

Communication

Electron-Beam Mediated Rearrangement and Fragmentation of Bis(diphenylphosphino)alkane Derivatives in Gas Phase

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ABSTRACT: The irradiation of electron-beam onto bis-(diphenylphosphino)methane, ethane, propane and butane initiated phenyl-shift from a phosphine to another phosphine atom and subsequent fragmentation resulted in the formation of triphenylphosphine derivative as key intermediate. The mechanism of those processes is speculated.

Photochemical functional group conversion on a solid surface provides diverse properties on the surface which have shown potential applications in the area of nanopatterning,¹ lithography,² tribology and diagnosis.³ For a practical application in industry, the conversion should be clean, simple to lead group-to-group transformation resulting only one component as possible.

In our previous research regarding fragmentation of alkyne-cobalt-phosphino complex by E-beam irradiation, we found that 1,3-bis(diphenylphosphino)methane ligand showed unexpected fragmentation suggesting an intramolecular phenyl transfer from phosphine to P atom.⁴ From this motivation, we carried out E-beam mediated fragmentation of bis (diphenylphosphino) alkanes (DPA) in gas phase using a mass spectrometer (Micromass Inc, Autospec, at Korea Research Institute of Chemical Technology) and observed that phenyl-group migration and P-P bond formation are involved in the fragmentation pathway as key step depending on the chain length of DPA.

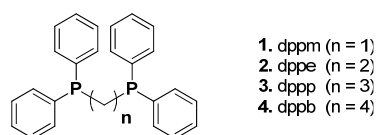


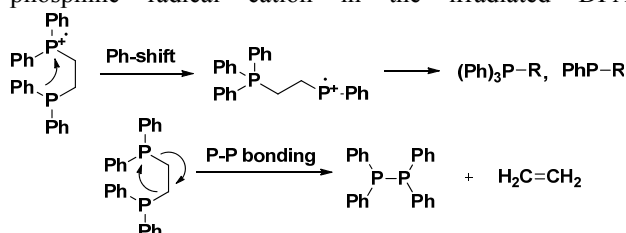
Figure 1. Chemical structure of bis(diphenylphosphino)alkanes.

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The fragmentation of phosphinoalkanes **1-4** was processed upon 20 or 70eV e-beam at 200 °C in gas phase and their data are listed in Table 1. Mass spectra of dppe and dppp are shown in Figures 2 and 3, respectively. Various fragmentation intermediates are observed including arylphosphine derivatives and representative fragments are assigned as M^+ (molecular ion), M-Ph (M-77), Ph-P-R, Ph_2P-R , Ph_3P-R and Ph_2P-PPh_2 (P-P bond formation) where R represents C0-C4 hydrocarbon.

For the generation of triphenylphosphine (Ph_3P-R) fragment, phenyl migration from a phosphine to cationic P atom is proposed as in Scheme 1. Depending on the number of alkyl-carbon of DPA, a subsequent fragmentation of cationic $Ph_3P-(CH_2)_n-P-Ph$ gave the intermediates Ph_3P-R or $R-P-Ph$. A serial $Ph_3P-(CH_2)_n$ peaks appeared with $m/z=14$ or 13 difference at $m/z=262$ (Ph_3P), 275 (Ph_3PCH), 289 ($Ph_3PC_2H_3$), 303 ($Ph_3PC_3H_5$) and 317 ($Ph_3PC_4H_7$) in 0.8-100% relative intensity as shown in Figure 2, 3. Similarly, Ph_2P-R (R=C1-C4 alkyl) peaks appeared with $m/z=14$ or 13 difference at $m/z=199$ (Ph_2PCH_2), 213 ($Ph_2PC_2H_4$), 227 ($Ph_2PC_3H_6$) and 241 ($Ph_2PC_4H_8$) from $z/m=185$. Interestingly, the base peaks of DPA were observed at various intermediates such as Ph_3P (dppm, $z/m=262$), M-Ph (dppp, dppb) and M^+ (dppe, $z/m=398$). In addition, BP ($m/z=183$) is assigned for phosphindole-dehydride.⁵

Phenyl-group migration from a phosphine to the other P atom of DPA is quite interesting. The migration of phenyl group seems to be processed via intramolecular 1,5-shift derived by electrophilic phosphine radical cation in the irradiated DPA.⁶

