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α-Substituted Toluenes and 3-Substituted Propenes. Evaluation of Substituent Effects via Carbon-13 Nuclear Magnetic Resonance Spectroscopy

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The ^{13}C NMR shielding effects for 12 α-substituted toluenes and nine 3-substituted propenes have been determined. The substituent effects were analyzed by the Taft σ_I and σ_R and by the Swain–Lupton **F** and **R** parameters. No significant difference was observed between the two methods. In the α-substituted toluenes substantial substituent shifts were observed at C_4 (para to methylene), five bonds removed from the substituent. Excellent correlation between the toluenes and propenes was obtained for the methylene and C_1 carbons. A substantial resonance interaction was found to be important to describe the substituent effects at C_1 in toluene and C_2 in propene.

The correlation of the effects of substituents on carbon-13 shieldings is an important facet of the current research in ^{13}C NMR spectroscopy.[1] Once determined, these substituent effects can, in principle, be used to predict chemical shifts and thus lend valuable aid to the interpretation of complex spectra. Substituent effect studies have also played a significant role in the correlation of chemical and physical properties with molecular structure.[2] From the studies of substituent effects on fluorine-19, proton, and carbon-13 chemical shifts in substituted benzenes, it is apparent that the substituent is capable of altering the electronic structure of the aromatic ring in a predictive fashion.[3] Recently, a significant carbon-13 substituent effect through eight covalent bonds was observed for substituted biphenyls.[4] Similar results have been reported using ^{19}F NMR where the substituent effect was transmitted through an "insulating" methylene cavity.[5]

The nature of the transmission of substituent effects in α-substituted toluenes, particularly the halogenated cases, has been addressed by various methods. It has been shown that α-substitution, even by a nitro group, does not markedly affect the ortho–para directability in these systems.[6] The acidity of α-substituted *p*-toluic acids as a function of the α substituent indicated that a π-inductive mechanism was operating.[7] Other studies, including PES spectra, have attributed the substituent effect to a hyperconjugative mechanism.[8,9] Since it has been established that the carbon-13 chemical shift is sensitive to π-charge density,[3a] it would be of interest to see how the carbon-13 chemical shifts behave with respect to a variety of substituents at the benzylic position. Additionally, it should prove informative to compare the substituent effects obtained from aromatic systems to those of the ethylene derivatives, in this instance 3-substituted propenes.

The use of linear free energy relationships has found great utility in the study of substituent effects in NMR spectroscopy.[3b,c] In general, the contributions to the chemical shift changes induced by the substituent are attributable to either inductive or field and resonance effects.[10] In order to obtain the relative importance of these interactions a two (or more) parameter equation such as eq 1 can be used[11]

$$\Delta\delta = aA + bB + i \qquad (1)$$

where Δδ is the chemical shift difference for a particular carbon in the parent compound vs. the same carbon in the substituted case; *A* is the inductive and field parameter taken together, and *B* is the resonance parameter. For the purpose of the study herein two different but equally diagnostic forms of eq 1 will be evaluated: that of Swain and Lupton,[11b] where $A = \mathbf{F}$ and $B = \mathbf{R}$, and that of Taft,[11a] where $A = \sigma_I$ and $B = \sigma_{R^\circ}$. The terms *a* and *b* (correlation factors) are determined by a minimization of the difference between the experimental chemical shifts and the chemical shifts calculated on the basis of eq 1. The term *i* is the intercept of the regression analysis and corresponds to the calculated shift of a particular carbon in the parent system.[12] The percent of contribution for each of the correlation factors can be obtained by the relative magnitudes of the absolute *a* and *b* values.[11b]

Results

The ^{13}C NMR spectra were recorded in deuteriochloroform solution, and all chemical shifts were determined from proton decoupled spectra using Me_4Si as internal reference.

