Stability of Carbonium Ions. Part 3.[1] The Transmission of Substituent Effects across the Fluorene and Biphenyl Systems

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The effects of substituents (X) upon the rates of solvolysis of α-(7-X-fluoren-2-yl)benzyl chlorides parallel those of substituents in the corresponding reaction of α-(4-X-fluoren-2-yl)benzyl chlorides, although the former is the more susceptible system. These results are consistent with regarding fluorene as a planar biphenyl structure. Both aromatic systems transmit substituent effects less well than the benzene system, but the relative abilities of substituents to affect the rates of the solvolysis are the same in all three systems. This suggests that the composite electronic (*I*,*M*) contribution of substituents is similar regardless of the system through which it is transmitted, so that there is no evidence of a selective, distance-dependent, dampening of one of the electronic contributors, and hence that both *I* and *M* contributions are perhaps substantially developed at, and transmitted from, the aromatic atoms bearing the substituents.

FLUORENE and biphenyl show considerable similarities in their reactions, and both the direction and the rates of electrophilic substitution are consistent with a planar biphenyl structure of fluorene (2,2′-methylenebiphenyl).[2] Similarly the rates of solvolysis of some derivatives of 2-(α-chloromethyl)fluorene are greater than those of the corresponding 4-(α-chloromethyl)biphenyl;[3] the trend in the rates of unimolecular solvolysis of a number of α-arylbenzyl chlorides, in which the aryl component may be regarded as derived from the biphenyl-4-yl system, follows the changes in the interplanar angle,[1,4] as does the rate of molecular chlorination of some similarly derived bridged biphenyl structures.[5] The results are usually explained by attributing the greater degree of resonance stabilisation of the resulting carbonium ion intermediate to the greater degree of overlap of the two rings in the biphenyl fragment. The variations of the Arrhenius parameters in both the molecular chlorination studies[6] and the solvolysis work[1,4] agree with this explanation.

In contrast, the effects of substituents upon the rate of protodetritiation of either 7-X-2-tritiofluorenes or 4′-X-4-tritiobiphenyls are the same in the two systems.[7] Although the extent of transmission of the substituent

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[1] Part 2, R. Bolton, *J. Chem. Soc.*, 1965, 1542.

[2] M. J. S. Dewar and D. S. Urch, *J. Chem. Soc.*, 1958, 3079.

[3] E. Berliner and N. Shieh, *J. Amer. Chem. Soc.*, 1957, **79**, 3849; L. Verbit and E. Berliner, *ibid.*, 1964, **86**, 3307.

[4] R. Bolton, M. E. Jones, and S. W. Tucker, *J. Chem. Soc.*, 1964, 1464.

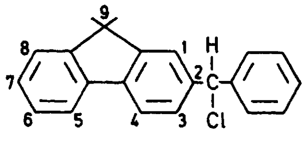
[5] P. B. D. de la Mare, E. A. Johnson, and J. S. Lomas, *J. Chem. Soc.*, 1964, 5317.

[6] P. B. D. de la Mare and J. S. Lomas, *J. Chem. Soc.*, 1965, 5739.

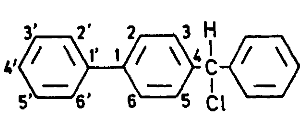
[7] R. Baker, R. W. Tolt, C. Eaborn, and P. M. Greasley, *J. Chem. Soc.*, 1964, 627.

effect in biphenyl is not nearly as great as that in benzene,[8] the change to the fluorene system would be expected to show some increased transmission of such effects if the coplanarity of the two rings allowed greater resonance interaction.

We therefore began a study of substituent effects in the rates of solvolysis of some α-(fluoren-2-yl)benzyl chlorides (1) and some α-(biphenyl-4-yl)benzyl chlorides (2) in



(1)



(2)

ethanol–acetone (9 : 1, v/v). If the acceleration resulting from bridging the biphenyl structure does arise from the consequent coplanarity of the two rings, the substituent effects ought similarly to be more readily relayed across the fluorene system rather than the biphenyl system.

