# Kinetics of Reaction of Picryl Bromide with Substituted Biphenyl-4-carboxylate Ions

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**Second-order rate constants have been measured for the reactions of picryl bromide with 2'-, 3'-, and 4'-substituted biphenyl-4-carboxylate ions in 80% methanol–water at several temperatures and activation parameters have been calculated. The Hammett equation applies very well to the reactions of 3'- and 4'-substituted biphenyl-4-carboxylate ions with $\sigma$ values calculated by the FMMF method. The effect of 2'-substituents is understandable in terms of $\pi$-electron steric effects. The rate constants correlate with the p$K_a$ values of the correspondingly substituted biphenyl-4-carboxylic acids. In the case of 3'- and 4'-substituted biphenyl-4-carboxylate ions such a correlation leads to an $\alpha$-value of 0.52 indicating substantial bonding in the transition state.**

ALTHOUGH the study of bimolecular nucleophilic substitutions involving benzene derivatives as nucleophiles has received much attention,[1] no such study has so far been undertaken with biphenyl derivatives as nucleophiles. In continuation of our studies of the effect of substituents in the biphenyl system,[2] we have now investigated the kinetics of the reactions of several 2'-, 3'-, and 4'-substituted biphenyl-4-carboxylate ions with picryl bromide.

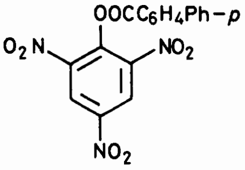
## EXPERIMENTAL

*Materials.*—Picryl bromide was prepared as described [3] and recrystallized from ethanol, m.p. 123—124 °C. The biphenyl-4-carboxylic acids were prepared by literature methods.[4] Methanol was purified by the method of Lund and Bjerrum.[5] Triply distilled water was used for dilution. Sodium salts of the biphenyl-4-carboxylic acids were prepared by the usual procedure in ethanol.

*Rate Measurements.*—The solvent used was 80% v/v methanol–water. The temperature was controlled to ±0.1 °C. The reactions were studied under second-order conditions. Low concentrations of the reactants (0.01M in both) were found suitable for following the kinetics satisfactorily. The reactions were followed by the same method described earlier.[6]

*Reaction Path and Products.*—The reaction was followed by estimating the bromide ion which would arise from the nucleophilic attack of biphenyl-4-carboxylate ion at C-1 of picryl bromide. Bromide ion could also arise by attack of hydroxide ion formed by the hydrolysis of sodium salts of the acids. There is a further possibility of liberation of bromide ion by general base catalysed attack of water or methanol. Given these possibilities, the situation is not simple. However, that the process being followed is mainly nucleophilic attack on picryl bromide by biphenyl-4-carboxylate ion is confirmed by almost quantitative isolation of the picryl ester (1) in all cases. The product mixture did not contain methyl picryl ether. The amount of picric acid formed is so small that it does not affect the overall order of the reaction.

Standard solutions of the appropriate sodium biphenyl-4-carboxylate and picryl bromide were mixed in an equimolar ratio and maintained at the kinetic temperature until completion. After concentration of the solution to small volume under reduced pressure the picryl esters precipitated were filtered off, and recrystallized from suitable solvents. In all cases the amount of ester formed was *ca.* 95%. Table 1 lists the new compounds isolated, their m.p.s, and analyses.



(1)

## RESULTS AND DISCUSSION

It was observed that the reactions followed second-order kinetics, first-order in each reactant. The usual procedure was employed to establish this in a few representative cases. The second-order rate constants are given in Table 2. The data indicate that electron-withdrawing groups decrease and electron-donating groups increase the rate showing that it depends on the electron density on the oxygen atom of the nucleophile.

*Activation Parameters.*—The activation energies were computed from the linear plots of log $k$ against $1/T$. The values of the activation energies show a regular variation with substituents: electron-withdrawing groups increase and electron-donating groups decrease $E_a$. The entropies of activation are negative as for bimolecular reactions.

