Inductive and Field Effects in Aromatic Substitution. Part V.[1] Kinetics of Nitration of the Quaternary Salts of Diazacyclophanes and of Related Unbridged Ions

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The rates of nitration of the open-chain ions (I) in aqueous sulphuric acid are compared with those of the corresponding bridged ions (II). The comparison is used to provide evidence on how the substituent effects of the groups $-[CH_2]_n\cdot{}^+NR_3$ depend on the conformation of the carbon chain. The results indicate that for $n \geqslant 2$, the deactivation produced by the nitrogen poles depends more directly on the distance of the poles from the centre of the ring than on the number of carbon atoms in the carbon chain. This is interpreted in terms of the field effect of the pole. For $n = 1$, there is evidence for additional modes of deactivation but the field effect still appears to be the major factor.

THIS paper continues the study of the substituent effect of groups of the type $-[CH_2]_n\cdot{}^+NR_3$ with particular reference to the dependence of the substituent effect on the conformation of the carbon chain. A comparison is made of the reactivities in aromatic nitration of open-chain systems of structure (I) with those of the related bridged systems (II). The use of these 1,4-disubstituted

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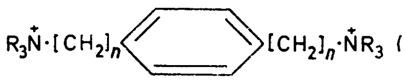
[1] Part IV, A. Ricci and J. H. Ridd, preceding paper.

aromatic rings has the advantage that all the positions available for substitution are equivalent; the relative reactivity of positions in different ions can therefore be discussed without reference to the orientation of the monosubstituted product.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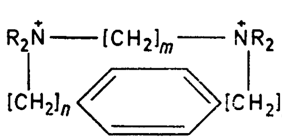

(II) R = H or Me

In the open-chain ions (I) the distance between the nitrogen poles and the ring in the transition state should increase with n, for the carbon chains should adopt an extended conformation to minimise the electrostatic interaction between these poles and the charge on the ring and on the electrophile. In contrast, in those bridged ions (II) with the minimum number (10) of atoms in the bridge to provide a strainless system the distance of the nitrogen pole from the centre of the ring is not very sensitive to the value of n (for $n \geqslant 1$), since to a good approximation the nitrogen poles then occupy points on part of a semicircle centred at the centre of the ring. This difference between the bridged and unbridged systems is of particular value in the analysis of the inductive and field effects of the nitrogen poles.

Kinetics.—The rates of nitration of the bridged and open-chain ions were followed from the changes in the u.v. spectra as described previously for other positive ions.[1] Second-order rate constants (k_2) at a given acidity were calculated from equation (1) and are listed

$$\text{Rate} = k_2[\text{ArH}][\text{nitric acid}] \qquad (1)$$

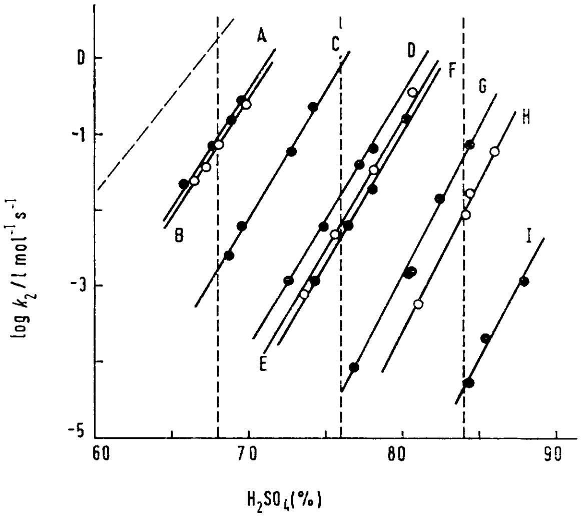
for different concentrations of sulphuric acid in Table 1.

