b})
1y	2y	91(40)	93(15)	3280, 1651	232 (234 ^{26a})
1z	2z	93(30)	93(15)	3320, 1644	238-240 (241-242 ^{26c})
1a'	2a'	83(120)	93(10)	1650	101-103 (101-102 ^{26b})
1b'	2b'	92(30)	93(3)	3210, 1750, 1714	247 (248 ^{26b})
1c'	2c'	70(300)	80(30)	1646	106-107 (107 ^{26c})
1d'	2d'	70(300)	96(20)	1637	127-130 (128-130 ^{26c})
1e'	2e'	70(300)	96(20)	1638	89-90 (89-91 ^{26c})
1f'	2f'	94(70)	95(5)	1720	210-212/760 (212/760 ^{26d})
1g'	2g'	90(70)	90(5)	1725	196-197/760 (198-199/760 ^{26d})
1h'	2h'	94(70)	94(5)	1653	75-77 (75-77 ^{26d})
1i'	2i'	90(70)	90(5)	1650	136-137 (136-138 ^{26d})
1j'	2j'	93(70)	94(5)	1650	49 (48-49 ^{26d})
1k'	2k'	90(70)	90(5)	1660	41-43 (42-44 ^{26d})
1l'	2l'	90(35)	91(10)	1715	82-84 (82-85 ^{26d})

^aIsolated yield.

Experimental Section

General: The products were identified by comparison of their physical and spectral data with those of authentic samples. Yields refer to isolated products. The thiocarbonyl compounds are either commercially available or were prepared as following: thioamides from the reaction of the corresponding amides with P_4S_{10} ²⁴; thiono esters and thioketones from the reaction of the corresponding carbonyl compounds with Lawesson's reagent.²⁵ *n*-Butyltriphenylphosphonium dichromate was prepared according to the described procedure.²³

General procedure for the conversion of thiocarbonyls to carbonyl compounds in acetonitrile solvent. In a round-bottomed flask (50 mL), a solution of thiocarbonyl compound (1 mmol) in CH_3CN (10 mL) was treated with $(Bu^nPPh_3)_2Cr_2O_7$ (3 mmol) and the reaction mixture was stirred under reflux conditions for the time indicated in Table 1. The progress of the reaction was monitored by TLC (eluent: $CCl_4/EtOAc$: 4/1). The reaction mixture was filtered and the solid material was washed with CH_3CN (15 mL). The filtrate was evaporated and the crude product was either recrystallized from $EtOH/H_2O$ or purified by chromatography on silica gel to afford the pure product (Table 1).

General procedure for the conversion of thiocarbonyls to carbonyl compounds under microwave irradiation. Thiocarbonyl compound (1 mmol) and $(Bu^nPPh_3)_2Cr_2O_7$ (2.5 mmol) were mixed and then 0.5 mL CH_3CN was added. The mixture was subjected to microwave irradiation at 900 W for the appropriate time according to Table 1. After completion of the reaction (TLC), the mixture was extracted with CH_2Cl_2 . The solvent was evaporated and the crude product was either recrystallized from $EtOH/H_2O$ or subjected to chromatography on silica-gel to afford the pure product (Table 1).

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