The Stabilities of Meisenheimer Complexes. Part XI.[1] The Effects of Ring-size on Spiro-complex Formation

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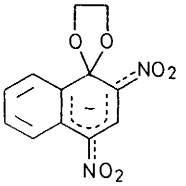
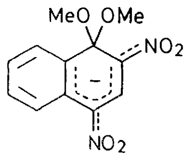
^1H N.m.r. measurements show that in dimethyl sulphoxide containing base 1-(3-hydroxypropoxy)- and 1-(4-hydroxybutoxy)-2,4-dinitronaphthalene cyclise to give spiro-Meisenheimer complexes containing respectively six- and seven-membered rings. Evidence is presented for a similar mode of action in water. Kinetic and equilibrium measurements are reported and compared with corresponding data for formation of the analogous complex containing a five-membered dioxolan ring. It is found that there is a dramatic decrease in complex stability on increasing the ring size from five to six or seven members. This reflects a large decrease in the rate of ring formation while the rates of ring opening are affected little by ring size.

SPIRO-MEISENHEIMER complexes are of current interest and have been used by Bernasconi and his co-workers[2] as models for the intermediates in nucleophilic aromatic substitution reactions. Our previous studies[3] have involved comparisons of the values of rate and equilibrium constants for formation of spiro-complexes with those for similarly activated 1,1-dimethoxy-complexes. We found, for example, in the 2,4-dinitronaphthyl system that the stability of (I) is considerably greater than that of (II). In general rates of formation of spiro-complexes are many orders of magnitude greater than those for their dimethoxy-analogues and also, perhaps surprisingly, rates of ring opening of the spiro-complexes are higher than rates of methoxide expulsion from the dimethoxy-complexes. A possible reason for this latter observation is relief of ring strain on opening of the spiro-complexes.[3,4]



(I)



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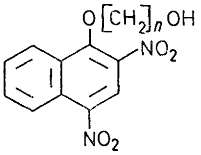
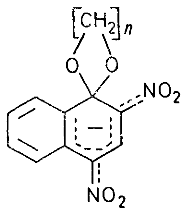


(III)



(IV)

So far all quantitative measurements have involved the formation of five-membered rings. In order to obtain more information regarding the factors affecting spiro-complex formation we have in the present work investigated the cyclisation of the ethers (III; $n = 3$ and 4) to give complexes (IV; $n = 3$ and 4) containing six- and seven-membered rings.

EXPERIMENTAL

1-(3-Hydroxypropoxy)-2,4-dinitronaphthalene was prepared by the reaction of 1-chloro-2,4-dinitronaphthalene with sodium 3-hydroxypropoxide in propane-1,3-diol. Recrystallisation from benzene–light petroleum yielded pale orange crystals, m.p. 95° (Found: C, 52.9; H, 4.1; N, 10.0. Calc. for $C_{13}H_{12}N_2O_6$: C, 53.4; H, 4.1; N, 9.6%). 1-(4-Hydroxybutoxy)-2,4-dinitronaphthalene was prepared similarly by the reaction of 1-chloro-2,4-dinitronaphthalene with sodium 4-hydroxybutoxide in butane-1,4-diol. Recrystallisation from benzene–light petroleum gave a pale yellow solid, m.p. 72° (Found: C, 55.5; H, 5.0; N, 8.6. Calc. for $C_{14}H_{14}N_2O_6$: C, 54.9; H, 4.6; N, 9.1%). 1-(2-Methoxyethoxy)-2,4-dinitronaphthalene was prepared from 1-chloro-2,4-dinitronaphthalene and the sodium salt of 2-methoxyethanol in the alcohol. Recrystallisation from benzene–light petroleum gave pale yellow crystals, m.p. 78°. Elemental analyses for these compounds were in satisfactory agreement with calculated values. The ^1H n.m.r. spectra, described later, were consistent with the proposed structures and indicated negligible proportions of impurities. Solvents and solutions of base were prepared and/or purified as before.[3]

