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PREPARATION OF TRIAZOLYLMETHYLPHOSPHONATES AND OF TRIAZOLYLMETHYLPHOSPHONIUMSALTS AND THEIR APPLICATION IN THE WITTIGHORNER REACTION

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<u>Abstract</u> 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 ($\underline{4}$, and $\underline{5}$) by a Mannichtype reaction or by transesterification of 1-hydroxymethyl-1H1,2,4-triazol 1 with tertiary phosphites failed.

$$N-H + CH2O \longrightarrow N-CH2OH \xrightarrow{HP(0)(OR)_{2}} N-CH2P(OR)_{2}$$

$$\frac{1}{4}, R = C2H5, \frac{5}{5}, R = i-C3H7$$

On the other hand $\underline{4}$ and $\underline{5}$ 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 $\underline{4}$ and $\underline{5}$.

$$\underline{1} + SOC1_2 \xrightarrow{NaOH} \underbrace{\stackrel{N=}{\longrightarrow}}_{NaOH} - CH_2C1 \xrightarrow{+NaOP(OR)_2} \underbrace{\stackrel{N=}{\longrightarrow}}_{N-CH_2P(OR)_2}$$

$$\underline{3} \qquad \underline{4}, \underline{5}$$

 $\underline{3}$ is obtained in good yield as a water clear liquid, b.p. 52-54°C /0.2 torr, from the interaction of $\underline{1}$ 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.

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

$$(c_6H_5)_3P + c_1CH_2 - N \longrightarrow CH_3CN \longrightarrow \left[(c_6H_5)_3PCH_2 - N \longrightarrow C_1C_1 - C_$$

Not successful was an attempt to prepare $\underline{4}$ 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.

$$(c_2H_50)_2$$
 $\stackrel{0}{\stackrel{\text{\tiny PCH}}}_2$ $\stackrel{C_2H_5}{\stackrel{\text{\tiny N}}}_2$ $\stackrel{\text{\tiny DMSO}}{\stackrel{\text{\tiny M}}}_2$ $\stackrel{\text{\tiny M}}{\stackrel{\text{\tiny N}}}_2$

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

$$(RO)_{2_{\parallel}^{PCH}2}^{PCH} - \stackrel{N}{\underset{N}{\stackrel{N}{\longrightarrow}}} + C1 \stackrel{C1}{\longleftarrow} \stackrel{C1}{\underset{0}{\stackrel{NaH}{\longrightarrow}}} C1 \stackrel{C1}{\longleftarrow} \stackrel{C1}{\underset{CH_{3}}{\longleftarrow}} \stackrel{N=1}{\underset{N}{\longrightarrow}} \stackrel{N=1}{\underset{CH_{3}}{\longleftarrow}} \stackrel{N=1}{\underset{N}{\longrightarrow}} \stackrel{$$

In several cases this mixture could be separated into the cisand trans compounds by colomn chromatography. Several of these compounds possess a high fungicidal activity¹.

Alkylation of the carbanion, prepared from $\underline{4}$ and butyllithium, with methyland ethyl iodide produced the alkylated 1-(1H-1,2,4-triazol-1-yl)-ethyl-1 and -propyl-1-phosphonates $\underline{7}$ and $\underline{8}$.

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

$$(C_2H_5O)_2P-CH-N=N$$
 + HC1 ----- (HO) $_2P-CH-N=N$
 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 $^{31}\text{P-chemical}$ shift on the pH of the solution (Table 1).

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

Compound	рН	1	4	7	9	11
<u>9,</u> 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-chloromethylimidazolyl- and -pyrazolyl-compounds were not successful.

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

 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.