Rates of Base Cleavage of $X{\cdot}C_6H_4{\cdot}[C{\equiv}C]_n{\cdot}MEt_3$ Compounds (n = 2 and 3, M = Si and Ge), and their Significance for Theories of Substituent Effects

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The rates of cleavage of $X{\cdot}C_6H_4{\cdot}[C{\equiv}C]_n{\cdot}MEt_3$ compounds (n = 2 and 3, M = Si and Ge) by aqueous-methanolic alkali at 29·6 °C have been measured spectrophotometrically. The ease of cleavage increases as n is raised; *e.g.*, for the $C_6H_5{\cdot}[C{\equiv}C]_n{\cdot}SiEt_3$ compounds with n = 1, 2, and 3 the approximate relative rates are 1:240:4100. Germanium compounds are less reactive than the corresponding silicon compounds.

The rates of cleavage of $X{\cdot}C_6H_4{\cdot}[C{\equiv}C]_3{\cdot}SiEt_3$ compounds with X = *p*-OMe, H, *p*-F, *m*-Br, and *p*-NO_2 correlate well with the simple Hammett substituent constants, σ, which normally refer to reactions involving markedly smaller distances between the substituent X and the reaction site. This casts some doubt on the validity of treatments of substituent effects which involve separation into (*a*) field effects which depend only on the distance between the substituent site and the reaction site, and (*b*) resonance effects which depend on the effectiveness of conjugation between the sites. Substituent constants calculated according to one such treatment (that by Dewar and Grisdale) are less satisfactory than σ-constants for the cleavages studied.

Recent advances in preparative methods[1] have made available to us compounds of the types $X{\cdot}C_6H_4{\cdot}[C{\equiv}C]_n{\cdot}MR_3$ in which $n = 2$ and 3, and M = Si and Ge. These compounds have the following features which make them especially useful for a study of the nature of the effects of the substituents X in the aromatic ring: (*a*) the rates of alkali and acid cleavage of the alkynyl–M bond (the former reaction generating negative and the latter positive charge in the side-chain) can be easily measured spectrophotometrically, as has been demonstrated for the $X{\cdot}C_6H_4{\cdot}C{\equiv}C{\cdot}MR_3$ compounds;[2,3] (*b*) for $n = 3$, the reaction centre is much further removed from the substituent X than in most reactions used in substituent effect studies; and (*c*) the molecular backbone is rigid and linear, so that not only is the distance between the substituent and the reaction centre precisely known but also electrostatic effects can operate largely through the substrate cavity. This paper deals with the alkali cleavages.

Details of the rates of cleavage in aqueous methanolic alkali of several groups of $X{\cdot}C_6H_4{\cdot}[C{\equiv}C]_n{\cdot}MR_3$ compounds, with the groups X chosen to give a spread of substituent types, are shown in Tables 1—4. In each case the observed first-order rate constant, k, is listed along with the rate, k_{rel}, relative to that of the appropriate parent $Ph{\cdot}[C{\equiv}C]_n{\cdot}MR_3$ compound, the concentration of the aqueous alkali which was mixed with a methanolic solution of the alkynyl compound, and the wavelength, λ, used in recording the progress of the reaction. The water : methanol ratio in the medium was varied to take account of differing solubilities and reactivities.

TABLE 1

Cleavage of $X{\cdot}C_6H_4{\cdot}(C{\equiv}C)_2{\cdot}SiEt_3$ compounds in aqueous-methanolic alkali at 29·6 °C

X	[NaOH] ^{a}/M	10^3k/min^{-1}	k_{rel}	λ/nm
p-MeO	0·06	103	0·50	307
m-Me	0·06	170	0·825	298
	0·0255	66·2		299·6
H	0·0255	80·3	1·00	298
p-F	0·0255	103	1·28	297·8
m-Br	0·0255	206	2·56	299·2
	0·01095	81·5		299·2
p-NO_2	0·01095	280	8·80	335

[a] Concentration of the aqueous alkali, 1 vol. of which was added to 5 vol. of a methanolic solution of the silane.

TABLE 2

Cleavage of $X{\cdot}C_6H_4{\cdot}[C{\equiv}C]_2{\cdot}GeEt_3$ compounds in aqueous-methanolic alkali at 29·6 °C

X	[NaOH] ^{a}/M	10^3k/min^{-1}	k_{rel}	λ/nm
p-MeO	0·123	72·4	0·55	304
m-Me	0·123	113	0·86	298
H	0·123	131	1·00	296·5
p-F	0·123	149	1·14	295·5
m-Br	0·123	260	1·98	298
	0·0251	50·1		
p-NO_2	0·0251	140	5·54	340

[a] Concentration of aqueous alkali, 3 vol. of which was added to 5 vol. of a methanolic solution of the germane.