^1H N.m.r. measurements were made at 20° with a Bruker HX90 instrument using tetramethylsilane as internal reference. U.v.–visible spectral measurements were made with Unicam SP 500 or 8000 instruments or with a 'Canterbury' stopped-flow spectrophotometer described previously.[3] The path-length of the measuring cell in the latter instrument was 2 mm. The rate constants associated with spiro-complex formation were determined by the stopped-flow method. Thus measurements were made at the absorption maxima of the coloured adducts, at which wavelengths the reactants were transparent. In all cases the base concentration was in large excess of the substrate concentration so that first-order kinetics were observed. Typical data are in Table 1. The baseline after completion of the initial colour-forming reaction was sufficiently stable to allow an 'infinity' value to be obtained. A slower reaction yielding 2,4-dinitronaphthol was also observed. Rate constants for this latter reaction in water were determined, using the SP 500 spectrophotometer, by measuring the increase with time of optical density at 430 nm. Measurements were made with both substrates (III; $n = 3$ and 4) at several sodium hydroxide concentrations. In each case the value of the second-order rate constant was found to be $(6 \pm 1) \times 10^{-2}\,l\,mol^{-1}\,s^{-1}$.

In addition to its use for kinetic measurements the

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[1] Part X, M. R. Crampton, *J.C.S. Perkin II*, 1975, 825.

[2] C. F. Bernasconi and R. H. de Rossi, *J. Org. Chem.*, 1973, **38**, 500; C. F. Bernasconi, R. H. de Rossi, and C. L. Gehriger, *ibid.*, p. 2838; C. F. Bernasconi and H. S. Cross, *ibid.*, 1974, **39**, 1054; C. F. Bernasconi and C. L. Gehriger, *J. Amer. Chem. Soc.*, 1974, **96**, 1092.

[3] M. R. Crampton, *J.C.S. Perkin II*, 1973, 2157; M. R. Crampton and M. J. Willison, *ibid.*, 1974, 1681, 1686.

[4] J. F. Bunnett, quoted in ref. 2.

stopped-flow spectrophotometer was used to determine equilibrium optical densities. Because of the ability to measure small voltage changes (1 part in 2×10^3) small values of optical density could be determined with better accuracy than with a normal spectrophotometer. The spectra of the red species initially produced from (III; $n = 3$ or 4) in aqueous sodium hydroxide were found to have maxima at 495 ± 2 nm.

TABLE 1

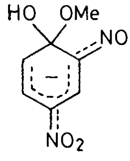
Reaction of 1-(3-hydroxypropoxy)-2,4-dinitronaphthalene (2.34×10^{-5}M) with sodium hydroxide (0.10M) in water at 25°. Measurements at 500 nm

t/s	Scale reading (arbitrary units)	k_{obs}/s^{-1}
0.20	2.77	1.04
0.40	3.35	1.05
0.60	3.78	1.02
0.80	4.17	1.03
1.00	4.46	1.02
1.20	4.73	1.04
1.40	4.93	1.04
1.60	5.10	1.04
1.80	5.20	1.02
∞	5.80	

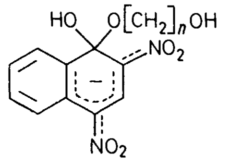
Measurements with 1-(2-methoxyethoxy)-2,4-dinitronaphthalene in aqueous base indicated the absence of a fast colour-forming reaction at 500 nm. Thus in solutions containing 10^{-5}M-substrate and 0.5M-sodium hydroxide the change in optical density at 500 nm was <0.001 (quoted for 1 cm cell). The assumption of a value for the extinction coefficient at this wavelength of 1.5×10^4 l mol^{-1} cm^{-1} allows an upper limit of 2×10^{-2} l mol^{-1} to be set for an equilibrium constant for complex formation. However we note that in media rich in dimethyl sulphoxide this substrate gives with base an initial orange colour which may signify hydroxide ion addition.

RESULTS AND DISCUSSION

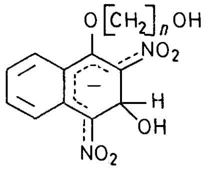
In the presence of dilute (<0.1M) aqueous sodium hydroxide both the parent ethers (III; $n = 3$ or 4) immediately gave a red colour. This was followed by the fairly fast formation of the yellow 2,4-dinitronaphthol, identified by the u.v.–visible spectrum[3] which showed maxima at 390 and 430 nm. In media containing dimethyl sulphoxide (DMSO) the initial red colour was more intense and faded less rapidly. We note that in a related system Hasegawa and Abe[5] have obtained evidence for the formation of (V) as an observable intermediate from 2,4-dinitroanisole and hydroxide ions in aqueous DMSO. We must therefore consider the possibility that the red colour we observe results not from spiro-complex formation but rather from hydroxide addition. The most likely adducts are (VI) or (VII). N.m.r. spectroscopy should be definitive in this context.[6] Measurements in water were precluded by the low solubility and fast decomposition of the substrate. However measurements in DMSO were more successful.



