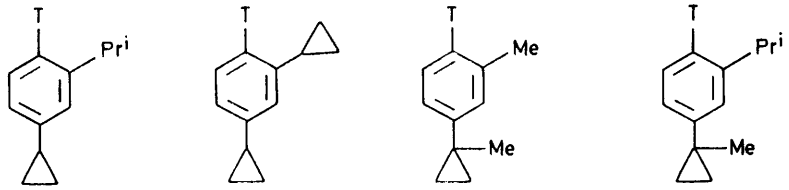
# Electrophilic Aromatic Substitution. Part 26.[1] The Effect of the Cyclopropyl Substituent in Aromatic Detritiation

By **Peter Fischer**, Organic Chemistry Institute, University of Stuttgart, D–7000, Stuttgart 1, W. Germany
**Roger Taylor,*** School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ, Sussex

The effects of the *ortho*- and *para*-cyclopropyl and *para*-1-methylcyclopropyl substituents in acid-catalysed hydrogen exchange have been determined through detritiation of a range of disubstituted aromatics in various acetic acid–trifluoroacetic acid media at 70°. The *p*-cyclopropyl substituent gives *f* 13 900 and $\sigma^+$ −0.473, the latter being in excellent agreement with values obtained in other reactions. The *o*-cyclopropyl substituent is much less activating, *f* 1 630, and this confirms that the very high *ortho* : *para* ratios obtained in nitration (especially in acetic anhydride) are anomalous, as they are for certain other substituents. The value for log $f_o$/log $f_p$ for cyclopropylbenzene in hydrogen exchange (0.77) is significantly lower than for other alkyl- and cycloalkyl-benzenes (each of which gives a value of −0.875 ± 0.01) implying that the bisected conformation of the *o*-cyclopropyl group is not quite achieved in the (normally) unhindered exchange reaction. The *p*-1-methylcyclopropyl substituent is more activating than the *p*-cyclopropyl substituent ($f_p$ 39 200, $\sigma^+$ −0.525) just as *p*-t-butyl is more activating than *p*-isopropyl in trifluoroacetic acid media, and may be attributed to the same cause *viz.* the greater inductive and hyperconjugative effect of the methylated species. In these poorly solvating media, the greater importance of C–C hyperconjugation over C–H hyperconjugation is not masked by steric hindrance to solvation. All the cyclopropyl substituents are slightly more activating (relative to methyl) in media containing less trifluoroacetic acid, suggesting that the former are more polarisable. However, since this behaviour parallels, though to a much lesser extent, that of the methoxy-substituent (which is strongly hydrogen-bonded in trifluoroacetic acid), we cannot exclude the possibility that cyclopropyl is similarly, but slightly, hydrogen-bonded. Rate factors were therefore determined in media in which hydrogen bonding is insignificant even for methoxy. The rate *versus* acidity profile for exchange in a wide range of acetic acid–trifluoroacetic acid media has been determined and shows that at 70°, exchange in acetic acid is $10^{8.2}$ times slower than in trifluoroacetic acid. Between acetic acid and trifluoromethanesulphonic acid, a reactivity range of $10^{20}$ is therefore encompassed.

DURING the past 15 years there have been a large number of studies of the electrophilic reactivity of cyclopropylbenzene and its derivatives.[2-19] In nitration, a common feature for cyclopropylbenzene itself is the high *ortho* : *para* product ratio, which varies from 2.0 using nitric acid–sulphuric acid as the nitrating medium,[3] to as high as 4.7 using acetyl nitrate.[3] (The actual value obtained under the latter conditions can vary according to the method of preparation of the reagent.[2,4,5,10,19]) A high ratio (1.7) is also obtained in nitration of *trans*-1,2-diphenylcyclopropane, though 2,2-dichlorocyclopropylbenzene gave a substantially lower ratio,[13] due most probably to the intervention of a strong $-I$ effect; likewise 1,1-diphenylcyclopropane, in which the *ortho* positions are severely sterically hindered, gave a low ratio.[9] The specific *ortho*-orientation in nitration is shown in the reaction with 4-cyclopropylbiphenyl and 4,4′-dicyclopropylbiphenyl,[15] where substitution occurs to a significant extent *ortho* to the cyclopropyl group, even though this position is *meta* to phenyl and therefore normally unreactive. Likewise a ratio of 1.0 is obtained in nitration of 2-cyclopropylbiphenyl [16] (in which there is only one position *ortho* and one position *para* to the cyclopropyl substituent) and a ratio of 3.0 is obtained (relative to cyclopropyl) in nitration of *o*-methylcyclopropylbenzene.[14]

