Synthesis and Solvolysis of *o*-, *m*-, and *p*-Ethynylbenzyl Chloride and Closely Related Structures. The Electronic Nature of the Acetylene Group[1]

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o-, *m*-, and *p*-ethynylbenzyl chloride and *m*- and *p*-ethynylbenzoic acid have been synthesized and used to determine substituent constants for the ethynyl group (σ_m, 0.205; σ_p, 0.233; $\sigma_m{}^+$, 0.330; $\sigma_p{}^+$, 0.179). Unlike any other group for which these constants have been determined, the acetylene function exhibits a resonance effect which is reflected in both the σ and σ^+ values but in opposite directions. This and other aspects of the electronic nature of the ethynyl group are discussed together with solvolysis data for the *cis* and *trans* isomers of 5-chloro-3-hexen-1-yne and the ethynyl substituted benzyl chlorides. Evidence is presented regarding the possibility of proximity effects of acetylene functions in solvolytic, displacement reactions.

In view of the frequency with which the acetylene function is encountered in studies of organic reactions, it would be of interest to have a more detailed understanding of the electronic nature of the group as reflected by carefully measured substituent constants. Brown[3] and Taft[4] have determined σ^* for the ethynyl and phenylethynyl group, respectively (Table I), and these values represent an electron-withdrawing effect considerably greater than that of either the ethylene or β-styryl group.[5]

TABLE I

SELECTED TAFT SUBSTITUENT CONSTANTS[a]

Substituent	σ^*	Substituent	σ^*
Cl_3C	2.65	$CH_2 = CH$	0.653[b]
CH_3CO	1.65	$C_6H_5CH{=}CH$	0.410
$HC{\equiv}C$	1.43[c]	$C_6H_5CH_2CH_2$	0.080
$C_6H_5C{\equiv}C$	1.35	CH_3CH_2	−0.100

[a] Unless otherwise indicated values are from ref 4. [b] See ref 12. [c] See ref 3.

The relative importance of the inductive effect is clearly apparent when one notes that the rate of solvolysis of propargyl bromide (*ca.* 50% aqueous dioxane at 60°) is less by a factor of 28.8 than that of allyl bromide under the same conditions. However, the substitution of ethynyl for the methane hydrogen of isopropyl chloride enhances the solvolysis rate (80% aqueous ethanol at 25°) by a factor of 100. Using the data of Hennion and Nelson,[8] and of Brown and Fletcher[9] for the solvolyses of 3-chloro-3-methyl-1-butyne and 2-chloro-2-methylbutane, respectively (80% ethanol at 25°), one can estimate the resonance acceleration effect of the ethynyl group by application of the Taft equation[10] with a σ^* value of 1.43 for ethynyl[3] and a ρ^* value of −3.29 for the solvolyses of tertiary alkyl halides under the specified conditions.[11] The calculated factor of 960 is 63 times *less* than the resonance accelerating effect calculated for the vinyl group from solvolysis data on 3-chloro-3-methyl-1-butene[8] and a σ^* value of 0.653 for the vinyl group.[12] These results are supported by the $\sigma_p{}^+$ values determined for the phenylethynyl and β-styryl groups[13] (see discussion).

Although determination of σ_m and σ_p for the phenylethynyl group[13] (Table VI) reveals that it can act as a resonance electron acceptor in the appropriately substituted benzoic acid systems, the role of the phenyl group in promoting this kind of behavior is not clearly defined. Recent estimates of σ_m and σ_p for the ethynyl group[14] do not resolve the problem in view of the questionable value of σ_m (see discussion).

The following study provides data from which reliable σ and σ^+ values can be calculated for the acetylene group and, in addition, yields evidence about the effect of a neighboring ethynyl group in a unimolecular solvolysis reaction.

Synthesis.—Both *m*- and *p*-ethynylbenzoic acids (**6**) and the corresponding benzyl chlorides **8** were conveniently prepared according to Scheme I. Intermediates in the synthetic sequence were identified from their infrared and nmr spectral characteristics (see Experimental Section).

The ethylene ketal of bromobenzaldehyde **1** was converted to phthalaldehydic acid **2** in *ca.* 90% yield by carbonation of the Grignard reagent prepared in tetrahydrofuran, followed by acidic hydrolysis of the reaction product. This method is superior to other preparations of either terephalaldehydic[15] or isophalaldehydic acid.[15,16] Condensation of isophalaldehydic acid with malonic acid in a solution of ethanol and pyridine and of terephalaldehydic acid with acetic anhydride and sodium acetate produced the corresponding cinnamic acids **3** in a yield of 67 and 52%, respectively.

Treatment of *para* isomer **3** with aqueous bromine afforded α,β-dibromo-*p*-carboxyhydrocinnamic acid, which resisted attempted dehydrohalogenation with 25% alcoholic potassium hydroxide, 20% methanolic sodium methoxide, and 25% aqueous potassium hydroxide, each at reflux for several hours. Similar results were encountered in the *meta* series, but the difficulty could be circumvented in both series by prior conversion of diacid **3** to the diethyl ester followed by

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[1] Taken from the Ph.D. dissertation of R. H. Rynbrandt, University of Kansas, 1965. Partial support of this work by a University of Kansas Research Grant and a grant from the Socony Mobil Co. is gratefully acknowledged.

[2] Phillips Petroleum Fellow, 1964, 1965. National Science Foundation Summer Fellow, 1964, 1965.

[3] T. L. Brown, *Chem. Rev.*, **58**, 595 (1958).

[4] R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 619.

[5] The work of Lucken[6] and Bykov[7] indicates higher intrinsic electronegativity for a hybridized carbon atom as the per cent *s* character increases.

[6] E. A. C. Lucken, *J. Chem. Soc.*, 2954 (1959).

[7] G. V. Bykov, "Electronic Charges of Bonds in Organic Compounds," The Macmillan Co., New York, N. Y., 1964, p 23.

[8] G. F. Hennion and K. W. Nelson, *J. Am. Chem. Soc.*, **79**, 2142 (1957).

[9] H. C. Brown and R. S. Fletcher, *ibid.*, **71**, 1845 (1949).

[10] R. W. Taft, Jr., in M. S. Newman's, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p 606.

[11] A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **78**, 4935 (1956).

[12] J. Hine and W. C. Bailey, *ibid.*, **81**, 2075 (1959).

[13] J. Kochi and G. Hammond, *ibid.*, **75**, 3452 (1953).

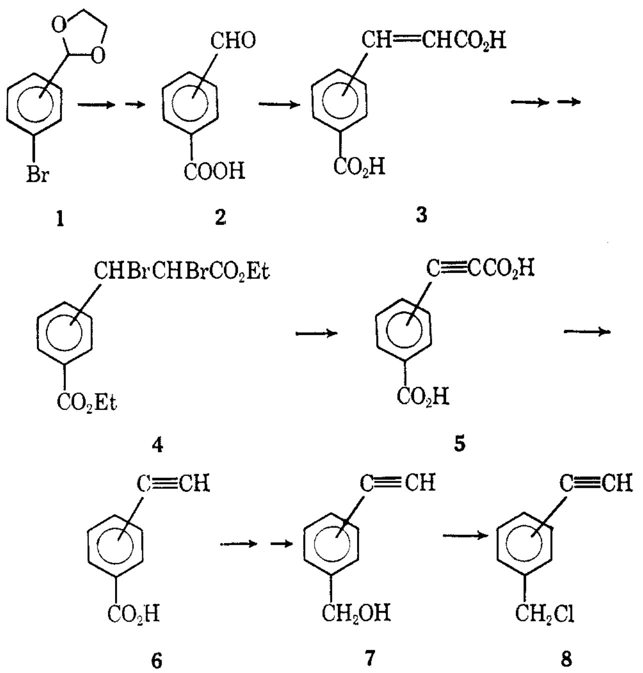
[14] M. Charton, *J. Org. Chem.*, **30**, 552 (1965).

[15] W. Davies and W. H. Perkins, *J. Chem. Soc.*, **121**, 2202 (1922).

[16] H. Simmons, *Chem. Ber.*, **45**, 1584 (1912).

treatment with bromine in chloroform. Dehydrohalogenation of the resulting dibromodihydrocinnamate **4** was effected in 70–80% yield by treatment with hot alcoholic potassium hydroxide. Decarboxylation of carboxypropiolic acid **5** was carried out with copper in quinoline at 90–110° and the *m*- and *p*-ethynylbenzoic acids (**6**) were purified as simple ester derivatives. The over-all acid yield in either series was *ca.* 10% based upon ketal **1**. The triply recrystallized *para* acid **6**, mp 218° dec, and *meta* acid, mp 170.5–171°, both of which gave a good analysis for $C_9H_6O_2$, were used for the potentiometric determination of the acid dissociation constants (*vide infra*).