The carbon-13 chemical shifts for the α-substituted toluenes are given in Table I. The aromatic assignments were determined as follows. The C_1 carbon (methylene substituted carbon) was readily identified by its low intensity and its singlet nature in the proton coupled spectrum. Likewise the assignment of the C_4 carbon could be easily established via intensity considerations since it is only ca. one-half the area of the other two signals. The $C_{2,6}$ and $C_{3,5}$ carbon shift assignments were more difficult to make, and in those cases where the chemical shifts are close, the assignments given in Table I may be reversed. However, when the $C_{2,6}$ and $C_{3,5}$ carbon shifts are separated by more than ca. 0.5 ppm and no overlap with the C_4 resonance occurs, the assignments could be obtained from inspection of the proton coupled spectrum. The $C_{2,6}$ carbon resonance appears as a broad multiplet owing to two different three-bond couplings (protons meta to $C_{2,6}$), a two-bond coupling (protons ortho to $C_{2,6}$) and a four-bond coupling (from the proton para to $C_{2,6}$), while the $C_{3,5}$ carbon resonance appears as a broad doublet owing to one three-bond, two two-bond, and one four-bond couplings.[13] The assignments, see Table III, for the 3-propenes are straightforward,

Table I. Chemical Shift of Toluene Compounds (ppm Relative to Internal Me_4Si) [a]

Registry no.	X	CH_2	C_1	$C_{2,6}$	$C_{3,5}$	C_4	Other
108-88-3	H	21.3	137.8	129.3	128.5	125.6	
100-41-4	CH_3	29.3	144.1	128.1	128.5	125.9	16.8 (CH_3)
101-81-5	Ph	42.0	141.3	129.0	128.5	126.2	
350-50-5	F[b]	84.9	137.0	127.8[c]	128.7[c]	125.9	
100-44-7	Cl	46.2	137.5	128.6[c]	128.5[c]	128.3	
100-39-0	Br[b]	33.4	137.8	129.0[c]	128.6[c]	129.0	
620-05-3	I	5.9	139.0	128.5	128.5	127.6	
140-29-4	CN	23.4	130.2	129.0	127.7	127.9	118.0 (CN)
622-42-4	NO_2[b]	81.0	130.7	130.7	130.7	129.7	
100-46-9	NH_2	46.4	143.3	127.0	128.4	126.6	
100-51-6	OH	64.9	140.5	127.2	128.6	127.7	
140-11-4	$OCOCH_3$	66.3	136.4	128.4[c]	128.6[c]	128.4	20.9 (CH_3) 170.7 (CO)

[a] Ca. 20% v/v in deuteriochloroform. [b] L. Zetta and G. Gatta, *Org. Magn. Reson.*, **4**, 585 (1972). [c] Shifts in the same row may be reversed.

Table II. Relative Chemical Shifts of Benzyl Substituted Compounds vs. Toluene [a]

X	CH_2	C_1	$C_{2,6}$	$C_{3,5}$	C_4
CH_3	8.0	6.3	−1.2	0.0	0.3
Ph	20.7	3.5	−0.3	0.0	0.6
F[c]	63.6	−0.8	−1.5 (−0.4)[b]	0.4 (−0.7)	0.3
Cl	24.9	−0.3	−0.7 (−0.8)	0.0 (0.1)	2.7
Br	12.1	0.0	−0.3 (−0.7)	0.1 (−0.3)	3.4
I	−15.4	1.2	−0.8	0.0	2.0
CN	2.1	−7.6	−1.4 (−0.3)	0.5 (−0.6)	2.3
NO_2[c]	59.7	−7.1	1.4	2.2	4.1
NH_2	25.1	5.5	−2.3	−0.1	1.0
OH	43.6	2.7	−2.1	0.1	2.1
$OCOCH_3$	45.0	−1.4	−0.9 (−0.7)	0.1 (−0.1)	2.8

[a] Negative sign indicates an upfield shift. [b] Values in parentheses are for alternate assignments. [c] See Table I.

