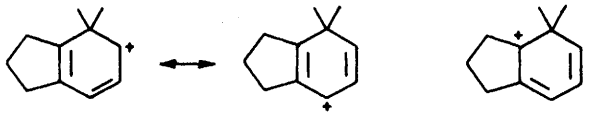
Electrophilic Aromatic Substitution. Part 19.[1] Protiodetritiation of 1,2-Diphenylethane and 9,10-Dihydrophenanthrene: Effect of Strain on Aromatic Reactivity

By **Herbert V. Ansell** and **Roger Taylor,*** School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ, Sussex

Rates of protiodetritiation of 1,2-diphenylethane and 9,10-dihydrophenanthrene in anhydrous trifluoroacetic acid at 70 °C have been measured and yield the following partial rate factors (positions in parentheses): diphenylethane, 100(2); 5.73(3); 200(4); 9,10-dihydrophenanthrene, 100(1); 2 840(2); 189(3); 1 970(4); the corresponding σ^+ values are −0.23, −0.085, −0.26, −0.23, −0.395, −0.26, and −0.375. The overall reactivity of 9,10-dihydrophenanthrene relative to that of fluorene is compatible with the differences in coplanarity between the molecules. The ratio of the reactivities of the positions α and β to the central ring in 9,10-dihydrophenanthrene is higher than in fluorene and confirms that the low reactivity of the α-positions of the latter arises from an increase in strain produced on going to the transition state for α-substitution. The bond-strain theory accounts for the anomalously low reactivity of the 7-position, and of the 3-bromo-substituent effect in detritiation of fluoranthene. A linear free energy correlation exists between molecular chlorination and detritiation of 9,10-dihydrophenanthrene, fluorene, biphenyl, naphthalene, and benzene.

VAUGHAN *et al.*[2] proposed that the low reactivity of the aromatic α-position of indane relative to that of tetralin (and hence the Mills–Nixon effect) arose from the increase in bond strain produced in the five-membered ring on going to the transition state. Thus the bond common to each ring has $\frac{2}{3}$ double bond character in the transition state (I) as opposed to $\frac{1}{2}$ double bond character



(I)

in the ground state. For molecules with six-membered rings as side chains, *e.g.* tetralin, the increase in strain is not significant. One of us argued that as a converse the aromatic β-position should show enhanced reactivity (since the common bond only has $\frac{1}{3}$ double bond character in the transition state) and moreover, that the overall theory could account for the low aromatic α-reactivity in benzocyclobutene, biphenylene, triptycene,[3] fluorene, dibenzofuran, dibenzothiophen, and carbazole,[4] and strained aromatic systems in general.[3] Subsequently, Streitwieser *et al.*[5] re-proposed the same correlation (their paper shows that they were aware of our prior publication); their explanation of the phenomenon was based upon changes in hybridisation of the bridgehead carbon atom, produced by strain. A difference between the two theories is that the bond strain theory predicts that the aromatic β-positions will have enhanced reactivity, whereas the theory of amended hybridisation predicts that they will have diminished reactivity; in no case has the latter been observed.[6] As a further test of

[1] Part 18, H. V. Ansell, M. M. Hirschler, and R. Taylor, *J.C.S. Perkin II*, 1977, **353**.

[2] J. Vaughan, G. J. Welch, and G. J. Wright, *Tetrahedron*, 1965, **21**, 1665.

[3] R. Taylor, G. J. Wright, and A. J. Homes, *J. Chem. Soc.* (*B*), 1967, 780; R. Taylor, *Chimia* (*Switz.*), 1968, **22**, 1.

[4] R. Taylor, *J. Chem. Soc.* (*B*), 1968, 1559.

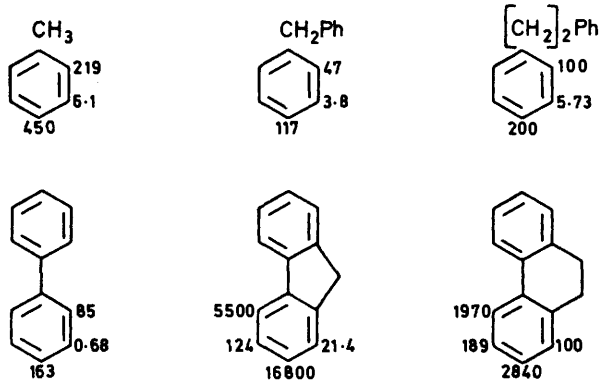
[5] A. Streitwieser, G. R. Ziegler, P. C. Mowery, A. Lewis, and R. G. Lawler, *J. Amer. Chem. Soc.*, 1968, **90**, 1357.