As shown in Table 1, the compounds studied include those with protonated (R = H) and those with methylated (R = Me) poles. In principle, the former could undergo reaction through either the free amine, the monoconjugate acid, or the diconjugate acid. The similar slopes of the rate profile (see Figure) for the ions with protonated poles (lines A, C, E, G, H, I) to those with fully alkylated poles (lines B, D, F) makes it clear that the former are reacting as the diconjugate acids. The comparison of the results for the two pairs of ions (I; $n = 3$, R = H or Me) (lines A and B) and (II; $n = 2$, $m = 4$, R = H or Me) (lines E and F) suggests that when $n \geqslant 2$ the difference between the substituent effects of the protonated and methylated poles is slight. This accords with previous studies on monosubstituted benzenes.[2,3] The comparison of the results for the ions (I; $n = 1$, $^+NR_3 = {}^+NH_3$ or $^+NH_2Me$) (lines G and H) shows that when $n = 1$, the rate of nitration is much more sensitive to the extent of alkylation at the nitrogen pole. This also accords with previous studies.[4]

TABLE 1

Second-order rate coefficients [k_2, eqn. (1)/l mol^{-1} s^{-1}] for the nitration of the open-chain and bridged ions illustrated in structures (I) and (II) in aqueous sulphuric acid at 25 °C

Open-chain ions (I)					
$n = 3$, R = H	H_2SO_4 (%)	65·78	67·67	68·90	69·53
	10^4k_2	218	706	1520	2820
$n = 3$, R = Me	H_2SO_4 (%)	66·50	67·50	68·10	69·72
	10^4k_2	238	355	728	2500
$n = 2$, R = H	H_2SO_4 (%)	68·70	69·53	72·79	74·22
	10^4k_2	24·6	61·4	575	2190
$n = 1$, R = H	H_2SO (%)	76·80	80·34	82·46	84·95
	10^4k_2	0·81	14·5	141	724
$n = 1$, $^+NR_3 =$ $^+NH_2Me$	H_2SO_4 (%)	81·00	84·20	84·40	85·95
	10^4k_2	5·76	83·1	132	575
Bridged ions (II)					
$n = 3$, $m = 2$, R = Me	H_2SO_4 (%)	72·52	74·89	77·20	78·65
	10^4k_2	11·5	60·2	389	831
$n = 2$, $m = 4$, R = H	H_2SO_4 (%)	73·65	75·61	78·16	80·58
	10^4k_2	7·76	46·9	331	3550
$n = 2$, $m = 4$, R = Me	H_2SO_4 (%)	74·30	76·50	78·06	80·25
	10^4k_2	11·5	61·7	18·2	1660
$n = 1$, $m = 8$, R = H	H_2SO_4 (%)	84·31	85·40	85·96	87·88
	10^4k_2	0·52	1·99	3·01	11·2



Plot of log k_2 for the nitration of ions of structure (I) and (II) in aqueous sulphuric acid at 25 °C; A, (I; $n = 3$, R = H); B, (I; $n = 3$, R = Me); C, (I; $n = 2$, R = H); D, (II; $n = 3$, $m = 2$, R = Me); E, (II; $n = 2$, $m = 4$, R = H); F, (II; $n = 2$, $m = 4$, R = Me); G, (I; $n = 1$, R = H); H, (I; $n = 1$, $^+NR_3 = {}^+NH_2Me$); I, (II; $n = 1$, $m = 8$, R = H). The broken rate profile is for *p*-xylene (ref. 6)

For all the substrates listed in Table 1, the change in the u.v. spectrum during reaction was that expected for mononitration and this was confirmed by a product analysis for the ion (II; $n = 2$, $m = 4$, R = H).

The wide range of acidity and reactivity covered by the results in the Figure makes it difficult to extrapolate

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[2] F. De Sarlo, G. Grynkiewicz, A. Ricci, and J. H. Ridd, *J. Chem. Soc.* (*B*), 1971, 719.

[3] T. A. Modro and J. H. Ridd, *J. Chem. Soc.* (*B*), 1968, 528.

[4] M. Brickman, J. H. P. Utley, and J. H. Ridd, *J. Chem. Soc.*, 1965, 6851.

the rate of nitration of each ion to a single acidity. The reactivities relative to benzene and the partial rate factors have therefore been calculated by a series of stepwise comparisons based on the relative reactivities at the acidities indicated by lines in the Figure. These results are listed in Table 2. This procedure is a little different from that used in the preliminary communication of some of these results[5] where the partial rate factors were based on the relative reactivity with respect to benzene at a higher acidity (74% H_2SO_4). The slope of the rate profile for the nitration of benzene becomes steeper relative to those of most other substrates at acidities above 70% sulphuric acid[6] and so the previous values of the partial rate factors are somewhat smaller than those now reported. Our further studies have also led us to modify slightly the slopes of the rate profiles previously reported[5] so that the rate difference between the ions (I; $n = 2$, R = H) and (II; $n = 2$, $m = 4$, R = H) becomes a factor of 109 not 200.

