Comparing Nucleophilic Substitutions Versus Elimination Reactions in Comprehensive Introductory Organic Chemistry Textbooks

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Abstract: In order to facilitate learning nucleophilic substitution and elimination, 17 comprehensive introductory organic chemistry textbooks are compared with respect to topic ordering, term abbreviation selection, including important topics, and content accuracy. Differences among texts are noted, and detailed comparisons are discussed. Pedagogically useful, consistent, and concise descriptions are given to understand the differences.

Introduction

Nucleophilic substitutions versus elimination reactions constitute an integral part of introductory organic chemistry, which is required for many graduate and professional programs in science.[1] The underlying chemistry principles governing these reactions are critical for comprehending material in other scientific disciplines. The importance of introductory organic chemistry is evidenced by its being a prerequisite for nursing, medicine, engineering, dentistry, pharmacy, biochemistry, and many sciences. If students in these majors do not understand material in the text adopted for their organic chemistry courses, then this can influence them to consult other textbooks, for additional and/or alternative explanations. Complex or weak points in course-designated texts can similarly compel students to supplement the course-designated textbook with other organic texts, which could present different definitions, terminology, acronyms, and abbreviations. While multiple explanations can provide the supplement or clarification which students seek, these explanations must be unequivocal, and multiple sources should at least agree on basic facts, terminology, acronyms, and abbreviations.

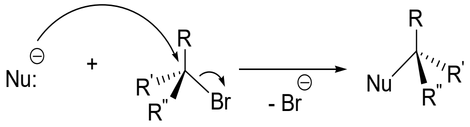
Many introductory organic chemistry students identify nucleophilic substitution versus elimination reactions as the most confusing section in the first semester introductory organic chemistry course.[2] This is due to the concurrent nature of these reactions and their similarities in reagents and reaction conditions, which hinder predicting the predominant reaction. Such confusion in students is further intensified when these texts disagree on basic facts, terminology, acronyms, and abbreviations. Variations and inconsistencies, in facts and terminology of some topics across introductory organic chemistry texts have previously been identified.[1,3] These variations and inconsistencies can originate from personal preferences of the authors and/or instructors.[4] Therefore, an analysis differentiating the two could (a) limit confusion originating from personal preferences, (b) prevent the dissemination of such discrepancies in subsequent texts, and (c) spawn general agreement on the presentation of facts, terminology, and abbreviations. The benefits of limiting such discrepancies due to personal preferences of authors and instructors have been highlighted.[1,3-5] Therefore, the treatment of these reactions in current texts is analyzed herein in order to (1) reveal discrepancies identified in nucleophilic substitutions versus elimination reactions across current organic chemistry texts and (2) spawn a general consensus among authors and instructors.

Background

In nucleophilic substitution, a molecule or atom with an electron pair replaces a leaving group on a substrate. The attacking molecule or atom is referred to as a nucleophile, and the molecule containing the positive or partially positive leaving group is called an electrophile. An example of nucleophilic substitution is hydrolysis of alkyl bromide R-Br, under alkaline conditions (eq 1), where the nucleophile is OH^- and the leaving group is Br^-.

$$\text{R-Br} + OH^- \rightarrow \text{R-OH} + Br^- \qquad (1)$$

Nucleophilic substitution can involve two molecules (S_N2) or one molecule (S_N1) in the rate-determining transition state (eqs. 2 and 3 respectively). For S_N2, the departure of the leaving group from the electrophile is simultaneous with a backside attack by the nucleophile, producing stereochemical inversion in the product. In S_N1, the leaving group departs to produce a positively charged planar carbocation intermediate. Because the nucleophile can attack the resulting carbocation with equal probability from either side, S_N1 substitution is associated with racemization.



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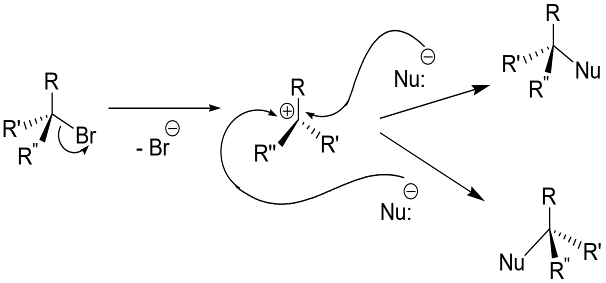

