togram attributed to the nucleosides. Such data treatment is validated by the great similarity in extinction coefficient observed for the starting nucleoside and its methyl derivatives at the wavelength of detection.

Methylation of Adenosine. Solutions of adenosine (0.005 M) in 0.1 M buffers (pH 1.4–12.4) were prepared. A tenfold excess of BPA was added to each solution which was placed in a clear tube and irradiated for 20 h with a water-cooled 450-W mercury lamp (Pyrex filter) at 32 °C and a distance of 2 cm. Since some deribosylation occurred during this reaction, the reaction mixtures were totally deribosylated to the free bases by acid hydrolysis (1.0 M HCl, 100 °C, 1 h) before analysis by high-pressure LC. This simplifies data analysis without sacrificing the accuracy of the methylation pattern or the product yield as indicated by controls.

Methylation of Guanosine. The methylation of guanosine at 0.001 and 0.005 M concentrations was conducted in the same manner. Guanosine and its methylated derivatives were analyzed by high-pressure LC.

Methylation of Cytidine. The methylation of cytidine was conducted in the same manner. One of the products, N^4-methylcytidine, was isolated from a large-scale reaction by preparative high-pressue LC using a Partisil 10 ODS (Magnum 9) column (50 cm × 9 mm) with 10% methanol in water at 8 mL/min as eluent. The eluted material was deribosylated by acid hydrolysis (4 N HCl, 130 °C, 16 h) and was identified as N^4-methylcytosine by coinjection with an authentic sample.

Methylation of Thymidine. The methylation of thymidine was conducted in the usual manner except a nitrogen atmosphere was maintained. The nucleoside and its methylation product were analyzed by high-pressure LC.

Methylation of Uridine. The methylation of uridine was conducted in the same manner. Since some deribosylation occurred during this reaction, the reaction mixtures were totally deribosylated by acid hydrolysis (4.0 M HCL, 130 °C, 16 h) and analyzed by high-pressure LC. There were no changes observed in either the site or extent of methylation by this acidic workup procedure as indicated by controls.

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Registry No. Adenosine, 58-61-7; guanosine, 118-00-3; cytidine, 65-46-3; thymidine, 50-89-5; uridine, 58-96-8; A, 73-24-5; 2-MeA, 1445-08-5; 8-MeA, 22387-37-7; 6-MeA, 443-72-1; 2,8-Me_2A, 25680-62-0; 2-MeG, 2140-77-4; 8-MeG, 36799-17-4; 3-MeC, 2140-64-9; 4-MeC, 10578-79-7; 3-MeT, 958-74-7; U, 66-22-8; 6-MeU, 626-48-2; 5-MeU, 65-71-4; 3-MeU, 608-34-4.

Vinyl Cation Intermediates in Electrophilic Additions to Triple Bonds. 1. Chlorination of Arylacetylenes

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The products of ionic addition of chlorine to phenylacetylene, β-methylphenylacetylene, 4-methylphenylacetylene, β-ethylphenylacetylene, and tolan have been investigated in anhydrous acetic acid. The major products are the α,β-dichlorostyrenes arising from simple 1,2 addition, but significant yields of solvent-incoroprated products are also found. In some cases significant yields of β-chlorophenylacetylenes are found, presumably arising from an addition–elimination process. No products arising from addition of 2 mol of Cl_2 were observed. The reactions are clearly nonstereospecific and show only weak stereoselectivity varying from predominant syn to predominant anti addition. However, the reactions are all completely regiospecific in the Markovnikov sense. In the presence of low concentrations of added salts such as lithium chloride, acetate, and perchlorate, the product distribution and stereochemistry are hardly affected. Only at high concentrations of these salts is there any significant change in product distribution. The second-order rates of addition have been measured for five additional phenyl-substituted compounds. The seven ring-substituted phenylacetylenes show an excellent correlation with σ^+, giving a large negative ρ value (−4.19). The effects of β-substitution on the rate of chlorination are very small. The results are interpreted in terms of a simple Ad-E2 process, in which the rate-determining transition state is an open vinyl-cation-like species, with most of the positive charge being developed at C_α. The subsequent product-determining intermediate is considered to be a tight ion pair between an open α-phenylvinyl cation and a chloride counterion. This ion pair can react by ion-pair collapse, solvent attack, or internal proton elimination. Activation parameters determined for three of the above compounds show that the higher rates of chlorination (over bromination) of the acetylene system are due almost entirely to lower ΔH^* values.

Despite the recent wave of activity in studying reactions involving vinyl cations[1] as reactive intermediates and the resurgence of interest in electrophilic additions generally, very little mechanistic work has been reported to date on the addition of molecular chlorine to the triple bond. This reaction presumably involves the formation of vinyl cationic intermediates of some kind, yet a recent review on electrophilic additions to carbon–carbon triple bonds[2] shows relatively little in the way of systematic results in this area.

We have recently completed a detailed study of the kinetics and mechanism of additions of chlorine to two types of acetylene, namely, those substituted with phenyl groups and those substituted only with alkyl groups. Since the reactions of the arylacetylenes appear to be less complex and the results more easily interpreted mechanistically, these will be reported on first in this paper. The accompanying paper[3] reports an analogous study of the chlorinations of alkylacetylenes. All the reactions have been studied in anhydrous acetic acid as solvent to make

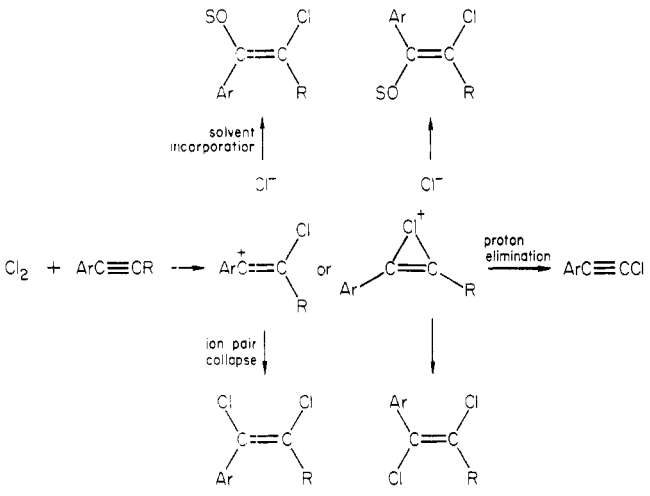
(1) M. Hanack, *Angew. Chem., Int. Ed. Engl.*, 17, 333 (1978); P. J. Stang, *Prog. Phys. Org. Chem.*, 10, 205 (1973); G. Modena and U. Tonellato, *Adv. Phys. Org. Chem.*, 9, 185 (1971).