TABLE 2

Partial rate factors (f) and rates of nitration of the ions (I) and (II) relative to benzene and *p*-xylene[a]

	log (Relative rate)		
Open-chain ions (I)	To benzene	To *p*-xylene[b]	f
$n = 3$, R = H	0·27	−1·32	2·8
$n = 3$, R = Me	0·15	−1·44	2·1
$n = 2$, R = H	−1·45	−3·04	$5{\cdot}4 \times 10^{-2}$
$n = 1$, R = H	−5·71	−7·30	$2{\cdot}95 \times 10^{-6}$
$n = 1$, $^+NR_3 = {}^+NMeH_2$	−6·43	−8·02	$5{\cdot}6 \times 10^{-7}$
Bridged ions (II)			
$n = 3$, $m = 2$, R = Me	−3·11	−4·70	$1{\cdot}2 \times 10^{-3}$
$n = 2$, $m = 4$, R = H	−3·49	−5·08	$4{\cdot}9 \times 10^{-4}$
$n = 2$, $m = 4$, R = Me	−3·65	−5·24	$3{\cdot}4 \times 10^{-4}$
$n = 1$, $m = 8$, R = H	−8·73	−10·32	$2{\cdot}8 \times 10^{-9}$

[a] Based on the rate coefficients for benzene and *p*-xylene given by ref. 6. [b] Calculated with respect to the rate of nitration of benzene and *p*-xylene in 68% sulphuric acid.

The reactivity of the open-chain and bridged ions relative to *para*-xylene is included in Table 2 in order to provide a guide to the effect of the nitrogen poles on the reactivity of 1,4-dialkylbenzene. The use of *p*-xylene as the reference compound could perhaps be criticised on the grounds that it reacts with nitronium ions at the encounter rate;[6] its reactivity may not therefore reflect the true activating effect of two *p*-methyl groups. Coombes, Moodie, and Schofield[6] however have shown that the reactivity of *p*-xylene is only 24% less than that expected from the reactivity of toluene and the additivity principle. Such a small influence on the reaction rate is not significant in comparison with the large rate ratios reported here.

DISCUSSION

The main purpose of this study was to test two very simple hypotheses concerning the deactivating effect of the nitrogen pole in substituents of the type $Ar{\cdot}[CH_2]_n{\cdot}{}^+NR_3$: (*a*) that this deactivating effect is propagated along the carbon chain by the classical inductive effect and (*b*) that the deactivating effect operates through space and is dependent mainly on the distance of the nitrogen pole from the centre of the aromatic ring.

In analysing the data in terms of these hypotheses it is convenient to start with the compounds with two or more carbon atoms between the pole and the ring for these results present a simple and self-consistent picture.

The Open-chain and Bridged Ions with $n \geqslant 2$.—Consider first the open-chain ion (I; $n = 3$, R = Me). This ion is less reactive than *p*-xylene by a factor of 28 (Table 2), a result consistent with both the hypotheses above. However, when the conformation of the carbon chain is modified by linking the nitrogen poles by two methylene groups as in the ion (II; $n = 3$, $m = 2$, R = Me) the reactivity decreases by a further factor of 1800 (Table 2).

This decrease cannot be attributed to the classical inductive effect for the number of intervening methylene groups between each pole and the ring is the same in the open-chain and bridged ions. Any contribution to the classical inductive effect of the pole through the longer arm of the bridge should be much less than that in the open-chain ion because of the greater number of intervening atoms. The lower reactivity of the bridged ion is most unlikely to arise from steric hindrance to the attack of the nitronium ion because even if this ion were completely prevented from approaching from one side of the ring, the decrease in the reaction rate should be only a factor of 2. Steric hindrance in the stage involving proton loss need not be considered since it is unlikely that this stage is rate-determining.

