Rates of Tritium Exchange in a series of *N*-Phenyl Substituted Pyrroles

John R. Jones, [a] **Stephen Hunt,**[a] **François Terrier**[b] **and Erwin Buncel**[c]
[a] *Chemistry Department, University of Surrey, Guildford, Surrey GU2 5XH, UK*
[b] *ENSCP, Physicochimie des Solutions, 11 rue Curie, F-75231 Paris 05, France*
[c] *Department of Chemistry, Queens University, Kingston, Canada K7L 3N6*

Rate constants $k_{\text{exch}}^{\text{H}_3\text{O}^+}$ for the H^+-catalysed protiodetritiation of a number of *N*-phenyl substituted 2,5-dimethyl-3,4-[$^3\text{H}_2$]pyrroles have been measured in aqueous solution. For the series of *N*-(*para*-X-phenyl substituted) derivatives studied (**1a–h**), the rate constants are found to obey a satisfactory linear Hammett relationship with a negative reaction constant ρ of -0.90. The low ρ value is attributed to reduced transmission of the electronic influence of the X substituent caused by steric hindrance to conjugation between the phenyl and pyrrole rings. While decreasing the thermodynamic basicity at β-C of the pyrrole ring, *ortho*-dimethylation of the phenyl ring increases appreciably the rate of exchange, consistent with the idea that the resulting tetramethyl-substituted pyrrolium cation but not the transition state of reaction, is subject to inhibition of solvation of positive charge which develops on the nitrogen atom. Methoxy substitution of the phenyl ring gives results which reflect a balance between the opposite resonance and inductive effects of the OCH_3 group, as well as steric effects around the methoxy-bearing positions.

Pyrrole and indole derivatives are part of a relatively small group of aza-aromatic compounds which undergo exclusive protonation at carbon.[1,2] In recent years, much effort has been devoted to obtain mechanistic information on this process, commonly regarded as a model for the addition step of $\text{S}_\text{E}\text{Ar}$ electrophilic aromatic substitution.[3] However, the formation of most pyrrolium and indolium cations occurs only in strongly acidic media,[4–8] where the rates for the equilibrium formation of these σ-adducts have generally proven to be inaccessible by conventional kinetic techniques. Only in the case of 3-ethyl-2,4-dimethylpyrrole (kryptopyrrole), 1,2,5-trimethylpyrrole and 3,4-dimethylpyrrole, which are among the most basic pyrroles known, could a direct kinetic study of the *C*-protonation process be made by using stopped-flow spectrophotometry.[9,10] Accordingly, data on the protonation of pyrroles and indoles are most often obtainable only through tritium or deuterium isotope exchange in acid media.[7,8,11,12] The situation is reminiscent of that which prevails for *C*-protonation of benzenoid compounds.[13–15] Here, direct kinetic studies have so far been restricted to the pioneering NMR investigation by Kresge of the protonation of 1,3,5-trimethyoxybenzene[16] and the recent stopped-flow work by Knoche on the protonation of various 1,3,5-tris(*N*,*N*-dialkylamino)benzenes.[17] A direct kinetic study of the *C*-protonation of guaiazulene (1,4-dimethyl-7-isopropylazulene) was also successful.[18]

Considering tritium or deuterium isotopic exchanges, these processes occur as described in eqn. (1), with the second-order rate constant, k_{exch}, being derived on the assumption that the intermediate σ-complex is a low concentration, 'steady-state', intermediate, eqn. (2).

$$\text{ArL} + \text{HA} \underset{k_{-1}^{\text{H}}}{\overset{k_1^{\text{HA}}}{\rightleftharpoons}} [\text{L–Ar–H}]^+ + \text{A}^- \xrightleftharpoons{k_{-1}^{\text{L}}} \text{ArH} + \text{LA} \qquad (1)$$

$$k_{\text{exch}} = \frac{k_1^{\text{HA}}}{1 + k_{-1}^{\text{H}}/k_{-1}^{\text{L}}} \qquad (2)$$

