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BASE-CATALYSED CLEAVAGE OF SILYL-SUBSTITUTED POLYYNES. ATTENUATION OF HYDROCARBON ACIDITY AND TRANSMISSION OF SUBSTITUENT ELECTRICAL EFFECTS IN LONG-CHAIN CONJUGATED POLYACETYLENES

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SUMMARY

The rates of cleavage of alkynyl–silicon bonds in (a) $Et_3Si(C{\equiv}C)_nSiEt_3$, (b) $Et_3Si(C{\equiv}C)_nH$, and (c) $Mesityl(C{\equiv}C)_nSiEt_3$ compounds at 29.6° in aqueous methanol containing alkali or a base buffer have been measured in order to assess both the attenuation of hydrocarbon acidity and the maximum electron-withdrawing effect attained by long-chain conjugated terminal polyyne systems. The results, expressed as relative rates within each of the series, are as follows: (a) (n, rel. rate) 2, 1.0; 3, 17.4; 4, 86.8; 6, 357; 8, 570; 9, 575. (b) 1, 1.0; 2, 98; 3, 1790; 4, 8017; 6, 27450; 8, 42530. (c) 2, 1.0; 3, 40; 4, 220; 5, 760. In so far as the systems studied are representative, the figures indicate that both the acidity of the parent polyynes, $H(C{\equiv}C)_nH$, and the electron-withdrawal by $H(C{\equiv}C)_n$ groups attenuate rapidly as n increases, reaching limiting values for $n = 8$–10.

INTRODUCTION

Terminal acetylenes exhibit high acidities in comparison with other hydrocarbons[1]. This fact, rationalised in terms of the intrinsic electronegativity of *sp*-hybridised carbon, is embodied in the MSAD acidity scale[2]; for example, whereas saturated, olefinic and aromatic hydrocarbons normally require strongly basic conditions for proton abstraction*, the ethynyl–hydrogen atom undergoes rapid exchange in protic solvents in the pH range 7–9[3,4]. It follows that the acetylene entity is strongly electron-withdrawing, a property demonstrated by the greater acidity of tetrolic ($MeC{\equiv}CCO_2H$, pK_a 2.7) as compared with *trans*-crotonic ($MeCH{=}CHCO_2H$, pK_a 4.7) and butyric acid (pK_a 4.8)[1], and characterised by the positive σ, σ^+ and σ^--constants[5,6] of the ethynyl group. Intuitively one would expect diacetylenes, $R(C{\equiv}C)_2H$, to be more acidic, and the butadiynyl group to be even more electron-attracting, and there is some evidence that this is indeed the case. For example, in the acid-catalysed cleavage of aryl–tin bonds in $XC_6H_4SnMe_3$ compounds (an electro-

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* Hydrocarbons giving rise to conjugatively stabilised anions, or small strained rings approximating to *sp*-situations, must be excluded from this category.

philic aromatic substitution), in which electron-withdrawing substituents, X, lower the rate of cleavage[7], the butadiynyl group lowers the rate more than ethynyl[8], which in turn lowers the rate relative to hydrogen ($X = H$)[6]. Again, calculated proton affinities for the acetylide and diacetylide (*i.e.* butadiynide) anions predict greater acidity for diacetylene[9], however a value for the latter has yet to be determined experimentally. In view of the considerable instability of both higher terminal and parent polyynes, $R(C\equiv C)_nH$ or $H(C\equiv C)_nH$ $n \geqslant 2$, the relevant experimental data for these compounds are difficult to obtain by direct means*, but it is of interest to pose the interrelated questions: to what extent does acetylene hydrocarbon acidity increase and, presumably, attenuate as the number of conjugated triple bonds increases, and at what stage does the electron-withdrawing capacity of a polyyne chain as a substituent attain an effectively limiting value?