(2) G. H. Schmid, "Electrophilic Additions to Carbon–Carbon Triple Bonds. The Chemistry of the Carbon–Carbon Triple Bond", S. Patai, Ed., Wiley, New York, 1978, Chapter 8, p 279.

(3) K. Yates and T. A. Go, *J. Org. Chem.*, following paper in this issue.

0022-3263/80/1945-2377$01.00/0

Scheme I[a]



[a] R = H, alkyl, or phenyl.

the results more directly comparable with the large body of data available on the corresponding bromine additions and also with a recently reported study of chlorine additions to substituted styrenes.[4]

The major questions to be answered concern the nature of the rate-determining transition states and the product-determining intermediates in these reactions, namely, as to whether either or both of these are best represented as open or bridged vinyl-cation-like species in the general mechanistic scheme (Scheme I) for chlorine additions to the triple bond. Other important questions concern which of the various mechanistic categories set out by Schmid and Garratt for Ad-E reactions[5] best describes these chlorination reactions.

Results

Products of Chlorination of Arylacetylenes. In order to simulate the kinetic conditions to be used, we added the chlorine solutions in acetic acid to the acetylene solutions in the same solvent in dropwise fashion. However, the products obtained in this way were identical within experimental error with those obtained by mixing the two reactant solutions instantaneously. The solvent was also saturated with oxygen to inhibit possible free-radical pathways, but it was found that the presence or absence of oxygen had no effect on the product distribution or stereochemistry.[6] In general the acetylene concentrations were kept at about 10–15% in excess of the chlorine to minimize possible further chlorination of the primary reaction products.

All the reactions studied were very fast and most were essentially complete within a few minutes. To determine whether the products formed are those of kinetic or thermodynamic control, we carried out experiments in which product mixtures were added to solutions of chlorine

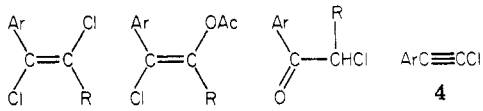
Table I. Product Distributions in the Chlorination of Arylacetylenes in Acetic Acid at 25 °C

	% products[a]			
	1,2-dichlorides			
substr	*E* (anti)	*Z* (syn)	SI[b]	chloro-acetylene
PhC≡CH	15	31	42	12
PhC≡CMe	36	38	26	
4-MePhC≡CH	37	38	14	11
PhC≡CEt	38	42	20	
PhC≡CPh	49	23	25	

[a] Estimated error in product analysis is 1–2%. [b] Solvent-incorporated products of types 2 and 3 (see text).

in acetic acid. After 30 min, there was no detectable change in product composition, but if the mixture were left overnight, some higher chlorinated products were found. It is therefore reasonable to assume that the initially formed products do not easily isomerize under the experimental conditions used and are those of kinetic control. The product mixtures are, in fact, quite stable in the dark, and analysis of the same product mixture after 2 months showed no significant change. However, if product mixtures were left exposed to light, decomposition occurred within hours.

The major products found in each case are the isomeric 1,2-dichloro olefins 1 (where R = H, alkyl, or phenyl), as



1 2 3 4

shown in Table I. In the case of phenylacetylene itself, the major isomer is the (*Z*)-α,β-dichlorostyrene arising from syn addition to the triple bond. With the two methylphenylacetylenes and β-ethylphenylacetylene, the ratio of *E* to *Z* isomer is not far from unity, so that syn and anti modes of addition are almost equally probable. Only in the case of tolan does the anti mode of addition predominate, but even then only by a factor of 2:1. These reactions are thus nonstereospecific, and indeed not even very stereoselective. Secondary products of two types are found. In all cases, there are significant amounts of solvent-incorporated products, which are either chloro enol acetates (2) or the corresponding chloro ketones (3) formed by hydrolysis of the former during workup. Again, these products are formed nonstereospecifically, since both *E* and *Z* chloro enol acetates are found in every case.[9] The reactions are nonetheless completely regiospecific in the Markovnikov sense, since electrophilic chlorine is found only at the β-carbon of the original phenylacetylene and the acetate (or keto) group only at the α-position. No anti-Markovnikov products were ever detected. These solvent-incorporated products are all grouped together under the heading SI in Table I.

A third (minor) type of product arises when the β-carbon of the phenylacetylene bears a hydrogen. This is the β-chloroacetylene (4), presumably formed by addition–elimination, analogously to similar products found in the

(4) K. Yates and H.-W. Leung, *J. Org. Chem.*, in press.
(5) G. H. Schmid and D. G. Garratt, "Chemistry of Double Bonded Functional Groups", S. Patai, Ed., Wiley, London, 1977, Supplement A, Part 2, Chapter 9.
(6) Although in the absence of oxygen chlorinations in nonpolar solvents can occur spontaneously by a radical mechanism[7] even in the dark, the present results, including the kinetics and linear free-energy relationships, strongly indicate that these reactions in anhydrous acetic acid go exclusively by polar or ionic pathways. Heasley and co-workers[8] have recently suggested that chlorination of olefins in acetic acid can proceed by a molecule-induced radical pathway, but they did not elaborate on the nature of this process or offer any direct evidence to substantiate it.
(7) M. L. Poutsma, *J. Am. Chem. Soc.*, 87, 4293 (1965).
(8) V. L. Heasley, D. F. Shellhamer, J. A. Iskikian, D. L. Street, and G. E. Heasley, *J. Org. Chem.*, 43, 3139 (1978).
(9) Since separation and identification of the isomeric chloro enol acetates was difficult (see Experimental Section), the exact stereoselectivity shown by these solvent-incorporated products is not known. The situation is further complicated by the fact that the *E* and *Z* isomers may not hydrolyze to chloro ketone at similar rates during workup. In general, however, it appears that the *E* chloro enol acetate either is the major isomer or is at least formed to the same extent as the *Z* isomer, so that solvent incorporation shows some preference for the anti mode of addition, as has been observed previously in olefin additions.