[6] R. Taylor, M. P. David, and J. F. W. McOmie, *J.C.S. Perkin II*, 1972, 162.

these theories we decided to investigate the reactivity of 9,10-dihydrophenanthrene (which does not have a strained central ring) for comparison with that of fluorene (which does). For complete analysis of the data, rates of exchange were measured for each position of 1,2-diphenylethane.

RESULTS AND DISCUSSION

Rates of protiodetritiation in trifluoroacetic acid at 70 °C, compared with the rate of exchange of benzene under the same conditions,[7] lead to the partial rate factors shown in Scheme 1 together with those previously obtained from related molecules.[8]



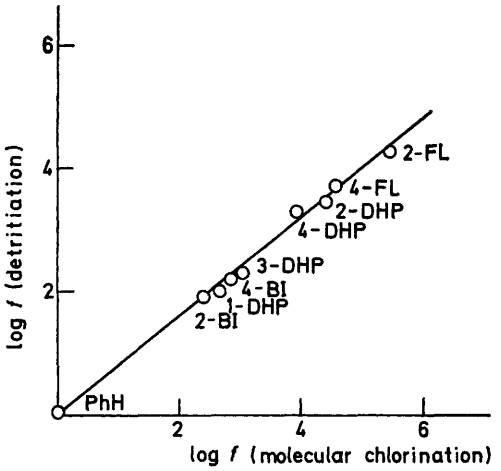
SCHEME 1 Partial rate factors for protiodetritiation in anhydrous trifluoroacetic acid at 70 °C

1,2-Diphenylethane.—Each position in this molecule has a reactivity intermediate between those of toluene and diphenylmethane, as expected in view of the inductive (—*I*) effect of the phenyl substituent. Iodination of 1,2-diphenylethane with iodine acetate also showed its reactivity at the *para*-position to be intermediate between those of toluene and diphenylmethane.[9]

1,2-Diphenylethane gives a log f_o/log f_p value of 0.87 (*cf.* 0.88 for toluene and 0.865 for a whole range of compounds in hydrogen exchange).[10] The following σ^+ values may be assigned for the 2-, 3-, and 4-positions, respectively, in 1,2-diphenylethane: —0.23, —0.085, and —0.26.

9,10-Dihydrophenanthrene.—(i) The reactivities of the 2- and 4-positions in 9,10-dihydrophenanthrene are greater than those of the corresponding positions in biphenyl and less than those in fluorene; this is the result expected on the basis of the differences in planarity between the molecules.

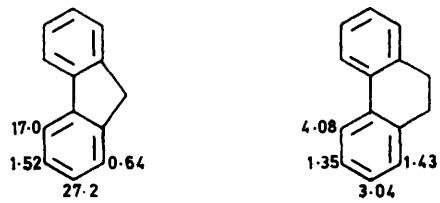
(ii) This intermediate reactivity is paralleled by results for molecular chlorination in acetic acid; [11] indeed there is an excellent linear free energy relationship involving the reactivities of the 2- and 4-positions in biphenyl and fluorene and all positions in 9,10-dihydrophenanthrene (Figure). This shows that steric hindrance is relatively



Linear free energy correlation of rates of molecular chlorination and protiodetritiation (BI = biphenyl; FL = fluorene; DHP = 9,10-dihydrophenanthrene)

unimportant in molecular chlorination, as indicated previously by log f_o/log f_p values for toluene and anisole.[10] We may therefore assign with some confidence the following σ^+ values for 9,10-dihydrophenanthrene (positions in parentheses): —0.23(1); —0.395(2); —0.26(3); and —0.375(4).