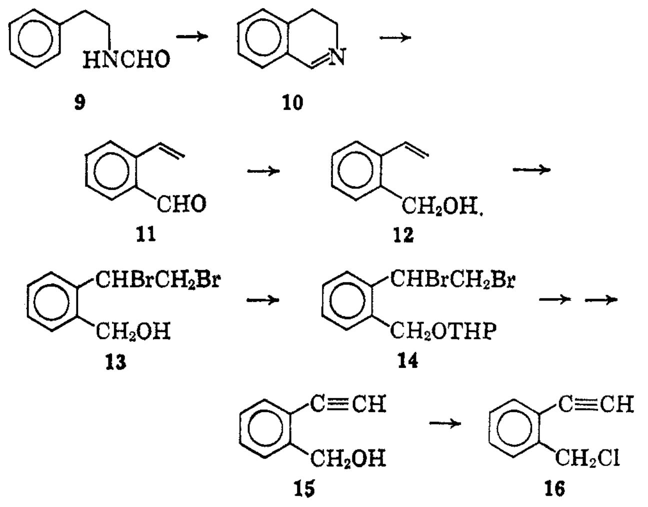
SCHEME I



m- and *p*-ethynylbenzyl chlorides (**8**) were prepared in an over-all yield of 50% by lithium aluminum hydride reduction of the methyl or ethyl ester of ethynyl acid **6**, followed by treatment of benzyl alcohol **7** with thionyl chloride at 70°. The pure chlorides **8** had infrared and nmr spectra consistent only with the indicated structures (see Experimental Section).

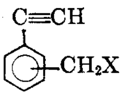
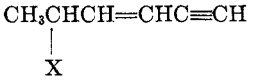
The preparation of *o*-ethynylbenzyl chloride (**16**) was accomplished according to the sequence in Scheme II.[17] *o*-Vinylbenzaldehyde (**11**) was prepared in a two-step sequence from N-phenethylformamide (**9**) according to the procedure described by Dale, Starr, and Strobel.[18] Reduction and bromination of aldehyde **11** gave an excellent yield of dibromide **13**, which was converted to the tetrahydropyranyl ether prior to dehydrohalogenation with methanolic sodium ethoxide in order to avoid intramolecular displacement of bromide or nucleophilic cyclization of *o*-ethynylbenzyl alcohol under strongly basic conditions. Removal of the tetrahydropyranyl group was accomplished by mild treatment with acidic methanol[19] and the resulting alcohol **15** was converted in 58% yield to *o*-ethynylbenzyl chloride (**16**) by treatment with thionyl chloride at 70°. The over-all yield of **16** from formamide **9** was *ca.* 10%.

SCHEME II



Nmr data (Table II) on several *o*-, *m*-, and *p*-ethynylbenzyl and *cis*- and *trans*-5-substituted 3-hexen-1-yne derivatives which were prepared in this study show a characteristic downfield shift of 0.23–0.50 ppm for the *ortho* proton (relative to the *meta* or *para* proton) or the *cis* allylic proton (relative to the *trans* allylic proton). A similar deshielding effect of 0.27–0.32 ppm was observed for the acetylenic proton of the *ortho* and *cis* isomers relative to the *meta*, *para*, or *trans* counterparts.

TABLE II
NMR CHEMICAL SHIFT DATA

	Orientation	X	δ H (τ) -CHX	δ H (τ) C≡CH
 C≡CH, CH₂X	*ortho*	OH	5.22	6.73
	meta	OH	5.59	7.02
	para	OH	5.58	7.05
	ortho	Cl	5.28	6.73
	meta	Cl	5.51	7.00
	para	Cl	5.52	7.01
 $CH_3\underset{X}{C}HCH{=}CHC{\equiv}CH$	*cis*	OH	5.10	6.74
	trans	OH	5.59	7.03
	cis	Cl	4.85	6.73
	trans	Cl	5.35	7.05

Substituent Constants.—Hammett *meta* and *para* substituent constants for the ethynyl group were obtained by potentiometric determination of the dissociation constants for pure samples of *meta* and *para* acids **6** in 50 vol % aqueous ethanol at 25° (Table III). Conditions and procedures were so chosen as to enable

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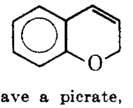
[17] An attempt to prepare chloride **16** by a route similar to that in Scheme I produced a mixture after bromination and attempted dehydrohalogenation of ethyl *o*-carbethoxycinnamate. The crude reaction product showed infrared absorptions at 1600, 1720, and 1770 cm⁻¹, but no absorption characteristic of the ethynyl group.

[18] W. J. Dale, L. Starr, and C. W. Strobel, *J. Org. Chem.*, **26**, 2226 (1961).

[19] Excess *p*-toluenesulfonic acid must be carefully neutralized with sodium bicarbonate prior to the isolation of **15**. Addition of potassium hydroxide pellets followed by distillation produced a material which showed, among others, a strong infrared absorption at 1660 cm⁻¹ but no absorption characteristic of the acetylene or hydroxyl function. Upon standing, the compound polymerized. It gave a picrate, mp 83–84.5°, which allowed a tentative identification as isochromen (lit.[20] mp 85°).



[20] J. N. Chatterjea, *Chem. Ber.*, **91**, 2637 (1958).

Table III

Apparent pK Values for Substituted Benzoic Acids in 50 Vol % Aqueous Ethanol at 25.0 ± 0.1°

Substituent	Orientation	pK_a'[a]
H	...	5.750[b]
C≡CH	*meta*	5.450[c]
C≡CH	*para*	5.410[c]

[a] Precision ±0.005. [b] Adjusted to agree with the data of ref 21 and 22. [c] Represents the average of two determinations.

careful correlation of our data with those of Roberts, *et al.*[21,22] (Experimental Section). The substituent constants were calculated directly from the simple Hammett expression for which $\rho = 1.464 \pm 0.025$ for substituted benzoic acids at the specified equilibrium conditions.[22] Values obtained by this method are listed in Table IV together with values estimated by Charton from extrathermodynamic relationships.[14,23] Both our value for σ_p, +0.233 ± 0.006, and that of Charton, +0.270 ± 0.04, are within experimental error of being identical.[24] The value determined by Charton was obtained from a free energy correlation of the dissociation constants for a series of β-substituted acrylic acids for which $\rho = 2.230 \pm 0.117$.[25] The σ_m value, +0.205 ± 0.006, differs from that of Charton, +0.32, by a substantial amount.[27]

Table IV

Substituent Constants for the Ethynyl Group

Constant	Value	Ref
σ^* (Taft)	1.43	*a*
σ_m	0.205 ± 0.006	*b*
	0.32[c]	*d*
σ_p	0.233 ± 0.006	*b*
	0.270 ± 0.04[e]	*d,f*
σ_m^+	0.330 ± 0.014	*b*
σ_p^+	0.179 ± 0.010	*b*

[a] See ref 3. [b] This work. [c] See ref 27. [d] See ref 14. [e] The error was calculated from data in ref 23 and 26. [f] Referral is made to data in ref 23 from which $\sigma_p = 0.288 \pm 0.04$ can be calculated although the value reported in ref 14 is 0.281. See ref 24.

The electrophilic substitutent constants[28] for the ethynyl group were determined by first establishing an extrathermodynamic relationship between log k/k_0 for Oliver's data[29] on the solvolysis of substituted benzyl chlorides in 50 vol % aqueous ethanol at 83° *vs.* σ^+ as shown in Figure 1. Simple linear regression analysis gave $\rho = -1.748 \pm 0.068$. Data for the solvolysis of *m*- and *p*-ethynylbenzyl chloride under the same conditions (Table V) led to the electrophilic substituent constants given in Table IV.

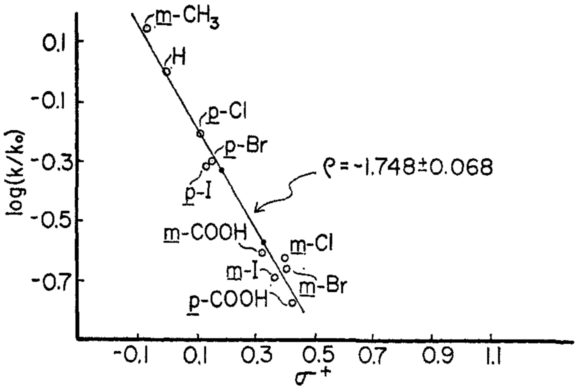


Figure 1.—Hammett-type plot for solvolysis of substituted benzyl chlorides in 50 vol % aqueous ethanol at 83.0°. Shaded circles represent data from Table V for the *p*- and *m*-ethynylbenzyl chlorides.

Table V

Relative and Absolute Solvolysis Rates in 50 Vol % Aqueous Ethanol

Compd	Temp, °C[a]	k, sec^{-1} [b]	k_{rel}
3-Chloro-1-butene	30	2.81×10^{-5} [c]	1.00
5-Chloro-*cis*-3-hexen-1-yne	24	7.126×10^{-6}	
5-Chloro-*cis*-3-hexen-1-yne	30	1.691×10^{-5} [d]	0.602
5-Chloro-*cis*-3-hexen-1-yne	40	6.583×10^{-5}	
5-Chloro-*trans*-3-hexen-1-yne	20	2.774×10^{-5}	
5-Chloro-*trans*-3-hexen-1-yne	30	1.048×10^{-4}	3.73
5-Chloro-*trans*-3-hexen-1-yne	40	3.651×10^{-4}	
Benzyl chloride	63	4.067×10^{-5}	1.00
Benzyl chloride	83	2.235×10^{-4}	
o-Ethynylbenzyl chloride	63	1.574×10^{-5} [d]	0.387
o-Ethynylbenzyl chloride	83	8.991×10^{-5}	
m-Ethynylbenzyl chloride	63	9.727×10^{-6}	0.239
m-Ethynylbenzyl chloride	83	5.917×10^{-5}	
p-Ethynylbenzyl chloride	63	1.910×10^{-5}	0.470
p-Ethynylbenzyl chloride	83	1.087×10^{-4}	

[a] Variation in the temperature was ≤±0.05°. [b] All rate constants were determined by the method of least squares and have a least-squares probable error of ≤±1%. Each value represents the average of two runs with an average deviation of ≤±1% except where indicated. [c] C. A. Vernon, *J. Chem. Soc.*, 423 (1954). [d] Average deviation for two runs is ±1.3%.

