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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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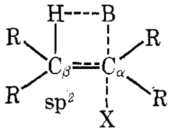
Rates and olefinic products of dehydrotosylation of secondary tosylates under conditions suitable for E2C, E2H, and solvolysis (E1) reactions, respectively, have been measured. The kinetic products are compared with those from equilibration. Quite different proportions of olefins are obtained according 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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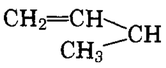
Table I. Products [d] of Dehydrotosylation of Secondary Alkyl Tosylates $R_1CH(OTs)R_2$ and Equilibration of Olefins

No.	$R_1CH(OTs)R_2$ R_1	 R_2	Mech	Log k[e]	Conjugated[a] hyperconjugated	Other[b] olefins, %	Trans[c,m] cis	
III	$PhCH_2$	$CH(CH_3)_2$	E2C[g]	−2.9	0.10	0.8	18	
			Eq[h]		1.8	3.4	130	
			Sol.[i]	−3.3[f]	0.16	13.3	9	
			E2H[j]	−2.8	37	0.2	60	
IV	CH_3CH_2	$CH(CH_3)_2$	E2C	−2.8	0.043[a]	2.7	>35	
			Eq		0.092[a]	<1	6	
			Sol.[k]	>−4[f]	0.20[a]	13	>35[k]	
			E2H	−2.6	0.96[a]	<1	2	
V	 $CH_2{=}CH(CH_3)CH$	$CH(CH_3)_2$	E2C	−2.9	1.0	1.7	1.6	
			Eq		4.0	1.7	1.2	
			Sol.	−2.3[f]	0.53	2.2	1.0	
			E2H	−3.45	3.5	5.4	2.6	
VI	CH_3COCH_2	$CH(CH_3)_2$	E2C	−2.5	35	0.2	100	
			Eq		110	0.7	200	
			Sol.	−2.7[f]	20.3	10.4	33	
			E2H	≥1.3	13	0.3	130	
VII	$PhCH_2$	CH_2CH_3	E2C	−4.35	1.6	1	14.5	9.5[l]
			Eq		15.6	<0.1	52	3.5[l]
			Sol.	−3.8[f]	0.50	0.3	5.2	2.2[l]
			E2H	−2.6	41	<0.1	15	0.6[l]

[a] Ratio of trans + cis conjugated olefin to trans + cis olefin hyperconjugated with a methyl group. Note that the term conjugated does not apply in compound IV. [b] Percentage of rearranged olefins relative to total of olefinic products, mostly 1-ene. [c] Ratio of trans to cis olefin in the products of dehydrotosylation or equilibration. [d] VPC analysis after extraction of reaction mixture with petroleum ether. Olefins were characterized by synthesis or by preparative VPC, followed by uv and NMR analysis of the separated olefins. [e] k in $M^{-1}\ s^{-1}$ at 75 °C. [f] Initial second-order rate constant from rate of solvolysis assuming second-order reaction with 0.20 M base. [g] Tosylate was 0.02–0.05 M, NBu_4Br was 0.1–0.2 M in acetone containing 0.05–0.1 M 2,6-lutidine. [h] Equilibrated with excess KOBu-*t* in Me_2SO at 30 °C for 30 min. [i] Solvolysis in 50/50 acetone/water at 75 °C. [j] Tosylate was 0.02–0.05 M, KOBu-*t* was 0.05–0.10 M, in *t*-BuOH. [k] A. K. Colter and D. R. McKelvey, *Can. J. Chem.*, **43,** 1282 (1965). [l] Ratio of trans/cis hyperconjugated olefin. [m] Ratio trans/cis of conjugated olefin.

to give olefins having conjugation with a phenyl group (III), a vinyl group (V), and an acyl group (VI), or an olefin hyperconjugated with two methyl groups (III, V, and IV). Two other tosylates are shown: IV, in which dehydrotosylation gives either a trans and cis olefin hyperconjugated with one methyl group or an olefin hyperconjugated with two methyl groups; and VII, in which competition gives trans, cis olefins conjugated with a phenyl group or hyperconjugated with a methyl group.