The one major factor remaining is the field effect of the nitrogen pole.* This should be greater in the bridged ion because the pole is then nearer the centre of the ring (a distance of *ca.* 3·5 Å compared with 6·3 Å for the extended conformation of the open-chain ions) and possibly also because the bridged ion constitutes a greater ' cavity ' in the solvent. The last factor could reduce the effective dielectric constant for intramolecular electrostatic interactions.[7]

Consider next the open-chain ion with one fewer methylene group between the pole and the ring (I; $n = 2$, R = H). This ion is less reactive than the corresponding ion with three methylene groups by a factor of 52 (Table 2). In itself, this difference in reactivity could be ascribed either to the increased inductive effect or to the increased field effect of the nitrogen pole. However, if the former interpretation were correct, the same factor should appear in the comparison of the corresponding bridged ions. In fact the bridged ion with two intervening methylene groups (II; $n = 2$, $m = 4$, R = Me) is less reactive than that

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* The possibility that the existence of the bridge might in itself seriously modify the aromatic reactivity by reducing the solvation of the transition state is discussed in the following section.

[5] G. Mossa, A. Ricci, and J. H. Ridd, *Chem. Comm.*, 1971, 332.

[6] R. G. Coombes, R. B. Moodie, and K. Schofield, *J. Chem. Soc.* (*B*), 1968, 800.

[7] J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, 1938, **6**, 506, 513.

with three methylene groups (II; $n = 3$, $m = 2$, R = Me) but the difference is only a factor of 3·4. We conclude therefore that the decrease in the reaction rate when the number of methylene groups in the open-chain ions is reduced from three to two comes largely from the field effect of the nitrogen poles. Since this conclusion arises from a comparison of the kinetic effects of structural changes within the open-chain and bridged systems, it should not be invalidated by any general effect of bridging on the reaction rate (see following section).

If this conclusion is true for the change in the reactivity of the open-chain system when the number of methylene groups is changed from two to three, the same should be true for the further addition of methylene groups to the carbon chain. This follows because the field effect is generally recognised to be of longer range than the classical inductive effect and hence becomes more important relative to the inductive effect as n increases.* By mentally increasing the number of methylene groups to $n = \infty$, we can see that the reactivity of the open-chain systems with $n > 2$ relative to a 1,4-dialkylbenzene should also reflect mainly the field effect of the pole.

The Open-chain and Bridged Ions with n = 1.—These ions need to be considered separately because the distance of each nitrogen pole from the centre of the ring in the open-chain ion does not depend on the conformation of the substituent. As a result the distance should be unchanged (apart from any slight distortion of bond angles) when the nitrogen atoms are linked by a methylene chain. This distance (3·7 Å) is similar to that in the bridged ions discussed above. On the simple interpretation of these substituent effects in terms of electrostatic interaction between the nitrogen poles and the charge on the ring in the transition state,[3] the reactivity of both the open-chain and the bridged ions with $n = 1$ should be similar to that of the other bridged ions.

Neither of these consequences is observed. If we take the reactivity of the bridged ion (II; $n = 2$, $m = 4$, R = Me) as standard, the reactivity of the open-chain ion (I; $n = 1$, R = H) is less by a factor of 115 (Table 2) and that of the bridged ion (II; $n = 1$, $m = 8$, R = H) is less by a further factor of 1050.

The simplest interpretation of the increased deactivation of the open-chain ion with $n = 1$ over the bridged ions with $n = 2$ is in terms of the classical inductive effect of the nitrogen pole transmitted through the single methylene group. However, it is probably important to consider also the extent to which the nitrogen pole modifies the activation of the aromatic ring by the methylene group. The activation of the aromatic ring in *p*-xylene corresponds to a partial rate factor[6] of 59 and so the absence of this activation could account for much of the deactivation of the open-chain ion (I; $n = 1$, R = H) relative to the bridged ion (II; $n = 2$, $m = 4$, R = Me). The fact that the percentage of *meta*-substitution in the ions $Ph\cdot[CH_2]_n\cdot{}^+NMe_3$ increases[9] from 17% when $n = 2$ to 88% when $n = 1$ accords with both these interpretations. The deactivation of the open-chain ion (I; $n = 1$, R = H) relative to the bridged ions with $n = 2$ (a factor of *ca.* 10^2) is small in comparison with the deactivation of the open-chain ion with respect to *p*-xylene (a factor of *ca.* 10^7). Thus, in free-energy terms, the major part of the deactivation of the open-chain ion with $n = 1$ relative to *p*-xylene can still be considered as a field effect.