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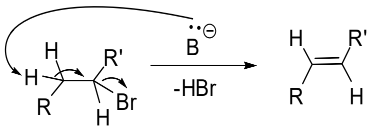
Elimination is a reaction in which two substituents are removed from a molecule, usually to form a π bond. Either the unsaturation of the molecule increases by one (to form a π bond) or the valence of an atom in the molecule decreases by two; the latter process is also known as reductive elimination.

$$PhCH_2CH_2Br + MeO^- \rightarrow PhCH{=}CH_2 + MeOH + Br^- \qquad (4)$$

The one- and two-step mechanisms are known as E1 and E2, respectively. Often an alkane bearing a good leaving group reacts with a base to form an alkene, such as an alkyl bromide reacting with methoxide to yield an alkene (eq 4). When leaving group departure is simultaneous with proton abstraction by base, a concerted bimolecular elimination (E2) mechanism is favored, in which two molecules participate in the rate-determining transition state (eq 5). When the leaving group departs first in order to form a carbocation, followed by rapid proton abstraction by base, a unimolecular elimination (E1) mechanism is effected (eq 6). If the proton is removed first in order to form a carbanion, followed by slow loss of the leaving group (eq 7), this mechanism (eq 7) is known as unimolecular elimination conjugate base (E1cb). The E1cb mechanism is common when there is at least one good electron-withdrawing group (EWG) adjacent to the alkane proton to be abstracted. The EWG serves to increase the Bronsted acidity of the adjacent alkane proton by stabilizing the resultant conjugate base. However, the weak acidity of alkane protons dictates that most organic molecules will not undergo E1cb.



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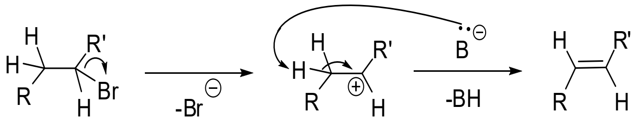

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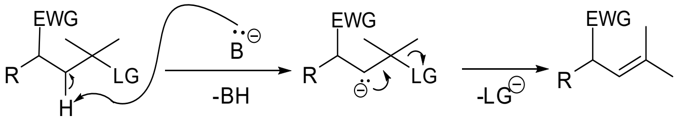

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EWG = Electron Withdrawing Group

Methodology

There were selected 15 commonly used current comprehensive introductory organic chemistry textbooks (Solomons,[6] Klein,[7] J. G. Smith,[8] Hornback,[9] McMurry,[10] Jones,[11] Loudon,[12] M. B. Smith,[13] Clayden,[14] Bruice,[15] Wade,[16] Carey,[17] Brown,[18] Vollhardt,[21] and Sorrell)[22] and two additional recently used ones (Eğe[19]and Fox),[20] both of which were very popular while they were available. These textbooks were published before COVID came and posed problems for education generally, including publishing textbooks. The textbooks selected for comparison were provided by publishers; textbook descriptors (senior author, publisher, edition, and year) are listed in the extreme left four columns of Table 1.

A group of undergraduate students, who recently had completed Organic Chemistry I and Organic Chemistry II, each enrolled in an independent study course in order to assist with the project and help formulate the recommendations discussed herein. Over two semesters, about 20 students participated, joining and leaving at different times, with flexibility in their participation. Each student brought a fresh eye to the project, so each brought the valuable perspective of a student who was learning the material, rather than the perspective of a professor who had taught the course for years. Each came in at regular intervals, reviewed pertinent sections of each textbook, and offered his/her individual evaluation of each text. The results from the students for each book are compiled and compared in Tables 1-4.

Results and Discussion

There were 17 comprehensive introductory organic chemistry textbooks[6-22] selected for comparison perused, and characteristics critical to nucleophilic substitution versus elimination reactions were identified. Results of the comparisons are listed in Table 1. Many variations and inconsistencies were identified in the chapter(s) covering the reactions (Tables 1-4). For clarity, results have been grouped into subsections, and corresponding recommendations are given in each subsection, based on the patterns observed across the texts.

