Stabilization of phosphobetaines that form in the reaction of trialkylphosphines with methoxyallene

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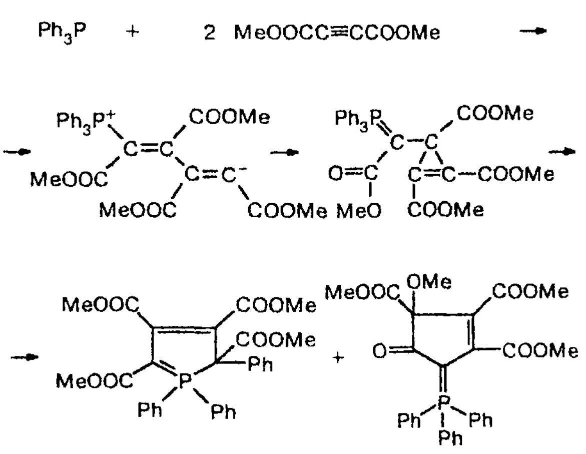
Reactions of tripropyl- and tributylphosphines with methoxyallene were studied. In the case of tripropylphosphine, a mixture of tripropylphosphine oxide and tripropyl-1-formylethylidenephosphorane (the latter in equilibrium with its *O*-betaine) was obtained. The reaction with tributylphosphine yields, along with tributylphosphine oxide, two homologous ylides, namely, tributyl-1-formylethylidene- and tributyl-1-formylpropylidenephosphoranes, which are also in equilibria with their *O*-betaines. A possible scheme of formation of these ylides is discussed.

Key words: tripropylphosphine, tributylphosphine, methoxyallene, ylide, *O*-betaine, phosphobetaine, protonation, demethylation, cationotropic migration.

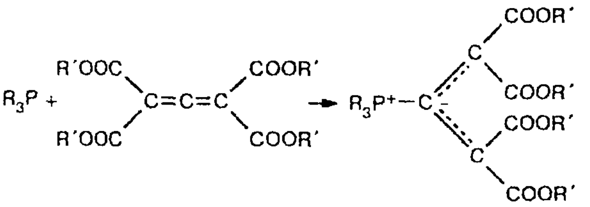
It is known[1—6] that tertiary phosphines react with activated unsaturated compounds in the absence of proton-donor reagents to give phosphobetaines. Depending on their structure, the latter are stabilized in different ways, mostly, either by transprotonation involving the α-H atoms to form stable ylides or by dissipation of the negative charge over the system of C atoms with the electron-acceptor substituents. Thus the reaction of triphenylphosphine with dimethyl acetylenedicarboxylate results in an unstable 1 : 2 adduct (cyclopropenylphosphonium ylide), which is transformed into allylidenephosphorane, and trimethyl 3-methoxy-4-oxo-5-(triphenylphosphoranylidene)cyclopentene-1,2,3-tricarboxylate (Scheme 1).[7]

Scheme 1



The products of addition of tertiary phosphines to tetraethyl allenetetracarboxylate are stable crystalline bipolar compounds (Scheme 2).[8]

Scheme 2



β-Phosphobetaine, which has a similar structure with the negative charge distributed over the allylic bond system and is stabilized by the mesomeric effect, was obtained by us earlier by reaction of tributylphosphine with phenylallene.[9]

In continuation of these investigations, we studied the reactions of trialkylphosphines with methoxyallene with the goal of gaining insight into the influence of the structure of the starting allene on the stability of the resulting phosphobetaine. It was shown that tripropylphosphine reacts with methoxyallene at 100 °C, but higher yields were obtained upon heating in a sealed tube at 120 °C. The reaction results in tripropylphosphine oxide and *O*-betaine **A**, which is in equilibrium with its ylide form **B**.

Apparently, tripropylphosphine oxide is formed as a result of an abnormal nucleophilic substitution of tripropylphosphine for the methoxy group. The corresponding cumulene was not isolated from the reaction mixture (Scheme 3).