Table II. Effect of Added Salts on the Products of Chlorination of Phenylacetylene and Methylphenylacetylene

salt	concn, M	% products[a] dichlorides anti	dichlorides syn	SI[b]	chloroacetylene
		Phenylacetylene			
		15	31	42	12
LiCl	0.1	15	30	42	13
	1.0	26	29	37	8
LiOAc	0.1	15	29	43	13
	1.0	8	24	54	14
$LiClO_4$	0.1	16	26	47	11
	1.0	10	23	57	10
		Methylphenylacetylene			
		36	38	26	
LiCl	0.1	39	33	28	
	1.0	48	29	23	
LiOAc	0.1	37	33	30	
	1.0	26	29	45	
$LiClO_4$	0.1	38	37	25	
	1.0	34	25	41	

[a] Estimated error of 2%. [b] Solvent-incorporated products (see text).

bromination of phenylacetylene[10] and chlorination of styrene.[4]

It is to be noted that under the conditions used no products arising from addition of two molecules of chlorine were found. Thus the initially formed products are sufficiently deactivated that a second electrophilic addition to the resulting double bond is much slower than the first addition to the triple bond.

Effects of Added Salts. For the examination of the ease with which the reactive intermediates can be intercepted or diverted by external anions, the chlorinations of phenylacetylene and methylphenylacetylene were repeated in the presence of added chloride, acetate, and perchlorate, and the products analyzed. The results for each acetylene are very similar, as shown in Table II. Low concentrations of added salt (0.1 M) do not affect the product distribution to any significant extent. Unusually high[11] salt concentrations (1.0 M) favor the formation of specific products, depending on the nature of the added salt. High lithium chloride content in the reaction mixture increases the (*E*)-dichloride (from anti addition) largely at the expense of solvent-incorporated products. High acetate concentration results in increased chloro enol acetate formation, largely at the expense of *anti*-dichloride formation, but the *syn*-dichloride is also reduced in the presence of acetate. Lithium perchlorate at high concentration tends to increase the solvent incorporation, mainly at the expense of *anti*-dichloride formation from the phenylacetylene and of *syn*-dichloride from the methylphenylacetylene. The percentage of chloroacetylene formed from phenylacetylene is largely unaffected by the added anions, even at high concentrations. These results are in marked contrast to analogous brominations, where, for example, addition of 0.1 M LiBr results in almost exclusive *anti*-bromide fromation from phenylacetylene, as opposed to the nonstereospecific formation of the five products (dibromides, solvent-incorporated products, and bromoacetylene) normally observed in the absence of added salts.[10] The above results on chlorination of acetylenes are closely analogous to the effects of addition of the same salts on the chlorination of styrenes and 1-phenylpropenes.[4]

Table III. Second-Order Rate Constants for the Chlorination of Ring-Substituted Phenylacetylenes

substituent	k_2,[a] M^{-1} s^{-1}	log k_2	σ[b]	σ^+[c]
p-CH_3	(1.83 ± 0.02) × 10^2	2.262	+0.170	−0.311
p-F	(1.49 ± 0.02) × 10	1.173	+0.062	−0.073
H	(1.06 ± 0.01) × 10	1.025	0	0
p-Cl	4.15 ± 0.04	0.618	+0.227	+0.114
p-Br	2.81 ± 0.02	0.449	+0.232	+0.150
m-NO_2	(1.65 ± 0.02) × 10^{-2}	−1.783	+0.710	+0.674
p-NO_2	(3.25 ± 0.04) × 10^{-3}	−2.488	+0.778	+0.790

[a] Measured in anhydrous acetic acid at 25 °C. [b] Taken from ref 16. [c] Taken from ref 15.

It has been suggested that in the presence of chloride ion, the rate expression for chlorination may change to include a kinetic term in halide,[12] similar to that commonly found in bromination.[10,13] To test this possibility, we determined the rates of chlorination of the same two acetylenes as above in the presence (1.0 M) and absence of the three salts used in the product studies. Despite the addition of a very large excess of chloride (over the two reagents) the rate only changed by about 10%. Similar small increases in rate were observed with acetate and perchlorate. Furthermore, the reactions remain cleanly second order (see the next section), and the observed variations in rate can be attributed to small salt effects arising from the increased polarity of the solvent due to the high concentrations of added salt.

Rates of Chlorination and Linear Free-Energy Relationships. Without exception, the rate law obtained for the kinetics of chlorination to the phenylaceylene derivatives studied exhibited a simple second-order dependence overall, first order in acetylene and first order in chlorine (eq 1). As pointed out above, no evidence was

$$-d[Cl_2]/dt = k[Cl_2][\text{acetylene}] \quad (1)$$

found for kinetic dependence on chloride ion, nor was any higher order dependence on $[Cl_2]$ found. Except for two nitro-substituted substrates, rates were followed by stopped-flow spectrophotometry, using the disappearance of the Cl_2 absorption at 321 nm. The rates were determined under pseudo-first-order conditions, with at least a 20-fold excess of acetylene over chlorine. For the nitro derivatives the intense UV absorption of the nitro aromatic system ($\epsilon \simeq 10^4$) obscured the weak absorption of Cl_2 (ϵ 80) at the usual wavelengths studied. Fortunately, the rates for these compounds were sufficiently slow to allow use of a titrimetric method (see Experimental Section). The rate constants (k_2) obtained by using both methods are listed in Table III for the several ring-substituted acetylenes investigated. Unfortunately, the rate of chlorination of the *p*-methoxy derivative was too high to be followed, even by stopped-flow methods, so that the range of substituents

(10) J. A. Pincock and K. Yates, *J. Am. Chem. Soc.*, **90**, 5643 (1968); J. A. Pincock and K. Yates, *Can. J. Chem.*, **48**, 3332 (1970).

(11) The addition of 1.0 M concentrations of salts would be very unusual in solvolytic work where the usual range of salt concentration is 0.1 M or less, and even in previous bromination work the added salts rarely exceed 0.2 M in concentration.

(12) P. B. D. de la Mare, "Electrophilic Additions to Unsaturated Systems", Cambridge University Press, London, 1976, p 66.

(13) J. E. Dubois and X. Q. Huynh, *Tetrahedron Lett.*, 3369 (1971).

(14) K. Yates, R. S. McDonald, and S. A. Shapiro, *J. Org. Chem.*, **38**, 2460 (1973).

