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# Cetyltrimethylammonium dichromate: a mild oxidant for coupling amines and thiols

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**Abstract**—A novel lipopathic oxidizing agent, cetyltrimethylammonium dichromate, was used for coupling aromatic amines and thiols to yield the corresponding diazo compounds and disulfides, respectively.


Oxidation of amino compounds to the corresponding azo compounds has been carried out using oxidizing agents like phenyl iodoacetate,[1] lead tetraacetate,[2] sodium hypochlorite,[3] manganese dioxide,[4] potassium ferricyanide[5] and barium ferrate monohydrate,[6] etc. For the oxidation of substituted anilines by ferricyanide, Wang et al.[7] proposed a free radical mechanism, where the aniline is converted into a symmetrical *N*,*N*′-diaryl hydrazine, which on further oxidation yields the azobenzene. They achieved a substantial increase in the yield of product by carrying out the reaction in a biphasic system using 2,4,6-tri-*tert*-butylphenol as the phase transfer catalyst. Similar oxidants can also oxidize thiols to the corresponding disulfides.[6,8]

In continuation of our search for oxidants having lipopathic characteristics, we have reported the oxidation kinetics of cetyltrimethylammonium permanganate[9,10] and the synthesis and oxidative application of cetyltrimethylammonium cerate.[11] In the present investigation, the dichromate ion is associated with the cetyltrimethylammonium counterion and the behavior of the salt towards aromatic amines and thiols in organic solvents is studied.

The oxidant, cetyltrimethylammonium dichromate (CTADC) was prepared by simply stirring cetyltrimethylammonium bromide and potassium dichromate in aqueous solution at room temperature. The results of elemental analysis (C, H, N and Cr), IR and NMR spectral studies suggest the product to be $[C_{16}H_{33}N(CH_3)_3]_2Cr_2O_7$. The oxidant, Cr(VI) in the form of dichromate, attached to a carrier cetyltrimethylammonium ion, is carried into the organic phase. It does not oxidize the carrier, as cetyltrimethylammonium permanganate (CTAP) does, giving pentadecanal, trimethylamine and carbon dioxide.[9] CTADC is found to be stable in chloroform and dichloromethane at reflux temperature for around 48 h.

While attempting the oxidation of 2-aminobenzothiazole with CTADC with a view to obtain the sulfur oxidized product, the corresponding sulfone,[12] we obtained instead a red colored crystalline product characterized as 2,2′-azodibenzothiazole. The FABMS (M+1) ion peak, NMR and IR spectral data corroborated the formation of the compound, which was also synthesized by electrochemical oxidation of 2-aminobenzothiazole by the method reported by Goyal et al.[13] or by oxidation of 2-hydrazinobenzothiazole with nickel oxide using the method of Balachandran and George.[14] To examine the generality of this reactivity of CTADC on amino functions, we oxidized a series of substituted anilines and the results are given in Table 1. The progress of the reaction was followed by TLC. The products were separated from the reaction mixtures using a silica gel column and benzene–ether as eluent. The products were identified by IR, NMR and melting/boiling point measurements.

We extended the oxidation to thiols. The oxidation of aromatic and aliphatic thiols resulted in the formation of the corresponding disulfides. The experimental conditions and analytical results are provided in Table 2. The stoichiometry of the reaction was found to be 1:3

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**Table 1.** Reflux time, yield, melting points and UV–vis (in ethanol) of the symmetrical diaryl diazo compounds

| Substrate | Reflux (h) | Product | Yield (%) | Mp (°C) | $\lambda_{max}$ (nm) |
|---|---|---|---|---|---|
| Aniline | 6 | Azobenzene | 95 | 68 | 320.5 |
| *p*-Chloroaniline | 4 | 4,4′-Dichloro-azobenzene | 90 | 185 | 329.5 |
| *p*-Methoxyaniline | 2 | 4,4′-Dimethoxy-azobenzene | 95 | 160 | 356 |
| *p*-Methylaniline | 3 | 4,4′-Dimethyl-azobenzene | 80 | 144–145 | 328 |
| *p*-Hydroxyaniline | 3 | 4,4′-Hydroxy-azobenzene | 85 | 190–192 | 361 |
| *o*-Hydroxyaniline | 6 | 2,2′-Dihydroxy-azobenzene | 75 | 173–175 | 431.5 |
| 2-Aminobenzothiazole | 6 | 2,2′-Azodibenzothiazole | 65 | 294 | 424 |

**Table 2.** Reflux time, yield and melting point of the symmetrical disulfides

| Substrate | Reflux (h) | Product | Yield (%) | Mp/bp (°C) |
|---|---|---|---|---|
| *n*-$C_4H_9SH$ | 6 | $C_4H_9SSC_4H_9$ | 80 | 117–118(l)[6] |
| $C_6H_5SH$ | 5 | $C_6H_5SSC_6H_5$ | 85 | 60–61(s)[6] |
| *p*-$CH_3C_6H_4SH$ | 4 | *p*-$CH_3C_6H_4SSC_6H_4CH_3$-*p* | 75 | 40–41(s)[8] |
| *o*-$CH_3C_6H_4SH$ | 5 | *o*-$CH_3C_6H_4SSC_6H_4CH_3$-*o* | 65 | 71–72(s)[6] |
| $C_6H_5CH_2SH$ | 3 | $C_6H_5CH_2SSCH_2C_6H_5$ | 70 | 70–71(s)[8] |
| 2-Mercapto benzothiazole | 3 | 2,2′-Benzothiazolyl disulfide | 80 | 181–182(s)[6] |

for oxidant and substrate in both types of reactions. When acrylonitrile was added to the reaction mixture under nitrogen, turbidity appeared indicating the involvement of free radicals in the reaction. No nitroanilines could be converted to corresponding azobenzenes even after 24 h of reflux. Possibly the free radicals were captured by the nitro group.[15] The reduced product of chromium was found to be Cr(III).

In conclusion, the reagent is found to be effective in coupling amino and mercapto groups to give the corresponding diazo and disulfides, respectively.

*Synthesis of cetyltrimethylammonium dichromate*: Potassium dichromate (2.94 g, 0.01 M) in 100 mL of water was added slowly to an aqueous solution of cetyltrimethylammonium bromide (7.38 g, 0.02 M) with continuous stirring with a Teflon coated magnetic bar at room temperature. A yellow colored compound appeared immediately. Stirring was continued for 15 min more after completion of the addition of dichromate solution. The resulting yellow product was filtered off and washed with water several times until no $Br^-$ or dichromate were detected in the filtrate. The product was vacuum dried and kept in a desiccator in the dark. Mp 212 °C (dec), yield: 98%. Elemental analysis: C, 58.14; H, 10.65; N, 3.54; Cr, 13.11. $C_{38}H_{84}O_7N_2Cr_2$ requires C, 58.16; H, 10.71; N, 3.57; Cr, 13.26. IR ($cm^{-1}$): 771, 879, 933, 1467, 2850, 2921, 3028, 3471. NMR ($CDCl_3$, 300 MHz): $\delta$ 0.86 (t, 6H), 1.29 (m, 48H), 1.67 (m, 4H), 1.74 (m, 4H), 3.42 (s, 18H), 3.51 (m, 4H).

*General procedure for oxidation of aromatic amino/thiol compounds*: To a solution of the substrate in chloroform, half an equivalent of CTADC in chloroform was added and the mixture was refluxed on a water bath. With aniline substrates, the development of a red color in the reaction mixture was observed. The volume of the solution was reduced until a pasty mass remained and this was then purified by silica gel column chromatography to provide the azo compound. For mercaptans, the color of reaction mixture was green.

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