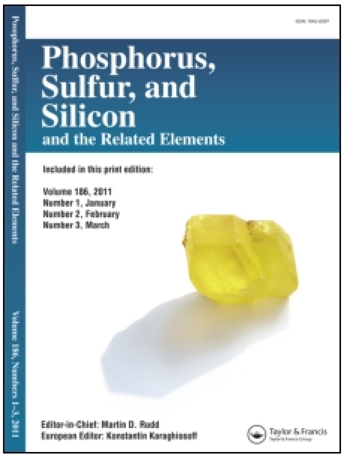

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The Synthesis and Application of 3,6-Bis(triphenylphosphonium) Cyclohexene Dichromate: An Efficient Oxidizing Agent

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The synthesis of 3,6-bis(triphenylphosphonium) cyclohexene dichromate is described. This reagent oxidizes primary and secondary alcohols to their corresponding carbonyl compounds thiols to disulfides, and amines to their azo compounds.

Keywords Alcohol; aromatic amines; azo compounds; BTPCD; carbonyl compounds; dichromate anion; disulfides; MeCN; oxidation; thio; triphenylphosphine

INTRODUCTION

The oxidation of organic substrates with chromium (VI)-based oxidants such as dichromate anion ($Cr_2O_7^{2-}$) and chromium trioxide, which are used alone or with an organic ligand, is an important reaction in synthetic organic chemistry.[1–6] Most procedures using these oxidants are usually conducted under aqueous acidic conditions. Methods using these kind of reagents are faced with limitations: The low pH of the medium is not suitable for acid-sensitive compounds; long reaction times and low selectivity are observed with some reactions; some reagents are hygroscopic and photochemically unstable; and a large excess of the reagent and an unsatisfactory yield are usually accompanied with reactions. However, for the oxidation of organic substrates under nonaqueous and aprotic conditions, a condition that is very useful in modern organic synthesis, a number of different chromium (VI)-based oxidants are reported in the literature, such as n-butyltriphenylphosphoniumdichromate,[7] benzyltriphenylphosphonium dichromate,[8] potassium dichromate in

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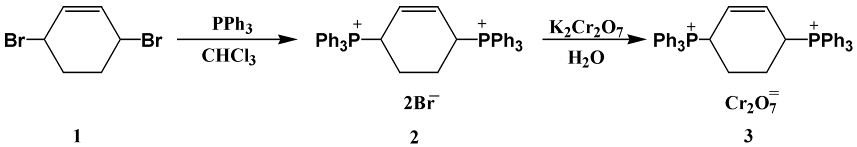
dimethylformamide,[9] zincchlorochro-mate,[10] and potassium dichromate in a benzene-water system.[11]

In this article, we wish to report the synthesis and application of 3,6-bis-(triphenylphosphonium) cyclohexene dichromate (BTPCD) as a mild and selective oxidant for the effective oxidation under neutral and nonaqueous conditions.

RESULTS AND DISCUSSION

The synthesis of the BTPCD is shown in Scheme 1. The required starting material, 3,6-dibromocyclohexene **1**, was prepared via the reaction of cyclohexene with N-bromosuccinimide (NBS) according to the procedure reported by Engman and Bystrom.[12] Dibromide **1** was stirred with triphenylphosphine in refluxing $CHCl_3$ for 2.5 h to produce, on cooling and treatment first with diethylether and then with acetone, 3,6-bis(triphenyl-phosphonium) cyclohexene dibromaide **2** as a white solid in an 80% yield. The reaction of **2** with $K_2Cr_2O_7$ in water at an ambient temperature for 1 h yielded, after filtration and washing with acetone and drying, BTPCD **3** as a yellow solid in an 78% yield (Scheme 1).