These high ratios are inexplicable in electronic terms, and indicate a special mechanism for *ortho* nitration; one possibility is that the electrophile co-ordinates initially with the substituent,[12] in the manner proposed for anisole [20] and biphenyl.[21] Another follows from the fact that nitration *ipso* to a cyclopropyl substituent has been observed.[18] It is a common feature of all *ipso*-nitrations that the initial attack takes place at the point of highest electron density in the aromatic ring, and this is followed by 1,2- or 1,3-migration of the nitro-group.[22]




(I) (II) (III) (IV)

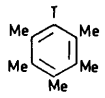
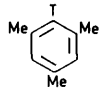
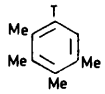
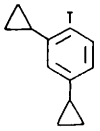
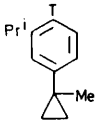
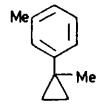
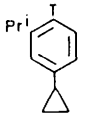
By contrast, halogenation of cyclopropylbenzene gives very low *ortho* : *para* ratios.[12,17,23,24] Unfortunately, neither of these results give much idea of the electronic effect of the *ortho*-cyclopropyl substituent, because halogenation is subject to moderate to severe steric hindrance, whilst nitration gives anomalously high *ortho* : *para* ratios for other substituents. Consequently we felt it would be of value to determine the effect in hydrogen exchange since in this reaction almost every aromatic compound is almost entirely free of steric hindrance. Previously one of us attempted such a study (see ref. 25) but this was defeated by the ease with which

the cyclopropyl ring opened in the presence of anhydrous trifluoroacetic acid at 70 °C, the standard condition for acid-catalysed detritiation. However, it appeared that with suitable activation by other substituents the reactivity of the aromatic could be increased to the point where weaker acids, which would not produce ring-opening, could be employed. Accordingly we have now prepared the tritiated compounds (I)—(IV) and measured their rates of acid-catalysed hydrogen exchange, from which substituent effects may be determined, as follows: (i) comparison of the rate of exchange of (I) and [*o*-$^3$H]-isopropylbenzene gives $f_p$ (cyclopropyl); (ii) comparisons of the rate of exchange of (II) and the value of $f_p$ (cyclopropyl) determined in (i) gives $f_o$ (cyclopropyl); and (iii) comparison of the rates of exchange of (III) and (IV) with [*o*-$^3$H]toluene and [*o*-$^3$H]isopropylbenzene, respectively, gives $f_p$ (1-methylcyclopropyl).

These data also provide information on the relative electron-releasing abilities of *p*-cyclopropyl and *p*-1-methylcyclopropyl substituents which is of interest because the former is more activating in nitration,[12,19] whereas the latter is more reactive in bromination.[12]

TABLE 1

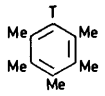
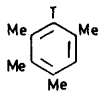
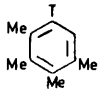
Rate coefficients ($10^7k$/s$^{-1}$) for detritiation in TFA–HOAc mixtures

| Aromatic | Vol % TFA in HOAc 100 | 50 | 35 | 25 | 15 |
|---|---|---|---|---|---|
|  | 7 011 000 [a] | 18 520 | 1 360 | 245 | 34.0 |
|  | 674 500 [a] | 1 674 | 129 | 21.1 | 3.45 |
|  | 113 050 [a] | 247 | 18.7 | 3.20 | 0.51 |
|  | | 908 | 94 | 17 | 2.6 |
|  | | 414 | | 8.00 | 1.21 [c] |
|  | | 387 | | 7.40 | 1.12 [c] |
|  | | 183 | | 3.33 | 0.52 [c] |
|  | 17 000 [b] | | 23.7 | | 1.89 |
|  | $9.5 \times 10^{-2}$ | $1.2 \times 10^{-4}$ [c] | $8.9 \times 10^{-6}$ [c] | $1.61 \times 10^{-6}$ [c] | $2.23 \times 10^{-7}$ [c] |

[a] Ref. 26. [b] Ref. 27. [c] Calculated values (see text).