It is more difficult to explain the further rate decrease by a factor of 1050 (Table 2) between the open-chain ion (I; $n = 1$, R = H) and the bridged ion (II; $n = 1$, $m = 8$, R = H). This rate decrease is inconsistent with both the simple theories outlined at the beginning of this discussion. Certain difficulties in the preparation of the bridged ions led us to make this bridged ion with a 12-atom rather than a 10-atom bridge but this change was not expected to have a significant effect on the aromatic reactivity.

TABLE 3

Rate ratios for the variation of n [structures (I) and (II)] in open-chain and bridged ions

n	Open-chain ions	Bridged ions
3 → 2	$\frac{k(n = 3, R = H)}{k(n = 2, R = H)} = 52$	$\frac{k(n = 3, m = 2, R = Me)}{k(n = 2, m = 4, R = Me)} = 3\cdot4$
2 → 1	$\frac{k(n = 2, R = H)}{k(n = 1, R = H)} = 1\cdot8 \times 10^4$	$\frac{k(n = 2, m = 4, R = H)}{k(n = 1, m = 8, R = H)} = 1\cdot7 \times 10^5$

One possible explanation of the above rate difference would be that the presence of a bridge between the two nitrogen poles decreases the reactivity of the aromatic system by decreasing the solvation of the transition state by the medium. However, even if this factor were significant it can hardly explain the relative rates observed here, for the rate ratios in Table 3 show that a related anomaly exists for comparisons within the series of open-chain and bridged ions. For the comparison of the compounds with $n = 3$ and $n = 2$, the rate ratio is, as outlined above, much greater for the open-chain series than for the bridged series. However, for the comparison of the compounds with $n = 2$ and $n = 1$, the reverse is true. The cause of this difference cannot lie in any special property of all the bridged compounds;

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* The classical inductive effect is usually represented[8] as decreasing exponentially with n: the field effect as decreasing (to a first approximation) inversely with the distance between the charges.

[8] G. E. K. Branch and M. Calvin, 'Theory of Organic Chemistry,' Prentice-Hall, New York, 1944, pp. 183 *et seq.*

[9] C. K. Ingold and I. S. Wilson, *J. Chem. Soc.*, 1927, 810.

it can and probably does lie in the unexpectedly low reactivity of the bridged ion with $n = 1$.

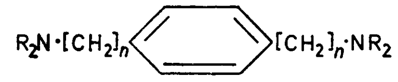
We have no completely satisfactory explanation of the low reactivity of this ion. The fact that the rate of nitration of monosubstituted [1] and 1,4-disubstituted ions containing the group $-CH_2\cdot{}^+NH_3$ is considerably reduced when the N–H hydrogens are replaced by methyl groups (compare the rate constants for plots G and H in the Figure) suggests that when $n = 1$ the deactivating effect of poles is very sensitive to the size of the molecular cavity. When $n = 2$, this effect is much less important. It is possible therefore that the increase in the size of the molecular cavity produced by bridging is particularly important for the ions with $n = 1$. It is also possible that the deactivating effect of a $-CH_2\cdot{}^+NR_3$ group is sensitive to the conformation of this group with respect to the ring; * this conformation is constrained in the bridged compound with the C–N bond approximately parallel to the axis of the *p*-orbitals of the ring. These points are under further investigation.

Comparison with Previous Work.—The main conclusions concerning the substituent effects of the groups $-[CH_2]_n\cdot{}^+NR_3$ in aromatic nitration are as follows. (*a*) For $n \geqslant 2$, the deactivation produced by a $-[CH_2]_n\cdot{}^+NR_3$ group relative to a methyl group comes mainly from the field effect of the nitrogen pole. The deactivation is more dependent on the distance of the nitrogen pole from the centre of the ring than on the number of carbon atoms in the methylene chain. (*b*) For $n = 1$, the overall deactivation is still mainly a field effect but there is a significant contribution from an additional mode of deactivation which could be either the inductive effect of the nitrogen pole operating through the methylene group or the effect of this pole on electron release (hyperconjugative or inductomeric) by the methylene group.

