

## Stable Carbocations. Part 12.<sup>1</sup> Generation, Observation, and Properties of Ferrocenyl-stabilised Vinyl Cations

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A series of stable ferrocenylvinyl cations has been prepared by protonation of alkynylferrocenes in trifluoroacetic acid, and their structural and chemical properties have been investigated by spectroscopic means. Their stability towards nucleophilic addition is enhanced by alkyl substitution in the ferrocene rings and by steric shielding of the reaction centre. For cations bearing a vinyl  $\beta$ -substituent, torsional isomerisation by rotation around the ring-C<sup>+</sup> bond has been studied by <sup>1</sup>H n.m.r. spectroscopy.

ALTHOUGH the intermediacy of vinyl cations in solvolyses of substituted ethylenes and in electrophilic addition reactions of alkynes is well established,<sup>2-4</sup> few have been prepared in solution with lifetimes sufficiently long to permit study by spectral methods.<sup>3,4</sup> Taking advantage of the powerful electron-releasing capacity of the ferrocenyl group, we have prepared a series of stable ferrocenylvinyl cations and we now report their spectroscopic and chemical properties.<sup>3</sup> These cations were generated in trifluoroacetic acid by protonation of the alkynes (1a-f), (2a-e), and (3a-e), prepared as described previously,<sup>5</sup> and their <sup>1</sup>H n.m.r. spectra were recorded where possible for solutions in the same solvent.

*Protonation of Ethynylferrocenes.*—The alkynes (1a-f)

<sup>1</sup> Part 11, W. Crawford and W. E. Watts, *J. Organometallic Chem.*, 1976, **110**, 257.

<sup>2</sup> M. Hanack, *Accounts Chem. Res.*, 1970, **30**, 209; G. Modena and U. Tonnellato, *Adv. Phys. Org. Chem.*, 1971, **9**, 185; P. J. Stang, *Progr. Phys. Org. Chem.*, 1973, **10**, 205; L. R. Subramanian and M. Hanack, *J. Chem. Educ.*, 1975, **52**, 80.

<sup>3</sup> Preliminary communication, T. S. Abram and W. E. Watts, *J.C.S. Chem. Comm.*, 1974, 857.

<sup>4</sup> H.-U. Siehl, J. C. Carnahan, L. Eckes, and M. Hanack, *Angew. Chem. Internat. Edn.*, 1974, **13**, 675; S. Masamune, M. Sakai, and K. Morio, *Canad. J. Chem.*, 1975, **53**, 784.

dissolved readily in trifluoroacetic acid giving green solutions containing the corresponding vinyl cations (4a-f), which were quickly captured by solvent to give violet trifluoroacetoxycarbenium derivatives (5a-f). Quantitative yields of the ketones (6a-f) were isolated following hydrolysis of these solutions with aqueous sodium hydrogen carbonate.<sup>6</sup> Ferrocenylvinyl cations of type (4) are thus more reactive towards nucleophilic addition of trifluoroacetic acid than ferrocenylalkylium ions, including the simplest (ferrocenylmethylium), which are stable in this solvent.<sup>7</sup>

With ethynylferrocene (1a), the high rate of solvent addition to the first-formed cation (4a) prevented determination of its <sup>1</sup>H n.m.r. spectrum, and only that of the product (5a) of further addition of trifluoroacetic acid was observed.<sup>8</sup> However, the resonances of the other vinyl

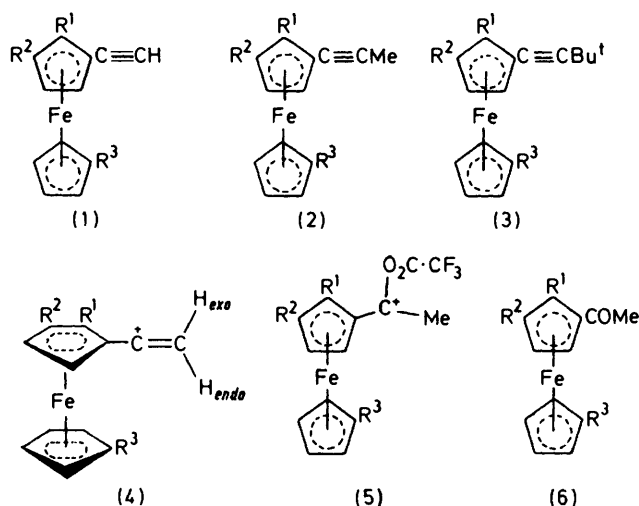
<sup>5</sup> T. S. Abram and W. E. Watts, *Synthesis and Reactivity in Inorganic and Metal-Organic Chem.*, 1976, **6**, 31.