(iii) Neglecting for the moment coplanarity effects, we may calculate the positional reactivities in fluorene and 9,10-dihydrophenanthrene from those in diphenylmethane and 1,2-diphenylethane, respectively, and biphenyl. The ratios of the observed to the calculated reactivities are shown in Scheme 2; the fact that these



SCHEME 2 Ratios of observed to calculated reactivities for protiodetritiation

values differ considerably from the expected value of 1.0 reflects in the main the planarity differences (the discrepancies being greatest at the 2- and 4-positions). But an outstanding feature is that the ratios of α- to β-substitution in fluorene are low, being 0.625 (4- and 2-positions) and 0.415 (1- and 3-positions) whereas in 9,10-dihydrophenanthrene the ratios are considerably higher, being 1.33 (4- and 2-positions) and 1.05 (1- and

[7] H. V. Ansell and R. Taylor, *J.C.S. Chem. Comm.*, 1973, 952.
[8] R. Baker, C. Eaborn, and R. Taylor, *J. Chem. Soc.*, 1961, 4927; K. C. C. Bancroft, R. W. Bott, and C. Eaborn, *ibid.*, 1964, 4806; R. Baker, R. W. Bott and C. Eaborn, *ibid.*, 1963, 2136; C. Eaborn and R. Taylor, *ibid.*, 1961, 1012; Y. El-din Shafig and R. Taylor, unpublished results.
[9] Y. Ogata, I. Urasaki, and T. Ishibashi, *J.C.S. Perkin I*, 1972, 180.
[10] H. V. Ansell, M. M. J. Le Guen, and R. Taylor, *Tetrahedron Letters*, 1973, 13; C. Eaborn, T. A. Emokpae, V. I. Sidorov, and R. Taylor, *J.C.S. Perkin II*, 1974, 1454; M. M. J. Le Guen and R. Taylor, *ibid.*, 1976, 559.
[11] P. B. D. de la Mare, E. A. Johnson, and J. S. Lomas, *J. Chem. Soc.*, 1963, 5973; 1964, 5317.

3-positions). Moreover, in 9,10-dihydrophenanthrene, the positions relatively unaffected by coplanarity and conjugative effects (1- and 3-) are more reactive than calculated by closely similar factors (which almost certainly reflects the secondary relay of the extra conjugation arising from the coplanarity). In fluorene, for comparison, the 1- (α-) position is much less reactive than calculated (and in fact less reactive overall than the 1-position in 9,10-dihydrophenanthrene) whereas the 3- (β-) position is significantly more reactive than calculated relative to the corresponding position in 9,10-dihydrophenanthrene. Both observations are predicted by the theory based upon bond strain effects; by contrast the amended-hybridisation theory predicts that the reactivity of the β-position in fluorene should be less than calculated, and this is not observed.

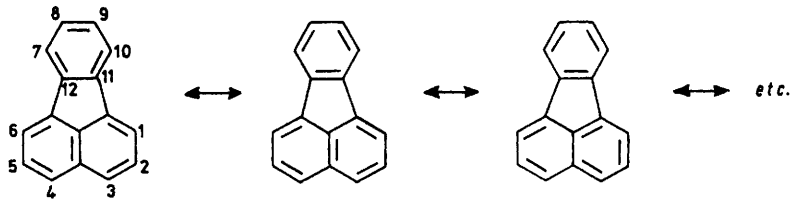
(iv) Similar arguments to those given in (iii) may be applied to the 2- and 4-positions. The situation is less unambiguous here because of the superimposed effect of increased conjugation. Nevertheless the general trend is apparent, for whereas the reactivities of the 2- and 4-positions in 9,10-dihydrophenanthrene exceed those calculated by fairly similar factors (3.04 and 4.08, respectively; *i.e.* relatively more at the α- than at the β-position) [the reason for this is not entirely clear—see (v) below], in fluorene the factors are much more dissimilar being greatest at the β-position (27.2) and least at the α-position (17.0).

(v) The results for 9,10-dihydrophenanthrene suggest that for aromatic systems with six-membered side chains, the α-reactivity is somewhat greater than predicted relative to the β-reactivity, or that the β-reactivity is diminished relative to the α-reactivity. It would be possible to invoke various additional and minor bond-strain effects to account for either possibility, but at this stage we note only that this slightly enhanced β : α reactivity ratio is evident in hydrogen exchange of tetralin (which also has a six-membered side chain) relative to *o*-xylene.[3,12]

An Explanation of the Anomalous Reactivity of Fluoranthenes and Substituted Fluoranthenes in Detritiation.—In recent studies of the rates of detritiation of fluoranthene and substituted fluoranthenes, Bancroft and Howe noted two anomalies which they were unable to explain.[13] (i) The reactivity of the 7-position of fluoranthene was much lower than predicted by a range of theoretical methods; the reactivities of the other positions were in the predicted order. (ii) In comparison with the effects at the analogous positions in naphthalene, bromine in the 3-position produced deactivation at the 2- and 4-positions which was anomalously weak, especially at the latter position.