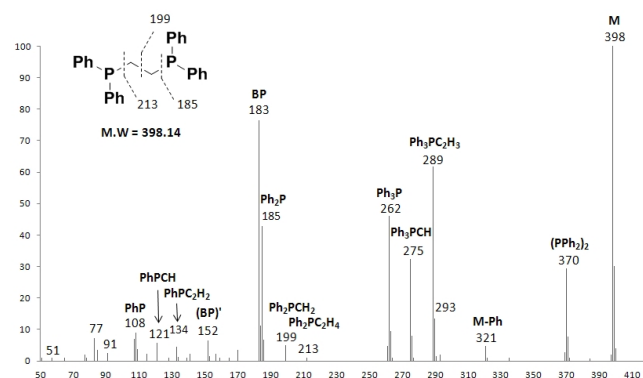


Scheme 1. A proposed mechanism for fragmentation of dppe via phenyl group migration and P-P bond formation by e-beam irradiation (R; C0-C4).

Table 1. The relative intensities of intermediates from diphenylphosphinoalkanes 1-4 irradiated with 70eV e-beam.

	Ph-P (108)	PhPCH (121)	Ph ₂ P (185)	Ph ₂ PCH ₂ (199)	Ph ₂ PC ₂ H ₄ (212)	Ph ₃ P (262)	Ph ₃ PCH (275)	Ph ₃ PC ₂ H ₃ (289)	Ph ₃ PC ₃ H ₅ (303)	M-Ph	(PPh ₂) ₂ (370)	M ⁺
DPPB	13.9	9.0	15.9	6.7	10.9	15.0	a	0.8	a	100 (349)	0.9	42.6 (426)
DPPP	7.4	19.4	23.1	17.9	5.53	13.7	1.9	9.1	6.9	100 (335)	a	75.8 (412)
DPPE*	9.0	5.8	42.8	5.0	1.0	46.1	32.3	61.7	-	4.6 (321)	29.3	100 (398)
DPPM	4.8	48.5	7.1	44.2	-	100	-	-	-	1.3 (307)	a	83.6 (384)

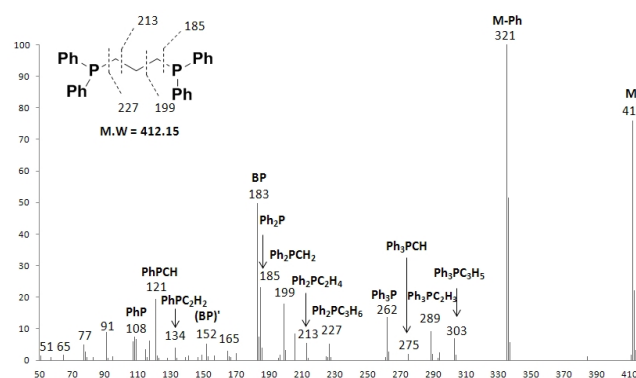
Numbers in parenthesis are m/z values; (a), not observed; (-), not available; (*), at 70eV. For dppb, Ph₃PC₄H₇ peak appeared at m/z=317(3.4).

**Figure 2.** MS spectrum of dpepe irradiated at 70eV.

Another noticeable intermediate, tetraphenylbisphosphine Ph₂P-PPh₂ (m/z=370), was observed from dpepe and dppb containing even number of alkyl carbons representing P-P bond formation. Meanwhile, dppm and dppp containing odd number of alkyl carbon did not show Ph₂P-PPh₂. These results suggest that P-P bond forming seems to be derived by the evolution of ethylene gas. To our best knowledge, phosphine-related photochemistry has been reported only in case of phosphite (PH₃) of which photolysis triggered P-P bond formation to give P₄ or P₂H₄.^{7,8} For the mechanism of P-P bond formation in an e-beam mediated fragmentation of DPA, it is not sure whether it occur via recombination of Ph₂P or concerted cyclic transition state releasing ethylene gas resembling the Norrish type II cleavage.⁹ Thus, further photochemical studies of phosphinoalkanes in solution would be a practical tool for the mechanism of P-P bond formation.

ACKNOWLEDGEMENT

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**Figure 3.** MS spectrum of dppp irradiated at 70eV.

KEYWORDS

Bis(diphenylphosphino)alkane, electron-beam, fragmentation, phenyl migration, P-P bonding.

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