*Linear Free Energy Relationship.*—With a view to seeking a Hammett correlation,[7] we converted Byron *et al.*'s [8] p$K_a$ values of 3'- and 4'-substituted biphenyl-4-carboxylic acids into $\sigma_{ij}$ values by dividing the $\Delta$p$K_a$ values by a $\rho$ value of 1.32 based on benzoic acid ionization in 50% 2-n-butoxyethanol–water.[9] The new $\sigma$ values thus calculated are given in Table 3. The Hammett correlation with these values was very poor ($r$ 0.869 at 30 °C). The reason for the poor correlation may possibly lie in the p$K_a$ values of Byron *et al.*, which generated separate lines for 3'- and 4'-substituted biphenyl-4-carboxylic acids when plotted against ordinary $\sigma$ values. Also the p$K_a$ value reported for 4'-cyanobiphenyl-4-carboxylic acid must be regarded as very approximate, for the acid could not be properly purified by them. However, a plot of log $k$ at 30 °C for 3'- and 4'-substituted biphenyl-4-carboxylate ions against ordinary Hammett

TABLE 1

Picryl biphenyl-4-carboxylates

| Substituent | M.p. (°C) | Recryst. solvent | Found (%) C | Found (%) H | Formula | Required (%) C | Required (%) H |
|---|---|---|---|---|---|---|---|
| H | 198—199 | A | 56.0 | 2.8 | $C_{19}H_{11}N_3O_8$ | 55.8 | 2.7 |
| 3′-F | 206—207 | B | 53.8 | 2.4 | $C_{19}H_{10}FN_3O_8$ | 53.4 | 2.3 |
| 3′-Cl | 218—219 | A | 51.7 | 2.4 | $C_{19}H_{10}ClN_3O_8$ | 51.4 | 2.3 |
| 3′-Br | 212—213 | A | 47.0 | 2.3 | $C_{19}H_{10}BrN_3O_8$ | 46.7 | 2.1 |
| 3′-CN | 220—221 | B | 55.6 | 2.5 | $C_{20}H_{10}N_4O_8$ | 55.3 | 2.3 |
| 3′-$NO_2$ | 224—225 | B | 50.6 | 2.5 | $C_{19}H_{10}N_4O_{10}$ | 50.2 | 2.2 |
| 3′-$CH_3$ | 215—216 | A | 57.1 | 3.3 | $C_{20}H_{13}N_3O_8$ | 56.7 | 3.1 |
| 3′-$OCH_3$ | 210—211 | B | 54.8 | 3.0 | $C_{20}H_{13}N_3O_9$ | 54.7 | 3.0 |
| 4′-F | 192—193 | B | 53.3 | 2.4 | $C_{19}H_{10}FN_3O_8$ | 53.4 | 2.3 |
| 4′-Cl | 197—198 | A | 51.6 | 2.3 | $C_{19}H_{10}ClN_3O_8$ | 51.4 | 2.3 |
| 4′-Br | 190—191 | A | 47.0 | 2.1 | $C_{19}H_{10}BrN_3O_8$ | 46.7 | 2.1 |
| 4′-CN | 200—201 | A | 55.7 | 2.5 | $C_{20}H_{10}N_4O_8$ | 55.3 | 2.3 |
| 4′-$NO_2$ | 210—211 | B | 50.4 | 2.5 | $C_{19}H_{10}N_4O_{10}$ | 50.2 | 2.2 |
| 4′-$CH_3$ | 183—184 | B | 56.8 | 3.1 | $C_{20}H_{13}N_3O_8$ | 56.7 | 3.1 |
| 4′-$OCH_3$ | 219—220 | B | 55.0 | 3.1 | $C_{20}H_{13}N_3O_9$ | 54.7 | 3.0 |
| 2′-F | 180—181 | A | 53.9 | 2.4 | $C_{19}H_{10}FN_3O_8$ | 53.4 | 2.3 |
| 2′-Cl | 185—186 | B | 51.8 | 2.4 | $C_{19}H_{10}ClN_3O_8$ | 51.4 | 2.3 |
| 2′-Br | 188—189 | B | 47.0 | 2.1 | $C_{19}H_{10}BrN_3O_8$ | 46.7 | 2.1 |
| 2′-CN | 195—196 | A | 55.6 | 2.3 | $C_{20}H_{10}N_4O_8$ | 55.3 | 2.3 |
| 2′-$NO_2$ | 161—162 | A | 50.5 | 2.4 | $C_{19}H_{10}N_4O_{10}$ | 50.2 | 2.2 |
| 2′-$CH_3$ | 177—178 | B | 57.0 | 3.2 | $C_{20}H_{13}N_3O_8$ | 56.7 | 3.1 |
| 2′-$OCH_3$ | 165—166 | A | 54.9 | 3.0 | $C_{20}H_{13}N_3O_9$ | 54.7 | 3.0 |

A, Aqueous methanol; B, aqueous ethanol.