TABLE 2

Relative reactivities of polymethylbenzenes

| | Vol % TFA in HOAc 100 | 50 | 35 | 25 | 15 |
|---|---|---|---|---|---|
|  | 62 | 75 | 73 | 76 | 67 |
|  | 6.0 | 6.8 | 6.9 | 6.6 | 6.8 |
|  | 1 | 1 | 1 | 1 | 1 |
| ρ | −8.75 | −9.1 | −9.1 | −9.1 | −9.1 |

## RESULTS AND DISCUSSION

Rate coefficients for detritiation of (I)—(IV) and for some polymethylbenzenes and [*p*-$^3$H]anisole, were measured in various acetic acid–trifluoroacetic acid (TFA) media, and are given in Table 1. The following features are notable.

(i) The rate spread for the polymethylbenzenes (shown in Table 2) appears to be greater in the acetic acid-containing media as expected (though it is difficult to be certain of this because the rate coefficients for exchange in TFA alone are so high [26] that the possibility of errors being introduced by the difficulty in measuring the rates cannot be excluded); a ρ factor of *ca.* −9.1 may be calculated for the acetic acid-containing media. From the partial rate factor for pentamethylbenzene in anhydrous TFA (73 800 000) [27] and the exchange rate coefficient for this compound in each medium, the rate coefficient for benzene in each medium may be calculated. (This is too low to measure except in anhydrous TFA.) The absolute accuracy of these values is unimportant for it depends upon ρ, and any error in ρ largely cancels out in the calculations which follow.

(ii) From the rate coefficients for detritiation of [*p*-$^3$H]anisole (Table 1) and the calculated coefficients for detritiation of [$^3$H]benzene (Table 2), $\sigma^+_{p\text{-OMe}}$ may be calculated as −0.705 (50% TFA–50% HOAc) and −0.76 (15% TFA–85% HOAc). These values may be compared with the value of −0.60 which is obtained in TFA above,[28] and the standard value of −0.778, and

show that hydrogen-bonding (which decreases as the TFA content of the acetic acid media decreases) [29] is almost non-existent in the weakest acid medium we have used. The need for this conclusion is evident from (iii).

(iii) The rates of exchange of the cyclopropyl-substituted aromatics relative to the polymethylbenzenes are slightly greater in the weaker acids than in the 50% TFA–50% HOAc medium [but are constant relative to each other (Table 3)]. This could thus be due either to

TABLE 3

Relative reactivities of cyclopropylbenzenes

| | Vol % TFA in HOAc | |
|---|---|---|
| Compound | 50 | 25 |
| (II) | 4.96 | 5.10 |
| (IV) | 2.26 | 2.40 |
| (III) | 2.10 | 2.22 |
| (I) | 1.0 | 1.0 |

greater polarisability of cyclopropyl relative to methyl (so that the $+E$ effect becomes greater in the reaction of the weaker electrophile), or to slight hydrogen-bonding of the cyclopropyl substituent (in view of its high π-density). However, this rate effect is very much smaller than for anisole (the rate of exchange of which in the 35% TFA–65% HOAc medium is only 22% of that predicted) and since hydrogen-bonding of the latter has almost disappeared in the 15% TFA–85% HOAc medium, we may use the rate coefficients for exchange of the cyclopropyl-substituted compounds in this medium, with confidence.

