435. *The Deoxygenation of Heterocyclic* N*-Oxides. Part III.*[1] *Kinetics of Their Reactions with Phosphorus Trichloride in Chloroform.*

By T. R. Emerson and C. W. Rees.

The very rapid deoxygenation of certain heterocyclic mono- and di-*N*-oxides with excess of phosphorus trichloride in chloroform at 25° is kinetically complex. The reactions are strongly inhibited by small amounts of hydrochloric acid, and the results are reproducible only when this is removed by the addition of another base (2,6-lutidine). In the presence of this base the deoxygenation of 4-nitropyridine 1-oxide and phenazine 5-oxide are first-order in phosphorus trichloride and second-order, with respect to time but not with respect to concentration, in *N*-oxide. The rate constants decrease rapidly with increasing initial concentration of *N*-oxide.

The di-*N*-oxides of quinoxaline and phenazine are deoxygenated stepwise, by way of the mono-oxides, but azoxybenzene and 3,4-benzocinnoline 5-oxide and 5,6-dioxide are inert to phosphorus trichloride under these conditions.

Earlier parts of this series [1,2] described attempts to provide a quantitative comparison of the reactivity towards deoxygenation of heterocyclic *N*-oxides, *i.e.*, of their effectiveness as reagents for oxygen-atom transfer. These reactions are of synthetic and of potential biological importance, and rate data would help in elucidation of the mechanism of this novel type of attack on an aromatic system.

For the purpose of this comparison the use of triethyl phosphite in diethylene glycol diethyl ether was unsatisfactory because of the complex sequence of reactions necessary for deoxygenation,[2] and polarographic reduction was unsuitable since, with all but the simplest oxides, the $N^+–O^-$ bond was not the first to be reduced at the dropping-mercury electrode.[1] It was therefore decided to investigate the kinetics of the reaction of certain heteroaromatic *N*-oxides with phosphorus trichloride in chloroform:

$$R_3N^+–O^- + PCl_3 \longrightarrow R_3N + POCl_3$$

This reaction is the one most commonly used for deoxygenation in synthetic work.

Experimental

A Unicam S.P. 500 spectrophotometer and a Perkin-Elmer Vapour Fraktometer were used.

Materials.—Commercial specimens of 2- and 4-picoline and 2,6-lutidine, and their 1-oxides, were recrystallised or fractionated, to give samples with m. p.s (or b. p.s) and refractive indices in agreement with literature values; these criteria of purity were supplemented where possible by gas chromatography. The picrates also had m. p.s in agreement with literature values. 3-Nitropyridine, m. p. 37°, was prepared by oxidation of 2-hydrazino-5-nitropyridine with aqueous silver acetate,[3] and converted into its 1-oxide, m. p. 171°, with peracetic acid. Preparation and purification of the other *N*-oxides were as described in Parts I and II.[2,1] Phosphorus trichloride (from May and Baker) was redistilled and periodically degassed with a stream of dry nitrogen under reduced pressure; batches were used for up to about 8 weeks before being replaced by a freshly redistilled sample. Chloroform was purified, dried, and stored in bulk in tightly stoppered brown bottles in the conventional way until the very marked sensitivity of our reactions to hydrogen chloride was recognised. Hydrogen chloride and phosgene rapidly appeared in batches of this solvent, even in the dark. In a modified procedure, small quantities (1 l.) were shaken with concentrated sulphuric acid (3 × 50 ml.) and washed with water until the washings were neutral. The wet chloroform was stored in the dark until required, and a portion (*ca.* 300 ml.) was dried ($CaSO_4$ and then P_2O_5) and distilled from fresh phosphorus pentoxide, under nitrogen, into a receiver, protected from atmospheric moisture,

[1] Part II, Emerson and Rees, *J.*, 1962, 1923.
[2] Emerson and Rees, *J.*, 1962, 1917.
[3] Deavin and Rees, unpublished work.

TABLE 1.

Ultraviolet absorption spectra; analytical wavelengths ($\lambda_{max.}$) and extinction coefficients for the *N*-oxides, in ethanol.