Interestingly, the $k_{-1}^{\text{H}}/k_{-1}^{\text{L}}$ ratios have been shown to be rather insensitive to the structure and basicity of the parent aromatic or heteroaromatic substrate, having average values of 18 and 6.5 in detritiation and dedeuteriation experiments, respectively.[9,11,13,18,19] Using these values, the rate constants $k^{\text{H}_3\text{O}^+}$ for carbon protonation can be readily evaluated, allowing useful comparisons of the reactivity of the hydronium ion and other general acid catalysts with other electrophiles which can be involved in $\text{S}_\text{E}\text{Ar}$ substitutions of aromatic and heteroaromatic substrates, *e.g.* benzenediazonium cations.[9,10]

Even though rate exchange data are available for unsubstituted pyrrole and some simple alkyl derivatives,[7,8,12,20] *C*-protonation studies in the pyrrole series remain relatively scarce compared to those in the indole series. This is essentially because investigation of pyrroles is hampered by their high susceptibility to aerial oxidation as well as polymerization in acid solutions.[1] In this respect, an *N*-phenyl substituent can render the pyrrole ring less reactive, thus reducing the importance of the above side reactions.

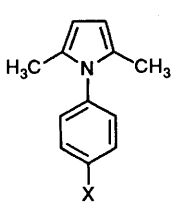
In connection with our studies of structure–reactivity relationships in electrophilic aromatic substitutions of pyrroles,[21–23] it appeared to us that a study of the detritiation of a homogeneous series of *N*-phenyl substituted pyrroles was particularly desirable. Such substrates have recently proven to be interesting compounds, being prone to polymerization under some experimental conditions to give polypyrrole films whose electrical properties are related to the electronic character of the substituents in the phenyl ring of the monomers.[24,25] The present work reports the results of a study of the detritiation of a series of *N*-phenyl substituted 2,5-dimethyl pyrroles **1a–n** in dilute aqueous hydrochloric acid media. Some additional pyrroles (**1o–r**) bearing benzyl, pyridinyl and morpholino substituents on the pyrrole nitrogen have also been examined and the results are reported herein.

Results and Discussion

Table 1 summarizes the second-order rate constants, $k_{\text{exch}}^{\text{H}_3\text{O}^+}$, measured for the hydronium ion catalysed protiodetritiation of the various *N*-phenyl substituted 2,5-dimethylpyrroles studied. For the series of *para*-substituted *N*-phenyl derivatives **1a–1h** the rate constant $k_{\text{exch}}^{\text{H}_3\text{O}^+}$ increases regularly on going from the most electron-withdrawing (NO_2) to the most electron-releasing (OCH_3) group. The Hammett relationship obtained by plotting the log $k_{\text{exch}}^{\text{H}_3\text{O}^+}$ values *versus* the substituent constants σ_p°

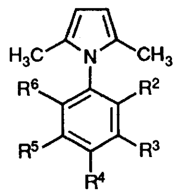
Table 1 Second-order rate constants $k_{exch}^{H_3O^+}$ for the protiodetritiation of *N*-phenyl substituted 2,5-dimethylpyrroles **1a–n** in aqueous solution at 25 °C

Substituent(s) in the phenyl ring	Pyrrole	$k_{exch}^{H_3O^+}$/ $dm^3\ mol^{-1}\ s^{-1}$	Substituent(s) in the phenyl ring	Pyrrole	$k_{exch}^{H_3O^+}$/ $cm^3\ mol^{-1}\ s^{-1}$
4-NO_2	**1a**	0.53	4-OCH_3	**1h**	4.48
4-CN	**1b**	0.72	2,4-Di-CH_3	**1i**	6.48
4-CF_3	**1c**	1.07	2,6-Di-CH_3	**1j**	6.60
4-$COCH_3$	**1d**	0.99	2,4,6-Tri-CH_3	**1k**	7.89
4-Br	**1e**	1.89	2,4-Di-OCH_3	**1l**	4.77
None (4-H)	**1f**	2.55	3,5-Di-OCH_3	**1m**	2.72
4-CH_3	**1g**	4.29	3,4,5-Tri-OCH_3	**1n**	2.54