This evidence for the field effect of the nitrogen poles supports the simple electrostatic picture of those substituent effects previously given [3] for *meta*-substitution in monosubstituted benzenes. The work also accords with the evidence in the preceding paper on the dependence of these substituent effects on the conformation of the carbon chain. The work in that paper also provided evidence for some additional deactivation when $n = 1$ above that expected from the distance of the nitrogen pole from the centre of the ring. Since this referred to *meta*-substitution, it seems unlikely that the additional deactivation operates only by the effect of the pole on electron release from the methylene group.

The field effect of the nitrogen poles does not appear to discriminate markedly between the *meta*- and the *ortho–para*-positions. Thus a comparison of the rate profiles for nitration of toluene [6] and the ion [3] $Ph\cdot[CH_2]_3\cdot{}^+NMe_3$ shows that the latter is deactivated relative to toluene by a factor of *ca*. 8; however the percentage of *meta*-substitution in this ion (5%) [9] is little different from that for the nitration of toluene (3 ± 1%).[6] Hence, although the field effect of the nitrogen pole appears to be the major cause of the deactivation produced by substituents of the type $-[CH_2]_n\cdot{}^+NR_3$, it does not follow that the field effect of the nitrogen pole is the major factor in determining the orientation of substitution. As de la Mare has pointed out,[10] the orientation of substitution may be much more sensitive to the extent of hyperconjugative electron release from the C–H bonds since this type of interaction discriminates strongly between the *ortho–para*-positions and the *meta*-positions. Thus the electrostatic interpretation provided here and in previous papers [2,3] is not intended as a complete account of the substituent effects of $-[CH_2]_n\cdot{}^+NR_3$ groups.

EXPERIMENTAL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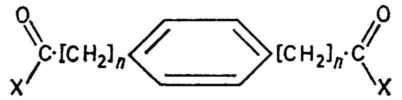
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Synthesis of the Open-chain Diamines (III).—The diamine (III; $n = 1$, R = H) was prepared as described by Lustig [11] and had m.p. 36 °C (lit.,[10] 35 °C). The partially methylated derivative (III; $n = 1$, NR_2 = NHMe) was prepared by the reaction of terephthalic acid dichloride with methylamine in dioxan followed by reduction of the diamide formed with excess of lithium aluminium hydride in dry tetrahydrofuran. The product had b.p. 127 °C at 15 mmHg (lit.,[12] 141 °C at 15 mmHg) and gave a dipicrate, m.p. 214 °C (lit.,[12] 216 °C). The diamine (III; $n = 2$, R = H) was prepared by the reduction [13] of *p*-phenylenediacetonitrile and had b.p. 139—140 °C at 3·5 mmHg. The diamine (III; $n = 3$, R = H) was prepared from the acid (IV; $n = 2$, X = OH) by treatment with thionyl chloride to give the dichloride (IV; $n = 2$, X = Cl), m.p. 50 °C, followed by reaction with ammonia to give the diamide (IV; $n = 2$, X = NH_2), m.p. 254—256°. This diamide was then reduced with lithium aluminium hydride in dry tetrahydrofuran to the diamine (III; $n = 3$, R = H), b.p. 114—115°, 0·8 mmHg. The diamine was analysed as the *dihydrochloride* (Found: C, 54·2; H, 8·2; N, 10·4. $C_{12}H_{22}Cl_2N_2$ requires C, 54·35; H, 8·4; N, 10·6%). The n.m.r. spectra of all the above diamines accorded with the stated structure.

The quaternary ion (I; $n = 3$, R = Me) was prepared from the diacid chloride (IV; $n = 2$, X = Cl) by reaction with dimethylamine to form the diamide (IV; $n = 2$, X = NMe_2), m.p. 120—121°, followed by reduction with excess of lithium aluminium hydride in tetrahydrofuran to form the diamine (III; $n = 3$, R = Me), b.p. 126 °C at 0·3 mmHg. This diamine was methylated with methyl iodide. The *diperchlorate* of (I; $n = 3$, R = Me) was prepared by the addition of a saturated solution of lithium

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* We owe this suggestion to Professor A. R. Katritzky.

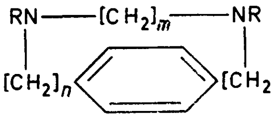
[10] P. B. D. de la Mare, in 'Rodd's Chemistry of Carbon Compounds,' Elsevier, Amsterdam, 1971, vol. IIIA, p. 45.