I. Presentation of Nucleophilic Substitution versus Elimination Reactions.

The comparison herein of Nucleophilic Substitution versus Elimination Reactions is extremely important because it is a topic which undergraduates enrolled in organic chemistry consider to be difficult and confusing. All texts canvassed[6-22] covered nucleophilic substitution and elimination reactions, but they differed in the number and/or order of chapters in which they were presented (Table 1). While six texts[12,13,17,20-22] cover nucleophilic substitution and elimination reactions in more than two chapters, six other texts[7-9,11,14,15] limit discussions of the reactions to only two chapters. The material is condensed into a single chapter by the remaining five texts.[6,10,16,18,19]

The preferred paradigm for ordering substitution and elimination mechanisms begins with the simplest reaction mechanism and trends with increasing mechanistic complexity. The S_N2 mechanism is relatively straightforward and therefore should be presented before the S_N1, because the S_N1 mechanism typically leads to a mixture of product stereoisomers and may involve a carbocation rearrangement. Similarly, nucleophilic substitution should be discussed before elimination, because the concepts learned for the former assist learning the latter. E1cb is the most complicated of the elimination reaction mechanisms, so it should be discussed last. Therefore, the preferred order of presentation of these reactions (Table 1) is bimolecular nucleophilic substitution (S_N2), unimolecular nucleophilic substitution (S_N1), bimolecular elimination (E2), unimolecular elimination (E1), and elimination unimolecular conjugate base (E1cb).

This ordering is consistent with three texts,[7-9] and four other texts[6,12,13,15] use the same order except omitting E1cb. All texts except one cover the S_N2 reaction first; one text,[22] presents the S_N1 reaction first followed by S_N2, E1, E2, then E1cb. Three texts[10,11,20] use the recommended order, except they reverse the order of the E1 and E2 reactions; three additional texts[16,17,21] do the same except they omit the E1cb reaction also. One text[14] discusses S_N2 and S_N1 together and then E2, E1, and E1cb in the recommended order. Two texts[18,19] present the S_N2 and S_N1 reactions together and the E2 and E1 reactions together also.

II. Nucleophilicity versus Basicity.

Some students find the concept of nucleophilicity versus basicity confusing. Given that nucleophilicity and basicity are kinetic and thermodynamic phenomena respectively, a clear discussion of the competition between substitution and elimination is crucial, especially in borderline situations where both are possible. To this end, it is imperative to compare nucleophilicity versus basicity in nucleophilic substitution and elimination reactions. Fifteen texts[6-18,21,22] detail such comparisons between nucleophilicity and basicity in these reactions, but two texts[19,20] omit them (Table 1).

III. Abbreviations for Leaving Group and Nucleophile.

There is great variation in abbreviations used for leaving group and nucleophile (Table 2). Eight texts[6,8-11,14,18,21] use Nu to represent nucleophile, while four texts[7,12,16,20] use Nuc. Some[13,15,17,22] opt for Y, while one[19] uses B as an abbreviation for nucleophile. We favor using Nu with a lone pair of electrons (Nu:). Using only Nu: for nucleophile avoids the ambiguity that could emerge with Nuc, B, or Y, because these could be construed to mean nucleus, base, and yield, respectively. Because nucleophiles can be neutral or negatively charged, Nu can be used for the neutral nucleophile and Nu^- for the anion.

Table 1. Substitution vs. Elimination Presentation in Comprehensive Introductory Organic Chemistry Textbooks.

	Textbooks				Substitution and Elimination Presentation								Nucleophilicity vs Basicity Comparision	
	First Author	Publisher	Current Edition	Pub. Year	# of Chapters			Presentation Ordering				Incl. E1cb		
					1	2	2+	S_N2	S_N1	E2	E1			
Preferred Entries ⟶					x			1	2	3	4	y	y	Ref
1	Solomons	Wiley	11	2013	x			1	2	3	4	n	y	6
2	Klein	Wiley	1	2012		x		1	2	3	4	y	y	7
3	Smith, JG	McGraw Hill	4	2014		x		1	2	3	4	y	y	8
4	Hornback	Cengage	2	2006		x		1	2	3	4	y	y	9
5	McMurry	Cengage	8	2012	x			1	2	4	3	y	y	10
6	Jones	Norton	5	2014		x		1	2	4	3	y	y	11
7	Loudon	Roberts	5	2009			x	1	2	3	4	n	y	12
8	Smith, MB	CRC Press	1	2010			x	1	2	3	4	n	y	13
9	Clayden	Oxford Univ.	2	2012		x		1	1	3	4	y	y	14
10	Bruice	Pearson	7	2013		x		1	2	3	4	n	y	15
11	Wade	Pearson	8	2013	x			1	2	4	3	n	y	16
12	Carey	McGraw Hill	9	2014			x	1	2	4	3	n	y	17
13	Brown	Cengage	7	2014	x			1	1	3	3	n	y	18
14	Ege	Houghton Mifflin	5	2004	x			1	1	3	3	n	n	19
15	Fox	Jones/Barlett	3	2004			x	1	2	4	3	y	n	20
16	Vollhardt	Macmillan	7	2014			x	1	2	4	3	n	y	21
17	Sorrell	Univ. Science	2	2006			x	2	1	4	3	y	y	22