TABLE 3

Cleavage of $X{\cdot}C_6H_4{\cdot}[C{\equiv}C]_3{\cdot}SiEt_3$ compounds in aqueous-methanolic alkali at 29·6 °C

X	[NaOH] ^{a}/M	10^3k/min^{-1}	k_{rel}	λ/nm
p-MeO	0·01095	87·0	0·59	349
H	0·01095	147	1·00	343
	0·0092	123		
p-F	0·0092	152	1·24	343
m-Br	0·0092	237	1·93	343
p-NO_2	0·01095	489	3·33	354

[a] Concentration of aqueous alkali, 2 vol. of which were added to 25 vol. of a methanolic solution of the silane.

TABLE 4

Reactivities of different types of $X{\cdot}C_6H_4{\cdot}[C{\equiv}C]_n{\cdot}MR_3$ compounds at 29·6 °C

X	n	MR_3	[NaOH] ^{a}/M	H_2O/MeOH (v/v)	10^3k/min^{-1}
H	2	$SiEt_3$	0·0255	1 : 5	80·3
H	1	$SiMe_3$	0·0255	1 : 5	93·5
H	2	$GeEt_3$	0·123	1 : 5	16·5
m-Me	2	$SiEt_3$	0·123	1 : 5	346
H	3	$SiEt_3$	0·0255	2 : 25	382
m-Br	2	$SiEt_3$	0·0255	2 : 25	55·8

[a] Concentration of the aqueous alkali used.

It can reasonably be assumed that the mechanism of

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[1] R. Eastmond and D. R. M. Walton, *Chem. Comm.*, 1968, 204, and unpublished work.

[2] C. Eaborn and D. R. M. Walton, *J. Organometallic Chem.*, 1965, **4**, 217.

[3] R. W. Bott, C. Eaborn, and D. R. M. Walton, *J. Organometallic Chem.*, 1964, **1**, 420.

the cleavage is the same for all the $X{\cdot}C_6H_4{\cdot}[C{\equiv}C]_n{\cdot}MR_3$ compounds. The simplest mechanism is one in which the MR_3 group is attacked by the nucleophile YO^- (Y = H or Me) to give a free carbanion [step (1)], which then rapidly acquires a proton from the solvent [step (2)].[2] It is probable that, as is known to be the case for alkali cleavage of benzyl-silicon bonds,[4] the carbanion

$$X{\cdot}C_6H_4{\cdot}[C{\equiv}C]_n{\cdot}MR_3 + YO^- \longrightarrow X{\cdot}C_6H_4{\cdot}[C{\equiv}C]_{n-1}{\cdot}C{\equiv}C^- + R_3MOY \quad (1)$$

$$X{\cdot}C_6H_4{\cdot}[C{\equiv}C]_{n-1}{\cdot}C{\equiv}C^- + YOH \longrightarrow X{\cdot}C_6H_4{\cdot}[C{\equiv}C]_n{\cdot}H + YO^- \quad (2)$$

is never wholly free, *i.e.*, that steps (1) and (2) are synchronous,[2] but this is relatively unimportant for consideration of substituent effects, since in either mechanism a substantial fraction of negative charge must develop at the terminal carbon atom, and it is the interaction of this with the group X which is important. For simplicity in presentation, we write as though the free carbanion were formed.

