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# HOFMANN ELIMINATION REACTION WITH PHOSPHORUS CONTAINING ALKYLAMMONIUM SALTS

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### SHORT COMMUNICATION

# Hofmann Elimination Reaction with Phosphorus Containing Alkylammonium Salts

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Ethylammonium phosphite salts, formed by alkyl transfer from dialkyl phosphites to tertiary amines, undergo a Hofmann elimination of ethylene.

Key words: Hofmann; elimination; alkylammonium; phosphite; ethylene; alkylation.

The formation of olefins by the decomposition of quaternary ammonium hydroxides, the Hofmann elimination reaction, is well-known.<sup>1</sup> Previously it has been reported that ethylene is evolved in the cleavage of the alkylammonium salt obtained through the alkylation of ethylendiamine with dimethyl phosphite.<sup>2</sup> In this paper we report that ethylammonium salts of alkyl phosphites, formed by alkyl transfer to amines from dialkyl phosphites, undergo a Hofmann elimination reaction. This discovery is an unusual example of a Hofmann elimination induced by an Arbuzov-type alkylation reaction.

The <sup>1</sup>H-NMR spectrum (200 MHz, DMSO- $d_6$ ) of the product of the reaction (90°C for 7 hrs) of dimethyl phosphite with triethylamine reveals the following signals:  $\delta$  6.55 (d,  $J_{PH}$  = 578 Hz, PH);  $\delta$  3.55 (d,  $J_{CH}$  = 12 Hz, POCH<sub>3</sub>);  $\delta$  2.93 (s, NCH<sub>3</sub>);  $\delta$  4.63 (broad, NH);  $\delta$  3.47–3.74 (m, NCH<sub>2</sub>CH<sub>3</sub>) and  $\delta$  1.15 (t,  $J_{CH}$  = 4.5 Hz, NCH<sub>2</sub>CH<sub>3</sub>). The NH signal in the reaction product exchanges with deuterium after the sample is treated with D<sub>2</sub>O. These data are consistent with the formation of I in Scheme I. Thus, the alkylammonium salt which forms in the first stage of the reaction of dimethyl phosphite with triethylamine<sup>3–5</sup> undergoes a subsequent Hofmann elimination reaction. The evolution of ethylene has been independently confirmed from the IR spectrum of the evolved gas which shows characteristic absorption bands for ethylene.<sup>6</sup> The yield of ethylene according to the difference between the weight of the pressure reactor before and after heating for 7 hrs, is 48%.

A gas with the same IR spectra is also evolved from the reaction of diethyl phosphite and dimethylaniline at 150-152°C. For this reaction 41% of ethylene is

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$$(RO)_{2}P(O)H + N(CH_{2}CH_{3})_{3} \longrightarrow RO - P - O - NR(CH_{2}CH_{3})_{3} + H$$

$$\begin{array}{c}
\bigcirc \\
\parallel \\
\text{RO-P-O-NHR}(\text{CH}_2\text{CH}_3)_2^+ \\
\text{H}
\end{array}$$

$$\begin{array}{c}
\text{CH}_2=\text{CH}_2\\
\text{CH}_3
\end{array}$$

SCHEME I

formed after 48 hrs, along with 16% of a solid material. The solution  $^1\text{H-NMR}$  spectrum of this solid product reveals signals at  $\delta$  1.13 and 3.41. By  $^{31}\text{P}$  NMR spectroscopy this product does not contain phosphorus. Thus the initially formed ethylene undergoes subsequent cyclization and polymerization reactions because of the higher temperature reaction conditions. In this second case an ethyl group transfers from diethyl phosphite to dimethylaniline prior to the nucleophile induced Hofmann elimination step (Equation 1). A second product  $(\text{CH}_3\text{O})\text{P}(\text{H})\text{O}_2^-\text{NC}_6\text{H}_5(\text{C}_2\text{H}_5)_2\text{CH}_3^+$ , resulting from an alkyl group rearrangement, is expected to be formed at these

$$(C_2H_5O)_2P(H)O + NC_6H_5(CH_3)_2 \rightarrow (C_2H_5O)P(H)O_2^-NC_6H_5(CH_3)_2C_2H_5^+$$

$$\rightarrow (C_2H_5O)P(H)O_2^-NC_6H_5(CH_3)_2H^+ + C_2H_4$$
(1)

higher temperature conditions.9

On the basis of these results, we propose that the cleavage of these phosphorus-containing alkylammonium salts proceeds by the Hofmann elimination mechanism (Scheme II). This observation of ethylene elimination confirms our previous suggestion that these phosphorus-containing alkylammonium salts exist as free-ions.<sup>2,5</sup> Further details on the extension of this reaction to other phosphorus-containing alkylammonium salts will be published in due course.

$$(RO)_{2}P(O)H + NR_{2}'R'' \longrightarrow RO_{P-O}^{O}CH_{3}CH_{2}NR_{2}'R''^{+}$$

$$RO_{P-O}^{O}NHR_{2}'R''^{+} + CH_{2}=CH_{2}$$

$$R = CH_{3}, R' = R'' = CH_{2}CH_{3}; R = CH_{2}CH_{3}, R' = CH_{3}, R'' = C_{6}H_{5}.$$
SCHEME II

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- 6. IR spectra (gas) =CH group at 3120-2880 cm<sup>-1</sup>; CH=CH<sub>2</sub> at 950 cm<sup>-1</sup>; CH and CH<sub>2</sub> at 1410 cm<sup>-1</sup>.
- 7. The <sup>1</sup>H NMR spectrum of cyclohexane shows  $\delta = 1.54$ .
- 8. IR spectrum (KBr) shows (CH<sub>2</sub>) at 2920–2830 cm<sup>-1</sup> and  $\delta$ (CH<sub>2</sub>) at 1450 cm<sup>-1</sup>.
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