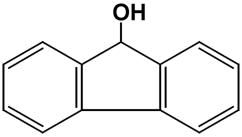
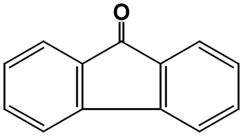
SCHEME 1

The structures of **2** and **3** were confirmed by IR, ^{1}H NMR, ^{13}C NMR, and elemental analysis. Compound **3** is a yellow solid, which decomposes above 130°C and is stable for long periods without losing its activity. This reagent is insoluble and stable in solvents, such as $CHCI_3$, CCl_4, CH_2Cl_2, CH_3CN, CH_2C1CH_2C1, THF, benzene, toluene, and acetone. In this study, we found that BTPCD is able to oxidize primary and secondary alcohols to their corresponding carbonyl compounds, amines to their azo compounds, and thiols to disulfides.

The Oxidation of Alcohols

The oxidation of primary and secondary alcohols with BTPCD was performed in refluxing acetonitril. Benzilic alcohols were converted to their corresponding aldehydes and ketones in high yields (Table I, entries 1–11). Other primary and secondary alcohols were also oxidized with this

TABLE I The Oxidation of Alcohols with BTPCD in Refluxing MeCN

Entry	Substrate	Time (h)	Yield(%)[a]	Product[b]
1	$PhCH_2OH$	1.5	94	$PhCHO$
2	$p\text{-}ClC_6H_4CH_2OH$	2	84	$p\text{-}ClC_6H_4CHO$
3	$PhCH(OH)CH{=}CHCO_2Et$	2	76	$PhCOCH{=}CHCO_2Et$
4	$o\text{-}MeOC_6H_4CH_2OH$	1.5	90	$o\text{-}MeOC_6H_4CHO$
5	$p\text{-}NO_2C_6H_4CH_2OH$	2.5	81	$p\text{-}NO_2C_8H_4CHO$
6	$PhCH(OH)COPh$	2	80	$PhCOCOPh$
7	$PhCHOHPh$	2.5	87	$PhCOPh$
8	$p\text{-}BrC_6H_4CHOHCH_3$	2.5	81	$p\text{-}BrC_6H_4COCH_3$
9	$o\text{-}CIC_6H_4CH_2OH$	2	86	$o\text{-}CIC_6H_4CHO$
10	$p\text{-}CH_3C_6H_4CH_2OH$	2.5	92	$p\text{-}CH_3C_6H_4CHO$
11		2	87	
12	$PhCH{=}CHCH_2OH$	2	77	$PhCH{=}CHCHO$
13	$PhCH{=}CHCH(OH)CH_3$	2.5	72	$PhCH{=}CHCOCH_3$
14	$PhCH(CH_3)OH$	2.5	75	$PhCOCH_3$
15	$Ph(CH_2)_3OH$	2.5	70	$Ph(CH_2)_2CHO$
16	$Ph(CH_2)_2OH$	2.5	82	$PhCH_2CHO$
17	$CH_3(CH_2)_6CH_2OH$	2	93	$CH_3(CH_2)_6CHO$

[a] Yields refer to isolated yields.

[b] Products were characterized by a comparison of their physical and spectral data with authentic samples.

oxidant and afforded carbonyl compounds in good yields (Table I, entries 14–17). Under the same reaction conditions, allylic alcohols were selectively converted to the corresponding α,β-unsaturated carbonyl compounds. Carbon–carbon double bounds remained intact during the oxidation process (Table I, entries 3, 12, and 13). It is noteworthy that the further oxidation of aldehydes to their carboxylic acids were not observed in this investigation.

The effect of various solvents, such as CCl_4, CH_2Cl_2, $CHCl_3$, DMSO, DMF, CH_3CN, THF, and Et_2O, on the oxidation of p-methoxybenzylalcohol to p-methoxybenzaldehyde with BTPCD were also investigated. The experimental results show that CH_3CN is the best choice for this purpose (Table II).