Table IV. Effects of β-Substitution on the Rate of Chlorination of Phenylacetylene

substr	k_2, M^{-1} s^{-1}	k_{rel}
PhC≡CH	10.6 ± 0.1	1.0
PhC≡CMe	30.3 ± 0.4	2.8
PhC≡CEt	55.0 ± 0.6	5.2
PhC≡CPh	2.97 ± 0.04	0.3

Table V. Rate Constants for the Chlorination of Acetylenes in Acetic Acid at Different Temperatures

substr	temp, °C	k_2, M^{-1} s^{-1}	n^a
PhC≡CH	21.0	9.1 ± 0.2	3
	25.0	10.6 ± 0.2	5
	30.0	14.2 ± 0.2	3
	35.0	15.6 ± 0.2	3
	40.0	20.0 ± 0.3	3
	45.0	23.3 ± 0.4	3
PhC≡CMe	16.5	22.3 ± 0.4	4
	20.1	26.1 ± 0.4	4
	25.0	30.3 ± 0.4	5
	29.0	40.9 ± 0.6	4
	32.0	46.6 ± 0.7	4
	40.7	62.1 ± 0.8	4
PhC≡CPh	25.0	2.97 ± 0.03	4
	32.0	4.19 ± 0.05	3
	37.0	5.17 ± 0.07	2
	41.0	6.00 ± 0.08	2
	47.0	8.06 ± 0.09	2
	54.0	10.4 ± 0.1	2

[a] Number of kinetic runs.

used was necessarily somewhat limited. Nonetheless the rates ranged over five orders of magnitude, and sufficient data were accessible to establish reasonable linear free-energy relationships of the Hammett type. A correlation of log k_2 vs. Brown's σ^+ scale[15] gives a ρ value of −4.19 with a correlation coefficient of 0.998. This correlation was significantly better than that from a plot of log k_2 vs. σ, which yielded $\rho = -4.71$ and $r = 0.991$.

The effects of β substitution on the rate were also investigated by replacing the hydrogen of phenylacetylene with methyl, ethyl, and phenyl. The results are given in Table IV. It can be seen that the rate variations are quite small, even when H is replaced by phenyl. These effects are consistent with the large (negative) ρ value already observed, which indicates substantial charge development at C_α. They are also very similar to the small effects shown in solvolysis of vinylic systems, where β substitution is not expected to affect the stability of the vinyl cationic center at C_α to a large extent. It is to be noted that tolan is the slowest reacting of the four acetylenes listed in Table IV. This is also the case in the bromination of the same four compounds.[17]

Activation Parameters. Rate constants were measured for three of the phenylacetylenes over the range of 16–54 °C, and the results are shown in Table V. The calculated values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are given in Table VI, with some reported values from bromination for comparison. The $\Delta H^\ddagger$ values for chlorination are of the order of 6–8 kcal, which is about 5 kcal lower than the corresponding bromination value[10] in the two cases given. This is similar to the results obtained from double bond additions of Cl_2 and Br_2, where the faster rates of chlorination are mainly due to a lower $\Delta H^\ddagger$ term.[4] The values of $\Delta S^\ddagger$

Table VI. Activation Parameters for Chlorination and Bromination of Phenylacetylenes

substr	halogen	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, eu
PhC≡CH	Cl_2	6.3 ± 0.2	−33 ± 1
	Br_2[a]	12	−31
PhC≡CMe	Cl_2	7.6 ± 0.3	−26 ± 2
	Br_2[a]	12	−29
PhC≡CPh	Cl_2	7.7 ± 0.3	−30 ± 1

[a] Values taken from ref 10.

of around −30 eu are reasonable for a polar bimolecular process involving some solvent restriction and are very similar to the $\Delta S^\ddagger$ values frequently obtained in other electrophilic additions to both double[5] and triple[2] bond systems.

Discussion

The reaction is clearly electrophilic in nature, from the sign and magnitude of the ρ value. The product studies, including the effect of added salts, show that the mechanism involves a cationic intermediate, which can react to give final products in several ways. The fact that the reactions are not very stereoselective (let alone stereospecific) but yet are completely regiospecific means that the reactive intermediate is best represented as an open β-chloro-α-phenylvinyl cation. If there is any chlorine bridging at all in this intermediate, it must be very weak and highly unsymmetrical. The effects of added nucleophile and perchlorate show that the initially formed vinyl cation must be very tightly ion paired with its chloride counterion, since it is very difficult to intercept or to divert to the solvent-separated ion-pair stage. The sterochemistry shows, however, that the intimate ion-pair, although tightly held, can interconvert to the ion pair with chloride ion on the opposite side from the electrophilic chlorine at C_β. Whether this occurs by rotation about the C_{phenyl}–C_α bond or by migration of chloride to the opposite side of the vinyl cation is difficult to say, but the former process seems more probable.

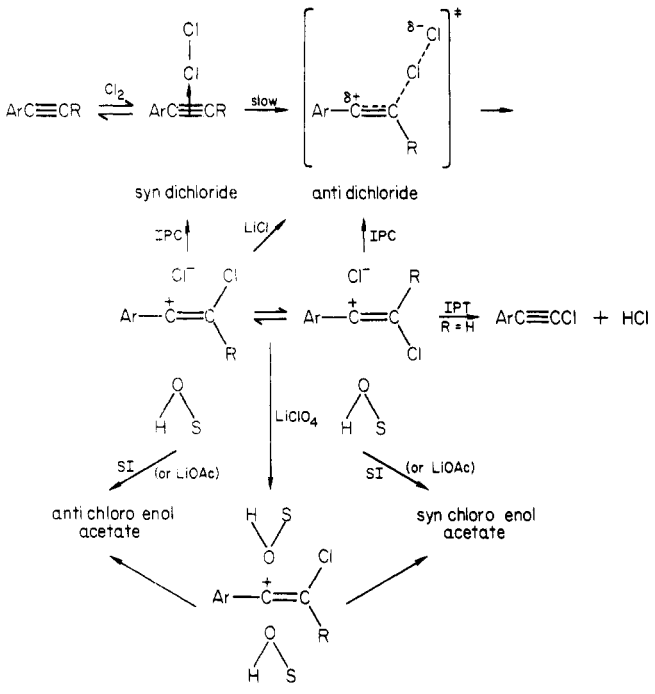
It appears from the strong rate dependence on ring substituents and the better correlation of log k_2 with σ^+ than with σ that the rate-determining transition state is also open vinyl-cation-like, with at best very weak, unsymmetrical chlorenium ion character. This is also supported by the very small rate dependence on β-substitution. The range of β substituents Et > Me > H > Ph produces only an overall variation in rate of a factor of 17, whereas simply replacing H by Me at the para position of the phenylacetylene produces a similar rate difference.

