Stable Carbonium Ions. Part V.[1] Distribution of Positive Charge in Ferrocenylalkylium Ions and Factors influencing their Relative Thermodynamic Stabilities

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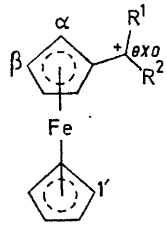
From pK_{R^+} measurements, evidence relating to the distribution of positive charge in ferrocenylalkylium ions has been obtained. The 1-ferrocenyl-1-methylethylium cation is more stabilised by methyl substitution at the β- than at the 1′-position while substitution at the α-position exerts a destabilising effect. Cation stability is also sensitive to structural deformation of the system caused by interannular bridging. The mixtures of products formed in the reactions of a series of 1-(acetylferrocenyl)-3-phenylallylium cations with sodium methoxide have been analysed. An acetyl substituent reduces the capacity of the ferrocenyl group to delocalise positive charge. A ruthenocenyl group is more effective than a ferrocenyl group in stabilising a carbonium ion.

As discussed in Part IV,[1] the unique properties of ferrocenylalkylium ions (1) have prompted several conflicting descriptions of the bonding in the system. Since the high intrinsic stability of these cations requires a substantial measure of charge delocalisation, it was thought that a knowledge of the relative amounts of charge associated with the *exo*-, α-, β-, and 1′-carbon atoms [see (1)] would provide some insight into the electronic structure of the system. In this connection, a recent theoretical treatment[2] of the structure of the ferrocenylmethylium cation (1; $R^1 = R^2 = H$) is relevant. From S.C.C. extended Hückel calculations, it was concluded that the iron atom in this cation bears about one half the total positive charge with the remainder distributed to the eleven carbon atoms of the ligands. The concentration of charge at the individual carbon atoms, calculated from the figures[2] of Gleiter and Seeger, increases through the series β (0·022+) < α (0·033+) < 1′ (0·052+) < *exo* (0·065+).

For carbonium ions in which there is extensive charge delocalisation (*e.g.* benzylic, polyenylic systems), it is well known[3] that the extent to which the system is stabilised by an electron-donating substituent increases with increasing positive charge concentration at the carbon atom which bears the substituent. Similarly, maximum destabilisation occurs when an electron-withdrawing substituent is attached to the site of highest positive charge in the ion. With this phenomenon in mind, we have studied the extent of stabilisation of the 1-ferrocenyl-1-methylethylium cation (3a) conferred by substitution of an electron-donating (+*I*) methyl group at the α-, β-, and 1′-positions (3b—f), taking the pK_{R^+} scale[4] as a convenient index of relative thermodynamic stability.

The required tertiary alcohol precursors (2b—f) were prepared in high yields by the addition of methyllithium to the corresponding acetyl derivatives which, in turn, were obtained by Friedel–Crafts acetylation of methylferrocene and 1,1′-dimethylferrocene according to reported methods.[5] The α-methyl alcohol (2b) could be more conveniently prepared by specific α-lithiation[6] of 2-ferrocenylpropan-2-ol (2a) and *in situ* treatment of the α-lithio-intermediate with iodomethane. Final, rigorous purification of each alcohol was achieved by preparative t.l.c. on silica. Determinations of the pK_{R^+} values for the carbonium ion $\rightleftharpoons$ alcohol equilibria [equation (1)] were carried out according to the method of Hill[7] using aqueous sulphuric acid as solvent (see Experimental section). The results obtained together with selected literature values are in Table 1.



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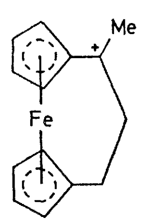

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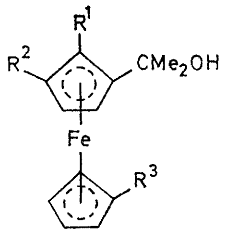

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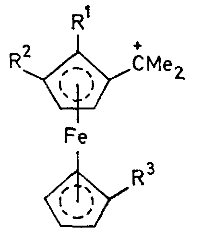

