Aromatic Substitution. XXIX.[1] Friedel–Crafts Acylation of Benzene and Toluene with Substituted Acyl Halides. Effect of Substituents on Substrate and Positional Selectivity

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Abstract: Friedel–Crafts acylation of benzene and toluene with substituted acyl halides was investigated. Effect of substituents in the acylating agents showed that both substrate selectivity (as expressed by $k_t{:}k_b$ rate ratios) and positional selectivity (ortho:para ratio) were governed by the nature of the electrophiles. These results are to be explained if one assumes that the position of the transition state of highest energy lies earlier along the reaction coordinate for reactions with stronger electrophiles and later with weaker electrophiles, resembling in the first case more starting aromatics and in the latter the Wheland intermediates.

The extensively studied Friedel–Crafts acylations of aromatic hydrocarbons, such as toluene and benzene, are characterized by high selectivity of the reactions. This has been evidenced by high comparative substrate rate ratios (generally $k_{\text{toluene}}{:}k_{\text{benzene}}$). Furthermore, in Friedel–Crafts acylations generally predominant para substitution is observed.[3] The latter was considered to be a consequence of steric ortho hindrance to the acylating agent.[4] Recently we have shown in Friedel–Crafts benzylation a relationship between the electrophilicity of the reagent and substrate and positional selectivity.[5] We report now results of Friedel–Crafts formylation, acetylation, and benzoylation of toluene and benzene with acyl and substituted acyl halides. This study centers on the comparison of the effects of substituents on the reactivity and selectivity of the acylating agent both in acetylations and benzoylations. The results clearly show that electronic substituent effects in the reagent influence both substrate and positional selectivity. This evidence substantially strengthens the views expressed in our previous work relating to substituent effects in Friedel–Crafts alkylations.[5]

Results and Discussion

Acetylation and Formylation. Acetylation of toluene and benzene with acetyl chloride (aluminum chloride catalyst) and acetyl fluoride (boron trifluoride catalyst) shows high substrate ($k_t{:}k_b = 141$ and 130, respectively) and high para positional selectivity (95.5 and 97.7% para isomer). This reflects the weak electrophilic nature of the acetyl cation and the generally σ complex nature of the transition states.

$$\text{ArH} + \text{RCOX} \xrightarrow{\text{AlCl}_3 \text{ or } \text{BF}_3} \text{ArCOR} + \text{HX}$$

$$\text{R} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5, i\text{-C}_3\text{H}_7, \text{CH}_2\text{Cl}, \text{CHCl}_2$$

$$\text{X} = \text{Cl}, \text{F}$$

When hydrogen is substituted for the methyl group, *i.e.*, in the formylation reaction of Olah and Kuhn[6] using formyl fluoride and boron trifluoride catalyst, the $k_{\text{toluene}}{:}k_{\text{benzene}}$ ratio is decreased substantially to 34.6, as is the degree of para substitution. A concomitant increase of ortho substitution (53.2% para and 43.3% ortho isomer) with only a modest increase of meta isomer is also noted (3.5%). As obviously the methyl group is larger than the hydrogen atom, steric reasons used to explain the very high degree of para substitution in acetylation of toluene over that of ortho isomer formations could be used to explain the isomer distribution. As, however, simultaneously substrate selectivity is also substantially changed, we suggest that these differences are due also to the greater electrophilic reactivity of the formylating agent ($\text{HCOF}\rightarrow\text{BF}_3$ complex or HCO^+, probably exchanging with the system) relative to that of the acetylating agent (CH_3CO^+). The stronger the electrophile, the lesser the demand there is in the transition state on the aromatic substrate. This means an "earlier" transition state which resembles more the starting hydrocarbons (toluene, benzene) than the intermediate benzenium ions (σ complexes).

It was demonstrated by Jensen[3a] that acylations can occur by both second- and third-order processes. Since kinetic hydrogen isotope effects can effect both substrate and positional selectivity in these reactions, we measured $k_H{:}k_D$ (by comparing benzene with benzene-d_6; see Experimental Section) of both the acylation and the formylation reactions and found them to be similar (2.45 and 2.68, respectively). Thus differences in kinetic hydrogen isotope effects cannot be responsible for observed substantial differences in the acetylation and formylation reaction and they must be due to a substituent effect, *i.e.*, H *vs.* CH_3. The idea that isomer distributions are effected primarily by the bulkiness of the acylating agent can be tested, when the methyl hydrogens of the reagent acetyl group are subsequently substituted by methyl groups of chlorine atoms. De-

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[1] Part XXVIII: G. A. Olah, *Accounts Chem. Res.*, **4**, 240 (1971).

