SYNTHESIS OF SOME HETEROCYCLIC COMPOUNDS FROM PHOSPHORUS YLIDES

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Abstract - A series of phosphorus heterocyclic compounds have been prepared from phosphorus ylides and carbonyl compounds. The ylides have been prepared using carbene method under different experimental conditions giving rise to new types of ylides.

Synthetic application of ylides was first of all discovered by Wittig et al.[1] in 1953. After that a number of papers have appeared on the various aspects of ylide chemistry and Wittig reaction.

The main application of ylides is the synthesis of olefins. Here we report their application in the synthesis of various heterocyclic compounds. The ylides have been prepared by carbene method under three different conditions :

1. Using excess of potassium t-butoxide only
2. Using excess of triphenyl phosphine only
3. Using excess of potassium t-butoxide and triphenyl phosphine.

The treatment of potassium t-butoxide, triphenyl phosphine and bromoform in the molar ratio of 2:1:1 in dried and distilled pet.ether yielded a new compound which was identified as (di-t-butoxy methylene)-triphenyl phosphorane (II) by element analysis and spectroscopy.

$$(CH_3)_3COK + CHBr_3 + Ph_3P \longrightarrow \underset{(I)}{Ph_3P = CBr_2} + (CH_3)_3COH + KBr$$

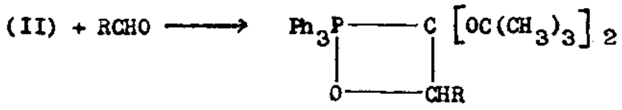
$$(I) + 2(CH_3)_3\ COK \longrightarrow \underset{(II)}{Ph_3P{=}C\left[OC(CH_3)_3\right]_2} + 2KBr$$

The formation of the dihalo ylide(I) was indicated by the development of golden yellow colour on addition of bromoform. But soon the colour disappears.

Potassium t-butoxide is a strong base and the ylide(I) is a very reactive moiety. Therefore, the replacement of halogens by the base seems placid. Seyferth et al.[2]

have also shown that the use of a strong base gives halogen free product in higher yield.

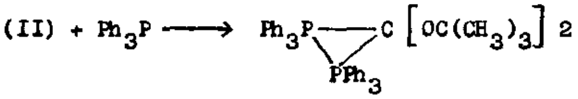
The formation of the ylide(II) has further been confirmed by treating it with various carbonyl compounds whereupon it yielded a series of stable oxaphosphetanes (III-VII).



(III-VII)

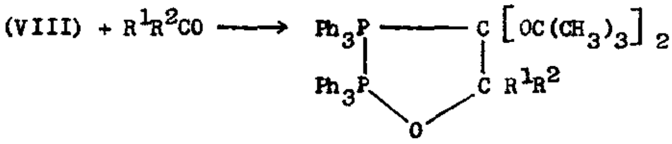
(III) R = C_6H_4-p-CH_3, (IV) R = C_3H_7, (V) R = $CH{=}CHCH_3$, (VI) R = $CH{=}CHC_6H_5$
(VII) R = C_6H_4-p-Cl .

Diphosphirane is formed when triphenyl phosphine is also taken in excess i.e. the molar ratio of potassium t-butoxide, triphenyl phosphine and bromoform is taken as 2:2:1. Triphenyl phosphine, being a reactive moiety, attacks the ylide(II) to give the diphosphirane (VIII).



(VIII)

5-Membered oxadiphospholanes (IX-X) have been synthesized by treating the diphosphirane (VIII) with carbonyl compounds.



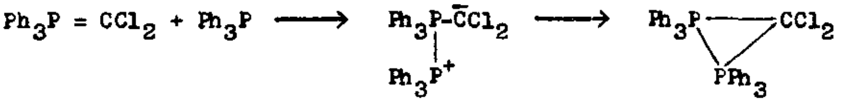
(IX-X)

(IX) $R^1 = R^2 = C_6H_5$; (X) $R^1 = H$, $R^2 = C_6H_4pOCH_3$

All the oxaphosphetanes and oxadiphospholanes give main IR bands due to Ph_3P (near 1440 cm^{-1})[3], and C-O-C-O-C (near 1190, 1120, 1070 and 1030 cm^{-1})[4]. Oxadiphospholanes show a band near 460 cm^{-1} due to P-P[5]. The ylide(II) shows absorption at 1190 cm^{-1} which is characteristic of phosphine methylenes[6]. The compounds (II-X) show aliphatic signals in the range 8-9 (τ) and complex aromatic signals in 2-3 (τ) in their H NMR spectra.