For leaving group abbreviation, the letter X is used by ten texts,[8,10,12-17,21,22] LG is preferred in five,[6,7,11,19,20] Lv in one,[18] and L in one.[9] We recommend that LG represent leaving group, because it is most self-explanatory. It is not surprising that the letter X might be used to represent leaving group, since X is often used to represent halide, and halide could serve as a leaving group in alkyl halides during nucleophilic substitution and elimination reactions. However, halides are not the only leaving groups on alkanes, which undergo nucleophilic substitution and elimination reactions. This supports LG being used to represent leaving group instead of the letter X, because it is self-explanatory and encompasses leaving groups other than halide, such as tosylate and mesylate. The use of Lv should be avoided, because it is unclear.

IV. Comparing Pairs of Competing Mechanisms

A. S_N2 versus S_N1

The majority of texts[6-8,10,11,16,17,19,22] examined herein compare the reactivity of substrates toward S_N2 versus S_N1 reactions by listing the substrates as a series. In these nine texts, substrates most reactive toward S_N2 and least reactive towards S_N1 are listed first, then the trend is to substrates least reactive toward S_N2 and most reactive towards S_N1 (Table 2). Six texts[9,12,14,15,20,21] compile similar substrates in the form of a table, while maintaining the trend. In both series and table treatments, borderline cases can be found mid-way through the trend where either S_N1 or S_N2 is plausible, depending upon reaction conditions and reagents involved. However, one text[18] implements both series and table representations for S_N2 versus S_N1 reactions, and one[13] omits the comparison totally.

Most texts present S_N2 reactivity as a series, two in charts,[14,21] one in a table,[12] and two[6,13] in both series and table formats. While one text[6] employs only a series presentation for S_N2 versus S_N1 reactivity, it utilizes both series and table presentations for correlating S_N2 reactivity. Similarly, one text[13] omits the S_N2 versus S_N1 comparison, but it presents reactivity just for S_N2 using both series and table presentations. When discussing S_N2 reactivity, only eight texts[6,11,15-17,19,20,22] include the bulky neopentyl substrate.

We recommend that the reactivities of substrates toward S_N2 versus S_N1 be presented together, and the data be outlined both in series and in a table. This will help students to contrast

Table 2. Reactivity Toward S_N2/S_N1 and Abbreviations Used in Comprehensive Introductory Organic Chemistry Textbooks.

	S_N2 Reactivity		S_N2/S_N1 Reactivity	Abbreviation		
	Include Neopentyl	Presentation		Leaving Group	Nucleophile	
Preferred Entries ⟶	y	Series or Both		LG	Nu:	Ref
1	y	both[a]	series	LG	Nu	6
2	n	series	series	LG	Nuc	7
3	n	series	series	X	Nu	8
4	n	series	table	L	Nu	9
5	n	series	series	X	Nu	10
6	y	series	series	LG	Nu	11
7	n	table	table	X	Nuc	12
8	n	both[a]	none	X	Y	13
9	n	chart	table	X	Nu	14
10	y	series	table	X	Y	15
11	y	series	series	X	Nuc	16
12	y	series	series	X	Y	17
13	n	series	both[a]	Lv	Nu	18
14	y	series	series	LG	B	19
15	y	series	table	LG	Nuc	20
16	n	chart	table	X	Nu	21
17	y	series	series	X	Y	22

[a]Both = series and table

the contributing role of steric and electronic requirements in S_N2 versus S_N1 reactions. Both formats should be used throughout, in analyzing S_N2 and S_N1 reactions individually as well. This is because using both tables and series for comparisons or one reaction, and then switching to only a series presentation for a different reaction within the same text, can hinder grasping and assimilating information. Also, using only a series presentation for S_N2 and S_N1 reactions separately, introduces unnecessary separation between the concepts. Therefore, we suggest that reactivities of S_N2 and S_N1, as well as their comparisons, should be treated simultaneously and should use both series and table presentations.