Both these anomalies find a ready explanation in the bond-strain theory. The central ring of fluoranthene is strained, and considerably more so than in indane. Accordingly, any shortening of the 11,12-bond will be very unfavourable, all the more so since this bond has to bridge the *peri*-naphthalene positions. The 7-position is α to this five-membered ring, and the transition state for 7-substitution involves shortening of the 11,12-bond [*cf.* (I)]; 7-substitution will therefore be unfavourable. The low 1 : 3-reactivity ratio (0.032) compared to that for the corresponding positions in naphthalene (0.13) may also reflect the fact that the 1-position is α to the strained ring.

Because of the strain in the five-membered ring, the most stable canonical form for fluoranthene will be that in which the bonds in this ring will be more nearly single, *i.e.* (II) rather than (III), (IV), *etc.* The bonds in the naphthalene portion should therefore be more fixed than in naphthalene itself. This being so, the 3-bromo-substituent effect will be less readily transmitted to the 4-position (less charge is in any case delocalized to a given position than to the corresponding position in naphthalene because there are more sites for delocalization in fluoranthene). The 3-bromo-substituent should therefore deactivate the 4-position less than the corresponding position in naphthalene. The 2-position is conjugated with the 3-position and since the bond order of the 2,3-bond is expected to be higher than the corresponding bond in naphthalene, the $+M$ effect of bromine should be transmitted more effectively across this bond; the deactivation should be considerably less than in naphthalene. No *X*-ray studies of the bond lengths in fluoranthene have, to our knowledge, been carried out; it would be interesting to see if the predictions from kinetic studies could be verified.



(II) (III) (IV)

The difficulty of forming a double bond in the central ring also inhibits conjugation between the benzene and naphthalene moieties. Thus whereas a 4'-bromo- and 4'-nitro-substituent deactivates the 4-position of fluorene in detritiation by 4.7 and 2 670 times, respectively,[14] the

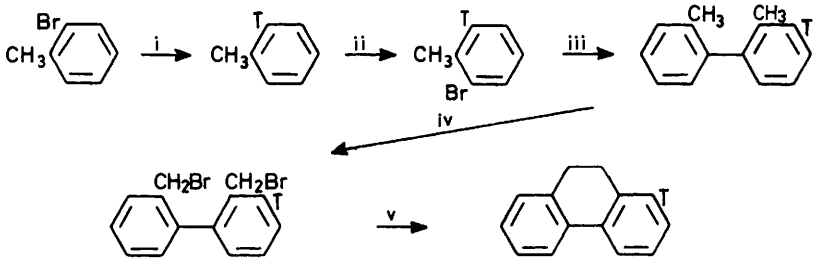
[12] J. Vaughan, and G. J. Wright, *J. Org. Chem.*, 1968, **33**, 2580.
[13] K. C. C. Bancroft and G. R. Howe, *J.C.S. Perkin II*, 1970, 1541; 1971, 400.
[14] R. Baker, R. W. Bott, C. Eaborn, and P. M. Greasley, *J. Chem. Soc.*, 1964, 627.

analogous deactivation of the 3-position by an 8-substituent in fluoranthene is halved, being 2.33 and 1 260 times for bromo and nitro respectively. The relative deactivation of the 3- and 4-positions by the non-conjugating 6-nitro-substituent is a factor of 9.7 and closely similar to that (13.7) produced by the 7-nitro-substituent which, although in a conjugating position, is substantially prevented from doing so because of the restrictions on bond shortening.

EXPERIMENTAL

1-[2-, 3-, *or* 4-^{3}H]*Phenyl-2-phenylethane*.—[2-, 3-, and 4-^{3}H]Toluene were each prepared by hydrolysis, with tritiated water, of the Grignard reagent prepared from the appropriate bromo-compound. Each isomer was brominated in the side chain with *N*-bromosuccinimide, and the Grignard reagent prepared from each active benzyl bromide was coupled with an equimolar quantity of benzyl bromide to give, after work-up involving two recrystallisations from ethanol, 1-[2-, 3-, or 4-^{3}H]phenyl-2-phenylethane, m.p. 52° (lit.,[15] 52°).