[2] Postdoctoral Research Associate, 1970–1971.

[3] For reviews see (a) F. R. Jensen and G. Goodman in "Friedel–Crafts and Related Reactions," G. A. Olah, Ed., Vol. III, Part 2, Wiley-Interscience, New York–London, 1964, pp 1024–1032; (b) H. C. Brown and K. L. Nelson, in "Chemistry of Petroleum Hydrocarbons," Vol. III, B. T. Brooks, S. S. Kurtz, C. B. Board, and L. Schmerling, Ed., Reinhold Publishing Corp., New York, N. Y., 1955, pp 465–578.

[4] (a) H. C. Brown and G. Marino, *J. Amer. Chem. Soc.*, **81**, 5611, 5929 (1959); (b) G. A. Olah, M. E. Moffatt, S. J. Kuhn, and B. A. Hardie, *ibid.*, **86**, 2198 (1964); G. A. Olah, S. J. Kuhn, S. H. Flood, and B. A. Hardie, *ibid.*, **86**, 2203 (1964); G. A. Olah, J. Lukas, and E. Lukas, *ibid.*, **91**, 5319 (1969).

[5] G. A. Olah, M. Tashiro, and S. Kobayashi, *ibid.*, **92**, 6369 (1970).

[6] G. A. Olah and S. J. Kuhn, *ibid.*, **82**, 2380 (1960); *Chem. Ber.*, **89**, 866 (1956).

Table I. Relative Rates and Isomer Distributions in the Boron Trifluoride and Aluminum Chloride Catalyzed Acetylation (Formylation) of Toluene and Benzene in Carbon Disulfide Solution at 25°

Acyl halide	Catalyst	$k_t:k_b$	% ortho	% meta	% para	ortho:para
HCOF	BF_3[a]	34.6	43.3	3.5	53.2	0.81
CH_3COF	BF_3[a]	130.0	1.2	1.1	97.7	0.01
CH_3COCl	$AlCl_3$	141.0	2.5	2.0	95.5	0.03
CH_3CH_2COCl	$AlCl_3$	89.2	2.6	3.1	94.3	0.03
$(CH_3)_2CHCOCl$	$AlCl_3$	84.4	3.2	2.4	94.4	0.03
$CH_2ClCOCl$	$AlCl_3$	78.2	11.1	2.3	86.6	0.13
$CHCl_2COCl$	$AlCl_3$	51.4	17.3	3.2	79.5	0.22

[a] Reaction carried out without solvent at −30 to +25°.

spite the obvious *increase* in the size of the reagent, substituent effects are observed which correlate with the increase of electron deficiency of the reagent (not only chlorine atoms, but methyl groups are inductively electron-withdrawing substituents when attached to sp^3 carbon). Thus, the increase in electrophilicity of the attacking oxocarbenium ion causes the transition state of highest energy to be "early" on the reaction coordinate and results, therefore, in lower substrate selectivity and increased ortho substitution (see data summarized in Table I).

Benzoylation. Substituent effects in the attacking electrophile and related effects on selectivity in Friedel–Crafts acylations can be studied advantageously for benzoylations with substituted benzoyl chlorides. Data summarized in Table II show that the weakly electrophilic parent benzoyl cation give high substrate and positional selectivity, in accordance with previous observations. Introduction of p-CH_3, p-F, 2,4,6-$(CH_3)_3$, and p-CH_3O substituents into the benzoyl cation (being electron-donating substituents on the aromatic ring) decreases its electrophilicity and gives slight further increase in selectivity. In contrast, the presence of electron-withdrawing substituents which increase the electrophilicity of the benzoyl cations is reflected by lower $k_t:k_b$ rate ratios and an increase in the amount of ortho (and to a lesser degree, meta) substitution. Again the latter effect is observed despite the obvious increase in size and thus increased steric requirement of the reagents. The spread of $k_t:k_b$ from 16 to 233 and a similar substantial charge in ortho:para isomer ratios clearly demonstrate the effect of substituents on the electrophilicity of the reagent and through this on the nature of the transition states.