	$\lambda_{max.}$ (mμ)	log ε		$\lambda_{max.}$ (mμ)	log ε
Pyridine 1-oxide	265	4·09 (3·10)	Phenazine 5,10-dioxide	285	4·90 (—, 3·40)
2-Picoline 1-oxide	262	4·08 (3·53)	Phenazine 5-oxide	265	4·96 (3·40)
4-Picoline 1-oxide	266	4·21 (2·70)	Phenazine	248	5·08 —
2,6-Lutidine 1-oxide	259	4·00 (3·49)	3,4-Benzocinnoline 5,6-di-	292	4·12 (3·81, 3·92)
4-Methoxypyridine 1-oxide	269	4·22 —	oxide	302	4·10 (3·94, 3·73)
3-Nitropyridine 1-oxide	279	3·98 (3·51)		345	4·04 (3·18, 3·92)
4-Nitropyridine 1-oxide	330	4·14 —	3,4-Benzocinnoline 5-oxide	330	3·97 (3·12)
Quinoxaline 1,4-dioxide	385	4·09 —		363	3·78 (3·18)
Quinoxaline 1-oxide	325	3·97 (3·48)		382	3·64 (2·80)
Quinoxaline	315	3·80 —	3,4-Benzocinnoline	307	3·97 —

* Log ε for the parent base is shown in parentheses where correction for absorption by the base was necessary; a second such figure is the corresponding value for the mono-*N*-oxide.

TABLE 2.

Deoxygenation of *N*-oxides with phosphorus trichloride in anhydrous chloroform containing 2,6-lutidine, at 25 ± 1°.

Run no.	*N*-Oxide	Concn. of *N*-oxide (M × 10^3)	Concn. of PCl_3 (M × 10^2)	Concn. of 2,6-lutidine (M × 10^3)	Overall k_3 (× 10^{-2}) (l.^{2} mole^{-2} min.$^{-1}$)
30	Pyridine 1-oxide	1·25	1·06	4·0	> 5 × 10^3 *
31	2,6-Lutidine 1-oxide	1·39	0·97	4·7	— *
32	3-Nitropyridine 1-oxide	0·98	5·95	18·2	— *
33	4-Nitropyridine 1-oxide	0·70	2·60	4·4	37
34	,,	1·02	6·70	237	35
35	,,	1·08	2·05	4·4	37
36	,,	1·10	6·10	12·2	29
37	,,	1·11	6·40	13·2	35 †
38	,,	1·13	6·20	13·6	37
39	,,	1·17	1·15	4·4	33
40	,,	1·90	4·70	4·0	14
41	,,	2·08	5·20	4·4	9·2
42	,,	2·13	2·36	4·2	5·9
43	,,	2·13	1·60	4·2	5·4
44	,,	9·8	5·60	13·5	0·12
45	Phenazine 5-oxide	0·51	4·90	14·4	96 (93) ‡
46	,,	1·05	5·15	14·9	39 (41) ‡
47	,,	1·07	5·30	15·5	27 (under N_2)
48	,,	1·08	5·83	15·8	38 §
49	,,	1·11	6·00	15·3	31 (in dark)
50	,,	1·51	5·75	14·3	25
51	,,	2·00	5·95	14·1	16
52	,,	2·03	5·85	14·7	11
53	,,	2·80	5·60	14·1	9·6 (11) ‡
54	,,	3·90	5·20	14·1	4·8 (under O_2)
55	,,	3·94	5·40	21·4	3·8 ¶
56	,,	4·53	6·10	22·9	1·6
57	Phenazine 5,10-dioxide	0·97	4·88	15·8	22 (24) ‡**
58	,,	1·11	5·00	16·3	55 (56) ‡**
59	Quinoxaline 1-oxide	1·00	5·05	18·8	37
60	,,	1·03	5·20	13·3	31
61	,,	1·12	5·15	13·3	21
62	Quinoxaline 1,4-dioxide	0·99	5·20	17·3	19
63	,,	1·04	5·25	17·7	35
64	3,4-Benzocinnoline 5-oxide	0·99	5·40	23·1	No reaction in 20 hr.
65	3,4-Benzocinnoline 5,6-dioxide	1·00	5·45	22·7	