DISCUSSION

A number of derivatives of both α-(biphenyl-4-yl)-benzyl chloride and α-(fluoren-2-yl)benzyl chloride were studied. Tables 1 and 2 list the substituents, the corresponding rate constant for solvolysis at 25°, and the derived Arrhenius parameters for the fluorene and the biphenyl derivatives repsectively. Both sets of results gave good plots of $\log_{10}k_1$ (k_1 is the first-order rate constant for solvolysis at 25°) against σ^+. In reactions of high electron demand, σ^+ is more appropriate than σ.[9] The slopes of these graphs showed that the solvolysis of substituted (biphenyl)benzyl chlorides (ρ^+ −1.20 ± 0.1) was less sensitive to substituent effects than the corresponding reaction of the fluorene compounds (ρ −1.7 ± 0.1). The fluorene system therefore seems to transmit more of the electronic effect across the two phenyl rings than does the biphenyl fragment, in agreement with the hypothesis that delocalisation of charge and the interplanar angle are linked.

TABLE 1

Results of kinetic studies of some α-(X-fluoren-2-yl)benzyl chlorides

Substituent (X)	$k_1(25°)/s^{-1}$ *	$\Delta E/$ kcal mol^{-1}	$-\Delta S/$cal mol^{-1} K^{-1}
H	9.9×10^{-3}	17.8 ± 0.2	8
7-Cl	4.0×10^{-3}	18.0 ± 0.4	9
7-Et	3.4×10^{-2}	20.1 ± 0.2	2
7-F	7.8×10^{-3}	17.7 ± 0.2	9
7-OMe	160×10^{-3}	16.9 ± 0.4	6
7-NO_2	3.3×10^{-4}	19.6 ± 0.3	9
6-Cl	2.2×10^{-3}	16.8 ± 0.3	15

* Internal probable error (mean deviation from the mean) is ±3%. Reproducibility is ±10%.

TABLE 2

Results of kinetic studies of some α-(X-biphenyl-4-yl)benzyl chlorides

Substituent (X)	k_1 (25°)/s^{-1}	$\Delta E/$ kcal mol^{-1}	$-\Delta S/$cal mol^{-1} K^{-1}
H	5.13×10^{-4} *	19.8 ± 0.2	8
3-Br	1.45×10^{-4}	17.7 ± 0.7	17
3-F	1.88×10^{-4}	18.2 ± 0.2	15
3-OMe	4.5×10^{-4}	19.2 ± 0.4	10
3-NO_2	5.6×10^{-5}	18.3 ± 0.9	16
4-Br	2.8×10^{-4}	17.4 ± 0.5	16
4-Cl	2.5×10^{-4}	19.8 ± 0.3	9
4-F	3.9×10^{-4}	18.7 ± 0.8	11
4-Me	9.87×10^{-4}	19.9 ± 0.4	6
4-OMe	3.51×10^{-3}	19.6 ± 0.3	5
4-NO_2	5.0×10^{-5}	20.8 ± 1.0	8
4-Ph	6.12×10^{-4}	20.1 ± 0.2	6

* As in Table 1.

Whether the interplanar angle, θ, and the extent of mesomeric relay are linked by the equation $E = E_0 \cos^2\theta$ or in some other way,[5] the effects of similarly situated substituents in biphenyl and in fluorene should parallel each other. If, in the fluorene system, the result of a substituent effect ($\delta\Delta G = RT\log k_X/k_H$) is dependent upon some function of θ, then the corresponding result in the biphenyl system ($\delta\Delta G'$) depends similarly upon θ′, the interplanar angle in biphenyl. As fluorene is planar, θ is zero. Because this solvolysis reaction is one which makes maximum demands for stabilisation from the system, the biphenyl residue will be as nearly coplanar as steric interactions will permit, *i.e.* θ will be minimal and nearly constant for all 3′- or 4′-substituted (biphenyl-4-yl)benzyl carbonium ion intermediates.

