CHEMISTRY LETTERS, pp.575-576, 1974. Published by the Chemical Society of Japan

FORMATION OF IMINOPHOSPHORANES FROM ANTHRANILS AND TRIPHENYLPHOSPHINE

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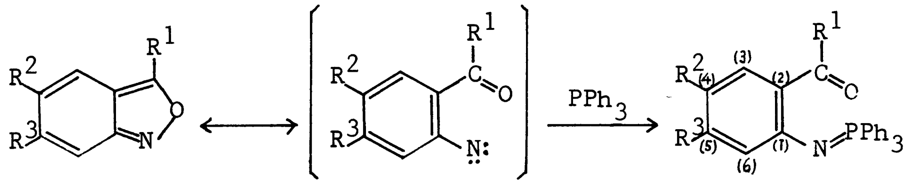
It was found that benz[c]isoxazoles gave (2-acylphenyl)iminotriphenylphosphoranes upon heating with triphenylphosphine in toluene. These iminophosphoranes were considerably stable although they have two reactive groups for the Wittig-type reaction in ortho-position in a molecule. This fact as well as their spectral data suggested the existence of the resonance-stabilized chelate ring.

It is well known that isoxazole ring of benz[c]isoxazole (anthranil) (1a) opens with various reagents to yield many different products.[1)] We have found that triphenylphosphine (PPh_3) reacted with 1 to give (2-acylphenyl)iminotriphenylphosphoranes (2). In a typical run, a solution of equimolar amount of 1a (2.4g, 20 mmol) and PPh_3 (5.2g, 20 mmol) in toluene was heated to reflux for 24 hr. Addition of n-hexane gave powder which was recrystallized from benzene—n-hexane as yellow prisms (2a), mp 173-174°C, yield 3.2g (42%).



1 1' 2

	R^1	R^2	R^3
a	H	H	H
b	H	H	Cl
c	CH_3	H	H
d	CH_3	NO_2	H
e	Ph	Br	H

It may be reasonable to assume that anthranil behaves as a nitrenoid such as 1' in this reaction.[2)]

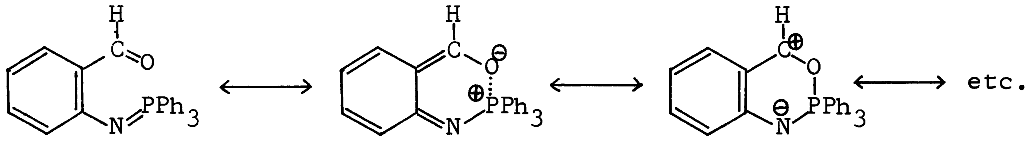
Substituted anthranils also gave corresponding iminophosphoranes as listed in Table 1. The structures of 2 were confirmed on the basis of the elemental analyses and data of NMR, IR, and Mass spectra.

It is interesting to notice that the product is stable (in refluxing toluene) although it containes the two reactive groups ($-N=P<$ and $>C=O$) for the Wittig-type reaction.[3)] This stability is most probably due to the formation of resonance-stabilized

Table 1. Iminophosphoranes (2)[4] Produced by the Reaction of Anthranils with Triphenylphosphine

2	Mp(°C)	Yield (%)	ν(cm^{-1})		NMR: δ(ppm) (TMS as an internal standard, in $CDCl_3$)
			C=O	N=P	
a	173-174	42	1670	1340	11.40(s, 1H, -CHO), 8.3-7.5(m, 16H, (3)-H + PPh_3), 7.25(dt, 1H, (5)-H), 6.80(t, 1H, (4)-H), 6.65(d, 1H, (6)-H)
b	163-164	51	1665	1320	11.20(s, 1H, -CHO), 8.1-7.3(m, 16H, (3)-H + PPh_3), 6.75(dd, 1H, (4)-H), 6.55(d, 1H, (6)-H)
c	121	51	1645	1345	8.0-7.4(m, 16H, (3)-H + PPh_3), 7.05(dt, 1H, (5)-H), 6.75(dt, 1H, (4)-H), 6.55(d, 1H, (6)-H), 2.80(s, 3H, CH_3)
d	162-163	95	1655	1310	8.50(m, 1H, (3)-H), 8.0-7.4(m, 16H, (5)-H + PPh_3), 6.45(d, 1H, (6)-H), 2.80(s, 3H, CH_3)
e	205-206	16	1655	1340	8.10(dd, 1H, (5)-H), 7.9-7.15(m, 21H, (3)-H + COPh + PPh_3), 6.45(d, 1H, (6)-H)

chelate ring such as given below.



This interpretation is supported by the fact that (i) the iminophosphorane (2a) itself made no intra- nor intermolecular Wittig-type reaction, but gave readily hydrolyzable (p-chlorobenzylidene)-o-formylaniline and triphenylphosphine oxide almost quantitatively upon prolonged heating with p-chlorobenzaldehyde, (ii) the chemical shift of aldehyde proton is almost 1 ppm lower than for the normal aromatic aldehyde and the peaks of (4)-H and (6)-H appear at relatively high field (see Table 1) probably due to the existence of a strong electron-donating substituent, and (iii) $\nu_{C=O}$ is also considerably lower than the standard value.

Further studies on the chemical properties of 2 are now in progress.

References and Note

1) K. H. Wünsch and A. J. Boulton, "Advances in Heterocyclic Chemistry," Vol. 8, ed. by A. R. Katritzky and A. J. Boulton, Academic Press, N. Y.(1967), p. 303.
2) W. Lwowski, "Nitrenes," Interscience, London(1970), p. 286.
3) A. W. Johnson, "Ylid Chemistry," Academic Press, N. Y.(1966), p. 227.
4) All the products gave satisfactory elemental analyses.

(Received April 20, 1974)