# NEW EVIDENCE FOR AND NEW REACTIONS OF
ORTHO-LITHIO YLIDS

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Summary: While α-lithio ylid 2 *may be generated from triphenylphosphonio-bromomethylid through halogen/metal exchange, the reaction of triphenyl-phosphonio-methylid* 1 *with sec- or tert-butyllithium produces nearly quantitatively the o-lithio ylid* 3 *, which is stable at -60° but slowly decomposes at higher temperatures via a cyclization product* 5 *to give the α-lithio phosphine* 4 *.*

In contradiction to other reports [1, 2], the reaction between triphenylphosphonio-methylid 1 (fig. 1) and *sec-* or *tert*-lithium was claimed to generate mainly if not exclusively α-lithio ylid 2 and to afford derivatives in 54 - 87% yields [3]. These results, however, are in conflict with our own findings. We have been able to identify other reactions which extensively take place when triphenylphosphonio-methylid is treated with organolithium reagents : ligand exchange and *ortho*-metalation [4]. Consequently, product mixtures are inevitable and products that *may*, though must not be attributed to an α-lithio ylid intermediate 2 are found in only poor yields [4].
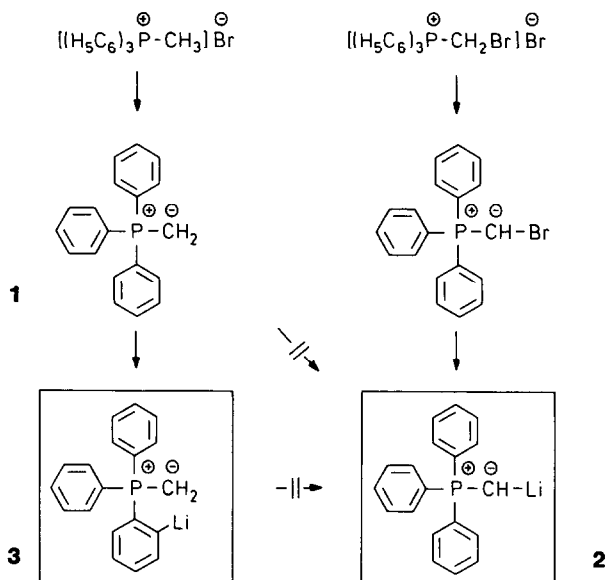

In order to study the behavior of phosphorus ylids as P-electrophiles and CH-acids in greater detail, we have embarked on a careful ^{1}H-, ^{13}C- and ^{31}P-nmr spectroscopic investigation. We summarize here our observations and conclusions.

1. When a suspension of bromomethyltriphenylphosphonium bromide (10 mmol) in 25 mL tetrahydro-furan (THF) was treated dropwise with a solution of LiBr-complexed phenyllithium [5] (0.8 M; 1.1 equiv.) in diethyl ether (DEE) at -100°C and stirred 1 h at -40°C before *tert*-butyllithium (1.5 M; 2.0 equiv.) in hexane was added at -75°C, an orange red mixture resulted. It exhibited ^{1}H-, ^{13}C- (coupled and decoupled) and ^{31}P-nmr signals which are in perfect agreement with an α-lithio ylid structure **2** (see fig. 2) [6]. Moreover, treatment with methyl iodide under conditions of little trans-ylidation [7] gave isopropyltriphenylphosphonium iodide (mp 190 - 192°C, dec.) as the main product (63%).

2. No α-lithio ylid **2** was obtained, however, when *tert*-butyllithium (or *sec*-butyllithium) was allowed to react with "salt-free" [8] ylid **1** in THF or DEE (2 h at -75°C). In contrast, the orange-yellow *ortho*-lithiated ylid **3** was found to form nearly quantitatively, provided the metalating agent was applied in moderate excess (1.2 equiv.). The ^{1}H-nmr spectrum (fig. 3) allows an unambiguous structure assignment [9]. Additional evidence came from the conversion of *o*-lithio ylid **3** with methyl iodide to ethyl-diphenyl-*o*-tolyl-phosphonium iodide (81%, mp 176 - 180°C, dec.).