9,10-*Dihydro*[1-^{3}H]*phenanthrene*.—The overall method of preparation of this compound is shown in Scheme 3.



SCHEME 3

6-*Bromo*[2-^{3}H]*toluene*. Bromine (0.7 ml, 0.028 mol) dissolved in aqueous 85% acetic acid (20 ml) was added during 2 days to a stirred solution of [2-^{3}H]toluene (1.233 g, 0.013 4 mol; prepared as above) in aqueous 85% acetic acid (25 ml) and stirring was continued during a further day. Normal work-up with addition of inactive *o*-bromotoluene (10 g) gave 6-bromo[2-^{3}H]toluene (9.5 g), shown by g.l.c. to contain 93% of the required *ortho*-isomer (the presence of the other isomers is not important as they cannot lead to a cyclized product). The specific activity was >0.2 mCi ml^{-1} (half the tritium is lost in the bromination).

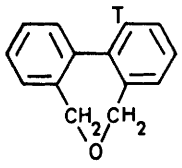
2,2′-*Dimethyl*[3-^{3}H]*biphenyl*. This was prepared from 6-bromo[2-^{3}H]toluene (step iii in Scheme 3) by the general method of Kharasch and Fields;[16] work-up involving fractional distillation gave a 44% yield of 2,2′-dimethyl-[3-^{3}H]biphenyl, b.p. 70—71° at 0.2 mmHg, specific activity 0.35 mCi g^{-1}; g.l.c. analysis showed this to be 95% pure.

2,2′-*Bis*(*bromomethyl*)[3-^{3}H]*biphenyl*. 2,2′-Dimethyl-[3-$^3H_2$]biphenyl (2.08 g, 0.011 4 mol) dissolved in redistilled carbon tetrachloride (6 ml) was heated with dried *N*-bromosuccinimide (4.07 g, 0.022 8 mol) during 30 h. The succinimide which precipitated was filtered off and the filtrate was washed (aq. Na_2SO_4, aq. NaOH, dil. HCl, and aq. Na_2SO_4) and dried (Na_2SO_4). G.l.c. analysis showed the presence of three compounds, one of which was starting material and another of which was subsequently found to be the required product; however the major component (*m/e* 196) separated by column chromatography, had m.p. 72—73°. This was therefore the dihydrodibenzoxepin (V) previously prepared (m.p. 72.5—73°) by Wittig *et al.*[17] by the reaction of 2,2′-bis(hydroxymethyl)biphenyl with hydrobromic acid. Presumably the work-up procedure caused nucleophilic substitution of hydroxide for one of the bromo-substituents followed by elimination of hydrogen bromide; alternatively disubstitution of hydroxide was followed by elimination of water in the subsequent washing with hydrochloric acid; in either event the ease of formation of the seven-membered ring is remarkable.

The procedure was repeated but without any washing after removal of succinimide. Recrystallisation of the crude product from carbon tetrachloride gave 2,2′-bis(bromomethyl)[3-^{3}H]biphenyl (39%), m.p. 91° (lit.,[18] 91—93°). This product (1.51 g, 0.004 4 mol) was cyclized with phenyllithium by the method of Hall *et al.*,[18] and 9,10-dihydrophenanthrene (0.5 g) was added to the crude product. Fractional distillation yielded 9,10-dihydro[1-^{3}H]phenanthrene (0.85 g), specific activity 0.05 mCi g^{-1}, m.p. 35° (lit.,[18] 35—35.5°) (from methanol).

9,10-*Dihydro*[3-^{3}H]*phenanthrene*.—This was prepared by the above route, but from [4-^{3}H]toluene. The final product had a higher specific activity, since in step ii of Scheme 3 bromination does not cause displacement of half the tritium in the toluene.

9,10-*Dihydro*[4-^{3}H]*phenanthrene*.—This was initially prepared, along with an equal amount of the 2-isomer, by the above route from [3-^{3}H]toluene. Because the rates of exchange differed by a factor of only 1.89, however, it was not possible to resolve the curved log(activity) *vs.* time plots into two first-order components. The following route was therefore adopted for preparation of the 4-isomer.



(V)

9,10-*Dihydro*-4-*nitrophenanthrene*. Since nitration of biphenyl in acetic anhydride at low temperature gives

[15] R. A. Smith and S. Natelson, *J. Amer. Chem. Soc.*, 1931, **53**, 3476.