TABLE 2

Second-order rate constants and activation parameters for the reaction of substituted biphenyl-4-carboxylate ions with picryl bromide in 80% v/v methanol–water

| | | $10^4k$/l $mol^{-1}$ $s^{-1}$ | | | | | |
|---|---|---|---|---|---|---|---|
| No. | Substituents | 30 °C | 40 °C | 50 °C | $\Delta H^\ddagger$/kcal $mol^{-1}$ | $-\Delta S^\ddagger$/cal $mol^{-1}$ $K^{-1}$ | log $A/s^{-1}$ |
| 1 | H | 11.0 ± 0.2 | 25.0 ± 0.3 | 50.6 ± 0.5 | 14.2 ± 0.2 | 25.1 ± 0.2 | 7.8 |
| 2 | 3′-F | 9.2 ± 0.1 | 21.3 ± 0.4 | 44.6 ± 0.2 | 14.8 ± 0.2 | 23.8 ± 0.2 | 8.1 |
| 3 | 3′-Cl | 8.9 ± 0.1 | 21.0 ± 0.3 | 43.9 ± 0.4 | 14.9 ± 0.1 | 23.2 ± 0.1 | 8.2 |
| 4 | 3′-Br | 8.7 ± 0.1 | 20.9 ± 0.3 | 43.6 ± 0.4 | 15.1 ± 0.1 | 22.8 ± 0.1 | 8.3 |
| 5 | 3′-CN | 8.0 ± 0.1 | 19.2 ± 0.4 | 41.1 ± 0.4 | 15.3 ± 0.1 | 22.2 ± 0.1 | 8.4 |
| 6 | 3′-$NO_2$ | 7.2 ± 0.1 | 18.1 ± 0.2 | 38.4 ± 0.5 | 15.7 ± 0.1 | 21.1 ± 0.1 | 8.7 |
| 7 | 3′-$CH_3$ | 11.5 ± 0.1 | 25.8 ± 0.2 | 51.8 ± 0.2 | 14.0 ± 0.3 | 25.7 ± 0.1 | 7.7 |
| 8 | 3′-$OCH_3$ | 11.3 ± 0.2 | 25.3 ± 0.1 | 50.7 ± 0.4 | 14.0 ± 0.3 | 25.8 ± 0.1 | 7.6 |
| 9 | 4′-F | 10.6 ± 0.2 | 24.4 ± 0.3 | 48.9 ± 0.4 | 14.3 ± 0.3 | 25.0 ± 0.2 | 7.8 |
| 10 | 4′-Cl | 9.7 ± 0.1 | 22.5 ± 0.3 | 46.5 ± 0.3 | 14.6 ± 0.2 | 24.0 ± 0.1 | 8.0 |
| 11 | 4′-Br | 9.5 ± 0.1 | 22.3 ± 0.4 | 46.3 ± 0.4 | 14.8 ± 0.1 | 23.5 ± 0.1 | 8.1 |
| 12 | 4′-CN | 7.6 ± 0.1 | 18.3 ± 0.2 | 39.7 ± 0.3 | 15.5 ± 0.2 | 21.7 ± 0.1 | 8.5 |
| 13 | 4′-$NO_2$ | 7.0 ± 0.2 | 17.5 ± 0.3 | 37.7 ± 0.5 | 15.8 ± 0.3 | 20.9 ± 0.1 | 8.7 |
| 14 | 4′-$CH_3$ | 12.1 ± 0.1 | 26.9 ± 0.3 | 53.7 ± 0.3 | 13.9 ± 0.1 | 26.0 ± 0.1 | 7.6 |
| 15 | 4′-$OCH_3$ | 12.8 ± 0.2 | 28.3 ± 0.3 | 55.6 ± 0.5 | 13.7 ± 0.6 | 26.5 ± 0.1 | 7.5 |
| 16 | 2′-F | 11.2 ± 0.1 | 25.6 ± 0.4 | 51.5 ± 0.6 | 14.2 ± 0.2 | 25.1 ± 0.1 | 7.8 |
| 17 | 2′-Cl | 12.0 ± 0.1 | 26.6 ± 0.4 | 53.0 ± 0.4 | 13.9 ± 0.2 | 26.2 ± 0.2 | 7.5 |
| 18 | 2′-Br | 12.0 ± 0.1 | 26.7 ± 0.3 | 53.6 ± 0.5 | 14.0 ± 0.2 | 25.8 ± 0.1 | 7.6 |
| 19 | 2′-CN | 12.7 ± 0.2 | 28.8 ± 0.3 | 60.1 ± 0.2 | 14.5 ± 0.3 | 23.9 ± 0.1 | 8.0 |
| 20 | 2′-$NO_2$ | 10.0 ± 0.1 | 22.8 ± 0.4 | 49.1 ± 0.3 | 14.9 ± 0.2 | 23.2 ± 0.1 | 8.2 |
| 21 | 2′-$CH_3$ | 12.4 ± 0.2 | 28.1 ± 0.3 | 56.0 ± 0.4 | 14.1 ± 0.3 | 25.4 ± 0.1 | 7.7 |
| 22 | 2′-$OCH_3$ | 13.0 ± 0.2 | 30.0 ± 0.3 | 60.5 ± 0.4 | 14.1 ± 0.4 | 25.0 ± 0.2 | 7.8 |