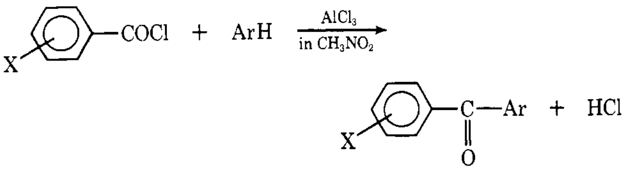

Table II. Relative Rates and Isomer Distribution in the Aluminum Chloride Catalyzed Benzoylation of Toluene and Benzene with Substituted Benzoyl Chlorides in Nitromethane Solution at 25°

Benzoyl chloride	$k_t:k_b$	% ortho	% meta	% para	Ortho: para
C_6F_5COCl	16.1	35.4	7.8	56.8	0.62
2,4-$(NO_2)_2C_6H_3COCl$[a]	29.0	42.4	3.0	54.6	0.78
3,5-$(NO_2)_2C_6H_3COCl$[a]	38.9	9.4	6.8	83.8	0.11
p-$NO_2C_6H_4COCl$[a]	52.0	9.5	1.2	89.3	0.14
2,5-$F_2C_6H_3COCl$	96.2	12.3	1.6	86.1	0.09
C_6H_5COCl	153.5	8.1	1.2	90.7	0.09
p-$CH_3C_6H_4COCl$	164.4	7.8	1.1	91.1	0.02
p-FC_6H_4COCl	170.0	8.0	1.1	90.7	0.09
2,4,6-$(CH_3)_3C_6H_2COCl$	196.0	2.3	0.6	97.1	0.02
p-$CH_3OC_6H_4COCl$	233.0	14.9	1.5	83.6	0.18

[a] Results obtained from gas–liquid chromatographic analysis after conversion to denitrated benzophenones.

Conclusions

In electrophilic aromatic substitutions the transition states of highest energy can resemble either the Wheland intermediates (σ complex) or starting aromatics (π complex).

It is evident that the nature of the transition states in aromatic substitutions has a profound effect on both substrate and positional selectivity. In exothermic reactions of low substrate selectivity, the transition state of highest energy is of π complex nature. In this case, a highly reactive electrophile interacts with the aromatic substrate (such as benzene and toluene) with relatively little deformation of the latter in the transition state. The generally very fast reactions take place with little substrate discrimination (as π bases). Subsequent σ complex formation leads to positional selectivity. In these reactions the σ complexes themselves also lie relatively early on the reaction path and therefore ortho substitution is favored over para, as there are two ortho, but only one para position giving σ complexes of about comparable energy, the meta complexes being less favorable. Steric ortho hindrance can also influence the ortho:para ratio in acylations of toluene. This effect, however, cannot be considered the only major effect influencing isomer ratios.

On the other hand, in selective reactions with increasingly weaker electrophiles (or with aromatics of lesser nucleophilicity) which show higher substrate selectivity, the σ transition states are of "late" nature resembling the intermediates and the ortho:para ratio decreases, *i.e.*, para substitution becoming predominant.

Reactions indicating early transition state of highest energy reflect charge distribution of the starting aromatics. In alkylbenzenes, like toluene, charge density is highest around the ortho and para positions. Further, as there are two ortho, but only one para position, the ortho:para ratio will be high ($\gtrsim$ 2).

In reactions indicating late transition states, of highest energy, *e.g.*, resembling the Wheland intermediates, the isomer distributions obtained relate to the relative stabilities of the cyclohexadienyl cations (Wheland intermediates, σ complexes). Nmr studies of σ complexes[7]

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(7) For a review, see D. M. Brouwer, E. L. Mackor, and C. L. McLean, in "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, Chapter 20.

including the recent study of the $C_6H_7^+$ ion itself[8] clearly show that a substituent will exert a more powerful effect on the benzenium ion (σ complex) when it is para to the entering reagent than when it is ortho and even more so than when it is meta. With an electron-donating substituent, like the methyl group in toluene, the stability of intermediate ions will decrease in the order para > ortho ≫ meta, resulting in a low ortho:para isomer ratio, as indeed found experimentally in high selectivity reactions. The electrophilicity of the reagent plays a major role in influencing the nature of the transition state of highest energy, and thus is a significant factor affecting positional and substrate selectivity. The nucleophilicity of the substrate (aromatics) can also contribute to the same effect. This is reflected by the extensive literature data of Friedel–Crafts acylations[3,4] showing that the high selectivity observed in the reactions of toluene compared to benzene is not increasing with further methyl substitution of the aromatics as fast as would be expected based on known σ basicities.[1,9] Thus with increasingly more basic aromatics even a relatively weak electrophile will result in earlier (more π type) transition states.