<sup>6</sup> Cf. D. Kaufman and R. Kupper, *J. Org. Chem.*, 1974, **39**, 1438.

<sup>7</sup> (a) M. Hisatome and K. Yamakawa, *Tetrahedron*, 1971, **27**, 2101; (b) T. D. Turbitt and W. E. Watts, *J.C.S. Perkin II*, 1974, 189; (c) S. Braun, T. S. Abram, and W. E. Watts, *J. Organometallic Chem.*, 1975, **97**, 429.

<sup>8</sup> Cf. J. R. Sutton, *Diss. Abs.*, 1971-1972, **32**, 845-B.

cations (4b—f) were obtained by recording the spectra of solutions of the alkynes (1b—f) in cold trifluoroacetic



- a:  $R^1 = R^2 = R^3 = H$   
 b:  $R^1 = R^3 = Me, R^2 = H$   
 c:  $R^1 = H, R^2 = R^3 = Me$   
 d:  $R^1 = R^3 = Bu^t, R^2 = H$   
 e:  $R^1 = H, R^2 = R^3 = Bu^t$   
 f:  $R^1 = Bu^t, R^2 = R^3 = H$

acid ( $-10^\circ C$  initially) immediately after their preparation. The original signals in these spectra quickly

spectra (Table 1) of the vinyl cations are similar to those of related ferrocenylalkylium ions<sup>7b</sup> and the vinyl resonances appear in each case as a clean AB quartet ( $\tau$  ca. 3.3 and 3.8;  $J$  12 Hz) in accord with the expected<sup>10</sup> 'linear' geometry ( $C_{sp}-C_{sp}$ ) of the vinyl group. Restricted rotation about the exocyclic bond of such species,<sup>11</sup> resulting from  $p(d)\pi-p\pi$  conjugation of the ferrocenyl group and the vacant vinyl  $p$  orbital, leads to differential shielding of the vinyl protons which occupy different locations (*exo* and *endo*) relative to the ferrocenyl group (see later). The most compelling evidence for the stereochemistry (4) is provided by the magnitudes of the geminal vinyl coupling constants (Table 1), which may be compared with the corresponding values<sup>12</sup> for keten (15.8 Hz) and 1,1-dimethylallene (9.0 Hz). For molecules of such orbital geometry, hyperconjugative interaction between the  $CH_2$  bonds and the adjacent coplanar  $p\pi$  system leads to an enhancement of the geminal coupling constant from the much lower values (ca. 2 Hz) normally associated with terminal alkenes.<sup>12</sup>

In the formation of the vinyl cations of this series, stereochemically indiscriminate protonation of the triple bonds of the precursors was indicated by the  $^1H$  n.m.r. spectrum of the alkyne (1d) in trifluoroacetic [ $^2H$ ]acid, which contained both *exo*- and *endo*-vinyl proton signals ( $\dot{C}=\text{CHD}$ ) of approximately equal intensity.

The rate of solvent ( $CF_3CO_2H$ ) capture by these vinyl cations was found sensitive to alkyl substitution in the ferrocenyl rings; at  $33^\circ C$ , observation ( $^1H$  n.m.r.) life-

