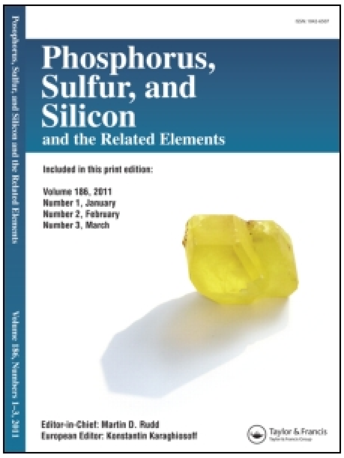

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Commercial Synthesis 1,3-Bis(Dialkylphosphino)Propanes

Allan J. Robertson[a]; Colleen E. Micklethwaite[a]
[a] Cyanamid Canada Inc., Niagara Falls, Ontario, Canada

To cite this Article Robertson, Allan J. and Micklethwaite, Colleen E.(1993) 'Commercial Synthesis 1,3-Bis(Dialkylphosphino)Propanes', Phosphorus, Sulfur, and Silicon and the Related Elements, 75: 1, 79 — 82
To link to this Article: DOI: 10.1080/10426509308037369
URL: http://dx.doi.org/10.1080/10426509308037369

Phosphorus, Sulfur, and Silicon, 1993, Vol. 75, pp. 79–82
Reprints available directly from the publisher
Photocopying permitted by license only

COMMERCIAL SYNTHESIS 1,3-BIS(DIALKYLPHOSPHINO)PROPANES

ALLAN J. ROBERTSON, COLLEEN E. MICKLETHWAITE
Cyanamid Canada Inc., P.O. Box 240 Niagara Falls,
Ontario, Canada, L2E 6T4

Abstract This paper reports a simple two step process by which a large variety of 1,3-bis(dialkylphosphino)propanes can be prepared on an industrial scale. The first stage is the preparation of an allyldialkylphosphine which is then followed by free radical addition of a dialkylphosphine to the allyl functional group to yield the subject compound

INTRODUCTION

Metal complexes containing bidentate ligands of the type $R_1R_2P(CH_2)^nPR_3R_4$ have found utility as catalysts. In particular compounds in which n=3, such as 1,3-bis(diphenylphosphino)propane, have been demonstrated as being superior to triphenylphosphine as catalyst ligands in the decarbonylation of aldehydes.(1)
The classical routes to diphos C3 bridged ligands generally involve reactions between 1-alkylphosphino Grignard reagents and halophosphines or 1-chloroalkylphosphines and metal phosphides.(2,3) 1,3-bis(dialkyl- phosphino)propanes have also been prepared by ethoxide promoted elimination of 2-cyanoethyl groups bis (1,3-dialkyl(2-cyanoethyl)phosphonium) propanes.(4) All routes give good to excellent yields but are not generally amenable to large scale industrial production.

RESULTS AND DISCUSSIONS

The starting materials for the synthesis are dialkylphosphines prepared from the free radical addition of phosphine to olefins and allylbromide. The intermediate allyldialkylphosphine is formed as a result of nucleophilic displacement of bromine from allylbromide by a dialkylphosphine. Although tertiary phosphines will readily quarternize with alkylbromides, secondary phosphines which are much less nucleophilic are very slow to react.(5) However, in the case of the more reactive allylbromide, quantitative reaction with dialkylphosphines takes place in 1-2 hours at 70-80°C.

Allylbromide is added over 1 hour at 80°C to an equal molar amount of dialkylphosphine in a hydrocarbon/acetonitrile mixture. After an additional 1 hour the reaction is complete with the allyldialkylphosphine being present in the lower acetonitrile layer as the hydrobromide salt. Water and an equal molar quantity of $NaHCO_3$ are then added. Three layers form. The lower aqueous layer contains NaBr. The middle layer is essentially acetonitrile with traces of phosphine oxides while the upper layer contains the hydrocarbon diluent and allyldialkylphosphine.

After decanting the lower layers, an additional mole of dialkylphosphine is added slowly at 70-80°C with 1-2 molar % of a free radical initiator such as azobis(isobutyronitrile). Generally 70-80% conversion is obtained in 4-6 hours. Unconverted dialkylphosphine and intermediate allyldialkylphosphine are removed with the diluent by distillation and are subsequently recycled. Removal of the last traces of intermediate is facilitated by choosing a diluent which has a boiling point between that of the intermediate and the product.

The synthesis is general for a wide range of dialkylphosphines as well as diphenylphosphine. However, there are some practical restrictions. All dialkylphosphines readily undergo the first step, however, some dialkylphosphines containing secondary alkyl groups such as s-butyl or cy-hexyl react slowly with olefins under free radical conditions.

Another restriction is the boiling point of the intermediate which places a practical limit of 10-12 carbons per alkyl group.

