Pentafluorophenyl Group. Electronic Effect as a Substituent

William A. Sheppard

Contribution No. 1652 from the Central Research Department,
Experimental Station, E. I. du Pont de Nemours and Company,
Wilmington, Delaware 19898. *Received January 17, 1970*

Abstract: The substituent parameters for the pentafluorophenyl group have been determined by classical pK_a measurements and ^{19}F nmr calibrations on the appropriate pentafluorobiphenyl derivatives. The pentafluorophenyl group inductively withdraws electrons more strongly than a phenyl group but much less than a trifluoromethyl group. Resonance effects were not significant but would be prevented in these systems by steric interactions. The pentachlorophenyl group was similar to pentafluorophenyl. The results are interpreted in terms of p–π interactions.

Perfluoroaromatic chemistry has recently become a subject of considerable interest, particularly in preparation of organometallic derivatives and in aromatic nucleophilic substitution studies.[1] The pentafluorophenyl group has been assumed to be strongly electron withdrawing but the only quantitative data are the pK_a of pentafluorophenol[2] and pentafluorobenzoic acid[3] (Table I). As expected the inductive effect of the five fluorines increases the acidity of the phenol or benzoic acid but the *ortho* fluorines are too near the site of measurements to allow proper evaluation of the group as a substituent. The Hammett substituent parameters for C_6F_5 were crudely estimated as σ_m of 0.22 from ^{19}F nmr chemical shift correlation on a series of pentafluorophenyl phosphorus compounds, C_6F_5PXY,[4] and σ_p of 0.42 from a correlation of rates of reaction of substituted pentafluorobenzenes with sodium pentafluorophenolate.[5]

Table I. Ionization Constants of Phenols[a] and Benzoic Acids[b]

	pK_a
C_6H_5OH	9.9
C_6F_5OH	5.5
C_6Cl_5OH	5.2
$C_6H_5CO_2H$	4.21
$C_6F_5CO_2H$	3.38

[a] See ref 2. [b] See ref 3.

We have now obtained quantitative measure of the electronic effect of the pentafluorophenyl group by classical methods. The needed pentafluorobiphenyl derivatives (*meta* and *para* substituted) **1**, **2**, **3**, and **4** were prepared by using the coupling reaction of the new pentafluorophenylcopper reagent.[6,7] The pentachlorofluorobiphenyls **5** were prepared by oxidative coupling of lithium (pentachlorophenyl)(fluorophenyl)-copper.[8]

$$C_6F_5Cu + IC_6H_4CO_2CH_3 \longrightarrow C_6F_5C_6H_4CO_2CH_3 \xrightarrow{H_3O^+} C_6F_5C_6H_4CO_2H$$

1

$$C_6F_5Cu + BrC_6H_4NO_2 \longrightarrow C_6F_5C_6H_4NO_2 \xrightarrow[HCl]{H_2} C_6F_5C_6H_4NH_2$$

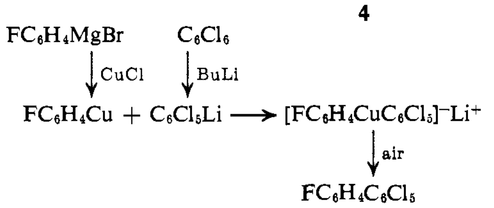
2

$$C_6F_5Cu + IC_6H_4N(CH_3)_2 \longrightarrow C_6F_5C_6H_4N(CH_3)_2$$

3

$$C_6F_5Cu + IC_6H_4F \longrightarrow C_6F_5C_6H_4F$$

4



$$\begin{tikzcd}
FC_6H_4MgBr \arrow[d, "CuCl"] & C_6Cl_6 \arrow[d, "BuLi"] & \\
FC_6H_4Cu & + \; C_6Cl_5Li \arrow[r] & {[FC_6H_4CuC_6Cl_5]^-Li^+} \arrow[d, "air"] \\
& & FC_6H_4C_6Cl_5
\end{tikzcd}$$