[16] M. S. Kharasch and E. K. Fields, *J. Amer. Chem. Soc.*, 1941, **63**, 2319.

[17] G. Wittig, P. Davis, and G. Koeing, *Chem. Ber.*, 1951, **84**, 627.

[18] D. M. Hall, M. S. Lesslie, and E. E. Turner, *J. Chem. Soc.*, 1950. 711.

maximum *ortho*-substitution [19] we reasoned that the same conditions would give the maximum of 4-substitution in 9,10-dihydrophenanthrene. Nitration of 9,10-dihydrophenanthrene (15 g, 0.073 mol) in acetic anhydride (90 ml) with fuming nitric acid (6.9 g, 0.11 mol) in acetic anhydride (15 ml) during 1 h at 0 °C and a further 1 h while room temperature was attained yielded, after work-up and fractional distillation at 0.05 mmHg, three fractions, b.p. 100—150, 150—180, and >180 °C. G.l.c. indicated the second fraction to contain the required isomer. This fraction was chromatographed; elution with light petroleum (b.p. 60—80 °C) produced unchanged 9,10-dihydrophenanthrene. Elution with benzene–light petroleum (1 : 4) produced almost pure 9,10-dihydro-4-nitrophenanthrene followed by a mixture of this with the 2-isomer. Recrystallisation from ethyl acetate gave pure 9,10-dihydro-4-nitrophenanthrene (1.30 g, 8%), m.p. 98.5 (lit.,[20] 97—98°).

4-Amino-9,10-dihydrophenanthrene. The method of Krueger and Mossetig was modified in that the catalyst was palladium–charcoal, and the hydrogen was under pressure of 45 lb in^{-2}. The product (1.026 g, 91%) has m.p. 55° (lit.,[20] 52—54°).

The amino-group in this compound was replaced by bromine; treatment of the bromo-compound with n-butyllithium followed by hydrolysis with tritiated water gave 9,10-dihydro[4-^{3}H]phenanthrene.

9,10-Dihydro[2-^{3}H]*phenanthrene*.—Since bromination by bromine in trifluoroacetic acid is very *para*-selective,[21] 9,10-dihydrophenanthrene was brominated with bromine in this solvent. G.l.c. analysis showed the 2-isomer to be the main component (it had the longest retention time). 2-Bromo-9,10-dihydrophenanthrene (contaminated with a little 9,10-dihydrophenanthrene) was obtained by column chromatography [light petroleum (b.p. 60—80 °C) as eluant]. Hydrolysis of the lithium derivative prepared from this, with tritiated water, gave, after normal work-up, 9,10-dihydro[2-^{3}H]phenanthrene. Kinetic studies on this compound gave a rate within 3% of that obtained by Bancroft [22] with the same isomer prepared by a different route.

Kinetic Studies.—These were carried out as previously described.[23] Rate coefficients were reproducible to better than ±1.5% and were measured over a range of temperatures (Table). The significance of the values at temperatures other than 70 °C will be discussed later along with other data; only the values obtained at 70 °C were used in calculating the partial rate factors.

Rates ($10^7k/s^{-1}$) for protiodetritiation of ArH in trifluoroacetic acid

	t/°C			
ArH	70	110	160	180
1-[2-^{3}H]Phenyl-2-phenylethane	9.47, 9.49	198		
1-[3-^{3}H]Phenyl-2-phenylethane	0.544	17.3	297	716
1-[4-^{3}H]Phenyl-2-phenylethane	18.9, 19.2	408		
9,10-Dihydro[1-^{3}H]phenanthrene	9.48, 9.55			
9,10-Dihydro[2-^{3}H]phenanthrene	270, 278			
9,10-Dihydro[3-^{3}H]phenanthrene	17.9, 18.0			
9,10-Dihydro[4-^{3}H]phenanthrene	187, 187			

[6/1645 *Received*, 24*th August*, 1976]

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[20] J. W. Krueger and E. Mossetig, *J. Org. Chem.*, 138, **3**, 343.
[21] H. V. Ansell and R. Taylor, *J. Chem. Soc.* (*B*), 1968, 526.
[22] K. C. C. Bancroft, Ph.D. Thesis, University of Leicester, 1963.
[23] J. M. Blatchly and R. Taylor, *J. Chem. Soc.*, 1964, 4641.