[11] F. Lustig, *Ber.*, 1895, **28**, 2986.

[12] M. Sander and D. Burmeister, *Chem. Ber.*, 1962, **95**, 964.

[13] P. Ruggli, H. Steiger, and P. Schobel, *Helv. Chim. Acta*, 1945, **28**, 333.

perchlorate to an aqueous solution of the iodide. The product, after two recrystallisations from aqueous perchloric acid, had m.p. 268—269 °C (Found: C, 45·3; H, 7·2; N, 5·8. $C_{18}H_{34}Cl_2N_2O_8$ requires C, 45·3; H, 7·2; N, 5·9%).



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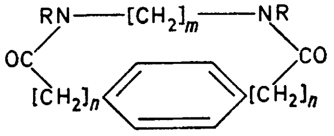

(VI)

$RHN\cdot[CH_2]_m\cdot NHR$ (VII)

Synthesis of the Bridged Diamines (V).—The bridged diamines were prepared by the reduction of the cyclic diamides (VI). These were prepared by the reaction [14] of the diacid chlorides (IV; X = Cl) with the diamines (VII). The diamide (VI; *n* = 0, *m* = 8, R = H) prepared in this way from the diacid chloride of terephthalic acid and octane-1,8-diamine. had m.p. 296—298 °C (lit.,[13] 290 °C). Reduction with lithium aluminium hydride in dry tetrahydrofuran gave the *diamine* (V; *n* = 1, *m* = 8, R = H), b.p. 156—158 °C at 0·3 mmHg (Found: C, 77·6; H, 10·5; N, 11·0. $C_{16}H_{28}N_2$ requires C, 78·0; H, 10·6; N, 11·4%). The mass spectrum showed a large parent peak at *m/e* 246 in accord with the expected formula.

The preparation of the bridged diamine (V; *n* = 2, *m* = 4, R = H) will be described in more detail since the corresponding cyclic amide is new. The diacid (IV; *n* = 1, X = OH) was refluxed with thionyl chloride for 5 h giving the diacid chloride (IV; *n* = 1, X = Cl) (m.p. 64—65 °C). A solution of this diacid chloride (15·3 g) in dry benzene (500 ml) and a solution of the diamine (VII; *m* = 4) (11·8 g) in dry benzene (500 ml) were added simultaneously and at constant rate to a well stirred volume of dry benzene (700 ml) during 5 h. The reaction was carried out under nitrogen at *ca.* 80 °C. After addition, the reaction mixture was heated under reflux for 40 min and then the hot solution was filtered. On cooling, the cyclic diamide (VI; *n* = 1, *m* = 4, R = H) crystallised out and a further portion was obtained by partial evaporation of the benzene. Recrystallisation from chlorobenzene gave 7·5 g of the *diamide,* m.p. 186—187 °C (Found: C, 68·2; H, 7·3; N, 11·0. $C_{14}H_{18}N_2O_2$ requires C, 68·25; H, 7·4; N, 11·4%).

Reduction of this diamide was carried out by the gradual addition of lithium aluminium hydride (6·0 g) to a stirred solution of the diamide (8 g) in dry tetrahydrofuran. After being heated under reflux for 19 h, the solvent was distilled off and the residue treated with wet ether (300 ml) and sufficient water to decompose the excess of lithium aluminium hydride. The ether layer was separated, dried ($MgSO_4$), and the ether evaporated. Distillation of the product, b.p. 130—131 °C at 0·3 mmHg, gave 4 g of the cyclic *diamine* (V; *n* = 2, *m* = 4, R = H) (Found: C, 76·2; H, 9·8; N, 12·5. $C_{14}H_{22}N_2$ requires C, 77·0; H, 10·2; N, 12·8%).