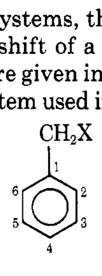
Table III. Chemical Shift Values for Propene Systems (ppm relative to Me_4Si)

Registry no.	X	$CH_2{=}CHCH_2X$		
		CH_2	C_1	C_2
115-07-1	H[a]	18.7	136.2	115.9
106-98-9	CH_3[c]	26.8 (8.1)[b]	140.2 (4.0)	113.5 (−2.4)
300-57-2	Ph	40.3 (21.6)	137.5 (1.3)	115.7 (−0.2)
107-05-1	Cl	45.3 (25.8)	134.0 (−2.2)	118.4 (2.5)
106-95-6	Br	32.8 (14.1)	134.5 (−1.7)	118.9 (3.0)
109-75-1	CN	21.4 (2.7)	126.5 (−9.7)	119.3 (3.4) (117.2) CN
107-11-9	NH_2	44.6 (25.9)	141.0 (4.8)	112.9 (−3.0)
107-18-6	OH	63.3 (44.6)	137.5 (1.7)	114.9 (−1.0)
591-87-7	$OCOCH_3$	64.7 (46.0)	133.1 (−3.1)	117.8 (1.9)

[a] J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972. [b] Values in parentheses are Δδ values vs. propene. [c] See T. Vonemoto, *J. Magn. Reson.*, **13**, 153 (1974).

and except for propenyl cyanide the shifts compare well with those already reported in the literature.[14] The shift values for propenyl cyanide reported here are consistent with observed substituent effects for this moiety; thus the value reported in ref 14a is in error.

In order to facilitate the discussion of the general trends observed for the substituent effects in the toluene and 3-propene systems, the Δδ values (the difference between the chemical shift of a particular carbon vs. that of the parent system) are given in Tables I and III, respectively. The numbering system used in this study is shown below. On inspection of these data, it is apparent that the Δδ values for the benzylic and allylic methylene carbons vary over a range of ca. 80 ppm. By plotting the respective Δδ values for the methylene carbons in these two systems against each other, an excellent straight line is obtained, see Figure 1, with a correlation coefficient of >0.99 and a slope of 1.02. Good correlation is also found if these methylene Δδ values are plotted vs. the Δδ values obtained for simple aliphatic systems (Figure 2).[14a,15] A plot of the Δδ values vs. group electronegativity[16] does not correlate to a high degree; however, the order of the shifts suggests that the α-substituent effect is primarily inductive in nature.



$$H_2\overset{2}{C}{=}\overset{1}{C}H{-}CH_2X$$

The C_1 carbon of the toluene and the C_1 carbon of the propene systems are also found to experience similar substituent shifts. A plot (Figure 3) of the carbon shifts for these two systems yields a straight line with a correlation coefficient of 0.98 and a slope of 1.08. The correlation of the substituent

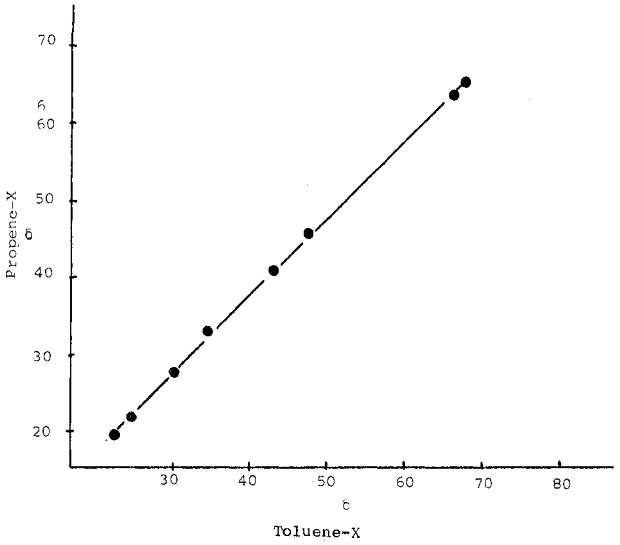


Figure 1. Comparison of the methylene carbon substituent effects for the toluene and propene systems.