Carbon–silicon bonds are broken by base[13,14], the rates of cleavage broadly paralleling the ease of proton abstraction from the parent hydrocarbon, *i.e.* the greater

TABLE 1

CLEAVAGE OF $Et_3Si(C\equiv C)_nH$ AND OF $Et_3Si(C\equiv C)_nSiEt_3$ COMPOUNDS IN ALKALINE OR BUFFERED AQUEOUS METHANOL AT 29.6°

Compound	*Medium*[a]	$10^3\,k$ (*min*$^{-1}$)	k_{rel}	k'_{rel}	λ[b] (*nm*)
$Et_3SiC\equiv CH$	A	118		1.0	240
$Et_3Si(C\equiv C)_2H$	B	115		98[c]	263
	C	45.2			
$Et_3Si(C\equiv C)_2SiEt_3$	C	67.6	1.0		279
$p\text{-}NO_2C_6H_4(C\equiv C)_2SiEt_3$	C	240			335
	D	3.93			
$Et_3Si(C\equiv C)_3H$	D	13.5		1790	215
$Et_3Si(C\equiv C)_3SiEt_3$	D	19.1	17.4		235
$Et_3Si(C\equiv C)_4H$	D	59.1		8017	224
$Et_3Si(C\equiv C)_4SiEt_3$	D	95.8	86.8		256
$Et_3Si(C\equiv C)_6H$	D	207		27450	287
$Et_3Si(C\equiv C)_6SiEt_3$	D	395	357		299
	E	155.5			
$Et_3Si(C\equiv C)_8H$	E	125		42530	326
$Et_3Si(C\equiv C)_8SiEt_3$	E	247.5	570		335
$Et_3Si(C\equiv C)_9SiEt_3$	E	249.5	575		350

[a] A solution of the polyyne in MeOH (5 vol) was mixed with water (1 vol) containing alkali or buffer of the following concentration: A, 2.00 *M* NaOH; B, 0.20 *M* NaOH; C, 0.01 *M* K_2CO_3/0.01 *M* $KHCO_3$; D, 0.1 *M* borax; E, 0.001 *M* borax. [b] Wavelength used to follow progress of reaction. [c] Calculated by assuming the rate to be proportional to the alkali concentration[13,14,17].

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* Enhanced acidity may be inferred from the decrease in rate for oxidative couplings of $Ph(C\equiv C)_nH$ compounds at pH$\sim$3 as *n* increases[10], the increasing ease of decarboxylation of the acids $R(C\equiv C)_nCO_2H$ as *n* increases[11], and the extremely facile dehydrohalogenation of certain dichloropolyynes: *e.g.* $t\text{-}Bu(C\equiv C)_2CHClC\equiv CCHClC\equiv CH$, in the presence of basic alumina[12].

the hydrocarbon acidity the faster the cleavage rate[*], and the increase in polyyne acidity with implied attenuation is similarly reflected in the rates of cleavage of $Ph(C{\equiv}C)_nSiEt_3$ compounds in aqueous methanolic alkali (*viz.* $n = 1, 2, 3$: rel. rate = 1/240/4100)[17]. The successful utilisation of trialkylsilyl groups as protecting agents for terminal alkynes in oxidative couplings[18] has now provided a series of mono- and bissilylpolyynes, $Et_3Si(C{\equiv}C)_nH$ ($n = 2$–8) and $Et_3Si(C{\equiv}C)_nSiEt_3$ ($n = 2$–16) for study, and we have consequently measured the rates of cleavage for a selection of these compounds, and also of a series of available silylated mesitylpolyynes, 1,3,5-$Me_3C_6H_2$-$(C{\equiv}C)_nSiEt_3$ ($n = 2$–5)[19], in order to arrive at an approximate assessment of hydrocarbon acidity variation as conjugated polyyne chains are lengthened.

