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CATALYTIC ACTIVITY OF SOME 1-ARYL-3-METHYL-3-PHOSPHOLENE-1-OXIDES* IN THE DISPROPORTIONATION OF PHENYL ISOCYANATE TO DIPHENYLCARBODIIMIDE AND CARBON DIOXIDE

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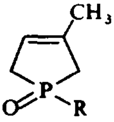
Abstract—The catalytic (second order) rate constants, obtained in benzene solution at 80°. for six various substituted 1-phenyl-phospholene oxides obeyed a linear $\rho\sigma^\circ$ relationship excellently (where $\rho = -0{\cdot}750$ and σ° are the "normal" substituent constants). These data indicate a lack of conjugation between aromatic ring and phosphoryl group.

INTRODUCTION

THE 1-substituted 3-methyl-3-phospholene-1-oxides (I) have been obtained for the first time by McCormack[1]. They were remarkable due to their unexpected high catalytic activity in converting isocyanates almost quantitatively to carbodiimides (1).



I

$$2R'{-}N{=}C{=}O \xrightarrow{\text{I}} R'{-}N{=}C{=}N{-}R' + CO_2 \qquad (1)$$

The report of this interesting reaction[2] was followed by studies concerning its mechanism,[3] as well as by some attempts to prepare several compounds with similar structure and the same catalytic effect.[4]

Now it is well known[5] that most of P=O bond containing compounds possess a similar property and their catalytic activity is generally proportional to P=O bond polarity. But we have not found any report concerning a quantitative correlation between the structural parameters and this activity, apart from a recent unsuccessful attempt[4b] to correlate the first-order rate constants of reaction (1) with dipole moments of some phospholene oxides.

In order to establish such a correlation we synthesized some 1-aryl-substituted phospholene oxides (I) and tested their activity upon phenyl isocyanate (Eq 1 $R' = C_6H_5$).

According to Monagle *et al.*[3] the mechanism of this reaction is illustrated by Eqs 2 and 3:

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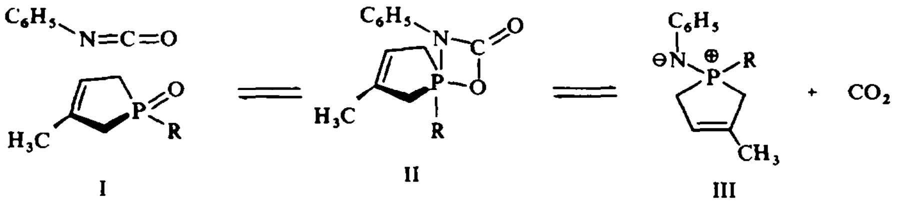
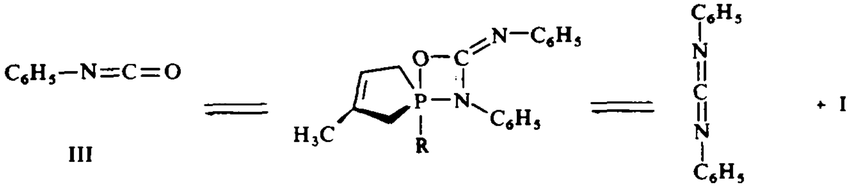
* Nomenclature according to *Chem. Abstr.* (1967).



(2)



(3)

The rate determining step proved to be[3a] the decomposition of intermediate II into phospholenimide III and CO_2.

RESULTS AND DISCUSSION

The kinetics of reaction (1) was followed measuring carbon dioxide evolution rate. Using in all cases the same initial phenyl isocyanate concentration (0·42 mol/l in anhydrous benzene at 80°*) we obtained several but in all cases first order rate constants (k_x). For all phospholene oxides the determined k_x value shows a first-order dependence on phospholene oxide concentration [PO] (Fig. 1).

The catalytic (second-order) rate constants calculated from the slopes of Fig. 1 ($k_x^{cat} = k_x/[PO]$) are listed in Table 1. The log (k_x^{cat}/k_a^{cat}) versus Hammett standard σ

TABLE 1. VALUES OF CATALYTIC RATE CONSTANTS DEPENDING ON SUBSTITUENT R FROM I

I_x	R	$k_x^{cat} \times 10^4$ l. mol^{-1} sec^{-1}
Ia	C_6H_5—	1·030
Ib	*p*-Me—C_6H_4—	1·420
Ic	*p*-Et—C_6H_4—	1·300
Id	*p*-iPr—C_6H_4—	1·315
Ie	3′,4′—$Me_2C_6H_3$—	1·560
If	*p*-Et_2N—C_6H_4—	2·060