1

a X = NO_2
b X = CN
c X = CF_3
d X = $COCH_3$
e X = Br
f X = H
g X = CH_3
h X = OCH_3



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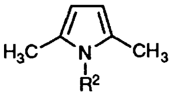
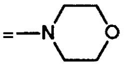
i $R^2 = R^4 = CH_3$, $R^3 = R^5 = R^6 = H$
j $R^2 = R^6 = CH_3$, $R^3 = R^4 = R^5 = H$
k $R^2 = R^4 = R^6 = CH_3$, $R^3 = R^5 = H$
l $R^2 = R^4 = OCH_3$, $R^3 = R^5 = R^6 = H$
m $R^3 = R^5 = OCH_3$, $R^2 = R^4 = R^6 = H$
n $R^3 = R^4 = R^5 = OCH_3$, $R^2 = R^6 = H$



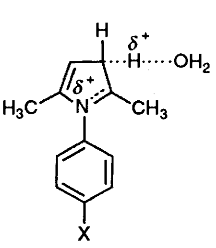
1

o $R^2 = CH_3$
p $R^2 = CH_2–C_6H_5$
q R^2 = 4-pyridinyl
r R^2 =

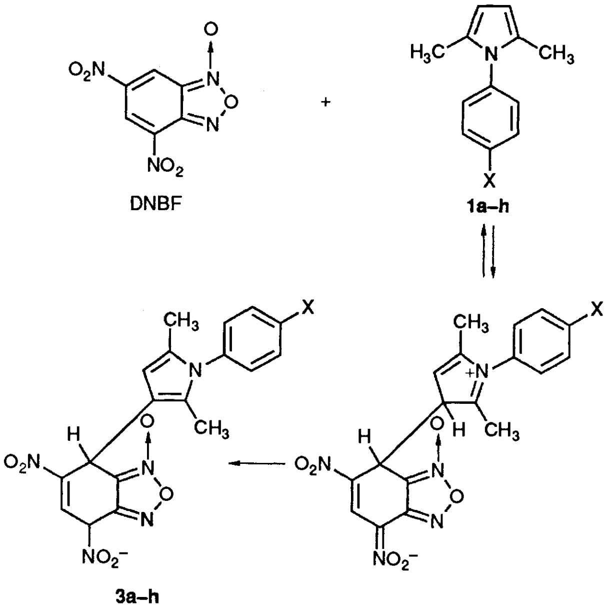


is satisfactorily linear with a reaction constant, $\rho = -0.90 \pm 0.1$.[26] It is clear from the similarity of the measured $k_{exch}^{H_3O^+}$ values of the *p*-OMe and *p*-Me derivatives, that a correlation based on σ_p^+ or even the classical Hammett σ_p substituent constants can readily be eliminated.

While the negative ρ is consistent with the expected development of a partial positive charge on the pyrrole nitrogen in the transition state of the reactions,[4,9,14] as shown in **2**, the absolute value of ρ is remarkably low. In this regard, it is of interest to recall that the two α-methyl groups have been shown to prevent the coplanarity of the phenyl and pyrrole rings in 2,5-dimethyl-1-phenylpyrrole **1f**, thereby reducing the interannular conjugation to a considerable extent in this derivative.[27,28] It thus appears reasonable to assume that the low ρ value associated with protiodetritiation of the series **1a–h**, is more the reflection of the fact that the transmission of electronic influence of the X substituent to the β position *via* the C–N bond occurs largely through a π-inductive interaction, than a reflection of the remoteness of this substituent from β-C. Interestingly, a ρ value of similar order of magnitude ($\rho = -1.02$) has been found for the rate-determining addition of 4,6-dinitrobenzofuroxan (DNBF)—a very powerful neutral electrophile—to the β position of **1a–h**, to give the *C*-adducts **3a–h** in methanol, eqn. (3).[23]