(3)

a; $R^1 = R^2 = R^3 = H$
b; $R^1 = Me$; $R^2 = R^3 = H$
c; $R^2 = Me$; $R^1 = R^3 = H$
d; $R^3 = Me$; $R^1 = R^2 = H$
e; $R^1 = R^3 = Me$; $R^2 = H$
f; $R^2 = R^3 = Me$; $R^1 = H$
g; $R^2,R^3 = [CH_2]_3$; $R^1 = H$

$$(3) + 2H_2O \rightleftharpoons (2) + H_3O^+ \qquad (1)$$

Before discussion of these results, an important qualification must be made. Since the pK_{R^+} value characterises an equilibrium attained in aqueous acidic media between an alcohol and the derived carbonium ion [equation (1)], comparison of such values in relation to thermodynamic stabilities is meaningful only if differences in the free energies of the alcohols in the

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[1] Part IV, T. D. Turbitt and W. E. Watts, preceding paper.

[2] R. Gleiter and R. Seeger, *Helv. Chim. Acta*, 1971, **54**, 1217.

[3] See N. C. Deno in 'Carbonium Ions,' eds. G. A. Olah and P. von R. Schleyer, Interscience, New York, 1970, vol. II, ch. 18; T. S. Sorensen, vol. II, ch. 19.

[4] N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Amer. Chem. Soc.*, 1955, **77**, 3044.

[5] K. L. Rinehart, K. L. Motz, and S. Moon, *J. Amer. Chem. Soc.*, 1957, **79**, 2749; R. A. Benkeser, Y. Nagai, and J. Hooz, *ibid.*, 1964, **86**, 3742.

[6] *Cf.* R. A. Benkeser, W. P. Fitzgerald, and M. S. Meltzer, *J. Org. Chem.*, 1961, **26**, 2659.

[7] E. A. Hill and R. Wiesner, *J. Amer. Chem. Soc.*, 1969, **91**, 509; E. A. Hill, *J. Organometallic Chem.*, 1970, **24**, 457.

particular solvent medium are insignificant. However, since the structures of the alcohols under disdiscussion are closely similar, it may be reasonably assumed that a more positive $\mathrm{p}K_{\mathrm{R+}}$ value corresponds to a carbonium ion of greater thermodynamic stability.*

Comparison of the $\mathrm{p}K_{\mathrm{R+}}$ values for the ferrocenylmethylium, 1-ferrocenylethylium, and 1-ferrocenyl-1-methylethylium cations (1; $R^1 = R^2 = H$; $R^1 = Me$, $R^2 = H$; $R^1 = R^2 = Me$) shows that substitution of methyl groups at C_{exo} of the parent cation exerts a cumulative stabilising effect, suggesting that C_{exo} bears a significant proportion of the charge on the ion. Substitution of a methyl group at a β- or 1′-carbon atom (3c and d respectively) of the 1-ferrocenyl-1-methylethylium cation (3a) also confers stabilisation, the β-methyl group providing the larger effect. This would suggest that there is extensive charge delocalisation to the β- and 1′-carbon atoms of the ion (3a) and that the former bear a higher charge per atom (*cf.* Gleiter and Seeger calculations[2]). The presence of a second methyl substituent in the rings of the cation (3f) confers further stabilisation although the effect of multiple methyl substitution does not appear to be strictly cumulative [*cf.* $\mathrm{p}K_{\mathrm{R+}}$ values for (3a, c, d, and f). The higher charge inferred for the β-carbon atoms may in part account for the specific deshielding of attached protons[8] observed in the ^1H n.m.r. spectra of ferrocenylalkylium ions although other effects (anisotropic[9] or structural[10]) may also be important.

TABLE 1

$\mathrm{p}K_{\mathrm{R+}}$ Values for ferrocenylalkylium ions[a]

Cation	λ_{max}/nm[b]	$\mathrm{p}K_{\mathrm{R+}}$	Ref.[c]
(1; $R^1 = R^2 = H$)	256	−1·28	*d*
		−1·75[e]	*f*
		−0·55	*g*
(1; $R^1 = Me$, $R^2 = H$)	259	−0·66	*d*
		−0·92[e]	*f*
		−0·10	*g*
		−0·65	
(1; $R^1 = R^2 = Me) \equiv$ (3a)	261	−0·01	*d*
		0·00	
(3b)	258	−0·50	
(3c)	262	+1·10	
(3d)	264	+0·72	
(3e)	260	+0·40	
(3f)	260	+1·40	
(3g)	258	+2·50	
(4)	258	−2·52	
$(\pi\text{-}C_5H_5RuC_5H_4CHMe)^+$	250	+1·20	