At first glance it would appear that unsymmetrical ligands of the type $R_2PCH_2CH_2CH_2PR'_2$ can also be prepared by selecting a second dialkylphosphine for the final step. The radical addition product from such reactions, $R_2PCH_2\dot{C}HCH_2PR'_2$, undergoes reversible P-C bond fission at both the 1 and 3 positions to generate $R_2P^\cdot$,$R'_2P^\cdot$, (allyl)$R_2P^\cdot$ and (allyl)$R'_2P^\cdot$(6). This results in a mixed product containing $R_2P(CH_2)_3PR_2$, $R_2P(CH_2)_3PR'_2$ and $R'_2P(CH_2)_3PR'_2$. The above synthesis is thus restricted to symmetrical ligands although mixed dialkylphosphines of the type RR'PH may be used.

The product mixture becomes even more complex if one attempts to prepare tridentate ligands of the type $RP(-CH_2CH_2CH_2PR_2)_2$ or $R'P(-CH_2CH_2CH_2PR_2)_2$ by allowing two moles of the allylic intermediate to react under free radical conditions with one mole of a primary phosphine.

The bidentate ligands were characterized by their ^{31}P NMR and mass spectra. The isobutyl, cyclopentyl, cyclohexyl, n-hexyl and n-octyl homologues diluted in IPA, had chemical shifts of -41.02, -5.90, -6.85, -32.46 and -32.63 ppm respectively. Figure 1 contains the mass spectra of the isobutyl homolog and intermediate alkyl phosphine. All ligands typically have low abundance of the molecular ion. P-C bond cleavage occurs preferentially at the alkyl P-C bond rather than at the P-C bond in the three carbon bridge. Typical spectra of homologues containing up to 6 carbons in the alkyl group show successive losses of the alkyl fragments. The ion with m/e of 106 and found in such spectra is the ion associated with $H_2P-CH_2CH_2CH_2-PH_2$. In homologs with eight or more carbons in the alkyl group, P-C bond cleavage in the bridge system occurs with losses of R_2P fragments.

CONCLUSIONS

This is a general method for preparing $R_2PCH_2CH_2CH_2PR_2$ systems in which R contains up to 10 carbons and where R is not cyclohexyl or a secondary or tertiary alkyl group such as sec-butyl or tert-butyl. Unsymmetrical systems such as $R_2PCH2CH_2CH_2PR'_2$ will in general result in a mixture of other products.

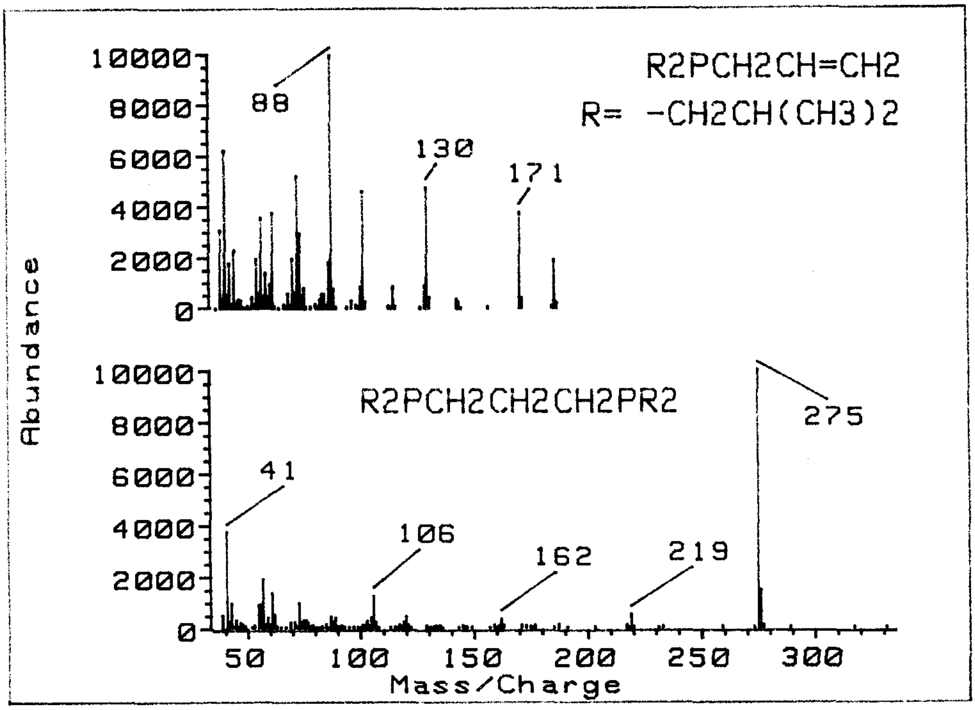

FIGURE 1 Mass spectra of allyl diisobutylphosphine and 1,3-bis(diisobutylphosphino)propane

REFERENCES

(1) "Catalytic Aspects of Metal Phosphine Complexes"; American Chemical Society, Washington DC, 1982; Chapter 4.

(2) S.O. Grim, R.C. Barth; Journal of Organometallic Chemistry, 94 327 (1975).

(3) R. Uriarte, T.J. Mazanec, K.D. Tau and D. Meek, Inorganic Chemistry, 19 79 (1980)

(4) M. Grayson, P. Keough, G. Johnson; Journal of the American Chemical Society, 81 4083 (1959).

(5) W. Henderson, Jr, S. Buckler; Journal of the American Chemical Society, 82 5794 (1960).

(6) J. Pellon; Journal of the American Chemical Society, 83 1915 (1961).