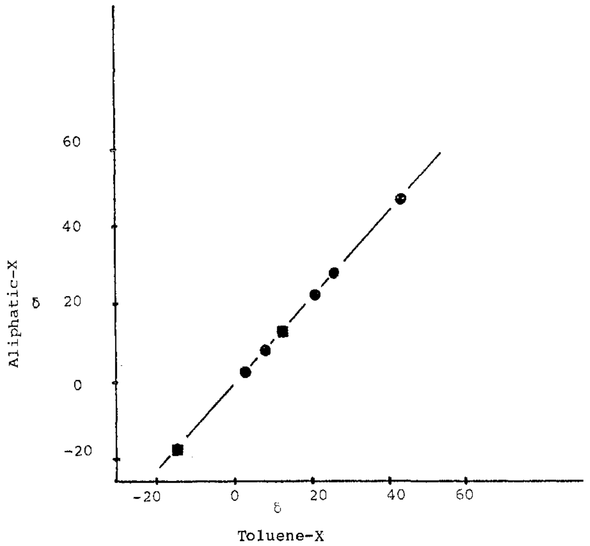


Figure 2. Comparison of the methylene carbon substituent effect for the toluene system with that of similarly substituted aliphatic systems: ●, data from ref 14a; ■, data from ref 15b.

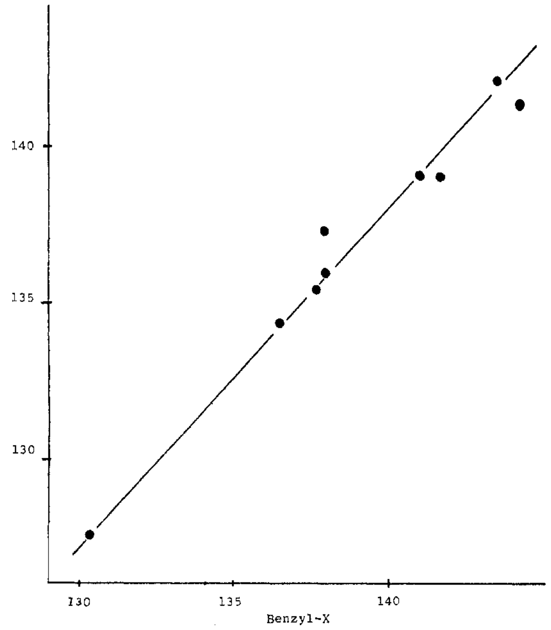


Figure 3. Comparison of the C_1 chemical shift for the toluene-X and propene-X systems.

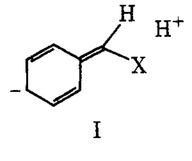
effect at these carbons is not surprising in that the substituent is in the same relative position in space for both systems. Similar results have been obtained on comparison of monosubstituted benzenes with monosubstituted ethylenes.[17]

The remaining carbons which can be directly compared are $C_{2,6}$ (toluene) and C_2 (propene) carbons. A reasonable assumption based upon previous studies concerning aromatic ortho carbon shifts vs. olefinic β carbon shifts is that these carbon substituent shifts should be similar in magnitude and direction. In the benzene vs. ethylene series it was found that the $\Delta\delta$ values in the ethylene system are about twice that in the benzene analogues.[17] However, in the present instance poor correlation was obtained, and this suggests that the mechanism(s) responsible for the substituent shift at these carbons is different. For the propene systems both positive and negative $\Delta\delta$ values are obtained for the C_2 substituent shift, whereas in the toluene system, $C_{2,6}$ is seen generally to have negative values of $\Delta\delta$.