Consideration of the nature of the transition states enables an understanding of substrate selectivities separate from positional selectivities. It also brings to light the importance of ortho:para isomer ratios in the context of positional selectivities and further allows their correlation with substrate selectivities. This realization supplements the well-demonstrated importance of meta:para isomeric substitution ratios on which the Brown selectivity treatment is based.

It should be pointed out that Norman and Taylor[10] must be credited with first emphasizing the importance of the ortho:para ratio discussing contributions from: (a) steric hindrance; (b) steric acceleration; (c) interaction between the substituent and the reagent; (d) electronic effects; and (e) solvent effects. They considered that due to the complexity of factors involved it is difficult to evaluate individual effects separately. Our work, however, shows clear indication for the dependence of the ortho:para isomer ratios on the nature of the transition states, effected through electrophilicity of the reagents or nucleophilicity of the aromatics. Steric effects obviously play an important role in effecting the isomer distributions in Friedel–Crafts acylations (particularly ortho substitution) but they cannot any longer be considered as the only major reason for orientation.

Experimental Section

Materials. Benzene, toluene, carbon disulfide, and nitromethane were commercially available as spectroquality chemicals and were used after drying over molecular sieves. Acetyl fluoride and acetyl, propionyl, isobutyryl, chloroacetyl, and dichloroacetyl chlorides were commercially obtained and distilled before use. Formyl fluoride was prepared by established procedures.[6] Benzoyl, *p*-fluorobenzoyl, and *p*-methoxybenzoyl chlorides used were available from commercial sources. 2,4-Dinitrobenzoyl (mp 47° from CCl_4), 2,5-difluorobenzoyl (bp 92–93°, 34 mm), and 2,4,6-trimethylbenzoyl (bp 120–123°, 30 mm) chloride were prepared by reaction with thionyl chloride of the corresponding acids which were obtained from commercial sources. Benzene-d_6 was purchased from Merck Sharp and Dohme, Ltd., Montreal, Canada.

General Procedure for Competitive Acylation of Benzene and Toluene. (a) In Carbon Disulfide (or Nitromethane) Solution. To a solution of 0.01 mol of aluminum chloride catalyst in 20 g of solvent (see Tables I and II) were added 0.05 mol each of benzene and toluene in a three-necked reaction flask equipped with a thermometer, reflux condenser (connected through a drying tube to a hydrogen halide absorber), and a dropping funnel. The reaction flask was then placed in a constant temperature bath at 25 ± 0.5°

Table III. Gas–Liquid Chromatography Retention Times of Reaction Products[a]

