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Heterocyclic Fused Tropylium Ions

IV. Stabilities and Electrophilic Deuteriation of Some Dithieno- and Furothienoannelated Tropylium Ions*

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Unusually stable tropylium ions with pK_{R^+} values of 6.65, 5.40, 6.9 and 6.8 have been found in dithieno[2,1-b;4,5-b′]tropylium perchlorate (V), dithieno[2,1-b;5,4-b′]tropylium perchlorate (VI), furo[3,2-a]thieno[2′,3′-d]tropylium perchlorate (VII) and furo[2,3-a]thieno[3′,2′-d]tropylium perchlorate (VIII), respectively. Thus thieno- and furoannelation stabilize the tropylium ion, while the result of the corresponding benzoannelations is strong destabilization. Attempts are made to explain these differences.

It was found that V, VI, and VII smoothly underwent deuterium exchange with concentrated deuteriosulphuric acid in the heterocyclic β-positions. This was proven in the case of V and VI by the synthesis of authentic 3-deuterio derivatives.

A few years ago Pettit *et al.*[1] made the interesting observation that the fusion of a thiophene ring with its b-side onto the tropylium ion increased the stability (pK_{R^+} of I $= +6.0$), while it was known that benzoannelation decreased the stability[2] (p$K_{R^+} = +1.7$), compared to that of the tropylium ion[3] (p$K_{R^+} = 4.7$). Further annelation of benzene rings decreased the stability of the carbonium ion even more (p$K_{R^+} = -1.9$ for the dibenzotropylium ion IV).[4] The reason for the destabilizing effect of benzoannelation is not well understood.[4,5] It has been suggested that fusion of benzene rings, which in principle should cause an extension of the conjugated system, stabilizes the conjugate base or bases to a greater extent than the ion itself. One contribution to the relative destabilization has in some cases been ascribed to *peri* hydrogen interference, which could cause deviation from coplanarity.[6–8] Angular strain has also been mentioned as a factor contributing to the lower stability of benzoannelated systems.[8]

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[*] Taken in part from the Ph.D. theses of U. Michael, University of Lund 1971 and B. Yom-Tov, University of Lund 1972.

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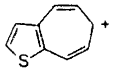
SYNTHESES AND QUALITATIVE OBSERVATIONS

In order to obtain a better understanding of the annelation effects in tropylium ion chemistry, we have prepared some dithieno- and furothieno-annelated tropylium ions and studied their stabilities, their spectroscopical properties and electrophilic deuteriation. We were also interested in such compounds in connection with investigations on isoelectronic borepins.[9] The syntheses of dithieno[2,1-b;4,5-b']tropylium perchlorate (V) and dithieno[1,2-b;5,4-b']tropylium perchlorate (VI) have been described previously,[10],[11] and preliminary reports of some physical and chemical properties have been given.[10] Furo[2,1-b]thieno[4,5-b]tropylium perchlorate (VII) and furo[1,2-b]-thieno[5,4-b]tropylium perchlorate (VIII) were prepared[12] in a similar way as that described for the dithieno analogues.[11] Thus 4,5-dihydro-9H-thieno-[4,5-b']cyclohepta[2,1-b]furan-9-one (IX)[12] was transformed to 9H-thieno-[4,5-b']cyclohepta[2,1-b]furan-9-one (X) by side-chain bromination-dehydrobromination. Reduction of X with lithium aluminium hydride gave 9H-thieno-[4,5-b']cyclohepta[2,1-b]furan (XI), which was difficult to obtain pure and therefore was directly transformed to the tropylium perchlorate VII, by reaction with triphenylmethyl perchlorate. Following the same reaction sequence, VIII was prepared *via* 8,9-dihydro-4H-thieno[5,4-b']cyclohepta[1,2-b]furan-4-one (XII),[12] 4H-thieno[5,4-b']cyclohepta[1,2-b]furan-4-one (XIII) and 4H-thieno[5,4-b']cyclohepta[1,2-b]furan (XIV). The structures of the compounds were evident from the mode of synthesis, and from IR, NMR, and mass spectral data.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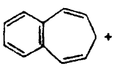
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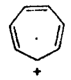
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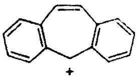
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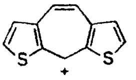
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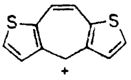
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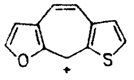
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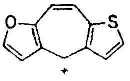
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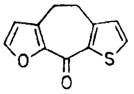
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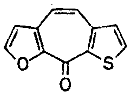
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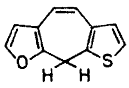
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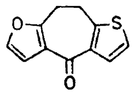
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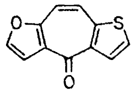
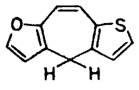

XIII

Qualitatively, the high stability of the tropylium ions V to VIII is demonstrated by several observations. The first indication stems from the ease with which IX, XII, 4,5-dihydro-9H-cyclohepta[2,1-b;4,5-b']dithiophene-9-one (XV)[13] and 8,9-dihydro-4H-cyclohepta[1,2-b;5,4-b']dithiophene-4-one (XVI),[13] in contrast to 8,9-dihydro-4H-cyclohepta[2,1-c;4,5-c']dithiophene-4-one

(XVII),[13] underwent bromination-dehydrobromination to the cycloheptatrienone derivatives. The driving force for the spontaneous dehydrobromination is probably the fact that the newly introduced unsaturation is part of an aromatic system. (The unsaturated ketones have tropylium ion structures in one of their dipolar forms.)

The lithium aluminium hydride reduction of X, XIII, 9H-cyclohepta-[2,1-b;4,5-b′]dithiophene-9-one (XVIII)[10] and 4H-cyclohepta[1,2-b;5,4-b′]-dithiophene-9-one (XIX)[10] yields the methylene derivatives and not the carbinols, corresponding to the ketones. A mixture of lithium aluminium hydride and aluminium chloride reduces some ketones to the methylene stage.[14] In this reducing mixture the aluminium chloride enhances the electrophilicity of the carbonyl carbon and eases the C–O bond cleavage. In the cases of ketones X, XIII, XVIII, and XIX, the carbon is electrophilic enough so that the Lewis acid is not necessary. The tropylium ions might be intermediates in these cases. The saturated ketone XII yielded only the corresponding carbinol upon reaction with lithium aluminium hydride. Furthermore the dibenzocycloheptatrienone (XX) also yielded the corresponding carbinol. This is understandable if it is considered that the corresponding dibenzotropylium ion IV is 10^8-10^9 times less stable than the corresponding dithieno- or furothienoannelated tropylium ions (*cf.* below). The difficulty experienced in the reduction of 4H-cyclohepta[2,1-c;4,5-c′]dithiophene-4-one (XXI)[13] might also be associated with the expected lower stability of the corresponding tropylium ion.