This suggests that the two free energy terms will be linearly linked for all pairs of substituents [equations (1)—(3)].

$$\delta\Delta G = RT\log k_X/k_H f(\theta) \qquad (1)$$

$$\delta\Delta G' = RT\log k_X'/k_H' f(\theta') \qquad (2)$$

$$i.e.\ \delta\Delta G/\delta\Delta G' = \text{constant} \qquad (3)$$

A plot of log k_X/k_H against log k'_X/k'_H for six *para*-substituents gives a good straight line of slope 1.45 ± 0.04. (k_H and k_X are the first-order rate constants at 25° for the fluorenyl- and substituted fluorenyl-benzyl chlorides. k'_H and k'_X are the analogous rate constants for the biphenyl system.) This represents a closer linear relation than either of the component free energy terms show with respect to benzene analogues (*i.e.* σ^+) and implies that proportional changes in the various energetic contributions are occurring in the fluorene and in the biphenyl series. If $f(\theta') = \cos^2\theta'$, then the constant in equation (3) becomes $1/\cos^2\theta'$, which is the slope of the graph, 1.45. This in turn gives a value of θ′(45°) in complete agreement with that found in the molecular chlorination studies [5] and close to various estimates made from spectroscopic work.[10]

Since the difference in activation energies between fluorene and biphenyl analogues also is close to 1—3 kcal mol^{-1}, this gives a value of 2—6 kcal mol^{-1} as the difference in energy arising from forcing planarity upon the

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[8] D. J. Byron, G. W. Gray, and R. C. Wilson, *J. Chem. Soc.* (*C*), 1966, 831 and references therein.

[9] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

[10] O. Bastiansen, *Acta Chem. Scand.*, 1949, **3**, 408; 1950, **4**, 926.

biphenyl system (*i.e.* in making the fluorene and the biphenyl structures equally able to transmit electronic effects). The similarity between this energy and calculated values [11] of the rotational energy barrier (*ca.* 4 kcal mol^{-1}) is encouraging, but might arise from other, unconsidered factors.

The difference in entropy changes for the pairs of substituents 4- and 3-nitro, 4- and 3-fluoro, *etc.* is related in a general way to the magnitude of the electronic effect of the substituent. The greater the electronic effect, the greater the difference in entropy change between a given pair. Thus, the 3- and 4-fluoro-substituents which have low substituent constants, reflecting their low electronic contributions give values of -10 and -11 cal mol^{-1} K^{-1} respectively for their associated entropy changes. Similarly the 3- and 4-bromo-substituents have values of -17 and -16 cal mol^{-1} K^{-1}. However, the highly electron donating methoxy-group and the highly withdrawing nitro-group both show differences of a factor of 2 between these terms. Due to synthetic difficulties the analogous 6- and 7-substituted fluorenyl derivatives could not be studied in depth. The only pair that was obtained were the 6- and 7-chlorofluoren-2-ylbenzyl chlorides. Again the change in entropy for the *meta* or fluoren-6-yl substituent (-15 cal mol^{-1} K^{-1}) is greater than that for the *para* or fluoren-7-yl substituent (-9 cal mol^{-1} K^{-1}).

Since the mesomeric contribution of *meta*-substituents is mainly confined to the ring containing them, and since there would be differences in the extents to which mesomeric contributions could be relayed from the 3′- and 4′-positions in biphenyl (*cf.* ref. 8), these derivatives of biphenyl and of fluorene were not studied intensively. This study was further thwarted by difficulties in preparing 3-nitrofluorene, our chosen starting material in obtaining α-(6-X-fluoren-2-yl)benzyl chlorides. A reported method [12] gave very low yields ($\ngtr 5\%$) after some modification, but never allowed the preparation of adequate amounts of 3-nitrofluorene. Other synthetic routes to this compound were tedious and also gave minimal yields.

EXPERIMENTAL

2-Aminofluorene [13] was the source of 2-fluoro- and 2-hydroxyfluorene by conventional diazonium ion reactions.[14,15] 2-Methoxyfluorene was obtained by methylation of the phenol.[14] 2-Chlorofluorene was prepared by the reduction of 2-chlorofluorenone, itself isolated by oxidation of the products of chlorination of fluorene. Direct isolation of the chlorofluorene was not a viable synthetic route. 3-Methyl- and 3-chloro-fluorene were similarly obtained from the corresponding fluorenones, themselves prepared from toluene or from chlorobenzene through ring closure of the 2-amino-4′-substituted benzophenones arising from Friedel–Crafts acylations using *N*-(*p*-tolylsulphonyl)-anthranilic acid.[15] 1-Methylfluorene was similarly prepared from 2-amino-2′-methylbenzophenone.[16] 2-Ethylfluorene was prepared by reduction (Hüang-Minlon) of 2-acetylfluorene.