TABLE 1

$^1H$  N.m.r. spectra ( $\tau$  values) of ferrocenylvinyl cations<sup>a</sup>

Cation	Cyclopentadienyl protons			Ring alkyl protons	Other protons ( $\dot{C}=\text{CHR}$ ) <sup>b</sup>
	H-2, -5	H-3, -4	H-1'-5'		
(4b) <sup>c</sup>	5.49—5.76	3.74 (d)	4.76—5.12	8.06, 8.32 (2 × s, Me)	3.16, 3.76 (2 × d, $CH_2$ )
(4c)	5.47—5.73	3.70—3.83	4.87—5.23	7.60, 8.01 (2 × s, Me)	3.36, 4.00 (2 × d, $CH_2$ )
(4d)	5.62 (t)	3.55—3.66	4.62—5.08	8.80br (s, 2 × $Bu^t$ )	3.24, 3.83 (2 × d, $CH_2$ )
(4e)	5.71—5.96	3.45—3.60	4.68—5.17	8.56, 8.83 (2 × s, $Bu^t$ )	3.34, 3.94 (2 × d, $CH_2$ )
(4f)	5.60—5.72	3.55—3.73	4.76 (s)	8.82 (s, $Bu^t$ )	3.26, 3.84 (2 × d, $CH_2$ )
(7Ab)	5.62—5.80	3.79—3.90	4.84—5.27	7.97, 8.20 (2 × s, Me)	3.84 (q, CH), 7.57 (d, Me)
(7Ac)	5.55—5.77	3.69—3.81	4.54—5.01	7.66, 8.16 (2 × s, Me)	3.63 (q, CH), 7.57 (d, Me)
(7Ad)	5.72 (t)	3.71—3.86	4.75—5.20	8.85br (s, 2 × $Bu^t$ )	3.75 (q, CH), 7.60 (d, Me)
(7Ae)	5.23—5.45	3.39—3.51	4.80—5.10	8.69, 8.80 (2 × s, $Bu^t$ )	3.32 (q, CH), 7.51 (d, Me)
(7Bb)	5.62—5.80	3.79—3.90	4.84—5.27	7.97, 8.20 (2 × s, Me)	2.79 (q, CH), 7.57 (d, Me)
(7Bc)	5.55—5.77	3.69—3.81	4.54—5.01	7.66, 8.16 (2 × s, Me)	2.89 (q, CH), 7.81 (d, Me)
(7Bd)	5.72 (t)	3.71—3.86	4.75—5.20	8.85br (s, 2 × $Bu^t$ )	2.95 (q, CH), 7.64 (d, Me)
(7Be)	5.23—5.45	3.39—3.51	4.80—5.10	8.69, 8.80 (2 × s, $Bu^t$ )	2.85 (q, CH), 7.50 (d, Me)
(10Aa)	5.48 (t)	3.65 (t)	4.91 (s)		3.61 (s, CH), 8.70 (s, $Bu^t$ )
(10Ab)	5.70 (t)	3.90 (d)	4.96—5.30	8.15, 8.41 (2 × s, Me)	3.52 (s, CH), 8.69 (s, $Bu^t$ )
(10Ac)	5.59—5.88	3.87—3.98	4.93—5.32	7.69, 8.11 (2 × s, Me)	3.78 (s, CH), 8.72 (s, $Bu^t$ )
(10Ad)	5.72—5.82	3.68—3.80	4.83—5.14	8.82br (s, 2 × $Bu^t$ )	3.72 (s, CH), 8.65 (s, $Bu^t$ )
(10Ae)	5.40—5.70	3.56—3.65	4.60—5.17	8.58, 8.84 (2 × s, $Bu^t$ )	3.66 (s, CH), 8.68 (s, $Bu^t$ )
(16)	5.14 (t)	3.30 (t)	4.48 (s)		0.63—1.14 ( $C_7H_6$ ), 1.93 (s, CH)

<sup>a</sup> Solvent  $CF_3CO_2H$ ;  $Me_4Si$  as internal reference; integrated relative intensities of signals agreed with proton assignments; multiplets unless indicated otherwise. <sup>b</sup> Coupling constants associated with  $\dot{C}=\text{CH}_2$  (4) and  $\dot{C}=\text{CHMe}$  (7) were 12.0 and 7.2 Hz, respectively. <sup>c</sup> Cation obtained by dissolution of either alkyne (1b) or (13) in  $CF_3CO_2H$ .

decayed and were replaced after a few minutes by those characteristic \* of the addition products (5b—f).