(iv) The value of $f_{p\text{-cyclopropyl}}$ is determined by the principle noted in the introduction, as follows. For compound (I) the overall partial rate factor is $0.52/2.23 \times 10^{-7} = 2.33 \times 10^6$, and in order to separate this into the components due to *o*-isopropyl and *p*-cyclopropyl we must first correct for the fact that additivity does not precisely hold for the polyalkylbenzenes due to the reactivity–selectivity effect.[26,27] Fortunately, a smooth curve connects the observed and predicted polyalkylaromatic reactivities (not shown) from which we can calculate a 'true' additive partial rate factor of $5.62 \times 10^6$. This in turn must be corrected to the partial rate factor that would apply in pure TFA, *i.e.* antilog $[(\log 5.62 \times 10^6) \times 8.75/9.1] = 3.09 \times 10^6$. Since $f_{o\text{-isopropyl}} = 223$,[25] then $f_{p\text{-cyclopropyl}} = 13{,}900$ and $\sigma^+_{p\text{-cyclopropyl}} = 0.473$. An error of 0.2 ρ units in our estimation of ρ (which seems improbable) produces an error in $\sigma^+$ of only 0.014 σ units, due to cancellation of errors in the method of calculation. The derived $\sigma^+$ value may therefore be used with some confidence, and we note that it compares well with the literature values which range from −0.41 to −0.54.[5-8] (This variation may not be the result of genuine physical phenomena such as polarisability, since the ρ factors are somewhat imprecisely defined in some of the reactions used.) The data of Hahn *et al.*[5] are probably the most reliable, and in Table 4 are gathered the values for the *p*-cycloalkyl substituents determined in detritiation,[25] and in solvolysis of 1-aryl-1-methylpropyl chlorides in 90% aqueous acetone.[5] The pattern which one of us noted previously for the cycloalkyl substituents, *viz.* that the $\sigma^+$ value is depressed in solvolysis due to substantial steric hindrance to solvation,[25,30] is confirmed for cyclopropyl. Since this latter is the smallest substituent we should expect that $\delta\sigma^+$ would be smallest, as observed. (However, it must be borne in mind that the $\sigma^+$ values for this substituent are the least accurate extrapolations or approximations being used in both methods to derive the values.)

TABLE 4

Values of $\sigma_p^+$ from detritiation (TFA) and solvolysis of 1-aryl-1-methylpropyl chlorides (90% aqueous acetone

| | Cyclopropyl | Cyclobutyl | Cyclopentyl | Cyclohexyl |
|---|---|---|---|---|
| Detritiation | −0.473 | −0.346 | −0.352 | −0.338 |
| Solvolysis | −0.462 | −0.290 | −0.303 | −0.285 |
| $\delta\sigma^+$ | 0.011 | 0.056 | 0.049 | 0.053 |

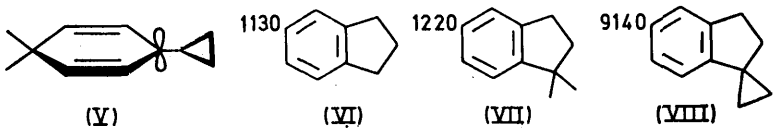
In nitration, Stock and Young [19] obtained a value of 947 for $f_{p\text{-cyclopropyl}}$ (under conditions which gave $\rho = -7.3$, based on $f_{p\text{-Me}}$ and $\sigma^+_{p\text{-Me}}$) and this gives $\sigma^+_{p\text{-cyclopropyl}} = -0.41$, somewhat lower than our value. However they did not consider this value related to the fully bisected conformation (V), in which electron release should be greatest,* because along the series of compounds (VI)—(VIII), the partial rate factors were obtained as shown. In (VIII) the cyclopropyl group is constrained in the bisected conformation (relative to the aromatic ring) and from these data a value of $f_{p\text{-cyclopropyl}}$ of 1 880 was calculated, hence $\sigma^+ = -0.449$. Unfortunately this result is not unambiguous, because in (VIII) the cyclopropyl substituent will significantly increase the strain in the five-membered ring, which is known to increase the reactivity of the β-aryl position.[31] Secondly, although the conformation arguments which are accepted for biphenyl are here applied to the cyclopropyl substituent, there is a major difference in the amount of steric hindrance to coplanarity in biphenyl compared to cyclopropylbenzene. Thus any variation in electron-releasing ability by the *p*-cyclopropyl substituent may (in the absence of *ortho*-substituents) be a polarisability effect rather than a conformational one.