DISCUSSION

The results of the kinetic study are shown in Tables 1 and 2, for the mono- and bissilylpolyynes and for the silylated mesitylpolyynes respectively. Owing to the spread in reactivity within each series, it proved impossible to carry out all rate measurements (determined spectrophotometrically as pseudo first-order constants, k, at wavelengths, λ, indicated in the Tables) in a single medium, hence an overlap procedure, also involving auxiliary compounds, was employed. As is evident from the data in Table 1, the conversion of any bis- to the corresponding monosilylpolyyne, *i.e.* $Et_3Si(C{\equiv}C)_nSiEt_3 \rightarrow Et_3Si(C{\equiv}C)_nH$, is accompanied by cleavage of the product to give the parent polyyne, $H(C{\equiv}C)_nH$. Fortunately, however, optical density changes associated with the conversion $Et_3Si(C{\equiv}C)_nH \rightarrow H(C{\equiv}C)H$, are negligible in the region of high intensity absorption used to monitor the decomposition of the relevant bissilylpolyynes[18], and so the rates for the latter are not subject to error from this source.

TABLE 2

CLEAVAGE OF $Mesityl(C{\equiv}C)_nSiEt_3$ COMPOUNDS IN ALKALINE OR BUFFERED AQUEOUS METHANOL AT 29.6°

Compound or n	*Medium*[a]	$10^3\,k$ (*min*$^{-1}$)	k_{rel}	λ[b] (*nm*)
2	A	57.2	1.0	307
$Ph(C{\equiv}C)_2SiEt_3$	A	161.7		298
	B	7.16		
3	B	101.3	40	349.5
$Ph(C{\equiv}C)_3SiEt_3$	B	147.7		342
	C	7.17		
4	C	27.2	220	392
5	C	93.2	760	318

[a] A solution of the polyyne in MeOH (5 vol) was mixed with water (1 vol) containing alkali or buffer of the following concentration: A, 0.025 *M* NaOH; B, 0.004 *M* K_2CO_3/0.008 *M* $KHCO_3$; C, 0.1 *M* borax.
[b] Wavelength used to follow progress of reaction.

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[*] Recent attempts[15] to represent rates of cleavage as a linear function of hydrocarbon acidity are subject to criticism[16].

The essential features of the results are summarized as follows:

(a). $Et_3Si(C{\equiv}C)_nSiEt_3$ series ($n=2, 3, 4, 6, 8, 9$)

The measured rate constants for these compounds should be divided by a factor of 2 in order to arrive at the cleavage rate for a single $Si{-}(C{\equiv}C)_n$ bond because two sites are available for attack, but this does not affect the k_{rel} values for these compounds listed in Table 1. Following the pattern previously established for $Ph(C{\equiv}C)_nSiEt_3$ compounds[17], the rates of cleavage, k_{rel}, relative to $Et_3Si(C{\equiv}C)_2SiEt_3$* increase as n increases, but the rate of increase, conveniently expressed in terms of incremental factors (Table 3), falls rapidly and becomes vanishingly small for $n=8, 9$ at a k_{rel} value of ~580. From this we infer that the acidity of the parent polyynes, $H(C{\equiv}C)_nH$, probably attains a maximum value for $n=8$–10; in other words, an octayne unit effectively suffices to insulate the terminal $C{\equiv}CH$ site from the electron-withdrawing (acid strength enhancing) influence of any additional triple bonds. This finding is consistent with the trends revealed in linear free energy analyses of the rates of alkali cleavage of $XC_6H_4(C{\equiv}C)_nSiEt_3$ compounds, for which the effects of substituents, X, (albeit additionally transmitted through the phenylene system) fall off rapidly as n increases from 1 to 3. The electron-attracting capacity of a polyyne substituent, $H(C{\equiv}C)_n$, already showing signs of attenuation under conditions favourable to enhanced electron withdrawal [*viz.* $n=1$, $\sigma_p^-=0.52(5)$ (ref. 6); $n=2$, $\sigma_p^-=0.72$ (ref. 8)] is therefore likely to reach a limiting value (unspecified) when $n=8$.

TABLE 3

RELATIVE CLEAVAGE RATES FOR SILYLATED POLYYNES EXPRESSED AS INCREMENTAL FACTORS

Series (*R*)	*Reactivity Factors:* $R(C{\equiv}C)_mSiEt_3/R(C{\equiv}C)_nSiEt_3$ *for m/n is*						
	2/1	3/2	4/3	5/4	6/4	8/6	9/8
H	98	18.3	4.4		3.4	1.6	
Et_3Si		17.4	5.0		4.1	1.6	1.0
Mesityl		40	5.5	3.4			
Ph	240[a]	20[b]					

[a] Ref. 17. [b] Calcd. from data in Table 2.

