

Kinetic Study of the Intramolecular Decomposition of Some Phosphine *N*-Benzoyl Imines

GUNNAR AKSNES and PAUL FRØYEN

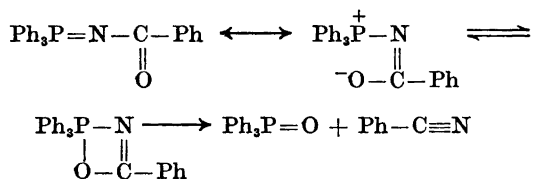
Chemical Institute, University of Bergen, Bergen, Norway

The intramolecular thermal decomposition of several phosphine *N*-benzoyl imines are studied in mesitylene. The compounds investigated are: triphenyl-, diphenyl ethyl-, diethyl phenyl-, triethyl-, and phospholane-1-phenyl phosphine *N*-benzoyl imine.

It is found that the rate of decomposition obeys first order kinetics. The activation energies and the frequency factors for the decomposition of the compounds are calculated, and are discussed in relation to substituent effects.

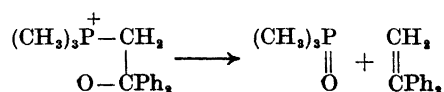
Staudinger and Hauser¹ reported in 1921 several unsuccessful attempts to react triphenylphosphine *N*-benzoyl imine with compounds containing cumulated double bonds. When the imine was heated with carbon disulphide at 150°C in an autoclave, no carbodiimide or benzoyl isothiocyanate was detected in the reaction mixture.

The imine was quantitatively cleaved in triphenylphosphine oxide and benzonitrile. The reaction is believed to proceed *via* a four membered ring transition state:²



The delocalisation of charge from nitrogen through the carbonyl group is reflected in the low infrared stretching frequency of the carbonyl group, 1558 cm⁻¹, and demonstrates the importance of the betaine form in the resonance hybrid. The strong delocalisation of charge through the carbon portion of the imine may explain why the intramolecular reaction path is preferred. The purpose of this work has been to investigate the effect of the

substituents linked to phosphorus on the reaction. It was originally expected that electron donating substituents on phosphorus would make the nucleophilic attack on phosphorus by the oxygen atom more difficult because of the increased electron density on phosphorus. This effect seems to be of considerable importance in the Wittig reaction between unstabilized ylids and carbonyl compounds. Methylene triphenyl phosphorane reacts thus with benzophenone to afford 1,1-diphenyl ethene, whereas methylene trimethyl phosphorane does not afford olefine under the same conditions.³ Treatment of the latter reaction mixture with mineral acid, resulted in the conjugated acid of the betaine, showing that the betaine is unchanged during the reaction. The inductive effect of the methyl groups linked to phosphorus was believed to increase the electron density on phosphorus sufficiently to make the attack of the oxygen atom in the Wittig intermediate very difficult:



It must be noted, however, that since the phosphoranes were generated from the phosphonium salts with phenyl lithium, the complex formation of the betaines with lithium salts may have modified their reactivity.

However, the situation is more complicated with the phosphine *N*-benzoyl imines than with the intermediates in the Wittig reaction since a change in the substituents on phosphorus in the former case, also affects the degree of $p\pi-d\pi$ overlap between phosphorus and nitrogen and thereby also affects the electron density on the oxygen atom.

EXPERIMENTAL

The phosphine *N*-benzoyl imines were synthesized according to Staudinger¹ from the respective phosphines and benzoyl azide.

Triphenylphosphine N-benzoyl imine was recrystallized two times from methylene chloride-petrol ether, m.p. 191–93° (Lit.¹ 193–194°).

Diphenylethylphosphine N-benzoyl imine recrystallized from petrol ether, thereafter two times from ether, m.p. 81–83°.

Phenyl diethylphosphine N-benzoyl imine was recrystallized three times from ether. (The ether-solution must be cooled before the crystallisation will start) m.p. 74°. (Lit.¹ 73–74°).

Phospholane-1-phenyl N-benzoyl imine. The product crystallized by strong cooling of the reaction mixture. It was recrystallized three times from ether, m.p. 80–83°.

Triethylphosphine N-benzoyl imine was recrystallized three times from ether; during the crystallisation the ether solution was cooled, m.p. 63° (Lit.¹ 62.5–63°).

Mesitylene (Fluka *puriss.*) was redistilled, and the fraction boiling at 63° and 26 mm Hg was used.

