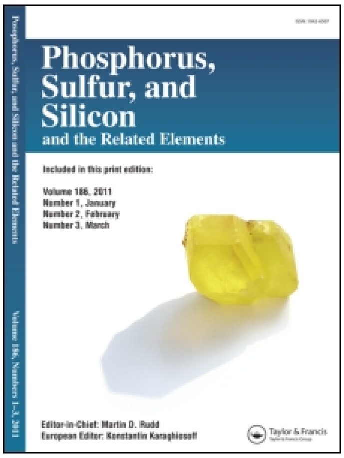

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Troev, K. and Roundhill, D. Max(1988) 'NOVEL REARRANGEMENT OF PHOSPHORUS-CONTAINING ALKYLAMMONIUM SALTS', Phosphorus, Sulfur, and Silicon and the Related Elements, 37: 3, 247 — 249

To link to this Article: DOI: 10.1080/03086648808079045

URL: http://dx.doi.org/10.1080/03086648808079045

Phosphorus and Sulfur, 1988, Vol. 37, pp. 247–249
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SHORT COMMUNICATION

Novel Rearrangement of Phosphorus-Containing Alkylammonium Salts

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(Received December 11, 1988; in final form January 22, 1988)

Phosphorus containing alkylammonium salts, obtained through the *in situ* alkylation of tertiary amines with diethyl phosphite, undergo a novel rearrangement involving alkyl group transfer between the phosphite anion and the alkylammonium cation.

Key words: Rearrangement; alkylammonium; phosphite; alkylation; amines; novel.

The alkylation of amines with dialkyl phosphites is well-known.[1–5] In this paper we wish to report a novel rearrangement reaction of phosphorus-containing alkylammonium salts, which are formed *in situ* by the alkylation of tertiary amines with diethyl phosphite. The reaction product from the thermal reaction between diethyl phosphite and dimethylaniline at 150°C for 7 hrs shows the presence of two different phosphorus containing compounds in solution. The ^{31}P NMR spectrum (81.02 MHz, DMSO-$\underline{d}_6$) of this product mixture (I and II) shows a doublet of triplets at δ 2.63 with $^1J_{PH} = 632$ Hz and $^3J_{PCH} = 9$ Hz. This spin multiplicity is characteristic of a $CH_3CH_2OP(O)(H)O^-$ fragment. The second ^{31}P resonance is a doublet of quartets centered at δ 4.55 with $^1J_{PCH} =$ 629 Hz and $^3J_{PH} = 12$ Hz, which is characteristic of a $CH_3OP(O)(H)O^-$ fragment. As confirmation of the presence of these moieties, the ^{1}H NMR spectrum (200 MHz, DMSO-$\underline{d}_6$) of this same product mixture shows the expected resonances for compounds I and II. Compound I shows resonances at δ 6.64 (*d*, $J_{PH} = 631$ Hz, $P\underline{H}$); δ 1.26 (*t*, $J_{CH} = 8$ Hz, $POCH_2C\underline{H}_3$) and δ 3.44 – 3.49 (*m*, $POC\underline{H}_2CH_3$). The $NC_6H_5(CH_3)_2C_2H_5^+$ cation shows resonances at δ 2.97 (*s*, $NC\underline{H}_3$); δ 0.99 (*t*, $NCH_2C\underline{H}_3$); δ 3.52–3.68 (*m*, $NC\underline{H}_2CH_3$); δ 7.91–8.16 (*m*, $C_6\underline{H}_5$). Compound II has resonances at δ 6.58 (*d*, $J_{PH} = 629$ Hz, $P\underline{H}$) and δ 3.48 (*d*, $J_{CH} = 12$ Hz, $POC\underline{H}_3$). These data support the formulation of I as $CH_3CH_2OP(O)(H)O^-$ $NC_6H_5(CH_3)_2C_2H_5^+$ and II as $CH_3OP(O)(H)O^-$ $NC_6H_5(CH_3)(C_2H_5)_2^+$ (Scheme I). An analogous product mixture is obtained from the reaction between diethyl phosphite and trimethylamine (Scheme I,

