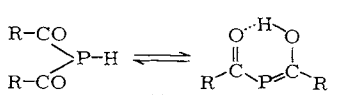
Lithium Dibenzoylphosphide · 1,2-Dimethoxyethane —A New 2-Phospha-1,3-dionate[**]

By *Gerd Becker, Matthias Birkhahn, Werner Massa,* and *Werner Uhl*[*]

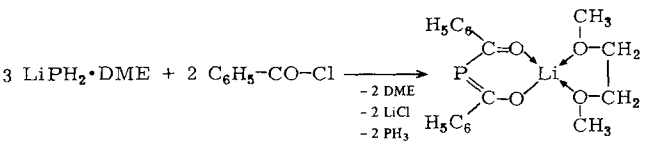
Dedicated to Professor Karl Dimroth on the occasion of his 70th birthday

The diacylphosphanes *(1)*, $R = CH_3$, $(CH_3)_3C$, synthesized so far show a remarkable keto-enol tautomerism and resemble 1,3-diketones in their properties[1]. According to X-ray structure analyses of nickel bis(dipivaloylphosphide)·DME[2] (DME = 1,2-dimethoxyethane) and of aluminum tris(dibenzoylphosphide)[3a] this similarity is also shown by 2-phospha-1,3-dionates; the metal ions are not coordinated to the phosphorus atoms but in chelate rings to the oxygen atoms of the anions.



(1)

In order to synthesize the hitherto unknown dibenzoylphosphane *(1)*, $R = C_6H_5$, we treated monolithium phosphide·DME[4] with benzoyl chloride in DME. However, instead of the expected monobenzoylphosphane, lithium dibenzoylphosphide·DME *(2)* was formed with slow evolution of phosphane.



(2)

The reaction course can be rationalized by assuming formation of the monosubstituted compound, subsequent lithium/hydrogen exchange, and renewed reaction with an excess of benzoyl chloride. The resulting dibenzoylphosphane reacts with lithium phosphide to form *(2)*.

Compound *(2)* was characterized by elemental analysis and by its NMR and IR data. The ^{31}P- and ^{13}C-NMR signals of the C—P—C group show a downfield shift[5] as has been observed in similar compounds[1b,3]. Since the poor solubility in apolar solvents containing no DME precluded determination of the molecular size and constitution, we investigated *(2)* by an X-ray structure analysis (see Fig. 1).

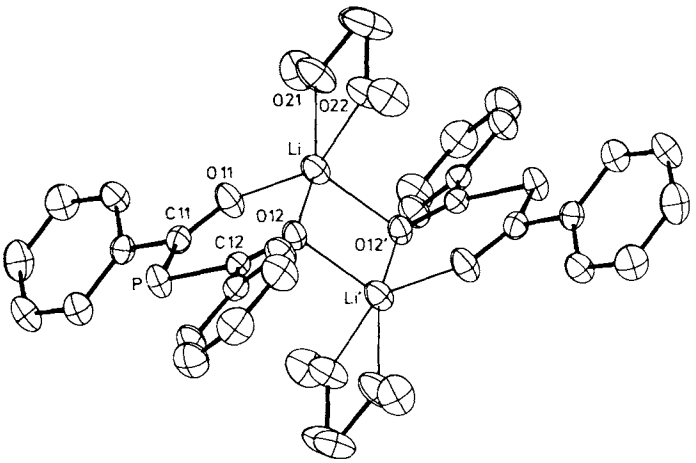


Fig. 1. ORTEP plot of the molecular structure of dimeric lithium dibenzoylphosphide·1,2-dimethoxyethane. The vibrational ellipsoids correspond to 50% probability. *(2)*, space group $P2_1/c$, with $a = 1907.1(7)$, $b = 762.6(7)$, $c = 1259(2)$ pm; $\beta = 104.5(1)°$; 4 formula units. 1907 independent, observed ($F > \sigma$) reflections recorded on an automatic four-circle diffractometer CAD4 (Enraf-Nonius) at $-80\,°C$ ($Mo_{K\alpha}$ radiation, $4° < 2\theta < 48°$) and corrected in the conventional way; $R_w = 0.034$.

