

Note

Regeneration of the carbonyl compounds from their semicarbazones using tetra-*n*-alkylammonium bromates

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Tetra alkyl ammonium bromates are prepared by a simple procedure and used for the oxidative regeneration of the parent carbonyl compound from their semicarbazones. Reaction conditions are simple and the deprotection gives satisfactory yield of the carbonyl compound.

Keywords: Tetraalkylammoniumbromate, oxidative cleavage, semicarbazones, carbonyl compounds, deprotection

IPC Code: Int.Cl.⁸ C07C

Quaternary ammonium salts are versatile phase transfer catalysts and some of them have been used to assist oxidation of a variety of organic substrates using inexpensive primary oxidants such as O₂ (ref. 1), NaOCl (ref. 2), KMnO₄ (ref. 3) H₂O₂ (ref. 4) and others (refs 5,6). Efforts are now directed towards the use of modified quaternary ammonium salts as reagents rather than as catalyst. In our previous communications⁷⁻¹⁰, the preparation of a quaternary-ammonium bromate from the easily available bromide by a simple procedure was reported and these bromates used for the oxidation of aromatic amines to nitro compounds⁷, benzyl alcohols and halides to the aldehydes⁸ and for the oxidative deoxygenation⁹ were reported. We have since modified the reported procedure⁷⁻⁹ for the preparation of the quaternary ammonium bromates and observed that the procedure reported herein gives better and cleaner yield of the bromates. Two different bromates were prepared namely the tetraethylammoniumbromate **I** and the *N*-cetyl-*N,N,N*-trimethylammoniumbromate **II**. These bromates were soluble in organic solvents as well as in water, albeit sparingly. Bromates are seldom used as oxidants in organic synthesis primarily because of their insolubility in organic solvents. Favourable solubility characteristics of these tetraalkylammonium bromates offer opportunity not only as for their use a

primary oxidant but also resulted in easier product recovery techniques.

Semicarbazones are easily prepared derivatives of the carbonyl compounds and give well characterized crystalline products which are used frequently for the detection and identification of the carbonyl compounds. However, the semicarbazones are seldom used as a good protective group for the carbonyl compound as there are very few procedures for the regeneration of the parent carbonyl compound¹⁰⁻¹⁴. Herein we wish to report a very useful and easy method for the oxidative regeneration of the carbonyl compounds from their semicarbazone derivatives. The procedure involves the refluxing of quaternary-ammonium bromate and semicarbazone in an appropriate solvent for a stipulated period of time as shown in **Table I**. Product recovery is simple and the resulting carbonyl compounds are obtained in good yields. The transformation is shown in **Scheme I**.

Experimental Section

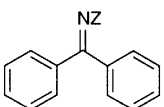
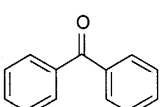
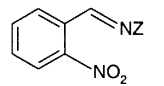
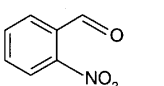
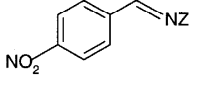
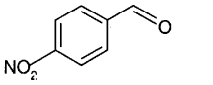
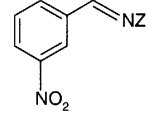
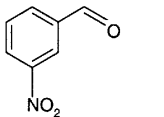
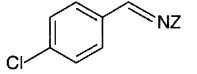
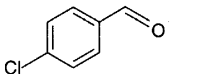
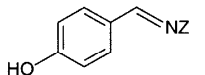
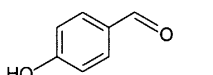
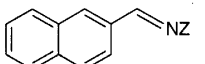
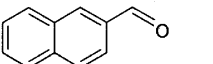
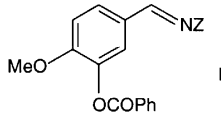
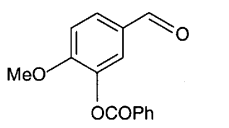
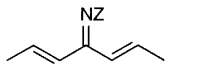
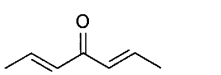
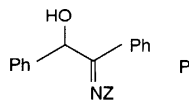
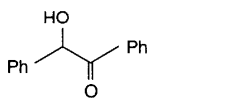
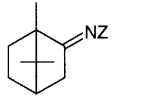
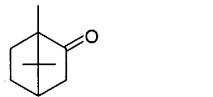
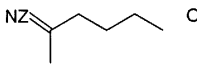
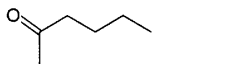
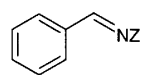
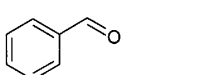
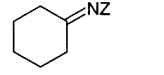
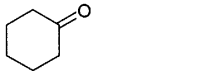
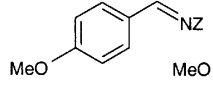
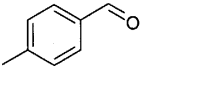
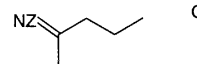
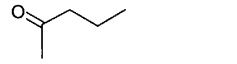
All reagents and solvents were purified by methods reported in literature^{15,16}. The quaternary ammonium bromides were procured from E. Merck Inc. Melting points were recorded in an apparatus from Scientific Devices, India, Type MP-D in open capillaries. ¹H NMR spectra recorded in EM 360, 60 MHz spectrophotometer, IR in Perkin-Elmer 1600 FT IR spectrometer and C, H, N, analyses were obtained from facilities available at RRL, Jorhat and IIT, Guwahati.