Comparison of substituent constants for various groups constitutes a widely used method for the study of resonance and polar effects. From the selected constants shown in Table VI it is apparent that the ethynyl group exhibits unique behavior markedly dependent on the nature of the system to which it is attached. The *meta* substituent constant, 0.205, indicates a moderate electron-withdrawing effect, less than that of the halo-

Table VI

Selected Substituent Constant Data[a]

Substituent	σ_m	σ_p	$\sigma_p - \sigma_m$[b]	σ_m^+	σ_p^+	$\sigma_p^+ - \sigma_m^+$[b]
OCH_3	0.115	−0.268	−0.38	0.047	−0.778	−0.73
I	0.352	0.18	−0.17	0.359	0.135	−0.22
Br	0.391	0.232	−0.16	0.405	0.150	−0.26
Cl	0.373	0.227	−0.15	0.399	0.114	−0.28
$C_6H_5CH{=}CH$[c]	0.030	−0.070	−0.10	...	−1.0	...
C_6H_5	0.06	−0.01	−0.07[d]	0.109	−0.179	−0.29
$C_6H_5C{\equiv}C$[c]	0.140	0.165	0.03[e]	...	−0.03	...
$HC{\equiv}C$[f]	0.205	0.233	0.03[g]	0.334	0.179	−0.16[e]
NO_2	0.710	0.778	0.07	0.674	0.790	0.12
CO_2Et	0.37	0.45	0.08	0.366	0.482	0.12

[a] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 173, 204. [b] Estimated error ±0.03 except where indicated. [c] See ref 13. [d] Error ±0.07. [e] Error ±0.01. [f] This work. [g] Error ±0.007.

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(21) J. D. Roberts and W. T. Moreland, Jr., *J. Am. Chem. Soc.*, **75**, 2167 (1953).

(22) J. D. Roberts, E. A. McElhill, and R. Armstrong, *ibid.*, **71**, 2923 (1949).

(23) M. Charton and H. Meislich, *ibid.*, **80**, 5940 (1958).

(24) The value of +0.270 quoted in ref 14 differs slightly from that in the original article[23] from which it was taken, +0.281, and is not in exact agreement with the value that the present authors calculate from the data of ref 23, +0.288.

(25) A value of 3.75 ± 0.05 was used for the pK_a of the β-ethynyl acid.[26]

(26) G. H. Mansfield and M. C. Whiting, *J. Chem. Soc.*, 4761 (1956).

(27) Professor Charton has indicated to me that his value for σ_m unlike that for σ_p was calculated from the equation $\sigma_m = (2\sigma_I + \sigma_p)/3$ in which the value for σ_I and σ_p were taken as 0.35 and 0.270, respectively. Since Charton's value for σ_p is in substantial agreement with our value we can only assume that either the estimate of σ_I is in error or the above equation is not so generally useful as has been previously supposed.

(28) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

(29) S. C. J. Oliver, *Rec. Trav. Chim.*, **49**, 697 (1930).

gen, nitro, or carbethoxy group but significantly greater than that of the styryl, phenyl, or methoxy group. This same trend is reflected in the *meta* electrophilic substituent constants (σ_m^+) even though the relative values are somewhat different.

If one assumes that inductive effects are transmitted to the reaction center almost as effectively from the *para* as from the *meta* position,[30] the values for $\sigma_p - \sigma_m$ and $\sigma_p^+ - \sigma_m^+$ can be used as a crude measure of direct resonance effects.[32] Although the value of 0.03 for $\sigma_p - \sigma_m$ for the ethnyl group reflects a distinct resonance electron-withdrawing effect, that of -0.16 for $\sigma_p^+ - \sigma_m^+$ clearly indicates the presence of a substantial resonance electron-donating effect. *No other group for which these requisite substituent constants have been measured exhibits this behavior.* Replacement of the acetylenic proton with phenyl decreases the value for both σ_m and σ_p but the difference, 0.03, remains the same as that for ethynyl possibly owing to a fortuitous cancellation of several factors.[34] This small resonance electron-withdrawing effect is less than one-half that of the nitro or carbethoxy group. Particularly interesting is the -0.10 value of $\sigma_p - \sigma_m$ for the styryl group, indicative of a resonance releasing effect in the same direction as that of the halogens and of a similar order of magnitude. When the ethynyl group is directly conjugated with an electron deficient center as it is in the transition state for solvolysis of *p*-ethynylbenzyl chloride, resonance electron donation occurs to give a negative value to $\sigma_p^+ - \sigma_m^+$, the magnitude of which is about one-fifth that for the methoxy group but similar to that of the halogens. The unusally large difference (0.13) between σ_m^+ and σ_m for the ethynyl group is noteworthy in view of the general similarity of these values for groups other than those which possess a substantial resonance interaction with the aromatic ring.[35]

Kinetic Results.—In an effort to gain further information about electronic and/or proximity effects of the ethynyl group in unimolecular solvolytic displacement reactions, kinetic measurements were made on the 5-chloro-3-hexen-1-yne system **18**. The results

$$\underset{\mathbf{17}}{CH_2{=}CHCHClCH_3} \qquad \underset{\mathbf{18}}{HC{\equiv}CCH{=}CHCHClCH_3}$$

are included in Table V. A comparison of the rate of solvolysis for *cis*-**18** with that for *trans*-**18** should reflect only those effects dependent on the spatial distance and/or relative orientation of the acetylene group to the reaction site. In support of this suggestion is the observaion that "normal"[36] electrical effects of *ortho* substituents are proportional to those of *para* substituents.[37] In addition, extrathermodynamic relationships applied to *cis*- and *trans*-vinylene sets has allowed differences in the ρ values to be correlated with field effects.[38]

A comparison of the solvolysis rates for 3-chloro-1-butene (**17**) and 5-chloro-*trans*-3-hexen-1-yne (**18**) indicates a rate increase of *ca.* 4 upon introduction of the ethynyl group into α-methylallyl system **17**. This result is in sharp contrast with the rate retardation effect of introducing the ethynyl group at any ring position on benzyl chloride (Table V). The relative rates for solvolysis of *ortho* isomer **16** and *para*-**8**, 0.387 and 0.470 relative to benzyl chloride at 63°, clearly indicate the predominance of the inductive effect reflected in the positive substituent constants previously discussed. Since resonance effects are not transmitted as well by aromatic as by olefinic systems,[39,40] the apparent preponderance of a resonance stabilizing effect in the transition state for solvolysis of *trans*-**18** can be reasonably explained. These results are further reflected in the activation parameters (Table VII). The more positive entropy of activation for *trans* chloride **18** relative to 3-chloro-1-butene is undoubtedly associated with an increase in positive charge delocalization in the transition state for solvolysis.[41] The kinetic results are similar to those encountered during the solvolysis of *trans*-1,3-dichloropropene[42] in which the chlorine behaves like the ethynyl group of **18** as one might expect from the relative similarity of the electrophilic substituent constants (Table VI).

TABLE VII

SUMMARY OF ACTIVATION PARAMETERS[a]

Compd	ΔH^*, kcal/mole[b]	ΔS^*, eu[b]
3-Chloro-1-butene	20.4[c]	−12.2[c]
5-Chloro-*cis*-3-hexen-1-yne	25.1	2.5
5-Chloro-*trans*-3-hexen-1-yne	22.9	− 1.2
Benzyl chloride	19.6	−20.6
o-Ethynylbenzyl chloride	20.0	−21.1
m-Ethynylbenzyl chloride	20.8	−19.9
p-Ethynylbenzyl chloride	20.0	−20.9

[a] Values were determined from rate data at three temperatures for the aliphatic compounds and at two temperatures for the aromatic compounds. [b] The average deviation for ΔH^* and ΔS^* is ±0.2 kcal/mole and ±0.5 eu, respectively. [c] Calculated from the data of ref 42.

If the ethynyl group of **18** is in the *cis* orientation, the solvolysis rate is slower by a factor of 6.2 than if it is in the *trans* orientation, and slower than unsubstituted chloride **17** by 1.66. Clearly there is no obvious rate enhancement by neighboring group participation of the *cis* acetylene function. Instead one must rationalize a net rate decrease. The observed relative rates are in accord with data for the solvolyses of isomeric 1,3-dichloropropenes[42,43] and 1-chloro-2-butenes[44] for which the *trans* isomers react 2–6 times faster than the corresponding *cis* isomers.

Bank[45] has ascribed the slower solvolysis rate for 1-chloro-*cis*-2-butene (relative to the *trans* isomer) to

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(30) Hine[31] has calculated that inductive effects should be 1.074 times as large in the *meta* as in the *para* position.

(31) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, Book Co., Inc., New York, N. Y., 1962, p. 92.