The following features of the results are noteworthy. (i) For a given set of $C_6H_5{\cdot}[C{\equiv}C]_n{\cdot}MEt_3$ compounds, the ease of cleavage increases with the change in n from 1 to 2 to 3. The effect, which is to be attributed to the inductive withdrawal of electrons by the additional alkynyl groups, is particularly marked for the change from $n = 1$ to $n = 2$. An approximate assessment of the reactivity increase can be derived for the triethylsilyl compounds from data in Table 4 as follows: (*a*) The rate ratio $Ph{\cdot}[C{\equiv}C]_3{\cdot}SiEt_3/m\text{-}Br{\cdot}C_6H_4{\cdot}[C{\equiv}C]_2{\cdot}SiEt_3$ is 382 : 55·8 in a mixture of methanol (25 vol.) and aqueous 0·0255M-sodium hydroxide (2 vol.) at 29·6 °C; since the rate ratio $Ph{\cdot}[C{\equiv}C]_2{\cdot}SiEt_3/m\text{-}Br{\cdot}C_6H_4{\cdot}[C{\equiv}C]_2{\cdot}SiEt_3$ is 1 : 2·56, the ratio $Ph{\cdot}[C{\equiv}C]_3{\cdot}SiEt_3/Ph{\cdot}[C{\equiv}C]_2{\cdot}SiEt_3$ is (382 × 2·56)/55·8 = 17·5. (*b*) In a mixture of methanol (10 vol.) and aqueous 0·0255M-sodium hydroxide (2 vol.) at 29·6 °C, the rate ratio $Ph{\cdot}[C{\equiv}C]_2{\cdot}SiEt_3/Ph{\cdot}C{\equiv}C{\cdot}SiMe_3$ is 80·3/93·5; since $Ph{\cdot}C{\equiv}C{\cdot}SiMe_3/Ph{\cdot}C{\equiv}C{\cdot}SiEt_3$ = 277 (ref. 1), the ratio $Ph{\cdot}[C{\equiv}C]_2{\cdot}SiEt_3/Ph{\cdot}C{\equiv}C{\cdot}SiEt_3$ is (277 × 80·3)/93·5, *i.e.*, 236. Thus, if the medium change is neglected, the variations for the $Ph{\cdot}[C{\equiv}C]_n{\cdot}SiEt_3$ compounds are as shown in Table 5. By use of several ratios

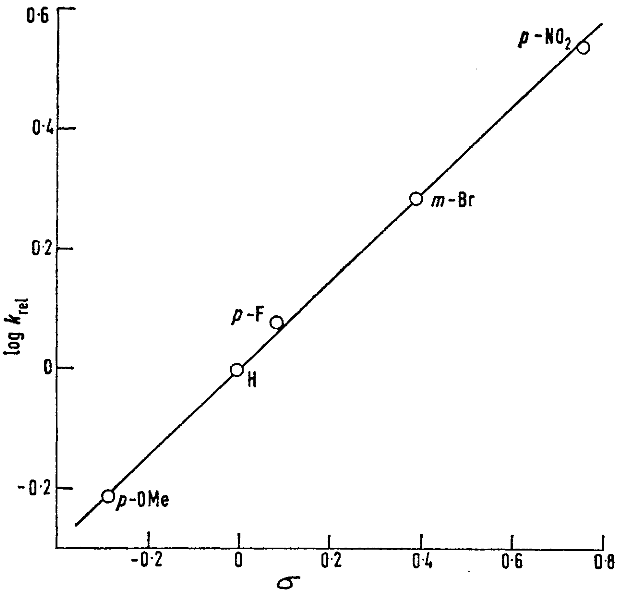
TABLE 5

n	1	2	3
Relative rate	1	240	4100

from the Tables and from ref. 2 it can be shown that the rate ratio $Ph{\cdot}[C{\equiv}C]_2{\cdot}GeEt_3/Ph{\cdot}C{\equiv}C{\cdot}GeEt_3$ has a value of *ca.* 130.

(ii) The germanium compounds are somewhat less reactive and somewhat less sensitive to changes in X than the corresponding silicon compounds, as noted and discussed for the $X{\cdot}C_6H_4{\cdot}C{\equiv}C{\cdot}MR_3$ series.[2] As might be expected in view of the close similarity between the systems, satisfactorily linear plots (not shown) are obtained if log k_{rel} values for $X{\cdot}C_6H_4{\cdot}[C{\equiv}C]_n{\cdot}GeEt_3$ are plotted against those for the corresponding $X{\cdot}C_6H_4{\cdot}[C{\equiv}C]_n{\cdot}SiEt_3$ compounds.

(iii) While the point for X = p-NO_2 deviates by more than the experimental error from a plot (not shown) of log k'_{rel} for $X{\cdot}C_6H_4{\cdot}[C{\equiv}C]_2{\cdot}SiEt_3$ against log k_{rel} for $X{\cdot}C_6H_4{\cdot}[C{\equiv}C]_3{\cdot}SiEt_3$, the separate plots of either log k'_{rel} or log k_{rel} against σ are satisfactory linear, as shown for log k_{rel} in the Figure. A similar plot for $X{\cdot}C_6H_4{\cdot}C{\equiv}C{\cdot}SiEt_3$ compounds is likewise satisfactorily linear for the substituents considered here and for many additional substituents.[2]



Plot of log k_{rel} for the cleavage of $X{\cdot}C_6H_4{\cdot}[C{\equiv}C]_3{\cdot}SiEt_3$ compounds against σ