Additional evidence for the stability of the tropylium ions and the delocalization of the positive charge in the tricyclic system is obtained from a study of the C=O stretching region in the IR spectra of the ketones. Due to the high contribution of dipolar resonance forms having C–O single bonds, low frequencies for the C=O stretching are expected. However, the situation is somewhat complicated as several bands are observed in the pertinent region



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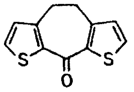

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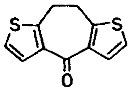

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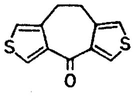

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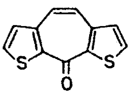

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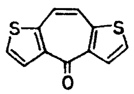

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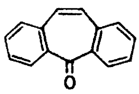

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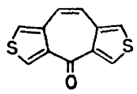
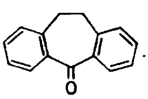
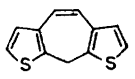


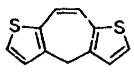
XXI



XXII



XXIII



XXIV

for the unsaturated ketone. This was already found by Doering and Detert[15] in their classical work on tropone, for which they observed two bands at 1638 cm^{-1} and 1582 cm^{-1}. By extrapolation from benzoannelated derivatives, Heilbronner *et al.* assigned the lower frequency band to carbonyl stretching.[5] For the unsaturated ketones X, XIII, XVIII, and XIX, we have assigned the broad high-intensity bands to the carbonyl stretching frequency (Table 1). The sharper peaks of lower intensity (given in parentheses) are most probably due to $C=C$ stretching, or perhaps are ring stretching bands. For XXI only one band was observed in this region.

The IR spectra were measured both in the solid state and in $CHCl_3$ solution. It is obvious that on going from the saturated to the unsaturated b-annelated dithieno or furothieno systems a shift of about 50 cm^{-1} towards lower frequency is observed. This effect is absent in the c-annelated dithieno derivatives XXI and XVII, and in the dibenzo systems XX and 10,11-dihydro-5H-dibenzo[a,d]cyclohepta-5-one (XXII).

Table 1. Frequencies in the $C=O$ stretching region of some dithieno- and furothieno-annelated cycloheptanones.

Unsaturated ketone No.	Frequency cm^{-1}		Saturated ketone No.	Frequency cm^{-1}	
	in KBr	in $CDCl_3$ (≈ 5 %)		in KBr	in $CDCl_3$ (≈ 5 %)
X	1565 (1622)	1573 (1613)	IX	1612	1618 (1575)
XIII	1582 (1612)	1575 (1604)	XII	1630	1625
XVIII	1545 (1602)	1550 (1575) (1600) (1612)	XV	1595	1598
XIX	1568 (1598)	1568 (1598) (1612) (1585)	XVI	1621	1618 (1595)
XXI	1617	1616	XVII	1621	1625
XX	1650 (1600)		XXII	1648 (1595)	

It has recently been shown by X-ray analysis that compound XX is not planar.[16] The more extensive conjugation of a carbonyl group attached to the 2-position of thiophene or furan, compared to one attached through the 3-position, first pointed out for 2- and 3-thiophene aldehyde,[17] is also evident from the data given in Table 1.

pK_{R^+} Values

The pK_{R^+} values of V, VI, and VIII could easily be determined by titrating dilute ($< 2 \times 10^{-4}$ molar) aqueous carbon dioxide-free solutions of the perchlorate with dilute sodium hydroxide solution. Under these conditions reproducible ʃ-shaped curves were obtained. The pH at half neutralization was taken as pK_{R^+}. Solutions with higher concentration of tropylium ion became turbid on standing, and the titration curves obtained from such solutions deviated more from the classical ʃ shape the more concentrated the solution was. The pK_{R^+} value of tropylium ion VII could not be determined by this technique, since this ion did not show a normal response towards added base. However, the pK_{R^+} value for VII was determined by measuring initial pH values of the aqueous solutions of the perchlorate, a method used by Pettit and coworkers.[1] The stability constant can be estimated, if it is assumed that $(H_3O^+) \approx (ROH)$ and that the concentration of the carbonium ion is given by the difference between the concentration of added R^+ and the concentration of hydronium ion. This method is not very suitable for the determination of the pK_{R^+} of this particular tropylium ion, since over a wide range of concentrations the initial pH values were between 5.0 – 5.3, a region where small amounts of dissolved carbon dioxide can introduce a significant error. When the water was carefully treated to remove dissolved carbon dioxide and the measurements were carried out under an argon atmosphere, a reproducible value of $pK_{R^+} = 6.9 \pm 0.3$ was obtained. Application of the same method to the isomeric tropylium ion VIII and to tropylium ion (III) [18] gave pK_{R^+} values in excellent agreement with those obtained from potentiometric titrations.

The difficulties in determining the pK_{R^+} values of the tropylium salts at higher concentration is most probably due to some irreversible reactions of the tropylium ion-carbinol system. One possibility consists in a bimolecular hydride transfer between the carbinol and the tropylium ion, giving the methylene derivative and the ketone (after proton loss). These difficulties could perhaps be circumvented by using alkoxide in the corresponding alcohol as solvent (provided the carbonium ion is in rapid equilibrium with the corresponding ether).

The pK_{R^+} values measured in this investigation, together with some pertinent values of other tropylium ions, are given in Table 2. The dithieno- or furothienoannelated tropylium ions are thus 10^7 to 10^9 times more stable (less acidic) than the corresponding dibenzotropylium ion, and are among the most stable carbonium ions known.