[a] For aqueous H_2SO_4 solutions unless indicated otherwise; values given from this study are the average of at least three independent determinations (spread ±0·1). [b] For aqueous 50% H_2SO_4 solutions. [c] Unless present study. [d] Ref. 7. [e] For aqueous $HClO_4$ solutions. [f] Ref. 19. [g] J. Tirouflet, E. Laviron, C. Moïse, and Y. Mugnier, *J. Organometallic Chem.*, 1973, **50**, 241.

The $\mathrm{p}K_{\mathrm{R+}}$ values for the cations (3b and e) show that, despite its electron-donating ability, an α-methyl group exerts a destabilising effect [*cf.* $\mathrm{p}K_{\mathrm{R+}}$ values for (3a and b); (3d and e)]. In the cations (3b and e), therefore, steric repulsion between the α-methyl substituent and the proximate methyl group of the (Me_2C^+) substituent must raise the energy of the conformation in which the ion achieves maximum stabilisation (see later). The same conclusion was reached[1] previously from the conformational behaviour of a 1-ferrocenylethylium cation bearing an α-methyl substituent.

We have previously shown[1] that the energy barrier to rotation around the exocyclic bond of the 1-ruthenocenylethylium cation $(\pi\text{-}C_5H_5RuC_5H_4\overset{+}{C}HMe)$ is appreciably higher than that of the iron analogue (1; $R^1 = Me$, $R^2 = H$). It has also been reported[11] that the rate of formation of the former cation in the solvolysis of 1-acetoxyethylruthenocene is significantly faster than the corresponding rate of formation in the ferrocenyl case. In order to compare the free energies of carbonium ions stabilised by ruthenocenyl and ferrocenyl groups, we have measured the $\mathrm{p}K_{\mathrm{R+}}$ values of the two 1-metallocenylethylium cations. The difference between the values for these cations is large (Table 1) with the ruthenocenyl system the more stable.* This may result from stronger bonding interactions between the hydrocarbon ligand and the more extended orbitals of the ruthenium atom, as suggested previously.[1]

We have also determined the $\mathrm{p}K_{\mathrm{R+}}$ values of two carbonium ions (3g) and (4) derived from 1,1′-trimethyleneferrocene. The alcohol precursors of these ions were obtained by the addition of methyl-lithium to 3-acetyl-1,1′-trimethyleneferrocene[12] and 1,1′-(1-oxotrimethylene)ferrocene[13] respectively. Comparison of the values for the cation (3g) and for a similarly alkylated unbridged analogue (3f) reveals that a modest increase in thermodynamic stability accrues upon interannular bridging. This finding weighs against the Richards ring-slip structure, at least for tertiary ferrocenylalkylium ions, since movement of the iron atom towards C_{exo} in this ion (3g) is prohibited by the presence of the bridging alkyl group. A similar conclusion was reached by Rosenblum from an ^1H n.m.r. study.[14] The enhanced stability of this ion may be a consequence of cyclopentadienyl ring tilting, which is known to occur for compounds of the 1,1′-trimethyleneferrocene class.[15] Such deformation of the ferrocene residue would result in the projection of nonbonding electron density from the iron atom in the direction of the sandwich opening[16] (*i.e.*, away from the bridging

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* With the proviso mentioned in the text, a difference of one unit between $\mathrm{p}K_{\mathrm{R+}}$ values corresponds to a free energy difference between cations of *ca.* 5·7 kJ mol^{-1}.

[8] M. Cais, J. J. Dannenberg, A. Eisenstadt, M. I. Levenberg, and J. H. Richards, *Tetrahedron Letters*, 1966, 1695; W. M. Horspool and R. G. Sutherland, *Chem. Comm.*, 1967, 786; *cf.* H. L. Lentzner and W. E. Watts, *Tetrahedron*, 1972, **28**, 121.

[9] J. J. Dannenberg, M. K. Levenberg, and J. H. Richards, *Tetrahedron*, 1973, **29**, 1575.

[10] M. Cais, *Organometallic Chem. Rev.*, 1966, **1**, 435.