* Too fast to measure; reaction complete in 1 min. † Phosphorus oxychloride (4·6 × 10^{-3}M) added. ‡ Rate constants calculated, independently, for the appearance of phenazine. § Phosphorus oxychloride (1·47 × 10^{-2}M) and phenazine (1·78 × 10^{-3}M) added. ¶ Bromochloromethane (10% v/v) added to the solvent. ** Rate constant for deoxygenation of the mono-oxide; first step too fast to measure.

through which pure nitrogen was passed. This receiver had a tap at the bottom through which solvent could be removed without exposure of the stock. This solvent did not react with calcium hydride or with aqueous silver nitrate, and was always used within 24 hr. of being dried and distilled.

Kinetic Method.—The deoxygenation reactions were followed spectrophotometrically by measuring the decrease in extinction for the *N*-oxide at a wavelength of maximum absorption ($\lambda_{max.}$), and sometimes by also measuring the increase in extinction of the base formed at its $\lambda_{max.}$ (see Table 1). Readings for each component were corrected graphically, where necessary,

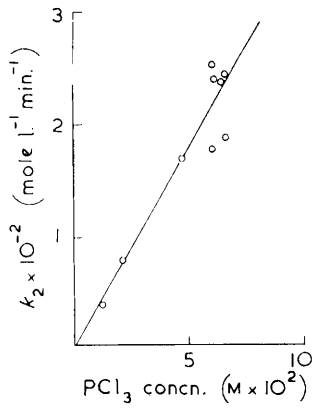


FIG. 1. Deoxygenation of 4-nitropyridine 1-oxide (*ca.* $1{\cdot}1 \times 10^{-3}$M) with phosphorus trichloride, in chloroform at 25°.

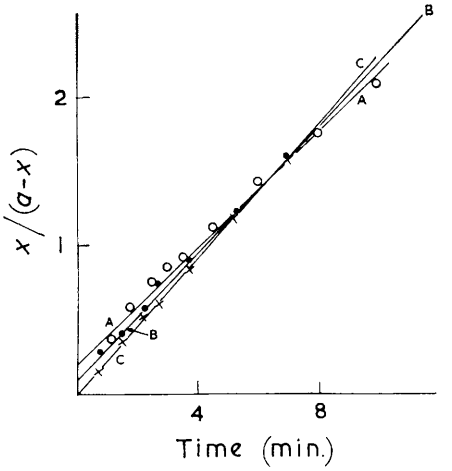


FIG. 2. Second-order reactions with phosphorus trichloride in chloroform, at 25°.

A (run 36): 4-nitropyridine 1-oxide ($2{\cdot}19 \times 10^{-3}$M; 20 ml.), 2,6-lutidine (0·0529 g.), and PCl_3 ($1{\cdot}21 \times 10^{-1}$M; 20 ml.).

B and C (run 46; for disappearance of *N*-oxide and appearance of phenazine, respectively): phenazine 5-oxide ($2{\cdot}1 \times 10^{-3}$M; 20 ml.), 2,6-lutidine (0·0630 g.), and PCl_3 ($1{\cdot}03 \times 10^{-1}$M; 20 ml.).

for the extinction due to the other. The reaction vessel was an " automatic " pipette with a small bulb (2 ml.) in a side-limb which could be filled with solution from a larger bulb (100 ml.), and from which the solution could then be discharged; a fixed volume (2·02 ml.) could thus be rapidly and repeatedly delivered into the solution used to arrest the reaction. The reaction solution was protected from atmospheric moisture and the whole apparatus enclosed in an air thermostat at 25 ± 1°. In view of other more serious sources of error, described below, closer control of the reaction temperature was unnecessary. As phosphorus trichloride is very rapidly hydrolysed and small amounts of hydrogen chloride were found to affect the reaction markedly, stringent precautions were taken to exclude moisture from the apparatus and reagents. *N*-Oxides, many of which are hygroscopic, were dried over phosphorus pentoxide at 0·1 mm.