(V)

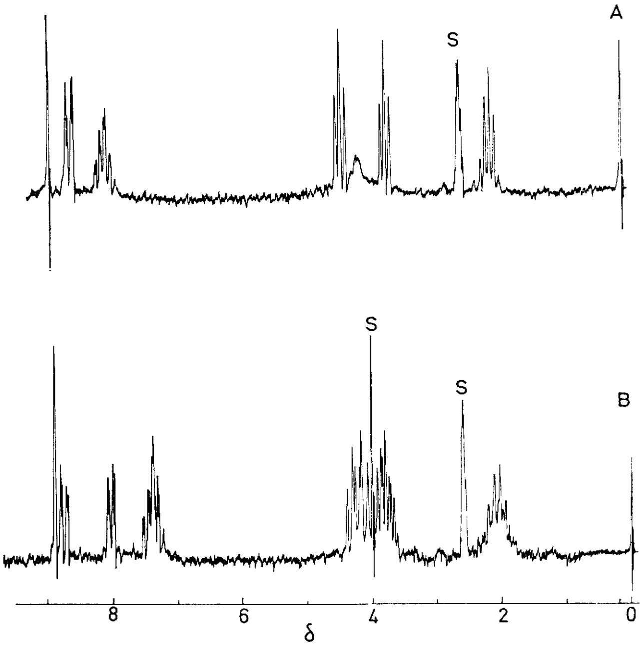


(VI)



(VII)

^{1}H *N.m.r. Spectra.*—The spectrum (Figure A) of 0.2M-1-(3-hydroxypropoxy)-2,4-dinitronaphthalene in [$^2H_6$]DMSO shows three sets of bands due to ring protons at δ 8.90 (s, H-3), 8.60 (dd, H-5 and -8), and 8.03 (m, H-6 and -7). These positions are close to those observed for other 2,4-dinitronaphthyl ethers.[3,7] The α-CH_2 absorbs at δ 4.40 (t, J 6.5 Hz), the β-CH_2 group at 2.08 (quintet, J 6.5 Hz), and the γ-CH_2 group at 3.70 (t, J 6 Hz), while the hydroxy-proton gives a broad band at δ 4.20.



A, ^{1}H n.m.r. spectrum of 0.2M-1-(3-hydroxypropoxy)-2,4-dinitronaphthalene in [$^2H_6$]DMSO. B, Spectrum after the addition of base. Bands marked ' S ' are due to solvent

On the addition of sodium deuterioxide in deuterium oxide the spectrum is that shown in Figure B. The aromatic ring protons now absorb at δ 8.92 (s, H-3), 8.77 (dd, H-8), 8.05 (dd, H-5), and 7.40 (m, H-6 and -7). The H-5—7 signals show the shifts to high field expected on formation of an anionic complex. The small shifts to low field on complex formation of the H-3 and -8 resonances are analogous to those observed previously in similar systems.[3,7] Of particular interest is the appearance of the bands due to methylene protons in the complex. These give two overlapping triplets at δ 4.26, two quartets at 3.81, and a multiplet at 2.08. The sharp band at δ 4.0 marked ' S ' in Figure B is due to

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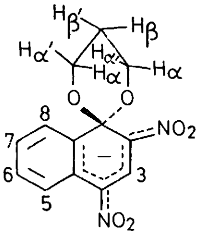
[5] Y. Hasegawa and T. Abe, *Chem. Letters*, 1972, 985; Y. Hasegawa, *Bull. Chem. Soc. Japan*, 1974, **47**, 2186.

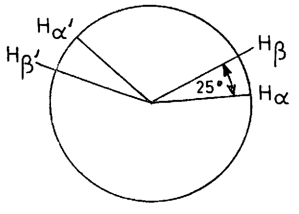
[6] M. R. Crampton, *Adv. Phys. Org. Chem.*, 1969, 211; M. J. Strauss, *Chem. Rev.*, 1970, 667.

[7] J. H. Fendler, E. J. Fendler, W. E. Byrne, and C. E. Griffin, *J. Org. Chem.*, 1968, **33**, 977, 4141.

rapidly exchanging hydroxylic protons in the solvent. Measurements at different base concentrations indicated that in Figure B no bands are obscured by this peak.