(b). $Et_3Si(C{\equiv}C)_nH$ series ($n=1, 2, 3, 4, 6, 8$)

As expected, the pattern within this series, as expressed by rates, k'_{rel}, relative to $Et_3SiC{\equiv}CH$ (Table 1) and incremental factors (Table 3) is much the same as that for the bissilylpolyynes, by far the greatest difference in reactivity occurring between $Et_3SiC{\equiv}CH$ and $Et_3Si(C{\equiv}C)_2H$. It is noteworthy that the statistically "corrected" rates for the bissilylpolyynes diverge from the rates for the corresponding monosilylpolyynes as n decreases, which reflects the slight electron-releasing (rate retarding)

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* The optical density change associated with the conversion of $Et_3SiC{\equiv}CSiEt_3$ to $Et_3SiC{\equiv}CH$ was too small to allow measurement of the rate constant by UV spectrometry.

effect (relative to hydrogen) of the (non-leaving) Et_3Si-group in the bis-series. As *n* increases, the effect diminishes, *viz.* $k\cdot[Et_3Si(C{\equiv}C)_nSiEt_3] \simeq 2\,k\cdot[Et_3Si(C{\equiv}C)_nH]$ for $n>6$, a fact which additionally denotes increasing insulation from substituent influences as the chain lengthens.

(*c*). *Mesityl*$(C{\equiv}C)_n$*SiEt*$_3$ *series* ($n=2, 3, 4, 5$)

Rates of cleavage for this series (Table 2) were measured in order to provide additional information on attenuation brought about by chain extension, as observed in the $Ph(C{\equiv}C)_nSiEt_3$ compounds[17]. The necessary compounds were not available to achieve the convergence limit, *i.e.* $(n+1)/n=1$, as found in the bissilylpolyynes, nevertheless the trend is clear and parallels the effects observed in (a) and (b) above. The somewhat larger incremental factors for low values of *n* in both phenyl and mesityl series (Table 3) merely reflect the greater electrical influence of aryl groups close to the site of reaction, an effect which falls off quickly as the chain lengths increase in each series.

It would be satisfying to find a simple relationship between the degree of attenuation and the number of polyyne units, but plots of the log k_{rel} in each of the three series (a, b, and c) against simple functions of the number of units (*e.g.* against the reciprocal of the chain-length or of the square of the chain-length) are non-linear. Further analyses must therefore await extended proton affinity calculations of the type already carried out for the acetylide and diacetylide anions[9].

EXPERIMENTAL

The methods of preparing silylated mesitylpolyynes[19] and mono- and bissilylpolyynes in solution[18] have been described elsewhere. AnalaR quality K_2CO_3, $KHCO_3$ and borax were used as supplied. With the unstable polyynes, a solution freshly eluted from neutral alumina with paraffinic hydrocarbon* was concentrated to ca. 0.5 ml then diluted with a large excess of methanol. Some of this methanolic solution was mixed with the appropriate quantity of aqueous alkali or buffer, and rate constants were determined spectrophotometrically at 29.6°, using a Unicam SP500 instrument fitted with an electrically thermostatted cell housing, by the methods previously described[14]. For the mono- and bissilylpolyynes, wavelengths corresponding to the characteristic high or ultra-high intensity absorptions[18] were selected. In each case, the optical density of a solution of monosilylpolyyne, recorded under run conditions at the wavelength used to follow the decomposition of the corresponding bissilylpolyyne, was found to be invariant. The stability of the buffer solution was checked by periodic rate measurements using appropriate standards, *e.g.* $Et_3Si(C{\equiv}C)_4SiEt_3$ was used for the 0.1 *M* borax solutions.

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* n-Hexane (spectroscopic grade) or light petroleum (b.p. 60–80°, free from aromatic hydrocarbons) was used.

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