(v) Application of the calculation method given in (iv) to compound (II) gives $f_{o\text{-cyclopropyl}} = 1\,630$ and hence $\sigma^+_{o\text{-cyclolpropyl}} = -0.365$. Two points follow. First, the *o*-cyclopropyl substituent is *not* more activating than the *p*-cyclopropyl substituent, so the nitration results are confirmed as anomalous. Secondly, the ratio $\log f_o : \log f_p$ for cyclopropyl (0.77) is significantly lower than that (0.875) which we obtained for other alkyl- and cycloalkylbenzenes.[25,32] Since our method of calculation takes into account any reactivity–selectivity effects, and since hydrogen exchange is unhindered except in the most

* Because overlap between the empty *p* orbital in the aromatic ring, and the σ electrons of the cyclopropyl ring (carbon–carbon hyperconjugation) will be maximal. Hyperconjugation will also relieve the strain in the three-membered ring, thereby accounting for the high overall electron release by the cyclopropyl substituents.

severe situations, it is difficult to account for this result. The simplest interpretation is that in the transition state the *o*-cyclopropyl substituent is prevented from attaining the bisected conformation, but models give no indication why this should be so.

(vi) The data for compounds (III) and (IV) show excellent self-consistency with the data for exchange of

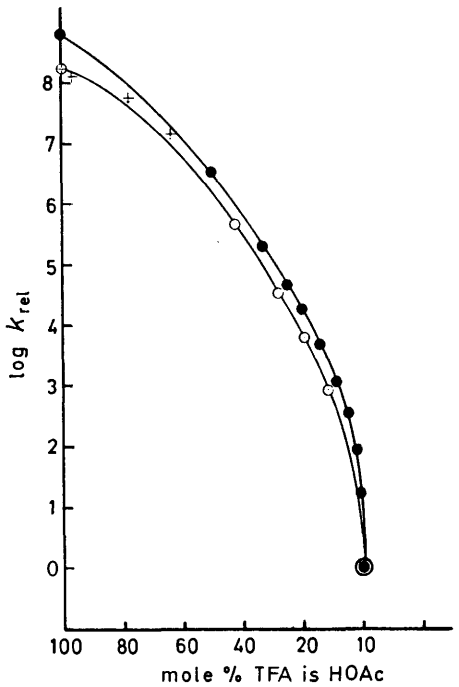



(V) (VI) (VII) (VIII)

[*o*-$^3$H]toluene and [*o*-$^3$H]isopropylbenzene, for which the partial rate factors are 219 [33] and 223,[25] respectively, *i.e.* in both sets of compounds the isopropyl substituent is slightly the more activating. Treatment of the data as in (iii) gives an average value of $f_{p\text{-1-methylcyclopropyl}} = 39\,200$ and $\sigma^+ = -0.525$. Thus the 1-methylcyclopropyl substituent is more activating than cyclopropyl, and this is the first determination in which this is found to be so. The reason is that in the poorly solvating trifluoroacetic acid-containing media, the true electron-releasing ability of the 1-methylcyclopropyl substituent (arising from the greater importance of C–C over C–H hyperconjugation) is not masked by steric hindrance to solvation; likewise in these media *p*-t-butyl is more activating than *p*-isopropyl (or *p*-methyl).[33] Steric hindrance to solvation causes the effects of these two sets of substituents to be paralleled in other reactions. Thus in molecular bromination, in which steric hindrance to solvation is severe, *p*-1-methylcyclopropyl is less activating than *p*-cyclopropyl,[12] and *p*-t-butyl is less activating than *p*-isopropyl [34] whilst in nitration the substituents in each set have closely similar reactivities.[12,19,35]