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* Boiling of solvent is necessary to expel CO_2 from the liquid phase. This proved to be a condition for the first order kinetics.[3a]

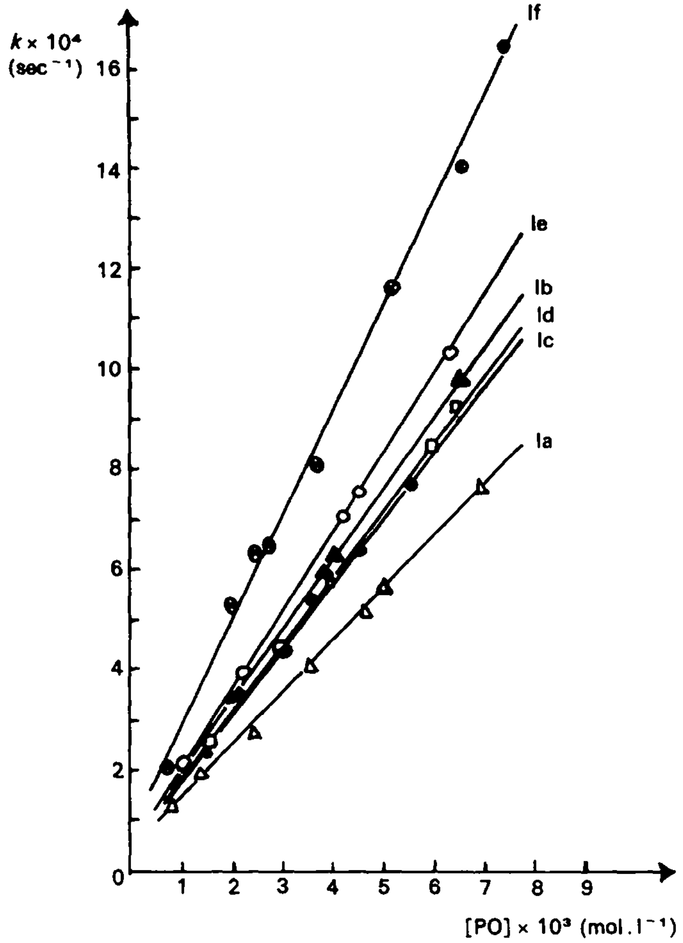


Fig. 1

values plot exhibits a good linear correlation for Ia–Ie while a considerable deviation occurs for If. From the experimental data is obtained $\sigma = -0{\cdot}41$ compared to that given[6] for p-Me_2N—. $\sigma = -0{\cdot}83$ which must be very close to σ for p-Et_2N. But using the values designated by Taft[7] as "normal" substituent constants, applicable to those substituted aryl-compounds in which conjugation between the reaction site and the aromatic ring is not possible (e.g. substituted phenylacetic acids) we obtained an excellent linear correlation (Fig. 2). For the compound Ic and Id, since there are no available σ° values we used the corresponding standard σ constants as the weakly conjugating substituents have σ° values very close to σ.[6]