5

The aniline derivatives **2** were too insoluble in the aqueous system commonly used for pK_a measurements, but the N,N-dimethylanilines **3** were soluble in 45% dioxane–55% water employed previously.[9] Because of solubility problems, the acidity of the benzoic acids was measured in 75% methanol–25% water at 39.8°.[10] Nmr ^{19}F measurements on the *meta*- and *para*-fluoro-substituted pentafluorobiphenyls **4** were used for determination of the σ_I and σ_R values by the method of Taft.[9,11] In addition σ_I and σ_R parameters were estimated from the chemical shifts of the *meta* and *para* fluorines in decafluorobiphenyl.[12]

Experimental Section

1. Synthesis. A. Coupling Reaction. Pentafluorophenylcopper was prepared by the literature procedure[6] and used directly as the dioxane complex. As an example of the coupling procedure, 0.010 mol of *p*-fluoroiodobenzene and 0.010 mol of $(C_6F_5Cu)_2$–dioxane in benzene solution were heated to reflux for 2 hr under nitrogen. The solution was cooled and filtered to remove cuprous halide, and the light yellow product sublimed and purified by recrystallization from ethanol. The physical and analytical properties of all products prepared by this procedure are given in Table II.

B. (Pentafluorophenyl)benzoic Acid. Methyl *p*-(pentafluorophenyl)benzoate (1.25 g, 0.0415 mol) was hydrolyzed by heating

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(1) For a review of perfluoroaromatic chemistry, see W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1969, pp 357, 439.

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(5) R. J. DePasquale and C. Tamborski, *J. Org. Chem.*, **32**, 3163 (1967).

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(7) R. J. DePasquale and C. Tamborski, *J. Org. Chem.*, **34**, 1736 (1969).

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(9) W. A. Sheppard, *J. Amer. Chem. Soc.*, **87**, 2410 (1965).

(10) W. N. White, R. Schlitt, and D. Gwynn, *J. Org. Chem.*, **26**, 3613 (1961).

(11) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *J. Amer. Chem. Soc.*, **85**, 709, 3146 (1963).

(12) M. G. Hogben and W. A. G. Graham, *ibid.*, **91**, 283 (1969).

Table II. Perhalophenyl Derivatives. Preparation and Properties

Compd	Isomer	Mp, °C	Re-crystallzn solvent	Method of prepn[a] (% yield)	Formula	Mol wt	Calcd, %				Found, %			
							C	H	F	N	C	H	F	N
$C_6F_5C_6H_4F$	*meta*	63–64	Ethanol	A (73)	$C_{12}H_4F_6$	262.2	55.0	1.54	43.5		54.8	1.60	43.5	
	para	118–119	Ethanol	A (78)							55.0	1.77	43.5	
$C_6F_5C_6H_4NO_2$	*meta*	106–108	Ethanol	A (85)	$C_{12}H_{11}F_5NO_2$	289.2	49.8	1.39	32.9	4.85	49.9	1.50	32.7	5.02
	para	87–89	Ethanol	A (85)							49.7	1.94		4.94
$C_6F_5C_6H_4NH_2$	*meta*	103–104	Hexane	C (90)	$C_{12}H_6F_5N$	259.2	55.6	2.34	36.7	5.41	55.9	2.09	35.6	5.40
	para	135–136	Hexane	C (81)							55.6	2.02	36.3	5.53
$C_6F_5C_6H_4N(CH_3)_2$	*meta*	90–90.5	Hexane	A (33)	$C_{14}H_{10}F_5N$	287.2	58.5	3.52	33.1	4.88	58.2	3.42	32.7	4.76
	para	158–160	Hexane	A (26)							58.2	3.28	33.0	4.73
$C_6F_5C_6H_4CO_2CH_3$	*meta*	107–108.5	Methanol	A (96)	$C_{14}H_7F_5O_2$	302.2	55.6	2.53	31.4		55.8	2.37	31.7	
	para	115–116.5	Methanol	A (97)							56.0	2.41	32.0	
$C_6F_5C_6H_4CO_2H$	*meta*	247–250	Benzene	B (87)	$C_{13}H_5F_5O_2$	288.2	54.2	1.75	33.0		54.6	1.89	33.1	
	para	221–223.5	Benzene	B (88)							54.3	1.75	33.2	
$C_6Cl_5C_6H_4F$	*meta*	87.5–88	Pentane	D (3)	$C_{12}H_4Cl_5F$	344.4	41.8	1.17			42.4	1.26		
	para	171–172	Hexane	D (3)							42.2	1.51		

[a] Letter refers to procedure listed in the Experimental Section.

at 110° in 15 ml of concentrated sulfuric acid for 30 min. The product was isolated by pouring the solution into ice and water, and filtering. The (pentafluorophenyl)benzoic acid, 1.05 g (88%), was purified by recrystallization from benzene and sublimations.