The detailed mechanism can be represented as in Scheme II. The initial attack of Cl_2 on the triple bond probably results in reversible formation of a charge-transfer complex.[18] (It should be pointed out that it is not yet certain that such complexes necessarily lie on the reaction coordinate for electrophilic addition, and in any event this may not be kinetically significant.) This is followed by rate-determining formation of an open vinyl cation, tightly ion paired with its chloride counterion. Thus the mechanism can be categorized as a simple Ad-E2 process.[5] There is no evidence for a competing chloride ion catalyzed Ad-E3 process, for electrophilic attack by Cl_3^-, or for a termolecular process involving two molecules of Cl_2.

The ion pairs then react by ion-pair collapse to give both *syn*- and *anti*-dichloride formation, and in fact this is

(15) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).
(16) L. P. Hammett, "Physical Organic Chemistry", 2nd ed., McGraw-Hill, New York, 1970, p 356.
(17) A. Modro, C. H. Schmid, and K. Yates, unpublished results.
(18) J. E. Dubois and F. Garnier, *Spectrochim. Acta, Part* A, **23**, 2279 (1967); J. E. Dubois and F. Garnier, *Tetrahedron Lett.*, 3047 (1966); 3961 (1965).

Scheme II[a]



[a] IPC = ion-pair collapse, IPT = internal proton transfer, and SI = solvent incorporation.

generally the predominant product-forming step. They can also react (in either configuration) with acetic acid to give both syn- and anti-formed solvent-incorporated products, which are β-chloro-α-acetoxystyrenes. Internal proton transfer[19] to chloride ion can result in β-chloroacetylene formation as a minor product, in cases where the starting acetylene bears a β-hydrogen. In the presence of added nucleophiles, the ion pairs can be trapped to give increased amounts of *anti*-dichloride (with LiCl) or of solvent-incorporated product (with LiOAc), but only when high concentrations of nucleophile are present. The ion pairs can go on to the solvent-separated ion-pair stage and be prevented from returning to the intimate ion-pair stage, but again only with considerable difficulty (by $LiClO_4$). This also results in increased solvent-incorporated product.

The fact that these chlorination reactions are much faster (by a factor of about 10^2) than analogous brominations is probably attributable to formation of a stronger C–Cl bond and less Cl–Cl bond breaking in the rate-determining step for the chlorination. This results in a significantly lower value (by about 5–6 kcal) of $\Delta H^{\ddagger}$ for chlorination, although $\Delta S^{\ddagger}$ values are comparable for both bromination and chlorination at about −30 eu. This is similar to the difference in rates and $\Delta H^{\ddagger}$ values found for corresponding additions to phenyl-substituted double bonds.[4]

Experimental Section

General Methods. All boiling points and melting points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer 237B or 337 spectrophotometer, using either neat samples or solutions in CCl_4. Routine UV spectra were measured on a Unicam SP800A. Mass spectra were determined on a CEC21-490 single-focussing magnetic sector spectrometer, operating at 70 eV. NMR spectra were obtained on a Varian T-60 or T-60A instrument, generally using CCl_4 solutions with Me_4Si as internal standard. GLC was used extensively in product separation and analysis. All instruments used were fitted with flame-ionization detectors, and most peak areas were determined by using a Varian CDS-111C computer-integrator system. Elemental analysis were carried out by A. Gygli, Ltd.

Table VII[a]

component	column A retn time, min	column A % of pdts	column B retn time, min	column B % of pdts
1	1.0	12	3.7	14
2	1.8	15	7.3	16
3	2.8	31	12.2	32
4	5.5	5	17.8	4
5	7.0	24	21.8	23
6	9.8	13	29.8	11

[a] Conditions: column A, 150–200 °C, flow rate 60 mL/min; column B, 140–200 °C, flow rate 40 mL/min.

Materials. Acetic acid was purified by the method previously described.[20] Chlorine (Matheson) was also dispensed and purified as described previously.[4] All chlorine solutions were prepared, stored, and used in the absence of light. Salts used were all analytical grade and dried as described previously.[4] Phenylacetylene, methylphenylacetylene, ethylphenylacetylene, and tolan were available commerically and were either recrystallized or distilled until GC showed better than 99.5% purity. All acetylenes had to be used within a few days of purification, since even when stored in the cold under N_2, the liquid samples started to turn yellow.

The ring-substituted phenylacetylenes have been prepared previously,[21] and the same two general methods were used. The physical properties (melting or boiling point) of all the acetylenes prepared corresponded with reported values.[21]

Kinetic Measurements. Except for the two nitro-substituted phenylacetylenes, all kinetic runs were followed spectrophotometrically. The change in Cl_2 absorption at 321 nm (ε 80) was used for all substrates except tolan. Here the tolan absorption at 296 nm (ε 29 530) was used to monitor the reaction rate. All runs were carried out at least in triplicate and with varying initial reagent concentrations. In most cases the second-order rate constants (k_2) agreed to within 3%. The initial concentrations of acetylenes were identified by direct weighing into a known volume of solvent. Initial Cl_2 concentrations were determined either by UV analysis or by titration with thiosulfate (after adding KI to the solution) using a 10% thyodene solution as indicator.[22]

For the more slowly reacting compounds, the absorbance was measured as a function of time on a Cary 16 instrument, with continuous recording. Runs were followed to at least 3 half-lives, and an infinity absorbance taken after 10 half-lives. In most cases reactions were followed under pseudo-first-order conditions, with at least a 20-fold excess of acetylene. For the more reactive compounds, a Durrum stopped-flow kinetics spectrophotometer was used, and the data were treated as described previously. More recently the kinetic data were handled directly by means of a Tektronix 4051 graphics system equipped with a printer–plotter. In the case of the two nitro compounds, the strong aromatic absorption made it impossible to follow the reactions at 321 nm. Fortunately these reactions are slow enough to use a sampling technique and the titrimetric method described previously.[22]

Product Analysis. The general procedures used previously for the products of chlorination of styrenes[4] were repeated essentially without change. At least two determinations were carried out under each set of conditions, and the product distributions agreed to within 2% in most cases. The detailed results are given below for each acetylene.