A solution of phosphorus trichloride, of known concentration, in chloroform, used for one run only, was added to a similar solution of the *N*-oxide in chloroform in the above pipette, to give the required concentration (see Table 2). Aliquot parts of the mixture were delivered from the pipette at appropriate times into AnalaR absolute ethanol containing enough piperidine to neutralise the hydrochloric acid formed; this strong base, transparent in the ultraviolet region in the concentration used, was added in 50% excess of that required to react with all the hydrochloric acid formed, since the *N*-oxide extinctions were found to be considerably reduced by

free acid. The extinctions for pyridine 1-oxide and of pyridine, in ethanol, were unaffected by the presence of this amount of piperidine; a much larger excess of piperidine caused a slow increase in absorption in the region 230—260 mμ. The solutions were then further diluted with ethanol and their spectra taken. In the case of the phenazine oxides these dilute solutions, which are unstable in light, were stored in the dark and the spectra measured as soon as possible.

A dry solution of hydrogen chloride in chloroform was standardised by conductimetric titration. In certain experiments the calculated quantity of this solution was added to the *N*-oxide solution, before the phosphorus trichloride, to give the required concentration of acid. All the later kinetic experiments were performed in the presence of 2,6-lutidine (see Table 2) which was added to the *N*-oxide solution before the phosphorus trichloride solution. The spectrophotometric readings were corrected for absorption by the lutidine.

Kinetic Results.—The *N*-oxides obeyed Beer's Law over the relevant range of concentrations. The spectra of reaction mixtures after complete deoxygenation agreed well with those of the corresponding bases, in the presence and absence of 2,6-lutidine. Phosphorus trichloride was present in large and effectively constant molar excess (*ca.* 50-fold, see Table 2). Its reactions with 4-nitropyridine 1-oxide and phenazine 5-oxide were first-order in phosphorus trichloride over the range 0·01—0·1M (see, *e.g.*, Fig. 1), and the other reactions were, by analogy, assumed to be first-order in phosphorus trichloride. Rate constants were calculated on the change in *N*-oxide concentration, and then divided by the phosphorus trichloride concentration, to give the overall rate constant. The former were obtained from the linear curves of log $(a - x)$

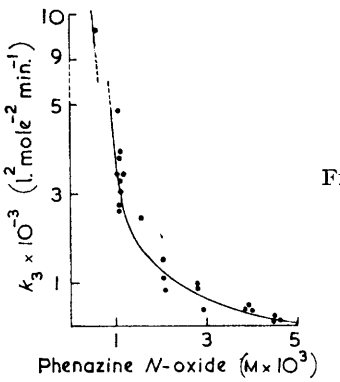


FIG. 3. Deoxygenation of phenazine 5-oxide with phosphorus trichloride, in chloroform at 25°.

or $x/(a - x)$ against time, t (in minutes), for reactions first-order or second-order, respectively, in *N*-oxide; a is the initial extinction of the *N*-oxide solution, and $(a - x)$ the extinction of the reaction mixture after time t. Some typical results are given in Fig. 2.

Stoicheiometry of the Reactions.—Since the kinetic solutions were too dilute for convenient isolation of reaction products some deoxygenations were performed in more concentrated solutions, but with a high ratio of phosphorus trichloride to *N*-oxide, to simulate the kinetic conditions. Pyridine 1-oxide, phenazine 5-oxide, and phenazine 5,10-dioxide were converted into the parent bases which were isolated in 78 (as picrate), 64, and 65% yield, respectively. After similar treatment with phosphorus trichloride in chloroform containing 2,6-lutidine, 3,4-benzocinnoline 5,6-dioxide and azoxybenzene were recovered unchanged in 82 and 79% respectively.