Compound	Retention time, min	Column[b]	Temp, °C
Benzaldehyde	17.2	A	80
o-Tolualdehyde	36.0	A	80
m-Tolualdehyde	37.6	A	80
p-Tolualdehyde	42.7	A	80
Acetophenone	9.0	A	130
o-Methylacetophenone	10.5	A	130
m-Methylacetophenone	13.5	A	130
p-Methylacetophenone	14.7	A	130
Propiophenone	10.7	A	140
o-Methylpropiophenone	12.6	A	140
m-Methylpropiophenone	16.9	A	140
p-Methylpropiophenone	18.5	A	140
Isobutyrophenone	11.5	A	140
o-Methylisobutyrophenone	12.8	A	140
m-Methylisobutyrophenone	17.0	A	140
p-Methylisobutyrophenone	19.0	A	140
α-Chloroacetophenone	22.0	A	140
o-Methyl-α-chloroacetophenone	26.6	A	140
m-Methyl-α-chloroacetophenone	36.0	A	140
p-Methyl-α-chloroacetophenone	42.0	A	140
α,α-Dichloroacetophenone	37.0	A	140
o-Methyl-α,α-dichloroacetophenone	42.0	A	140
m-Methyl-α,α-dichloroacetophenone	48.0	A	140
p-Methyl-α,α-dichloroacetophenone	54.0	A	140
Benzophenone	29.0	B	145
o-Methylbenzophenone	31.0	B	145
m-Methylbenzophenone	45.0	B	145
p-Methylbenzophenone	53.0	B	145
4,2′-Dimethylbenzophenone	57.0	B	145
4,3′-Dimethylbenzophenone	81.0	B	145
4,4′-Dimethylbenzophenone	97.0	B	145
2,3,4,5,6-Pentafluorobenzophenone	12.2	B	145
2,3,4,5,6-Pentafluoro-2′-methylbenzophenone	15.0	B	145
2,3,4,5,6-Pentafluoro-3′-methylbenzophenone	17.0	B	145
2,3,4,5,6-Pentafluoro-4′-methylbenzophenone	20.7	B	155
2,5-Difluorobenzophenone	12.1	C	130
2,5-Difluoro-2′-methylbenzophenone	13.0	C	130
2,5-Difluoro-3′-methylbenzophenone	16.0	C	130
2,5-Difluoro-4′-methylbenzophenone	20.7	C	130
4-Fluorobenzophenone	25.0	C	120
4-Fluoro-2′-methylbenzophenone	21.0	C	120
4-Fluoro-3′-methylbenzophenone	35.0	C	120
4-Fluoro-4′-methylbenzophenone	40.0	C	120
2,4,6-Trimethylbenzophenone	10.8	C	150
2,4,6,2′-Tetramethylbenzophenone	12.7	C	150
2,4,6,3′-Tetramethylbenzophenone	14.3	C	150
2,4,6,4′-Tetramethylbenzophenone	17.5	C	150
4-Methoxybenzophenone	24.0	C	150
4-Methoxy-2′-methylbenzophenone	19.0	C	150
4-Methoxy-3′-methylbenzophenone	32.0	C	150
4-Methoxy-4′-methylbenzophenone	36.0	C	150

[a] Carrier gas (helium) pressure was 30 psi. [b] A: stainless steel open tubular column, 150 ft × 0.01 in., wall coated with *m*-bis(*m*-phenoxyphenoxy)benzene and Apiezon L grease. B: stainless steel open tubular column, 150 ft × 0.01 in., wall coated with UCON Oil 550-X. C: stainless steel open tubular column, 100 ft × 0.02 in., wall coated with butanediol succinate.

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(8) G. A. Olah, R. H. Schlosberg, D. P. Kelly, and Gh. D. Mateescu, *J. Amer. Chem. Soc.*, **92**, 2546 (1970).

(9) E. L. Mackor, A. Hofstra, and J. H. van der Walls, *Trans. Faraday Soc.*, **54**, 186 (1958).

(10) R. O. C. Norman and R. Taylor in "Electrophilic Substitution in Benzenoid Compounds," Elsevier, Amsterdam–London–New York, 1965, pp 301–310.

and, with vigorous stirring, 0.01 mol of acyl chloride dissolved in 3 g of solvent was added at a constant rate over a period of 5 min. The reaction was allowed to proceed an additional 10 min after the additions were complete. The solution was then washed with ice water and extracted with ether. The organic layer was separated, dried (Na_2SO_4), condensed on a water bath, and analyzed by gas–liquid chromatography. The data obtained are summarized in Tables I and II.

(b) Without Solvent. To a solution of 0.1 mol each of benzene and toluene in a reaction flask fitted with a thermometer, reflux condenser, and gas inlet tube, was introduced 0.04 mol of formyl (or acetyl) fluoride at −30°. Stirring was begun and 0.04 mol of boron trifluoride gas was introduced into the solution at −30° over a period of 3 min. The reaction system was then allowed to warm to 25° and stirring was continued for another 10 min. The solution was then washed three times with water. The organic layer was extracted with ether, separated, dried (Na_2SO_4), and analyzed by gas–liquid chromatography. The data obtained are shown in Table I.

Determination of Kinetic Hydrogen Isotope Effect. Benzene-d_6 (0.02 mol) and toluene (0.02 mol) were used to obtain $k_H:k_D$ values for formylation and acetylation. The reaction conditions, work-up procedures, and gas–liquid chromatographic analyses were followed as described above (b). For formylation, $k_T:k_{B-d_6}$ was found to be 92.7. Calculations gave a $k_H:k_D$ value for benzene of 2.68 (92.7/34.6). For acetylation, $k_T:k_{B-d_6}$ was found to be 318; calculation gave a $k_H:k_D$ value for benzene of 2.45 (318/130).