3. When solutions of *o*-lithio ylid **3** in THF were warmed up to 25°C (50 h) or 50°C (5 h), 5-li-thiomethyl-5H-dibenzo-phosphole **4** was detected as the main product [10] (fig. 4). After hydro-lysis, 43% 5-methyl-5-H-dibenzophosphole [11] (δ_{CH_3} 1.39; J_{HP} 1.8; bp 88 - 90°C/10^{-3} mmHg; cor-responding oxide : mp 89 - 91°C) together with 10% of methyldiphenylphosphine (δ_{CH_3} 1.55; J_{HP} 3.2) were isolated and benzene was identified by gas chromatography. The degradation of **3** to **4** can be efficiently catalyzed by added potassium *tert*-butoxide. It finds some analogy in the base-pro-moted conversion of tetraphenylphosphonium bromide into 5-phenyl-5H-dibenzophosphole [12].
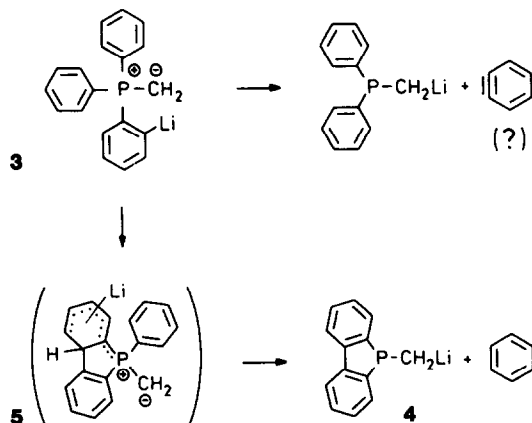
4. When hexamethylphosphorus triamide (HMPT) was added to 0.4 or 0.2 M solutions of *o*-lithio ylid **3** in THF (20 equiv. HMPT [13] per 1 equiv. **3** , *i.e.* 3.5 mL HMPT per 2.5 or 5.0 mL THF) and the mixture was kept 1 h at 20°C [13], it turned dark orange-brown and the ^{1}H-, ^{13}C- and ^{31}P-spectra changed in a very characteristic manner (fig. 5) [14]. All presently available data are compatible with the formation of intermediate **5** , the precursor to the phosphole **4** .
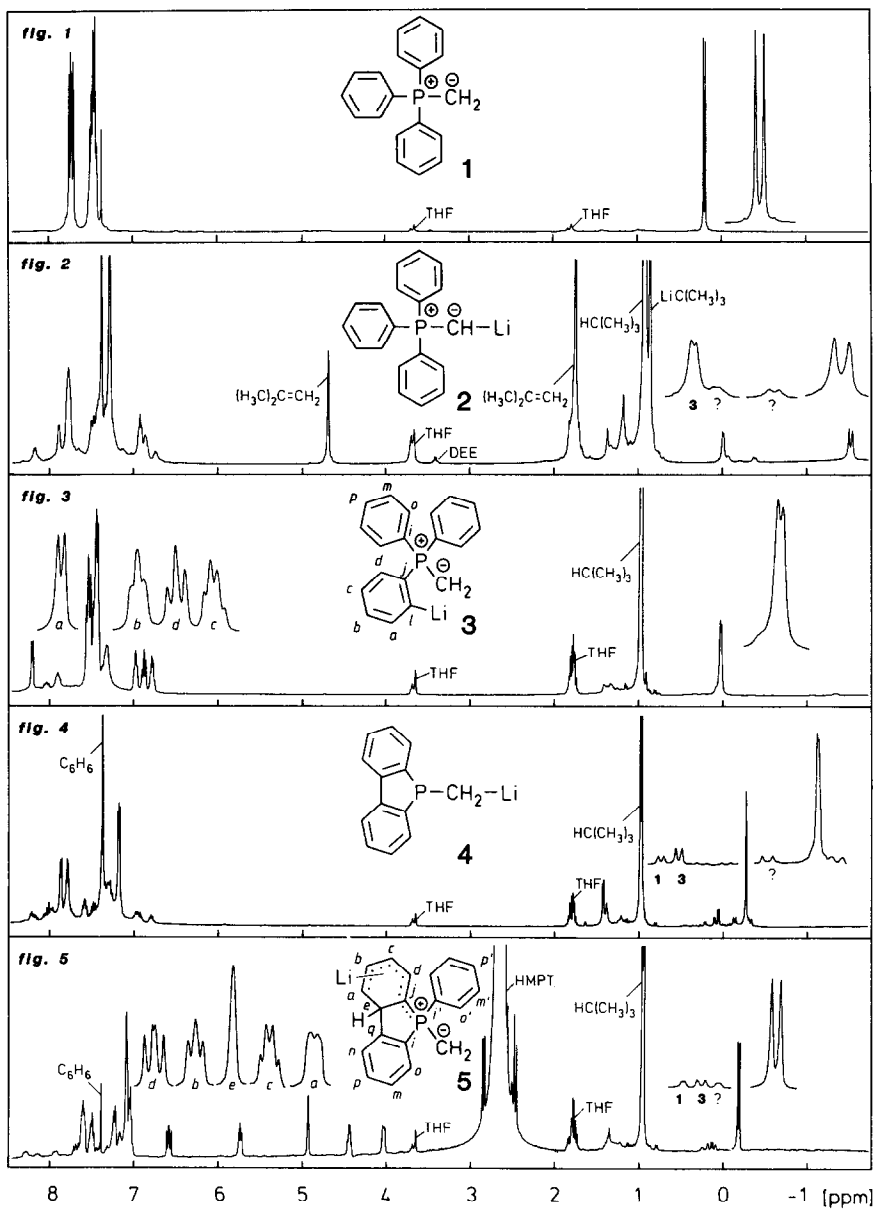
Figures 1 - 5 : ^{1}H-nmr spectra of triphenylphosphonio-methylid (1), α-lithio-triphenyl-phosphonio-methylid (2), o-lithio-triphenylphosphonio-methylid (3), 5-lithiomethyl-5H-dibenzophosphole (4), η^5-lithio-2,9-dihydro-5H-dibenzophospholio-methylid (5). Instrument : Bruker WH-360; spectral range : registered from +12.0 to -3.0 ppm, reproduced from +8.50 to -1.75 ppm; original scale : 90 Hz/cm for the main track, 20 Hz/cm for the expansions; sample temperature : -40°C; confirmation of signal assignments by double ir-radiation and two-dimensional ^{1}H/^{13}C-correlation.