(19) Although it is difficult to interpret the increases or decreases of the various dichlorides and chloro enol acetates as a function of added salts in any definitive way (see Table II), it seems clear that chloroacetylene formation is least affected by any of these salts. It is therefore reasonable to assume that the major proton-transfer agent is the chloride ion in the initially formed ion pair.

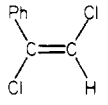
(20) A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Troops, Eds., "Techniques of Organic Chemistry", Vol. III, 2nd ed., Interscience, New York, 1955, p 145.

(21) A. D. Allen and C. D. Cook, *Can. J. Chem.*, 41, 1084 (1963).

(22) A. I. Vogel, "Quantitative Inorganic Analysis", 3rd ed., Wiley, New York, 1957, pp 348–50.

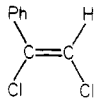
Phenylacetylene. The gas chromatogram of the crude product mixture showed components on two different columns[23] (see Table VII). The crude product mixture was distilled (0.2 mm, 120 °C). A dark residue remained, and a yellow liquid distillate was collected. This distillate was separated by preparative GC on column C (flow rates of 150, 220, and 100 mL/min). Four fractions were collected. Compound 1 has the following spectroscopic characteristics: NMR δ 7.23 (m); mass spectrum, m/e (relative intensity) 139 (10), 138 (62), 137 (29), 136 (100), 77 (51). Anal. Calcd for C_8H_5Cl: C, 70.35; H, 2.69; Cl, 25.96. Found: C, 69.99; H, 3.43; Cl, 26.05. On the basis of spectroscopic evidence, compound 1 was assigned the structure PhC≡CCl.

Compound 2 has the following spectroscopic characteristics: NMR δ 6.40 (s, 1 H), 7.35 (br s, 5 H); IR 6.3 μm (br and weak); mass spectrum, m/e (relative intensity) 177 (2), 176 (9), 175 (6), 174 (63), 173 (13), 172 (100), 139 (31), 137 (85), 125 (20), 102 (50), 89 (10), 77 (26). Anal. Calcd for $C_6H_3Cl_2$: C, 55.53; H, 3.50; Cl, 40.98. Found: C, 55.32; H, 3.20; Cl, 41.27. On the basis of the spectroscopic evidence, in comparison with that of compound 3, compound 2 was assigned the structure



2

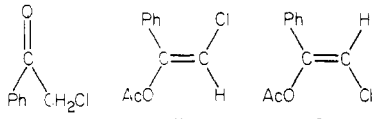
Compound 3 has the following spectroscopic characteristics: NMR δ 6.62 (s, 1 H), 7.35 (s, 5 H); IR 6.3 μm (stronger than that of compound 2); mass spectrum, similar to that of compound 2. Anal. Calcd for $C_8H_6Cl_2$: C, 55.53; H, 3.50; Cl, 40.98. Found: C, 55.27; H, 3.94; Cl, 40.66. On the basis of the spectroscopic evidence, in comparison with that of compound 2, compound 3 was assigned the structure



3

There are interesting and useful differences in the spectroscopic data for these two geometrically isomeric dichlorides. First, the retention times in the GC's, both analytical and preparative, are different. The *trans*-dichloride, being less polar, has a shorter retention time on polar columns such as Carbowax and UCON-(polar). Second, the C=C stretching frequency at 6.3 μm of the *trans*-dichloride in the IR is broad and weak, while that of the *cis*-dichloride is relatively sharper and stronger. Third, the proton cis to the phenyl ring in the *cis*-dichloride appears at lower field than that trans to the phenyl ring in the trans isomer in the NMR. The phenyl proton signals in the *trans*-dichloride are also broad compared to the phenyl protons in the cis case in the aromatic region of the NMR. Similar observations have been made previously in such pairs of geometrical isomers.[10]

Due to their long retention times on the preparative GC column, compounds 4, 5, and 6 were collected as a mixture by increasing



4 5 6

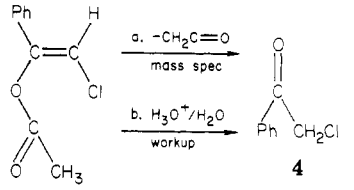
the column temperature, from 150 °C to 200 °C. They are deduced to have the structures shown on the basis of the following observations. The NMR of the mixture showed peaks at δ 2.06 and 2.10 which were assigned to the methyl groups of the isomeric chloro enol acetates. The peak at δ 4.42 was assigned to the methyl protons of the chloro ketone compound, 4. The mass spectrum of the mixture is consistent with the proposed structures, in that the base peak is found at m/e 154, which is the molecular ion for

(23) Details of the columns used for the GC separations are as follows: column A, 30% Carbowax 20M on 60/80 Chrom P; column B, 5% Carbowax 20M on 80/100 Chrom W; column C, 10% Carbowax 20M on 80/100 Chrom W; column D, 50% QF-1 on 80/100 Chrom W.

Table VIII

component	retn time, min	% of pdts
7	5.0	38
8	6.5	36
9	10.6	26

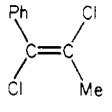
compound 4 and also arises from a loss of ketene from the chloro enol acetates 5 and 6 (eq 2, path a). The molecular ion peaks



5 or 6 4 (2)

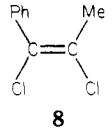
M^+ and $(M + 1)^+$ for the chloro enol acetates are found, showing the presence of compounds 5 and 6. Compound 4 is thought to arise from either compound 5 or 6 by a hydrolysis process in the acidic aqueous workup (eq 2, path b). Therefore, these are all solvent-incorporated products of the chlorination and are grouped under one heading in the Results and Discussion sections.