Preparation of the semicarbazone. The semicarbazones were prepared as per procedure obtained from literature¹⁵.

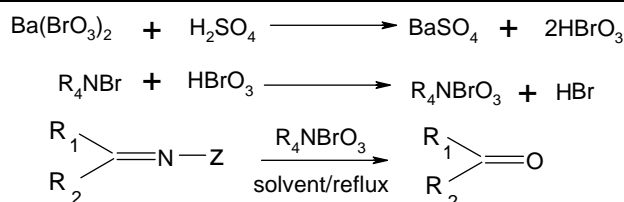
Preparation of bromic acid (HBrO₃). Finely ground Ba(BrO₃)₂ (10 g) was taken in an Erlenmeyer flask and to it was added dilute sulphuric acid (5 mL in 50 mL water) dropwise with constant shaking. After addition, the flask was kept for 24 hr in an ice-bath with frequent shaking. The contents of the flask are diluted with water (60 mL). A 10% solution of Ba(OH)₂ was added to remove the excess H₂SO₄. The mixture was allowed to stand overnight and the clear HBrO₃ solution was filtered.

Preparation of the tetraalkylammonium bromates. Tetraethylammoniumbromide (0.01 mole) was dissolved in minimum amount of water. To this

Table I—Experimental details of the generation of carbonyl from semicarbazone

| Sl. No. | Substrate | Product | Oxidant | Reflux time (min) | Yield % | m.p. | b.p. | Solvent |
|---------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|---------|-------------------|---------|---------|---------|---------|
| 1 |  |  | I | 180 | 92 | 48 | 48 | MeOH |
| | | | II | 24 | 90 | | | |
| 2 |  |  | I | 120 | 77 | 44 | 44 | dioxan |
| 3 |  |  | I | 72 | 70 | 132 | 130 | dioxan |
| 4 |  |  | I | 75 | 72 | 58 | 58 | toluene |
| 5 |  |  | II | 150 | 78 | 47 | 47 | dioxan |
| 6 |  |  | I | 120 | 70 | 110 | 109 | EtOH |
| 7 |  |  | II | 300 | 66 | 52 | 53 | dioxan |
| 8 |  |  | I | 240 | 78 | 76 | 78 | DCM |
| 9 |  |  | I | 360 | 55 | 110 | 110 | dioxan |
| 10 |  |  | II | 120 | 85 | 95 | 95 | dioxan |
| 11 |  |  | I | 180 | 92 | 48 | 48 | EtOH |
| | | | II | 240 | 90 | | | |
| 12 |  |  | I | 120 | 64 | 127b.p. | 127b.p. | EtOH |
| 13 |  |  | I | 90 | 82 | 177b.p. | 179b.p. | EtOH |
| 14 |  |  | I | 120 | 85 | 158b.p. | 156b.p. | EtOH |
| 15 |  |  | I | 420 | 77 | 244b.p. | 247b.p. | EtOH |
| 16 |  |  | I | 300 | 72 | 250b.p. | 252b.p. | EtOH |

NZ=NHCONH₂ Ph=Phenyl



Scheme I — Regeneration of carbonyl group from semicarbazones

aqueous solution of the bromide, the solution of HBrO_3 was added dropwise with constant shaking till a coloured precipitate of the tetraalkylammonium bromate was obtained. The solid bromate was filtered and washed several times with ice-cold water and dried.

The tetraethylammonium bromate was obtained as a yellow solid, m.p. 54°C and *N*-cetyl-*N,N,N*-trimethylammonium bromate was obtained as a light yellow solid m.p. 84°C . The bromates obtained responded to all the test of bromates and confirmed by the C, H, analysis.

