

Synthesis and characterization of series of promising decontaminants for organophosphorus compounds

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ABSTRACT

A novel 6,7-epoxy, N N', N'-trichloro-t-cinnamaldehyde semicarbazone has been synthesized, by conversion of t-cinnamaldehyde into its very stable semicarbazone derivative, followed by both epoxidation and N-chlorination (electrophilic) respectively. Calcium hypochlorite was the source of electrophilic chlorine. The physical characterization is reported and achieved for each member of the series by mass, FT-IR and ¹H NMR studies. Both the epoxide as well as the trichloro-derivatives are expected to act as suitable and efficient decontaminants for the toxic organophosphorus (C-O-P and C-N-P) compounds due to their functions as the oxidizing agents mainly.

Key words: t-cinnamaldehyde, electrophilic chlorination, decontamination, oxidation.

INTRODUCTION

In general, organic chemicals may be either toxic or non-toxic in nature depending upon both their basic structure as well as their nature. Organophosphorus¹ compounds (C-O-P and C-N-P) may be placed in the category to toxic chemicals and pose a threat to the humanity when used as chemical Warfare (CW) agents². Thus, decontamination³ of such toxic chemicals is a big challenge and the progress in this direction has led to the formation as well as application of N-chloramines having active (electrophilic) chlorine in them. The simplest N-chloro compound reported⁴ is chloramine-T (N-Chloro-4-methylbenzene sulphonamide, sodium salt). The present research work consists in the development of a set of compounds consisting of the chlorine rich N-chloramine derived via the epoxy derivative on an α , β -unsaturated aldehyde semicarbazone.

EXPERIMENTAL

During the present study, the simplest member of the α , β -unsaturated aromatic aldehyde, t-cinnamaldehyde was chosen as the parent compound and it was converted into its characteristic semicarbazone⁵ derivative using semicarbazide hydrochloride in the presence of sodium acetate in an aqueous-alcoholic medium. The reaction was carried out with constant stirring for nearly 1 hr. at room temperature and the yellow semicarbazone (Table 1) separated out. This crude product (m.pt 202-205°) was again purified with ethanol and the now the m.pt was of 207-208°C. The ratio of the substrate to reagent was kept as 1:1. During the study, the preparation of semicarbazone was also prepared under reflux condition and it only took about 20 mins. to complete the reaction.

In the next step, the above semicarbazone was epoxidised⁶ under acidic condition using hydrogen peroxide (30%). The reaction was performed by stirring at r.t. followed by warming (40-60°C) for about half an hour. During the course of the reaction it was observed that the pH of the reaction mixture changed from 2.0 to 3.0. On cooling and dilution with enough water, the precipitate of the epoxy derivative separated out and was later extracted with ether. On evaporation, a pale yellow solids was obtained. This product the epoxy compound (Table 1) gave a m.pt of 158-163°C. The yield of the epoxy derivative was only 34%. This was finally transformed into its chloro derivative having the three chloro groups at the two nitrogen position.

For this final step, the ratio of 6,7-epoxy t-cinnamaldehyde semicarbazone and calcium hypochlorite⁷ (for chlorination) was kept as 1:2. The reaction was carried out in excess of acetic acid by stirring for 1.40 hrs. at room temperature. It was noticed that during the reaction pH was increased from 2.0 to 3.0 (i.e. the acidity was reduced). The pH was brought to 7.0 by the addition of sodium carbonate solution and the precipitate thus separated out was collected by filtration. The yield of the product (Table 1) was ca. 27% only and the m.pt of 6,7-epoxy N,N',N'-trichloro compound was observed to be 128-130°C. During the three-step preparation, each product was checked for its purity by the absorption spectroscopic⁹⁻¹⁰ technique like FT-IR, ¹H NMR and mass spectrometry were used for its characterization.

RESULTS AND DISCUSSION

t-Cinnamaldehyde semicarbazone (Scheme 1, Table 1) was prepared as above the its

identification was possible with the help of mass spectrometry. It may be mentioned here that this study was already done by Blytin¹¹ and Waight¹¹ and the present data i.e. m/e: 189(28%); 146(14%); 145 (50%); 130(74%); 129(100%); 128 (26%); 115(32%); 91(10%); 77(18% 0 and 69(43%) only supports it.

On the other hand, ¹H NMR (400MHz) data has also been obtained and accounts for the various protons present in t-cinnamaldehyde semicarbazone (Scheme 1) derivative. This spectrum shows a doublet (1, 2-H); a multiplet (3, 4,5-H); two doublets (6,7-H) at δ 6.3 and 6.46; a doublet (8-H); and the protons (-NH and -NH₂) are exchangeable and these being present at 10(1H) and 12(2H) nitrogen atoms. These sometimes do not appear when water is present. The protons at N(12) may thus appear at a much lower value i.e. δ 1.0 or nearby. During this spectral examination CDCl₃ was used and the NMR signal appears at 1.76 ppm. From this spectral data the semicarbazone has been both identified and confirmed for its structural details to a large extent.