[1] M. Schlosser, G. Steinhoff & T. Kadibelban, *Angew. Chem.* 1966 , *78*, 1018; *Angew. Chem., Int. Ed. Engl.* 1966 , *5*, 968; *Justus Liebigs Ann. Chem.* 1971 , *743*, 25.

[2] See also M. Schlosser, Huynh Ba Tuong, J. Respondek & B. Schaub, *Chimia* 1983 , *37*, 10.

[3] E.J. Corey & J. Kang, *J. Am. Chem. Soc.* 1982 , *104*, 4724.

[4] B. Schaub, T. Jenny & M. Schlosser, *Tetrahedron Lett.* 1984, 4097.

[5] G. Wittig, *Angew. Chem.* 1940 , *53*, 242; H. Gilman & J.W. Morton, *Org. Reactions* 1954 , *8*, 286. - Under these conditions a bromine/lithium exchange leading to ylid 1 (25%; δ_{CH_2} 0.14, J_{HP} 7.5) competes with the generation of the triphenylphosphonio-bromomethylid (70%; δ_{CHBr} 2.50, J_{HP} = 14.0) by deprotonation. The former by-product can be suppressed when lithium diisopropylamide or lithium piperidide is chosen as the base (see also G. Köbrich, *Angew. Chem.* 1962 , *74*, 33).

[6] ^{1}H-nmr : δ_α -1.51 (J_{HP} 13.5); ^{13}C-nmr : δ_{CHLi} 5.3 (J_{CH} 108.0, J_{CP} 14.2); ^{31}P-nmr : δ +9.5. Upon warming up a reversible temperature effect on the width and position of the ^{1}H-, ^{13}C- and ^{31}P-signals is observed. We tentatively attribute it to the existence of an equilibrium between monomers and dimers or contact species and ion pairs.