It was not found possible to obtain a completely satisfactory analysis of this diamine but the correctness of the structure is indicated by the mass spectrum, the n.m.r. spectrum, and the conversion into the perchlorate of the diquaternary ion (II; *n* = 2, *m* = 4, R = Me). The high-resolution mass spectrum of the diamine indicated a strong parent peak at 218·1794 ($C_{14}H_{22}N_2$ has *M*, 218·1783). The n.m.r. spectrum was as expected for the diamine except that the methylene protons on the carbon atoms α and β to the phenyl group gave a single peak. The addition of tris(dipivaloylmethanato)europium gave the expected [15] splitting into four peaks corresponding to four types of methylene proton. The reaction of the diamine with 4 equivalents of methyl iodide in alcoholic potassium hydroxide gave the diquaternary iodide and this was converted into the *perchlorate* of the diquaternary ion (II; *n* = 2, *m* = 4, R = Me) by the addition of an aqueous solution of the iodide to saturated sodium perchlorate. The product after recrystallisation from acetonitrile–ether had m.p. 254—255 °C (Found: C, 45·3; H, 6·7; N, 6·1. $C_{18}H_{32}Cl_2N_2O_8$ requires C, 45·5; H, 6·8; N, 5·9%).

The perchlorate of the related ion (II; *n* = 3, *m* = 2, R = Me) was prepared in a similar series of reactions starting with the diacid chloride (IV; *n* = 2, X = Cl) and the diamine (VII; *m* = 2, R = Me). The intermediate diamide (VI; *n* = 2, *m* = 2, R = Me), m.p. 185—186 °C was reduced to the diamine (V; *n* = 3, *m* = 2, R = Me), b.p. 125 °C at 0·3 mmHg, which was then methylated to the diquaternary iodide with excess of methyl iodide in ether. The diquaternary iodide was converted into the *perchlorate* of the ion (II; *n* = 2, *m* = 3, R = H) by treatment with lithium perchlorate in aqueous solution. The product after recrystallisation from ethanol and aqueous perchloric acid (30%) had m.p. 256 °C (Found: C, 45·3; H, 6·5; N, 6·0. $C_{18}H_{32}Cl_2N_2O_8$ requires C, 45·5; H, 6·8; N, 5·9%).

Nitrations.—The procedure for the kinetic studies closely followed that described previously [1] except that 100% nitric acid was used, freshly distilled before use. The nitrations were followed from the change in the optical density of diluted samples of the reaction mixture at *ca.* 270 nm. At this wavelength, the extinction coefficient of the aromatic substrate is 200—800 and that of the mono-nitro-product (calculated from the optical density after complete reaction) is *ca.* 5000. The protonated substrates were added as the perchlorate salts. The stability of the

TABLE 4

The nitration of the bridged ion (II; *n* = 2, *m* = 4, R = Me) in 80·2% sulphuric acid at 25 °C. Initial concentrations [aromatic substrate] = 2·90 × 10^{-3}, [nitric acid] = 2·61 × 10^{-3}

t/s	390	880	1830	2670	4520	8100
O.D.[a] (270 nm)	0·150	0·210	0·285	0·315	0·375	0·428
10^3x [b]	0·433	0·804	1·27	1·45	1·82	2·15
k_2/l mol^{-1} s^{-1}	0·168	0·169	0·169	0·164	0·160	0·164

[a] Optical density of diluted sample of reaction mixture.
[b] *x* = Concentration of nitro-compound in reaction mixture. For calculation see ref. 1. The extinction coefficients of the substrate and product were 800 and 4912 respectively.

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[14] H. Stetter, L. Marx-Moll, and H. Rutzen, *Chem. Ber.*, 1958, **91**, 1775.

[15] J. K. M. Sanders and D. H. Williams, *J. Amer. Chem. Soc.*, 1971, **93**, 641.

substrates in the concentrations of sulphuric acid used was checked from the n.m.r. spectra, no evidence of sulphonation or other side reactions being obtained during the periods involved in the nitration. The product from the nitration of the bridged ion (II; $n = 2$, $m = 4$, R = H) with a two-fold excess of nitric acid in 78% sulphuric acid was isolated by ether extraction from a diluted reaction mixture made alkaline with potassium hydroxide. The n.m.r. spectrum of the product in carbon tetrachloride was as expected for the mono-nitro-product, the pattern shown by the aromatic protons corresponding closely to that for the mononitro-derivative of *p*-xylene. The analysis of the crude product is largely consistent with the mononitro-compound although the nitrogen percentage is a little low (Found: C, 63·6; H, 8·3; N, 14·9. Calc. for $C_{14}H_{21}N_3O_2$: C, 63·8; H, 8·0; N, 15·95%). An example of a typical kinetic run is given in Table 4.

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