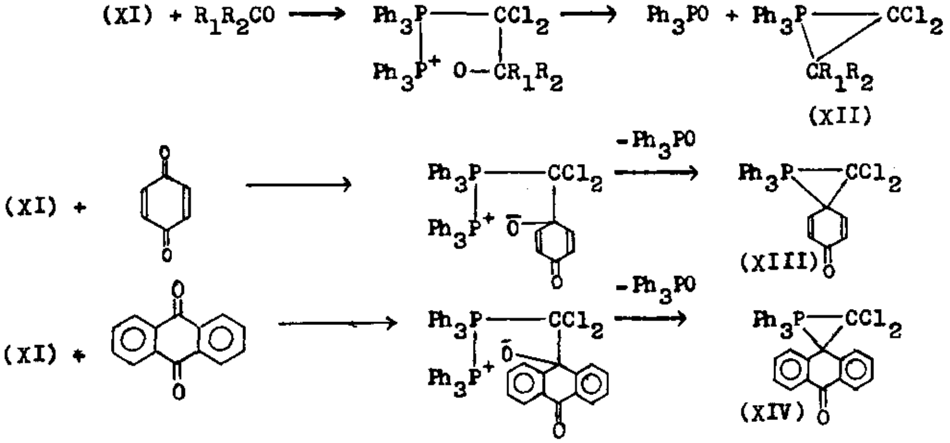
The third condition which has been tried out is by using only triphenyl phosphine in excess. Thus, the molar ratio of triphenyl phosphine, potassium t-butoxide and chloroform was taken as 2:1:1 and they were treated at 0°C in dried and distilled pet.ether. The product obtained was identified as a diphosphirane(XI).

$$Ph_3P + (CH_3)_3COK + CHCl_3 \longrightarrow Ph_3P{=}CCl_2 + (CH_3)_3COH + KCl$$



(XI)

The diphosphirane (XI) on treatment with ketones and quinones gives cyclic phosphirane derivatives (XII-XIV).

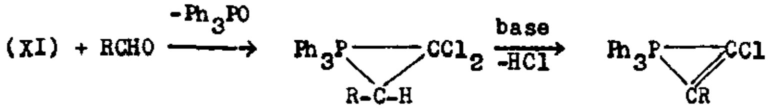


(XII)

(XIII)

(XIV)

In case of aldehydes, where α-hydrogen is available, one molecule of hydrogen chloride is eliminated by the influence of the base and phosphirene derivatives (XV-X X) are formed.



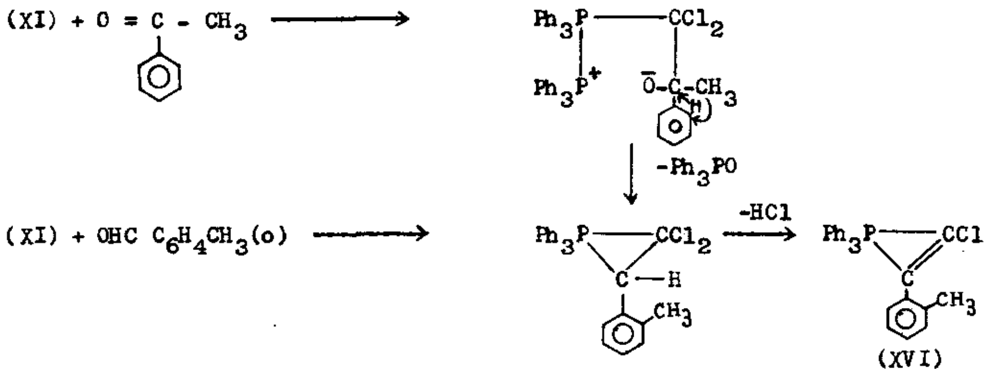
(XV-XX)

(XV) $R=C_6H_5$; (XVI) $R = C_6H_4\text{-o-}CH_3$; (XVII) $R = C_6H_4\text{-o-}NO_2$;

(XVIII) $R = C_6H_4\text{-o-}OH$; (XIX) $R = CH{=}CH\ C_6H_5$; (XX) $R = C_3H_7$

Phosphirenes are not formed with those aldehydes which carry an electron donating group e.g. anisaldehyde. With such aldehydes, phosphiranes are formed.

It has been found that the reaction of (XI) with acetophenone gives the same product as is obtained with o-tolualdehyde. This indicates that in the former case, the methyl group is migrated from the side chain to the nucleus.



(XVI)

The IR spectra of the products from acetophenone and o-tolualdehyde are superimposable and the mixed melting point is not depressed. The products give a singlet at 7.7 (τ) for Ar-CH_3 protons and multiplets for aromatic protons in the range 2.4-2.8 (τ).

The products (XI-XX) show main absorption bands in their IR spectra due to P-Ph (near 1435 cm^{-1}) and C-Cl (near 540 cm^{-1}) in addition to other bands. The products (XIII) and (XIV) and (XV-XX) show strong absorption near 1600 cm^{-1} due to C=O group, and C=C stretching respectively.