(32) It is recognized that values for $\sigma_m - \sigma_I$ clearly imply the existence of resonance interactions between *meta* substituents and the aromatic ring.[33]

(33) R. W. Taft, Jr., N. C. Deno, and P. S. Skell, *Ann. Rev. Phys. Chem.*, **9**, 287 (1958).

(34) Because of the errors in the values of $\sigma_p - \sigma_m$ for ethynyl and β-phenylethynyl, a difference as great as ±0.06 may be present.

(35) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p 206.

(36) Excluding field effects.

(37) M. Charton, *J. Am. Chem. Soc.*, **86**, 2033 (1964).

(38) M. Charton, *J. Org. Chem.*, **30**, 974 (1965).

(39) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(40) M. Charton, *J. Org. Chem.*, **26**, 735 (1961).

(41) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, pp 132–142.

(42) C. A. Vernon, *J. Chem. Soc.*, 423 (1954).

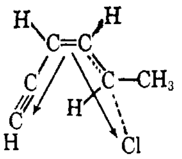
(43) S. Oae and C. A. VanderWerf, *J. Am. Chem. Soc.*, **75**, 2724 (1953).

(44) C. Prevost and C. Georgoulis, *Compt. Rend.*, **248**, 3450 (1959).

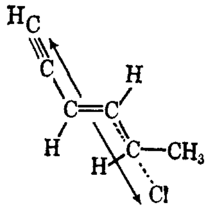
(45) S. Bank, *J. Am. Chem. Soc.*, **87**, 3245 (1965).

repulsive electrostatic forces between the dipole of the methyl–carbon bond and the electron deficiency on the terminal methylene position of the *cis* allylic cation. However, application of this reasoning to *cis*- and *trans*-1,3-dichloropropene or *cis*- and *trans*-**18** suggests that attactive forces between the dipole of the ethynyl–carbon bond or the chloromethyl–carbon bond and the cationic methylene group should stabilize the solvolysis transition states for the *cis* isomers in contradiction to the observed reactivity order. Prevost and Georgoulis[44] have attempted to explain the lower reactivity for silver ion assisted solvolysis of 1-chloro-*cis*-2-butene (relative to the *trans* isomers) by considering the existence of a weak bonding interaction between the methyl hydrogens and the chlorine atom, which makes the latter less susceptible to attack by the silver ion.

The slower solvolysis rate of *cis*-**18** compared with *trans*-**18** can be explained, at least in part, by a consideration of field effects in the transition state. Careful examination of the expected dipoles in the assumed transition states, **19** and **20**, for solvolysis of the two isomers suggests the presence of a repulsive dipole-dipole interaction which should destabilize *cis* transition state **19** relative to **20**.[46] Similar arguments have been used to explain certain conformational equilibria.[47] Although the ethynyl group in the *cis* orientation may interfere with normal solvation at the site of positive charge development in the transition state, these activation parameters suggest that this may not be an important factor. The data from Table VII indicate that the faster solvolysis rate of the *trans* compared to the *cis* isomer is primarily the result of a smaller (2.2 kcal/mole) enthalpy of activation. Although the more positive entropy of activation of the *cis* compound (relative to the *trans*) may be ascribed to steric interference to solvation in the transition state, the difference ($\Delta\Delta S^* = 3.7$ eu) is small and might be equally well explained by a reduced demand for external solvation because of charge stabilization from intramolecular interaction by the π electrons of the ethynyl group in the *cis* transition state. By analogy, the more positive entropy of activation for the solvolysis of *o*-nitrobenzyl chloride relative to the *para* isomer has been attributed to "intramolecular solvation" by the nitro group.[48]



19



20

The products of solvolysis of the 5-chloro-3-hexen-1-yne system are summarized in Table VIII. All were identified by comparison with authentic samples (see Experimental Section). As expected the reaction proceeded with high retention of geometrical configuration.[49] Although *trans* chloride **18** solvolyzed to a mixture of the corresponding *trans* alcohol (67%) and the *trans* ether (33%), *cis* chloride **18** produced a small amount (8.1%) of the isomeric *trans* products. Because the products appear to be stable to the reaction conditions (see Experimental Section) and isomerization of *cis* chloride **18** is unlikely in view of its stability when shaken with concentrated hydrochloric acid at 30°, the small observed loss of configuration probably occurs in the intermediate carbonium ion.

TABLE VIII

SOLVOLYSIS PRODUCTS OF 5-CHLORO-3-HEXEN-1-YNE IN 50% (VOL) ETHANOL–WATER

Chloride composition	Product composition
97% *trans*, 3% *cis*	*trans* 97%,[a] *cis* 3%[a]
10% *trans*, 90% *cis*	*trans* 17.3%, *cis* 82.7%

[a] 67% 3-hexen-5-yn-2-ol and 33% 5-ethoxy-3-hexen-1-yne.

Because solvolysis of 5-chloro-3-hexen-1-yne (**18**) provided no definite evidence for the existence of a rate accelerating proximity effect by the *cis* ethynyl group, it would be of interest to compare this result with that from the structurally related *o*-ethynylbenzyl chloride system. The k_o/k_p ratio has been extensively used as a qualitative measure of the "*ortho* effect."[50] From the rate ratios listed in Table IX for the solvolyses of substituted benzyl chlorides in 50 vol % aqueous ethanol at 83°, one notes that only the value for nitro is greater than one. Evidence has been presented which suggests that the *o*-nitro substituent participates as an internal nucleophile in promoting the dissociation of *o*-nitroiodobenzene dichloride,[50b] and in the solvolysis of *o*-nitobenzhydryl bromide.[50c] Methyl, chlorine, bromine, and iodine have values for k_o/k_p which cover a small range, 0.46–0.60, in spite of the differences in size, polarizability, inductive, and resonance characteristics. The k_o/k_p value of 0.83 for the acetylene function infers that it may either be participating in the stabilization of positive charge development in the transition state, but to a lesser extent than nitro, or that factors[51] which cause the methyl and halogen groups to have a lower reactivity in the *ortho* orientation (compared with *para*) are not so severe for the

TABLE IX

ortho–para RATE RATIOS FOR SOLVOLYSES OF BENZYL CHLORIDES IN 50 VOL % AQUEOUS ETHANOL AT 83°

Substituent	k_o/k_p	Ref
CH_3	0.46	*a*
Cl	0.57	*a*
Br	0.57	*a*
I	0.60	*a*
HC≡C	0.83	*b*
NO_2	1.13	*a*

[a] See ref 29. [b] This work.

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(46) We feel that the highly stretched carbon–chlorine bond in the transition state for solvolysis of **18** should establish a strongly directed dipole moment which could interact with the ethynyl–carbon bond moment. The assumption that the transition state has essentially the structure of a solvated carbonium ion intermediate would not necessarily lead to a similar result, since the chloride ion no longer has a specific orientation (see S. Bank[45]).

(47) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, p 461.

(48) J. B. Hyne and R. Willis, *J. Am. Chem. Soc.*, **85**, 3650 (1963).

(49) W. G. Young, S. H. Sharman, and S. Winstein, *ibid.*, **82**, 1376 (1960).

(50) (a) T. W. Taft in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp 648–652; (b) E. A. Jeffery, L. J. Andrews, and R. M. Keefer, *J. Org. Chem.*, **30**, 617 (1965); (c) E. A. Jeffery, R. K. Bausel, L. J. Andrews, and R. M. Keefer, *ibid.*, **29**, 3365 (1964); (d) A. Singh, L. A. Andrews, and R. M. Keefer, *J. Am. Chem. Soc.*, **84**, 1179 (1962).

(51) One possible factor is the interference of the *ortho* substituent to solvation of the reaction center in the transition state.

ethynyl group. The present results do not allow a distinction to be made between these possibilities.

Experimental Section[52]

***p*-Bromobenzaldehyde Ethylene Acetal** (**1**).—*p*-Bromobenzaldehyde (40 g, 0.22 mole), which had been prepared in 60% yield by the oxidation of *p*-bromotoluene (Eastman, practical) with chromium trioxide[53] (mp 55–57°; lit.[53] mp 55–57°), was dissoved in 0.5 l. of anhydrous benzene together with ethylene glycol (13.6 g, 0.22 mole; redistilled bp 195–197°) and *p*-toluenesulfonic acid (0.5 g). Water was removed with a Dean–Stark trap as the solution refluxed (10 hr). After the benzene was removed on a rotary evaporator, the crude acetal (50 g) was isolated by vacuum distillation, bp 90–97° (0.3 mm). Excess ethylene glycol was removed by distillation first from calcium hydride (5 g) and then from lithium aluminum hydride (0.5 g) to give 43 g (0.19 mole, 85% yield) of the pure acetal, bp 94–96° (0.3 mm). The material showed no carbonyl absorption in the infrared spectrum and gave an nmr spectrum which consisted of a multiplet at 2.57 (area 4), a singlet at 4.27 (area 1), and a singlet at 6.08 (area 4)

Terephthalaldehydic Acid (**2**).—*p*-Bromobenzaldehyde ethylene acetal (43 g, 0.19 mole) in 200 ml of dry tetrahydrofuran (distilled from lithium aluminum hydride) was added (*ca.* 2 hr) to a suspension of magnesium turnings (7.7 g, 0.187 mole; dried at 80° for 24 hr) in 25 ml of dry tetrahydrofuran (nitrogen atmosphere) so as to maintain the temperature at 25–30°. The mixture was stirred for one additional hour at 25° and poured onto *ca.* 200 g of crushed dry ice. Tetrahydrofuran was removed on a rotary evaporator and the residue was dissolved in hot water (500 ml), boiled 10 min with Norit-A (5 g), filtered, cooled, and acidified with 10% sulfuric acid. The acid product (25 g, 0.17 mole, 89% yield) was dried at 80° for 24 hr and recrystallized from 95% ethanol, mp 245–248° (lit.[15] mp 248–250°).