Bromochloromethane in the Solvent.—Bromochloromethane, an impurity in chloroform which reacts with trimethylamine to form chloromethyltrimethylammonium bromide,[4] was tested for as follows. Trimethylamine was passed through chloroform (50 ml.) for 3 hr. Fine colourless needles (0·22 g.) were deposited, and collected after 2 days. Further passage of the amine gave more (0·02 g.) of the product, m. p. 163°. This corresponds to *ca.* 0·25% of the impurity in our solvent. However, the addition of 10% (v/v) of bromochloromethane to chloroform (run 55) was without significant effect on the rate of deoxygenation of phenazine 5-oxide.

[4] Williams, *Chem. and Ind.*, 1960, 900.

Discussion

In the early experiments with pyridine 1-oxide the reactions were first-order in *N*-oxide but the slopes of the linear curves of log $(a - x)$ against t varied from run to run, the rate constants being irreproducible. For these experiments the chloroform had been purified in the usual way and stored in bulk, and it was noticed that the rate of reaction decreased with the age of the solvent and then sharply increased when freshly distilled solvent was used (k_2 = 1·2, 0·98, 0·58, and then 3·6, 1·2, and 0·7 l. mole^{-1} min.$^{-1}$ for runs 1—6). Under these conditions two other *N*-oxides, 4-nitropyridine 1-oxide and phenazine 5-oxide, were investigated (runs 7—12); their reactions were slower than with pyridine 1-oxide and gave fairly consistent results, again being first-order in *N*-oxide.

The purification of solvent, and the kinetic technique were then altered so that the solutions were kept as dry as possible, and the rates of deoxygenation of several *N*-oxides measured. Results were now often more erratic than before and the curves of log $(a - x)$ against t were not always linear. Indeed, as the technique was steadily improved the reaction rate tended to increase, and individual runs often appeared to be more close to second-order in *N*-oxide. As variable amounts of hydrochloric acid, present in the phosphorus trichloride and formed by its hydrolysis, were considered to be the most likely cause of this irreproducibility, the effect of adding more acid to the reaction mixture was determined. The rates of deoxygenation of pyridine 1-oxide and 2,6-lutidine 1-oxide were decreased rapidly as the acid concentration increased. When dry nitrogen was previously bubbled through the phosphorus trichloride under reduced pressure the deoxygenation rate was abnormally high, indicating that the phosphorus trichloride contained appreciable amounts of hydrogen chloride.

In view of the great difficulty of removing all traces of hydrogen chloride (and excluding all traces of water) from the system, a base was added to neutralise this acid. 2,6-Lutidine, a weak nucleophile but a very much stronger base than the *N*-oxides, was added to all subsequent reaction mixtures (see Table 2). The base increased the rate so much that the reactions with the *N*-oxides of pyridine, 3-nitropyridine, and 2,6-lutidine were too fast (90% reaction in 1 min.) to measure accurately by the present method (runs 30—32); later work suggested that these reactions might, however, be slow enough at considerably higher initial concentrations of *N*-oxide. The less reactive 4-nitropyridine 1-oxide and phenazine 5-oxide were also deoxygenated much faster in the presence of lutidine, but their reactions, and that of quinoxaline 1-oxide, were slow enough for fairly accurate kinetic measurement. Lutidine was usually added to 5—10-fold molar excess of the *N*-oxide (Table 2) but an increase in its concentration to fifty times this was without further effect on the reaction rate (run 34). Thus, there appears to be no formation of a complex between the lutidine and phosphorus trichloride of the type claimed [5] for triethylamine and phosphorus trichloride, though this claim was later refuted.[6]

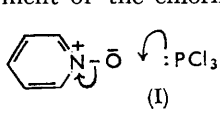
The reactions of 4-nitropyridine 1-oxide, quinoxaline 1-oxide, and phenazine 5-oxide, in the presence of lutidine, were, however, second-order in the oxide (see Fig. 2). This is in contrast to the early reactions, which were first-order in *N*-oxide, when hydrogen chloride, present adventitiously, was probably in excess of the oxide concentration (10^{-3}M). The change from first- to second-order, and the apparent non-integral order of many of the intervening runs, was thus presumably caused by the steady decrease in acid concentration as the reaction solutions were obtained, and kept, more and more anhydrous. With different initial concentrations of phosphorus trichloride these reactions were first-order in phosphorus trichloride (see, *e.g.*, Fig. 1) in the presence of 2,6-lutidine, and the overall third-order rate constants, k_3, were obtained by correction of the second-order rate constant to unit phosphorus trichloride concentration.