C. **(Pentafluorophenyl)aniline.** (Pentafluorophenyl)nitrobenzene was hydrogenated in ethanol containing 1 equiv of hydrogen chloride.[9]

D. **(Pentachlorophenyl)fluorobenzene.** Fluorophenylcopper, 0.1 mol, prepared in tetrahydrofuran (THF) solvent from fluorophenylmagnesium bromide and cuprous bromide,[6] was added to 0.1 mol of pentachlorophenyllithium[13] (prepared from hexachlorobenzene in THF and *n*-BuLi in pentane at −78° over 30 min). The mixture was stirred at −78° for 30 min and then dry air was passed over the stirred solution for 1 hr as it warmed to room temperature.[8] The mixture was hydrolyzed with ammonium chloride and the organic phase extracted into benzene. After drying and evaporation of the solvent, the organic product was purified by chromatography over neutral alumina using pentane as elutant. Decachlorobiphenyl by-product was eluted first, the desired (pentachlorophenyl)fluorobenzene next, and finally the difluorobiphenyl by-product.

2. **Physical Measurements. A. Ionization Constant Measurements.** The ionization constants of the benzoic acids and N,N-dimethylanilines were determined by literature methods. Because of poor solubility, the benzoic acids were titrated in 75% methanol–25% water at 39.8°,[10] a method developed for the highly insoluble benzoylbenzoic acids. To check our experimental procedure, a series of known benzoic acids were run by this procedure (Table III); all gave acceptable values except those with more highly fluorinated substituents. The ionization constants of the N,N-dimethylanilines were determined in 45% dioxane–55% water at 25° by the uv method as reported previously[9] for other N,N-dimethylanilines with fluorinated substituents. The results are reported in Table IV.

Table III. Ionization Constant Data on Benzoic Acids in 75% Methanol–25% Water at 39.8 ± 0.1°

$$XC_6H_4CO_2H \rightleftharpoons XC_6H_4CO_2^- + H^+$$

X of $XC_6H_4CO_2H$	−Log k[a]	Lit.[b] −log k	Calcd σ[c]	Lit. σ
H	6.05	5.995 ± 0.013	0	0
p-NO_2	4.90	4.920	0.78	0.78[d]
m-Cl	5.48		0.35	0.37[d]
m-CF_3	5.31		0.48	0.43[e]
p-CF_3	5.30		0.48	0.54[e]
m-OCF_3	5.38		0.42	0.40[f]
m-$CF(CF_3)_2$	5.61		0.25	0.37[e]
p-$CF(CF_3)_2$	5.41		0.40	0.53[e]
m-C_6F_5	6.11		−0.12	
p-C_6F_5	5.99		−0.03	

[a] Average of at least two determinations with precision of ±0.01. [b] Reference 10. [c] For calculation[10] $\rho = -1.339$, $\log k_0 = 5.947$. [d] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958). [e] Reference 9. [f] W. A. Sheppard, *J. Amer. Chem. Soc.*, **85**, 1314 (1963).

Table IV. Ionization Constants of N,N-Dimethylanilines in 45% Dioxane–55% Water at 25°

X of $XC_6H_4N(CH_3)_2$	λ_{max}, mμ	pK_a	σ[a]
H	252	4.14 (4.00)[b]	0
m-C_6F_5	318	2.64	0.34
p-C_6F_5	308	2.33	0.41

[a] Calculated using $\rho = +4.053$. [b] Intercept value used in calculation.

B. **Nmr Calibrations.** The ^{19}F nmr calibrations were carried out as described previously,[9] following the procedure of Taft.[11] The measurements were made in trichlorofluoromethane (also serves as internal standard) or in solvent containing 5% 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane at 20, 10, and 5% concentration; the reported chemical shifts values are from extrapolation to infinite dilution. The ^{19}F chemical shifts on the monofluorobenzene group are given in Table V. The chemical shifts for the pentafluorobenzene ring are given in Table VI.