EXPERIMENTAL :-

The IR spectra have been recorded on Perkin-Elmer-377. The melting points have been noted on Galen-kemp apparatus and are uncorrected.

Preparation of the ylide, di-t-butoxymethylenetriphenyl phosphorane(II):

Bromoform (0.01 mole) in pet.ether was added to the ice-cold mixture of potassium t-butoxide (0.02 mole) and triphenyl phosphine (0.01 mole) in dried and distilled pet.ether. The reaction mixture was stirred for two hrs and left for one day. The column chromatographic separation of the reaction mixture gave unreacted triphenyl phosphine with pet.ether and the product with benzene-ether. The product was recrystallized from benzene-pet.ether.

Reaction of the ylide(II) with aldehydes :

The ylide(II) was prepared in situ and the aldehyde (0.01 mole) in pet.ether (20 ml) was added slowly with constant stirring at room temperature. After the complete addition, the reaction mixture was stirred for 2 hrs at 50-60° and then left for one day. The column chromatographic separation of the reaction mixture gave unreacted triphenyl phosphine with pet. ether, unreacted substrate with benzene and the product with ether. The products were crystallized from benzene.

Preparation of 3,3-di(t-butoxy)-1,1,1,2,2,2-hexaphenyl diphosphirane(VIII) and its reaction with carbonyl compounds:

The diphosphirane(VIII) was prepared by the same experimental procedure as in first experiment by taking the triphenyl phosphine, potassium t-butoxide and bromoform in the molar ratio of 2:2:1. The addition of the carbonyl compound to the diphosphirane (VIII) in situ gave the products (IX) and (X), which were recrystallized from benzene or benzene-pet.ether.

Preparation of 3,3-dichloro-1,1,1,2,2,2-hexaphenyl diphosphirane(XI) and its reaction with carbonyl compounds :

Following the same experimental procedure as above, the treatment of triphenyl phosphine (0.02 mole), potassium t-butoxide (0.01 mole) and chloroform (0.01 mole) gave the diphosphirane (XI) with benzene-ether fraction. The addition of benzophenone (0.01 mole), benzoquinone (0.01 mole) and anthraquinone (0.01 mole) to the diphosphirane(XI) at room temperature and then elevating the temp. to 60°, gave the products (XII-XIV) respectively. The same procedure was followed for the reaction of the diphosphirane (XI) with aldehydes namely benzaldehyde, tolualdehyde, o-nitrobenzaldehyde, salicylaldehyde, cinnamaldehyde and crotonaldehyde to give the phosphirenes (XV-XX).

TABLE - 1

Product	m.p.	Yield %	Observed				Calculated			
			C%	H%	P%	Cl%	C%	H%	P%	Cl%
(II)	160°	50	76.7	7.7	7.9	-	77.1	7.8	7.4	-
(III)	148°	40	77.7	7.5	8.0	-	77.7	7.6	8.3	-
(IV)	152°	35	75.5	8.0	6.3	-	75.6	8.3	6.1	-
(V)	156°	37	76.2	7.6	5.8	-	75.9	7.9	6.0	-
(VI)	154°	36	78.5	7.8	5.9	-	78.2	7.4	5.6	-
(VII)	150°	38	73.1	6.9	5.1	-	72.8	6.8	5.5	-
(VIII)	161°	40	78.8	7.5	9.6	-	79.1	7.0	9.1	-
(IX)	168°	30	80.2	6.4	7.7	-	80.5	6.7	7.2	-
(X)	165°	35	77.5	6.4	7.9	-	77.7	6.8	7.5	-
(XI)	166°	33	73.6	4.8	10.0	11.5	73.1	4.9	10.2	11.6
(XII)	140°	41.4	76.1	5.2	5.9	14.3	75.1	4.9	6.1	13.9
(XIII)	147°	10	69.2	4.6	6.9	15.8	68.6	4.3	7.0	16.2
(XIV)	154°	15	74.2	4.5	6.1	12.3	73.7	4.2	5.7	13.2
(XV)	160°	37.5	78.2	4.8	7.8	8.8	78.1	5.0	7.7	9.1
(XVI)	158°	33.9	78.6	5.3	8.1	9.4	78.5	5.3	7.5	8.6
(XVII)	162°	40	70.9	4.4	7.0	8.6	70.3	4.2	6.9	8.0
(XVIII)	160°	31.4	75.8	5.1	7.5	-	75.3	4.8	7.7	-
(XIX)	165°	37.7	79.5	5.3	7.5	-	79.1	5.2	7.3	-
(XX)	155°	38	75.9	5.6	8.0	-	75.7	6.0	8.5	-

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