A Facile Synthesis of Bis-alkylmercaptomethanephosphonates

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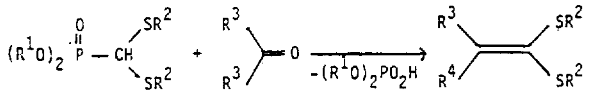
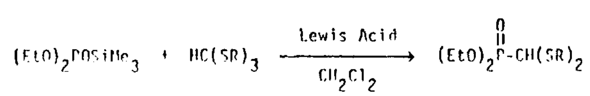
Bis-alkylmercaptomethanephosphonates which are the derivatives of the practically unknown formylphosponate are the intermediates of the conversion under Wittig-Horner reaction condition into the corresponding ketene thioacetals[1]. Ketene thioacetals are key intermediates in a wide variety of organic syntheses[2].



Until now, bis-alkylmercaptomethanephosphonate have been obtained by the following methods; Arbuzov reaction of trialkyl phosphites with bis-(alkylmercapto) methyl chlorides[3], addition of dialkyl sulfide to alkylthiomethanephosphonate carbanion[4], and reaction of diethoxymethanephosphonate with mercaptans[3b]. These known methods are successful to some extent but not sufficient both in yields and in reaction conditions.

In the course of our studies on α-heterosubstituted phosphonates we have recently reported a synthesis of 1-alkoxy-1-arylmethanephosphonates[5] which involves the Arbuzov reaction of diethyl trimethylsilyl phosphite (DTSP) with arylaldehyde dialkylacetals. In an extension of this work we now wish to report a convenient synthetic method for the preparation of bis-alkylmercaptomethanephosphonates by the reaction of DTSP with orthothioformates.



DTSP reacted with orthothioformates in the presence of Lewis acid highly to yield the desired phosphonates (Table 1). In order to find out optimum condition, we have studied the reaction of DTSP and tributyl orthothioformate in the presence of four different Lewis acids. The best yield was obtained in stannic chloride. Treatment of orthothioformates with the Lewis acid presumably leads to formation of intermediate thionium ions[6]. In a subsequent nucleophilic reaction DTSP reacts with this ions to yield product.

The advantages of this approach are to give the high yield, to shorten the reaction time and to be easy preparation of starting materials[7].

The following is a typical experimental procedure. To a solution of orthothioformate (2 mmol) in methylene chloride under nitrogen at $-10°C$ is added dropwise stannic chloride (2.1 mmol). After 10 min stirring at $-10°C$, DTSP (2 mmol) is added into the reaction mixture. The resulting solution is left to slowly return to room temperature for 3-4h, diluted with methylene chloride (5 m*l*) and water (5 m*l*), and stirred for 10 min. The organic layer is separated, dried with magnesium sulfate, and evaporated to leave a yellow or colourless oil. The product was purified by Kugelrohr distillation.

Talbe 1. Preparation of Bis-alkylmercaptomethanephosphonates

R	Lewis Acid	Yield(%)[a]	b.p(°C/mmHg)	^{31}p-NMR[b]($CDCl_3/H_3PO_4$) (ppm)
$CH_2CH_2CH_2CH_3$	$SnCl_4$	92	140-143/0.4	+19.14
	$TiCl_4$	80		
	BF_3Et_2O	83		
	ZnI_2	65		
$CH_2CH(CH_3)_2$	$SnCl_4$	94	136-38/0.4	+19.10
$CH_2CH_2CH_3$	$SnCl_4$	88	133-135/0.4	+19.50
$CH(CH_3)_2$	$SnCl_4$	83	131–134/0.4	+19.70
CH_2CH_3	$SnCl_4$	85	134-136/0.6[c]	+19.85

[a] Isolated yeild by Kugelrohr distillation. [b] The conversion of positive ^{31}p-NMR to down field from H_3PO_4 is used. [c] Lit[3b]; 95-100°C/0.05.

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Formation of *p*-Cymene from the Catalytic Reactions of Unsaturated Aldehydes and Alcohols with a Rhodium(I) Complex

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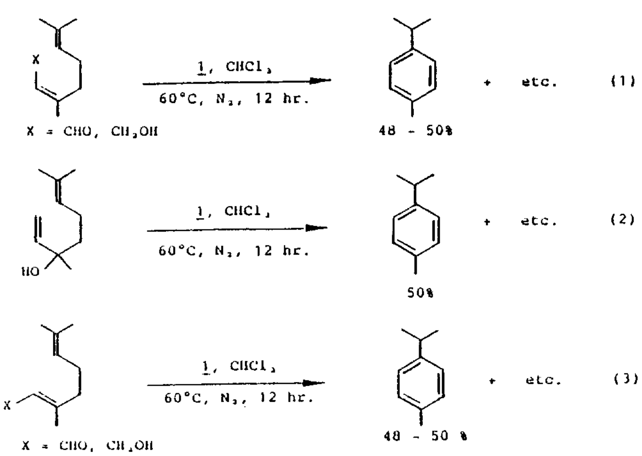
Catalytic cyclization of unsaturated aldehydes to give cycloketones[1-5] and unsaturated cycloalcohols[6] with various transition metal complexes has been observed. Aromatization of olefin substituted cyclohexenones by a transition metal conplex has been also reported.[7] In the presence of transition metal catalyst, alcohols and ketones undergo the hydrogenation reaction to give hydrocarbons under H_2,[8-11] in the presence of hydrogen donor,[12] or simply under N_2 (bimolecular disproportionation reaction, $2R_2CHOH \rightarrow R_2CH_2 + R_2CO + H_2O$).[13] Dehydrogenation of cyclohexanes with transition metal complexes has been known.[14,15]



During our investigation on the catalytic activities of $M(ClO_4)(CO)(PPh_3)_2$ (M = Rh, Ir) for the reactions of unsaturated nitriles,[16,17] aldehydes[18] and alcohols,[19] we have found the formation of *p*-cymene from the catalytic reactions of the unsaturated aldehydes (neral and geranial) and alcohols (nerol, geraniol and linalool) with $Rh(ClO_4)(CO)(PPh_3)_2$ (**1**) (eqs. 1-3). In all experiments, 0.7 mmole of **1** and 14 mmoles of the corresponding aldehyde or alcohol were used in 5 m*l* of $CHCl_3$ to produce *ca.* 7.0 mmoles of *p*-cymene. The product, *p*-cymene was identified by GC, mass (m/e = 134) and ^{1}H-NMR spectra. The reactions also yield some other products (besides *p*-cymene) which have not been fully characterized. It should, however, be mentioned that *p*-isopropenyl toluene (*ca.* 12%) has been found in the reactions of unsaturated aldehydes, and H_2O in all reactions (eqs. 1-3). It is noticed in eqs. 1-3 that the yield is always close to 50%. Accordingly, it may be suggested that the catalytic reactions (eqs. 1-3) involve a bimolecular disproportionation reaction such as $2R_2CHOH \rightarrow R_2CH_2 + R_2CO + H_2O$ as previously reported.[13]

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