The monosubstituted fluorenes were treated individually with a solution of the Perrier complex from benzoyl chloride (1.2 mol. equiv.) and aluminium chloride (1.1 mol. equiv.) in dichloromethane. After the evolution of hydrogen chloride, the complex between the products and aluminium chloride often precipitated. Hydrolysis of the complex gave the ketone, which was recrystallised from ethanol. Reduction, usually by sodium borohydride in methanol or by lithium aluminium hydride in ether, gave the secondary alcohol which with thionyl chloride gave the required chloride. Where these were solid, they were recrystallised from light petroleum, b.p. 60—80°.

TABLE 3

Physical properties of substituted biphenyls and fluorenes (XArCYZPh)

Substituent (X)	Ketone (YZ = O)	Alcohol (Y = H, Z = OH)	Chloride (Y = H, Z = Cl)
A Fluoren-2-yl derivatives (Ar = $C_{13}H_8$)			
		M.p. (°C)	
6-Cl	133—134	105—106	Oil
7-Br	126—127		
7-Cl	112—113	136—137	105—106
7-Et	108—109	86—90	94—95
7-F	114—115	78—80	77—78
7-OMe	132—134	128—129	149—150
7-NO_2	211—212 [a]	176—177	159
B Biphenyl-4-yl derivatives (Ar = $C_{12}H_8$)			
		M.p. (°C)	
3′-Br	87—88	Oil	Oil
3′-F	74—77	61—63	Oil
3′-OMe	Oil	Oil	Oil
3′-NO_2	135—136	Oil	Oil
4′-Br	155—157	115—116	Oil
4′-Cl	129—130		76—77
4′-F	110—111	68—69	Semi-solid
4′-Me	128.5—129.5	129—130	Oil
4′-OMe	166—168 [b]	96—97	129—130
4′-NO_2	154—156 [b]		115—116

[a] Ref. 17. [b] D. H. Hey and E. R. B. Jackson, *J. Chem. Soc.*, 1936, 802.

2-Benzoyl-7-nitrofluorene was prepared by the nitration [17] of 2-benzoylfluorene. The yellow product, m.p. 210—212° (lit.,[17] 206°) from acetic acid or from nitromethane, gave an amine upon reduction with tin(II) chloride in hydrochloric acid–acetic acid, m.p. 156° (lit.,[17] 155°). This amine, upon diazotisation and subsequent treatment with copper(I) chloride, gave 2-benzoyl-7-chlorofluorene (m.p. and mixed m.p. 111—112°) and, from the base-soluble products, a very small amount of a phenol which gave 2-benzoyl-7-methoxyfluorene upon treatment with base and dimethyl sulphate. The orientation of the nitration was therefore proven.

The original nitro-benzoylfluorene gave the corresponding alcohol by reduction with lithium borohyride in tetrahydrofuran.[18]

4-Fluoro- and 4-chloro-biphenyl were obtained by standard methods from 4-aminobiphenyl. Methylation of 4-

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[11] K. E. Howlett, *J. Chem. Soc.*, 1960, 1055.

[12] N. Ishikawa and M. Hayashi, *Yuki Gosei Kagaku Kyokaishi*, 1957, **15**, 405 (*Chem. Abs.*, 1954, **51**, 16, 379).

[13] *Org. Synth.*, 1943, Coll. Vol. II, p. 447.

[14] G. W. Gray, J. B. Hartley, and A. Ibbotson, *J. Chem. Soc.*, 1955, 2686.

[15] F. Bell and J. A. Gibson, *J. Chem. Soc.*, 1955, 3560.

[16] W. C. Lothrop and P. A. Goodwin, *J. Amer. Chem. Soc.*, 1943, **65**, 363.

[17] K. Dziewonski and A. Obtulowicz, *Bull. Internat. Acad. polon.*, 1930, *A*, 399 (*Chem. Abs.*, 1931, **25**, 5157).