Conversion of Nitro-Substituted Benzophenones to Benzophenones (Replacement of NO_2 by H). Competitive reaction products of *p*-nitrobenzoyl, 3,5-dinitrobenzoyl, and 2,4-dinitrobenzoyl chlorides were converted to the corresponding benzophenones and analyzed as such by gas–liquid chromatography. A typical experiment was as follows. A mixture of 0.005 mol of competitive reaction products, 0.03 mol of stannous chloride crystals,[11] and 10 g of concentrated hydrochloric acid was placed at 0° in a flask equipped with a thermometer and reflux condenser, then warmed up to 80° and kept for 30 min. The solution was cooled in an ice water bath, neutralized with 30% sodium hydroxide solution, and extracted three times with ether. Evaporation of ether gave the corresponding anilines whose analysis by ir and nmr spectroscopy confirmed the conversion of the nitro groups to amino groups. The aminobenzophenones were diazotized at 5–10° by treating a mixture of 0.003 mol of amines, 0.9 g of concentrated hydrochloric acid, and 10 g of water with 0.009 mol of sodium nitrite in 2 g of water. The solution was then added to 30 g of 30% hypophosphorous acid solution[12] and placed in a refrigerator overnight. The reaction mixture was extracted with ether, dried over Na_2SO_4, concentrated, and analyzed by gas–liquid chromatography.

Gas–Liquid Chromatographic Analysis. The analyses of all products were carried out by gas–liquid chromatography on a Perkin-Elmer Model 226 gas chromatograph equipped with a hydrogen flame ionization detector system and open tubular capillary columns. Characteristic retention time of benzaldehyde, acetophenone, and benzophenone derivatives along with Golay-type capillary columns employed and column temperatures are listed in Table III. Peak areas were determined with an Infotronics Model CRS-1 electronic integrator. Products were identified by comparison with authentic samples.

Acknowledgment. Partial support of our work by the Petroleum Research Fund, administered by the American Chemical Society, and the C. F. Mabery Fund of Case Western Reserve University is gratefully acknowledged. Esso Research and Engineering Company is also thanked for their help.

[11] J. S. Buck and W. S. Ide, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 130.

[12] N. Kornblum, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 295.

Participation of Acetylenic Bonds in Pericyclic Reactions. Thermal Cleavage of β-Hydroxyacetylenes

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Received December 8, 1970

Abstract: The ability of acetylenic systems to participate in intramolecular reactions proceeding *via* six-membered cyclic transition states has been established by thermolyses of a number of substituted β-hydroxyacetylenes, in both the vapor and the liquid states. Thermolyses products consisted solely of those allenes and carbonyl compounds derivable from a 1,5-hydrogen transfer. The homogeneous reactions followed the first-order rate law. Activation energies with a variety of alkyl substituents were essentially within experimental error. The activation parameters, $E_a \sim 40$ kcal/mol and $\Delta S^{\ddagger} \sim -10$ eu, are indicative of a cyclic transition state and closely parallel the parameters for the cleavages of those analogous olefins whose data are available. However, the acetylenic compounds utilized reacted at rates varying from 1.3 to 7 times as fast as those of their olefinic analogs. The effects of alkyl, phenyl, and vinyl substituents, and relative rate comparisons with the reaction of analogous olefins, are in accord with a planar transition state for the participation of the triple bond.

The investigation reported herein concerns the participation of acetylenes in reactions whose olefinic analogs normally proceed *via* six-membered cyclic transition states. Although the acetylenic bond is considered to be linear in the ground state in acyclic molecules, the existence of cyclooctyne and the transitory formation of smaller cycloalkynes, down to cyclopentyne,[2] suggest that deviation from linearity is not improbable.[3]

Among the recent reports of reactions of acetylenes which fall into the above category are the following: thermolyses of vinyl propargyl ethers to yield 3,4-pentadienals[4] in the vapor as well as in the liquid phase

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[1] (a) Northeastern University; (b) Universidad del Valle.

[2] L. K. Montgomery and L. E. Applegate, *J. Amer. Chem. Soc.*, **89**, 5305 (1967), and references cited therein.

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