C. **Substituent Parameters.** The Hammett σ constants were calculated by standard methods[9] from the ionization constant data. Substituent parameters from ^{19}F nmr chemical shifts were calculated by the method of Taft[11] for the monofluorobenzene group. For the pentafluorophenyl group the recently defined relationships[12]

$$\phi_p = -49.05\sigma_R^0 - 16.00\sigma_I + 153.72$$

$$\phi_m = -9.36\sigma_R^0 - 6.91\sigma_I + 162.71$$

were employed to calculate σ_I and σ_R^0. The σ_I and σ_R or σ_R^0 parameters were calculated according to Taft.[14] The substituent parameters are summarized in Table VII with comparative values for the phenyl and trifluoromethyl substituents.

Discussion

The substituent constants for the pentafluorophenyl group, as summarized in Table VII, appeared to vary widely depending on the method of measurement. A certain amount of variation is expected, but the value determined from the pK_a of benzoic acids appears anomalous and will be discussed below. The parameters determined by ^{19}F chemical shifts by the method

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(14) M. D. Rausch, F. E. Tibbetts, and H. B. Gordon, *J. Organometal. Chem.*, **5**, 493 (1966).

(15) R. W. Taft, *J. Phys. Chem.*, 64, 1805 (1960).

Table V. ^{19}F Chemical Shifts for Fluorobenzenes (XC_6H_4F) at Infinite Dilution Relative to Fluorobenzene

		δ in solvents,[a] ppm					
X of XC_6H_4F	Isomer	CCl_3F	Benzene	Methylene chloride	Acetonitrile	Acetone	Methanol
C_6H_5[b]	*meta*	+0.15[c]	+0.03		−0.23	−0.08	+0.08
	para	+2.90				2.70	2.80
C_6F_5	*meta*	−1.15	−1.12	−1.03	−0.92	−0.87	−0.91
	para	−1.78	−1.65	−1.77	−1.70	−1.60	−1.77
C_6Cl_5	*meta*	−1.19	−1.03	−0.99	−0.91	−0.87	I[d]
	para	−0.83	−0.73	−0.85	I	−0.71	I

[a] Chemical shifts (in hertz) of fluorobenzene at infinite dilution in each solvent relative to internal standard of 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane are: benzene −34, methylene chloride +6, acetonitrile +32, acetone +15, methanol +12, and fluorotrichloromethane (internal standard) +6382 Hz. [b] Data from ref 12. [c] Data in CCl_4. [d] I, too insoluble for nmr measurements.

Table VI. ^{19}F Chemical Shifts of Pentafluorophenyl Group in Pentafluorobiphenyl Derivatives

	δ, ppm[a]				
Compd	ϕ_o	ϕ_m	ϕ_p	σ_I[b]	σ_R^0[b]
C_6F_6		163.01			
$C_6H_5C_6F_5$	143.9	163.5	156.8	−0.03	−0.07
m-$FC_6H_4C_6F_5$	143.5	162.8	155.6	+0.07	−0.06
p-$FC_6H_4C_6F_5$	144.0	163.2	156.3	−0.01	−0.05
$(C_6F_5)_2$	138.9	161.8	151.5	+0.15	0

[a] Chemical shifts (in parts per million) of *o*-, *p*-, and *m*-fluorines in chlorotrifluoromethane as solvent and internal calibrant, extrapolated to infinite dilution. The ϕ scale is based here on C_6F_6 = 163.0 ppm upfield from $CFCl_3$ (see ref 12). [b] Calculated from ϕ_m and ϕ_p by method given in ref 12.

Table VII. Substituent Parameters

Substituent	Method[a]	σ_m	σ_p	σ_I	σ_R^0
C_6F_5	Benzoic	−0.12	−0.03		
	DMA	+0.34	+0.41		
	^{19}F mono	0.26	0.27	0.25	0.02
	^{19}F penta			0.15	0.00
C_6Cl_5	^{19}F mono	0.25	0.24	0.25	−0.01
C_6H_5	Benzoic[b]	0.22	0.01		
	^{19}F mono[c]	0.04	0	+0.08	−0.09
	^{19}F penta			−0.03	−0.07
CF_3	Benzoic[d]	0.42	0.53	0.41	0.09
	DMA[d]	0.48	0.60		
	^{19}F mono[d]	0.44	0.49	0.39	0.10
	^{19}F penta			0.33[e]	0.01[e]