[11] E. A. Hill and J. H. Richards, *J. Amer. Chem. Soc.*, 1961, **83**, 3840.

[12] T. H. Barr, E. S. Bolton, H. L. Lentzner, and W. E. Watts, *Tetrahedron*, 1969, **25**, 5245.

[13] T. D. Turbitt and W. E. Watts, *J. Organometallic Chem.*, 1972, **46**, 109.

[14] J. Feinberg and M. Rosenblum, *J. Amer. Chem. Soc.*, 1971, **91**, 4324.

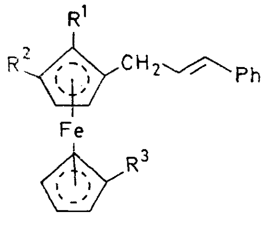
[15] W. E. Watts, *Organometallic Chem. Rev.*, 1967, **2**, 231.

[16] C. J. Ballhausen and J. P. Dahl, *Acta Chem. Scand.*, 1961, **15**, 1333; N. W. Alcock, *J. Chem. Soc. (A)*, 1967, 2001; J. C. Green, M. L. H. Green, and C. K. Prout, *J.C.S. Chem. Comm.*, 1972, 421.

group). Interaction between the C_{exo} p orbital and an iron d orbital would thereby be facilitated, particularly if the fulvene ligand were folded as has been suggested.[2,10]

The cation (4), in which the formal carbonium ion centre (C_{exo}) is located in the bridging group, proves to be much less stable than a similarly alkylated, unbridged analogue (3d). This bridged species would be unable to attain a conformation which would allow full conjugative overlap between the C_{exo} p orbital and the adjacent cyclopentadienyl π system.[17] Furthermore, the effect of ring tilting in this case would be to reduce the importance of a direct C_{exo}-Fe orbital interaction. The operation of either or both these effects could be responsible for the destabilisation of the system. A similar argument was advanced[18] to account for the slow rate of S_N1 solvolysis of 1,1′-(1-acetoxytrimethylene)ferrocene.

From pK_{R^+} measurements, Nesmeyanov *et al.* have already shown[19] that ferrocenylalkylium ions are destabilised by electron-withdrawing 1′-substituents (Cl, CN, and CO_2Me). As an alternative approach, we have investigated the reactions of three isomeric 1-(acetylferrocenyl)-3-phenylallylium cations (6b—d) with sodium methoxide. In an earlier study,[20] we showed that the parent cation (6a) of this series reacts with methoxide under kinetically controlled conditions to give a mixture of isomeric allylic ethers (7a) and (8a) in which the styryl isomer (7a) greatly predominates (*ca.* 88% of the mixture). From this result, it was inferred that C-1 bears a much higher proportion of the positive charge than C-3 in this ion (6a). Using arguments similar to those previously indicated, it was reasoned that the presence of an electron-withdrawing $(-I-R)$ acetyl substituent in ions (6b—d) would alter the C-1—C-3 charge allocation, that this change would be reflected in the (7) : (8) product ratio, and that the magnitude of the effect would be related to the concentration of positive charge at the ferrocenyl carbon atom bearing the acetyl substituent.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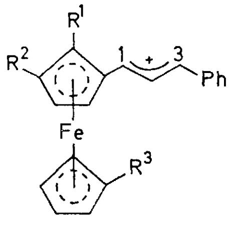
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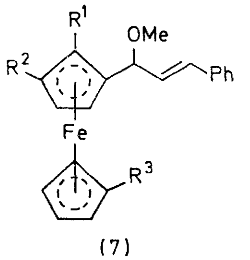
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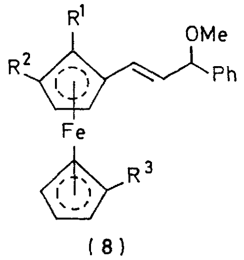
(8)

a; $R^1 = R^2 = R^3 = H$
b; $R^1 = Ac$; $R^2 = R^3 = H$
c; $R^2 = Ac$; $R^1 = R^3 = H$
d; $R^3 = Ac$; $R^1 = R^2 = H$

Cations (6b—d) were generated in dichloromethane solution by hydride abstraction ($Ph_3C^+BF_4^-$) from the phenylallyl precursors (5b—d) which were obtained by Friedel–Crafts acetylation of *trans*-3-ferrocenyl-1-phenylpropene[21] (5a) using Ac_2O–BF_3,Et_2O. These cations reacted instantaneously with methanolic sodium methoxide giving quantitative yields of mixtures of isomeric ethers * (7b—d) and (8b—d) which were analysed spectroscopically (see Experimental section). Since it was shown in separate experiments that these ethers do not isomerise in the presence of methoxide under the original reaction conditions, the relative proportions formed must result from kinetically controlled reactions of the cations (6b—d) with methoxide anion.