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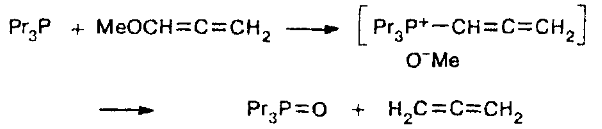
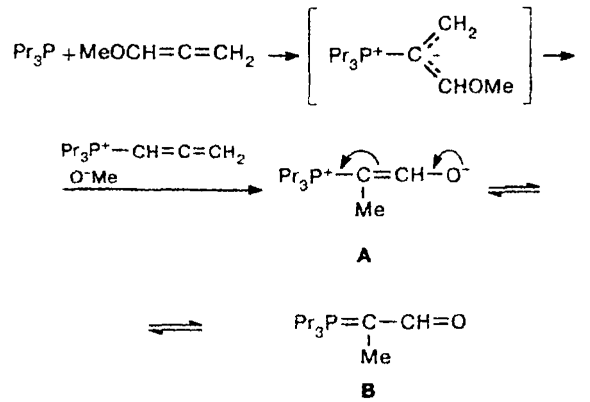
Scheme 3



The formation of the **A** ⇌ **B** equilibrium mixture may be explained by the initial attack of phosphine at the sp-hybridized carbon atom of the allene double bond system, which gives phosphobetaine, followed by its protonation and demethylation (Scheme 4). Thus, the reaction proceeds by two independent pathways.

Scheme 4



The ^{1}H NMR spectrum of the **A** ⇌ **B** equilibrium mixture isolated by distillation contains, along with the signals for all alkyl protons at δ 0.8—1.2, a low-field broadened singlet at δ 8.64 (J = 13.5 Hz) and a doublet at δ 9.09 ($^3J_{PH}$ = 29.8 Hz) with relative integral intensities of 1.0 and 1.6, respectively.

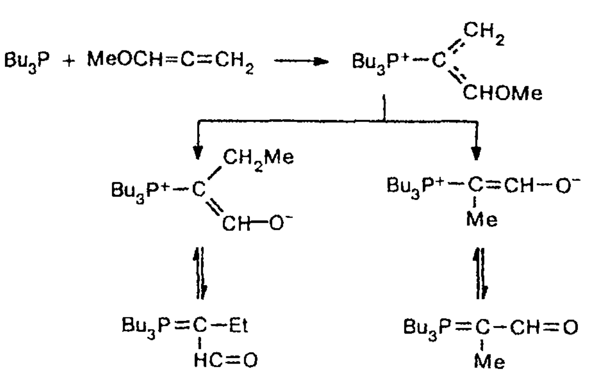
Additional splitting of both components of the doublet at δ 9.09 ($^4J_{HH}$ = 2 Hz) owing to spin-spin coupling of the aldehyde proton with the methyl protons allows us to assign this signal with a great degree of certainty to the proton of the =CH—O$^-$ group of compound **A**. The the values of the spin-spin coupling constant between the "aldehyde" proton of compound **B** and the phosphorus atom $^3J_{PH} \leq 6.6$ Hz. From the integral intensity ratio of the "aldehyde" protons, it follows that the content of compounds **A** and **B** in the mixture under study is 60 and 40%, respectively.

In the ^{13}C NMR spectrum of the **A** ⇌ **B** mixture, the following signals for the "aldehyde" carbon atoms are characteristic:

A, δ, 180.79, —CH=, $^2J_{PC}$ = 20, $^1J_{CH}$ = 152 Hz;
B, δ, 174.22, =CH—O$^-$, $^2J_{PC} \leq 20$, $^1J_{CH}$ = 152 Hz.

In contrast to tripropylphosphine, tributylphosphine reacts with methoxyallene to yield two homologous *O*-betaines that are in equilibrium with their ylide forms. The lower homolog seems to be formed according to the scheme proposed for the tripropyl analog, while the higher one results from cationotropic migration of the methyl group in the same phosphobetaine (Scheme 5).

Scheme 5



Attempts to separate the mixture of betaines by distillation failed. The ^{31}P NMR spectrum exhibits a single signal, and the structures of the reaction products were judged from their ^{1}H NMR spectrum.

After the above mixture was treated with methyl iodide, two new ^{1}H signals for the methyl protons appeared at δ 4.0 and 4.2, which suggests the presence of two isomeric salts.

The reason for the difference in reactivity of tripropyl- and tributylphosphines with respect to methoxyallene remains unclear. Probably, this is merely due to a steric factor, *viz*., the larger size of the tributylphosphonium cation, which favors intramolecular O—C interaction.

