extracted with three 100-ml portions of ether. After drying, the components of the ether solution were analyzed by glpc. Isolation of products could be accomplished by glpc or by liquid chromatography using acid-washed alumina. In the glpc separations, typical retention times observed for indole, 3-chloroquinoline, and 2-chloroquinoline were 39.7, 47.2, and 50.0 min, respectively. The following retention times were typical of the substituted indole experiments: 2-methylindole, 38.2; 3-chloro-2-methylquinoline, 44.2; 3-methylindole, 42.1; 3-chloro-4-methylquinoline, 51.7; 2,3-dimethylindole, 48.2; and 3-chloro-2,4-dimethylquinoline, 56.8 min. In the liquid chromatography separations, the pyrolyzate residue obtained by evaporating the ether extract was dissolved in Skellysolve B and added to the alumina column. The small quantities of unreacted indoles were eluted with Skellysolve B and the chloroquinoline products were eluted with 5% ether–Skellysolve B (3-chloroquinoline being eluted before the 2-chloroquinoline). After recrystallization from Skellysolve A, the physical properties (uv, nmr spectra, and melting point) were compared with literature values and/or authentic samples (see Table I).

Registry No.—3-Chloroquinoline, 612-59-9.

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Mechanism of the Reaction of Iminophosphoranes with Carbonyl Compounds. A Change in Rate-Determining Step[1]

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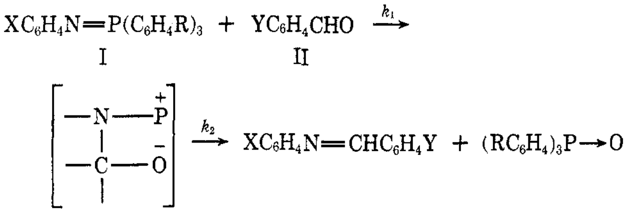
In an earlier study of the reaction of *N*-phenyliminotriphenylphosphoranes (I) with benzaldehydes (II) we demonstrated that, in general, the reaction was first order in both imine and aldehyde and that $k_2 > k_1$ for the mechanism[3]



The evidence for this conclusion, briefly, was the ρ value of +2.1 for variation of the aldehyde substituent Y, faster reaction in more polar solvents, a second-order reaction with a low energy of activation (8.46 kcal/mol), and a large negative entropy of activation (−42.0 eu at 40.5°).

Recently, Aksnes and Froyen[4] have confirmed our conclusions in the course of their studying the reaction of phosphine oxides with isocyanates to form carbodiimides, the second step of which appears to involve the reaction of an iminophosphorane with isocyanate. Specifically, they reported that gradual replacement of the *P*-phenyl groups in *N*-phenyliminotriphenylphosphorane (I, X = R = H) with ethyl groups led to a steady increase in k_{obsd} of the second step, presumably due to an increase in k_1 as a result of the increasing nucleophilic character of the nitrogen atom when *P*-phenyl is replaced by *P*-ethyl (*i.e.*, less $p\pi$–$d\pi$ overlap in the latter case due to the less electronegative ethyl group replacing the phenyl group[5]). The fact that the presence of a phosphorus atom with less positive character resulted in a higher k_{obsd} clearly indicates that betaine decomposition to products, involving the attack of an oxyanion on phosphorus, cannot have been the slow step. In other words, betaine formation was the rate-determining step and $k_2 > k_1$.

In our earlier work[3] we had reported that a Hammett plot of the reaction of *N*-phenyliminotri(substituted phenyl)phosphoranes (I, X = H, R = substituents) with *p*-nitrobenzaldehyde afforded a ρ value of −0.70, indicating that electron-withdrawing groups on phosphorus slowed the reaction and confirming that $k_2 > k_1$ (otherwise, oxyanion attack on phosphorus should have been facilitated with k_2 increased and reflected in an increase in k_{obsd}). It was speculated, however, that k_1 and k_2 must be similar in magnitude due to the small ρ value and the predicted opposite effect of any substituent on the two steps, betaine formation and betaine decomposition.