***p*-Carboxycinnamic Acid** (**3**).—The procedure of Low[54] was modified in the following manner. Terephthalaldehydic acid (15.0 g, 0.10 mole), anhydrous sodium acetate (15.0 g, 0.18 mole), and acetic anhydride (23.0 g, 0.23 mole) were thoroughly mixed and heated at 150–160° for 10 hr. The solid mass was then digested with 200 ml of water. The solid was filtered, dissolved in 200 ml of 10% sodium hydroxide solution, and acidified with 20% hydrochloric acid to yield *p*-carboxycinnamic acid as a white paste which was dried at 80° for 48 hr. The white granular solid product (10 g, 0.052 mole) was obtained in 52% of the theoretical amount and had mp 360° dec (lit.[54] mp 358° dec).

The nmr spectrum (dimethyl sulfoxide) showed doublets at 1.98 (area 2), 2.27 (area 2), 2.33 (area 1), and 3.41 (area 1).

α,β-Dibromo-*p*-carboxyhydrocinnamic Acid.—Finely powdered *p*-carboxycinnamic acid (1.9 g, 0.01 mole), water (4 ml), and bromine (1.9 g, 0.012 mole) in a sealed tube (1.5 × 25 cm) were heated in a boiling-water bath for 4 hr during which they were periodically shaken. The contents of the tube were digested with water (100 ml), cooled, and filtered to give the dibromide which was dried at 80° for 48 hr, mp >360° (lit.[54] mp >360°). The yield was 2.5 g (0.0072 mole) or 72%.

Attempted Dehydrohalogenation of α,β-Dibromo-*p*-carboxyhydrocinnamic Acid.—When the dibromo acid (2.0 g, 0.0057 mole) was treated with either 25% alcoholic potassium hydroxide (100 ml) or 20% sodium methoxide in methanol (100 ml) for several hours at reflux, only insoluble starting material was recovered. Similar results were obtained by using 25% aqueous potassium hydroxide at reflux for 4 hr.

Ethyl *p*-Carbethoxycinnamate.—*p*-Carboxycinnamic acid (17.0 g, 0.088 mole) was stirred with thionyl chloride (200 ml) at reflux for *ca.* 24 hr until solution was complete. Excess thionyl chloride was removed by distillation and absolute ethanol (200 ml) was slowly added to the cooled residue. After the solution was at reflux several hours, the excess ethanol was removed by distillation and a solidified sample (1 g) of the residue was recrystallized from 95% ethanol, mp 50–51° (lit.[55] mp 52°). The infrared and nmr spectra were consistent with the structural assignment. The over-all yield appeared to be nearly quantitative.

Ethyl α,β-Dibromo-*p*-carbethoxyhydrocinnamate (**4**).—The crude ethyl *p*-carbethoxycinnamate dissolved in chloroform (300 ml) was maintained at reflux while bromine (16.0 g, 0.10 mole) was slowly (10 hr) added. Excess bromine and solvent were removed at reduced pressure (30 mm) to give a reddish brown, viscous residue which showed no unsaturation in the infrared spectrum. The nmr spectrum showed doublets at 1.87 (area 2), 2.44 (area 2), 4.58 (area 1), and 5.18 (area 1); quartets at 5.59 and 5.62 (combined area 4); and triplets at 8.61 and 8.64 (combined area 6).

***p*-Carboxyphenylpropiolic Acid** (**5**).—After slow addition of a 25% solution of alcoholic potassium hydroxide (125 ml) to the dibromide from the previous experiment, the solution was maintained at reflux and stirred for 24 hr, after which the ethanol was removed at reduced pressure (*ca.* 30 mm). The solid residue was dissolved in water, heated to boiling with Norit-A (10 g), filtered through Filter-Cel, cooled (<10°), and acidified slowly with cold 20% sulfuric acid. The crude *p*-carboxyphenylpropiolic acid was stirred vigorously with cold water (250 ml) to dissolve inorganic impurities, filtered, and dried at 80° for 48 hr to give 13.1 g (0.068 mole, 77% yield) of product, mp > 360°.

The nmr spectrum (dimethyl sulfoxide) consisted of doublets at 2.00 and 2.34 (relative area 1:1).

Ethyl *p*-Carbethoxyphenylpropiolate.—The compound was prepared by the same procedure used for the preparation of ethyl *p*-carbethoxycinnamate. The infrared spectrum showed strong, sharp absorptions at 2265 and 2216 cm^{-1} characteristic of disubstituted acetylenes.[56] The nmr spectrum was in accord with the structure.

Decarboxylation of *p*-Carboxyphenylpropiolic Acid (**5**) **with Copper and Quinoline**.—Finely pulverized *p*-carboxyphenylpropiolic acid (13.0 g, 0.068 mole), quinoline (65 ml) (Eastman redistilled, bp 236–238°), and copper powder (2.5 g) were stirred and heated (nitrogen atmosphere) slowly (1 hr) to 90°, maintained at this temperature for 1 hr, cooled, and poured into a stirred mixture of crushed ice (250 g) and concentrated hydrochloric acid (65 ml). Crude *p*-ethynylbenzoic acid (10 g, 0.068 mole) was dried at 80° for 24 hr. Characterization was carried out on the purified ethyl ester.

Ethyl *p*-Ethynylbenzoate.—Crude *p*-ethynylbenzoic acid (10 g, 0.068 mole) was converted to its ethyl ester in the usual manner with thionyl chloride and ethanol. The product in ether (200 ml) was filtered, washed twice with 5% sodium carbonate solution (50 ml) and water (50 ml), dried over magnesium sulfate, and isolated by vacuum distillation, bp 77° (0.4 mm), after removal of the ether. The yield of 4.7 g (0.027 mole) corresponds to 31% of the theortical amount based on *p*-carboxycinnamic acid.

The infrared spectrum showed prominent absorptions at 2120 and 3310 cm^{-1}.[56] The nmr spectrum consisted of doublets at 1.92 and 2.41 (combined area 4), a quartet at 5.60 (area 2), a singlet at 6.60 (area 1), and a triplet at 8.65 (area 3).

***p*-Ethynylbenzoic Acid** (**6**).—Ethyl *p*-ethynylbenzoate (0.4 g, 0.0023 mole) in methanol (10 ml) was hydrolyzed with 25% aqueous potassium hydroxide (3.0 ml) over a period of 24 hr at 25°. The product, isolated by removal of the methanol on a rotary evaporator followed by addition of dilute hydrochloric acid to the residue, was recrystallized twice from hot water to afford pure *p*-ethynylbenzoic acid (0.28 g, 0.0019 mole), mp 218° dec.

Anal. Calcd for $C_9H_6O_2$: C, 73.96; H, 4.14. Found: C, 74.06; H, 4.20.

***p*-Ethynylbenzyl Alcohol** (**7**).—Ethyl *p*-ethynylbenzoate (3.0 g, 0.0172 mole) in tetrahydrofuran (25 ml) was slowly added to lithium aluminum hydride (0.54 g, 0.019 mole) in tetrahydrofuran

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[52] Elemental analyses were performed by the Huffman Laboratories, Inc., Wheatridge, Colo. Melting points were obtained on a Thomas–Hoover capillary melting point apparatus and were corrected. Boiling points are uncorrected. All nmr spectra were measured in carbon tetrachloride, unless otherwise specified, with a Varian A-60 spectrometer. Chemical shifts are expressed in parts per million relative to an internal tetramethylsilane standard, which is given an arbitrary position of 10 (τ scale). All infrared spectra were obtained in chloroform with either a Perkin-Elmer infracord or a Beckman Model IR-8 double-beam recording spectrometer with sodium chloride optics; a 1610- or 2920-cm^{-1} absorption (polystyrene *vs.* air) was used as a standard. The vapor phase chromatographic separations were performed on a 10-ft Carbowax 20-M column attached to a F & M Model 700 instrument with a thermal conductivity detector.

[53] S. V. Lieberman and R. Connor, in "Organic Syntheses," A. H. Blatt, Coll. Vol. II, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, p 441.

[54] W. Low, *Ann.*, **231**, 361 (1885).

[55] A. F. Titley, *J. Chem. Soc.*, 2581 (1928).

[56] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p 57–62.

(120 ml) at −20°. The reaction mixture was allowed to warm to 25° and then heated at 50° for 1 hr. After the addition of water (6 ml), the tetrahydrofuran was removed by vacuum distillation and the residue was dissolved in water (100 ml) and acidified with dilute sulfuric acid to pH 5–6. The product was isolated in the usual manner by extraction of the aqueous solution with ether. The crude alcohol (2.0 g, 0.0151 mole, 88% yield) was purified by distillation, bp 64–66° (0.2 mm) (white solid).