The cyclopentadienyl proton resonance patterns in the

\* The spectra of the cations (5) are similar in feature to those of the ketones (6) in trifluoroacetic acid (*i.e.*  $\text{COMe} \rightarrow \dot{\text{C}}\text{MeOH}$ );<sup>9</sup> in particular, the  $(\text{Me}\dot{\text{C}})$  protons give rise to a characteristic singlet resonance around  $\tau$  7.4

times increased through the series: (4a) (a few s) < (4b)  $\approx$  (4e) (2—3 min) < (4c) (6—8 min) < (4d)  $\approx$  (4f) (10—311.

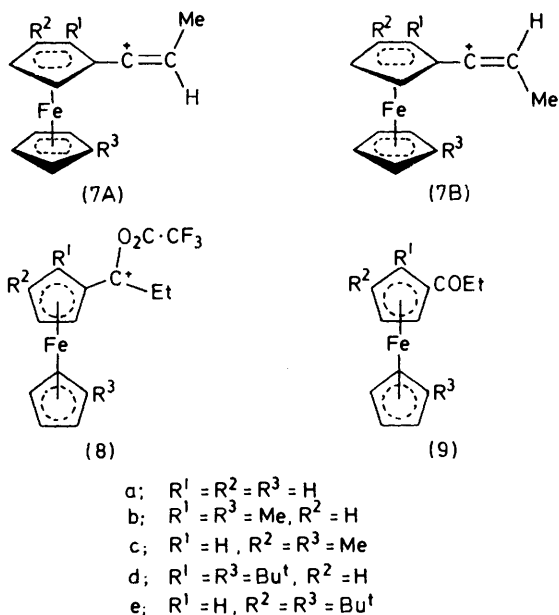
<sup>9</sup> G. A. Olah and Y. K. Mo, *J. Organometallic Chem.*, 1973, **80**, 311.

<sup>10</sup> See R. H. Summerville and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1974, **96**, 1110.

<sup>11</sup> T. D. Turbitt and W. E. Watts, *J.C.S. Perkin II*, 1974, 177.

<sup>12</sup> E. L. Allred, D. M. Grant, and W. Goodlet, *J. Amer. Chem. Soc.*, 1965, **87**, 673.

15 min). The extended lifetimes of those cations (4d and f) bearing a 2-*t*-butyl group adjacent to the reaction centre must reflect steric hindrance towards nucleophilic addition since the 1',2-dimethyl analogue (4b) is considerably more reactive. However, the enhanced stability of the latter cation over that of the parent (4a) suggests +*I* electronic stabilisation of the system by the ring methyl groups. This effect is more clearly shown by the



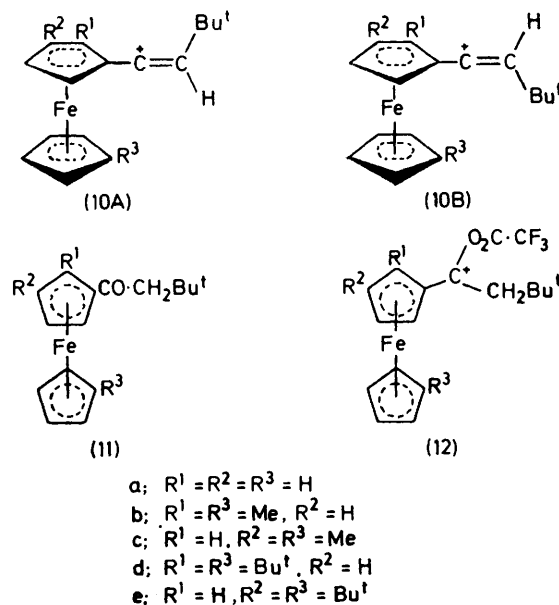
diminished reactivities, as compared with that of (4a), of the 1',3-dialkyl cations (4c and e) for which steric hindrance to reaction can be discounted. Methyl substituents appear more effective in this connection than *t*-butyl.\*

**Protonation of Propynylferrocenes.**—Dissolution of propynylferrocene (2a) in cold trifluoroacetic acid gave a green cation, presumably (7a); however, very fast solvent addition to form the violet cation (8a) prevented spectroscopic characterisation. Substitution of a vinylic hydrogen atom of the ferrocenylvinyl cation (4a) by a methyl group, therefore, provides no discernible stabilisation of the system towards nucleophilic addition (*cf.* influence of ring methyl substitution, described earlier), showing that little positive charge is delocalised to the vinyl  $\beta$ -carbon atom.