The higher stability of VIII than V could also be demonstrated by hydride ion transfer experiments.[18] The NMR spectrum of an equimolar mixture of VIII and 9H-cyclohepta[2,1-b;4,5-b′]dithiophene (XXIII), which was allowed to equilibrate (30 min at room temperature in anhydrous acetonitrile) revealed that the ratio of V to VIII was 2.0 – 2.2. The same ratio was obtained when XIV and V were allowed to equilibrate.

Several factors may contribute to the *increased* stabilization upon thieno- or furoannelation as compared to benzoannelation. Firstly it is well known that the π-excessive five-membered heterocyclic rings stabilize a positive charge of benzylic type much more efficiently than the benzene ring [19] and this has also been confirmed quantitatively by comparing pK_{R^+} values for dithienyl and trithienyl carbonium ions with those for analogous benzene derivatives.[1] MO calculations carried out by Pettit *et al.* also are in agreement with this observation.[1] In general, greater resonance stabilization can always be expected upon annelation of strongly π-excessive aromatic rings onto strongly π-deficient rings. It is possible that the same factors also are involved in tropylium ions. Secondly, as indicated by others,[8] ring-strain effects could operate upon the annelation of benzene rings onto tropylium ions. The ideal angle of the six-membered ring is 120°, and that of the regular seven-membered ring is 129°. In thiophene the $H_2-C_2-C_3$ angle is 128.68° and the $C_2-C_3-H_3$ angle is 123.28°.[20] On this basis one might expect less angular strain upon annelation of thiophene rings onto tropylium ions. The same geometrical considerations are also true for furan rings.[21] Thirdly, due to the hetero atoms *peri* interactions between hydrogens are diminished or completely excluded. X-Ray analysis shows that V is planar.[22] No point of the cation's surface deviates more than 0.05 Å from the best plane.

Heilbronner and coworkers [5] and Pettit and coworkers [1] have found linear correlations between the "excessive" π-energy ΔE_π of the cation and the pK_{R^+} values for tropylium ions and for other types of carbonium ions with varying pK_{R^+} values. An estimation of ΔE_π may be obtained from the difference between the calculated π-energies of the cation and a model of its conjugate base. As a model for the conjugate bases of the dithienotropylium and furothienotropylium ions we chose the corresponding dithienyl- and furylthienylethylenes. Calculations were carried out by the HMO method and by the ω-technique.[23] The following set of parameters for oxygen and sulphur were used:[23] $h_O=2.0$; $k_{CO}=0.6$; $h_S=1.0$; $k_{CS}=0.4$. The ΔE_π values obtained are given in Table 2. The calculated ΔE_π values do not show a linear correlation with the pK_{R^+} values, which might be due to the few values and small interval of the latter. Calculations, however, predict which of the two dithieno- and furothienotropylium ions are the more stable. This can also be inferred from simple considerations of "good resonance structure".[19]

Table 2. pK_{R^+} values of some tropylium ions and calculated ΔE_π values for the furothieno- and dithienotropylium ions.

Tropylium ion, No.	pK_{R^+}	Ref.	ΔE_π (in β-units) HMO	ω-techn.
III	4.7	3		
II	1.7 ±0.1	5		
I	6.0	1		
IV	−1.9 ±0.1	4		
V	6.65±0.05		1.50	2.64
VI	5.40±0.05		1.37	2.58
VII	6.9 ±0.3		1.50	2.63
VIII	6.8 ±0.1		1.37	2.57

A comparison of the NMR spectra of the four tropylium ions V−VIII and their methylene precursors XXIII, 9H-cyclohepta[1,2-b;5,4-b']dithiophene (XXIV), XI and XIV also indicates an extensive delocalization of the charge in the tropylium ions. The heterocyclic ring hydrogens are shifted 1.25 to 2.8 ppm towards lower field, and the formal ethylenic hydrogens 2.50−3.13 ppm, on going from the methylene derivatives to the tropylium ions. Attempts to correlate these chemical shift differences with the corresponding π-electron density differences[24] led to poor correlations. However, a rough correlation was obtained between the chemical shifts of the hydrogens of the tropylium ions in deuteriosulphuric acid and the π-electron densities on the carbons bearing these hydrogens (calculated by the ω-technique). Least square calculations gave a regression line with a proportionality constant of 7.1 ppm/electron and with a correlation coefficient of 0.84. In recent work, a proportionality constant of 13.56 ppm/electron was obtained for trithienylmethylcarbonium ions.[25] The electron densities and superdelocalizabilities for electrophilic substitution (S_{r^+}, in parentheses) of the tropylium ions are given in the diagrams in Fig. 1.

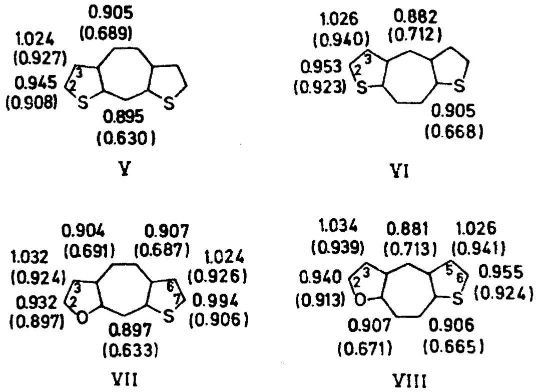


Fig. 1.

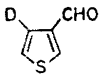
The UV spectra of the tropylium ions and their precursors will be discussed in a separate paper.

ELECTROPHILIC DEUTERIATIONS

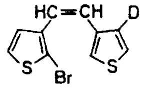
The NMR spectra of the tropylium ions V and VI run in D_2SO_4 at 68° showed that the high-field thiophenic doublets at δ 8.74 in V and 8.67 in VI, gradually disappeared, while a singlet simultaneously grew up in the middle of the lower field doublets, finally replacing these. Similarly with VII, the doublets at δ 8.21 (furanic) and δ 8.73 (thiophenic) gradually disappeared, while singlets grew up in the middle of the corresponding doublets at δ 9.17 and δ 9.35. From these results, it is quite obvious that deuterium exchange is occurring. Tropylium ion VIII, on the other hand, decomposed in concentrated D_2SO_4 before any exchange reaction could be observed. When mixtures of trifluoroacetic anhydride and D_2O or D_2SO_4 were used, no reaction could be detected. In order to prove the position of deuterium exchange, authentic 3-deuterio derivatives of V and VI were prepared.