$\sigma_m$ and $\sigma_p$ values based on benzoic acid ionization in water shows an excellent linear correlation (Figure 1) with $\rho$ −0.26 ($r$ 0.991); only the point for 3′-OMe showing a little deviation. The $\sigma$ value used by us for 3′-OMe substituent is 0.115. A good correlation exists at higher temperatures also. The $\rho$ values obtained at 40 and 50 °C are −0.20 ($r$ 0.993) and −0.16 ($r$ 0.993), respectively. The effective $\sigma$ value for *m*-OMe in our system appears to be *ca.* 0.0. Aslam *et al.*[10] found values for $\sigma_m$ for OMe in non-aqueous media of *ca.* +0.02—+0.05. It appears that a $\sigma$ value of +0.04 would bring the point for 3′-OMe in Figure 1 closer to the line. As the solvent used by us, 80% methanol-water, is sufficiently non-aqueous, the use of +0.04 as $\sigma$ for 3′-OMe may be quite permissible.

The good linear relationship in Figure 1 indicates that the additional aromatic ring in biphenyl does not affect the composition of the electrical effect which reaches the reaction centre, *i.e.* the relative importance of inductive and resonance effects. This also shows that an effect which was responsible for two separate lines for the 3′- and 4′-substituents with Byron *et al.*'s data[8] is seen from our results not to be operating in the biphenyl system.

Since the correlation was poor when $\sigma$ values based on ionization of biphenylcarboxylic acids were used, the correlation was attempted with calculated $\sigma_{ij}$ values (Table 3) based on the Dewar–Golden–Harris (DGH) treatment.[11] The log $k$ values at 30 °C give an excellent correlation ($r$ 0.994), $\rho$ −0.69, providing interesting confirmation that the DGH treatment is fairly successful for

TABLE 3

Calculated $\sigma_{ij}$ values

| Substituent | By FMMF method[11] | From $\Delta pK_a$ values |
|---|---|---|
| 3'-F | 0.107 | 0.146 |
| 3'-Cl | 0.122 | 0.146 |
| 3'-Br | 0.130 | 0.115 |
| 3'-CN | 0.201 | 0.131 |
| 3'-$NO_2$ | 0.255 | 0.162 |
| 3'-$CH_3$ | −0.030 | −0.054 |
| 3'-$OCH_3$ | 0.022 | −0.031 |
| 4'-F | 0.044 | 0.085 |
| 4'-Cl | 0.093 | 0.154 |
| 4'-Br | 0.102 | 0.154 |
| 4'-CN | 0.254 | 0.154 |
| 4'-$NO_2$ | 0.308 | 0.323 |
| 4'-$CH_3$ | −0.065 | −0.039 |
| 4'-$OCH_3$ | −0.084 | −0.108 |

biphenyl. This treatment gives $\rho$ values of −0.55 ($r$ 0.992) and −0.44 ($r$ 0.993) at 40 and 50 °C, respectively.

