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NOTE

Synthesis and Identification of 6,7-Epoxy *N,N′,N′*-Trichloro Derivative of α-Bromocinnamaldehyde Semicarbazone as an Active Decontaminating Agent for Toxic Compounds

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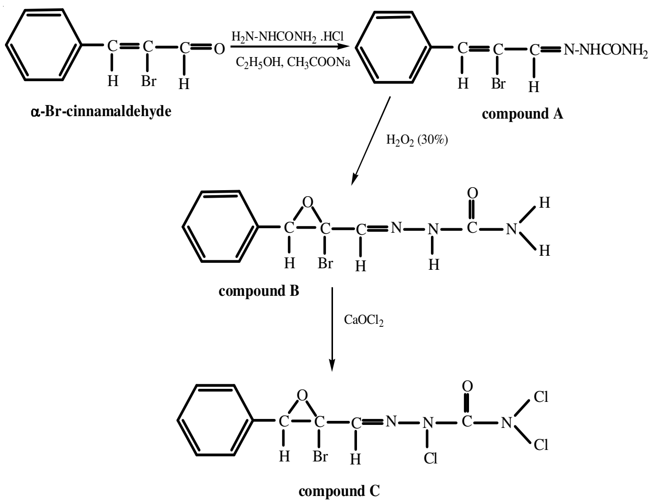
An approach was undertaken to synthesize 6,7-epoxy *N,N′,N′*-trichloro-α-bromo-cinnamaldehyde semicarbazone, by the conversion of α-bromo-cinnamaldehyde semicarbazone into its epoxy derivative and then finally the corresponding *N*-chloramine. Epoxidation was carried out with hydrogen peroxide and then chlorinated using calcium hypochlorite. The reaction between calcium hypochlorite and compounds containing a nitrogen atom with one or more hydrogen atoms attached to it will form chloramines which have lower disinfection efficiency but possess strong decontamination properties against toxic compounds and warfare agents. Their efficacy has to be tested on toxic compounds of phosphorus and CW agents under suitable conditions in sophisticated laboratory.

Key Words: Organophosphorus compounds, Chloramines, Decontamination, CW agents.

In general, decontamination of toxic chemicals[1] is an important task required to eliminate the hazard of toxic chemicals both in laboratories and field conditions. Semicarbazones[2] act as important synthetic intermediates and have been preferably used for the isolation, purification, characterization[3] and even protection of both aldehydes and ketones. Epoxidations under acidic conditions were a matter of debate for quite sometime because it was assumed that the end products were either α-glycols or their monoacetates when peracetic acid was employed for olefins. The first report about the formation of an epoxide successfully from methyl linoleate using peracetic acid came with the researches done by Boeseken, Smit and Gaster[4]. Calcium hypochlorite is one of the commonly used chlorinating agents for various chemical compounds. Various organic compounds containing either *N*-chloro groups or epoxide moiety are reported as efficient decontamination agents[5,6] for chemical warfare agents[7] and various chemical compounds.

During the present study, α-Br-cinnamaldehyde, one of the important members of α,β-unsaturated aldehyde was chosen as the starting compound and converted into the corresponding *N*-chloro compound which is expected to be formed as an active decontaminating agent in the following crucial three stepwise synthesis[8] (**Scheme-I**).

Synthesis of α-Br-cinnamaldehyde semicarbazone (compound A): α-Br-cinnamaldehyde, an α,β-unsaturated aldehyde, was converted[9] into the corresponding semicarbazone derivative using semicarbazide hydrochloride in presence of sodium acetate in an aqueous-alcoholic medium. The reaction was carried out with uninterrupted stirring for 1.5 h and obtained as the light yellow semicarbazone derivative. The same product was also obtained by refluxing method with much lesser time period, *ca.* 22 min. The final product was recrystallized with alcohol and recorded m.p. of 203-204 ºC.



Scheme-I: Stepwise synthesis of 6,7-epoxy *N,N',N'* -trichloro-α-Br-cinnamaldehyde semicarbazone

Synthesis of 6,7-epoxy α-Br-cinnamaldehyde semicarbazone (compound B): The next step was the epoxidation of the above semicarbazone derivative under acidic condition using hydrogen peroxide[14] (30 %). α-Br- cinnamaldehyde semicarbazone (10 g) was dissolved in acetic acid in the presence of one drop of conc. H_2SO_4 as catalyst with stirring at room temperature. It was epoxidized by gradual addition of hydrogen peroxide keeping the latter in excess. The reaction mixture was stirred on a magnetic stirrer for 3 h and 45 min and the pH of the solution was kept as 2.0 with the help of acetic acid. For this, excess of glacial acetic acid was added at intervals of time. The light greenish-yellow solution was diluted with excess of distilled water and extracted with ether. Then, the ethereal extract on evaporation gave a light-yellow solid, the epoxy derivative which has a m.p. of 168-170 ºC.