Benzonitrile (Fluka *pract.*) was distilled before use, b.p.₁₃ 72°.

Kinetic measurements

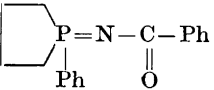
The reaction was studied in mesitylene. The rate was followed by measuring the infrared absorption band of benzonitrile at 2227 cm^{-1} . The start concentrations of the phosphine imines were in the range about 0.1 M. An infrared cell of 1 mm path length

was used. Samples withdrawn from the reaction solution were cooled to room temperature and transferred to the cell and recorded on a Unicam Spectrophotometer SP 200 G.

For every rate constant calculated, 10–12 separate determinations of concentration were performed in the region where 10–80 % of benzonitrile had been formed.

During the measurements there were some difficulties with the triphenylphosphine *N*-benzoyl imine, since this substance was sparingly soluble in mesitylene, and tended to crystallize in the infrared cell. This problem was solved by letting the samples stay for a couple of hours at room temperature, thus allowing some of the phosphine imines to crystallize before the measurements were done. The concentrations were corrected for the volume of the imine crystallized. Since the phosphine imine absorbs very weakly in the infrared region used in the present study, the change in concentration of the reactant had no influence on the C≡N absorption.

Table 1. Thermal decomposition of different phosphine *N*-benzoyl imine in mesitylene.

Compound	Conc. (mol/l) × 10	Temp. °C	<i>k</i> (min ⁻¹ × 10 ⁴)	<i>E_a</i> kcal/mol	log <i>A</i>	Δ <i>S</i> *
Et ₃ P=N-C(=O)-Ph	0.7709	158.4	23.9	34.1	12.8	-2.5
	1.301	157.9	23.0			
	0.9277	146.3	7.2			
	1.670	130.6	1.5			
Et ₂ PhP=N-C(=O)-Ph	0.7627	158.4	20.5	34.7	13.1	-1.3
	0.8127	157.9	19.6			
	0.8179	146.3	6.2			
	1.444	130.5	1.2			
	0.6835	147.0	145.0	33.3	13.7	1.5
	0.5845	138.4	62.8			
	1.015	131.0	26.9			
	1.293	118.2	8.4			
Ph ₂ EtP=N-C(=O)-Ph	0.8109	158.4	22.0	33.0	12.3	-5.0
	0.8758	157.9	20.1			
	0.8032	147.0	8.2			
	1.105	130.6	1.6			
Ph ₃ P=N-C(=O)-Ph	1.557	130.3	1.5	34.3	12.9	-2.1
	0.8018	163.0	31.2			
	0.8854	158.4	20.3			
	0.9395	146.3	6.6			

RESULT AND DISCUSSION

The rate data together with activation parameters for the reaction of the various phosphine imines are summarized in Table 1. As can be seen from the table, the activation energy of the reaction is independent of the substituents linked to phosphorus. The small differences actually observed in the activation energies are all within the limits of the experimental error. There is a slight increase in the rate of the reaction from triphenylphosphine *N*-benzoyl imine to the triethylphosphine analogue as phenyl groups are shifted with alkyl groups.

This weak increase in the rate of the decomposition may well be attributed to steric reasons. The result is interesting, because it shows that two opposing effects are balancing each other almost completely. As phenyl groups on phosphorus are shifted with alkyl, there will be an increase in the electron density on phosphorus. It is generally accepted, however, that π -bonding with an atom carrying vacant d -orbitals is becoming less efficient as the electron density on the atom is increased.^{4,5} If this is correct, the stabilization of the ylids through $p\pi-d\pi$ overlap between phosphorus and nitrogen, will diminish, thus leaving a higher electron density on the nitrogen atom as phenyl groups are shifted with alkyl.

As a result there will be an increase in the delocalisation of charge from nitrogen through the carbonyl group, thereby creating a more nucleophilic oxygen. Its higher nucleophilicity will counteract the lower electrophilicity of the phosphorus atom, resulting in an almost unchanged activation energy with substituents.

The *N*-benzoyl imine of 1-phenyl-1-phospholane is characterized by a much higher rate of reaction than any of the other compounds. The phospholane derivative is cleaved 23 times faster than the corresponding phenyl diethylphosphine *N*-benzoyl imine which is expected to have comparable inductive substituents effects. We attribute the higher rate to the "phospholane effect" mentioned in previous papers.^{6,7} The more positive entropy of activation of the decomposition of the phospholane compound, ($\Delta S = +1.5$), is typical for this effect.

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