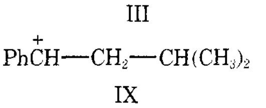
Methyl groups generally stabilize double bonds by hyperconjugation about two-thirds as strongly as do phenyl groups by conjugation[7] and follow additivity rules.[8] The equilibration of the conjugated and unconjugated olefins from III and VII suggests that in Me_2SO, a phenyl group is rather more effective than this, relative to methyl, in stabilizing olefins. By comparing the products of dehydrotosylation from the substrates of Table I via E2C-like, E2H-like, and solvolysis transition states with the products of olefinic equilibration in Me_2SO, information as to the product-like nature of the transition states may be obtained.

Equilibration. Equilibration with KOBu-*t*/Me_2SO shows that conjugation with a phenyl or a vinyl group (VII and V) is more effective in competition with a hyperconjugative methyl group in stabilizing olefins. Two hyperconjugative methyl groups are more effective than one hyperconjugative methyl group (IV) but are not quite as effective as one conjugative phenyl group (III). A conjugative acyl group (VI) is the most effective of the groups studied in stabilizing olefins. The equilibrium proportions in Me_2SO are consistent with the gas-phase thermodynamic properties of olefins.[7,8] Substituent effects tend to follow additivity rules,[7,8] so our observations may have some general application.

The equilibrium proportion in Me_2SO of trans olefin is higher (sometimes much higher) than that of cis olefin, for all the products studied in this work.

Solvolysis. Solvolysis of these secondary tosylates in 50% acetone–water is likely to be via carbonium ions which to some extent have undergone rearrangement, as shown by the presence of 1-ene in the products. For El elimination from a high-energy carbonium ion, the transition states leading to olefins will be carbonium ion-like. Thus there will be little discrimination of products between trans and cis or conjugated vs. hyperconjugated olefins. Ratios of trans/cis olefins from solvolysis should be nearer to unity than from equilibration and with one exception, such is the case in Table I. The proportion of conjugated to hyperconjugated olefin will depend to some extent on the proportions of rearranged carbonium ions, prior to elimination of a proton from them. With one exception, the ratio of conjugated to hyperconjugated olefin for solvolysis is nearer to unity than for equilibration.

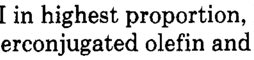
The effect of rearrangements on the solvolysis products of compound III illustrates the problem. Tertiary carbonium ions are slightly more stable than benzylic, than secondary, so that elimination is from a mixture of carbonium ions, VIII–X, with


$PhCH_2{-}CH(OTs){-}CH(CH_3)_2$

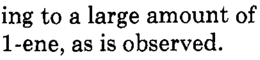
III


$PhCH_2CH_2{-}\overset{+}{C}(CH_3)_2$

VIII


$Ph\overset{+}{C}H{-}CH_2{-}CH(CH_3)_2$

IX

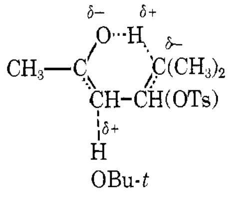

$PhCH_2{-}\overset{+}{C}H{-}CH(CH_3)_2$

X

VIII in highest proportion, leading to a large amount of the hyperconjugated olefin and the 1-ene, as is observed.

Clearly interpretation of solvolysis products is a complex matter because of rearrangements and little information which might help us in understanding E2C-like and E2H-like reactions can be obtained. In general, solvolysis is a less clean way of obtaining high yields of olefins than are E2C or E2H reactions.