To complete our preliminary inspection of the data concerning the substituent shifts, it is noticed that the $\Delta\delta$ values, except for α-nitrotoluene, for $C_{3,5}$ are negligible while the $\Delta\delta$ values for C_4 are substantial even though this carbon is five bonds removed from the substituent interchange, and transmission of the effect must take place through an "insulating" methylene group.

The above comparison of the substituent shift exerted at C_1 in the toluene and propene systems suggests that a similar mechanism is important in each case for the transfer of the substituent effect. Looking at the data in Table IV, obtained by utilizing eq 1, it is clear that this assumption is correct. Although the absolute magnitudes of *a* and *b* are different for the Swain–Lupton and Taft methods, the relative importance of each effect, inductive-field, and resonance, is the same within the experimental error. The difference in magnitude arises from the difference in the initial value of σ_I vs. **F** and σ_{R° vs. **R**. Swain and Lupton found that σ_I and σ_{R° are 0.60**F** and 0.63**R**, respectively. Normalization of the σ_I and σ_{R° regression coefficients by 0.6 yields numbers which compare favorably with the Swain–Lupton treatment. In any case, it is apparent that a large resonance type interaction occurs at C_1.

The analysis of the substituent effects transmitted to the toluene C_4 carbon also indicates some resonance interaction although it is reduced in magnitude. Here σ_R(BA) values, benzoic acid derived, were used as σ_{R° did not give adequate correlation.[3b] (This may indicate an advantage of the Swain–Lupton treatment as the *search* for values of the resonance parameter which give good correlation is unnecessary.) Since *all* the $\Delta\delta$ values observed at C_4 are positive (downfield shifts) any mechanism that is consistent with the data would logically have to indicate at least a partial positive charge on this carbon owing to a loss of charge density. CNDO calculations bear out this effect in monosubstituted benzenes.[3a] This observation would seem to rule out the hyperconjugative electron release interaction such as I, which is invoked in order to explain the ortho–para directivity of toluene systems,[6] as a major contributor to the observed shift values as it would place a negative charge at C_4—hence induce upfield shifts.



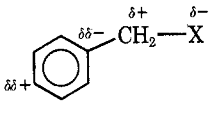
I

Table IV. Results of Linear Regression of $\delta = aA + bB + i$

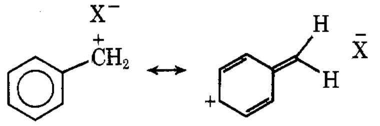
Position	a	b	c^d	d^d	i	r	Av dev	Range
			Toluene Compounds					
$C_1{}^a$	−7.30	−7.31	−0.81	−0.69	140.3	0.916	1.44	14.0
$C_1{}^b$	−12.65	−11.37	−0.81	−0.68	140.3	0.944	1.30	14.0
$C_4{}^a$	3.63	−1.43	0.93	0.09	125.6	0.964	0.27	4.1
$C_4{}^c$	5.48	−0.71	0.92	0.20	125.7	0.931	0.38	4.1
			Propene Compounds					
$C_1{}^a$	−6.92	−6.99	−0.81	−0.72	137.2	0.961	0.83	11.5
$C_1{}^b$	−12.51	−11.69	−0.83	−0.67	137.3	0.985	0.52	11.5
$C_2{}^a$	5.45	4.28	0.87	0.66	115.2	0.972	0.48	7.7
$C_2{}^b$	9.58	6.26	0.88	0.56	115.2	0.979	0.50	7.7

[a] $a\mathbf{F} + b\mathbf{R}$: Swain and Lupton.[11b] [b] $a\sigma_I + b\sigma_{R^\circ}$: Taft.[11a] [c] $a\sigma_I + b\sigma_{R(BA)}$; Taft.[3b] [d] Correlation coefficient (r) of a two-parameter equation A vs. δ and B vs. δ.