(2) exists as 2-phospha-1,3-dionate; the lithium ion is bonded to all oxygen atoms of the ligands. No monomer is present in the solid state; by the inversion as a crystallographic symmetry operation the molecules are linked pairwise to form dimers (Fig. 1). The coordination number of lithium is raised to 5 by bonding to a further oxygen atom O12′ belonging to the inverse dibenzoylphosphide ion; the two lithium atoms of the dimer are located 45 pm above the basal planes of two edge-linked, somewhat distorted square pyramids of O atoms. Although the Li—Li distance (283 pm) is shorter than in the element (304 pm)[6a], metal-metal interaction can be ruled out at a covalent radius of 134 pm[6b]. Similar association is observed in other 1,3-dionates[6c].

[*] Prof. Dr. G. Becker, M. Birkhahn, Dr. W. Massa, Dipl.-Chem. W. Uhl
Fachbereich Chemie der Universität
Hans-Meerwein-Strasse, D-3550 Marburg (Germany)

[**] Part 14 of Acyl- and Alkylidenephosphanes. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. 13. Mitteilung: *G. Becker, W. Uhl*, Z. Anorg. Allg. Chem., in press.

As in phosphamethinecyanines, λ^3-phosphorins[7], and phosphaferrocenes[8], the third valence of the phosphorus is involved in partial double bonds in the conjugated system of *(2)*. The bond lengths and angles (Table 1) in the dibenzoylphosphide ion are similar to those of the aluminum compound[3a]. The larger ionic radius of the lithium ion (59 pm), however[9], results in an increase of the intramolecular O11—O12 distance ("bite") to 279 pm. The bond lengths of the differently coordinated oxygen atoms O11 and O12 differ only slightly. As expected, the formally singly negatively charged phosphide anion is bound by shorter bonds to the lithium than the uncharged DME. Both chelate rings are not planar; lithium (72 pm) and phosphorus (11 pm) are located above the plane of the six-membered ring formed by the atoms C11, O11, O12, and C12.

Table 1. Selected structural parameters of *(2)*. For clarity, in Figure 1 the carbon atoms of the phenyl groups as well as C8n and C9n of the DME ligand have not been labeled. Atoms from the inverse molecule are marked with an apostrophe.

Bond lengths [pm]			Bond angles [°]	
	n=1	n=2		
P—C1n	181.5(3)	179.6(3)	C11—P—C12	101.8(1)
C1n—C2n	152.0(4)	151.1(4)	P—C11—O11	128.4(2)
C1n—O1n	125.4(3)	127.4(2)	P—C12—O12	128.4(2)
O1n—Li	194.4(5)	201.5(4)	C11—O11—Li	136.0(2)
O2n—Li	215.2(5)	210.4(5)	C12—O12—Li	132.4(2)
C8n—O2n	140.0(4)	138.0(4)	O11—Li—O12	89.7(2)
C81—C82	146.8(5)	—	O11—Li—O21	89.5(2)
O2n—C9n	141.3(4)	142.7(5)	O12—Li—O22	94.6(2)
Li—O12′	204.4	—	O21—Li—O22	75.6(2)
Li—Li′	283.2	—	O11—Li—O22	147.3(3)
			O12—Li—O21	159.7(3)

Procedure

All operations must be performed under highly pure Ar with dry (Na, $LiAlH_4$) solvents.—A solution of monolithium phosphide·DME (20.3 g, 156 mmol) in DME (200 ml) is added dropwise to a stirred, cooled (−35 °C) solution of benzoyl chloride (14.6 g, 104 mmol) in DME (50 ml). The mixture is then warmed to +20 °C and stirring is continued until evolution of phosphane has ceased (*ca.* 12 h). The precipitated lithium chloride is filtered off and washed with small amounts of DME. The solvent is vacuum distilled from the filtrate and the residue is dissolved in DME. At −25 °C, air-stable, orange-red, hexagonal prisms crystallize from the solution: yield 15.1 g (44.7 mmol, 86%), dec. p. 308 °C (under argon).

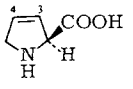
Received: March 10, 1980 [Z 563 IE]
German version: Angew. Chem. *92*, 756 (1980)