Starting from 3-bromo-4-deuteriothiophene,[26] 4-deuterio-3-thiophene aldehyde (XXV) was prepared, which was transformed to 1-(2-bromo-3-thienyl)-

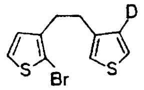
2-(4′-deuterio-3′-thienyl)ethene (XXVI) through the phosphonate carbanion[27,28] reaction with diethyl-2-bromo-3-thenylphosphonate. Catalytic hydrogenation using tris triphenylphosphine chlororhodium(I) gave 1-(2-bromo-3-thienyl)-2-(4′-deuterio-3′-thienyl)ethane (XXVII), which by halogen-metal exchange followed by carbonation yielded 1-(2-carboxy-3-thienyl)-2-(4′-deuterio-3′-thienyl)ethane (XXVIII). The acid XXVIII was ring-closed to 4,5-dihydro-3-deuterio-9H-cyclohepta[2,1-b;4,5-b′]dithiophene-9-one (XXIX) upon reaction with phosphorus pentachloride and tin tetrachloride. Ketone XXIX was brominated-dehydrobrominated with *N*-bromosuccinimide to give 3-deuterio-9H-cyclohepta[2,1-b;4,5-b′]dithiophene-9-one (XXX). Reduction of XXX with lithium aluminium hydride gave 3-deuterio-9H-cyclohepta[2,1-b;4,5-b′]dithiophene (XXXI), which finally through hydride transfer with trityl perchlorate was transformed to 3-deuterio-9H-dithieno[2,1-b;4,5-b′]-tropylium perchlorate (XXXII). 3-Deuterio-4H-dithieno[1,2-b;5,4-b′]tropylium perchlorate (XL) was prepared by an approach quite similar to that described for XXXII. The necessary 4-deuterio-2-thiophene aldehyde (XXXIII) was prepared in a one-pot procedure[29] from 2,4-dibromothiophene by halogen-metal exchange with butyllithium followed by reaction with *N*,*N*-dimethylformamide, renewed halogen-metal exchange and methanolysis with CH$_3$OD. Reaction of XXXIII with diethyl-3-bromo-2-thenylphosphonate gave



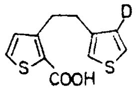
XXV



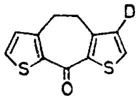
XXVI



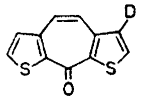
XXVII



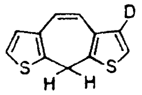
XXVIII



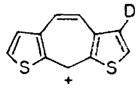
XXIX



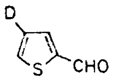
XXX



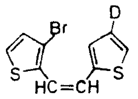
XXXI



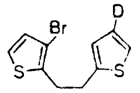
XXXII



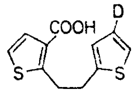
XXXIII



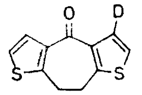
XXXIV



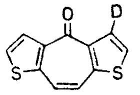
XXXV



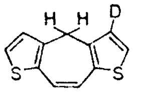
XXXVI



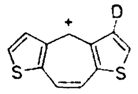
XXXVII



XXXVIII



XXXIX



XL

1-(3-bromo-2-thienyl)-2-(4′-deuterio-2′-thienyl)ethene (XXXIV), which *via* 1-(3-bromo-2-thienyl)-2-(4′-deuterio-2′-thienyl)ethane (XXXV), 1-(3-carboxy-2-thienyl)-2-(4′-deuterio-2′-thienyl)ethane (XXXVI), 8,9-dihydro-3-deuterio-4H-cyclohepta[1,2-b;5,4-b′]dithiophene-4-one (XXXVII), 3-deuterio-4H-cyclohepta[1,2-b;5,4-b′]dithiophene-4-one (XXXVIII) and 3-deuterio-4H-cyclohepta[1,2-b;5,4-b′]dithiophene (XXXIX), was transformed to XL. The full details of the synthetic approach have previously been discussed for the unlabelled compounds.[11,13]

From the NMR spectra of XXXII and XL it follows that hydrogen exchange has occurred in the β-positions of the two dithienotropylium ions (3- and 6-positions of V and 3- and 5-positions of VI). The assignments of the ring protons in the NMR spectrum of VII were not proven as rigorously. It is, however, evident that by analogy with V, the high-field thiophenic doublet of VII should be assigned to hydrogen 6. With the known larger shift difference between the high-field β-hydrogens and the low-field α-hydrogens in furans than in thiophenes,[31,32] it seems reasonable to also assume that the high-field furanic band of VII is that of the 3-hydrogen. In addition, a long-range coupling of 0.8 Hz to hydrogen 9 was observed in this band. Such long-range couplings across five bonds following the straightest zig-zag path from a β-hydrogen have for instance been observed in benzothiophenes,[32] benzofurans,[32,33] thienopyridines,[34] 4,5-borazarothieno[2,3-c]pyridines,[35] 4,5-borazarofuro[2,3-c]-pyridines,[36] thienobenzofurans,[37,38] and in benzodithiophenes [38] support the assignment of the δ 8.21 band to the 3-hydrogen. Similar long-range couplings ($J_{39} = 1.0$ Hz and $J_{58} = 0.6$ Hz), following the same pattern, are also observed in the NMR spectrum of VIII. It is thus clear that also in VII, it is the β-hydrogens (3- and 6-hydrogens), that are exchanged.

We have not yet undertaken a detailed kinetic investigation of the deuteriation. However, at 68°C half-lives in 97 % D_2SO_4 are around 5 h and exchange as far as can be seen by the NMR technique is complete in 24 h, except for the 3-hydrogen of VII, which is exchanged somewhat more slowly. The β-exchanged ions V and VI behaved differently on further heating with D_2SO_4. While no additional changes were observed in the NMR spectrum of V after heating for 100 h, two or more new peaks near each of the three original peaks of the fully β-deuteriated molecule appeared in the NMR spectrum of VI. These new peaks, which amounted to roughly 10 – 15 % of the original sample, could perhaps be attributed to mono- and disulphonated products.