Protonation of the 1',2-di-*t*-butyl-substituted compound (2d), on the other hand, gave a readily observable mixture of stereoisomeric vinyl cations (7Ad) and (7Bd) in the ratio 2 : 3, respectively ( $^1\text{H}$  n.m.r.). At  $-8^\circ\text{C}$  (spectrometer cavity temperature), these stereoisomers underwent rotational interconversion to give after 2.5 h an equilibrium mixture consisting predominantly (>95%) of the sterically less congested cation (7Ad), which was only slowly converted into (8d) by solvent

addition† (*ca.* 20% conversion after a further 6 h). Similar behaviour was found for the other alkynes (2b, c, and e) but the much faster solvent capture by the observable first-formed vinyl cations (7Ab, c, and e) and (7Bb, c, and e), giving the derivatives (8b, c, and e), made study of rotational equilibration less straightforward. Nevertheless, it is clear that, for cations of the type (7A)  $\rightleftharpoons$  (7B), rotation about the ring-C<sup>+</sup> bond occurs faster than addition of trifluoroacetic acid and that this latter process is retarded by ring alkyl substitution in a manner similar to that described previously for the related series (4a-f). Hydrolysis with aqueous sodium hydrogen carbonate of solutions of the cations (7) and/or (8) in trifluoroacetic acid gave exclusively the corresponding propanoylferrocenes (9).

The  $^1\text{H}$  n.m.r. signals of the cations (7Ab-e) and (7Bb-e) are given in Table 1. For each stereoisomeric pair the *exo*-vinyl proton of (7B) is substantially more deshielded (0.45–1.05 p.p.m.) than the *endo*-vinyl proton of the isomer (7A). Since this chemical-shift distinction reverses the situation which normally obtains for ferrocenyl substrates,<sup>14</sup> it appears likely that there is unequal hyperconjugative drain of electron density from the



vinylic  $\text{CH}_2$  bonds of cations of the type (4) such that the *exo*-CH bond experiences greater electron withdrawal.

**Protonation of (3,3-Dimethylbut-1-ynyl)ferrocenes.**—Protonation of the alkynes (3a-e) in trifluoroacetic acid gave a series of extremely unreactive vinyl cations whose  $^1\text{H}$  n.m.r. spectra (Table 1) showed the presence of a single stereoisomer (10Aa-e) in each case. Conceivably, protonation of the triple bonds from the *exo*-direction is strongly resisted by steric repulsion between the  $\beta$ -*t*-butyl

† The formation of (8d) may occur by the addition of trifluoroacetic acid to the minor stereoisomer (7Bd).

<sup>13</sup> T. D. Turbitt and W. E. Watts, *J.C.S. Perkin II*, 1974, 185.

<sup>14</sup> T. D. Turbitt and W. E. Watts, *Tetrahedron*, 1972, **28**, 1227.

\* It has been shown<sup>13</sup> that 3- and 1'-methyl substitution increases the thermodynamic stability of ferrocenylalkylium ions (*e.g.*  $\text{FcCMe}_2^+$ ).

group and the pendant cyclopentadienyliron moiety in the transition state [cf. (10B)].\*

These vinyl cations proved extremely resistant to

TABLE 2

Rate constants for solvent addition to vinyl cations <sup>a</sup>

Reaction	$10^5 k/s^{-1}$ <sup>b</sup>
(10Aa) $\rightarrow$ (12a)	240
(10Ab) $\rightarrow$ (12b)	7.65
(10Ac) $\rightarrow$ (12c)	22.6
(10Ad) $\rightarrow$ (12d)	ca. 0 <sup>c</sup>
(10Ae) $\rightarrow$ (12e)	61.5

<sup>a</sup> At 70 °C in  $CF_3CO_2H$ . <sup>b</sup> From the slope of linear  $\ln [\% (10A)]$ , vs.  $t$  plots; values considered accurate to within  $\pm 5\%$ . <sup>c</sup> No addition product was detected during 6 h at 70 °C.

nucleophilic addition. Earlier work<sup>15</sup> has established that ferrocenylcarbocations add nucleophiles preferentially from the *exo*-direction which, for the cations

however, lack pronounced absorption at wavelengths longer than 470 nm. This may be due to structural distortion. Steric repulsion between the *exo*- $\beta$ -t-butyl group and 2-alkyl ring substituent of these cations may cause twisting of the vinyl group from the preferred stereochemistry in which  $p_\pi-p(d)_\pi$  conjugation with the ferrocenyl group is maximised. In this connection, with the single exception of the  $\beta$ -methyl-1',2-di-t-butyl cation (7d), which is brown, all cations of the series (4) and (7) are green.