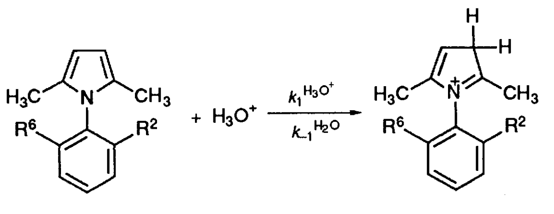


2



(3)

The changes in the rates of protiodetritiation brought about by the introduction of various methyl groups in the phenyl ring of 2,5-dimethyl-1-phenylpyrrole, **1f**, are worthy of comment. As can be seen from Table 1, the introduction of more methyl groups, either in the *ortho* or *para* positions, has the effect of further increasing the rate of detritiation at β-C. This is clearly consistent with the additivity of inductive (+I) effects exerted by these methyl groups. Contrasting with the changes in $k_{exch}^{H_3O^+}$, however, it has been reported that the introduction of two *ortho* methyl groups in **1f**, to give **1j**, has the effect of decreasing the thermodynamic basicity by 0.6 p*K* unit.[27] Inasmuch as the observed 2.5 increase in $k_{exch}^{H_3O^+}$ is necessarily the reflection of an increase in the protonation rate at β-C [$k_1^{H_3O^+}$ in eqn. (4)], the observed four-fold decrease in the K_a value ($pK_a = -\log k_{-1}^{H_2O}/k_1^{H_3O^+}$) for the equilibrium (4) on going from **1f** to **1j**, implies that the presence of the two *ortho* methyl groups in **1k** results in a significant increase (10-fold) in the rate constant $k_{-1}^{H_2O}$ for deprotonation of the resulting pyrrolium cation **4j** by solvent. This conclusion agrees with the explanation previously suggested to account for the observed decrease in the thermodynamic basicity at β-C, *i.e.*, the 2,5-dimethyl-1-(2,6-xylyl)pyr-



(4)

1f $R^2 = R^6 = H$

1j $R^2 = R^6 = CH_3$

4f

4j

Table 2 Second-order rate constants $k_{exch}^{H_3O^+}$ for the protiodetritiation of various *N*-substituted 2,5-dimethylpyrroles in aqueous solution at 25 °C

N-Substituent	Pyrrole	$k_{exch}^{H_3O^+}$ / dm^3 mol^{-1} s^{-1}
Methyl	**1o**	52
Phenyl	**1f**	2.55
Benzyl	**1p**	13.8
Pyridinyl	**1q**	4.9×10^{-3}
Morpholino	**1r**	4.4

rolium cation **4j** but not the 2,5-dimethyl-1-phenylpyrrolium cation **4f**, is subject to inhibition of solvation of the positive charge located on the nitrogen atom.[27] The increase in $k_{exch}^{H_3O^+}$ in the present work suggests, in turn, that the transition state of the reaction is much closer to the reactants than to the resulting cation.

Methoxy substitution in the phenyl ring of **1f** gives results which reflect the balance between the opposite resonance and inductive electronic effects of the OCH_3 group, as well as steric effects around the methoxy-bearing positions. As discussed above, the rate of tritium exchange is markedly increased on going from the *N*-phenyl to the *N*-*p*-methoxyphenyl derivative, in agreement with the expected contribution of the mesomeric (+M) effect of the *para*-methoxy group to stabilization of the developing positive nitrogen centre in the transition state.

Contrasting with this behaviour, the introduction of a second methoxy group in the *ortho* position of the phenyl ring, to form the *N*-(2,4-dimethoxyphenyl)-substituted compound **1l**, has essentially no effect on the rate of detritiation. This result suggests that full coplanarity of the *ortho* substituent with the phenyl ring cannot be reached in **1l** due to the presence of the two α-methyl substituents in the pyrrole ring. The + M effect of the *ortho*-methoxy group would thus be reduced to such an extent that it will just balance the opposite inductive (−I) effect, accounting for the absence of change in $k_{exch}^{H_3O^+}$.