The infrared spectrum showed significant absorptions at 2120, 3310, and 3690–3160 cm^{-1}. The nmr spectrum consisted of a multiplet at 2.50–3.00 (area 4) and singlets at 5.58 (area 2), 6.33 (area 1), and 7.05 (area 1).

***p*-Ethynylbenzyl Chloride** (**8**).—Cold (ice bath) *p*-ethynylbenzyl alcohol (**7**) (2.0 g, 0.0151 mole) was cautiously treated with thionyl chloride (1.8 g, 0.0151 mole) and the reaction mixture was then heated to 70° for 1 hr. Distillation, bp 60–61° (1.1 mm), gave 1.2 g (0.0080 mole, 53% yield) of chloride **8** which was shown to be >99% pure by vpc analysis (Carbowax 20-M) at 150°.

The infrared spectrum showed, among others, absorptions at 2120 and 3310 cm^{-1}. The nmr spectrum consisted of a multiplet at 2.46–2.82 (area 4) and singlets at 5.52 (area 2) and 7.01 (area 1).

***m*-Bromobenzaldehyde Ethylene Acetal** (**1**).—*m*-Bromobenzaldehyde (97 g, 0.52 mole) prepared by the method of Buck and Ide,[57] bp 67–70° (0.2 mm) [lit.[8] bp 90–92° (4 mm)], was converted to the ethylene acetal (80 g, 0.35 mole, 67% yield) by the same procedure previously described for the *para* isomer. The infrared spectrum showed the absence of a carbonyl function.

Isophthalaldehydic Acid (**2**).—Acetal **1** (76.0 g, 0.33 mole) was converted to isophthalaldehydic acid by carbonation of the correspondig Grignard reagent according to the procedure followed for the *para* isomer. The product **2** (45 g, 0.30 mole, 91% yield) was recrystallized from water, mp 174–175° (lit.[16] mp 175°).

***m*-Carboxycinnamic Acid** (**3**).—A procedure similar to that used for the preparation of *m*-nitrocinnamic acid was followed.[21] Isophthalaldehydic acid (40.0 g, 0.27 mole), malonic acid (31 g, 0.29 mole), 95% ethanol (65 ml), and pyridine (7 ml) were heated under gentle reflux (bath temperature 85–90°) for 8 hr and cooled. The large masses of crystals were broken up with a spatula and filtered. The *m*-carboxycinnamic acid was recrystallized from 95% ethanol and air dried, mp 268–270° (lit.[16] mp 275°). The yield was 36 g (0.187 mole) or 67% of the theoretical amount.

Methyl *m*-Carbomethoxycinnamate.—Acid **3** (31 g, 0.161 mole) was converted to the dimethyl ester according to the procedure described for the preparation of the *para* diester. The compound was a reddish oil, which gave an nmr spectrum consistent with the structure. No further purification was attempted.

Methyl α,β-Dibromo-*m*-carbomethoxyhydrocinnamate (**4**).—The crude *meta* diester was brominated according to the procedure described for bromination of the *para* diester. A sample (1 g) of product was recrystallized from 95% ethanol, mp 223–224° dec. The nmr spectrum consisted of a multiplet at 1.60–2.50 (area 4), doublets at 4.43 (area 1) and 5.02 (area 1), and singlets at 6.01 and 6.06 (combined area 6).

***m*-Carboxyphenylpropiolic Acid** (**5**).—The crude *m*-dibromide **4** (*ca.* 0.16 mole) was dehydrohalogenated according to the procedure used for the dehydrohalogenation of *para* dibromide **4**.

Because of the insolubility of the product, a sample (1 g) was converted into the diacid chloride with thionyl chloride in order to obtain spectral confirmation of the structure. The nmr spectrum consisted of a complex multiplet at 1.26–2.40. The infrared spectrum showed a strong absorption at 2190 cm^{-1}.

Decarboxylation of *m*-Carboxyphenylpropiolic Acid (**5**).—The finely pulverized acid (*ca.* 0.16 mole), quinoline (125 ml) (Eastman, redistilled, bp 236–238°), and copper powder (5.0 g) were heated at 110° for 1 hr. After the mixture was cooled and slowly poured into a well-stirred mixture of crushed ice (400 g) and concentrated hydrochloric acid (125 ml), the small amount of solid was filtered and discarded. The filtrate was extracted with three portions of ether (300 ml); the combined extracts were dried over magnesium sulfate. When the ether was removed on a rotary evaporator, a pale yellow solid (18 g) remained. The crude *m*-ethynylbenzoic acid was not purified as such but was converted into its methyl ester.

Methyl *m*-Ethynylbenzoate.—The crude acid **6** was converted to the methyl ester, bp 62–64° (0.3 mm), by a procedure analogous to that used for the preparation of ethyl *p*-carbethoxycinnamate. The product (4.0 g, 0.027 mole) was obtained in an over-all yield of 17% based on *m*-carboxycinnamic acid (**3**).

The infrared spectrum showed a weak absorption at 2110 and a strong absorption at 3310 cm^{-1}. The nmr spectrum consisted of a complex multiplet at 1.70–2.60 (area 4) and singlets at 6.02 (area 3) and 6.82 (area 1).

***m*-Ethynylbenzoic Acid** (**6**).—Methyl *m*-ethynylbenzoate (0.4 g, 0.0023 mole) was hydrolyzed in the same manner as ethyl *p*-ethynylbenzoate. Recrystallization from water afforded pure *m*-ethynylbenzoic acid (0.30 g, 0.0021 mole), mp 170.5–171°.

Anal. Calcd for $C_9H_6O_2$: C, 73.96; H, 4.14. Found: C, 73.61; H, 4.13.

***m*-Ethynylbenzyl Alcohol** (**7**).—Methyl *m*-ethynylbenzoate (7.1 g, 0.0443 mole) was treated with lithium aluminum hydride (1.3 g, 0.034 mole) in a manner analogous to that used for the corresponding *para* isomer. The product (4.5 g, 0.034 mole), bp 64–66° (0.2 mm), was obtained in a 77% yield.

The infrared spectrum showed absorptions at 2120, 3310, and 3690–3160 cm^{-1}. The nmr spectrum consisted of a multiplet at 2.61–2.92 (area 4) and singlets at 5.59 (area 2), 6.18 (area 1), and 7.02 (area 1).

***m*-Ethynylbenzyl Chloride** (**8**).—*m*-Ethynylbenzyl alcohol (1.5 g, 0.0114 mole) was treated with thionyl chloride (1.4 g, 0.012 mole) in a manner analogous to the corresponding *para* isomer. The product (1.0 g, 0.0067 mole, 59%), bp 61–62° (1.2 mm), was shown by vpc analysis (Carbowax 20-M, 150°) to be 98% pure.

The infrared spectrum showed a very weak absorption at 2120 and a strong absorption at 3310 cm^{-1}. The nmr spectrum consisted of a multiplet at 2.46–2.80 (area 4) and singlets at 5.51 (area 2) and 7.00 (area 1).

***o*-Vinylbenzaldehyde** (**11**).—*o*-Vinylbenzaldehyde (**11**), 25 g, 0.19 mole), bp 61–65° (0.2 mm) [lit.[18] bp 69–72° (2 mm)], was prepared in an over-all yield of 38% from β-phenylethylamine (60 g, 0.50 mole) by the procedures of Baumgarten[58] and Dale.[11]

The infrared spectrum was consistent with the assigned structure. The nmr spectrum showed a singlet at −042 (area 1), a multiplet at 2.00–2.68 (area 5), and doublets at 4.26 and 4.50 (combined area 2). An impurity showed singlets at 6.63 and 5.49 (relative areas 3:2).

***o*-Vinylbenzyl Alcohol** (**12**).—*o*-Vinylbenzaldehyde (22.0 g, 0.167 mole) dissolved in ether (100 ml) was cooled to −10° with a Dry Ice–isopropyl alcohol bath and lithium aluminum hydride (3.4 g, 0.09 mole) in ether (100 ml) was added to the stirred solution so as to maintain the temperature between −10° and 0°. The solution was stirred for 1 hr at 25° followed by the slow addition of water (10 ml) and 10% aqueous sodium hydroxide (60 ml). The precipitate was filtered and washed with ether; the etherate solutions were combined and washed once with 10% hydrochloric acid, five times with 10% sodium carbonate solution, and once with water. The solution was dried over magnesium sulfate and the ether was removed on a rotary evaporator. The crude yield was 22 g (0.164 mole) or 98% of the theoretical amount. Hydroquinone (1 g) was added as a radical inhibitor.

The nmr spectrum consisted of a complex multiplet at 2.23–2.77 (area 4), an ABC multiplet extending from 2.80–3.38 and from 4.1–4.8 (combined area 3), a singlet at 5.48 (area 2), and a broad singlet at 5.89 (area 1).

α,β-Dibromo-*o*-ethylbenzyl Alcohol (**13**).—*o*-Vinylbenzyl alcohol (**11**) (20 g, 0.149 mole) in methylene chloride (150 ml) was treated slowly with bromine (24 g, 0.149 mole) while the temperature was maintained between 20–30°. The crude dibromide (50 g, 0.147 mole, 98% yield) was isolated by evaporating the solvent and allowing the oil to solidify.

The nmr spectrum consisted of a complex multiplet at 2.18–2.67 (area 4), a triplet at 4.33 (area 1), a singlet at 5.24 (area 2), a singlet a 4.99 (area 1), and a doublet at 5.92 (area 2).