Confirmation of the similarity of k_1 and k_2 was obtained by studying the effect of the *N*-phenyl substituents on the reaction of I with *p*-nitrobenzaldehyde. A Hammett plot for this reaction afforded a curve which was "concave down." For the electron-donating substituents the ρ value was +0.95 and for the electron-withdrawing substituents the ρ value was −2.4. Since "concave down" Hammett plots generally are characteristic not of a change in the mechanism of a reaction, but rather of a change in the rate-determining step,[6] it was suggested that, at least for the reaction of the imines with the one aldehyde, *p*-nitrobenzaldehyde, k_1 and k_2 were similar in magnitude and their relative magnitudes changed position as the substituent X in the imines I was changed. Because of the considerable concern in ylide chemistry about the relative rates of betaine formation and betaine decomposition in the reactions of ylides and related substances, including imines (for example, effects on stereochemical control possibilities), it was deemed worthwhile to demonstrate that this apparent change in rate-determining step was a general phenomenon and not restricted just to the specific imines and aldehydes used in our earlier work.

In Table I are reported the rates of reaction of a series of *N*-phenyl-substituted imines (I, R = H, X = substituents) with a series of four substituted benzaldehydes (II). Included are the data for the reactions of the imines (I) with *p*-nitrobenzaldehyde and the aldehydes (II) with *N*-phenyliminotriphenylphosphorane (I, X = R = H) as reported in our original work.[3] A plot of log k/k_0 *vs.* σ of the substituents X for the reac-

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[1] Paper XXI in our series "The Chemistry of Ylides." For paper XX, see *J. Org. Chem.*, **35**, 2678 (1970).

[2] Department of Biological Chemistry, Harvard University Medical School, Boston, Mass. 02115. Deceased Dec 1971.

[3] A. W. Johnson and S. C. K. Wong, *Can. J. Chem.*, **44**, 2793 (1966).

[4] G. Aksnes and P. Froyen, *Acta Chem. Scan.*, **23**, 2697 (1969).

[5] A. W. Johnson, "Colloques Internationaux du Chimie Organique du Phosphore," Paris, 1970, pp 229–234.

[6] J. O. Schreck, *J. Chem. Educ.*, **48**, 103 (1971).

TABLE I

RATES OF REACTION OF *N*-(X-PHENYL)IMINOTRIPHENYLPHOSPHORANES WITH SUBSTITUTED BENZALDEHYDES[a]

$(C_6H_5)_3P{=}NC_6H_4X + YC_6H_4CHO$

Registry no.	Y	X = *p*-CH_3O (14796-89-5)[a]	X = *p*-CH_3 (2327-67-5)[a]	X = H (2325-27-1)[a]	X = *p*-Br (14987-96-3)[a]	X = *m*-Cl (14796-87-3)[a]	X = *m*-NO_2 (14796-86-2)[a]
528-75-6	2,4-$(NO_2)_2$	27.6[b]	29.6[b]	29.9[b]	9.0[b]	5.4[b]	1.03[b]
555-16-8	*p*-NO_2	19.3	23.3	34.6	24.0	16.7	2.03
105-07-7	*p*-CN			27.9			
587-04-2	*m*-Cl			8.82			
100-52-7	H	0.83	0.96	1.37	1.10	0.67	0.23
104-87-0	*p*-CH_3			0.66			
123-11-5	*p*-CH_3O	0.13	0.14	0.17	0.18	0.10	Too slow

[a] Registry number. [b] Rate constants are $\times 10^2$ l./mol sec at 40.5° in absolute ethanol solution.

tion of the *N*-phenyl-substituted imines with each of the four benzaldehydes results in four similar "concave down" curves. Accordingly, it may be concluded that the change in rate-determining step in the reaction of *N*-phenyliminotriphenylphosphoranes with aldehydes is a general phenomenon.