On the other hand, the rate of detritiation of *N*-(3,5-dimethoxyphenyl)-2,5-dimethylpyrrole, **1m**, ($k_{exch}^{H_3O^+} = 2.72$ dm^3 mol^{-1} s^{-1}), is almost the same as that of the parent unsubstituted 2,5-dimethyl-*N*-phenylpyrrole **1f** ($k_{exch}^{H_3O^+} = 2.51$ dm^3 mol^{-1} s^{-1}). This tends to indicate that the inductive effects of these two *meta*-methoxy groups are operating too far from the C–N bond to destabilize the transition state.

Interestingly, the $k_{exch}^{H_3O^+}$ rate constant for the *N*-(3,4,5-trimethoxyphenyl)-substituted pyrrole **1n** equals that of the parent **1f** ($k_{exch}^{H_3O^+} = 2.54$ dm^3 mol^{-1} s^{-1}). A reasonable explanation of this result seems to be that the steric interactions between the three methoxy groups prevent conjugation of the *para* methoxy group with the phenyl ring. Again, the reduced +M effect would approximately balance the inductive −I effects of the three methoxy substitutents.

The rate data reported for the various *N*-substituted 2,5-dimethylpyrroles listed in Table 2 reflect nicely the intrinsic electronic properties of the substituents. The 20-fold decrease in $k_{exch}^{H_3O^+}$ observed on substituting the 1-methyl group of 1,2,5-trimethylpyrrole (**1o**) for a phenyl group (**1f**), parallels the 2.5 p*K* unit decrease in the *C*-basicity of the β position of the pyrrole ring brought about by this substitution.[4a,27] Replacing the phenyl group by a 4-pyridinyl ring causes a 520-fold decrease in the rate of detritiation which can be readily accounted for in terms of protonation at the nitrogen atom of this heterocyclic moiety at the pH used for our tritium exchange experiments. The reactive pyrrole substrate must therefore be viewed as a 1-(4-pyridinium) substituted 2,5-dimethylpyrrole cation rather than a 2,5-dimethyl-1-(4-pyridinyl)pyrrole. Finally, the rate constant $k_{exch}^{H_3O^+}$ for the *N*-benzyl substituted pyrrole **1p** appears to be intermediate between those for the *N*-phenyl and *N*-methyl derivatives, as could reasonably be expected.

In conclusion, the present results clearly show that the susceptibility of the pyrrole ring to electrophilic attack is influenced by substituents on the *N*-phenyl moiety. However, it is also a significant characteristic feature that the transmission of the electronic effect from the substituted phenyl ring is strongly attenuated as a result of steric hindrance to conjugation between the phenyl and pyrrole rings caused by the 2,5-dimethyl substituents of the pyrrole ring.

Experimental

Materials.—1-(4-Acetylphenyl)-2,5-dimethylpyrrole (**1d**) and 2,5-dimethyl-1-phenylpyrrole (**1f**) were obtained from Lancaster Synthesis and recrystallised twice from methanol before use. A sample of 1,2,5-trimethylpyrrole (**1o**) was obtained from Aldrich and distilled under nitrogen before use. All other substrates were prepared by means of a Paal–Knorr type condensation reaction of hexane-2,5-dione with the appropriate amine, as described by Bruekelman *et al.*[29]

Tritiation Procedure.—Typically substrate (20 mg) was placed in a thick-walled glass tube, together with tritiated water (1–3 mm^3, 50 Ci cm^{-3}; 50–150 mCi) and *ca.* 1 mm^3 1 mol dm^{-3} aq. HCl. The tube was then evacuated, flame-sealed and immersed in an oil bath at 90 °C for 2–3 h. An exception was **1a**, the nitro-derivative which was labelled at 150 °C.

1,2,5-Trimethylpyrrole was labelled at room temperature by adding 3 mm^3 of 50 Ci cm^{-3} HTO to a solution of 0.1 g of the pyrrole in 0.5 cm^3 of dioxane.