(VIII)



(IX)

The observed spectrum can be interpreted in terms of structure (VIII) in which the molecule is symmetrical about the plane of the naphthalene ring. The two equivalent protons labelled H_{α} are *cis* and the two equivalent protons labelled $H_{\alpha'}$ are *trans* to the 2-nitro-group. From the spectrum a value for $J_{\alpha\alpha'}$ of 11 Hz is obtained which is in the range expected for geminal coupling constants for methylene groups attached to oxygen in six-membered rings.[8] The values of vicinal coupling constants are $J_{\alpha\beta}$ 8, $J_{\alpha\beta'}$ 8, $J_{\alpha'\beta}$ 4, and $J_{\alpha'\beta'}$ 7.5 Hz. These values provide information on the conformation of the molecule. Vicinal coupling constants are usually large [8,9] when the dihedral angle ϕ is close to 0 and 180°, and small when ϕ is close to 90°. Hence the observed values are best described by a situation represented diagramatically in (IX) where the dihedral angle between H_{α} and H_{β} is 20—30°. It should however be noted that we cannot rule out the possibility that the observed spectrum represents the time-average of two or more conformations in rapid equilibrium. If this situation does prevail, the measured coupling constants are weighted averages. Confirmation of the assignment of n.m.r. parameters was provided by irradiation of the β- and β'-methylene protons at δ 2.08 when the expected pair of doublets (J 11 Hz) was observed for the α- and α'-methylene protons. The observed spectrum is not consistent with the alternative structures (VI) and (VII).

TABLE 2

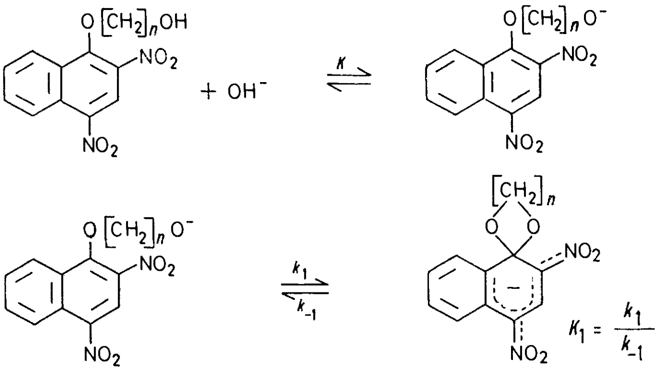
Kinetic and equilibrium data for spiro-complex formation from 1-(3-hydroxypropoxy)-2,4-dinitronaphthalene at 25°

Medium	[NaOH]/M	10^5[substrate]/M	k_{obs}/s^{-1}	O.D. (500 nm) [a]	K_c/l mol^{-1}
Water [b]	0.025	4.67	0.89 ± 0.02	0.020	1.3 [d]
	0.025 [c]	4.67	0.88		
	0.050	4.67	0.93	0.039	1.3
	0.075	4.67	0.99	0.056	1.3
	0.10	2.34	1.04	0.040	1.4
	0.15	2.34	1.12	0.056	1.4
80 : 20 (v/v) water–DMSO	0.012	4.4	0.32	0.060	8 [e]
	0.023	2.2	0.34	0.055	8
	0.047	2.2	0.41	0.100	8
	0.081	1.5	0.53	0.096	8
	0.110	1.2	0.60	0.087	8
60 : 40 (v/v) water–DMSO	0.012	1.0	0.185		
	0.024	1.0	0.30		
	0.050	1.0	0.56		
40 : 60 (v/v) water–DMSO	0.012	0.5	1.13		
	0.024	0.5	2.08		
	0.050	0.5	4.42		

[a] Values are quoted for cells of 1 cm pathlength. [b] Contains 0.5% DMSO from stock solution of substrate. [c] Containing 0.10M-sodium chloride. [d] Calculated for ε $(1.4 \pm 0.4) \times 10^4$ l mol^{-1} cm^{-1}. [e] Calculated for ε $(1.6 \pm 0.4) \times 10^4$ l mol^{-1} cm^{-1}.