Nothing is known about electrophilic substitution in the benzene derivatives isoelectronic with the tropylium ions, *viz.* benzodithiophenes and thienobenzofurans.[37-39] The closest related systems which have been studied in detail are benzo[b]thiophene and benzo[b]furan.[40] However, recent work by Marino and coworkers [40] on the influence of benzoannelation onto thiophene and furan upon electrophilic substitution, has shown that although the orientation in the two bicyclic systems is different, *i.e.* predominant substitution in the 3-position of benzo[b]thiophene and in the 2-position of benzo[b]furan, the effect caused by annelation on the reactivity of the α- and β-positions is substantially the same in the two rings. The reactivity of the α-position is always decreased by a similar factor and the reactivity of the β-position is increased in both systems. The different orientation observed in benzo[b]thiophene and benzo[b]furan is therefore not a consequence of a different effect of benzo-fusion, but must be attributed to the different $\alpha:\beta$-ratios in the two monocyclic systems. A consequence of this annelation effect is that in many electrophilic substitutions the β-position of benzo[b]thiophene is more reactive than the β-position of benzo[b]furan. Annelation of a tropylium ring onto furan as in VII apparently deactivates the α-position to a greater extent than the β-position, so that orientation is reversed.

MO calculations of electron-densities and superdelocalizabilities [41] for V – VIII by the ω-technique, given in the diagrams in Fig. 1, predict that electrophilic reagents should enter the β-positions, which is in agreement with the hydrogen-deuterium exchange experiments carried out with V – VII.

As far as we know, this is the first case in which electrophilic substitution has been carried out with tropylium ions, and we hope to be able to study hydrogen exchange in more detail and also to extend our investigations to other substitution reactions.

EXPERIMENTAL

4H-Thieno[5,4-b′]cyclohepta[1,2-b]furan-4-one (XIII). A mixture of 8.0 g (39 mmol) of 8,9-dihydro-4H-thieno[5,4-b′]cyclohepta[1,2-b]furan-4-one (XII) [12] and 100 mg of azobisisobutyronitrile (ABN) dissolved in 120 ml of anhydrous carbon tetrachloride was refluxed. A mixture of 7.0 g (39 mmol) of *N*-bromosuccinimide (NBS) and 150 mg of ABN was added in portions within 30 min. A red precipitate began to form 10 min after the addition was started. A few minutes later the evolution of hydrogen bromide could be detected. The mixture was refluxed for 6 h and was then cooled. The solid was filtered off (12.5 g), treated with water (3 x 50 ml at 45°) and dried, yielding 6.0 g of slightly greenish XIII. The carbon tetrachloride filtrate was treated with charcoal and evaporated, yielding 2.0 g of XII brominated in the side-chain. This product was dissolved in methanol containing 1.0 g of sodium methoxide and refluxed for 90 min. The methanol was evaporated, water was added and the solution was neutralized and extracted with ether. After drying over magnesium sulphate and evaporation, an additional 0.70 g of XIII was obtained, making a total yield of 84 %, m.p. 117 – 119° after recrystallization from hexane. NMR ($CDCl_3$): $\delta = 7.25$ ppm, centre of complex multiplet due to hydrogens 3, 8, and 9, $\delta_2 = 7.62$ ppm, $\delta_5 = 7.53$ ppm, $\delta_6 = 8.08$ ppm. $J_{23} = 2.0$ Hz, $J_{56} = 5.5$ Hz. [Found M. wt. 202: C 64.8; H 2.99; S 15.5. Calc. for $C_{11}H_6O_2S$ (202.2): C 65.33; H 2.99; S 15.86].

9H-Thieno[4,5-b′]cyclohepta[2,1-b]furan-9-one (X). A mixture of 4.0 g (20 mmol) of 4,5-dihydro-9H-thieno[4,5-b′]cyclohepta[2,1-b]furan-9-one (IX) and 80 ml of anhydrous carbon tetrachloride was refluxed. 70 mg of ABN was added, and then 3.5 g (20 mmol) of NBS was added in two portions. 2 min later, a vigorous reaction started and solid material precipitated from the solution. A few minutes later the evolution of hydrogen bromide could be observed. After 30 min the carbon tetrachloride was evaporated and methanol was added. The mixture was then refluxed for 2 h, the methanol evaporated and 50 ml of water was added. The slightly yellow solid was filtered off, washed with water (3 x 50 ml at 45°) and dried thoroughly, yielding 3.9 g (98 %) of the title compound X, m.p. 170 – 172° after recrystallization from isopropanol. NMR (CD_3SOCD_3): $\delta_3 = 7.27$ ppm, δ_4 or $\delta_5 = 7.57$ ppm, δ_5 or $\delta_4 = 7.86$ ppm, $\delta_6 = 7.77$ ppm, $\delta_7 = 8.28$ ppm, $\delta_2 = 8.43$ ppm. $J_{23} = 1.9$ Hz, $J_{45} = 11.5$ Hz, $J_{67} = 5.3$ Hz. [Found M. wt. 202: C 65.6; H 3.09; S 16.1. Calc. for $C_{11}H_6O_2S$ (202.2): C 65.33; H 2.99; S 15.86].

4H-Thieno[5,4-b′]cyclohepta[1,2-b]furan (XIV). 3.0 g (15 mmol) of 4H-thieno[5,4-b′]cyclohepta[1,2-b]furan-4-one (XIII) in 75 ml of anhydrous ether was refluxed with 1.5 g of lithium aluminium hydride for 6 h. The excess of lithium aluminium hydride was decomposed with methanol, and cold dilute hydrochloric acid was added until the layers were clearly separated. The aqueous phase was extracted a few times with ether and the combined organic phases were dried over magnesium sulphate and evaporated, yielding

2.7 g (96 %) of the title compound XIV, m.p. 65 – 68° after recrystallization from hexane. The compound should be stored in a cold dark place due to its instability to heat and light. NMR ($CDCl_3$): $\delta_{CH_2} = 3.87$ ppm, $\delta_2 = 7.35$ ppm, $\delta_3 = 6.18$ ppm, $\delta_5 = 6.71$ ppm, $\delta_6 = 7.20$ ppm, δ_8 and $\delta_9 = 6.47$ ppm. $J_{23} = 1.9$ Hz, $J_{56} = 5.0$ Hz. [Found M. wt. 188: C 70.1; H 4.34; S 16.9. Calc. for $C_{11}H_8OS$ (188.3): C 70.18; H 4.28; S 17.03].