*Protonation of Other Alkynylferrocenes.*—In trifluoroacetic acid, the silylalkyne (13) was converted into the vinyl cation (4b) and thence into the trifluoroacetoxycarbenium ion (5b). Presumably, the first-formed vinyl cation (not observed) fragments as shown (14) giving the alkyne (1b) and trimethylsilyl trifluoroacetate [ $\tau$  9.60(s)],

TABLE 3

Electronic spectra of ferrocenylvinyl cations <sup>a</sup>

Cation	$\lambda_{max}/nm$ (log $\epsilon$ )				
	Band 1	Band 2	Band 3	Band 4	Band 5
(10Aa)	255 (4.03)	280 (3.50)	400 (3.07)	455 (2.48)	680 (2.62)
(10Ab)	265 (4.01)	280 (3.52)	347 (2.78)	460 (2.51)	685 (2.61)
(10Ac)	266 (3.98)	290 (3.49)	412 (3.00)	475 (2.43)	685 (2.61)
(10Ad)	268 (3.99)	290 (3.53)	350 (2.77)	463 (2.45)	696 (2.38)
(10Ae)	269 (3.96)	295 (3.50)	417 (2.92)	486 (2.35)	696 (2.38)

<sup>a</sup> At 22 °C in  $CF_3CO_2H$ .

(10Aa—e), is seriously obstructed by the *exo*- $\beta$ -t-butyl group. In consequence, hydrolysis of these cations in trifluoroacetic acid solution with aqueous sodium hydrogen carbonate gave substantial amounts of deprotonation products (3a—e) together with the usual addition products (11a—e).

Capture of these cations by trifluoroacetic acid proceeded sluggishly, in contrast to the behaviour of the other series (4) and (7A). At 70 °C, the first-order rates of conversion of the cations (10Aa—c and e) were measured spectroscopically (Experimental section) and the rate constants are in Table 2. The  $\beta$ ,1',2-tri-t-butyl-substituted cation (10Ad) was totally resistant to addition of trifluoroacetic acid. These and the earlier results show that the reactivity of ferrocenylvinyl cations towards nucleophilic addition is diminished by groups providing steric shielding of the reaction centre, particularly an *exo*- $\beta$ -t-butyl group, and to a lesser extent by alkyl ring substituents which act to stabilise the system electronically.

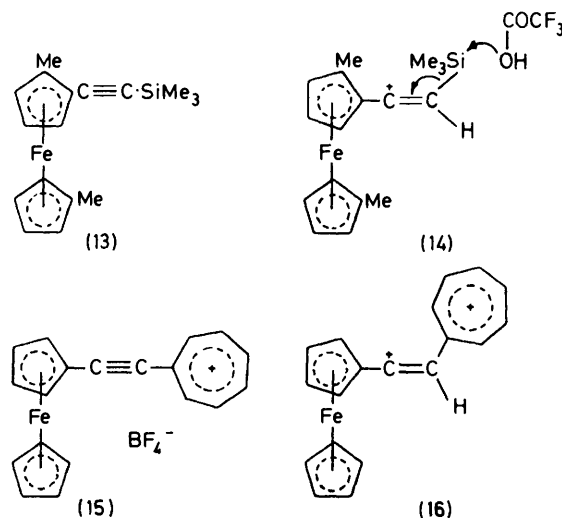
The electronic spectra of the cations (10Aa—e), obtained for freshly prepared solutions of the alkynes (3a—e) in trifluoroacetic acid, are summarised in Table 3. The parent cation (10Aa) and its 1',3-dialkyl derivatives (10Ac and e) give similar spectra containing five principal bands including a long wavelength absorption around 690 nm which imparts their green colour. The spectra of the orange-yellow 1',2-dialkyl derivatives (10Ab and d),

\* Alternatively, the rate constant for the isomerisation (10B)  $\rightarrow$  (10A) must be larger than ca.  $5 \times 10^{-2} s^{-1}$  with the equilibrium constant  $[(10A)]/[(10B)]$  greater than ca. 30 at 33 °C.

