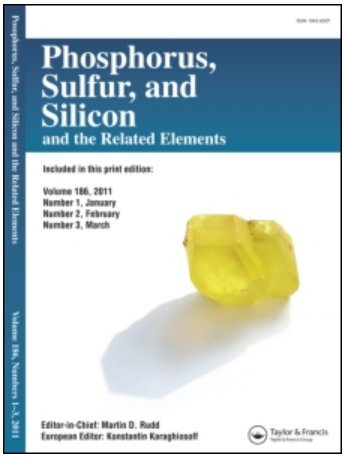

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Maier, Ludwig and Kunz, Walter(1987) 'Preparation of Triazolylmethylphosphonates and of Triazolyl-Methylphosphoniumsalts and their Application in the Wittig-Horner Reaction', Phosphorus, Sulfur, and Silicon and the Related Elements, 30: 1, 201 — 204
To link to this Article: DOI: 10.1080/03086648708080557
URL: http://dx.doi.org/10.1080/03086648708080557

Phosphorus and Sulfur, 1987, Vol. 30, pp. 201–204
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PREPARATION OF TRIAZOLYLMETHYLPHOSPHONATES AND OF TRIAZOLYLMETHYLPHOSPHONIUMSALTS AND THEIR APPLICATION IN THE WITTIG-HORNER REACTION

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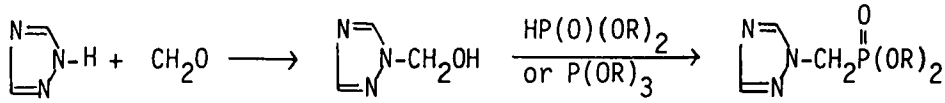
Abstract The preparation of triazolylmethylphosphonates and of triazolylmethylphosphoniumsalts and their application in the Wittig-Horner reaction is reported.

RESULTS AND DISCUSSION

Attempts to prepare 1H-1,2,4-triazol-1-ylmethylphosphonates (4, and 5) by a Mannichtype reaction or by transesterification of 1-hydroxymethyl-1H1,2,4-triazol 1 with tertiary phosphites failed.

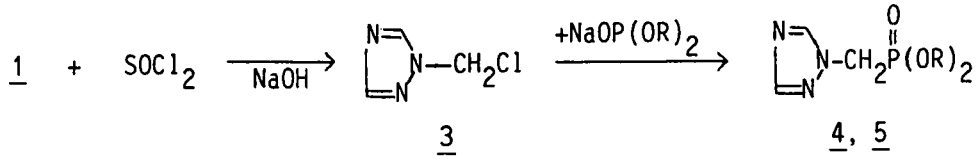


1

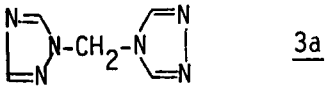
4, R = C_2H_5, 5, R = i-C_3H_7

On the other hand 4 and 5 are obtained by a Michaelis-Becker reaction from 1-chloromethyl-1H-1,2,4-triazol 3 and sodium phos-

phites in high yield. The Michaelis-Arbuzov reaction is less suited for the preparation of 4 and 5.

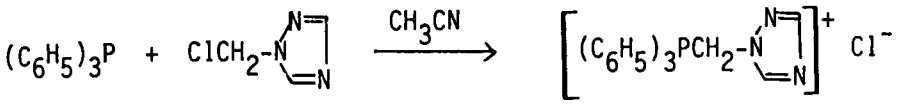


3 is obtained in good yield as a water clear liquid, b.p. 52-54°C /0.2 torr, from the interaction of 1 with thionyl chloride followed by treatment with a base. On standing at 0° or 20°C it decomposes within hours and yields the unsymmetrical methylen-bis-(triazol) 3a in addition to other products.