General procedure for the regeneration of carbonyl compounds from semicarbazones. Semicarbazone (0.001 mole) and quaternary-ammonium-bromate (0.001 mole) were dissolved in appropriate solvent (10 mL) and refluxed for stipulated time (**Table I**). The reaction was periodically monitored by TLC using ethanol as eluent. The completion of the reaction was observed from TLC. To the mixture ether was added which gave the parent carbonyl compound and was purified by column chromatography using silica gel column and ethyl acetate as eluent (**Table I**). The parent carbonyl compound was confirmed by mixed m.p., I.R. and ^1H NMR spectral data and by comparing with authentic samples.

Benzophenone 1: ^1H NMR (CDCl_3 , δ), 7.2 (broad 10H); IR (KBr, cm^{-1}): 1710; UV (95% EtOH): 282 nm; **2-nitrobenzophenone 2:** ^1H NMR (CDCl_3 , δ): 9.1 (s, 1H) 8.1(broad, 4H), IR (KBr cm^{-1}): 1730 (carbonyl) 1552, 1332 ($-\text{NO}_2$); UV (95% EtOH): 277 nm; **2-nitrobenzophenone 3:** ^1H NMR (CDCl_3 , δ): 9 (s, 1H), 7.7-7.9 (broad, 4H); IR (KBr cm^{-1}): 1745 1529, 1290 ($-\text{NO}_2$); UV (95% EtOH): 285 nm; **3-nitrobenzaldehyde 4:** ^1H NMR (CDCl_3 , δ): 8.7 (1H), 7.3-7.8 (4H, d), IR (KBr, cm^{-1}): 1713 carbonyl, 1515, 1320 ($-\text{NO}_2$), UV (95% EtOH): 295 nm; **4-chlorobenzaldehyde 5:** ^1H NMR (CDCl_3 , δ): 9.2

(1H), 7.3-7.7 (4H, d); IR (KBr cm^{-1}) 1740 (carbonyl) UV (95% EtOH): 285 nm; **4-hydroxybenzaldehyde 6:** ^1H NMR (CDCl_3 , δ): 8.8 (1H), 7.7-7.9 (4H, d); IR (KBr cm^{-1}): 1695 (carbonyl), 3455 ($-\text{OH}$); UV (95% EtOH): 280 nm; **2-naphthaldehyde 7:** ^1H NMR (CDCl_3 , δ): 9.3 (1H), 7.2-7.6 (broad, 7H); IR (KBr cm^{-1}): 1710 (carbonyl); UV (95% EtOH): 292 nm; **benzoyl vanillin 8:** ^1H NMR (CDCl_3 , δ): 7.6-8.1 (broad 8H), 4.2 (s, 3H); IR (KBr, cm^{-1}): 1725 (carbonyl) 1765 (carbonyl); UV(95% EtOH): 282 nm; **dibenzylidene acetone 9:** ^1H NMR (CDCl_3 , δ): 8.1 (1H), 6.9-7.4 (broad 10H), 3.8 (s 2H); IR (KBr cm^{-1}): 1690 (carbonyl); UV (95% EtOH): 314 nm. **benzil 10:** ^1H NMR (CDCl_3 , δ): 7.3-7.9 (broad) 2.4 (1H); IR (KBr cm^{-1}): 1720 (carbonyl), 3625 ($-\text{OH}$); UV (EtOH): 288 nm; **camphor 11:** ^1H NMR (CDCl_3 , δ): 2.1-2.5 (9H), 3.1-3.6 (6H); IR (KBr cm^{-1}): 1733 (carbonyl); UV (95% EtOH): 271 nm; **benzylmethylketone 12:** ^1H NMR (CDCl_3 , δ): 2.4 (3H), 1.2-1.6 (broad, 9H); IR (KBr, cm^{-1}): 1750 (carbonyl); UV (95% EtOH): 275 nm; **benzaldehyde 13:** ^1H NMR (CDCl_3 , δ): 9.1 (1H), 7.2-7.6 (5H); IR (KBr, cm^{-1}): 1730 (carbonyl); UV (95% EtOH): 275 nm; **cyclohexanone 14:** ^1H NMR (CDCl_3 , δ): 2.3-3.1 (broad 10H); IR (KBr, cm^{-1}): 1720 (carbonyl); UV (95% EtOH): 280 nm; **anisaldehyde 15:** ^1H NMR (CDCl_3 , δ): 8.8 (1H), 6.9-7.2 (4H), 3.6 (3H); IR (KBr cm^{-1}) 1715; UV (95% EtOH): 285 nm; **methylpropylketone 16:** ^1H NMR (CDCl_3 , δ): 2.2 (3H), 1.4-1.8 (7H); IR (KBr cm^{-1}): 1695 (carbonyl), UV (95% EtOH): 263 nm.

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