[5] Trost, *Canad. J. Chem.*, 1954, **32**, 356.
[6] Holmes and Bertant, *J. Amer. Chem. Soc.*, 1958, **80**, 2980.

The first series of results for reactions in the presence of 2,6-lutidine, obtained with 4-nitropyridine 1-oxide, were complex, since k_3 varied widely as the initial concentrations of the *N*-oxide, phosphorus trichloride, and lutidine were altered (runs **33** and **44**). The significance of this variation became clear only after the next series of experiments, with phenazine 5-oxide. An advantage here was that the rate of formation of phenazine could also be followed and compared with the rate of loss of *N*-oxide; good agreement was obtained (runs **45**, **46**, and **53**). In most of these runs the concentrations of phosphorus trichloride and lutidine were kept nearly constant, and the *N*-oxide concentration was varied considerably. The individual runs were second-order in *N*-oxide, but the overall third-order rate coefficients were very sensitive to the initial concentration of *N*-oxide. The variation of k_3 with this concentration is shown, for phenazine 5-oxide, in Fig. 3. The rate constant decreases, at first rapidly and then slowly, with increasing *N*-oxide concentration in an approximately hyperbolic manner. On this curve are also included results for reactions proceeding in the light (run **49**), under oxygen (run **54**), and under nitrogen (run **47**), and in the presence of initially added reaction products (run **48**) and of bromochloromethane (run **55**). All these factors are without appreciable effect, and thus, in contrast to the reaction of triethyl phosphite with pyridine 1-oxide,[2] free radicals do not seem to be involved in the phosphorus trichloride deoxygenations. Once this relationship between rate constant and concentration was established for phenazine 5-oxide the results with 4-nitropyridine 1-oxide could be understood. With one exception (run **44**), the range of initial concentrations of 4-nitropyridine 1-oxide ($0{\cdot}7 \times 10^{-3}$ to $2{\cdot}1 \times 10^{-3}$M) coincided with the very steep part of the curve where the rate constant is very sensitive to initial concentration. A plot of k_3 against this concentration of 4-nitropyridine 1-oxide does give a curve very similar in shape to that for phenazine 5-oxide though the initial concentrations are not as well separated.

This decrease in rate constant with increasing initial concentration suggests that under these experimental conditions, the *N*-oxides are present in various forms of markedly different reactivity, with the proportion of more reactive forms decreasing as the total concentration increases. It is reasonable to suppose that the polar *N*-oxide molecules will aggregate strongly in this non-polar solvent (dielectric constant = 4·7 at 25°), their ionic charges tending to be neutralised. However, the present kinetic results are not consistent with a simple rapid equilibrium between a reactive monomeric species and inert polymeric forms.* The system is thus a complex one which requires further detailed study for elucidation of the reaction mechanism, but is sufficiently unusual to warrant this. In particular, the marked dependence of rate constant upon initial concentrations of *N*-oxide means that comparative results for the deoxygenation of different *N*-oxides must be interpreted very cautiously.

It has been suggested [7] that phosphorus trichloride deoxygenates pyridine *N*-oxides by acting as a nucleophile, as in (I), but this mechansim is inconsistent with the present kinetics. Furthermore, the qualitative evidence available is in better agreement with nucleophilic attack upon phosphorus, by the oxide oxygen atom (cf. ref. 8). Thus, replacement of the chlorine atoms in phosphorus trichloride by the electron-releasing ethoxyl groups greatly decreases the rate of deoxygenation since much higher temperatures are required to effect reaction.[9] From a general comparison of results for pyridine 1-oxide and 4-nitropyridine 1-oxide, electron-withdrawal from the oxide group is seen to decrease the reaction rate markedly; protonation of the oxides, to give 1-hydroxypyridinium ion, does the same. Both are explained by the resulting decrease in nucleophilicity of the



