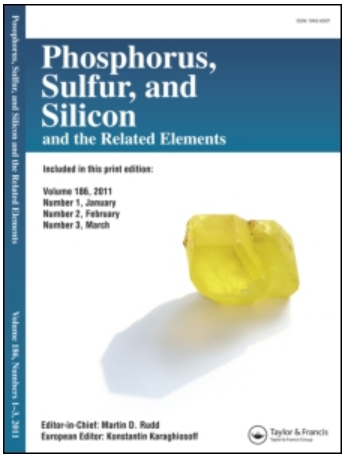

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HOFMANN ELIMINATION REACTION WITH PHOSPHORUS CONTAINING ALKYLAMMONIUM SALTS

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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.[1] 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.[2] 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 ^{1}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: δ 6.55 (*d*, J_{PH} = 578 Hz, PH); δ 3.55 (*d*, J_{CH} = 12 Hz, $POCH_3$); δ 2.93 (*s*, NCH_3); δ 4.63 (broad, NH); δ 3.47–3.74 (m, NCH_2CH_3) and δ 1.15 (*t*, J_{CH} = 4.5 Hz, NCH_2CH_3). The NH signal in the reaction product exchanges with deuterium after the sample is treated with D_2O. 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[3–5] 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.[6] 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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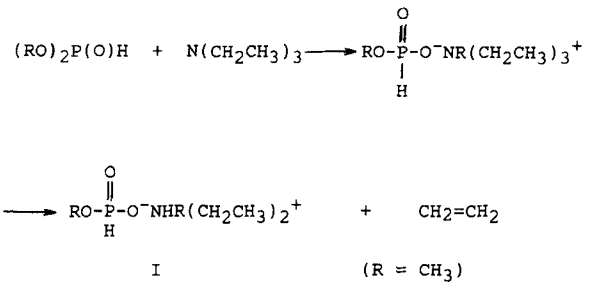


SCHEME I

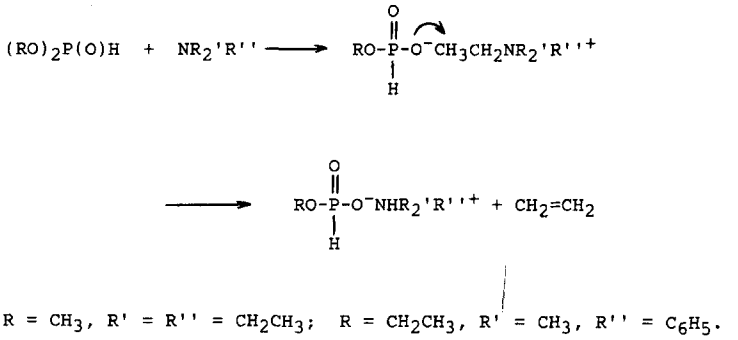
formed after 48 hrs, along with 16% of a solid material. The solution ^{1}H-NMR spectrum of this solid product reveals signals at δ 1.13 and 3.41. By ^{31}P NMR spectroscopy this product does not contain phosphorus. Thus the initially formed ethylene undergoes subsequent cyclization[7] and polymerization reactions because of the higher temperature reaction conditions.[8] 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 $(CH_3O)P(H)O_2^-NC_6H_5(C_2H_5)_2CH_3^+$, resulting from an alkyl group rearrangement, is expected to be formed at these

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

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

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.[2,5] Further details on the extension of this reaction to other phosphorus-containing alkylammonium salts will be published in due course.



SCHEME II

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6. IR spectra (gas) =CH group at 3120–2880 cm^{-1}; $CH{=}CH_2$ at 950 cm^{-1}; CH and CH_2 at 1410 cm^{-1}.
7. The ^1H NMR spectrum of cyclohexane shows $\delta = 1.54$.
8. IR spectrum (KBr) shows (CH_2) at 2920–2830 cm^{-1} and $\delta(CH_2)$ at 1450 cm^{-1}.
9. K. Troev and D. M. Roundhill, *Phosphorus and Sulfur,* (succeeding) paper.