Spectroscopic analysis of these ether mixtures showed that, in each case, the products of addition of methoxide to the position (C-3) adjacent to the phenyl group, *i.e.* (8b—d), predominated (60—65% of the mixtures). Since a much greater proportion of the styryl isomer (7a) is formed in the reaction of the parent cation (6a) with methoxide,[20] it may be concluded that the presence of an α-, β-, or 1′-acetyl substituent reduces the capacity of the ferrocenyl group to delocalise positive charge. A differential steric effect disfavouring addition to C-1 may be superimposed upon this electronic effect, particularly in the case of the cation (6b). Unfortunately, in view of the limits of error associated with the method of analysis of the various product mixtures, further information concerning the charge distribution through the ferrocenyl residue of the cation (6a) could not be obtained.

From the results described herein and in the preceding paper,[1] the following conclusions concerning the structure in solution of ferrocenylcarbonium ions appear justified.

(a) There is no evidence for special stabilisation of the system by ring slip displacement of the fulvene ligand, as suggested[9,11] by Richards.

(b) The 16-electron formulation originally proposed[22] by Pettit is ruled out from the results of several independent investigations.

(c) There is no evidence for a *strong* bond between the iron atom and C_{exo} of the fulvene ligand.

(d) The presence of restricted ligand rotation in

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* The α- and β-acetyl derivatives (7b and c), (8b and c) each exist as diastereoisomers owing to the asymmetry of the α(β)-acetylferrocenyl group.

[17] T. H. Barr and W. E. Watts, *Tetrahedron*, 1968, **24**, 6111.

[18] J. H. Richards and E. A. Hill, *J. Amer. Chem. Soc.*, 1959, **81**, 3484.

[19] A. N. Nesmeyanov, L. I. Kazakova, M. D. Reshetova, L. A. Kazitsina, and E. G. Perevalova, *Isvest. Akad. Nauk, S.S.S.R., Ser. Khim.*, 1970, 2804.

[20] M. J. A. Habib, J. Park, and W. E. Watts, *J. Chem. Soc. (C)*, 1970, 2556.

[21] M. J. A. Habib and W. E. Watts, *J. Organometallic Chem.*, 1969, **18**, 361.

[22] J. J. Dannenberg, L. Watts, and R. Pettit, *Tetrahedron Letters*, 1966, 1299.

certain cases points to a structure containing a folded fulvene ligand, as suggested by Cais [10] and Gleiter.[2]

(e) The preferred geometry of the ion in the ground state may be a ring tilted structure with C_{exo} located at the open side of the sandwich.

EXPERIMENTAL

For general details, see Part IV.[1]

The required alcohols were prepared according to methods reported elsewhere (see Parts IV [1] and VI [23]).

Determination of pK_{R^+} *Values.*—The method [7] of Hill was adapted as follows. A stock solution of the alcohol in absolute ethanol (*ca.* 40 g l^{-1}) of accurately known concentration was prepared. Aliquot portions (0·025 ml) of this solution were withdrawn by micropipette and diluted in turn to 25 ml in a volumetric flask with aqueous H_2SO_4 of various, accurately known concentrations. The u.v. spectra of these solutions were immediately recorded over the range 210—300 nm using 1 cm silica cells with acid of the appropriate concentration in the reference cell. These spectra showed little change over periods up to 1 h. Complete conversion of alcohol into carbonium ion in aqueous 50% H_2SO_4 solution was assumed. The wavelengths of maximum absorbance for such solutions are given in Table 1. The spectra of the alcohols in absolute ethanol were taken to represent those in water which could not be obtained due to insolubility in this solvent.

