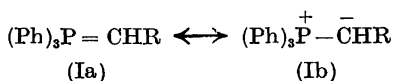


Infrared Studies of Some Phosphorus Ylids Containing Oxygen

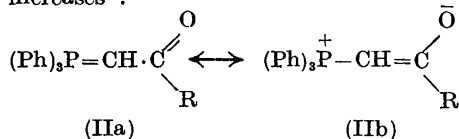
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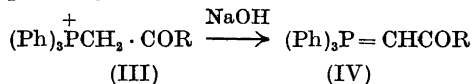
Alkaline treatment of triphenyl-substituted phosphonium salts containing a reactive hydrogen atom attached to the α -carbon atom of the phosphonium compounds (α -position with respect to P) results in the formation of phosphorus ylids¹⁻⁴. Due to the ability of phosphorus to expand its valence shell to a "ten electron shell" by utilization of one of its empty d -orbitals these compounds are most correctly described as resonance hybrids between the ylene form (Ia) and the ylid form (Ib):^{2,5}



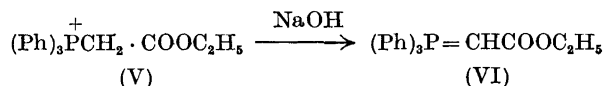
When the substituent R contains a keto group which can participate in the resonance stabilization of the phosphorus ylid the stability of such compounds greatly increases²:



The "keto betaine" described by Michaelis and Köhler⁶ which results from treatment of (III) with strong alkali was shown by Ramirez and Dershowitz² to be a phosphorus ylid:



In the same way the "phosphonium betaine" described by Michaelis and Gimborn⁷ obtained from (V) with concentrated alkali was found by Aksnes⁸ to be a phosphorus ylid:



In this paper we have compared the infrared absorption spectra of some phosphorus ylids containing keto groups with closely related phosphonium and keto compounds in order to assign the absorption bands of the C=O groups in different phosphorus ylids.

Experimental. Triphenyl phosphine was a sample from L. Light & Co, recrystallized from alcohol, m.p. 79.5°.

The phosphonium compound No. 2 of Table 1 was prepared in the following way: 4.5 g of bromoacetone was added to 8.6 g of triphenyl phosphine (equivalent amount). 10 ml of alcohol was added and the mixture was boiled for 10 min. After cooling of the reaction mixture the phosphonium compound crystallized, m.p. 226° (Michaelis and Köhler⁶, m.p. 226°).

The phosphorus ylid No. 3 was made by dissolving 4 g of No. 2 in 5 ml of cold water and adding 10 ml of cold concentrated sodium hydroxide solution. The white precipitate which immediately separated was filtered off and recrystallized from 60% water-alcohol mixture, m.p. 203–204° (Michaelis and Köhler⁶, m.p. 201°). (Found: C 79.3; H 5.8; P 9.6. Calc. for $\text{C}_{21}\text{H}_{19}\text{OP}$: C 79.0; H 6.0; P 10.0.)

The compound No. 4 was made from triphenyl phosphine (7.9 g) and chloroacetophenone (5 g) by heating the mixture to 80–90°C. The reaction was exothermic and a white crystalline mass separated upon cooling. The crystalline mass was washed several times with ether and recrystallized two times from water, m.p. 266° (decomp.).

Its corresponding phosphorus ylid, No. 5 of Table 1, was made from 4 g of No. 4 by dissolving it in 10 ml of water and adding 10 ml of cold concentrated sodium hydroxide solution. The compound which separated was recrystallized two times from 50% alcohol-water mixture, m.p. 182° (Michaelis and Köhler, m.p. 183–84°). (Found: C 81.8; H 5.4; P 8.0. Calc. for $\text{C}_{28}\text{H}_{21}\text{PO}$: C 81.9; H 5.6; P 8.4.)

Compounds Nos. 6 and 7 of Table 1 were synthesized according to descriptions in a previous paper.⁸

Compounds Nos. 8, 10 and 12 were made according to descriptions of Ramirez and Dershowitz¹⁰, Schönberg and Ismail⁹ and Schönberg and Michaelis¹⁴.

The infrared spectra were recorded on a Perkin-Elmer Spectrophotometer Model 21 using 1 mg of the compounds in KBr-briquets.


Compound	Frequencies (cm ⁻¹)					$\nu_{\text{C=O}}$ cm ⁻¹	$\Delta\nu_{\text{C=O}}$ cm ⁻¹
	1900	1800	1700	1600	1500		
1. (Ph) ₃ P							
2. [(Ph) ₃ P ⁺ -CH ₂ COCH ₃]Br ⁻			-----			1719	177
3. (Ph) ₃ P=CHCOCH ₃			-----	-----		1542	
4. [(Ph) ₃ P ⁺ -CH ₂ COPh]Cl ⁻			-----			1667	138
5. (Ph) ₃ P=CHCOPh			-----	-----		1529	
6. [(Ph) ₃ P ⁺ -CH ₂ COOC ₂ H ₅]Br ⁻			-----			1740	120
7. (Ph) ₃ P=CHCOOC ₂ H ₅			-----	-----		1620	
8. [(Ph) ₃ P ⁺ -C ₆ H ₃ (OH) ₂]Cl ⁻							
9. O=C ₆ H ₄ =O				-----		1662	135
10. (Ph) ₃ P=C ₆ H ₃ (OH) ₂				-----		1527	
11. 			-----	-----		1788, 1845	86, 40
12. (Ph) ₃ P=C(CH ₂ COOC ₂ H ₅) ₂			-----	-----		1702, 1805	

Table 1. The assignment of the stretching vibration frequencies of some oxygen containing phosphorus ylids.