[a] Method for calculation of substituent parameters described in the Experimental Section; designations are: benzoic, benzoic acid pK_a; DMA, N,N-dimethylanilinium ion pK_a; ^{19}F mono, from ^{19}F chemical shifts of *m*- and *p*-fluorobenzene derivatives by method of Taft; ^{19}F penta, from ^{19}F chemical shifts of *m*- and *p*-fluorines in pentafluorobenzene derivatives by method of ref 12. [b] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958). [c] Reference 11. [d] Reference 9. [e] Calculated using ϕ_m and ϕ_p values given in ref 12.

of Taft and from the pK_a of the N,N-dimethylanilinium ions do agree within the range normally found. The parameters calculated by the ^{19}F chemical shifts in the pentafluorophenyl ring gave σ_I values approximately 0.1 lower than by Taft's method (also noted for phenyl and trifluoromethyl). However, this type of correlation suffers because of p–p and p–π interactions involving fluorines adjacent to each other and sterically interacting with the substituent. The following observations are obvious from the data in Table VII.

1. The pentafluorophenyl group is inductively electron withdrawing, intermediate between nearly neutral phenyl and the much stronger trifluoromethyl.
2. The pentafluorophenyl group shows an insignificant electron-withdrawing effect by resonance.
3. The pentachlorophenyl group is inductively electron withdrawing, almost identical with the pentafluorophenyl. It also shows an insignificant resonance effect.

Several conclusions or explanations can be advanced for the above observations.

1. The inductive effect of a pentafluorophenyl group appears much less than might be predicted, particularly since the aromatic system with five fluorines is much weaker than the methyl with three fluorines. The weaker inductive effect of the pentafluorophenyl group may result from a partial cancellation of the inductive effect of the fluorines by donation of electron density from the p electrons of fluorine to the π system of the ring.[15a]

However, since the inductive effect is proportional to distance through space or through σ bonds, the measured effect could be considered normal. That is, the distances are such that the five fluorines on the pentafluorophenyl could be considered equivalent to a β-trifluoromethyl substituent. The σ_I values for phenyl and 2,2,2-trifluoroethyl[15b] add up to about 0.25, in agreement with the experimental value. However, this argument can be discounted because transmission through the π system is considerably different from that through saturated hydrocarbon so that the similar experimental and calculated values are probably fortuitous.

2. The resonance effect is negligible because steric interactions would prevent the pentafluorophenyl ring from becoming coplanar with the other phenyl. Indeed, examination of molecular models shows the pentafluorophenyl group must be twisted out of the plane by a greater amount than biphenyl because of interactions of the *ortho* fluorines with the *ortho* hydrogens of the other ring. Biphenyls have been estimated to be twisted 50° out of the plane through the *ortho* hydrogen interactions, and resonance interaction between the two rings is negligible.[16] The slight positive resonance effect noted could result from p–π electron donation of the unshared electrons of the *ortho* fluorines to the π system of the adjacent ring similar to that proposed for p–π interaction of a trifluoromethyl group with an aromatic ring.[9]

3. The apparent anomaly that the (pentafluorophenyl)benzoic acids are weaker than benzoic must

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(15) (a) For a discussion of p–π interactions, see ref 1, pp 33–40; (b) W. A. Sheppard, unpublished results.

(16) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1955, pp 158–159.

result from some unusual solvent interaction associated with the highly fluorinated substituent. The perfluoroisopropyl group also showed a decreased σ value when determined from the $\mathrm{p}K_a$ of benzoic acids in this solvent system; actually the σ_m of the perfluoroisopropyl group calculated from the $\mathrm{p}K_a$ of the benzoic acid in 50% ethanol–water had previously been noted to be low compared to parameters determined by other methods.[9] Whether this solvent interaction effect involves the un-ionized or ionized form is not clear at this point.

In conclusion, the pentafluorophenyl group is electron withdrawing inductively, but much weaker than the trifluoromethyl group or single halogen atoms.[17] The interaction between the p electrons of the five fluorines and the π system obviously greatly disturbs the electron distribution in the phenyl ring so that it no longer behaves as a typical aromatic system. Many of the unusual properties of perfluoroaromatic compounds, particularly perfluorophenylorganometallic, cannot be simply ascribed to a strong electron-withdrawing effect of the pentafluorophenyl ring but rather to the unusual π system that results from p–π interactions.

