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THE REACTION OF 2-OCTYL ARENESULFONATES WITH SODIUM METHOXIDE IN DIMETHYL SULFOXIDE.

ALKENIC PRODUCTS

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The recent report (2) that 2-methyl-3-pentyl arenesulfonates undergo E2 Hofmann elimination to produce unusually high trans/cis 4-methyl-2-pentene ratios in the presence of dimethyl sulfoxide prompts us to report a study of octenes generated in reactions of 2-octyl arenesulfonates with sodium methoxide in dimethyl sulfoxide. 2-Octyl p-toluenesulfonate, benzenesulfonate, p-chlorobenzenesulfonate, p-bromobenzenesulfonate, and p-nitrobenzenesulfonate were reacted with two equivalents of sodium methoxide at 20-25° for 30 minutes. Reaction and isolation conditions have been described (3). Gas chromatographic analyses of 1-octene and cis- and trans-2-octenes were performed on an adiponitrile column. Solvolytic and pyrolytic (i.e., in the gas chromatographic injector block) generation of octenes were ruled out as significantly contributing factors with the p-nitro ester. No isomerization of either 1- or trans-2-octene was observed under reaction conditions, although 3% conversion of cis- to trans-2-octene was observed. No 1-octene was obtained from the cis isomer. Duplicate reactions were carried out with each ester. Results are presented in Table 1.

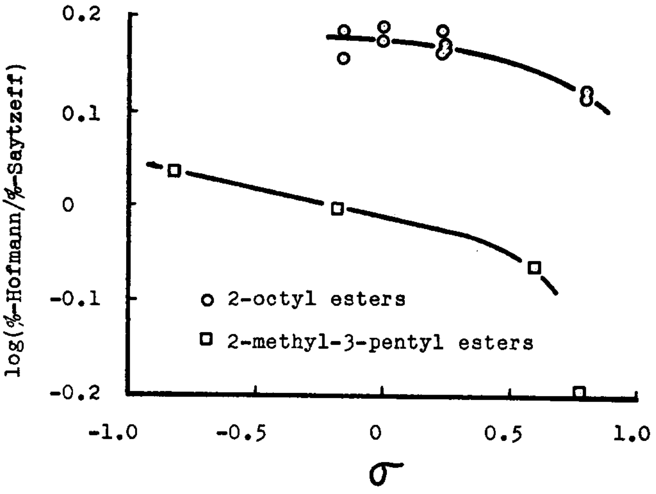
TABLE 1

p-Substituent	% 1-Octene	% trans- 2-Octene	% cis- 2-Octene	$\frac{\% \text{ trans}}{\% \text{ cis}}$	$\frac{\% \text{ 1-}}{\% \text{ 2-}}$
$-CH_3$	27.8	13.6	4.5	3.0	1.54
	18.2	9.1	3.5	2.6	1.44
-H	28.7	14.05	5.2	2.7	1.49
	27.2	12.7	4.9	2.6	1.55
-Cl	28.0	13.8	4.4	3.1	1.54
	26.4	13.6	4.6	3.0	1.45
-Br	29.3	15.1	4.6	3.3	1.49
	25.9	13.4	4.4	3.0	1.46
$-NO_2$	9.7	5.3	2.1	2.5	1.31
	7.7	4.2	1.6	2.6	1.32

These data indicate a trans/cis ratio in this study consistent with those normally obtained with secondary alkyl halides in E2 eliminations (4), including eliminations in dimethyl sulfoxide (5). These results contrast with Colter and McKelvey's considerably higher ratios of 20.7 (p-dimethylamino) to 34.8 (3,4-dichloro) of trans/cis 4-methyl-2-pentenes produced in E2 reactions of 2-methyl-3-pentyl arenesulfonates with potassium t-butoxide in 25% (volume) t-butyl alcohol-dimethyl sulfoxide at 50°. Conversely, our Hofmann/Saytzeff ratios are significantly higher than Colter and McKelvey's 1.09 (p-dimethylamino) to 0.64 (p-nitro) despite our use of the sterically smaller alkoxide.

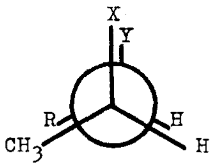
A plot of log (%-Hofmann product/ %-Saytzeff product) vs. σ^- (6) (Figure 1) suggests leaving-group electronic effects influence this ratio similarly in both studies. An analysis of the trans/cis ratio is less clear primarily because of relatively great scatter in our points.

FIG. 1

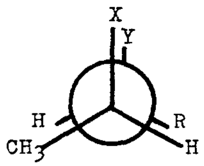


Because of the noted similarity in leaving-group electronic effects on the Hofmann/Saytzeff ratios, and because of the marked difference in ratios obtained with two simple aliphatic substrates, a non-electronic origin of the Hofmann/Saytzeff difference seems likely. Similarly, electronic effects do not seem to offer a simple rationalization of the trans/cis difference. Unusual catalytic effects of dimethyl sulfoxide (7) *per se* also appear to be an insufficient explanation. Substitution of this co-solvent for dioxane produced a remarkable effect on the trans/cis ratio in Colter and McKelvey's work but, as noted above, results obtained here in undiluted dimethyl sulfoxide are consistent with trans/cis ratios observed by others.

However, alkenic product ratios in *both* studies *are* consistent with the suggestion that the mode of elimination in the presence of dimethyl sulfoxide might differ from the normally accepted *trans* elimination mechanism (2). Thus if in this solvent a *cis* elimination (3) were obtained, transition states should resemble eclipsed conformations of the reacting esters. Trans/cis product-ratios should then be reflections of free energy differences of the following two conformations:



cis products

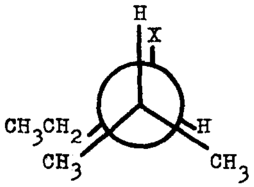


trans products

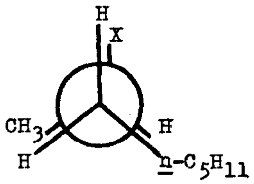
In 2-octyl esters, R = *n*-C_5H_{11}, X = the sulfonate group, and Y = H; in 2-methyl-3-pentyl esters, R = *iso*-C_3H_7, X = H, and

Y = the sulfonate group. Taft has calculated E_s values of -0.39 and -0.47 (8) for the n-butyl and isopropyl groups, respectively. Thus free energy differences due to eclipsing of alkyl groups in these two conformations may be significantly greater if R is isopropyl than if R is n-pentyl and may lead to the observed trans/cis differences.

The Hofmann/Saytzeff ratio in reactions of 2-octyl benzenesulfonate has been discussed elsewhere (3). We note here, however, that a cis-elimination to provide the Saytzeff products from 2-methyl-3-pentyl arenesulfonates does not involve the crowded transition state suggested (3) for the 2-octyl esters. For Saytzeff elimination from 2-methyl-3-pentyl esters, two methyl groups replace both the hydrogen and the n-pentyl group of the 2-octyl esters. While the n-pentyl group is assumed sufficiently bulky to effect a slight shielding of the reactive hydrogen in 2-octyl esters, the two methyl groups should have negligible steric effect on the base.



Saytzeff elimination:
2-methyl-3-pentyl esters



Saytzeff elimination:
2-octyl esters

While other explanations of the observed ratios may certainly be tenable, steric influences in cis-eliminations seem the simplest rationalization of the data at present.

Additional evidence for cis-eliminations in these systems is being sought.

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