The spectrum of the parent (III; $n = 4$) shows bands due to aromatic ring protons at positions very similar (±0.02 p.p.m.) to those observed for (III; $n = 3$). The α-CH_2 group absorbs at δ 4.32 (t, J 6 Hz), the β-CH_2 group at 1.98 (quintet, J 6 Hz), the γ-CH_2 group at 1.70 (quintet, J 6 Hz), and the δ-CH_2 group at 3.53 (t, J 6 Hz), while the hydroxy-proton gives a singlet at δ 4.35. The spectrum in the presence of base indicates cyclisation to give the spiro-complex (IV; $n = 4$) but provides less precise structural information than the spectrum of (IV; $n = 4$). Bands are observed due to aromatic protons at δ 8.90 (s, H-3), 8.73 (dd, H-8), 7.93 (dd, H-5), and 7.40 (m, H-6 and -7). The methylene protons α to the ring now give a multiplet at δ 3.85 and those β to the ring a band at δ 1.71.

Kinetic and Equilibrium Data.—Measurements made in water and in water–DMSO mixtures are reported in Tables 2 and 3. We will make the assumption, justified later, that in these media as in DMSO the initial colour forming reaction is spiro-complex formation. The probable mechanism [2,3] of complex formation in alkaline media, shown in the Scheme, involves a fast



SCHEME

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[8] A. A. Bothner-By, *Adv. Magnetic Resonance*, 1965, **1**, 195.

[9] M. Karplus, *J. Amer. Chem. Soc.*, 1963, **85**, 2870.

equilibrium transfer of the side-chain proton to base followed by slow internal cyclisation. As shown previously,[3] when the base concentration is in large excess of the substrate concentration the measured equilibrium constant K_c can be expressed as in equation (1) and the first-order rate constant for the attainment of equilibrium by equation (2).

$$K_c = KK_1/(1 + K[\mathrm{OH}^-]) \qquad (1)$$

$$k_{obs} = k_{-1} + k_1K[\mathrm{OH}^-]/(1 + K[\mathrm{OH}^-]) \qquad (2)$$

The parent molecules (III; $n = 3$ or 4) are unlikely[10] to have pK_a values much lower than 15, so that values of K will probably be less than 0.1 l mol^{-1}. Hence at the sodium hydroxide values used in the present work the values of the term $(1 + K[\mathrm{OH}^-])$ in equations (1) and (2) will be close to unity. Accordingly plots of k_{obs} *versus* base concentration were linear and yielded values of k_{-1} (intercept) and k_1K (slope). Combination of these data gave values of KK_1 (kinetic). In water the values of k_{-1} obtained are of good accuracy although because of the smallness of the slopes, particularly for formation of the seven-membered ring, values of k_1K are less good. As the proportion of DMSO is increased the accuracy of k_1K increases while that of k_{-1}, whose values approach zero, decreases.

TABLE 3

Kinetic and equilibrium data for spiro-complex formation from 1-(4-hydroxybutoxy)-2,4-dinitronaphthalene at 25°

Medium	[NaOH]/M	10^5[Substrate]/M	k_{obs}/s^{-1}	O.D. (500 nm) [a]	K_c/l mol^{-1}
Water [b]	0.075	4.4	0.68 ± 0.02	0.019	0.5 [c]
	0.10	4.4	0.70	0.026	0.5
	0.125	4.4	0.72	0.032	0.5
	0.15	4.4	0.73	0.037	0.5
	0.20	4.4	0.76	0.048	0.5
80 : 20 (v/v) water–DMSO	0.037	3.3	0.34	0.040	2.5 [d]
	0.055	6.5	0.37	0.125	2.5
	0.073	3.3	0.38	0.079	2.5
	0.092	3.3	0.41	0.095	2.5
	0.110	3.3	0.43	0.108	2.5
60 : 40 (v/v) water–DMSO	0.015	1.63	0.14	0.086	30 [e]
	0.037	1.63	0.22	0.145	30
	0.055	0.82	0.28	0.090	30
	0.092	0.82	0.42		

[a] Values are quoted for cells of 1 cm pathlength. [b] Contains 0.5% DMSO from stock solution of substrate. [c] Calculated for ε $(1.3 \pm 0.3) \times 10^4$ l mol^{-1} cm^{-1}. [d] ε $(1.5 \pm 0.3) \times 10^4$ l mol^{-1} cm^{-1}. [e] ε $(1.8 \pm 0.3) \times 10^4$ l mol^{-1} cm^{-1}.