*The Effect of 2'-Substituents.*—The data in Table 2 show that the Hammett equation is not applicable to the reactivity of 2'-substituted biphenyl-4-carboxylate ions. All the 2'-substituents (except $NO_2$) increase the rate of the parent reaction. This cannot be explained by the internally transmitted electronic effects of the substituents. This may readily be explained in terms of π-electron steric effect of the 2'-substituents.[8,12] None of the 2'-substituents is too large to prevent rotation about the 1,1'-bond. However, they may impose considerable strain upon the system which will result in diminished conjugative interaction between 2'- and 4-positions. The rate indicates that a substituent relays more electrons to the reaction centre from the 2'-position than it does from the 3'- or 4'-position. The 2'-substituents are in close proximity to the π-electrons of the ring carrying the reaction centre and a physical displacement of the π-electron cloud toward the 4-position needs to be envisaged as done previously by Byron *et al.*,[8] Idoux *et al.*,[12] and Bowden *et al.*[13] That the compressional effect on the π-electrons plays a decisive role is seen from the progressive increase in rate as the size of the 2'-halogeno-substituents increases. The rate data for the other substituents can also be interpreted in a similar way.

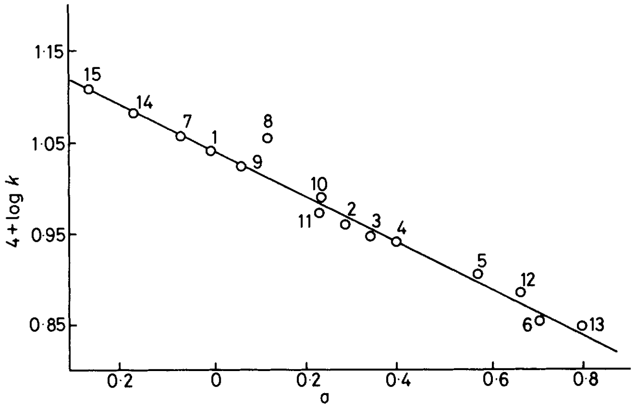


FIGURE 1 Plot of σ values against log $k$. Numbers as in Table 2

*Brönsted Relationship.*—The Brönsted equation has been widely employed in numerous general acid–base catalysis reactions.[14] It has been shown to be of great importance in the study of nucleophilic reactions.[15,16] For the reactions of 3'- and 4'-substituted biphenyl-4-carboxylate ions with picryl bromide, a plot of log $k$ *versus* $pK_a$ (Figure 2) shows 3'-Br, 3'-CN, and 3'-$NO_2$ markedly deviating from the straight line generated by the 4'-points and the 3'-points. The point for 4'-CN also deviates; but Byron *et al.*[8] say that their acid was impure, so the $pK_a$ value must be regarded as unreliable. The plot at 30 °C, ignoring the above points, gives a slope with Brönsted coefficient (α) of 0.52. This means that there is substantial bond formation in the transition state,[17] although the solvents for the two systems are not the same. The α value reported in the literature[18] for the reaction between picryl chloride and benzoate ions is 0.70 and those for the reactions of picryl bromide with 6-substituted 2-naphthoate and 6- and 4-substituted 1-naphthoate ions[6] are respectively 0.56 and 0.30.