Methylphenylacetylene. The gas chromatogram on column B of the crude product mixture had the components shown in Table VIII (from 120 to 200 °C at 6 °C/min; flow rate 240 or 40 mL/min). The distillate obtained from a distillation of the crude product mixture (50 μm 150 °C) was separated by preparative GC on column C (180–250 °C, flow rate 100 mL/min). Three fractions were collected. Compound 7 has the following spectroscopic characteristics: NMR δ 2.42 (s, 3 H), 7.35 (m, 5); mass spectrum, m/e (relative intensity) 190 (6), 188 (28), 186 (60), 153 (8), 151 (27), 155 (100), 89 (10). Anal. Calcd for $C_9H_8Cl_2$: C, 57.59; H, 4.31; Cl, 37.90. Found: C, 57.70; H, 4.30; Cl, 38.10. On the basis of the above data and also comparison with those of compound 8, compound 7 was assigned the following structure:



7

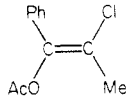
Compound 8 has the following spectroscopic characteristics: NMR δ 2.03 (s, 3 H), 7.25 (m, 5 H); mass spectrum, similar to that of compound 7. Anal. Calcd for $C_9H_8Cl_2$: C, 57.79; H, 4.31; Cl, 37.90. Found: C, 57.60; H, 4.51; Cl, 37.45. On the basis of above data and also comparison with those of compound 7, compound 8 was assigned the following structure:



8

The assignment of the geometrical isomerism for these two dichlorides is again based on the GC retention times and NMR data. In a β-methylstyrene system, the methyl group cis to the phenyl ring was found to absorb at a higher field than one trans to the phenyl ring.[24] The above assignment conforms with such results.

Compound 9 was shown by NMR to contain two components. They are deduced to be the isomeric chloro enol acetates on the basis of the following observations. The NMR showed two sets



9

(24) G. H. Schmid and M. Heinola, *J. Am. Chem. Soc.*, **90**, 3466 (1968).

Table IX[a]

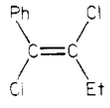
component	column A retn time, min	column A % of pdts	column B retn time, min	column B % of pdts
10	2.2	38	7.1	38
11	6.5	40	10.2	42
12	15.3	10	23.9	8
13	17.5	12	24.7	11

[a] Conditions: column A, 180–225 °C, flow rate 40 mL/min; column B, 150–210 °C, flow rate 30 mL/min.

of peaks, one in the aromatic region, δ 7.2 (m, 5 H), and the other at δ 2.0–2.1 (4 s, 6 H). The four singlets are assigned to the β-methyl groups and the methyl groups in the acetoxy functions of the two isomeric chloro enol acetates. Two sets of equal-intensity peaks are found for the singlets, showing the same number of protons for each type of proton in the chloro enol acetates. However, absolute assignment of the peaks is not possible at present due to the closeness of the peaks. The mass spectrum of these compounds showed small peaks at m/e 210 and 212 which corresponds to the molecular ions of the chloro enol acetates and the base peaks at m/e 168 which arise from the loss of ketene from the chloro enol acetates (cf. eq 2). Therefore, it appears that even GC cannot separate these chloro enol acetate isomers. This kind of problem was also encountered previously[10] in attempts to separate the bromo enol acetates which were products from the bromination of methylphenylacetylenes.

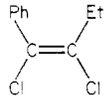
Ethylphenylacetylene. The gas chromatogram of the crude product mixture had the components shown in Table IX. After distillation (50 μm, 150 °C), the components were separated on a preparative GC column (column C, 200–250 °C, flow rate 100 mL/min).

Compound **10** has the following spectroscopic characteristics: NMR δ 1.23 (5, J = 7 Hz, 3 H), 2.73 (q, J = 7 Hz, 2 H), 7.30 (m, 5 H); mass spectrum, m/e (relative intensity) 205 (trace), 204 (8), 203 (5), 202 (45), 201 (8), 200 (73), 189 (trace), 187 (7), 185 (9), 168 (1), 167 (12), 166 (5), 165 (37), 152 (3), 151 (11), 150 (9), 149 (28), 129 (100), 115 (37), 77 (9). Anal. Calcd for $C_{10}H_{10}Cl_2$: C, 59.73; H, 5.01; Cl, 35.26. Found: C, 59.69; H, 5.45; Cl, 34.67. On the basis of the above data and comparison with those of compound **11**, compound **10** was assigned the following structure:



10

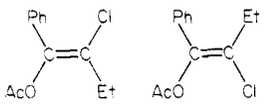
Compound **11** has the following spectroscopic characteristics: NMR 1.15 (t, J = 7 Hz, 3 H), 2.37 (q, J = 7 Hz, 2 H), 7.30 (s, 5 H); mass spectrum, similar to that of compound **10**. Anal. Calcd for $C_{10}H_{10}Cl_2$: C, 59.73; H, 5.01; Cl, 35.26. Found: C, 59.88; H, 4.76; Cl, 35.05. On the basis of the above data and comparison with those of compound **10**, compound **11** was assigned the following structure:



11

The assignment of the geometrical isomerism for these two dichlorides is again based on the GC retention times and the NMR data, similar to those given for the methylphenylacetylene case.

Compounds **12** and **13** were collected as one fraction. They



12 **13**

are shown to be the chloro enol acetates on the basis of the following observations. The NMR showed a singlet at δ 2.09 which was assigned to the methyl protons of the acetoxy function, a triplet at δ 1.17 (J = 7 Hz) which was assigned to the methyl group of the ethyl group, a quartet at δ 2.96 (J = 7 Hz) which was assigned to the methylene proton of the ethyl group (the peaks are quite broad, which could possibly arise from the poor resolution of the two isomeric compounds), and, finally, the aromatic protons at δ 7.30. The integration of the spectrum is consistent with such an assignment. The mass spectrum is also in agreement with the chloro enol acetates, in that the molecular peaks M^+ and $(M + 1)^+$ are present, and the base peak is attributed to the chloro ketone type ion which again is thought to arise from elimination of ketene from the molecular ions. The assignment of the absolute configuration of the two components in the GC mixture is based on the GC retention times of the components, since the most polar one, **13**, should have a longer retention time.

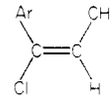
Table X[a]

component	column A retn time, min	column A % of pdts	column B retn time, min	column B % of pdts
14	7.1	11	3.2	12
15	14.3	36	6.9	38
16	24.1	38	10.3	38
17	46.0	9	18.4	8
18	62.6	6	21.2	4

[a] Conditions: column A, 150–200 °C, flow rate 60 mL/min; column B, 180–220 °C, flow rate 40 mL/min.