Acknowledgments. We wish to acknowledge with thanks the special assistance received from Mrs. Joan Hogan on $\mathrm{p}K_a$ measurements, Miss Ellen Wallace for ultraviolet measurements, Mr. Louis Walther for nmr calibrations, and Mr. Ed Wonchoba and Dr. Allan Cairncross on synthesis.

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[17] A similar conclusion has been reached by C. A. Tolman [*J. Amer. Chem. Soc.*, **92**, 2953 (1970)] from a spectroscopic study of the electron donor–acceptor properties of phosphorus ligands.

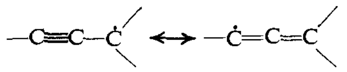
Stereochemistry of Addition Reactions of Allenes. III. Free-Radical Reactions of 2,3-Pentadiene and 2-Pentyne with *t*-Butyl Hypochlorite

Larry R. Byrd[1] and Marjorie C. Caserio[2,3]

Contribution from the Department of Chemistry, University of California, Irvine, California 92664. Received December 31, 1969

Abstract: Free-radical chlorination of 2,3-pentadiene with *t*-butyl hypochlorite has been found to give substitution products that may be formally considered as arising from both allylic and allenic hydrogen abstraction. Allenic abstraction led to formation of 4-chloro-2-pentyne which was also formed in the related chlorination of 2-pentyne. No 2-chloro-2,3-pentadiene was detected in the products from either hydrocarbon. Also, optically active 2,3-pentadiene gave racemic 4-chloro-2-pentyne. These results are discussed in terms of the radical intermediates involved, particularly with respect to the hybrid nature of the 2,3-pentadienyl radical. Competitive chlorination of 2,3-pentadiene and 2-pentyne indicates that the order of reactivity of hydrogen toward *t*-butoxy radicals is allenic ~ propargylic > allylic. Addition products were also formed in the chlorination of 2,3-pentadiene and were identified as *cis*- and *trans*-3,4-dichloro-2-pentene and *cis*- and *trans*-3-*t*-butoxy-4-chloro-2-pentene. Chlorination of optically active 2,3-pentadiene produced racemic adducts, which suggests the intervention of symmetrical resonance-stabilized allylic intermediates. Addition products were the major products of chlorination of 2,3-pentadiene and 2-pentyne in ether solution which reactions were observed to proceed by spontaneous initiation. The major product of reaction with either hydrocarbon as solvent was 4-chloro-2-pentyne. The effects of solvation of *t*-butoxy radicals in determining product distribution and the question of spontaneous initiation are briefly discussed.

Free-radical reactions of certain allenes and isomeric acetylenes and their derivatives can in principle lead to the formation of common resonance-stabilized radical intermediates which may be considered as hybrids of propargylic and allenic structures, A and B.



A B

The physical and chemical evidence pertaining to the hybrid nature of propargylic free radicals and the factors influencing the distribution of propargylic and allenic products obtained with various atom transfer agents have been carefully reviewed by Fantazier and Poutsma.[4] In summary, the relative energies of the two possible transition states and hence the product distribution for reactions at the two nonequivalent termini of propargylic radicals appear to depend in part on the relative thermodynamic stabilities of the derived products and in part on the relative spin densities at the two reacting termini. Steric effects may also play a role but their importance is difficult to evaluate.

In the case of photoinduced halogenation of allenes and acetylenes with chlorine and with *t*-butyl hypohalites, the major substitution products are propargylic halides even when the haloallene is known to be the more stable isomer. Reactions of this type therefore exhibit kinetic control and reflect a greater contribution of the propargylic structure A to the intermediate

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[1] N.D.E.A. Fellow, 1967–present.

[2] The authors wish to gratefully acknowledge the support of this work by the donors of the Petroleum Research Fund of the American Chemical Society (PRF 2357-A1,4).

[3] Part II: W. S. Linn, W. L. Waters, and M. C. Caserio, *J. Amer. Chem. Soc.*, **92**, 4018 (1970).

[4] R. M. Fantazier and M. L. Poutsma, *ibid.*, **90**, 5490 (1968).