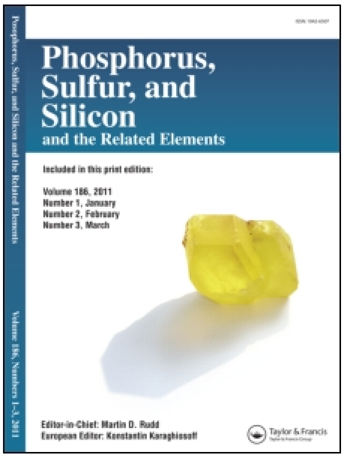

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Ylide Chemistry: An Account of Structural, Conformational and Redox Investigations

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To cite this Article Schmidbaur, Hubert , Bowmaker, Graham A. , Deschler, Ulrich , Dörzbach, Cornelia , Herr, Rudolf , Milewski-mahrla, Beatrix , Schier, Annette and Zybill, Christian E.(1983) 'Ylide Chemistry: An Account of Structural, Conformational and Redox Investigations', Phosphorus, Sulfur, and Silicon and the Related Elements, 18: 1, 167 — 170

To link to this Article: DOI: 10.1080/03086648308075993

URL: http://dx.doi.org/10.1080/03086648308075993

Phosphorus and Sulfur, 1983, Vol. 18 pp. 167-170
0308-664X/83/1801-0167/$18.50/0

YLIDE CHEMISTRY: AN ACCOUNT OF STRUCTURAL, CONFORMATIONAL AND REDOX INVESTIGATIONS

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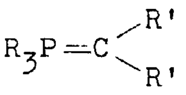
Abstract Structural data of phosphorus ylides are summarized and discussed. Conformational preferences in solution and in the solid state, as followed by NMR spectroscopy and X-ray diffraction, indicate a strong gauche effect for the lone pairs of electrons at the ylidic carbon atom. One- and two-electron oxydation of ylide carbanions is accomplished with copper(II) as the oxidant, leading to oxidative coupling or to halogenation, respectively.

INTRODUCTION

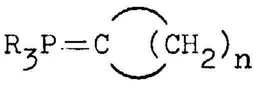
Phosphorus ylides are extremely important compounds in organic synthesis, in organometallic and coordination chemistry, and as classical cases of phosphorus-carbon multiple bonding. It is therefore surprising that information on their structure is still very limited. Only about two dozens of X-ray and electron diffraction studies are reported in the literature. Even less has been known on the conformations of species with ylidic bonds.

STRUCTURES

Summarizing some old and new results of these investigations it follows that all strain-free ylides **A** are found to have planar structures at the ylidic carbon atoms, associated with quasitetrahedral phosphorus centers. In molecules with the ylidic function integrated into a six- or five-membered ring the strain-free conditions **B** still allow the species to adopt a planar configuration at the ylide carbon, as also shown by ^{1}H, ^{13}C, and ^{31}P NMR techniques.



A



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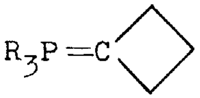
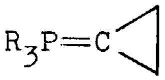


C



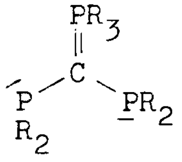
D

Already the smaller bond angles in the cyclobutane system, however, force the phosphorus atom out of the plane of the neighbouring $=C\!<^{C}_{C}$ plane. The ylidic bond forms an angle of 18° with this plane. The cyclobutane ring itself is folded by 16°, **C**. In the cyclopropylide case, finally, the P = C angle relative to the triangular plane is as high as almost 60°, **D**. In the ylides **C** and **D** the phosphonium geometry is strongly distorted by the lone pair of electrons at the ylidic carbon, and in the ground state one of the P-R bonds is pushed away from the ylide moiety by more than 10°. The idealized C_{3v} symmetry of the C_3PC group is thus reduced to C_s[1-3].

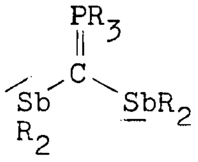
CONFORMATIONS

In phosphino-substituted ylides **E** a surprisingly high barrier to P-C rotation has been detected. Thus the

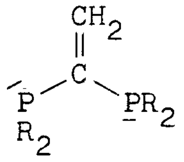
P(III) atoms in E are non-equivalent below room temperature in solution, as shown by NMR spectroscopy. An X-ray study of the perphenylated species confirmed the ground state geometry proposed in formula E. The geometry is directed by lone-pair/lone-pair repulsions which represent the first example of a gauche-effect in ylide chemistry.



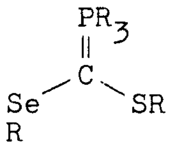
E



F



G



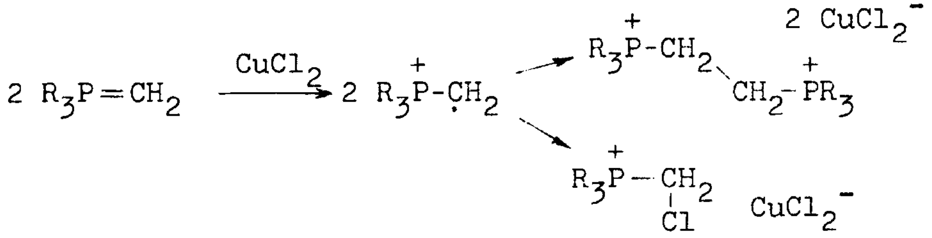
H

The antimony analogue F was found to have the same structure as E, though the Sb-C bonds are much longer than the P-C bonds, which should minimize steric effects on the rotational barrier and ground state structure. The lone-pair effect is making therefore the dominating contribution to the phenomenon. This becomes also obvious from a study of the 1,1-diphosphino-ethylene G, which has freely rotating PPh_2 groups in solution even though a structure analogous to that of E and F is found in the crystal. The results confirm the significance of the dipolar formula for the description of ylide bonding as compared to classical multiple bonding [4-6].

Similar conclusions can be drawn from thio- and seleno-substituted ylides H [7].

OXYDATION

oxydation of ylides under standard conditions is known to lead to P=C bond breaking with formation of phosphine oxides and a variety of P-free secondary products. It has now been discovered that oxydation with certain transition metal salts, copper(II) salts in particular, will induce formally a one-electron transfer process followed by C-C coupling. Diphosphonium salts are obtained in good yields from a very simple experimental procedure. Substituted ylides $R_3P{=}CHR'$ afford diastereomeric diphosphonium salts (RR, SS and RS). Radical cations $R_3P^{\oplus}{-}CH_2$ have previously been observed in UV-irradiated single crystals by ESR spectroscopy [8]. In cases with strong steric hindrance α-chlorination with $CuCl_2$ can also occur, corresponding to a two-electron transfer process, e.g.:



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