4-Methylphenylacetylene. Since the types of products obtainable from the chlorination of arylacetylenes have been established by the detailed studies of the three substrates presented above, the identities of the products of 4-methylphenylacetylene were inferred by analogy, with the aid of the gas chromatogram and the NMR spectrum of the product mixture.

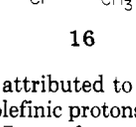
The gas chromatogram of the crude product mixture is listed in Table X. Compound **14** was assigned the structure ArC≡C-CH_3. Unfortunately, the aromatic region in the NMR is too complex to analyze in detail. However, the integration showed the correct excess of protons in this region (4:1) of the spectrum, which must be due to the presence of compound **14**. Compound **15** is assigned the structure shown. The following peaks in the



15

NMR are attributed to this compound: δ 2.33 (s, methyl group), 6.57 (s, olefinic protons).

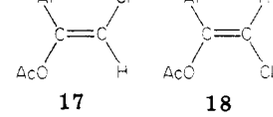
Compound **16** is assigned the structure shown. The following



16

peaks in the NMR are attributed to this compound: δ 2.33 (s, methyl group), 6.57 (s, olefinic protons). The two olefinic proton peaks at δ 6.40 and 6.57 are of equal intensity, showing equal amounts of dichloride, consistent with the GC data.

Compounds **17** and **18** are assigned as the isomeric chloro enol acetates. The following NMR peaks are attributed to these two



17 **18**

compounds: δ 2.00 and 2.10 (2 s, methyl groups on the acetoxy functions), 2.33 (s, methyl groups on the phenyl ring), 6.10 and

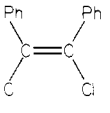
Table XI[a]

component	column D retn time, min	column D % of pdts	column A retn time, min	column A % of pdts
19	2.8	55	9.9	56
20	3.0	24	11.5	24
21	5.0	14	19.9	15
22	5.5	7	24.5	5

[a] Conditions: column D, 200–255 °C, flow rate 25 mL/min; column A, 200–275 °C, flow rate 25 mL/min.

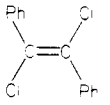
6.28 (2 s, olefinic protons). The peak at δ 6.1 is approximately twice as intense as the one at δ 6.28, showing an unequal distribution of the chloro enol acetates in favor of the trans isomer, which is consistent with the GC data.

Tolan. The gas chromatogram of the crude product mixture had the components shown in Table XI. The product mixture was partially dissolved in pentane, and the precipitate was filtered off. The precipitate was recrystallized from ethanol repeatedly until better than 98% purity was obtained as shown by analytical GC. The GC retention time of this purified compound is identical with that of compound **20**, and the following spectroscopic characteristics were observed: NMR δ 7.30 (br m); IR 6.25 μm (s); mass spectrum, *m/e* (relative intensity) 252 (4), 250 (23), 248 (37), 215 (7), 213 (19), 179 (15), 178 (100), 77 (12), 76 (24). Anal. Calcd for $C_{14}H_{10}Cl_2$: C, 67.49; H, 4.05; Cl, 28.46. Found: C, 67.33; H, 4.32; Cl, 28.99. On the basis of the above evidence and comparison with that obtained for compound **20** was assigned as the *cis*-dichloride, having the structure



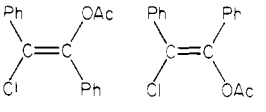
20

The component which was dissolved in pentane was recrystallized from pentane at very low temperature (−78 °C), and its GC retention time was identical with that of compound **19**. The following spectroscopic characteristics were observed: NMR δ 7.00 (s); IR 6.23 μm (w); mass spectrum, similar to that of compound **20**. Anal. Calcd for $C_{14}H_{10}Cl_2$: C, 67.49; H, 4.05; Cl, 28.46. Found: C, 67.23; H, 4.77; Cl, 27.86. On the basis of the above evidence and comparison with that obtained for compound **20**, compound **19** was assigned to be the *trans*-dichloride, having the structure



19

There are again interesting differences in the spectroscopic properties of these two isomeric dichlorides. The NMR peak of the trans isomer is a sharp singlet, while that of the cis isomer is a broad multiplet, showing nonequivalency of the aromatic protons in the cis case. This presumably arises from cis interaction between the adjacent phenyl rings in the cis isomer. As expected, the C=C stretching in the IR is weak for the *trans*-dichloride and strong for the cis compound. The residue from the recrystallization was analyzed by GC and NMR. The GC retention times of the components correspond to compounds **21** and **22**. In addition to the aromatic protons, the NMR contained two singlets of unequal intensities at δ 1.73 and 2.08, and these peaks were assigned to the methyl groups of the acetoxy functions in the chloro enol acetates. The mass spectrum of this mixture showed the molecular ions of the chloro enol acetates, and the base peak corresponds to the chloro ketone moiety. Therefore, on the basis of the evidence above, compounds **21** and **22** were assigned as the isomeric chloro enol acetates.



21 **22**

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Registry No. **1**, 1483-82-5; **2**, 58696-38-1; **3**, 58723-96-9; **4**, 532-27-4; **5**, 73496-66-9; **6**, 73496-67-0; **7**, 58696-47-2; **8**, 58696-54-1; **9**, 54034-56-9; **10**, 58696-39-2; **11**, 58696-40-5; **12**, 73496-68-1; **13**, 2749-93-1; **14**, 2749-93-1; **15**, 73496-69-2; **16**, 73496-70-5; **17**, 73496-71-6; **18**, 73496-72-7; **19**, 951-86-0; **20**, 5216-32-0; **21**, 73496-73-8; **22**, 73496-74-9; (*p*-methylphenyl)acetylene, 766-97-2; (*p*-fluorophenyl)acetylene, 766-98-3; phenylacetylene, 536-74-3; (*p*-chlorophenyl)acetylene, 873-73-4; (*p*-bromophenyl)acetylene, 766-96-1; (*m*-nitrophenyl)-acetylene, 3034-94-4; (*p*-nitrophenyl)acetylene, 937-31-5; (1-butynyl)benzene, 622-76-4; 1,2-diphenylethyne, 501-65-5; (*E*)-1-(*p*-methylphenyl)-1,2-dichloroethene, 73496-75-0; (*Z*)-1-(*p*-methylphenyl)-1,2-dichloroethene, 73496-76-1; (*p*-methylphenyl)chloroacetylene, 33491-04-2.