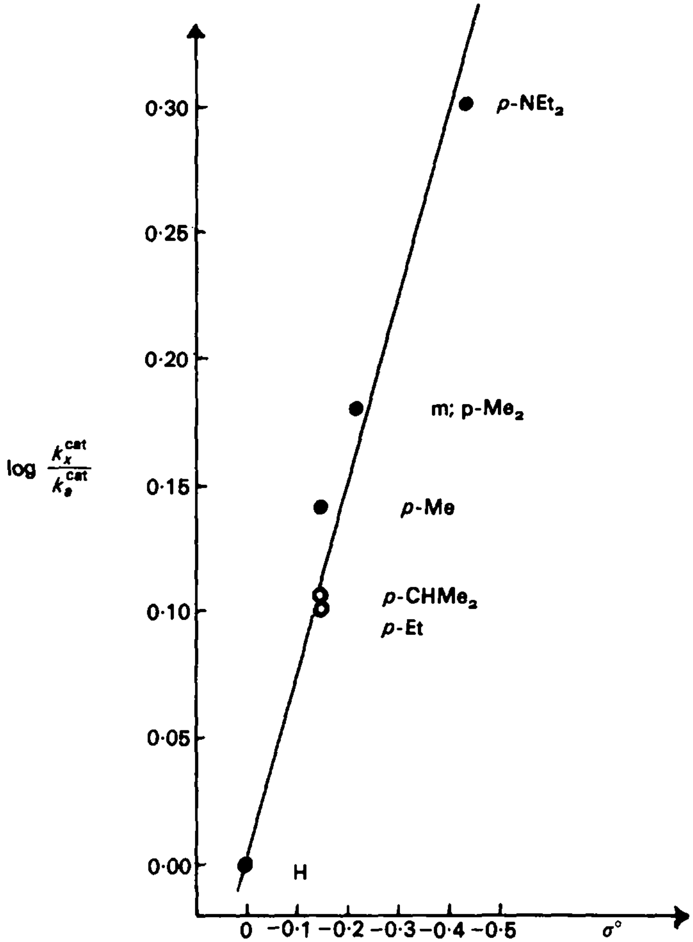


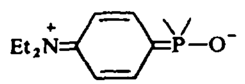
Fig. 2

● σ° values; ○ standard σ values

CONCLUSION

The negative value of ρ (−0·750) verified the fact, that electron releasing substituents increased the catalytic activity of P═O group.

The better correlation with the $\sigma°$ values (especially for the p-NEt$_2$ group) may be explained only if we exclude the possibility of conjugation between the P═O group and the benzene ring formally written as:



The P=O bond should be polarized through an inductive interaction between the P atom and the adjacent aryl carbon.

The latter becomes in its turn more or less negative, depending on the inductive and conjugation effect of para or meta substituents.

EXPERIMENTAL

Catalyst preparation. The phospholene oxides (Ia–If) were prepared according to McCormack's original method[1] from the corresponding aryl dichlorphosphines and isoprene.

For dichlorphosphines we used with some modifications the method recommended for $C_6H_5PCl_2$.[8] For phenyl, *p*-cumyl-, 4-(*o*-xylyl)dichlorsphosphines we tried Gefter's version[9] as well (pyridine instead of $POCl_3$ for the decomposition of the $RPCl_2 \cdot AlCl_3$ complexes) obtaining little improvement of yield.

The *p*-diethylaminophenyl-dichlorphosphine was obtained by heating alone equimolar amounts of $C_6H_5NEt_2$ and PCl_3 in a steam bath 5–7 hr[10] (yield: 51%).

The identity of our dichlorphosphines was established by means of their b.ps, IR spectra and refraction indices.[10,11a]

The reaction of dichlorphosphines with freshly distilled isoprene was performed[1,11b,12] in dried N_2 atmosphere in the presence of small quantities of copper stearate (as polymerization inhibitor) at room temp during 19–32 days. After a cautious hydrolysis, oxidation with H_2O_2, and repeated extractions with $CHCl_3$, the solns were dried over Na_2CO_3. The chloroform was removed at atmospheric press and the residue was distilled *in vacuo*.

The structure of phospholene oxides (Ia–If) was established by means of combustion analyses and IR spectra. Their purity was checked by paper chromatography using benzene as solvent. Detection was carried out with bromine vapour. There appeared a yellow spot for phospholene oxides since bromine adds readily to phospholene ring double bond.[11c]

TABLE 2. DATA FOR 1-ARYL-3-METHYL-3-PHOSPHOLENE-1-OXIDES

I_x	b.p. C°/mm Hg	Found			Requires			n_D^{25}
		C%	H%	P%	C%	H%	P%	
Ib	210–213°/5	69·4	7·5	14·5	69·8	7·3	14·5	1·5728
Ic	214–218/5	70·2	8·0	14·2	70·9	7·7	14·2	1·5672
Id	200–205/2–3	71·3	7·8	13·1	71·8	8·1	13·2	1·5689
Ie	215–220/3–4	70·2	7·7	13·8	70·9	7·7	14·2	1·5711
If*	215/4–5	68·2	8·4	11·6	68·4	8·4	11·8	1·5944

* It was found for this compound N%: 5·8 compared with those required: 5·3%.

Kinetics. Phenyl isocyanate (p.a.U.C.B.) was redistilled before use, benzene and catalyst (I) were carefully dried and freshly distilled according to the indications of Monagle *et al.*[3a] which were in general taken into account for all kinetic measurements.

A 150 ml thermostated cylindrical flask with a gas outlet tube covered with an efficient water condenser was used as a reaction vessel. The flask was equipped with a glass stirrer and a joint for the introduction of the catalyst.

The catalyst was best introduced by injecting or pipetting into the flask certain volumes of catalyst soln with exactly known concentration. For the evolved CO_2 volume, measured in a thermostated gas burette there were applied the corresponding corrections for atmospheric press, temp of gas burette and solvent vapour press.

The first-order rate constants were calculated from the log ($V_{\infty}^{CO_2} - V^{CO_2}$) versus time plot which was linear within the studied catalyst concentration range ($0{\cdot}8$–$8{\cdot}5 \cdot 10^{-3}$ mol/l).

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