[18] H. C. Brown, 'Hydroboration,' Benjamin, New York, 1962, p. 245.

hydroxybiphenyl gave 4-methoxybiphenyl. Standard homolytic arylation methods were used to obtain 3- and 4-methylbiphenyl from the appropriate toluidines, benzene, and pentyl nitrite.[19] 3-Nitrobiphenyl[19] was the starting material for 3-fluorobiphenyl, and 3-methoxybiphenyl was obtained *via* the corresponding phenol. 3-Bromobiphenyl was obtained by the method of Scarborough and Waters.[20]

TABLE 4

Measured rate constants in 9 : 1 ethanol–acetone

α-(2-Ethylfluoren-7-yl)benzyl chloride: $10^3k/s^{-1}$ = 2.1 3(2.8°), 4.30 (7.5°), 7.95 (12.7°), 9.66 (14.0°), 10.7 (15.4°), 19.3 (20.7°), 21.8 (21.5°)
α-(6-Chlorofluoren-2-yl)benzyl chloride: $10^3k/s^{-1}$ = 2.23 (25.0°), 3.45 (30.0°), 4.74 (34.0°), 8.22 (39.5°), 13.50 (44.0°)
α-(2-Chlorofluoren-7-yl)benzyl chloride: $10^3k/s^{-1}$ = 1.16 (13.6°), 1.98 (19.1°), 2.92 (22.0°), 4.27 (25.0°)
α-(2-Fluorofluoren-7-yl)benzyl chloride: $10^3k/s^{-1}$ = 3.06 (14.7°), 5.68 (18.0°), 4.80 (20.0°), 7.76 (24.7°), 12.64 (29.5°)
α-(2-Methoxyfluoren-7-yl)benzyl chloride: $10^2k/s^{-1}$ = 0.300 (−13.0°), 0.533 (−7.5°), 1.38 (0.0°), 3.24 (8.0°), 7.4 (15.6°)
α-(2-Nitrofluoren-7-yl)benzyl chloride: $10^4k/s^{-1}$ = 3.30 (25.2°), 14.85 (39.4°)
α-(4′-Fluorobiphenyl-4-yl)benzyl chloride: $10^3k/s^{-1}$ = 0.393 (24.8), 0.727 (30.5°), 1.78 (47.0°), 2.68 (51.0°), 4.58 (49.5°), 6.14 (62.8°)
α-(4′-Bromobiphenyl-4-yl)benzyl chloride: $10^3k/s^{-1}$ = 0.441 (30.8°), 1.04 (39.0°), 2.16 (47.0°), 2.68 (51.0°), 4.58 (57.0°), 6.14 (62.8°)
α-(4′-Nitrobiphenyl-4-yl)benzyl chloride: $10^4k/s^{-1}$ = 0.756 (36.2°), 2.89 (40.3°), 4.90 (46.6°), 7.33 (50.8°), 13.6 (56.5°), 21.5 (63.0°)
α-(4′-Chlorobiphenyl-4-yl)benzyl chloride: $10^4k/s^{-1}$ = 2.41 (26.1°), 11.3 (40.2°), 29.3 (49.8°)
α-(4′-Methylbiphenyl-4-yl)benzyl chloride: $10^4k/s^{-1}$ = 9.87 (24.7°), 32.8 (34.7°), 99.0 (44.0°)
α-(4′-Methoxybiphenyl-4-yl)benzyl chloride: $10^4k/s^{-1}$ = 1.93 (0.4°), 35.1 (24.7°), 45.5 (38.5°)
α-(4′-Phenylbiphenyl-4-yl)benzyl chloride: $10^4k/s^{-1}$ = 5.10 (24.5°), 6.11 (25.0°), 12.70 (31.2°), 29.1 (39.2°), 72.6 (50.2°)
α-(3′-Bromobiphenyl-4-yl)benzyl chloride: $10^4k/s^{-1}$ = 2.87 (28.5°), 5.68 (40.0°), 13.06 (48.0°), 22.87 (54.0°), 32.47 (60.5°), 44.87 (64.0°)
α-(3′-Fluorobiphenyl-4-yl)benzyl chloride: $10^4k/s^{-1}$ = 1.88 (25.6°), 5.93 (38.0°), 7.57 (41.0°), 12.85 (46.0°), 21.19 (51.0°), 36.3 (58.0°)
α-(3′-Methoxybiphenyl-4-yl)benzyl chloride: $10^4k/s^{-1}$ = 4.55 (25.2°), 7.46 (30.0°), 12.05 (34.0°), 20.95 (40.0°), 28.83 (42.5°), 33.88 (45.0°), 48.92 (49.0°)
α-(3′-Methylbiphenyl-4-yl)benzyl chloride: $10^4k/s^{-1}$ = 11.60 (24.0°), 18.65 (27.3°), 23.95 (30.0°), 34.7 (36.0°), 46.59 (40.0°), 110.3 (49.5°)
α-(3′-Nitrobiphenyl-4-yl)benzyl chloride: $10^4k/s^{-1}$ = 0.58 (24.5°), 0.88 (27.0°), 1.370 (30.0°), 1.808 (34.0°), 3.24 (40.5°), 6.86 (49.5°), 11.19 (54.5°)