The Oxidation of Amines and Thiols

The conversion of primary amines to their corresponding azo compounds under nonaqueous and aprotic conditions is an interesting reaction in organic synthesis.[7,12,13] We found that BTPCD is an

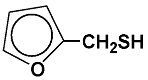
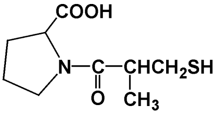
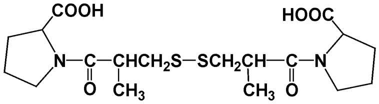
TABLE II Data for the p-Methoxybenzyl Alcohol Oxidation With BTPCD in Various Solvents

Entry	Solvent	Time (h)	Yield (%)[a]
1	CCl_4	8	Trace
2	CH_2Cl_2	8	20
3	$CHCl_3$	8	20
4	DMSO	2.5	70
5	DMF	2	54
6	CH_3CN	1.5	90
7	THF	8	—
8	Et_2O	8	—

[a] TLC yields.

effective oxidant for the transformation of aromatic amines to their corresponding azo compounds under neutral conditions in good yields (Table III, entries 1–6). New methods for the oxidation of thiols to their disulfides are reported in the literature.[7,14–16] BTPCD, however, is shown to be an effective reagent for the conversion of thiols to disulfides, a reaction which demonstrates the mildness of this oxidant (Table III, entries 7–12).

TABLE III The Oxidation of Amines and Thiols withs BTPCD in Dry CH_3CN

Entry	Substrate	Time (h)	Yield (%)[a]	Product[b]
1	$C_6H_5NH_2$	3	75	PhN=NPh
2	p- $MeC_6H_4NH_2$	3	81	p-$MeC_6H_4N{=}NC_6H_4Me$-p
3	p-$ClC_6H_4NH_2$	3.5	70	p-$ClC_6H_4N{=}NC_6H_4Cl$-p
4	p-$MeOC_6H_4NH_2$	3	76	p-$MeOC_6H_4N{=}NC_6H_4MeO$-p
5	o-$MeC_6H_4NH_2$	3	74	o-$MeC_6H_4N{=}NC_6H_4Me$-o
6	o-$BrC_6H_4NH_2$	3.5	60	o-$BrC_6H_4N{=}NC_6H_4Br$-o
7	C_6H_5SH	1.5	93	$C_6H_5S{-}SC_6H_5$
8	p-$NO_2C_6H_4SH$	1.5	86	p-$NO_2C_6H_4S{-}SC_6H_4NO_2$-p
9	p-ClC_6H_4SH	1	83	p-$ClC_6H_4S{-}SC_6H_4Cl$-p
10	n-C_4H_9SH	1	90	n-$C_4H_9S{-}SC_4H_9$-n
11		1	92	
12		1	40	

[a] Yields refer to isolated yields.

[b] Products were characterized by comparison of their physical and spectral data with authentic samples.

CONCLUSION

BTPCD is an oxidant that could be synthesized very easily from commercially available materials. It is a stable, mild, and selective oxidant that can be used under neutral and nonaqueous conditions for the oxidation of different substrates.

EXPERIMENTAL

General

^{1}H NMR spectra were recorded on a Bruker Advance DPX-250 MHz NMR spectrometer in $CDCl_3$ and d_6-DMSO. IR spectra were recorded on a Shimadzu 470 spectrophotometer (4000–400 cm^{-1} region). The C,H analysis was performed by the microanalysis service of the research institute of petroleum industry (NIOC). Melting points were measured on a Mettler FP5 apparatus. TLC confirmed the purity of the substrates, and reactions were monitored on silica gel plates. All yields refer to isolated products. Products were characterized by comparison of their physical and spectral data with those of authentic samples.

The Preparation of 3,6-Bis(triphenylphosphonium)-cyclohexene Dibromide (2)

To a solution of 3,6-dibromocyclohexene **1** (1.1 g, 5 mmol) in $CHCl_3$ (10 mL) in a 50 mL round-bottomed flask equipped with a magnetic stirrer and a reflux condenser, triphenylphosphine (2.62 g, 10 mmol) was added. The reaction mixture was refluxed on a water bath for 2.5 h. The solution was cooled to r.t. and then, while vigorously stirring, diethylether was added dropwise until an oily product was separated. The ether was removed by decantation, and acetone (40 mL) was added. Stirring the acetone solution for 40 min afforded a white precipitate, which was filtered, washed with acetone, and then dried. Yield (80%), m.p.: 276–277°C.