The linearity of the plot in the Figure is especially revealing, because it means that substituent constants derived from reactions at centres attached to the ring or separated from it by one carbon atom can be used satisfactorily for a reaction generating a (localized) negative charge at a centre separated by five atoms from the ring. This casts doubts on treatments of substituent effects in conjugated systems which involve separation into two independent effects, (*a*) inductive effects (wholly or partly field effects) which depend on the distance between the substituent and the reaction site, and (*b*) resonance effects which depend on the effectiveness of conjugation between the sites, for only by an improbable coincidence should the variations in the two effects maintain the balance in the polyacetylene systems exactly as it exists in the Hammett σ-constants. (While we studied only a small number of substituents, they were carefully chosen to include a good range of substituent types and provide the maximum information on the balance of resonance and inductive effects. In our experience, if the results for the substituents we used correlate well with σ-constants for a reaction, those for a much larger range of substituents will also correlate satisfactorily with such constants.)

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[4] R. Alexander, C. Eaborn, and T. G. Traylor, *J. Organometallic Chem.*, 1970, **21**, P65.

The best developed such treatment of substituent effects is that by Dewar and Grisdale.[5] For a substituent attached at atom i and reaction site attached to atom j, they derive substituent constants σ_{ij} given by equation (3) in which F is a measure of the field set up by the substituent (assumed to constitute the whole of its inductive effect), M a measure of the combined mesomeric and π-inductive effects of the substituent (henceforth referred to, for convenience, as the mesomeric effect), r_{ij} the

$$\sigma_{ij} = F/r_{ij} + Mq_{ij} \qquad (3)$$

distance between atoms i and j, and q_{ij} the formal charge at position j produced by attaching the CH_2^- group at position i. Values of F and M are derived from ordinary σ-constants for *meta*- and *para*-substituents in benzene derivatives by use of the appropriate r and q values.

In a variant on this treatment, the substituent constants, σ'_{ij}, are defined by equation (4), in which the mesomeric effect of the substituent is given by the

$$\sigma'_{ij} = F'/r_{ij} - M'\pi_{ij} \qquad (4)$$

quantity $-M'\pi_{ij}$, where π_{ij} is the atom–atom polarizability of atoms i and j.[5] For the systems considered by Dewar and Grisdale, differences between σ_{ij} and σ'_{ij} were very small, and they favour the use of equation (3).

Values of r_{ij} are expressed in units of the lengths of the C–C bonds in benzene, and for simplicity all the carbon–carbon bonds in $X{\cdot}C_6H_4{\cdot}[C{\equiv}C]_n{\cdot}MR_3$ compounds are assumed to be of this length. (Use of actual bond lengths would not lead to different conclusions in the discussions below.) Values of q_{ij} are obtained from the charge distributions shown in the Chart, derived by the Longuet-Higgins method.[6]

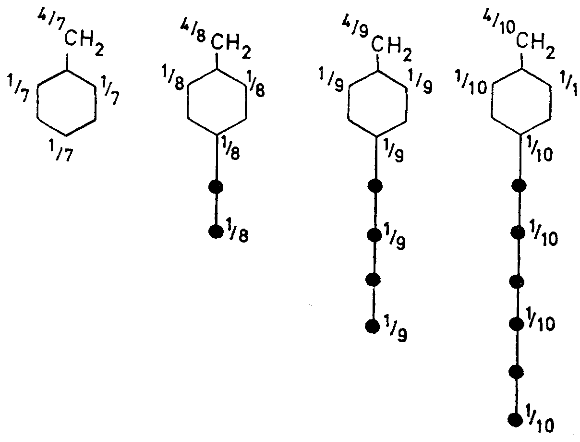

CHART Charge distributions in the ions $H{\cdot}[C{\equiv}C]_n{\cdot}C_6H_4{\cdot}CH_2^-$-*p*

It is necessary first to decide which carbon atom in $X{\cdot}C_6H_4{\cdot}[C{\equiv}C]_n{\cdot}SiEt_3$ compounds should be regarded as atom j. Dewar and Grisdale were concerned only with aromatic ring systems (although their treatment is not specific for such systems), and took atom j to be the ring carbon to which the side chain was attached.[5] At first sight, atom j in the $X{\cdot}C_6H_4{\cdot}[C{\equiv}C]_n{\cdot}SiEt_3$ compounds might seem to be the terminal atom, the reaction site,* but the analogy between the equilibrium (5), from which the σ-constants are derived, and reaction (6), suggests that for $X{\cdot}C_6H_4{\cdot}[C{\equiv}C]_n{\cdot}SiEt_3$ compounds atom j should be taken as the $(2n - 2)$th carbon from from the ring.