The labelled pyrroles were extracted by partitioning the reaction mixtures between *ca.* 10 cm^3 of diethyl ether and 5 cm^3 of aq. sodium hydrogencarbonate. The ether layer was removed and the aqueous layer was extracted with further portions of ether. Combined ether extracts were washed with water (3 × 10 cm^3) and dried over anhydrous $MgSO_4$. The solvent was then removed by a stream of N_2, to leave the labelled pyrrole. Specific activities were in the range 10–80 mCi mmol^{-1}.

^{3}H NMR Analysis.—^{3}H NMR spectroscopy was used throughout this work to verify the position of the label and the radiochemical purity of the products. Solutions of the labelled pyrroles were prepared in [$^2H_6$]DMSO to contain typically 0.5–2 mCi, so that ^{3}H NMR signals could be obtained in a few hours. The ^{1}H spectra of the tritiated materials were indicative of negligible decomposition during the labelling process. The ^{3}H spectra showed labelling to have occurred exclusively at the pyrrole β-positions. The only exception was 1-(3′,5′-dimethoxyphenyl)-2,5-dimethylpyrrole, the ^{3}H spectrum of which showed 1–2% of the tritium to be in the 4 position of the phenyl ring.

Kinetic Procedure.—Rates of detritiation were measured using the standard technique of quenching portions of the reaction mixture at timed intervals, extracting into a scintillant and assessing the radioactivity present in each extract by liquid scintillation counting. All measurements were made at 25.0 ± 0.1 °C. Owing to the low solubility of 2,5-dimethyl-*N*-phenylpyrroles in water, stock solutions had to be prepared by adding a few milligrams of the labelled compound to *ca.* 1 dm^3 of boiled-out, deionised water. Kinetic runs were then initiated by mixing portions of stock solution with portions of aqueous hydrochloric acid, both of which had been pre-equilibrated at 25 °C. Typically, 10–12 samples were taken, intervals being chosen so that 90% or more of the reaction was monitored. Samples were partitioned between scintillator solution (3.4 g dm^{-3} 2,5-diphenyloxazole in toluene) and aqueous sodium hydrogencarbonate solution. Toluene extracts were removed, dried and assayed for tritium using a Beckman LS 1800 scintillation counter.

Plots of ln (radioactivity) *versus* time were linear and rate constants were determined graphically.

Runs were performed at several acid concentrations, and in duplicate at each concentration, for all the compounds examined.

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References

1 R. A. Jones and G. P. Bean, *The Chemistry of Pyrroles*, Academic Press, London, New York, 1977, pp. 446–451.

2 A. H. Jackson, in *Comprehensive Organic Chemistry*; eds. D. H. R. Barton, W. D. Ollis and P. G. Sammes, Pergamon Press, Oxford, 1979, vol. 4, p. 276.

3 R. Taylor, *Electrophilic Aromatic Substitutions*, Wiley, New York, 1990.

4 (*a*) E. B. Whipple, Y. Chiang and R. L. Hinman, *J. Am. Chem. Soc.*, 1963, **85**, 26; (*b*) Y. Chiang and E. B. Whipple, *J. Am. Chem. Soc.*, 1963, **85**, 2763; (*c*) H. J. Chen, L. E. Hakka, R. L. Hinman, A. J. Kresge and E. B. Whipple, *J. Am. Chem. Soc.*, 1971, **93**, 5102.

5 R. L. Hinman and J. Lang, *J. Am. Chem. Soc.*, 1964, **86**, 3796.

6 R. J. Abraham, E. Bullock and S. S. Mitra, *Can. J. Chem.*, 1959, **37**, 1859.

7 (*a*) G. P. Bean, *J. Chem. Soc., Chem. Commun.*, 1971, 421; (*b*) G. P. Bean and T. J. Wilkinson, *J. Chem. Soc., Perkin Trans. 2*, 1978, 72.