IR (KBr): 3053, 2755, 1613, 1575, 1475, 1446, 1108, 750, 723, 692, 537 cm^{-1}. ^{1} H NMR (250 MHz), δ_h ($CDC1_3$): 2.37–2.85 (m, 4H), 5.78 (d, 2H), 6.47 (m, 2H), 7.12–7.96 (m, 30H). Anal. calc: C, 65.98; H, 5.01%; found: C, 66.02; H, 4.95%.

The Preparation of 3,6-Bis(triphenylphosphonium)-cyclohexene Dichromate (3)

To a stirring suspension of powdered **2** (1.14 g, 1.5 mmol) in water (20 mL), a solution of $K_2Cr_2O_7$ (0.45 g, 1.5 mmol) in water (5 mL) was added dropwise. A yellow precipitate was formed. The mixture was stirred for 1 additional h. The resulting yellow solid was separated by filtering and then poured into acetone (20 mL) and stirred for 15 min; it was separated by a Buchner funnel and dried. Yield (78%), m.p.: 130°C (dec).

IR(KBr): 3445, 3030, 2910, 1633, 1470, 1425, 1101, 990,933, 770, 745, 721, 690, 528 cm^{-1}. ^1H NMR (250 MHz), δ (d_6-DMSO): 2.46 (m, 4H), 6.38 (d, 2H), 6.68 (m, 2H), 7.39–7.94 (m, 30). ^{13}C NMR (250 MHz), δ (d_6 DMSO): 22.63, 31.12, 116.38, 130.91, 132.11, 134.78, 136.17. Anal. calc.: C, 61.46; H, 4.63%; found: C, 61.32; H, 4.57%).

The General Procedure for the Oxidation of Alcohols, Amines, and Thiols

To a refluxing solution of substrate (0.8 mmol) in dry acetonitril (20 mL) in a 50 mL round-bottomed flask equipped with a condenser and a magnetic stirrer was added 3,6-bis (triphynylphosphonium)cyclohexene dichromate (0.8 mmol) in small portions over a period of 1–3.5 h. At the end of the reaction, a greenish solution was obtained. The progress of the reaction, was monitored by TLC. The reaction mixtures were filtered and the solid was washed with ether (15 mL). The filterates were evaporated and the residue was purified on a silica-gel plate (eluent: $CC1_4/Et_2O$, 4/1). Pure products were obtained. Yields: carbonyl compounds 70–94% (Table I), azo compounds and sulfides 40–93% (Table III).

The Oxidation of Benzyl Alcohol: A Typical Procedure

A solution of benzyl alcohol (87.3 mg, 0.8 mmol) in dry acetonitril (20 mL) in a 50 mL round-bottomed flask equipped with a condenser, a magnetic stirrer is prepared. To this solution under reflux condition was added BTPCD (663 mg, 0.8 mmol) in 10–12 portions over a period of 1.5 h. After completion of the reaction, the solution was filtered, and the solid was washed with acetonitril (2 × 15 mL). The solvent was evaporated under reduced pressure at an ambient temperature. The resulting crude material was purified on a silica-gel plate (eluent: $CC1_4/Et_2O$, 4/1). Evaporation of the solvent afforded pure benzaldehyde. Yield 94%.

The Oxidation of p-Methoxyaniline: A Typical Procedure

In a 50 mL round-bottomed flask equipped with a condenser and a magnetic stirrer, a solution of p-methoxy aniline (98.4 mg, 0.8 mmol) acetonitril was prepared. To this solution, while stirred magnetically under reflux condition, was added BTPCD (656 mg, 0.8 mmol) in 10–12 portions over a period of 3 h. After completion of the reaction, the solution was filtered, and the solid was washed with acetonitril (2 × 15 mL). The solution was evaporated, and the residue was purified on a silica-gel plate (eluent: CCl_4/Et_2O, 6/1). Evaporation of the solvent afforded pure azo compounds. Yield 76%.

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