Results and discussion. In Table 1 are recorded the main absorption bands between 1900 and 1400 cm⁻¹ of the different phosphonium compounds, phosphorus ylids and keto compounds studied. The phosphorus compounds all contain the triphenyl phosphine residue and the characteristic bands of triphenyl phosphine at approx. 1440 cm⁻¹, 1490 cm⁻¹, and 1590 cm⁻¹ are found almost at the same positions in all of the phosphorus compounds.

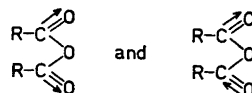
The assignment of the carbonyl bands of the phosphorus ylids and their corresponding "parent compounds" containing the C=O group are shown in Table 1 where dotted lines combine the corresponding bands. The assigned C=O bands of the compounds Nos. 3 and 5 correspond with the bands of the carbonyl groups proposed by Wittig and Schöllkopf⁴ and Ramirez and Dershowitz². The very strong displacements of the C=O bands (so far the strongest ever known) upon formation of the phosphorus ylids show that the ionic structure (IIb) must contribute very strongly to the resonance hybrid of the phosphorus ylids. This is also in accordance with the dipole moments 5.45 D and 5.54 D observed for the compounds Nos. 3 and 5

in Table 1². The somewhat smaller displacements of the carbonyl bands of the phosphorus ylids Nos. 7 and 12 may be explained as due to the opposing inductive effect of the oxygen atoms adjacent to the carbonyl groups in these two compounds. The same argument is used by Hartwell *et al.*¹¹ to explain the higher carbonyl frequencies of esters as compared with ketones.

Schönberg and Ismail⁹ have proposed

the structure: $\text{>P}^+-\text{O}-\text{C}_5\text{H}_3\text{O}^--$ for the addition compound between triphenyl phosphine and maleic anhydride.

Now it is known that all acid anhydrides give rise to two carbonyl bands in infrared due to the coupling between the following two types of stretching vibration:¹²



The two bands of maleic anhydride are found at 1788 cm⁻¹ and 1845 cm⁻¹

(reported ¹² 1 790 cm⁻¹ and 1 850 cm⁻¹). The addition compound between triphenyl phosphine and maleic anhydride has two strong bands at 1 702 cm⁻¹ and 1 805 cm⁻¹. We assume that these two bands are due to the coupling between two carbonyl groups and suggest therefore that the addition compound is a phosphorus ylid namely compound No. 12 in Table 1. This structure may also explain the unreactivity of 1,2-substituted maleic anhydrides ⁹.

My sincere thanks are due to *Norwegian Defence Research Establishment* for financial support and to Arnljot Nørland at the same institute for recording the infrared spectra.

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Received March 1, 1961.

"Pit-mapping" — a General Approach for Computer Refining of Equilibrium Constants

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The problem of determining the equilibrium constants for a number of simultaneous equilibria in solution may be expressed as a special case of the following well-known general problem. Having measured a quantity y and assumed a functional relationship:

$$y = f(k_1, k_2, \dots, k_N; a_1, a_2, \dots) \quad (1)$$

between y and some quantities a_1, a_2, \dots that can be varied but whose values are assumed to be known accurately in each experiment, one seeks to determine the set of unknown constants, $k_1 \dots k_N$.

Provided a) that the expression for f is correct, b) that there are no other errors (especially no systematic ones) except the random errors in y , c) that the errors in y are "normally" distributed around the correct value, and d) that the weight w_i given to each measurement y_i is inversely proportional to the square of its standard deviation, then the "best" values for $k_1 \dots k_N$ would be those that minimize the error-square sum:

$$U = \sum_i w_i (y_i - f(k_1 \dots k_N; a_{1i}, a_{2i} \dots))^2 \quad (2)$$

Even though one can seldom hope that all these assumptions are correct, the "least-squares" condition, $U = \text{minimum}$, is often employed in calculations. It is "objective" in the sense that the same set of data, and the same assumptions, should give the same answer in the hands of different workers. Perhaps, however, one should not forget the risk of over-estimating the significance of the answer.

If f is a linear function of the k 's, the "least-squares" condition leads to linear equations, which can be solved by straightforward methods. For instance, in studies of equilibria of step-wise complex formation, if one has measured the concentration of the central atom, or of one specific complex (as it is, for instance, usually done in extraction studies), this condition leads to