[7] When, for example, ylid 1 (10 mmol) in 20 mL THF is slowly added to a solution of methyl iodide (25 mmol) in 50 mL of hexane, kept at 25°C, 80% ethyl- together with 10% methyl- and 10% isopropyl-triphenylphosphonium iodide precipitate.

[8] The α-lithio ylid 2 does show up to the extent of 10% (plus 5% of a new, unidentified product) if the metalation of 1 is carried out in the presence of 1 equiv. [3] of LiBr.

[9] ^{1}H-nmr : δ_a 8.20 (*d, J* 5.5); δ_b 6.94 (*t, J* 5.6); δ_d 6.85 (*t*, J_{HH} = J_{HP} 8.5); δ_c 6.75 (*dd*, J_{HH} 6.5, J_{HP} 12.6); δ_α 0.01 (J_{HP} 5.5); ^{13}C-nmr : δ_l ?; δ_d 122.3 (J_{CP} 13.8, J_{CH} 158.0 and 6.6); δ_j 141.1 (J_{CP} 116.7, J_{CH}: broadening); δ_i 138.7 (J_{CP} 67.0); δ_m 128.7 (J_{CP} 10.3, J_{CH} 161.4); δ_c 131.4 (J_{CP} 25.3, J_{CH} 159.3); δ_p 130.4 (J_{CH} 139.0); δ_o 133.1 (J_{CP} 8.3; J_{CH} 161.8); δ_b 126.3 (J_{CP} 4.1, J_{CH} 147.8); δ_a 142.6 (J_{CP} 30.8; J_{CH} 153.8) δ_α -4.6 (J_{CP} = 51.6; J_{CH} 133.0); ^{31}P-nmr : δ 27.2.

[10] ^{1}H-nmr : δ_α -0.27 (J_{HP} = 1.5); ^{13}C-nmr : δ_α -2.0 (J_{CP} 50.1, J_{CH} 121.1); ^{31}P-nmr : δ 8.7).

[11] B.R. Ezzell & L.D. Freedman, *J. Org. Chem.* 1969 , *34*, 1777.

[12] H. Hoffmann, *Chem. Ber.* 1962 , *95*, 2563; see also G. Wittig & G. Geißler, *Justus Liebigs Ann. Chem.* 1953 , *580*, 44; E. Zbiral, *Tetrahedron Lett.* 1964, 1649.

[13] According to ref. [3], such conditions were applied for the reaction of supposed α-lithio ylid 2 with fenchone. By the way, fenchone *does* react with 1 , neat or in THF, at 25°C.

[14] ^{1}H-nmr : δ_d 6.56 (*dd*, J_{HH} 7.7; J_{HP} 10.1); δ_b 5.72 (*t, J* 6.8); δ_e 4.91 (*s*), δ_c 4.43 (*dd, J* 12.0, 6.0); δ_a 4.00 (*d, J* 5.8); δ_α -0.19 (*d, J* 8.5); ^{13}C-nmr : δ_q 155.7 (J_{CP} 21.1); δ_i 147.5 (J_{CP} 71.8; $\delta_{i'}$ 144.3 (J_{CP} 78.7); δ_o 136.1 (J_{CP} 15.7, J_{CH} 147.4); $\delta_{o'}$ 131.4 (J_{CP} 8.4, J_{CH} 156.2); $\delta_{p'}$ 129.8 (J_{CH} 144.8; δ_p 129.4 (J_{CH} ~ 160); δ_m 127.8 (J_{CP} 8.2, J_{CH} ~ 150); $\delta_{m'}$ 127.6 (J_{CP} 10.2, J_{CH} 157.3); δ_n 127.1 (J_{CP} 5.5, J_{CH} 154.0); δ_d 125.0 (J_{CP} 8.8, J_{CH} 163.0); δ_b 123.2 (J_{CP} 7.8, J_{CH} 155.0); δ_a 98.0 (J_{CP} 3.9, J_{CH} 155.5); δ_c 63.1 (J_{CP} 13.7, J_{CH} 155.6); δ_j 63.1 (J_{CP} 129.0); δ_e 47.0 (J_{CP} 19.5, J_{CH} 130.1); δ_t 1.4 (J_{CP} 111.4, J_{CH} 149.5); ^{31}P-nmr : 14.8.