$$X{\cdot}C_6H_4{\cdot}C(O){-}OH + H_2O \rightleftharpoons X{\cdot}C_6H_4{\cdot}C(O){-}O^- + H_3O^+ \qquad (5)$$

$$X{\cdot}C_6H_4{\cdot}C{\equiv}C{-}SiEt_3 + HO^- \rightleftharpoons X{\cdot}C_6H_4{\cdot}C{\equiv}C^- + Et_3SiOH \qquad (6)$$

The relevant values of r and q_{ij} are then as in Table 6.

TABLE 6

	p-X				*m*-X			
n	1	2	3	4	1	2	3	4
r	2	4	6	8	1·73	3·6	5·5	7·5
q_{ij}	1/7	1/8	1/9	1/10	0	0	0	0

It is clear that for *p*-X groups the field effect should fall off markedly more rapidly than the mesomeric effect, so that substituent constants, such as ordinary σ-constants, which are applicable for smaller values of n should not be proportional to those for $n = 3$. (The rate of fall-off of the field effect relative to the mesomeric effect would be even greater if the former effect were taken to be proportional to $1/r_{ij}^2$, and this probability is not considered further, even though there are some indications that this relationship between the magnitude of the field effect and the ij separation is the more justifiable.[7])

Values of σ_{ij} for the X groups in the $X{\cdot}C_6H_4{\cdot}[C{\equiv}C]_3{\cdot}SiEt_3$ system, based on values of 6 for r_{ij} and 1/9 for q_{ij}, are listed in Table 7. The statistical analysis in Table 8

TABLE 7

Calculated σ-constants for $X{\cdot}C_6H_4{\cdot}[C{\equiv}C]_3{\cdot}SiEt_3$

X	F	M	F'	M'	σ_{ij}	σ'_{ij}
p-OMe	+0·20	−2·58	+0·13	−3·36	−0·254	−0·106
H	0·00	0·00	0·00	0·00	0·00	0·00
p-F	+0·58	−1·61	+0·56	−2·10	−0·083	−0·006
p-NO_2	+1·23	+1·14	+1·26	+1·48	+0·332	+0·211
m-Br	+0·68	−0·77	+0·66	−1·00	+0·124	+0·088

TABLE 8

Statistical analysis of correlations of log k_{rel} for $X{\cdot}C_6H_4{\cdot}[C{\equiv}C]_3{\cdot}SiEt_3$ compounds with substituent constants

Constants	ρ	Intercept	Correlation coefficient	RD/RMS
(*a*) Constrained to pass through origin				
σ	0·694	0·00	0·994	0·110
σ_{ij}	1·384	0·00	0·964	0·419
σ'_{ij}	1·947	0·00	0·984	0·165
(*b*) Without constraint				
σ	0·698	−0·004	0·993	0·108
σ_{ij}	1·245	0·101	0·969	0·220
σ'_{ij}	1·798	0·038	0·989	0·127

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* The treatment gives even less satisfactory values of σ_{ij} if the terminal carbon atom *is* taken to be atom j.

[5] M. J. S. Dewar and P. J. Grisdale, *J. Amer. Chem. Soc.*, 1962, **84**, 3539, 3548.

[6] H. C. Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 265, 275, 283.

[7] M. J. S. Dewar and A. P. Marchand, *J. Amer. Chem. Soc.*, 1966, **88**, 3318.

reveals that the correlation with σ_{ij} is markedly less satisfactory than that with σ-constants, as judged by the quantity RD/RMS, which is thought to be the best measure of the dispersion.[8,9] The superiority of the σ-constants is greater when the correlation line is constrained to pass through the origin, and we believe such constraint is justified since the origin is the only point for which there can, by definition, be no doubt about the value of the substituent constant.