Furo[1,2-b]thieno[3,4-b]tropylium perchlorate (VIII). 2.0 g (11 mmol) of 4H-thieno-[5,4-b′]cyclohepta[1,2-b]furan (XIV) was dissolved in 200 ml of anhydrous ethyl acetate and a hot solution of 3.6 g (10.5 mmol) of triphenylmethyl perchlorate[42] dissolved in the minimum amount of anhydrous acetonitrile was added dropwise within 5 min. An immediate precipitation occurred. The mixture was stirred for another 5 min, filtered and dried, yielding 3.0 g (98 %) of the title compound, m.p. 271 – 275° after recrystallization from an ethyl acetate-acetonitrile mixture. NMR (CF_3COOH): $\delta_2 = 8.60$ ppm, $\delta_3 = 7.83$ ppm, $\delta_4 = 10.00$ ppm, $\delta_5 = 8.46$ ppm, $\delta_6 = 8.81$ ppm, $\delta_8 = 9.60$ ppm, $\delta_9 = 9.00$ ppm. $J_{23} = 2.2$ Hz, $J_{39} = 1.0$ Hz, $J_{56} = 5.4$ Hz, $J_{58} = 0.6$ Hz, $J_{89} = 10.8$ Hz. [Found: C 46.4; H 2.61; Cl 12.3; S 11.1. Calc. for $C_{11}H_7ClO_5S$ (286.7): C 46.08; H 2.46; Cl 12.37; S 11.18].

Furo[2,1-b]thieno[4,5-b]tropylium perchlorate (VII). 1.5 g (7.0 mmol) of 9H-thieno-[4,5-b′]cyclohepta[2,1-b]furan-9-one (X) in 100 ml of anhydrous ether was refluxed for 6 h with 350 mg of lithium aluminium hydride and worked up as described for hydrocarbon XIV. 1.3 g of crude labile 9H-thieno[4,5-b′]cyclohepta[2,1-b]furan (XI) was obtained, which without purification was used in the next step. NMR ($CDCl_3$): $\delta_9 = 4.23$ ppm, $\delta_3 = 6.33$ ppm, δ_4 or $\delta_5 = 6.33$ ppm, δ_5 or $\delta_4 = 6.62$ ppm, $\delta_6 = 6.86$ ppm, $\delta_7 = 7.05$ ppm, $\delta_2 = 7.25$ ppm. $J_{23} = 2.0$ Hz, $J_{39} \approx 0.4$ Hz, $J_{29} \approx 0.3$ Hz, $J_{67} = 5.0$ Hz, $J_{45} = 11.5$ Hz. 850 mg of crude XI was converted into the title compound in the same way as described above for the isomeric tropylium ion VIII. 820 mg (58 % based on the unsaturated ketone X) of furo[2,1-b]thieno[4,5-b]tropylium perchlorate, m.p. 236 – 239° after recrystallization from a mixture of ethyl acetate-acetonitrile, was obtained. NMR (CF_3COOH): $\delta_3 = 7.84$ ppm, $\delta_6 = 8.41$ ppm, $\delta_2 = 8.80$ ppm, $\delta_7 = 9.00$ ppm, δ_4 or $\delta_5 = 9.06$ ppm, δ_5 or $\delta_4 = 9.36$ ppm, $\delta_9 = 9.95$ ppm. $J_{23} = 2.0$ Hz, $J_{39} \approx 0.8$ Hz, $J_{45} = 10.5$ Hz, $J_{67} = 5.5$ Hz, $J_{69} \approx 0.4$ Hz. NMR (D_2SO_4): $\delta_3 = 8.21$ ppm, $\delta_6 = 8.73$ ppm, $\delta_2 = 9.17$ ppm, $\delta_7 = 9.35$ ppm, δ_4 or $\delta_5 = 9.40$ ppm, δ_5 or $\delta_4 = 9.68$ ppm, $\delta_9 = 10.23$ ppm. [Found: C 46.5; H 2.41; Cl 12.4; S 11.4. Calc. for $C_{11}H_7ClO_5S$ (286.7): C 46.08; H 2.46; Cl 12.37; S 11.18].

4-Deuterio-3-thiophene aldehyde (XXV). To 475 ml of 0.7 N ethereal butyllithium cooled to –70°, 49.2 g (0.30 mol) of 3-bromo-4-deuteriothiophene[26] in 200 ml of anhydrous ether was added in a slow stream. After stirring for 5 min, 36.0 g of anhydrous *N*,*N*-dimethylformamide in 100 ml of anhydrous ether was added during 5 min with efficient stirring. The cooling bath was removed after 30 min, stirring was continued until the reaction mixture reached room temperature, and it was then decomposed by pouring it into a 20 % ice-water solution of ammonium chloride. After the usual work-up, the ether phase was fractionated, yielding 24 g (70 %) of 4-deuterio-3-thiophene aldehyde, b.p. 40 – 45°/1 mmHg. NMR ($CDCl_3$): $\delta_5 = 7.30$ ppm, $\delta_2 = 8.07$ ppm, $\delta_{CHO} = 9.83$ ppm. $J_{25} = 2.9$ Hz, $J_{CHO-5} = 0.8$ Hz.

4-Deuterio-2-thiophene aldehyde (XXXII). To a solution of 42.2 g (0.17 mol) of 2,4-dibromothiophene[43] in 100 ml of anhydrous ether cooled to –70°, 110 ml of 1.6 N commercial butyllithium in hexane was added during 20 min under nitrogen. The mixture was stirred at –70° for an additional 5 min, and 13 g of anhydrous *N*,*N*-dimethylformamide in 100 ml of ether was added quickly. The cooling bath was removed, the mixture stirred for 30 min, and cooled again to –70°. 172 ml of 1.6 N butyllithium in hexane was added dropwise during 15 min. Stirring was continued for 75 min and 8.0 g of deuteriomethanol in 50 ml of anhydrous ether was added. The cooling bath was removed and the mixture poured into 20 % ice-cold ammonium chloride solution and worked up as usual. Distillation gave 10 g of 4-deuterio-2-thiophene aldehyde, b.p. 90 – 110°/15 mmHg, which VPC analysis showed to contain 20 % 2,4-dibromothiophene. Fractionation gave 8.0 g (41 %) of 4-deuterio-2-thiophene aldehyde, which was pure enough (> 95 %) for further use. NMR ($CDCl_3$): δ_3 and $\delta_5 = 7.78$ ppm, $\delta_{CHO} = 9.92$ ppm. $J_{CHO-5} = 1.0$ Hz.