TABLE 2

^{1}H N.m.r. spectra of allylic ethers [a]

Compound	Acetyl resonances (τ) [b]	Methoxy resonances (τ) [b]	Cyclopentadienyl resonances (τ)	Methine resonances (τ)	Vinyl resonances (τ)	Phenyl resonances (τ)
(7b) [c]	7·60	6·42	5·3—5·8 (3H); 5·74 (5H, s)	4·6—4·8	3·2—4·0	2·5—2·9
(7b) [c]	7·68	6·72	5·4—5·8 (3H); 5·95 (5H, s)	4·5—5·0	3·3—3·6	2·5—2·9
(7c) [d]	7·78	6·68	5·1—5·5 (3H); 5·86 (5H, s)	*e*	3·2—4·0	2·71br(s)
(7d) [d]	7·61	6·66	5·25—5·85	*e*	3·2—4·1	2·60br(s)
(8b) [f]	7·62	6·58, 6·65	5·1—5·7 (3H); 5·87, 5·97 (5H, 2 × s)	*e*	3·8—4·3	2·65br(s)
(8c) [d]	7·78	6·70	5·1—5·6 (3H); 5·96 (5H, s)	*e*	3·5—4·1	2·71br(s)
(8d) [d]	7·78	6·68	5·25—5·85	*e*	3·4—4·1	2·61br(s)

[a] For $CDCl_3$ solutions with Me_4Si as internal reference; integrated relative intensities of the resonance signals were in agreement with the assignments; multiplets unless indicated otherwise. [b] Singlet. [c] Diastereoisomeric ether. [d] Obtained impure (see text). [e] Resonance lies under the cyclopentadienyl envelope. [f] A 1 : 1 mixture of diastereoisomers.

For each solution, the relative concentrations of alcohol and carbonium ion were calculated from the absorbance at the $\lambda_{max.}$ value for the latter. The pK_{R^+} value was obtained conventionally [4] from a plot of log ($[R^+][ROH]^{-1}$) *vs.* H_R. At least three independent determinations were made for each system; good reproducibility was found. The results are in Table 1.

Acetylation of trans-3-*Ferrocenyl*-1-*phenylpropene*.—Acetic anhydride (6 ml) and BF_3,Et_2O (48% solution; 7 ml) were added to a stirred solution of the alkene [21] (5a) (10·0 g, 0·033 mol) in CH_2Cl_2 (75 ml) at 0°. The mixture was stirred and allowed to reach room temperature over 6 h, and then poured into water (200 ml). The organic layer was separated, washed (H_2O), dried ($MgSO_4$), and evaporated. The residue was chromatographed. Light petroleum eluted unchanged alkene (2·5 g, 25% recovery). Light petroleum–ether (9 : 1) eluted the *ketone* (5b) (1·1 g, 11%), an orange liquid (Found: C, 73·1; H, 5·8. $C_{21}H_{20}$-FeO requires C, 73·3; H, 5·9%), $\lambda_{max.}$ 253 nm (ε 22,500), τ 2·7 (5H, m, Ph), 3·45—3·55 (2H, m, vinyl), 5·35, 5·51, and 5·63 (3H, 3 × m, C_5H_3), 5·81 (5H, s, π-C_5H_5), 6·32 (2H, m, CH_2), and 7·59 (3H, s, Ac). Light petroleum–ether (4 : 1) eluted the *ketone* (5d) (3·9 g, 35%), an orange solid, m.p. 58—59° (Found: C, 73·4; H, 5·7%), $\lambda_{max.}$ 253 nm (ε 22,500), τ 2·7 (5H, m, Ph), 3·5—3·8 (2H, m, vinyl), 5·28, 5·53, and 5·90 (8H, 3 × m, ferrocenyl), 6·87 (2H, m, CH_2), and 7·66 (3H, s, Ac). Light petroleum–ether (4 : 1) eluted the *ketone* (5c) (2·4 g, 21%), a yellow solid, m.p. 111—112° (Found: C, 73·0; H, 5·8%), $\lambda_{max.}$ 252 nm (ε 22,000), τ 2·67 (5H, m, Ph), 3·5—3·7 (2H, m, vinyl), 5·24 and 5·50 (3H, 2 × m, C_5H_3), 5·81 (5H, s, π-C_5H_5), 6·72 (2H, m, CH_2), and 7·65 (3H, s, Ac).