From the above synthesized semicarbazone derivative (Scheme 1, I) the corresponding 6,7-epoxy compound (Scheme 1, II) was prepared using peracetic acid (H₂O₂/AcOH). The 6,7-epoxy derivative of derivative of t-cinnamaldehyde semicarbazone (Scheme 1, II) has also been subjected to similar spectral studies. The epoxy compound (MW=205) shows mass-to-charge (m/e) ratio and relative intensities (%) as: 189(1%); 186(12%); 163(12%); 147(34%); 144(10%); 122(96%); 105(100%); 103(22%); 91(17%); 77(70%) and 51(28%). The appearance of base peak at m/e 105 (100%) is quite indicative for the presence of benzaldehyde molecular ion

Table 1: Physical parameters of the series of compounds

S.No	Name	Mol. Wt.	Colour/State	M.Pt	Solubility
1.	t-Cinnamaldehyde semicarbazone	189.0	Light yellow solid	207-208°C	AcOH, MeOH (hot)
2.	6,7-Epoxy-t-cinnamaldehyde semicarbazone	205.0	Pale-yellow solid	158-163°C	AcOH, Et ₂ O
3.	6,7-Epoxy-N,N',N'-trichloro-t-cinnamaldehyde semicarbazone	308.5	Light brown solid	128-130°C	THF, CHCl ₃ , CH ₂ Cl ₂

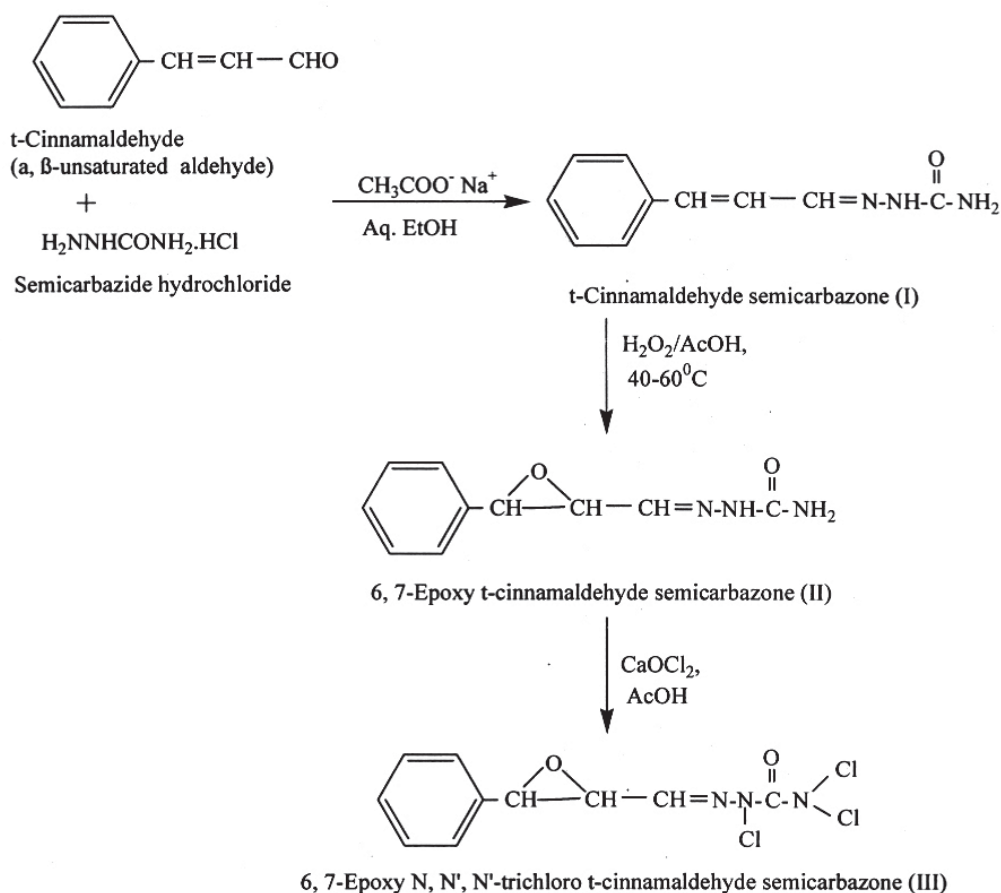
[($C_6H_5C=O^+$); 205-100=105] due to the formation of 6,7-epoxy-t-cinnamaldehyde semicarbazone.

The presence of C-O-C linkage (FT-IR) for epoxy compound is observed at 1070.49cm^{-1} and other related bands are: 1647.21cm^{-1} (C=O); 1056.41cm^{-1} (C=N) and 1114.86cm^{-1} (C-N str). As expected, ^1H NMR spectra shows the presence aromatic protons at δ 7.3 and the two epoxy protons appear at δ 2.05 and δ 2.3.

In continuation, the final product (Scheme, I, III) was also prepared from the epoxy compound (Scheme 1, II) utilizing calcium hypochlorite in acetic acid medium. Mass spectrometric study, 6,7-Epoxy-N,N',N'-trichloro-t-cinnamaldehyde semicarbazone (Scheme 1, 3) predicts changes in the molecular

structure on the basis of various m/e values. The presence of a base peak at m/e 186 (100%) corresponds to the loss (122.5) of three chlorine atoms and one oxygen (epox) atom from the present molecule (MW=308.5). Other important values are 187(0%); 186(100%); 115(37%); 103(7%); 77(6%) and 51 (3%), and these correspond to other possible important fragments.

^1H NMR spectrum of the final product (Scheme 1, 3) leads to the presence of much fewer numbers of protons than the former i.e epoxy derivatives. A multiplet at δ 7.6 indicates the presence of the aromatic protons and the epoxy protons also appear at δ 2.05 and δ 2.1 as usual. Indirectly, the absence of protons at the two nitrogen groups (-NH and NH_2) is decided.



Scheme 1: Stepwise conversion of t-cinnamaldehyde into 6,7-Epoxy-N,N',N'-trichloro-t-cinnamaldehyde semicarbazone.

CONCLUSION

On the basis of the experimental work and the results and discussions regarding the decontamination agents, it may be concluded that the above techniques mentioned therein are suitable for the preparation of 6,7-Epoxy-N,N',N'-trichloro-t-cinnamaldehyde semicarbazone. Both the epoxide and trichloro derivatives are significant and their use as decontamination agents will be tested for the

organosphosphorus compounds having both C-O-P and C-N-P linkages together in the same molecule.

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