As indicated by the relatively good fit of σ_I or **F** alone with the $\Delta\delta$ values observed at C_4, a π-bond polarization mechanism (π-inductive effect) such as II may be dominant.[18] Another possible contributor to the transmission of the substituent effect through the "insulating" methylene group involves participation of no-bond resonance forms,[5,19] e.g., III. A recent study concerning the substituent effect of a bromomethyl moiety supports a conjugative electron withdrawal by the C–Br bond.[20] As II and III work in the same direction it is difficult to distinguish between them.



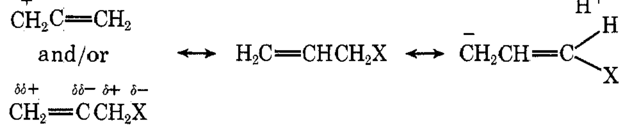
II



III

The data with respect to the propenyl system can be explained via considerations similar to those for the toluene derivatives. From eq 1, a considerable resonance interaction is observed at both C_1 and C_2. Interestingly, the regression coefficients for C_1 and C_2 are of opposite sign. This trend is readily apparent from the $\Delta\delta$ values in Table III, i.e., those functionalities which exert a positive shift at C_1 exert a negative shift at C_2. These substituents can be grouped as CN, OAc, Br, and Cl (negative shifts at C_1) and CH_3, phenyl, NH_2, and OH (positive shifts at C_1).

A mechanism which is consistent with these data involves resonance contributions of a hyperconjugative nature and inductive polarization (IV) and/or the no-bond resonance form (V). Groups like Br apparently favor IV and groups like NH_2 favor V. The high correlation coefficient obtained for the C_2 shift using only inductive and resonance interactions strongly suggests that other mechanisms[10] make at best minor contributions in the propene systems.



$$\overset{+}{C}H_2C{=}CH_2\ X^- \ \text{and/or}\ \overset{\delta\delta+}{CH_2}{=}\overset{\delta\delta-}{C}\overset{\delta+}{CH_2}\overset{\delta-}{X} \longleftrightarrow H_2C{=}CHCH_2X \longleftrightarrow \overset{-}{C}H_2CH{=}C(H)(X)\ H^+$$

IV V

This leaves us with the problem of the substituent effect observed at the toluene $C_{2,6}$ carbons. Adequate correlation was not obtained for these carbons using eq 1. Since the substituent shifts are generally upfield a steric interaction may be operative.[1,21] If such a mechanism is important then the order of substituent shift should be inverse to substituent A values, i.e., small A value, larger upfield shift. This order is a consequence of the substituents having smaller A values having more populated states in which the gauche interaction occurs.[1,15] The data in Table II suggest that the steric shift mechanism is not a dominant factor in the $C_{2,6}$ substituent shift. It is possible, then, that the "ortho effect" is important. The utility of the semiempirical Q parameter in assessing this effect has been previously exemplified.[3d,22] It appears from these reports that Q measures a property of the π system and is not a through-space effect. It has been suggested that Q reflects the paramagnetic shielding.[3d] Inclusion of Q into eq 1, using **F** and **R** values, greatly improves the correlation, r = 0.999, −1.48**F**, −0.45**R**, and 0.85Q, av dev 0.03 ppm. The reason for the difference between the C_2 propene carbon and the $C_{2,6}$ toluene carbons remain to be clarified. Further studies are in progress in order to explain this situation.

Experimental Section

All compounds were commercially available and of high purity, as indicated by a lack of significant signals in either the ^1H or ^{13}C NMR, and were used as received. The carbon-13 magnetic resonance spectra were obtained in the Fourier transform mode on a JEOL FX-60 spectrometer system equipped with a Texas Instruments computer with a 24K memory. The spectra were obtained at an observing frequency of 15.00 MHz. Sample concentrations were ca. 20% w/v in deuteriochloroform, in 10 mm o.d. sample tubes. General NMR spectral and instrumental parameters employed were internal deuterium lock to solvent; spectral width of 2500 Hz (166.6 ppm); a pulse width of 4 μs, corresponding to a 36° pulse angle; and a pulse repetition time of 1.8 s. For all decoupled spectra 8K time-domain data points were used while in some cases 16K time-domain data points were used for some of the coupled spectra. All shifts reported are referenced to internal Me_4Si, and are estimated to be accurate to ±0.05 ppm.