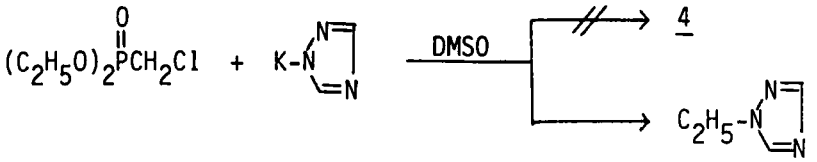
3a

However an acetonitrile solution of 3 is stable for months. Heating this solution with tertiary phosphines gives triazolylsubstituted phosphoniumsalts, e.g. 6

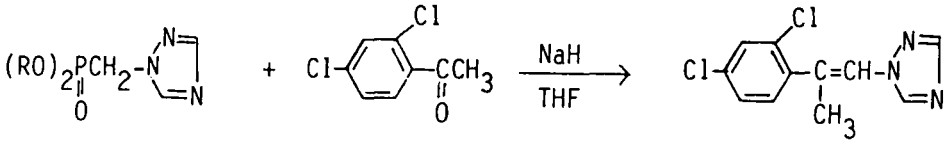


6

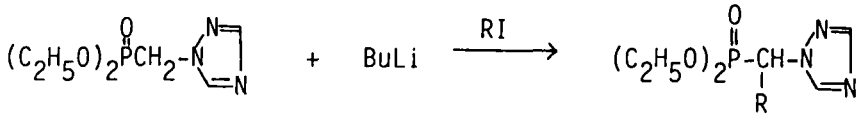
Not successful was an attempt to prepare 4 by reaction of 0,0-diethylchloromethylphosphonate with potassium-1H-1,2,4-triazol in DMSO as solvent. Rather 1-ethyl-1H-1,2,4-triazol was isolated in this experiment.



The Wittig-Horne reaction with 4 to 6 gives the olefinically substituted triazols as a cis/trans mixture in high yield, e.g.,

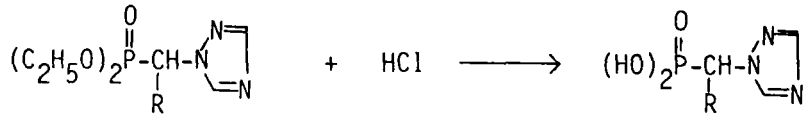


In several cases this mixture could be separated into the cis- and trans compounds by colomn chromatography. Several of these compounds possess a high fungicidal activity[1].
Alkylation of the carbanion, prepared from 4 and butyllithium, with methyland ethyl iodide produced the alkylated 1-(1H-1,2,4-triazol-1-yl)-ethyl-1 and -propyl-1-phosphonates 7 and 8.



7, R = CH_3 , 8, R = C_2H_5

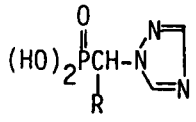
Hydrolysis with 20% of HCl under reflux yields the crystalline 1-(1H-1,2,4triazolyl)-alkylen-1-phosphonic acids 9, 10 and 11.



9, R = H, 10, R = CH_3, 11, R = C_2H_5

Like other phosphonic acids, but unlike aminosubstituted phosphonic acids, these acids show only a small dependence of the ^{31}P-chemical shift on the pH of the solution (Table 1).

Table 1: Dependence of the ^{31}P-chemical shift on the pH of



Compound	pH	1	4	7	9	11
9, R = H	chem. shift	8.65	10.7	9.21	9.30	9.21
10, R = CH_3	chem. shift	12.18	14.14	12.74	12.65	12.84
11, R = C_2H_5	chem. shift	11.53	13.21	12.37	12.28	12.28

1-Imidazolyl- and 1-pyrazolylmethylphosphonates could not be prepared since attempts to obtain the corresponding 1-chloromethyl-imidazolyl- and -pyrazolyl-compounds were not successful.

However the corresponding phosphine oxide compounds could be synthesized by a different route.

1. Ciba-Geigy AG, EP 63'099 (1982), Erf. L. Maier und W. Kunz;
Ciba-Geigy AG, EP 89'920 (1983), Erf. A. Meyer, W. Kunz, L. Maier und H. Rempfler;
Ciba-Geigy AG, EP 60'223 (1982), Erf. W. Kunz, R. Nyfeler, A. Meyer, W. Frick, L. Maier und E. Sturm.