1-(2-Bromo-3-thienyl)-2-(4′-deuterio-3′-thienyl)ethene (XXVI). This compound (25.6 g, 94 %) was prepared according to the general description given in Ref. 11 from 11.4 g (0.10 mol) of 4-deuterio-3-thiophene aldehyde and 31.3 g (0.10 mol) of diethyl-2-bromo-3-thenylphosphonate.

1-(2-Bromo-3-thienyl)-2-(4′-deuterio-3′-thienyl)ethane (XXVII). 20.0 g (73.5 mmol) of recrystallized 1-(2-bromo-3-thienyl)-2-(4′-deuterio-3-thienyl)ethene in 250 ml of 96 %

ethanol was hydrogenated using 0.6 g of tris triphenylphosphine chlororhodium(I) as catalyst, following the general procedure given in Ref. 11. 19.0 g (95 %) of the title compound, b.p. 100 – 115°/5 × 10^{-3} mmHg, was obtained. NMR ($CDCl_3$): $\delta_{CH_2-CH_2} = 2.84$ ppm, $\delta_4 = 6.65$ ppm, $\delta_{2'} = 6.84$ ppm, $\delta_5 = 7.05$ ppm, $\delta_{5'} = 7.15$ ppm. $J_{45} = 5.7$ Hz, $J_{2',5'} = 3.0$ Hz.

1-(2-Carboxy-3-thienyl)-2-(4′-deuterio-3′-thienyl)ethane (XVIII). From 6.8 g (2.5 mmol) of 1-(2-bromo-3-thienyl)-2-(4′-deuterio-3′-thienyl)ethane and 42 ml of 0.8 N ethereal ethyllithium and carbon dioxide, following the general procedure given in Ref. 11, 5.0 g (93 %) of the title compound, m.p. 176° after recrystallization from chloroform, was obtained. NMR (DMSO): $\delta_{CH_2-CH_2} = 2.8 - 3.2$ ppm (broad multiplet), $\delta_4 = 7.04$ ppm, $\delta_{2'} = 7.14$ ppm, $\delta_{5'} = 7.41$ ppm, $\delta_5 = 7.67$ ppm. $J_{2',5'} = 2.7$ Hz, $J_{45} = 5.0$ Hz.

4,5-Dihydro-3-deuterio-9H-cyclohepta[2,1-b;4,5-b′]dithiophene-9-one (XXIX). From 4.25 g (17.8 mmol) of 1-(2-carboxy-3-thienyl)-2-(4′-deuterio-3′-thienyl)ethane in 100 ml of anhydrous benzene, 4.4 g of phosphorus pentachloride and 4 ml of tin tetrachloride, 3.7 g (94 %) of the title compound, m.p. 105 – 106° after recrystallization from methanol, was obtained following the procedure given for the unlabelled compound in Ref. 11. NMR ($CDCl_3$): $\delta_{CH_2-CH_2} = 3.08$ ppm, $\delta_2 = 7.40$ ppm (singlet), $\delta_7 = 7.50$ ppm (doublet), $\delta_8 = 6.90$ ppm. $J_{67} = 5.0$ Hz.

3-Deuterio-9H-cyclohepta[2,1-b;4,5-b′]dithiophene-9-one (XXX). Following the procedure for the unlabelled compound in Ref. 13, 3.0 g (13.6 mmol) of 4,5-dihydro-3-deuterio-9H-cyclohepta[2,1-b;4,5-b′]dithiophene-9-one in 75 ml of carbon tetrachloride was heated with 2.43 g of *N*-bromosuccinimide and 0.4 g azobisisobutyronitrile, followed by treatment with 3 g of sodium methoxide, yielding 2.7 g (90 %) of the title compound, m.p. 151 – 152° after recrystallization from acetonitrile. NMR ($CDCl_3$): $\delta_2 = 7.70$ ppm (singlet), $\delta_4 = 7.36$ ppm, $\delta_6 = 7.35$ ppm, $\delta_7 = 7.70$ ppm (doublet). $J_{67} = 5.2$ Hz.

3-Deuterio-9H-cyclohepta[2,1-b;4,5-b′]dithiophene (XXXI). This compound was prepared in quantitative yield by reaction of 1.5 g of 3-deuterio-9H-cyclohepta[2,1-b;4,5-b′]dithiophene-9-one in 200 ml of anhydrous ether with 0.5 g of lithium aluminium hydride, according to the procedure in Ref. 13, m.p. 98 – 99° after recrystallization from hexane. NMR ($CDCl_3$): $\delta_2 = 7.00$ ppm (singlet), $\delta_4 = \delta_5 = 6.73$ ppm, $\delta_6 = 6.87$ ppm, $\delta_7 = 7.00$ ppm (doublet), $\delta_9 = 4.05$ ppm. $J_{67} = 5.3$ Hz.

3-Deuterio-9H-dithieno[2,1-b;4,5-b′]tropylium perchlorate (XXXII). From 0.5 g of 3-deuterio-9H-cyclohepta[2,1-b;4,5-b′]dithiophene in 75 ml of anhydrous ethyl acetate and 2 g of triphenylmethyl perchlorate in the minimum amount of acetonitrile, 0.7 g of the title compound was obtained, m.p. 288° after recrystallization from acetonitrile. NMR (H_2SO_4): $\delta_2 = 9.38$ ppm (singlet), $\delta_4 = \delta_5 = 9.43$ ppm, $\delta_6 = 8.67$ ppm, $\delta_7 = 9.38$ ppm (doublet), $\delta_9 = 10.34$ ppm. $J_{67} = 5.5$ Hz.

1-(3-Bromo-2-thienyl)-2-(4′-deuterio-2′-thienyl)ethene (XXXIV). From 11.4 g (0.10 mol) of 4-deuterio-2-thiophene aldehyde, 31.3 g diethyl-3-bromo-2-thenyl phosphonate and 8.1 g of sodium methoxide, 24.8 g (91 %) of the title compound was obtained, following the general procedure given in Ref. 11.