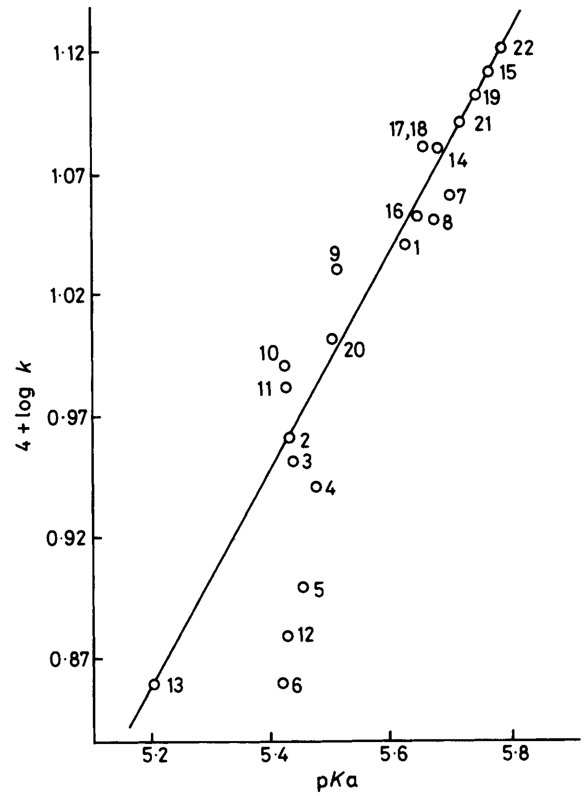


FIGURE 2 Plot of $pK_a$ against log $k$. Numbers as in Table 2

When the log $k$ values for the 2'-substituted compounds are put on the Brönsted plot described above using the $pK_a$ values of Byron *et al.*[8] all seven points lie reasonably close to the straight line. Thus both the carboxylate ion reactivities towards picryl bromide and the ionization of acids appear to show in comparable degree the π-electron steric effect of 2'-substituents mentioned above.

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## REFERENCES

[1] (*a*) J. F. Bunnett and R. E. Zaher, *Chem. Rev.*, 1951, **49**, 273; (*b*) J. F. Bunnett, *Quart. Rev.*, 1968, **12**, 1; (*c*) J. Miller, 'Aromatic Nucleophilic Substitution,' Elsevier, New York, 1968; (*d*) F. Pietra, *Quart. Rev.*, 1969, **23**, 504.

[2] P. Ananthakrishnanadar and N. Kannan, *J. Chem. Soc., Perkin Trans. 2*, 1980, 749; *Indian J. Chem.*, 1980, **19B**, 923; 1981, **20B**, 978.

[3] S. Sugden and J. B. Willis, *J. Chem. Soc.*, 1951, 1360.

[4] D. J. Byron, G. W. Gray, and R. C. Wilson, *J. Chem. Soc. C*, 1966, 840.

[5] H. Lund and J. Bjerrum, *Ber.*, 1931, **64**, 210.

[6] P. Ananthakrishnanadar and C. Gnanasekaran, *J. Chem. Soc., Perkin Trans. 2*, 1978, 671.

[7] (*a*) P. R. Wells, 'Linear Free Energy Relationships,' Academic Press, London, 1968; (*b*) J. Shorter, *Chem. Britain*, 1969, **5**, 269; (*c*) 'Advances in Linear Free Energy Relationships,' eds. N. B. Chapman and J. Shorter, Plenum, London, 1972.

[8] D. J. Byron, G. W. Gray, and R. C. Wilson, *J. Chem. Soc. C*, 1966, 831, 837.

[9] E. Berliner and E. A. Blommers, *J. Am. Chem. Soc.*, 1951, **73**, 2479.

[10] M. H. Aslam, N. B. Chapman, J. Shorter, and M. Charton, *J. Chem. Res.*, 1981, *S*188, *M*2301.

[11] M. J. S. Dewar, R. Golden, and J. M. Harris, *J. Am. Chem. Soc.*, 1970, **93**, 4187.

[12] J. P. Idoux, V. S. Cantwell, J. Hinton, S. O. Nelson, P. Hollier, and R. Zarrillo, *J. Org. Chem.*, 1974, **39**, 3946.

[13] K. Bowden and D. C. Parkin, *Can. J. Chem.*, 1969, **47**, 185.

[14] R. P. Bell, 'The Proton in Chemistry,' Methuen, London, 1959, p. 155.

[15] (*a*) J. R. Witaber, *J. Am. Chem. Soc.*, 1962, **84**, 1900; (*b*) G. Biggi and F. Pietra, *J. Chem. Soc. B*, 1971, 44; (*c*) W. Tagaki, T. Amada, Y. Yamashita, and Y. Yano, *J. Chem. Soc., Chem. Commun.*, 1972, 1131.

[16] (*a*) V. Baliah and P. Ananthakrishnanadar, *Indian J. Chem.*, 1977, **15B**, 277; (*b*) P. Ananthakrishnanadar and N. Kannan, *ibid.*, 1979, **18B**, 1129.

[17] (*a*) L. Senatore, E. Giuffarin, and A. Fava, *J. Am. Chem. Soc.*, 1970, **72**, 3035; (*b*) E. Guiffarin and L. Senatore, *J. Chem. Soc. B*, 1970, 1680.

[18] T. R. Mohanty and P. L. Nayak, *J. Chem. Soc., Perkin Trans. 2*, 1975, 242.