Tetrahydropyranyl α,β-Dibromo-*o*-ethylbenzyl Ether (**14**).—A mixture of crude dibromide (40 g, 0.136 mole) from the previous experiment, dihydropyran (11.8 g, 0.14 mole), and phosphorus oxychloride (1 drop) was magnetically stirred for 3 hr at 25–30°. The nmr spectrum was consistent with the assigned structure.

Tetrahydropyranyl *o*-Ethynylbenzyl Ether.—The crude material from the previous experiment (*ca.* 0.136 mole), potassium

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[57] J. S. Buck and W. S. Ide in "Organic Syntheses," A. H. Blatt, Ed., Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1955, p 130.

[58] H. E. Baumgarten, F. A. Bower, R. A. Setter, and R. E. Allen, *J. Am. Chem. Soc.*, **80**, 4591 (1958).

hydroxide (30 g), and absolute methanol (30 ml) were refluxed and magnetically sitrred for 20 hr. Water (200 ml) was added to the cooled solution, which was then acidified with dilute hydrochloric acid and extracted twice with ether (200 ml). The ether extract was washed once each with 10% hydrochloric acid, 10% sodium carbonate, and water, and dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the residual liquid was vacuum distilled, bp 115–125° (0.4 mm), to yield 15 g (0.069 mole) or 50% of the theoretical amount of the ether. The nmr spectrum was consistent with the assigned structure.

***o*-Ethynylbenzyl Alcohol (15).**—The crude ether (10 g, 0.046 mole) in methanol (175 ml), together with a trace of *p*-toluenesulfonic acid, was maintained at reflux for 2 hr, cooled, poured into ether (1 l.), and extracted twice each with 10% sodium carbonate and water. The ether was dried with magnesium sulfate and removed on a rotary evaporator. The residue was distilled to give fraction a (1.1 g), bp 60–72° (0.5 mm), and fraction b (5.0 g), bp 72–80° (0.5 mm).

An nmr spectrum of fraction a showed a complex multiplet at 2.20–2.80 (area 4) and singlets at 5.31 (area *ca.* 2), 6.55 (area *ca.* 3), and 6.72 (area 1). The compound was assigned the structure of *o*-ethynylanisole.

Fraction b (solid) was recrystallized from *n*-hexane to give 4.4 g (0.034 mole, 74% yield) of *o*-ethynylbenzyl alcohol, mp 63–64°. The infrared spectrum showed absorptions at 3700–3300, 3310, and 2100 cm^{-1} (weak).

Anal. Calcd for C_9H_8O: C, 81.79; H, 6,10. Found: C, 81.70; H, 6.03.

***o*-Ethynylbenzyl Chloride (16).**—*o*-Ethynylbenzyl alcohol (2.0 g, 0.0151 mole) was treated with thionyl chloride (1.8 g, 0.0151 mole) in a manner analogous to the corresponding *para*-isomer. Distillation yielded 1.3 g (0.0087 mole, 58% yield) of chloride 16, bp 60–61° (1 mm), which was shown by vpc analysis (Carbowax 20-M, 150°) to be >98% pure.

The infrared spectrum showed absorptions at 2120 (very weak) and 3310 cm^{-1}. The nmr spectrum consisted of a complex multiplet at 2.43–2.86 (area 4) and singlets at 5.28 (area 2) and 6.73 (area 1).

4-Hexen-1-yn-3-ol.—The procedure used is a modification of that used by Heilbron.[59] Crotonaldehyde (210 g, 3.0 moles) dissolved in an equal volume of anhydrous ether was slowly (*ca.* 4 hr) added to a liquid ammonia solution of sodium acetylide which had been prepared from ammonia (1 l.), ferric nitrate (1 g), sodium (69 g, 3.0 moles; added to the ammonia in 5-g portions), and excess dry acetylene (bubbled through the ammonia solution until the initially formed disodium acetylide precipitate dissolved). The solution was stirred for 1 hr, ammonium chloride (170 g) was added, and the ammonia was allowed to evaporate overnight. After water (500 ml) and ether (500 ml) had been added, the ether was separated, combined with ether extracts (200 ml) of the aqueous layer, washed with 10% aqueous hydrochloric acid and water, dried over magnesium sulfate, and removed on a rotary evaporator to give a residue of crude product which was vacuum distilled, bp 68–70° (20 mm) [(lit.[13] bp 74–75° (30 mm)]. The yield was 80 g (0.83 mole, 28%) of 4-hexen-1-yn-3-ol. The infrared and nmr spectra were in accord with the assigned structure. The nmr spectrum showed a complex multiplet at 3.60–4.50 (area 2), a mulitplet at 5.10 (area 1), a singlet at 6.22 (area 1), a doublet at 7.44 (area 1, J = 2.5 cps), and a doublet at 8.20 (area 3, J = 6 cps).

5-Chloro-3-hexen-1-yne (18).—The procedure is a modification of that used by Bell.[60] 4-Hexene-1-yn-3-ol (30 g, 0.31 mole) was slowly added to concentrated hydrochloric acid (90 ml) and shaken for 0.5 hr while the temperature was maintained between 20–25°. After dilution with an equal volume of water, the product was isolated from an ether extract in the usual manner. Distillation from calcium hydride produced a mixture of *cis*- and *trans*-**18** (30 g, 0.26 mole, 85% yield), bp 61–70° (*ca.* 70 mm) [lit.[60] bp 59–70° (70 mm)].

The infrared spectrum showed absorptions at 759 and 948 cm^{-1}, ascribed to the *cis* and *trans* isomers respectively.[61] The nmr spectrum showed acetylenic protons at 6.73 (area 0.24) and 7.05 (area 0.76) which were associated with the *cis* and *trans* isomers respectively, *vide infra*. Vapor phase chromatographic separation of the product at 100° showed two separate and distinct peaks. The first peak (25%) was collected and identified as *cis*-5-chloro-3-hexen-1-yne; the second peak (75%) was identified as the corresponding *trans* isomer.

The product (*ca.* 15 g) was distilled at *ca.* 75 mm through a column (60 × 1 cm) which contained a tantalum wire coil. The column was flooded and heated under total reflux for 2 hr. The reflux ratio was then adjusted to 100:1 and fractions were collected as follows: (a) bp 64.0–64.5° (discarded); (b) bp 64.5–65.5° (2.5 g); (c) bp 65.5–76.0° (discarded); (d) bp 76.0–76.5° (5.0 g).

The infrared spectrum of the *cis* isomer 18, fraction b, showed the olefinic carbon-hydrogen out-of-plane bending absorption at 759 cm^{-1} as reported by Allan.[61] The nmr spectrum showed the acetylenic hydrogen atom as a doublet at 6.73. Vapor phase chromatographic separation at 100° showed the presence of 7.0% of the corresponding *trans* isomer.

The ultraviolet spectrum of a sample of greater than 99% purity (collected from vapor phase chromatograph) showed λ_{max} at 2251 A with an extinction coefficient of 11,700.[60]

The infrared spectrum of *trans* isomer 18, fraction d, showed the olefinic carbon hydrogen out-of-plane deformation at 948 cm^{-1} as reported by Allan.[61] The nmr spectrum showed the acetylenic hydrogen as a doublet (J = 2.0 cps) at 7.05 and was consistent with the assigned structure. Vpc analysis (Carbowax 20-M, 100°) showed the presence of 3.0% of the corresponding *cis* isomer.

3-Hexen-5-yn-2-ol.—4-Hexen-1-yn-3-ol (3.0 g, 0.032 mole) was converted to the isomeric alcohol according to the procedure of Bell.[60] The infrared spectrum showed absorptions at 756 and 956 cm^{-1}, assigned to the *cis* and *trans* isomers respectively.[61] The nmr spectrum showed the acetylenic proton of the *cis* isomer at 6.74 (area 0.25) and that of the *trans* isomer at 7.03 (area 0.75). This is the same isomer content as that reported by Bell, Jones, and Whiting.[60]

5-Ethoxy-3-hexen-1-yne.—4-Hexen-1-yn-3-ol (3.0 g, 0.032 mole) was treated with acidic ethanol according to the procedure of Heilbron,[59] bp 82–83° (*ca.* 110 mm) [lit.[59] bp 81.5–82° (100 mm)]. Vpc analysis (Carbowax 20-M, 100°) showed two components, presumably the *cis* (8%) and *trans* (92%) isomers. The nmr spectrum showed acetylenic hydrogen atoms at 6.82 (area 0.08) and 7.12 (area 0.92).

Acetone–Water Hydrolysis of *trans*-5-Chloro-3-hexen-1-yne (18).—The halide **18** (3.0% *cis*) (1.0 g, 0.0088 mole) was dissolved in 50% (vol) acetone–water (100 ml) and maintained at 30° for 48 hr, after which the solution was diluted with water (700 ml) and extracted with ether. The extracts were dried and distilled through a 12-in. wire spiral column. Vpc analysis (Carbowax 20-M, 100°) on the residue (*ca.* 1 g) showed *trans*-3-hexen-5-yn-2-ol (95.7%), *cis*-3-hexen-5-yn-2-ol (3.0%), and 4-hexen-1-yn-3-ol (1.35%). Identifications were made by comparison with the previously prepared authentic material.