For completeness we also consider the use of equation (4), and Table 9 gives values of π_{ij} for *para*-substituents along with those of n and r. The variation in the ratio r/π_{ij} is smaller than that of the ratio r/q_{ij} and it follows that σ'_{ij} values (see Table 7), calculated according to equation (4), must fit our results better than do σ_{ij} values. The analysis in Table 8 shows that this is indeed the case, although correlation is still somewhat poorer than that with simple σ-constants. It is noteworthy that while use of q_{ij} leads to much the same results as use of π_{ij} in the naphthalene and biphenyl systems considered by Dewar and Grisdale,[5] q_{ij} and π_{ij} cannot be regarded generally as interchangeable, since the atom–atom polarizability, π_{ij}, is the same in both directions, whereas q_{ji} can differ substantially from q_{ij}, as shown for the Ph•[C≡C]$_n$•H systems in Table 10. [With the naphthalene systems, Dewar and Grisdale mistakenly used q_{ji} instead of q_{ij} values.[5] This was unimportant in that system,[9] but it is noteworthy that a similar erroneous use of q_{ji} in the Ph•[C≡C]$_n$•H system would lead to a more satisfactory set of σ_{ij} constants.]

TABLE 9

n	1	2	3	4
r	2	4	6	8
π_{ij}	−0·102	−0·0645	−0·0466	−0·0363

TABLE 10

n	1	2	3	4
q_{ij}	1/7	1/8	1/9	1/10
q_{ji}	1/7	1/11	1/15	1/19

The charge distribution which results when a CH_2^- group is attached to a conjugated system seems to us to provide an attractive model for assessing the resonance effects of substituents, and there is no reason to believe that the mesomeric effect of a substituent in position i on the reaction centre j *should* always be the same as that of the substituent at position j on a reaction centre at i, as is implied by use of π_{ij}. However, from our results we should have to conclude that if the Dewar–Grisdale treatment is valid then π_{ij} is better than q_{ij} as a measure of the transmission of mesomeric effects.

There are other examples of conjugated systems for which the simple σ-constants give better correlations than the calculated σ_{ij}-values, although the inferiority of the latter is not necessarily as marked as it is in the X•C_6H_4[C≡C]$_3$•$SiEt_3$ system. For example, the plot of the pK_a's of the acids 3'- and 4'-X•C_6H_4•C_6H_4•CO_2H-4 against σ_{ij}-constants ($r_{4'4} = 5$; $q_{4'4} = 1/31$), which has been used as a confirmation of the validity of the calculation of σ_{ij}-constants,[5] is less satisfactory than that against simple σ-constants. (The latter plot, while showing deviations, possibly because of uncertainties in the pK_a values, is actually better than the corresponding plot for the benzoic acids, X•C_6H_4•CO_2H, measured under identical conditions.[10]) Again, pK_a's [11] in the series (a) *p*-X•C_6H_4•C≡C–PyH$^+$ and (b) *trans*-*p*-X•C_6H_4•CH=CH–PyH$^+$ (where Py = 4-C_5H_4N) correlate well with σ_p-constants.

Our results suggest that in conjugated systems the variations in the transmission of inductive and conjugative effects are not as independent as is assumed in treatment of the Dewar–Grisdale type. (Dewar and his collaborators have themselves discussed the difficulties created by the simplifying assumptions involved in a two-parameter treatment, and have outlined various modes of transmission of electronic effects which can operate alongside simple field and classical mesomeric effects.[5,7,12]) In particular, in the Dewar–Grisdale treatment the inductive effects are assumed to be exclusively field effects, which would be identical with those in, say, an aliphatic system involving similar separation and orientation of the substituent and the reaction site, but there are good arguments in favour of the view that such a field effect contributes a minor part of the total inductive effect between conjugated centres, and that the major part is contributed by some transmission of the polar effect through the π-electron system [13] (see also ref. 12). Such transmission between two centres in a conjugated system might vary in much the same way as the normal mesomeric effect, so that the balance between the total inductive effect and the mesomeric effect would vary much less than between the simple field effect and the mesomeric effect.

EXPERIMENTAL

The preparation and properties of X•C_6H_4•[C≡C]$_n$•MEt_3 compounds will be described elsewhere.[1]

Rate Studies.—The spectrophotometric method described for alkali cleavage of X•C_6H_4•C≡C•MR_3 compounds was used.[2] The spectra of reaction solutions after 10 half-lives were identical with those of the corresponding cleavage products, aryl-buta-1,3-diynes and -hexa-1,3,5-triynes, in the reaction media. No change occurred in the u.v. absorption spectra of the latter solutions during times equivalent to 10 half-lives of the cleavages.

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[12] A. Adcock and M. J. S. Dewar, *J. Amer. Chem. Soc.*, 1967, **89**, 379; M. J. S. Dewar and T. G. Squires, *ibid.*, 1968, **90**, 212.

[13] P. R. Wells, 'Linear Free Energy Relationships,' Academic Press, London and New York, 1968, p. 52.