E2H Reactions. Dehydrotosylations with KOBu-*t*/*t*-BuOH are generally regarded as E2H-like reactions[1]. Rates of E2H-like reactions are much faster the more acidic the β hydrogen. Bronsted relationships are followed.[5] Thus since vinyl, phenyl, and acyl are more acidifying substituents than methyl, one would expect a high ratio of conjugated to hyperconjugated olefin from E2H-like reactions. Such is the case in Table I. There is, however, one surprising result, in that 7% hyperconjugated olefin is produced from tosylate VI, i.e., two methyl groups compete quite effectively with the very strongly acidifying acyl group in this E2H-like reaction. A potential problem with using the strong base KOBu-*t*/*t*-BuOH is that the products of elimination from VI (particularly the conjugated olefin) decompose slowly in the presence of excess of the *tert*-butoxide ion. However, similar product ratios to those for KOBu-*t*/*t*-BuOH were obtained after 1, 2, and 10 half-lives using the weaker NaOEt/EtOH base system. In the presence of this base the olefins are stable under the reaction conditions. We found no evidence for isomerization toward an equilibrium mixture of olefins under the reaction conditions with either base. An explanation for the high yield of hyperconjugated olefin may be that the carbonyl group is stabilizing the transition state for production of the hyperconjugated olefin via an enolate from as in XI, with return to the keto form on product isolation. This option is not available to E2C reactions which use very much weaker H bases.



XI

More trans than cis conjugated olefin is produced from the E2H-like reactions of Table I, but more important, the trans/cis proportions for E2H are *less than the equilibrium proportion*, with one exception.

E2C Reactions. E2C-like reactions of NBu_4Br in acetone containing 2,6-lutidine usually give very different proportions of olefins from E2H-like reactions, and from equilibration.[1] This has significance for the synthesis of olefins. The overall rates of dehydrotosylation under E2C conditions are similar (log k −2.5 to −3) for all tosylates in Table I having R_2 as an isopropyl group, no matter whether R_1 is methyl, phenyl, vinyl, or acyl. The proportion of conjugated to hyperconjugated olefin from E2C-like dehydrotosylation is less than the proportion from equilibration. Thus the E2C-like transition state is not *strongly* product-like in this respect. In general, although more olefin-like, E2C-like transition states lead to less of the conjugated olefin and more of the hyperconjugated olefin than do E2H-like reactions, which are governed by carbanion stability. The one exception is compound VI, where the unexpectedly high proportion of hyperconjugated olefin from the E2H-like reaction has already been commented on (cf. XI).

Proportions of trans to cis olefin from the E2C-like reactions shown in Table I are significantly greater than for solvolysis and greater than unity and this is a feature of most E2C-like reactions. However, the trans/cis ratios are often significantly different from the equilibrium proportions, when substituents capable of conjugation are involved. Sometimes the trans/cis ratio is greater, sometimes less for the E2C-like reaction than for the equilibrium proportion. For formation of a conjugated olefin, the trans/cis ratio is always less from the E2C-like than from the E2H-like reaction.

To summarize, E2C-like conditions often allow us to prepare a significantly different proprotion of olefins from a diastereotropic tosylate than would be obtained from a dehydrotosylation under E2H-like or solvolysis conditions, or from equilibration of olefins. This has advantages in preparative work. The behavior, under E2C-like conditions, of tosylates which contain substituents capable of conjugating with a developing double bond, is not entirely consistent with a very product-like E2C transition state. It may be that conjugating substituents are not able to achieve full conjugation of their π-electron systems with the developing double bond in E2C-like transition states, but we confess ourselves unable to give a completely satisfactory mechanistic explanation for the data in Table I.

Experimental Section

Preparation of Alcohols. 1-Phenyl-3-methyl-2-butanol, 1-phenyl-3-methyl-1-butanol, 1-phenyl-2-butanol, and 1-phenyl-1-butanol were prepared via the Grignard reaction using phenylacetaldehyde or benzaldehyde, and isopropyl bromide or ethyl bromide in the usual manner.[9] The alcohols were purified by spinning band vacuum distillation at 1 mmHg to >95% purity as determined by GC analysis using a 6 ft × 0.125 in. column of Apiezon L at 150 °C. An NMR of the purified alcohols confirmed their structure.

Methyl-2-hydroxy-3-methyl butyl ketone was prepared by slowly adding 2-methylpropionaldehyde dropwise to excess acetone at 5 °C containing 0.5% w/v tetraethylammonium hydroxide. The method was similar to that described by Eccott and Linstead.[10] The alcohol was purified by vacuum distillation (bp 92 °C, 23 mm) and analyzed by GC (Apiezon L at 80°) and NMR to confirm its purity and structure.