Aqueous Ethanolysis of *trans*-5-Chloro-3-hexen-1-yne (18).—The halide (3.0% *cis*) (1.0 g, 0.0088 mole) was dissolved in 50% (vol) ethanol–water (100 ml) and heated at 30° for 40 hr. The solution was diluted to 700 ml with water and extracted with either. The ether extracts were dried over magnesium sulfate and distilled on a 12-in. spiral wire column. Vpc analysis (Carbowax 20-M, 100°) of the residue (*ca.* 1 g) showed *trans*-3-hexen-5-yn-2-ol (65%), *cis*-3-hexen-5-yn-2-ol (2.0%), *trans*-5-ethoxy-3-hexen-1-yne (32%), and *cis*-5-ethoxy-3-hexen-1-yne (1.0%). Identifications were made by comparison with authentic samples.

Aqueous Ethanolysis of *cis*-5-Chloro-3-hexen-1-yne (18).—The halide **18** (10% *trans*) was solvolyzed in the same manner as the *trans* isomer. Integration of the acetylenic hydrogen atoms of the *cis* and *trans* isomers (nmr) showed 17.3% of *trans*-3-hexen-5-yn-2-ol and the corresponding ethyl ether and 82.7% of *cis*-3-hexen-5-yn-2-ol and the corresponding ethyl ether. This represents 8.1% geometrical isomerization.

Method of p*K* Measurements.—The dissociation constants of *m*- and *p*-ethynylbenzoic acids were determined potentiometrically in 50% (vol) ethanol–water by means of a glass electrode (Leeds and Northrup, STD. 1199-30) and a Heath pH recording electrometer (Model EUW-301) with a saturated aqueous potassium chloride calomel electrode (Leeds and Northrup, STD. 1199-31). In order to avoid solvent errors,[62] the glass electrodes were stored in 50% (vol) ethanol–water.

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(59) I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 81 (1945).

(60) I. Bell, E. R. H. Jones, and M. C. Whiting, *ibid.*, 2597 (1957).

(61) J. L. H. Allan, G. D. Meakins, and M. C. Whiting, *ibid.*, 1874 (1955).

(62) A. L. Bacarealla, E. Grunwald, H. P. Marshall, and E. L. Purlee, *J. Org. Chem.*, **20**, 747 (1955).

In order that the data could be combined with those of Roberts,[21,22] the following calibration procedure was used. A 3.127×10^{-3} M solution of benzoic acid (National Bureau of Standards) in 50% (vol) ethanol–water was half-neutralized and the meter was zeroed to 5.75, the apparent pK reported by Roberts.[21] The electrodes were cleaned, dried, and inserted into a 0.02 N potassium hydrogen phthalate buffer in 50% (vol) ethanol–water and readings of 5.50 ±0.005 were recorded. In subsequent runs the meter was standardized against this phthalate buffer solution.

All titrations were carried out with a 200-ml, covered beaker maintained at 25.0 ± 0.1° and a buret graduate to 0.01 ml. The base used was 0.06703 N sodium hydroxide in 50% (vol) ethanol–water and was prepared from carbonate-free water and base. The solutions were stirred with a magnetic stirring bar under a nitrogen atmosphere. Solutions of the acids (*ca.* 3.1×10^{-3} M) in 50% (vol) ethanol–water were prepared, and 50-ml aliquots were titrated. A plot of pH *vs.* volume of base was made for each titration and the pK values were determined graphically.

Ethanolysis Procedure (63–83° Range).—All kinetic experiments at 63 and 83° utilized a 12 × 12 in. pyrex bath which contained *ca.* 5 gal of oil (Cities Service, D.C.-915), a Lightnin Model L continuous duty stirrer, a hydrogen-jacketed thermoregulator, and a 500-w continuous heat source which was connected to a Variac. Fine heating was controlled by a 100-w light bulb connected through a relay to the thermoregulator. The entire bath was surrounded by *ca.* 3 in. of polyurethane foam and was covered with a 1-in. styrofoam lid.

The appropriate amount of halide (*ca.* 0.0013 mole) was dissolved in *ca.* 25 ml of water–ethanol (50% by volume at 20.0°) and the solution was distributed among 7–10 ampoules each containing *ca.* 2.3 ml. The ampoules were sealed and placed in the bath (clock started) and at appropriate time intervals ampoules were removed and quenched in ice–water. The necks were scored and snapped off, and an exact aliquot (*ca.* 2 ml) was removed with a pipet calibrated with the same ethanol–water solution. The aliquot was diluted with *ca.* 15 ml of cold distilled water and the acid solution was titrated to a phenolphthalein end point with 0.06307 N sodium hydroxide in 50% (vol) ethanol–water which had been standardized against potassium hydrogen phthalate. A 5-ml microburet which could be read directly to 0.01 ml was used. Infinity titers were taken after 10 half-lives.

Rate constants were determined by the method of least squares and the activation parameters were calculated from the Eyring equation.

The data for a typical run are indicated below for the ethanolysis of *p*-ethynylbenzyl chloride (**8**) at 83.00 ± 0.05°. Good first-order kinetics are shown in (Table X) for >69% reaction.

TABLE X[a]

Time elapsed, min	Titrated (HCl)	−ln (RCl)	Time elapsed, min	Titrated (HCl)	−ln (RCl)
∞	0.04974	...	075	0.02251	3.417
015	0.00684	3.027	105	0.02831	3.611
030	0.01121	3.121	135	0.03356	3.827
045	0.01539	3.220	180	0.03859	4.089

[a] Rate constant $(1.085 \pm 0.009) \times 10^{-4}$ sec^{-1}.

Ethanolysis Procedure (20–40° Range).—A constant-temperature bath similar to that previously described was used, except that water was used as the bath liquid and the bath was not insulated. A 10-ft coil of 0.25-in. copper tubing through which cold tap water circulated was utilized for the 20° temperature.

Approximately 240 ml of the ethanol–water solvent (50% by volume at 20.0°) was placed in a 250-ml volumetric flask and allowed to equilibrate for several hours in the bath. A sample of the halide (*ca.* 25 l.) was then quickly added (clock started) and the flask was shaken vigorously for several moments followed by reimmersion in the bath. At appropriate time intervals a sample of *ca.* 25 ml was poured from the flask into a 100-ml beaker (thermostated at the same temperature) equipped with a stirrer and a pair of electrodes.

The apparent pH of the solution was determined potentiometrically by means of a glass electrode (Leeds and Northrup, STD. 1199-30) and a Heath pH recording electrometer (Model EUW-301) with a saturated aqueous potassium chloride, calomel electrode (Leeds and Northrup, STD. 1199-31). A span setting of 5 on the electrometer was used which enabled one to read directly to 0.01 pH unit. The infinity pH was taken after at least 10 half-lives had elapsed.

Rate constants were determined from a plot of elapsed time *vs.* hydrogen ion concentration (calculated from pH reading).

The data for a typical run are indicated (Table XI) for the ethanolysis of *trans*-5-chloro-3-hexen-1-yne (**18**) at 20.00 ± 0.05°.

TABLE XI[a]

Time elapsed, hr	Titrated (HCl) × 10³	−ln (RCl)	Time elapsed, hr	Titrated (HCl) × 10³	−ln (RCl)
	4.170	...	2.5	0.646	5.652
1.0	0.0794	5.499	3.0	0.813	5.698
1.5	0.282	5.550	4.0	1.160	5.805
2.0	0.468	5.601	6.0	1.740	6.021

[a] Rate constant $(2.778 \pm 0.009) \times 10^{-5}$ sec^{-1}.

Amino Ketone Rearrangements. VI. Synthesis of 2-Alkylamino-2-phenylcyclohexanones[1a]

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The utility of the thermal rearrangement of α-amino ketones, α-hydroxy imines, and imine acid salts for the synthesis of a variety of 2-alkylamino-2-phenylcyclohexanones is described. The 2-aminocyclohexanones were reduced and the stereochemistry of four of the resulting amino alcohols determined.

Previous communications in this series have indicated the utility of the amino ketone rearrangement in the syntheses of 2-amino-2-methylcyclohexanones,[2] 2-anilino-2-phenylcyclohexanones,[3] and acyclic amino ketones.[4] Mechanistic aspects have also been discussed.[1,3] In this, and the accompanying communication,[5] the syntheses of a variety of aminocyclohexanones are reported and an evaluation made of the two pyrolytic routes employed. This rearrangement has

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(1) (a) Paper V: C. L. Stevens, H. T. Hanson, and K. G. Taylor, *J. Am. Chem. Soc.*, **88**, 2769 (1966). (b) Abstracted in part from the M.S. thesis of M. D. Pillai.

(2) C. L. Stevens, I. L. Klundt, M. E. Munk, and M. D. Pillai, *J. Org. Chem.*, **30**, 2967 (1965).

(3) C. L. Stevens, A. Thuillier, and F. A. Daniher, *ibid.*, **30**, 2962 (1965).

(4) C. L. Stevens, R. D. Elliott, and B. L. Winch, *J. Am. Chem. Soc.*, **85**, 1464 (1963).

(5) C. L. Stevens, A. Thuillier, K. G. Taylor, F. A. Daniher, J. P. Dickerson, H. T. Hanson, N. A. Nielsen, N. A. Tikotkar, and R. M. Weier, *J. Org. Chem.*, **31**, 2601 (1966).