<sup>15</sup> E. A. Hill and J. H. Richards, *J. Amer. Chem. Soc.*, 1961, **83**, 3840, 4216.

which was identified in the reaction mixture. Related fragmentations of benzyltrimethylsilanes in trifluoroacetic acid have been described.<sup>16</sup>

Finally, the tropylium salt (15) dissolved in trifluoroacetic acid to give the stable dication (16), characterised



by its <sup>1</sup>H n.m.r. spectrum (Table 1), which was totally resistant to solvent addition.

#### EXPERIMENTAL

For general details, see Part 4.<sup>11</sup> With the exception of the compound given below, the methods of preparation of all

<sup>16</sup> K. A. Andrianov, S. A. Igonina, V. I. Sidorov, C. Eaborn, and P. M. Jackson, *J. Organometallic Chem.*, 1976, **110**, 39; see also T. Kondo, K. Yamamoto, and M. Kumada, *ibid.*, 1973, **80**, 303.

of the alkynes used in this study have been described previously.<sup>5</sup>

1-(1',2-Dimethylferrocenyl)-2-(trimethylsilyl)ethyne (13).—A solution of the alkyne (1b)<sup>5</sup> (480 mg, 2 mmol) in ether (40 ml) was treated with methyl-lithium (4.8 mmol) in ether (2.5 ml) and the mixture was stirred for 0.5 h at room temperature, giving the corresponding lithium acetylide. Chlorotrimethylsilane (1.0 g, 9.3 mmol) was then added and the mixture was stirred for 0.5 h. The reaction was worked up in the usual manner and the product was purified by preparative t.l.c. [SiO<sub>2</sub>; light petroleum (b.p. 40–60 °C) as solvent]. The alkyne (13) (600 mg, 96%) was obtained as an amber liquid (Found: C, 66.0; H, 7.0 C<sub>17</sub>H<sub>22</sub>FeSi requires C, 65.8; H, 7.1%);  $\nu_{\max}$  (film) 2150 cm<sup>-1</sup> (C≡C);  $\tau$ (CDCl<sub>3</sub>) 5.72–5.83 (1 H) and 5.92–6.23 (6 H) (2 × m, ferrocenyl), 7.97 and 8.06 (3 H and 3 H, 2 × s, ring Me), and 9.77 (9 H, s, SiMe<sub>3</sub>).

<sup>1</sup>H N.m.r. Spectra.—The spectra of the vinyl cations (Table 1) were obtained by the following general procedure. Cold trifluoroacetic acid (ca. –10 °C), which had been deoxygenated by passage of nitrogen, was added rapidly to a cold n.m.r. sample tube containing the alkyne and tetramethylsilane reference under nitrogen. The spectrum of the resulting solution (ca. 0.2M) containing the vinyl cation was recorded immediately. In most cases, the spectrometer cavity temperature was 33 °C but a few spectra were obtained at –8 °C (see Discussion section).

Rate Studies.—Solutions of the alkynes (3a–e) in trifluoroacetic acid were prepared as described above in n.m.r. sample tubes which were sealed and thermostatted at 70 °C. The <sup>1</sup>H n.m.r. spectra were recorded at suitable time intervals and the relative proportions of vinyl cation (10A) and alkylion ion (12) were determined by integration of their sharp, well resolved t-butyl singlet resonances. Reactions were followed over at least three half-lives. Plots of log (% vinyl cation), vs. *t* were linear and the first-order rate constants, calculated conventionally, are given in Table 2. Duplicate kinetic runs gave acceptable agreement.

Hydrolysis Experiments.—Solutions of the alkynes in trifluoroacetic acid were poured with stirring into a large excess of saturated aqueous sodium hydrogen carbonate. The products were isolated by extraction with ether (ca. quantitative recovery of ferrocenyl substrates) and purified by preparative t.l.c. [SiO<sub>2</sub>; light petroleum (b.p. 40–60°) –ether mixtures].