8 R. S. Alexander and A. R. Butler, *J. Chem. Soc., Perkin Trans. 2*, 1980, 110.

9 F. Terrier, F. L. Debleds, J. F. Verchère and A. P. Chatrousse, *J. Am. Chem. Soc.*, 1985, **107**, 307.

10 F. Terrier, A. P. Chatrousse, J. R. Jones, S. Hunt and E. Buncel, *J. Phys. Org. Chem.*, 1990, **3**, 684.

11 (*a*) B. C. Challis and F. A. Long, *J. Am. Chem. Soc.*, 1963, **85**, 2524; (*b*) B. C. Challis and E. M. Millar, *J. Chem. Soc., Perkin Trans. 2*, 1972, 1116; (*c*) *J. Chem. Soc., Perkin Trans. 2*, 1972, 1618.

12 (*a*) D. M. Muir and M. C. Whiting, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1316; (*b*) 1976, 388.

13 (*a*) A. J. Kresge and Y. Chiang, *J. Am. Chem. Soc.*, 1961, **83**, 2877; (*b*) *J. Am. Chem. Soc.*, 1967, **89**, 4411; (*c*) A. J. Kresge, Y. Chiang and Y. Sato, *J. Am. Chem. Soc.*, 1967, **89**, 4418; (*d*) A. J. Kresge, S. Slae, D. W. Taylor, *J. Am. Chem. Soc.*, 1970, **92**, 6309; (*e*) A. J. Kresge, S. G. Mylonakis, Y. Sato and V. P. Vitullo, *J. Am. Chem. Soc.*, 1971, **93**, 6181.

14 A. J. Kresge in *Proton Transfer Reaction*; eds. V. Gold and E. F. Caldin, Chapman and Hall, London 1975, pp. 179–189.

15 (*a*) A. J. Kresge, Y. Chiang, G. W. Koeppl and R. A. More O'Ferrall, *J. Am. Chem. Soc.*, 1977, **99**, 2245; (*b*) A. J. Kresge, D. S. Sagatys and H. L. Chen, *J. Am. Chem. Soc.*, 1968, **90**, 4174.

16 A. J. Kresge, D. S. Sagatys and H. L. Chen, *J. Am. Chem. Soc.*, 1977, **99**, 7228.

17 W. Sachs, W. Knoche and C. Herrmann, *J. Chem. Soc., Perkin Trans. 2*, 1991, 701.

18 R. J. Thomas and F. A. Long, *J. Am. Chem. Soc.*, 1964, **86**, 4770.

19 (*a*) J. Schulze and F. A. Long, *J. Am. Chem. Soc.*, 1964, **86**, 1331; (*b*) J. L. Longridge and F. A. Long, *J. Am. Chem. Soc.*, 1967, **89**, 1292.

20 K. Schwetlick, K. Unverferth and R. Mayer, *Z. Chem.*, 1967, **7**, 58.

21 J. C. Hallé, M. J. Pouet, M. P. Simonnin, F. Debleds and F. Terrier, *Can. J. Chem.*, 1982, **60**, 1988.

22 F. Terrier, J. C. Hallé, M. P. Simonnin and M. J. Pouet, *J. Org. Chem.*, 1984, **49**, 4363.

23 F. Terrier, M. J. Pouet, E. Buncel, S. Hunt and J. R. Jones, manuscript in preparation.

24 M. Salmón, M. Aguilar and M. Saloma, *J. Chem. Soc., Chem. Commun.*, 1983, 570.

25 M. Salmón, M. E. Carbajal, J. C. Juarez, A. Diaz and M. C. Rock, *J. Electrochem. Soc.*, 1984, **131**, 1802.

26 The $\sigma_p{}^\circ$ values have been compiled from N. S. Isaacs, *Physical Organic Chemistry*, Longman, London, 1987, p. 134.

27 Y. Chiang, R. L. Hinman, S. Theodoropoulos and E. B. Whipple, *Tetrahedron*, 1967, **23**, 745.

28 H. Koford, L. E. Sutton and J. Jackson, *J. Chem. Soc.*, 1952, 1467.

29 S. P. Bruekelman, S. E. Leach, G. D. Meakins and M. D. Tirel, *J. Chem. Soc., Perkin Trans. 1*, 1984, 2801.

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