1-(3-Bromo-2-thienyl)-2-(4′-deuterio-2′-thienyl)ethane (XXXV). 15.0 g (55.1 mmol) of recrystallized 1-(3-bromo-2-thienyl)-2-(4′-deuterio-2′-thienyl)ethene in 200 ml of 96 % ethanol was hydrogenated, using 0.5 g of tris triphenylphosphine chlororhodium(I) as catalyst and following the general procedure given in Ref. 11. 14.0 g (93 %) of the title compound, b.p. 105 – 110°/5 × 10^{-3} mmHg, was obtained. NMR ($CDCl_3$): $\delta_{CH_2=CH_2} = 3.13$ ppm, $\delta_4 = 6.83$ ppm, $\delta_5 = 7.03$ ppm, $\delta_{3'} = 6.90$ ppm, $\delta_{5'} = 7.07$ ppm. $J_{45} = 5.2$ Hz, $J_{3',5'} = 1.4$ Hz.

1-(3-Carboxy-2-thienyl)-2-(4′-deuterio-2′-thienyl)ethane (XXXVI). From 11.5 g (42.3 mmol) of 1-(3-bromo-2-thienyl)-2-(4′-deuterio-2′-thienyl)ethane and 70 ml of 0.8 N ethereal ethyllithium and carbon dioxide, following the general procedure given in Ref. 11, 9.5 g (90 %) of the title compound was obtained, m.p. 135° after recrystallization from aqueous acetone. NMR (CD_3COCD_3): $\delta_{CH_2-CH_2} = 3.0 - 3.8$ ppm (broad multiplet), $\delta_{5'} = 7.18$ ppm, $\delta_{3'} = 6.90$ ppm, δ_4 or $\delta_5 = 7.21$ ppm, δ_5 or $\delta_4 = 7.43$ ppm. $J_{3',5'} = 1.5$ Hz, $J_{45} = 5.4$ Hz.

8,9-Dihydro-3-deuterio-4H-cyclohepta[1,2-b;5,4-b′]dithiophene-4-one (XXXVII). From 4.25 g (17.8 mmol) of 1-(3-carboxy-2-thienyl)-2-(4′-deuterio-2′-thienyl)ethane in 100 ml of anhydrous benzene, 4.4 g of phosphorus pentachloride and 4 ml of tin tetrachloride, 3.6 g (92 %) of the title compound was obtained, m.p. 95° after recrystallization from methanol, following the procedure given for the unlabelled compound in Ref. 11. NMR

($CDCl_3$): $\delta_{CH_2-CH_2} = 3.27$ ppm, $\delta_2 = 7.00$ ppm (singlet), $\delta_5 = 7.70$ ppm (doublet). $J_{56} = 5.5$ Hz.

3-Deuterio-4H-cyclohepta[1,2-b;5,4-b′]dithiophene-4-one (XXXVIII). Following the procedure for the unlabelled compound in Ref. 13, 3.0 g (13.6 mmol) of 8,9-dihydro-3-deuterio-4H-cyclohepta[1,2-b;5,4-b′]dithiophene-4-one in 75 ml of carbon tetrachloride was reacted with 2.43 g of NBS and 0.4 g ABN, followed by treatment with 3 g of sodium methoxide, yielding 2.55 g (85 %) of the title compound, m.p. 172 – 173° after recrystallization from acetonitrile. NMR ($CDCl_3$): $\delta_2 = 7.50$ ppm (singlet), $\delta_5 = 8.09$ ppm, $\delta_6 = 7.50$ ppm (doublet), $\delta_8 = \delta_9 = 7.24$ ppm. $J_{56} = 5.5$ Hz.

3-Deuterio-4H-cyclohepta[1,2-b;5,4-b′]dithiophene (XXXIX). 1.4 g (100 %) of the title compound, m.p. 132 – 133° after recrystallization from hexane, was obtained from 1.5 g (6.9 mmol) of 3-deuterio-4H-cyclohepta[1,2-b;5,4-b′]dithiophene-4-one in 200 ml of anhydrous ether and 0.5 g of lithium aluminium hydride, according to the procedure in Ref. 13. NMR ($CDCl_3$): $\delta_2 = 7.24$ ppm (singlet), $\delta_4 = 3.85$ ppm, $\delta_5 = 6.78$ ppm, $\delta_6 = 7.24$ ppm (doublet), $\delta_8 = \delta_9 = 6.72$ ppm. $J_{56} = 5.2$ Hz.

3-Deuterio-4H-dithieno[1,2-b;5,4-b′]tropylium perchlorate (XL). From 0.5 g of 3-deuterio-4H-cyclohepta[1,2-b;5,4-b′]dithiophene in 75 ml of anhydrous ethyl acetate and 2 g of triphenylmethyl perchlorate in the minimum amount of acetonitrile, 0.7 g of the title compound was obtained, m.p. 310° after recrystallization from acetonitrile. NMR (H_2SO_4): $\delta_2 = 9.04$ ppm (singlet), $\delta_4 = 10.31$ ppm, $\delta_5 = 8.74$ ppm, $\delta_6 = 9.04$ ppm (doublet), $\delta_8 = \delta_9 = 9.59$ ppm. $J_{56} = 5.5$ Hz.

Hydrogen-deuterium exchange experiments with the tropylium ions V, VI, and VII. 40 mg of the tropylium ion was dissolved in 0.5 ml of conc. D_2SO_4 (97 %) and the solution kept at 68°. The progress of the reaction was followed by NMR. The average value of four integrations of each absorption was taken. During the night the sample was stored at – 25°. No exchange reaction could be detected at this temperature.

In the pK_{R^+} determinations, sample titrations were made in a titration assembly consisting of a Radiometer Autoburette, ABU 11, in conjunction with a Radiometer pH-meter 26. Radiometer electrodes G202C and K410 were used. NMR spectra were recorded on a Varian A-60 NMR spectrometer, mass spectra on an LKB 9000 mass spectrometer and IR spectra on Perkin-Elmer 257 and Perkin-Elmer 221 spectrophotometers.

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