2-Methyl-3-hydroxy-4-methyl-5-hexene was prepared by the Grignard reaction with isobutyraldehyde and 1-bromo-2-butene added together to a well-stirred suspension of magnesium in ether. Although allylic bromides can react at either α or γ carbon, 1-bromo-2-butene reacts exclusively at γ carbon.[11] The product is complex because dimerization of the olefin and condensation of the aldehyde occur, and was fractionally distilled at atmospheric pressure and at 13 mmHg. Heptenols boil at 150–180 °C (40–70 °C, 13 mmHg) and a high-boiling aldol condensation product remains. The fraction recovered at 61 °C (13 mm) proved to be the required alcohol (NMR analysis) of 99% purity (GC analysis on Apiezon L at 100 °C). A GC analysis of this alcohol on Carbowax 20M at 60 °C resolved two peaks of equal intensity thought to be different diastereomers. The alcohol possesses two chiral centers.

Preparation of Tosylates. The tosylates were prepared by reacting the corresponding alcohols with a 50% excess of tosyl chloride which had been recrystallized from a 60:40 mixture of light petroleum and ethyl acetate. The reactants were dissolved in cold pyridine and allowed to react overnight. Excess tosyl chloride was removed by slowly adding a theoretical quantity of water and stirring. After 0.5 h, xcess 10% v/v ice-cold hydrochloric acid and ether were added and the tosylate was extracted into the ether layer and worked up in the usual manner. The isolated products were recrystallized or repeatedly oiled out at −70 °C from light petroleum. They were analyzed by ir to confirm the absence of residual alcohol and by NMR to confirm their purity and structure. Melting points were determined on a Kofler block and were found to be (structure; melting point): III, 79.5–80.5 °C; IV, oil; V, oil; VI, oil, ~31 °C; VII, 54–55 °C.

Preparation of Olefins. Conjugated olefins were generally prepared by refluxing the corresponding alcohol with 50% sulfuric acid while hyperconjugated olefins were generally prepared by refluxing the alcohol with iodine catalyst. Boiling points of the pure fraction corresponded to literature values and NMR analyses confirmed their structure. 1-Phenyl-3-methyl-2-butene was prepared independently by a Grignard reaction with bromobenzene and 1-chloro-3-methyl-2-butene. Olefin mixtures were separated and analyzed by GC using a 7 ft × 0.125 in. column of Carbowax 20M at 40–75 °C.

Registry No.—III, 33740-54-4; III alcohol derivative, 705-58-8; IV, 1516-13-8; IV alcohol derivative, 565-67-3; V, 59697-03-9; V alcohol derivative, 53045-65-1; VI, 59697-04-0; VI alcohol derivative, 38836-21-4; VII, 59697-05-1; VII alcohol derivative, 701-70-2; tosyl chloride, 98-59-9.

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Notes

Photochemistry of Organochalcogen Compounds. 2.[1] Photochemical Deselenation of Benzyl Diselenide by Triphenylphosphine

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Although the chemistry of organoselenides is well documented,[2] little is known about their photochemical reactions. By contrast, the photoreactions of many organosulfides have been studied and their mechanisms understood.[3] We have reported recently the first quantitative study on the photolysis of benzyl diselenide (1) in solution.[1] It was found that irradiation of 1 in degassed acetonitrile at wavelengths greater than 280 nm results in formation of elemental selenium and dibenzyl selenide. Photoinduced cleavages of Se–Se and C–Se bonds were proposed as possible primary processes.

Walling and Rabinowitz[4] discovered that trivalent phosphorus compounds convert thiyl radicals into alkyl radicals. This led us to investigate analogous reactions for organoselenides. A recent communication by Cross and Millington[5] on the deselenation of diethyl diselenide by tertiary phosphines prompts us now to report some quantitative details of our studies of photodeselenation of 1 by triphenylphosphine (2).