Synthesis of 6,7-epoxy *N,N',N'*-trichloro-α-Br-cinnamaldehyde semicarbazone (compound C): 6,7-Epoxy α-Br-cinnamaldehyde semicarbazone was dissolved in acetic acid by stirring on a magnetic stirrer. Then, it was chlorinated by the addition of (5.739 g) calcium hypochlorite[10] (maintaining the ratio 1:2) in instalments for 3 h with continuous stirring. During the process there was addition of acetic acid in excess so as to maintain the pH of the reaction mixture at 2.0 throughout the stirring. At the end, the reaction mixture was diluted with water and a creamish precipitate was obtained. It was then washed again thoroughly with water and kept for drying. The final product *N*-chloro-derivative is found to have a m.p. of 150-154 ºC.

Identification of compound A: The mass spectral data of compound **A** shows the formation of a base peak at *m/e* 188 (100 %) which is due to the loss of bromine atom (80). Other prominent peaks are 186 (20 %), 115 (24 %), 89 (2 %, 76 (2 %), *etc.*

^{1}H NMR data of compound **A** shows the absence of two doublets (due to the presence of an α-Br group) for the alkenyl protons (as seen in case of *t*-cinnamaldehyde semicarbazone) clearly indicates its formation. The presence of a multiplet at δ 7.2 further showed the presence of aromatic protons. The single olefinic proton appears at δ 6.9 and as expected forms a doublet in the NMR region. The appearance of a signal at δ 8.8 may be ascribed to the presence of the protons of the amide (nearly δ 8.5) type.

The above spectral studies establish the formation of α-bromo-cinnamaldehyde semicarbazone.

Identification of compound B: Mass spectral[11] data of 6,7-epoxy α-Br-cinnamaldehyde semicarbazone shows the following well defined ion peaks, *m/z* 225(4), 188(100), 186(10), 115(11). The presence of base peak at *m/e* 188 (100) due to the loss of oxygen (16) and bromine (80) atoms matches its formation.

IR spectral[12] of compound **B** shows the following characteristic absorption bands: 3153 cm^{-1} (Ar-H); 1697 cm^{-1} (C=O); 1587 cm^{-1} (C=N); 1109 cm^{-1} (C-N); 3458 cm^{-1} and 756 cm^{-1}(N-H); 1217 cm^{-1} and 1109 cm^{-1} (C-O-C).

^{1}H NMR study[13] shows no significant change in the NMR spectrum (in α-Br-derivative) even though an oxygen atom has been introduced at the double bond of the semicarbazone formed. Aromatic protons and exchangeable protons at the nitrogen nuclei are also observed just like the epoxy derivative of *t*-cinnamaldehyde itself.

Identification of compound C: ^{1}H NMR spectrum shows few signals which is due to lesser number of protons as three protons have been replaced by the chloro-groups. The aromatic protons are observed at the highest value *i.e.* 8.5 ppm. The appearance of a singlet at 2.4 ppm may be assigned to the proton at C-8. The presence of a doublet at 4.5-4.6 ppm is assigned to the epoxy ring proton (C-6). It is however, difficult to account for each and every signal seen in the spectrum. The above spectral study is able to identify and confirm the formation of 6,7-epoxy-*N*,*N'*,*N'*-trichloro-α-Br-cinnamaldehyde semicarbazone.

Conclusion

The epoxy compounds was converted into the trichloro-(*N*,*N'*,*N'*-) compound having chloro-substituents at the -NH and -NH_2 hydrogens. Such a class of compound is expected to bring about chlorination of organic compounds and particularly the organophosphorus compounds giving positive chlorine as the reactive species. The introduction of these chlorine substituents (Cl^+) is thus taken to behave quite differently and may attack[13] the organic compounds resulting in the introduction of the chlorine atom/s at very strategic positions only. Due to this typical nature of the above chloro- compounds (referred to as chloramines) organophosphorus compounds may lead to the formation of their chloro-derivatives, which may possess a non-toxic character, justifying the role of chloramines as chemical decontaminants. Such molecules bring about excessive chlorination with limited oxidation (due to the presence of epoxy ethereal linkage) and thus are expected to perform as better decontamination agents than the chloramines alone.

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