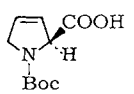
[1] a) *G. Becker*, Allg. Prakt. Chem. *23*, 73 (1972); *G. Becker, H. P. Beck*, Z. Anorg. Allg. Chem. *430*, 77 (1977); b) *G. Becker, M. Rössler, ibid.*, in press.
[2] *G. Becker, O. Mundt, M. Rössler*, Z. Anorg. Allg. Chem., in press.
[3] a) *G. Becker, H. P. Beck*, Z. Anorg. Allg. Chem. *430*, 91 (1977); b) *G. Becker, O. Mundt, ibid. 443*, 53 (1978).
[4] *H. Schäfer, G. Fritz, W. Hölderich*, Z. Anorg. Allg. Chem. *428*, 222 (1977).
[5] ^{13}C-NMR (C_6D_6 with small amounts of DME): δ=225, $^1J_{P,C}$=86.5 Hz; ^{31}P-NMR (DME): δ=64.0 (downfield shift).
[6] a) International Tables for X-Ray Crystallography. Vol. 3. Kynoch Press, Birmingham 1968, p. 278; b) *J. E. Huheey*: Inorganic Chemistry. Harper and Row, New York 1972, p. 184; c) *R. C. Mehrotra, R. Bohra, D. P. Gaur*: Metal β-Diketonates and Allied Derivatives. Academic Press, London 1978.
[7] *K. Dimroth*, Fortschr. Chem. Forschung *38*, 1 (1973).
[8] *F. Mathey, A. Mitschler, R. Weiss*, J. Am. Chem. Soc. *99*, 3537 (1977).
[9] *R. D. Shannon, C. T. Prewitt*, Acta Crystallogr. *B 25*, 925 (1969).

Direct Method for the Synthesis of *N*-Boc-L-3,4-didehydroproline[**]

By *Jean-Robert Dormoy, Bertrand Castro, Georges Chappuis, Ulrich Stefan Fritschi*, and *Peter Grogg*[*]

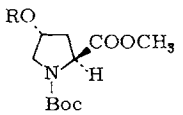
The incorporation of L-3,4-didehydroproline *(1)* into biologically active peptides very seldom results in loss of activity[1-3]; in fact, in some cases the activity even increases, with reduced toxicity of the product[3,4]. Deuterium and tritium can also be incorporated into biologically active peptides *via* dehydroproline[1,3].


(1)

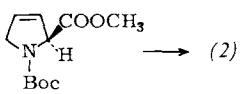

(2)

Boc = $(CH_3)_3COC-$

Hitherto, *(1)* had to be prepared by resolution[1,5] from the technically difficultly accessible racemic educt[6]. We have now succeeded in synthesizing *N*-Boc-L-3,4-didehydroproline *(2)* directly from the naturally occurring L-4-hydroxyproline.


(3), R = H

(4), R = $-\overset{S}{\overset{\|}{C}}-SCH_3$


(5)

N-Boc-L-4-hydroxyproline methyl ester *(3)*[7] was converted (90%) into the *S*-methyl xanthogenate *(4)*[8], which on Tschugaeff pyrolysis[9] gave the protected 3,4-didehydro ester *(5)* in 64% yield together with some protected 4,5-didehydro ester (3—5%) and educt *(3)* (5—9%). Hydrolysis of *(5)* afforded *(2)* in (70%) yield (see Procedure).—The 250-MHz ^{1}H-NMR spectra of the compounds *(4)* and *(5)* and of the 4,5-didehydro ester are given in Table 1.

Table 1. 250-MHz ^{1}H-NMR shifts of the ring protons in the compounds *(4)*, *(5)* and in the 4,5-didehydro isomer of *(5)* (δ values, in $CDCl_3$, TMS int., multiplets).

Cpd.	H-2 (1H)	H-3	H-4 (1H)	H-5
(4) [b]	4.39 [a] 4.47	2.27 [a] 2.33 (2H)	5.96	3.82 (2H)
(5)	4.95 [a] 5.01	5.74 (1H)	6.01	4.23 (2H)
(5)-isomer	4.61	3.06 (2H)	4.93	6.52 [a] 6.63 (1H)

[a] In some cases the conformers could be recognized by separate signals. *H. L. Maia, K. G. Orrell, H. N. Rydon*, Chem. Commun. *1971*, 1209; *J. Savrda* in *A. Loffet*: Peptides 1976, Brussels 1976, p. 653. [b] SCH_3: δ=2.56 (s, 3H).

Procedure

(4): *(3)* (10 mmol), tetrabutylammonium hydrogen sulfate (10 mmol) and CS_2 (12 mmol) were dissolved in benzene (20

[*] Prof. Dr. B. Castro, Dr. J. R. Dormoy
Laboratoire de Chimie Organique II, Université de Nancy I
Case officielle 140, F-54037 Nancy (France)
Dr. G. Chappuis, U. S. Fritschi, Dr. P. Grogg
Bachem Feinchemikalien AG
CH-4416 Bubendorf (Switzerland)

[**] Dehydroamino Acids, Part 1.