Attempts to carry out this acetylation reaction using either a twofold excess of Ac_2O,BF_3, or using MeCOCl–$AlCl_3$, were unsuccessful and only starting material was recovered.

Hydride Abstractions.—A solution of triphenylmethyl tetrafluoroborate (1·3 g, 0·0035 mol) in CH_2Cl_2 (25 ml) was added to solutions of each of the alkenes (5b—d) (1·1 g, 0·003 mol) in CH_2Cl_2 (50 ml). Dark brown solutions of the corresponding carbonium ions (6b—d) were formed instantaneously. These were treated as described below.

Methoxide Trapping Experiments.—A solution of sodium methoxide (from 0·2 g Na) in methanol (5 ml) was added to solutions of each of the cations (6b—d) in CH_2Cl_2. Orange-yellow solutions were immediately formed. These solutions were poured into water and the organic layer was separated, washed (H_2O), dried ($MgSO_4$), and evaporated. The residue was chromatographed on alumina which had been exposed to the atmosphere for 24 h. Light petroleum eluted triphenylmethane (1·0 g, 90%), m.p. 91—92°. Light petroleum–ether (4 : 1) eluted unchanged starting material (0·1 g, 9% recovery), followed by a mixture of isomeric ethers (7b—d) + (8b—d) (1·0 g, 83%). These mixtures were separated as follows.

(a) α-*Acetyl ethers* (7b) + (8b). The mixture of ethers obtained from the cation (6b) in the previous experiment was chromatographed on alumina. Three distinct bands developed and were eluted with light petroleum–ether (4 : 1). The first band afforded one *diastereoisomer* of the ether (7b) (0·024 g), an orange oil. The second band afforded a 1 : 1 mixture of the diastereoisomeric forms of the ether (8b) (0·120 g) as an orange oil. The third band afforded the other *diastereoisomer* of the ether (7b) (0·054 g). The product ratio (7b) : (8b) was 39 : 61 (average of two experiments).

(b) β-*Acetyl ethers* (7c) + (8c). The mixture of ethers obtained from the cation (6c) was subjected to preparative t.l.c. on silica using light petroleum–ether (9 : 1) as eluant. Clean separation of the constituents was not obtained.

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[23] T. D. Turbitt and W. E. Watts, following paper.

The top and tail of the band were removed and the absorbed material removed. The top of the band (less polar material) afforded a mixture containing *ca.* 80% of the ether (8c) while the bottom of the band (more polar material) afforded a mixture containing *ca.* 80% of the ether (7c). The ^1H n.m.r. spectra of the enriched fractions and of the original ether mixture (relative intensities of cyclopentadienyl singlet resonances) gave a product ratio (7c) : (8c) of 36 : 64 (average of two experiments).

(c) 1′-*Acetyl ethers* (7d) + (8d). The mixture of ethers obtained from the cation (6d) was subjected to preparative t.l.c. as described above. The top portion of the band gave a mixture enriched (*ca.* 80%) in the ether (7d) while the bottom portion gave a mixture enriched (*ca.* 80%) in the ether (8d). The product ratio (7d) : (8d) was 35 : 65 (from relative intensities of acetyl resonances; average of two experiments).

Identification of Ethers (7b—d) and (8b—d).—These ethers decomposed on standing and satisfactory analytical results were not obtained. Their ^1H n.m.r. spectra are summarised in Table 2. Each of the ethers obtained, either pure or as an enriched sample, was reduced with sodium borohydride (COMe ⟶ CHMeOH) in order to remove the acetyl chromophore. The ethers (7b—d) were thereby identified by the presence in the u.v. spectra of their reduction products of a characteristic styryl chromophore ($\lambda_{max.}$ 252 nm), while u.v. spectra of the reduction products of the ethers (8b—d) contained a characteristic ferrocenylvinyl chromophore ($\lambda_{max.}$ 234 nm) (see ref. 20).

Treatment of these ethers with methoxide under the conditions of their formation from the cations (6b—d) did not cause isomerisation.

We thank Mr. K. J. Baird for preliminary experiments and the Northern Ireland Ministry of Education for a maintenance grant (to T. D. T.).

[3/1850 *Received, 6th September,* 1973]