(I)

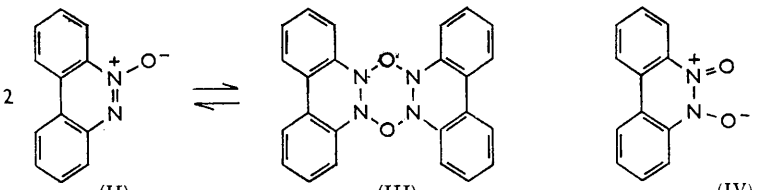
* We are grateful to a Referee for demonstrating this.

[7] Katritzky, *Quart. Rev.*, 1956, **10**, 399.
[8] Aguiar, *Diss. Abs.*, 1960, **21**, 457.
[9] Ramirez and Aguiar, Abstracts of Papers, 134th Meeting of the American Chemical Society, Sept. 1958, N42.

oxygen atom; if phosphorus trichloride were the nucleophile the reverse would be expected. This would explain the decreased reactivity of the *N*-oxide molecules as they form dipolar aggregates on increasing concentration; the negative charge on the oxide-oxygen atom becomes dispersed and its electron donating power consequently reduced.

Quinoxaline 1-oxide was deoxygenated at about the same rate as phenazine 5-oxide, and it, too, reacted more slowly at higher initial concentrations (runs 58—60). 3-Nitropyridine 1-oxide was deoxygenated too rapidly for measurement of the rate under our conditions at 25° (run 32). The di-*N*-oxides of quinoxaline (runs 62 and 63) and phenazine (runs 57 and 58) were deoxygenated stepwise, the first oxygen being removed at a rate too fast to measure, and the resulting mono-oxides, identified by their ultraviolet spectra, were then deoxygenated much more slowly. Although these rate constants for the mono-oxides were of the same order as those determined directly they were now much less reproducible. These results for the di-*N*-oxides may be contrasted with those for polarographic reduction,[1] where both oxygen atoms were removed simultaneously.

3,4-Benzocinnoline 5-oxide (II) and 5,6-dioxide (IV) did not react with phosphorus trichloride under our kinetic conditions, even after 20 hours, and the dioxide was recovered (82%) from an attempted large-scale deoxygenation with the same reagent. This result supports the polarographic evidence for a qualitative difference between this "*ortho*"



(II) (III) (IV)

di-*N*-oxide and the "para" di-*N*-oxides of quinoxaline and phenazine. Azoxybenzene, structurally somewhat similar to 3,4-benzocinnoline 5-oxide, was also stable to phosphorus trichloride in chloroform at room temperature. The inertness of the mono-*N*-oxide (II) would result, on the basis of the argument above, if it were virtually completely dimerised in the chloroform solution; compared with the other *N*-oxides studied, a particularly stable structure (III) may be envisaged for a dimer in this instance. The lack of reactivity of 3,4-benzocinnoline 5,6-dioxide is possibly due to extensive resonance stabilisation of the highly symmetrical ground-state, particularly by structures of type (IV) (cf. ref. 10). This di-*N*-oxide is sometimes referred to as 2,2′-dinitrosobiphenyl;[11] its chemical and physical properties, *e.g.*, its high melting point (243°), thermal stability, lack of colour in the solid state and in solution (cf. ref. 11), and inertness towards phosphorus trichloride, are incompatible with the presence of free nitroso-groups, but structure (IV) can, of course, be regarded as an unusually stable intramolecular "dimer" of the dinitroso-compound.

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Strand, London W.C.2. [*Received, March 16th*, 1963.]

[10] Ross and Kuntz, *J. Amer. Chem. Soc.*, 1952, **74**, 1297.
[11] "Chemistry of Carbon Compounds," ed. Rodd, Elsevier, Amsterdam, 1959, Vol. IVB, p. 1235.