The Friedel–Crafts acylation of these derivatives of biphenyl was carried out in carbon disulphide, but otherwise in a similar manner to that of the fluorene compounds. The reduction of the resulting ketones and the esterification of the derived alcohols, were similarly performed.

The rates and mechanism of the solvolyses were studied by the reported method.[1,4] Quantities of sodium ethoxide were added to the reaction mixture and the time at which aliquot portion was neutralized was noted. Bromothymol Blue was used as the internal indicator. Kinetic plots were obtained and first-order rate constants derived. Since the rate of this reaction has to be unaltered by the presence of varying low concentrations of sodium ethoxide, this technique is specific to S_N1 reactions.

Combustion analysis was not always used to establish the purity of the chloride, because isomeric chlorides with different rates of solvolysis would be undetectable. Similarly, the incomplete purification of a chloride could cause poor analysis, especially where the chloride was isolated as an oil, although the product was suitable for kinetic studies. Ultimately, the only criterion of purity which is appropriate is the kinetic behaviour of the sample. Trace amounts of acetic impurities (*e.g.* HCl) and of rapidly solvolysed compounds (*e.g.* $SOCl_2$) appeared as appreciable ' zero time ' titration readings; however, all the samples used in this study gave good linear, first-order plots often to more than 90% completion. The identity of the solvolysing species could usually be deduced from its approximate equivalent weight.

TABLE 5

Combustion analysis

	Required (%)			Found (%)		
	C	H	Cl	C	H	Cl
α-(X-Fluoren-2-yl)benzyl chloride						
X = 2-Et	82.9	6.08	11.1	82.8	6.0	11.0
= 2-Cl	73.8	4.3	21.8	73.7	4.2	21.7
= 2-F	87.9	5.1	6.9	87.7	5.0	6.8
= 2-OMe	78.6	5.3	11.1	78.5	5.2	11.1
= 2-NO_2	71.5	4.2	10.6	71.5	4.1	10.5
α-(X-Biphenyl-4-yl)benzyl chloride						
X = 4′-Cl	72.8	4.5	22.6	72.9	4.5	22.7
= 4′OMe	77.8	5.5	11.5	77.8	5.4	11.3
= 4′-NO_2	70.2	4.6	10.9	70.4	4.7	10.7
α-(X-Fluoren-2-yl)benzyl alcohol						
X = 6-Cl	78.6	4.6	11.6	78.3	4.7	11.6
α-(X-Biphenyl-4-yl)benzyl alcohol						
X = 3′-F	82.2	5.5	6.7 *	82.2	5.4	6.8 *
= 4′-Br	67.3	4.4		67.3	4.4	
= 4′-F	82.0	5.4		82.1	5.4	
= 4′-Me	87.6	6.6		87.5	6.7	

* = % Fluorine.

Combustion analyses are recorded for the solid alcohol precursors. The orientation of the ketones was confirmed by i.r. spectroscopy. The only series where the ketone, alcohol, and chloride were each oils was the 3′-methoxybiphenyl-4-yl system. However, 4-(3-methoxyphenyl)benzophenone was prepared *via* the corresponding phenol obtained as a diazotisation product of the characterised 4-(3-nitrophenyl)-benzophenone. The orientation is thereby assured.

[6/1022 *Received*, *27th May*, 1976]

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[19] J. I. G. Cadogan, *J. Chem. Soc.*, 1962, 4257.

[20] H. A. Scarborough and W. A. Waters, *J. Chem. Soc.*, 1927, 89.