Acknowledgments. Grateful acknowledgment is made to the Robert A. Welch Foundation for their financial support of this work and Professor P. D. Bartlett for his encouragement and helpful suggestions.

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The E2C Mechanism in Elimination Reactions. 8. Interaction of Conjugating Substituents with E2C- and E2H-Like Transition States

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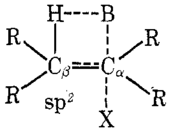
Rates and olefinic products of dehydrotosylation of secondary tosylates under conditions suitable for E2C, E2H, and solvolysis (E1) reactions, respectively, have been measured. The kinetic products are compared with those from equilibration. Quite different proportions of olefins are obtained according to the reaction conditions and this has obvious value for synthetic work. The tosylates studied contain groups, e.g., phenyl, acyl, vinyl, capable of conjugating with the developing double bond in the transition state leading to olefins. The product distribution from E2C-like reactions is not entirely consistent with the concept of a very product- (olefin-) like E2C transition state.

It is generally agreed that the olefin-forming elimination from secondary and tertiary alkyl halides and arenesulfonates induced by halide ions in aprotic solvents proceeds through a product-like transition state which has a large degree of carbon–carbon double bond character I.[1-3] There is little charge at C_α or C_β and the leaving group is only loosely bonded to C_α. Winstein and Parker suggested that the base B is bound to both β hydrogen and C_α in I and describe the mechanism as E2C but there is less agreement on this point.[1,4] A puzzling feature in terms of the product-like E2C transition state has been the similar substituent effect on rate of β-aryl and β-methyl groups,[1,2,5,6] which both strongly enhance the rate of E2C-like eliminations relative to hydrogen. Where there is a choice of elimination pathways, e.g., dehydrotosylation of II, β-phenyl substituents do not appear to dictate the direction of elimination to form an extended conjugated styrene system in preference to the methyl hyperconjugated system. The olefinic products are not close to their equilibrium proportions when phenyl substituents are involved.[6]



I

$PhCH_2CH(OTs)CH(CH_3)_2$

II

To establish whether these difficulties with our mechanistic interpretation of E2C reactions[1] were general for substituents capable of conjugation with developing double bonds, or were a peculiarity of aryl groups, e.g., steric factors inhibiting coplanarity of the phenyl ring with the developing double bond, we have studied the products of elimination from substrates having β-methyl, β-vinyl, β-acyl, and β-phenyl substituents.

Results and Discussion

We have difficulty in developing a consistent mechanistic description of the rates and proportions of olefinic products from the reactions of NBu_4Br in acetone containing 2,6-lutidine, the reactions of KOBu-*t* in *tert*-butyl alcohol, and the solvolysis in acetone–water of the tosylates shown in Table I. However, very small differences in the energy of transition states or of products can lead to what might at first appear to be rather different proportions of trans to cis olefin or of conjugated to unconjugated olefin. It may not be profitable to try to extend too far our E2C–E2H mechanistic thinking to explain differences in such small effects. Nevertheless, the results in Table I, together with some broad generalizations covering related compounds, could be of value to the organic chemist, anxious to decide between equilibration of olefins with KOBu-*t*/Me_2SO, reactions of tosylates with KOBu-*t*/*t*-BuOH or with NBu_4Br/acetone/lutidine, or solvolysis as a means of obtaining a desired proportion of olefins. For this reason we present the results and make a few very brief generalizations.

The tosylates III, V, and VI in Table I can be dehydrotosylated in two directions as well as giving trans and cis isomers,

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