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ALKENES FROM E2C-LIKE AND E2H-LIKE REACTIONS. DIFFERENCES IN HOFMANN-SAYTZEFF AND *trans-cis* PROPORTIONS.

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The olefinic products of β-elimination depend on the choice of base and solvent[1]. The following generalizations are illustrated in the Table. Alkyl bromides and sulphonate esters when treated under E2C-like conditions[2] with a strong carbon nucleophile, but very weak hydrogen base, in a dipolar aprotic solvent (e.g. NBu_4Br in acetone containing 2,6-lutidine) give very high proportions of Saytzeff olefin and very high proportions of *trans* olefin. Some of the *trans/cis* ratios in the Table for E2C-like reactions are among the highest ever reported for E2 reactions of these substrates. Under E2H-like (i.e. classical) conditions, the same substrates with strong hydrogen bases, but weak carbon nucleophiles (e.g. KOBu-*t* in *t*-butanol) give high proportions of Hofmann olefin and significant proportions of *cis*-olefin. With KOBu-*t* in DMSO - *t*-BuOH, proportions of *cis* isomer decrease with added DMSO[1].

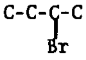
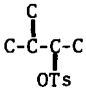
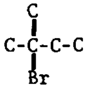
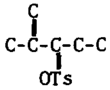
Solvolysis (E1) reactions in *t*-butanol of the substrates in the Table (but *not* of all substrates) usually give similar proportions of isomeric olefins to E2C-like reactions, but the E1 reactions often give high proportions of rearranged products, the E2C-like reactions give none. Equilibration of these olefins in DMSO, a solvent like acetone, gives *trans/cis* proportions between those for E2C-like and E2H-like reactions. Proportions of Hofmann olefin from E2C-like reactions in acetone are very close to those obtained by equilibration in DMSO, but these olefins are not isomerized under E2C-like conditions.

The mechanistic implications of these observations (cf. Ref. 1) will be discussed in detail elsewhere, they need not concern the synthetic organic chemist. He can predict the products of elimination from saturated alkyl and cycloalkyl tosylates and halides by applying the simple idea that E2C-like reactions have transition states which are very olefin-like with leaving group and β-hydrogen *anti* to each other and they, with the base, loosely incorporated in the p orbitals of sp^2-hybridized adjacent carbon atoms. On the other hand the double bond is much less developed and there is much more negative charge at C_β in the E2H-like transition state. The presence of bulky base and leaving group at C_α and the resulting non-bonding interactions in the E2C-like transition state, accounts for the fact that kinetic trans/cis proportions are much higher than equilibrated trans/cis proportions, but Hofmann proportions are close to the equilibrium values.

Tetrabutylammonium bromide in acetone containing 2,6-lutidine is recommended as the E2C base for producing quantitative yields of olefins containing high proportions of Saytzeff olefin and higher than thermodynamic proportions of trans olefin. The recommendation is for substrates in which it is not necessary to preserve a special configuration at C_α. Multiple Walden inversions (S_N2) prior to elimination can be avoided by using the more reactive NBu_4OAc in acetone, but the yields of olefin are lower, because the substitution product does not eliminate acetic acid under E2C-like conditions.

Elimination of HBr induced by NBu_4Br is much faster than elimination of HCl induced by NBu_4Cl, so that higher yields of olefin are obtained in a shorter time if NBu_4Br, rather than the more reactive NBu_4Cl, is used as base.

Table - Alkenes from E2C-like, E2H-like, E1 and Equilibration Reactions[m].

Substrate RX	Classification	Base	T°	% Hof[b]	% trans[c]	% cis[c]	$\frac{[\mathrm{Hof}]}{[\mathrm{Sayt}]}$[d]	$\frac{[\mathrm{trans}]}{[\mathrm{cis}]}$[c]
 $\mathrm{C{-}C{-}\underset{Br}{C}{-}C}$	E2C	$\mathrm{NBu_4Br/Me_2CO}$[a]	75	4	82	14	0.042	5.9
	E2H	KOBu-*t*/*t*-BuOH	50	54[e]	28[e]	18[e]	1.17	1.6
	Equil	KOBu-*t*/DMSO[f]	55	9	64	27	0.099	2.4
 $\mathrm{C{-}\overset{C}{C}{-}\underset{OTs}{C}{-}C}$	E2C	$\mathrm{NBu_4Br/Me_2CO}$[a]	75	0.3	-	-	0.003	-
	E2H	KOBu-*t*/*t*-BuOH	50	76.9[g]	-	-	3.19	-
	E1	Solv.[h]/*t*-BuOH	50	1.0[g]	-	-	0.01	-
	Equil.[i]	--	25	0.2	-	-	0.002[j]	-
 $\mathrm{C{-}\overset{C}{\underset{Br}{C}}{-}C{-}C}$	E2C	$\mathrm{NBu_4Cl/Me_2CO}$[a]	50	9	-	-	0.099	-
	E2H	KOBu-*t*/*t*-BuOH	50	73[e]	-	-	2.70	-
	E1	Solv.[h]/$\mathrm{Me_2CO}$[a]	50	50	-	-	1.00	-
	Equil.[i]	--	25	8.2[j]	-	-	0.090[k]	-
 $\mathrm{C{-}\overset{C}{C}{-}\underset{OTs}{C}{-}C{-}C}$	E2C	$\mathrm{NBu_4Br/Me_2CO}$[a]	75	7.5	7.4	0.1	0.081	70±20
	E2H	KOBu-*t*/*t*-BuOH	50	48.9[l]	32.6[l]	16.3[l]	0.957	2.0
	E1	Solv.[h]/*t*-BuOH[n]	50	7.0[l]	7.0	0	0.091[n]	>30[n]
	Equil.[f]	KOBu-*t*/DMSO[f,l]	55.5	8.4	7.2	1.2	0.105	6.0
	E2H	KOBu-*t*/25% *t*-BuOH[l]-DMSO	50	49.8	47.9	1.9	1.0	25.2

a) Solvent contains excess 2,6-lutidine. b) This represents that percentage of the quantitative yield of olefinic products which was the less substituted (Hofmann) olefin from β-elimination of HX. Unless stated otherwise, the Saytzeff olefin was the only other product. c) % *trans* and % *cis* denote percentages of total olefinic products which were *trans* and *cis* isomers from β-elimination of HX. d) This is the ratio of Hofmann olefin to Saytzeff (i.e. more substituted) olefin, from β-elimination of HX, taking the sum of *cis* and *trans* isomers as Hofmann or Saytzeff products, if necessary. e) H.C. Brown and R.L. Klimisch, *J. Am. Chem. Soc.*, **88**, 1425 (1966). f) Olefins are equilibrated with KOBu-*t* in DMSO under nitrogen, this result duplicates A. Schriesheim and C.A. Rowe, J. Am. Chem. Soc., 84, 3160 (1962). g) I.M. Feit and W.H. Saunders, J. Am. Chem. Soc., 92, 1630 (1970). h) Products from solvolysis in the solvent indicated. i) In gas phase at 25° from "Values of Physical and Thermodynamic Properties of Hydrocarbons," Carnegie Press, 1953, p.475. Equilibration of related olefins in DMSO and on activated alumina gives similar proportions. j) The equilibration product contains 8.2%-2-methyl-1-butene. k) The equilibration product contains 0.2%-3-methyl-1-butene. l) Reference 1. m) Estimated by vpc analysis. n) Contained 16%-2-methyl-1-pentene.

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