Experimental

^{1}H NMR spectra were recorded on a Perkin—Elmer R-12B spectrometer (60 MHz) with SiMe$_4$ as the internal standard. ^{13}C and ^{31}P NMR spectra were recorded on a Bruker 200 SU spectrometer (50.13 and 80.01 MHz, respectively) with 85% H$_3$PO$_4$ as the external standard. Mass spectra were obtained on an MKh-1321A GLC-MS spectrometer (EI, direct inlet of samples into the ion source).

Reaction of tripropylphosphine with methoxyallene. A mixture of tripropylphosphine (7.2 g) and methoxyallene (3.1 g) was heated in a sealed tube at 120 °C for 30 h. Distillation gave tripropylphosphine oxide (1.6 g, 20%), b.p. 100—102 °C (1 Torr), 270—273 °C (680 Torr) (*cf*. Ref. 10: b.p. 280—282 °C (760 Torr)) and a mixture of tripropyl-1-formylethylidenephosphorane with its *O*-betaine form (4.5 g, 46.4%), b.p. 145—155 °C (1 Torr). Found (%): C, 66.31; H, 11.26; P, 14.11. $C_{12}H_{25}OP$. Calculated (%): C, 66.67; H, 11.57; P, 14.35. IR, ν/cm^{-1}: 2750 (C=O), 1640 (C=C).

MeI (0.6 g) was added to a solution of the compound obtained (0.5 g) in 5 mL of ether. After 1 day, the precipitate that formed was filtered off, thoroughly washed with ether, and dried to give a mixture of iodides (0.8 g, 97.5%). Found (%): I, 34.89. $C_{13}H_{28}IOP$. Calculated (%): I, 35.47. IR, ν/cm^{-1}: 2750 (C=O), 1640 (C=C).

In addition, the nonconsumed tripropylphosphine (2.2 g, 30%) was isolated from the reaction mixture, b.p. 50—52 °C (1 Torr), 172—175 °C (680 Torr) (*cf*. Ref. 10: b.p. 187.5 °C (760 Torr)).

Reaction of tributylphosphine with methoxyallene. A mixture of tributylphosphine (3 g) and methoxyallene (2.5 g) was heated in a sealed tube at 120 °C for 25 h. Distillation *in vacuo* gave tributylphosphine (0.3 g, 10%), b.p. 75—80 °C (1 Torr), 106—109 °C (10 Torr) (*cf.* Ref. 11: b.p. 109—110 °C (10 Torr)), tributylphosphine oxide (0.9 g, 27.5%), b.p. 127—133 °C (1 Torr) (*cf.* Ref. 11: b.p. 146—147 °C (3.5 Torr), 127—133 °C (1 Torr)), and a mixture of tributyl-1-formylethylidene- and tributyl-1-formylpropylidenephosphoranes (1.5 g), which manifest themselves by a common ^{31}P signal at δ +24. MS, *m/z*: 258 and 272 $[M]^+$. ^1H NMR, δ: 0.9—1.0 (m, 9 H, $C\underline{H}_3CH_2CH_2CH_2$); 1.14 (m, 3 H, $C\underline{H}_3CH_2C=CH—O$, $J_{H,H}$ = 7.3 Hz); 1.2—1.3 (m, 12 H, $CH_3C\underline{H}_2C\underline{H}_2CH_2$); 1.8—2.1 (m, 6 H, CH_2P); 2.04 and 2.00 (both d, 3 H, CH_3CP, $^3J_{PH}$ = 16.7 and 16.5 Hz for *cis-* and *trans*-isomers); 2.0—2.15 (d.q, 2 H, $P—C—C\underline{H}_2CH_3$, J_{HH} = 6.6 Hz, $^3J_{PH}$ = 17 Hz); 8.8—8.9 (dd, 1 H, =CH, *cis*-J_{PH} = 2.8 Hz, *trans*-J_{PH} = 2.9 Hz); 9.23 (d, 1 H, CH=O, $^3J_{PH}$ = 29.5 Hz); 9.26 (d, 1 H, CH=O, $^3J_{PH}$ = 29.5 Hz).

MeI (0.8 g) was added to a solution of the mixture obtained (0.8 g) in anhydrous ether. The precipitate that formed was filtered off, washed with anhydrous ether, and dried *in vacuo* to give a mixture of iodides (0.8 g). Found: I, 32.22%. In the ^1H NMR spectrum of this mixture, two signals appeared at δ 4.0 and 4.2 (see above), characteristic of the methoxy groups at the sp^2-hybridized carbon atom.

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