TABLE 4

Variation of rate and equilibrium constants with solvent composition

		Water	80 : 20 (v/v) Water–DMSO	60 : 40 (v/v) Water–DMSO	40 : 60 (v/v) Water–DMSO
(IV; $n = 3$)	k_{-1}/s^{-1}	0.85 ± 0.2	0.28 ± 0.02	0.07 ± 0.01	
	k_1K/l mol^{-1} s^{-1}	1.7 ± 0.3	2.9 ± 0.3	10 ± 1	90 ± 5
	K_1K(kinetic)/l mol^{-1}	2.0 ± 0.5	10 ± 2	140 ± 30	
	K_1K(equil)/l mol^{-1}	1.3 ± 0.4	8 ± 2		
(IV; $n = 4$)	k_{-1}/s^{-1}	0.64 ± 0.04	0.30 ± 0.02	0.09 ± 0.01	
	k_1K/l mol^{-1} s^{-1}	0.6 ± 0.3	1.2 ± 0.1	3.5 ± 0.3	
	K_1K(kinetic)/l mol^{-1}	0.9 ± 0.5	4 ± 0.5	40 ± 5	
	K_1K(equil)/l mol^{-1}	0.5 ± 0.2	2.5 ± 1	30 ± 5	

An alternative approach to the calculation of K_c values, and hence KK_1, is afforded by the use of stopped-flow spectrophotometry to measure values of optical density after completion of the initial colour-forming reaction but before appreciable decomposition to 2,4-dinitronaphthol has occurred. Such values measured at the absorption maxima are in Tables 2 and 3. Unfortunately these measurements do not yield values for the extinction coefficients of the complexes in water since Benesi–Hildebrand plots[11] have intercepts close to zero. However in media rich in DMSO conversion into complex was complete so that extinction coefficients could be obtained directly. For example for (IV; $n = 3$) in 80% DMSO, $\lambda_{max.} = 508$ nm (ε 2.7×10^4 l mol^{-1} cm^{-1}). By analogy with previous results[3] values of ε will decrease with increasing proportion of water in the solvent. Extrapolation, as before,[3] of data obtained in water–DMSO mixtures gave the values of ε quoted in Tables 2 and 3. The necessarily high uncertainty associated with these values leads to the high error limits given for the calculated values of KK_1 (equilibrium). The data collected in Table 4 show that the agreement between KK_1 values determined kinetically and spectrophotometrically is not particularly good. This may indicate that the values used for ε are too high, or that measured values of k_1K are too high.

As expected[6] values of the equilibrium constants, KK_1, increase as the proportion of DMSO in the solvent is increased. These changes reflect increases in the values of rate constants for complex formation and

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[10] J. Murto, ' Chemistry of the Hydroxyl Group,' Interscience, New York, 1971, part 2, p. 1087.

[11] H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71**, 2703.

decreases in values of the rate constant for ring opening. Similar solvent effects have been observed with other spiro-complexes and the causes discussed.[2] We note that the steady change in values of the parameters with solvent composition is a strong argument that the mode of interaction does not change with solvent.

Evidence for Spiro-complex Formation in Water.—By use of stopped-flow spectrophotometry it was possible to determine the visible spectra of the initial complexes in water. The position of the absorption maxima, at 495 nm, is precisely the same as that for the spiro-complex (I). Addition at C-3, *ortho* to two nitro-groups, would be expected [6] to give rise to absorption at longer wavelengths. Thus hydroxide addition at C-3, to give (VII), or internal attack of the side-chain at C-3 are rendered unlikely. However by analogy with the dimethoxy-complex (II), where $\lambda_{\text{max.}}$ is 498 nm,[12] the adduct (VI) might be expected to show absorption at 495 nm. Further, this structure, (VI), is almost certain to be an intermediate in the substitution reaction leading to the reaction product, 2,4-dinitronaphthol. If the assumption is made that the data in Table 4 refer to formation of the adducts (VI; $n = 3$ or 4), then the knowledge that the second-order rate constants for nucleophilic displacement in water have values of $(6 \pm 1) \times 10^{-2}$ l mol^{-1} s^{-1} leads to the conclusion that expulsion of hydroxide from (VI) is faster than expulsion of alkoxide by at least an order of magnitude. Such a marked reversal of normal leaving-group tendencies [13] makes this hypothesis unattractive. Further evidence that the observed colour is unlikely to be due to (VI) comes from measurements with 1-(2-methoxyethoxy)-2,4-dinitronaphthalene. This compound which is structurally similar to the substrates under investigation but where spiro-complex formation is not possible hydrolyses in aqueous base without formation of an observable intermediate