*Hydrogen Exchange in Acetic Acid–Trifluoroacetic Acid Media.*—Because the ρ factor for hydrogen exchange is fairly large, it is not possible to cover a complete range of aromatic reactivities using trifluoroacetic acid as the exchanging medium. For unreactive aromatics, mixtures of mineral acids with trifluoroacetic acid may be used, but these have the disadvantages of introducing side reactions and, moreover, it is difficult to reproduce exchange rates between different acid batches because the rate is so sensitive to the medium composition. For these compounds, we consider that mixtures of trifluoroacetic acid and trifluoromethanesulphonic acid are best, and details of rate *versus* acidity plots will be published at a later date; trifluoromethanesulphonic acid accelerates exchange by a factor of $2.2 \times 10$.[11,36]

For very reactive aromatics, mixtures of acetic acid and trifluoroacetic acid have been favoured by various workers [37] and these have the advantage of substantially reducing the rates of side reactions (*e.g.* ring-opening in the present case) that can occur using trifluoroacetic acid alone. We therefore considered it useful to construct the rate *versus* acidity profile for detritiation in these media at 70°. Since pentamethylbenzene was too unreactive in AristaR acetic acid, the reactivity difference between this and 15 vol % trifluoroacetic acid was determined using [2-$^3$H]-5-methylthiophen, which gave rate coefficients of $7.0 \times 10^{-7}$ and $5\,850 \times 10^{-7}$ $s^{-1}$, respectively. The profile is given in the Figure (15, 25, 35, and 50 vol % TFA are 11.6, 19.9, 28.7, and 42.8 mol %, respectively) and also includes points (crosses) obtained by Baker and Eaborn [38] for [4-$^3$H]-4′-methylbiphenyl. The profile shows that exchange in acetic acid takes place $10^{8.2}$ times slower than in trifluoroacetic acid, and from the graph we may interpolate that in order to obtain successive ten-fold reductions in exchange rate, media of the following approximate composition (in mol % TFA) may be used: 69.0, 50.5, 36.0, 24.0, 14.5, 7.5, and 2.5.




Correlation of log (relative hydrogen exchange rate) *versus* concentration of acetic acid–trifluoroacetic acid media: ●, dedeuteriation, 25 °C; ○, detritiation, 70 °C, this work; +, detritiation, 70 °C, from ref. 29

From the work of Shatenshtein and his co-workers,[39,*] it is also possible to construct a rate *versus* acidity profile for dedeuteriation at 25 °C (Figure). This has a similar form to ours, but the rate spread is larger as expected for the lower temperature involved (and will also depend upon the fact that the ρ factor for detritiation is smaller than for dedeuteriation.[40] The rate spread will also

* There are typographical errors in this Table. The molar compositions on lines 1 and 11 should read 20 and 2, respectively. The medium on line 19 should read $CF_3CO_2H$ (not HOAc).

depend upon the reactivities of the aromatics involved (more reactive aromatics will give a smaller rate spread) and since more than one aromatic is used in constructing the profiles, small errors will be introduced by this also. Nevertheless, from the exchange rates obtained in a given medium it should be possible to calculate the exchange rate in trifluoroacetic acid with fairly high accuracy.

## EXPERIMENTAL

The tritiated aromatics were prepared from the corresponding bromoaromatics,[12] by reaction with n-butyllithium followed by hydrolysis of the organolithium intermediate with tritiated water. 5-Methyl[2-$^3$H]thiophen was kindly donated by Dr. A.R. Butler.

Kinetic studies were carried out in the usual manner.[41] Deviant points were found in some kinetic runs and these appeared to be more frequent with the weaker acid media. We attribute this to catalysis of exchange by Lewis acid sites on the glass ampoules, since such an effect could be expected to be more significant in the weaker media. Sufficient runs were carried out in each compound under each condition such that the derived rate coefficients were not significantly affected by these deviations. The occasional deviation apart, the kinetic plots were of good first-order linear form, and this confirmed that ring-opening of the cyclopropyl compounds did not take place under the exchange conditions, since this would have produced less reactive aromatics and a decrease in rate coefficient with time.

[9/1425 *Received*, 6*th September*, 1979]

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