The delicate balance in the rates of betaine formation and betaine decomposition in the imine–carbonyl reaction is a unique observation in the field of ylide chemistry. In the imine, electron-donating substituents are expected to increase the nucleophilicity of the nitrogen atom, but at the same time increase the electron density on the phosphorus atom, thereby decreasing its susceptibility to oxyanion attack (*i.e.*, increase k_1 and decrease k_2, respectively). Electron-withdrawing substituents are expected to decrease the nucleophilicity of the nitrogen atom but also decrease the electron density on the phosphorus atom, thereby increasing its susceptibility to oxyanion attack (*i.e.*, decrease k_1 and increase k_2, respectively). Thus, any imine substituent is expected to exert opposing effects on the two rate constants. The introduction of even a methyl group on the *N*-phenyl ring seems sufficient to increase k_1 to the point that betaine decomposition (oxyanion attack on phosphorus) becomes rate-determining. The difference in the effect exerted by an electron-donating substituent seems to indicate a far more effective transmission of electronic effect through a phenyl group to nitrogen than to phosphorus.

Coïncidentally, the use of 2,4-dinitrobenzaldehyde has permitted the observation of a steric effect in the imine–carbonyl reaction heretofore not observed. Although such a carbonyl group should be more electrophilic than that of *p*-nitrobenzaldehyde, in the reactions with those imines *not* carrying electron-donating groups k_{obsd} is lower for the dinitrobenzaldehyde. These observations are consistent with betaine formation being the slow step of the reaction in the former cases, and therefore the steric hindrance being reflected in k_{obsd}, but with betaine decomposition being the slow step in the latter case, and the steric effect apparently not being reflected in k_{obsd}. Steric hindrance seems to be a significant factor only in betaine formation and seems to be detectable only in those reactions in which betaine formation is the rate-determining step.

Experimental Section

The iminophosphoranes (I) were prepared as described in our earlier report.[3] The benzaldehydes were commercial samples which were purified by crystallization or distillation. The rates of the reactions of the imines with the benzaldehydes were determined at 40.5° in absolute ethanol solution according to the procedure described in our previous work.

1,2-Diazacyclooctanes

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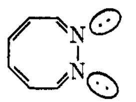
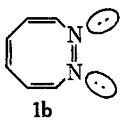
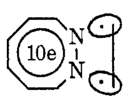
In light of the recent success of Trost and Cory[1] in uncovering an elegant route to 1,2-diazacyclooctatetraene (**1**), we have terminated our own studies in this



1a



1b



1c

area which were directed toward a synthesis of **1** *via* a classical halogenation–dehydrohalogenation sequence through the bis-protected diazacyclooctene **3**. Our interest in **1** derived from the conjecture that this compound might exist as the "aromatic" 10-π system **1c**.[2] Gund[3] has recently reported simple MO calculations on the classic structures **1a** and **1b** and has obtained delocalization energies similar to those calculated for cyclooctatetraene, whereas the "promoted" form **1c** leads to delocalization energies which are substantially higher. On the other hand, Trost's spectral results suggest nothing unusual about **1** but rather correlate well with structure **1a**.

Treatment of *cis*-1,6-dibromo-3-hexene (**2**) with *tert*-butyl hydrazodiformate and sodium hydride in dimethylformamide under relatively high dilution conditions gave **3** in 72% yield. A similar technique was used to obtain the saturated analog **7** (70%). Overberger and Stoddard[4] synthesized similarly the diethyl analog of **7**, although in only 22% yield.

Preliminary attempts to introduce further unsaturation into **3** were carried out by bromination followed by treatment with various bases. Thus addition of bromine to a solution of **3** in ether followed by addition of potassium *tert*-butoxide led to debromination with recovery of **3** rather than dehydrobromination. The less bulky sodium methoxide apparently attacked one

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(1) B. M. Trost and R. M. Cory, *J. Amer. Chem. Soc.*, **93**, 5572, 5573 (1971).

(2) For a consideration of a classical 10-π system which might also be obtainable *via* **3** see N. L. Allinger and G. A. Youngdale, *J. Org. Chem.*, **25**, 1509 (1960).

(3) P. H. Gund, Ph.D. Thesis, University of Massachusetts, Amherst, Mass., 1967.

(4) C. G. Overberger and J. W. Stoddard, *J. Amer. Chem. Soc.*, **92**, 4922 (1970).