Irradiation of 1 (2×10^{-2} M) and an excess of 2 (4×10^{-2} M) in degassed acetonitrile at 350 nm for 45 min yields 66.1% of dibenzyl selenide (3), 32.3% of bibenzyl (4), and 65.1% of triphenylphosphine selenide (5).

$$\underset{\mathbf{1}}{PhCH_2SeSeCH_2Ph} + \underset{\mathbf{2}}{Ph_3P} \xrightarrow[CH_3CN]{h\nu\ (350\ nm)} \underset{\mathbf{3}}{PhCH_2SeCH_2Ph} + \underset{\mathbf{4}}{PhCH_2CH_2Ph} + \underset{\mathbf{5}}{Ph_3PSe}$$

Under these conditions, the formation of elemental selenium is completely suppressed. If molecular oxygen is present, 5 reacts further to produce triphenylphosphine oxide and elemental selenium. The photoproducts were isolated by preparative layer chromatography and identified by comparison with authentic samples prepared by independent syntheses. The progress of the reaction was monitored by NMR as described previously.[1] The methylene protons of 1 (δ 3.81), 3 (δ 3.70), and 4 (δ 2.88) have sufficiently different chemical shifts to permit quantitative analysis. The results are shown in Figure 1. Formation of 5 cannot be monitored by NMR; however, it was demonstrated by GLC that 5 is formed rapidly and reaches constant concentration after about 40 min of irradiation (compare to Figure 1). NMR analyses indicate significant photoreaction in 10 min and complete disappearance of diselenide (1) in 45 min. No detectable reaction occurs in a nonirradiated aliquot of the degassed reaction mixture stored in the dark at room temperature for 7 days.

In contrast to the direct irradiation (quantum yield $\Phi = 0.16$ for disappearance of 1 in benzene at 313 nm),[1] the photodeselenation of 1 by 2 in benzene is remarkably efficient. Table I shows the increase of quantum yield with increasing concentration of 2. The large quantum yields provide strong evidence for a free-radical chain reaction.

For irradiations of 1, in the absence of 2, at 366 nm less than 7% decomposition of 1 was detected after 3 h exposure.[1] This result has been interpreted as evidence for a Se–Se bond cleavage (eq 1) as the major primary process in 1, followed by

$$RSeSeR \xrightarrow{h\nu} 2RSe\cdot \quad (R = PhCH_2) \tag{1}$$

$$RSeSeR \xrightarrow{h\nu} R\cdot + RSeSe\cdot \longrightarrow RSe\cdot + Se^0 + R\cdot \tag{2}$$

efficient benzylselenyl radical combination to give 1, or benzylselenyl radical displacement reaction at the Se–Se bond resulting in generation of 1 and an additional benzylselenyl radical.[1] We have no data on the relative importance of combination vs. displacement reactions for benzylselenyl radicals. Sayamol and Knight,[3] however, have reported that displacement reactions play a major role for thiyl radical reactions. Regardless of the relative importance of these reactions for benzylselenyl radicals these processes lead to no photoproduct formation.

The observed photoproducts can be explained on the basis of eq 2.[1] The very low quantum efficiency suggests that benzylselenyl radicals do not dissociate to yield Se^0 and benzyl radicals.

In contrast to these results, irradiation of 1 in the presence of 2 under identical reaction conditions results in total reaction

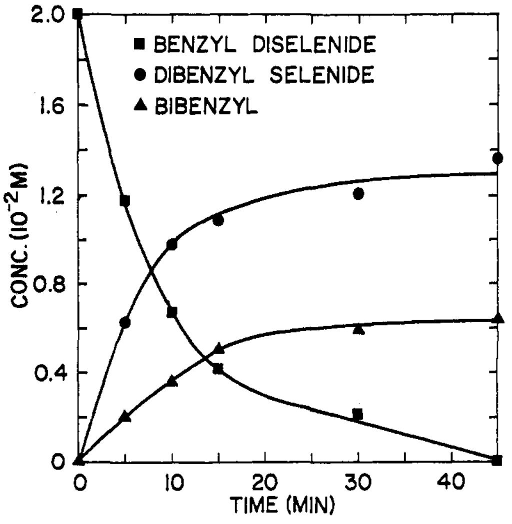

Figure 1. The concentration of reactant and photoproducts plotted vs. photolysis time.