The alkynes (1a–f) afforded exclusively the corresponding ketones (6a–f), which were identical with authentic samples.<sup>5</sup> Hydrolysis of solutions of the vinyl cations (10Aa–e) in trifluoroacetic acid gave mixtures of the corresponding alkynes (3a–e) and ketones (11a–e), identical with authentic samples.<sup>5</sup> In each case, the alkyne product predominated; the vinyl cation (10Ad) gave only a trace of the ketone (11d).

The alkynes (2) were converted quantitatively into the corresponding propanoylferrocenes (9), identified by their characteristic <sup>1</sup>H n.m.r. spectra: (2a) afforded (9a), an orange solid, m.p. 36–38° (lit.,<sup>17</sup> 38.0–38.2°);  $\tau$ (CDCl<sub>3</sub>) 5.16 and 5.48 (2 H and 2 H, 2 × t, C<sub>5</sub>H<sub>4</sub>), 5.77 (5 H, s, C<sub>5</sub>H<sub>5</sub>), 7.24 (2 H, q, CH<sub>2</sub>), and 8.81 (3 H, t, Me); (2b) afforded 1,1'-dimethyl-2-propanoylferrocene (9b), an orange liquid (Found: C, 66.9; H, 6.7. C<sub>15</sub>H<sub>18</sub>FeO requires C, 66.7; H, 6.7%);  $\tau$ (CDCl<sub>3</sub>) 5.47 and 5.62–5.85 (1 H and 2 H, t + m, C<sub>5</sub>H<sub>3</sub>), 5.59–6.15 (4 H, m, C<sub>5</sub>H<sub>4</sub>), 7.05–7.51 (2 H, m, CH<sub>2</sub>), 7.72 and 8.15 (3 H and 3 H, 2 × s, ring Me), and 8.83 (3 H, t, CH<sub>2</sub>Me); (2c) afforded 1,1'-dimethyl-3-propanoylferrocene (9c), an orange liquid (Found: C, 66.9; H, 6.9. C<sub>15</sub>H<sub>18</sub>FeO requires C, 66.7; H, 6.7%);  $\tau$ (CDCl<sub>3</sub>) 5.26–5.76 (3 H, m, C<sub>5</sub>H<sub>3</sub>), 5.93–6.14 (4 H, m, C<sub>5</sub>H<sub>4</sub>), 7.08–7.54 (2 H, m, CH<sub>2</sub>), 8.01 and 8.15 (3 H and 3 H, 2 × s, ring Me), and 8.84 (3 H, t, CH<sub>2</sub>Me); (2d) afforded 1-propanoyl-1',2-di-t-butylferrocene (9d), a red liquid (Found: C, 71.3; H, 8.4. C<sub>21</sub>H<sub>30</sub>FeO requires C, 71.2; H, 8.5%);  $\tau$ (CDCl<sub>3</sub>) 5.39 and 5.55–5.75 (1 H and 2 H, t + m, C<sub>5</sub>H<sub>3</sub>), 5.9–6.0 (4 H, m, C<sub>5</sub>H<sub>4</sub>), 7.05–7.5 (2 H, dq, CH<sub>2</sub>), 8.65 and 8.83 (9 H and 9 H, 2 × s, Bu<sup>t</sup>), and 8.82 (3 H, t, Me); (2e) afforded 1-propanoyl-1',3-di-t-butylferrocene (9e), a red liquid (Found: C, 71.2; H, 8.3. C<sub>21</sub>H<sub>30</sub>FeO requires C, 71.2; H, 8.5%);  $\tau$ (CDCl<sub>3</sub>) 5.3–5.4 and 5.65 (2 H and 1 H, m + t, C<sub>5</sub>H<sub>3</sub>), 5.75–6.15 (4 H, m, C<sub>5</sub>H<sub>4</sub>), 7.32 (2 H, q, CH<sub>2</sub>), 8.77 and 8.90 (9 H and 9 H, 2 × s, Bu<sup>t</sup>), and 8.84 (3 H, t, Me).

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<sup>17</sup> M. D. Rausch and L. E. Coleman, *J. Org. Chem.*, 1958, **23**, 107.