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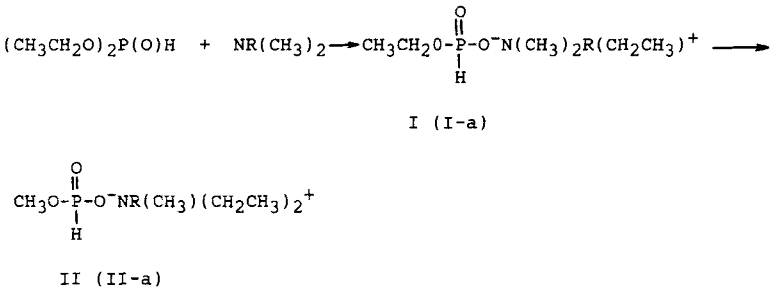


$$(CH_3CH_2O)_2P(O)H + NR(CH_3)_2 \longrightarrow CH_3CH_2O\text{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{P}}\text{-}O^- N(CH_3)_2R(CH_2CH_3)^+ \longrightarrow$$

I (I-a)

$$CH_3O\text{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{P}}\text{-}O^- NR(CH_3)(CH_2CH_3)_2^+$$

II (II-a)

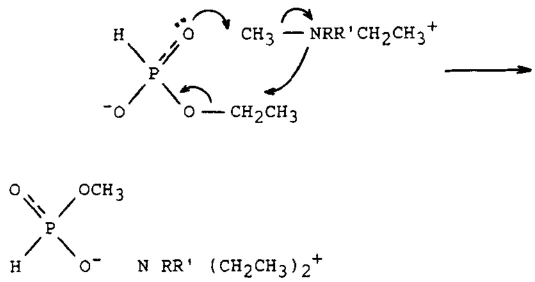
$R = C_6H_5$ (I and II), $R = CH_3$ (I-a and II-a))

SCHEME I

compound I-a and II-a).[6] The final reaction product obtained from dimethyl phosphite and triethylamine under the same experimental conditions consists of only one type of phosphorus atom, and is $CH_3OP(O)(H)O^-$ N $CH_3(C_2H_5)_3^+$.[7]

The formation of the compounds II and II-a (Scheme I) from the reaction of diethyl phosphite with either dimethylaniline or trimethylamine verifies that phosphorus-containing alkylammonium salts I and I-a undergo a unique alkyl transfer rearrangement between the phosphonate anion and the alkylammonium cation (Scheme I). A number of factors contribute to the driving force of this rearrangement. Firstly, a higher partial positive charge at the carbon atom of the N—CH_3 group is induced by the positive charge of the nitrogen atom, especially when its electrophilicity is compared with the α-carbon atom of the ethoxy group. Secondly, the nucleophilic oxygen atom present on the phosphoryl anion can attack at the methyl carbon on the intermediate alkylammonium cation. As shown in Scheme II this alkyl interchange reaction can occur without the generation of any free carbocations.

Under analogous experimental conditions with the ethyl dimethylanilinium cation, nucleophilic attack occurred at the ethyl group rather than the methyl, resulting in a Hofmann elimination reaction.[8] This elimination reaction yields a salt with the NH^+ rather than the $NCH_2CH_3^+$ cation, but with the same



($R = CH_3$; $R' = C_6H_5$, CH_3)

SCHEME II

phosphonato anion. Both reactions occur at 150°C, thereby lowering the selectivity of this rearrangement reaction.

Further details on the extension of this rearrangement reaction to other phosphorus-containing alkylammonium salts will be published in due course.

ACKNOWLEDGMENT

For the research at Tulane University, we thank the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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6. ^{31}P-NMR (200 MHz, DMSO-d_6): I-a $CH_3CH_2OP(O)(H)O^-$ $N(CH_3)_3(C_2H_5)^+$: δ 1.05 (*dt*, $J_{PH} =$ 534 Hz and $^3J_{PH} = 9$ Hz) II-a $CH_3OP(O)(H)O^-$ $N(CH_3)_2(C_2H_5)_2^+$): δ 3.32 (*dq*, $^1J_{PH} = 561$ Hz and $^3J_{PH} = 12$ Hz).
7. ^{31}P-NMR (200 MHz, DMSO-d_6): δ 3.52 (*dq*, $^1J_{PH} = 571$ Hz and $^3J_{PH} = 12$ Hz).
8. K. Troev and D. M. Roundhill, *Phosphorus and Sulfur,* (preceding) paper.