Effects of Ring-size on Spiro-complex Formation.—The results in Table 5 show that there is a very large decrease in stability on increasing the ring-size from five to six or seven members. This decrease reflects large changes in values of the rate constants for spiro-complex formation while values of the rate constant for ring opening are little affected by ring-size. Some decrease in the values of the equilibrium constant K governing proton loss from the side-chain might be expected as the number of methylene groups increases due to attenuation of inductive effects. However the pK_a values for ethane-1,2-, propane-1,3-, and butane-1,4-diol are reported to be equal.[10] A further possible reason for variations in the values of K might be differential stabilisation of the parent alcohols (III) by intramolecular hydrogen bonding to the 2-nitro-group. However there seems to be no compelling reason why such stabilisation should increase with increasing chain length. The main differences are, then, likely to be connected with the internal cyclisation step. The present observation that the rate of cyclisation falls dramatically on going from (III; $n = 2$) to (III; $n = 3$) has analogy with kinetic studies involving neighbouring-group participation.[14] For example measurements with halogenohydrin anions, Cl[CH$_2$]$_m$O$^-$, indicate that the rate of cyclisation decreases by 10^3 on going from $m = 4$ (five-membered ring) to $m = 5$ (six-membered ring). One important factor is likely to be the loss of rotational freedom of the side-chain on ring-formation. This will lead to an increasingly unfavourable entropy loss as the chain length increases. The effects of ring-size on ring-strain are less easy to predict. Formation of the five-membered ring in the spiro-complex (IV; $n = 2$) involves eclipsing interactions between adjacent methylene hydrogens.[3,4] However a model indicates that little deformation of bond-angles is required so that this may not be a particularly strained structure. The proposed structure (VIII) for the six-membered ring involves some expansion of bond angles, and unfavourable interactions between adjacent hydrogen atoms are still present. It may be that in this system the seven-membered ring of (IV; $n = 4$) is less strained than the six-membered ring. A decrease in ring strain working in opposition to the expected increase in entropy loss would provide an explanation for the unexpectedly similar stabilities of (IV; $n = 3$) and (IV; $n = 4$). There is a further factor which may lead to a decrease in complex stability when $n = 3$ or 4 relative to $n = 2$. Thus increasing steric bulk at the 1-position in the spiro-complexes may unfavourably affect the 2-nitro-group both by causing its rotation from the ring plane, leading to a decrease in conjugation, and by inhibition of its solvation.

TABLE 5

Equilibrium and rate data for spiro-complex formation in water at 25°

	KK_1/l mol^{-1}	k_1K/l mol^{-1} s^{-1}	k_{-1}/s^{-1}
(IV; $n = 2$) [a]	3×10^4	9×10^4	2.3
(IV; $n = 3$)	1.7 [b]	1.7	0.85
(IV; $n = 4$)	0.7 [b]	0.6	0.64

[a] Data from ref. 3. [b] Average from kinetic and spectrophotometric measurements.

The similarity of k_{-1} values in Table 5 probably indicates that most of the entropy loss and ring strain connected with cyclisation is already present in the transition state for ring formation. Thus the argument used previously [3] that the high rates of ring opening of spiro-complexes relative to their 1,1-dimethoxy-analogues derives from the relief of ring strain is probably not justified. An alternative explanation * may be found in terms of the conformational differences about C–O bonds in the two types of complex. Thus the preferred conformation of the 1,1-dimethoxy-complex

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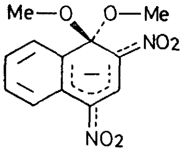
* We thank a referee for this suggestion.

[12] M. R. Crampton and H. A. Khan, *J.C.S. Perkin II*, 1972, 2286.

[13] C. F. Bernasconi and R. G. Bergstrom, *J. Org. Chem.*, 1971, **36**, 1325.

[14] B. Capon, *Quart. Rev.*, 1964, **18**, 45, and references therein.

will be (X) in which there is considerably more conformational freedom about C–O bonds than in the spirocomplexes. Much of this freedom may well be lost on passage to the transition state for C–O bond breaking; hence the lower rate of C–O bond breaking. The increasing demand for *p*–π overlap in the unbroken C–O bond could be important as could ion–dipole interaction.



(X)

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