B. S_N1 vs E1, and S_N2 vs E2

1. Presentation.

When competing nucleophilic substitutions and elimination reactions are plausible, it can be difficult to select the favored reaction pathway. It can be especially difficult to choose between S_N2 versus E2 reactions, and between S_N1 versus E1 reactions, because of similarities in each pair. S_N2 versus E2 reactions arising from a common reactant have similarities such as concerted mechanisms and an identical leaving group, while S_N1 and E1 reactions proceed through a common first step and cationic intermediate. These similarities in each reaction pair create similarities in the contributing roles of base strength, temperature, steric requirements, and nucleophile strength. Therefore, an effective discussion must compare not only nucleophilic substitution vs elimination pathways generally, but also the four sets of mechanism pairs which frequently compete: S_N1 versus S_N2, S_N1 versus E1, S_N2 versus E2, and E1 versus E2. Also, in each of these pairs, the factors which favor one selection over the other must be discussed.

However, there is little agreement among the textbooks about the comparisons which should be included. One point of agreement is that all textbooks examined do compare S_N1 versus S_N2 mechanisms and the factors which favor each.

Some texts do not compare these pairs of mechanisms or even nucleophilic substitution versus elimination generally. Only two[17,18] include both a general comparison between nucleophilic substitution versus elimination, as well as specific comparisons between S_N2 versus E2 mechanisms and between S_N1 versus E1 mechanisms.

While eleven texts[7,8,10,12-14,17-19,21,22] present general comparisons between nucleophilic substitution and elimination reactions, six texts[6,9,11,15,16,20] omit such comparisons, but effectively contrast S_N2 versus E2 and S_N1 versus E1.

However, we recommend thorough and comprehensive comparisons, not just between nucleophilic substitutions (S_N1 versus S_N2) and between elimination reactions (E1 versus E2), but for S_N2 versus E2, and for S_N1 versus E1 as well. Such information gives students criteria needed to predict the major product in each reaction, and the mechanism by which it is formed.

2. Factors Affecting the Reactions.

Predicting whether nucleophilic substitution or elimination predominates in these reactions eludes many organic chemistry students, due to similar reaction conditions and reagents involved. Factors affecting nucleophilic substitutions versus elimination reactions are crucial in predicting which mechanism predominates. Therefore, it is logical to include all factors and to discuss them thoroughly both for S_N1 versus E1, and for S_N2 versus E2 comparisons. Knowing the contributing roles of these factors will help students readily identify the dominant mechanism when competing mechanism are plausible. Competing reactions (S_N1 versus E1, and S_N2 versus E2) and side reactions (carbocation rearrangement in S_N1 and E1 reactions) warrant that factors (such as base strength, temperature, steric effects, and nucleophilicity) affecting these reactions be considered carefully.

Table 3. Substitution vs. Elimination Characteristics in Comprehensive Introductory Organic Chemistry Textbooks.

	Comparison			Factors Compared								Ref
				S_N1/E1				S_N2/E2				
	S vs. E	S_N1 vs. E1	S_N2 vs. E2	Base Strength	Temp-erature	Steric Effects	Nucleo-philicity	Base Strength	Temp-erature	Steric Effects	Nucleo-philicity	
Preferred Entries →	x	x	x	x	x	x	x	x	x	x	x	
1		x	x		x			x	x	x	x	6
2	x			x	x	x	x	x	x	x	x	7
3	x	x		x		x	x	x	x	x	x	8
4		x	x	x			x	x	x	x	x	9
5	x		x	x				x	x		x	10
6		x	x				x	x	x	x	x	11
7	x			x			x	x			x	12
8	x			x		x	x	x		x	x	13
9	x			x	x	x	x	x	x	x	x	14
10		x	x	x				x	x	x	x	15
11		x	x	x	x		x	x		x	x	16
12	x	x	x	x	x	x		x	x	x	x	17
13	x	x	x	x				x	x	x	x	18
14	x			x	x	x		x	x	x		19
15		x	x		x		x	x			x	20
16	x			x		x	x	x	x		x	21
17	x		x		x	x	x		x	x	x	22

In spite of the pivotal role of these factors in predicting whether substitution or elimination predominates, there seems little agreement among these texts, in presentation method, technique, or order for comparing S_N2 versus E2, or S_N1 versus E1. In general, the texts emphasize comparisons between S_N2 versus E2 more than those between S_N1 versus E1. This is demonstrated by fewer entries in the S_N1 versus E1 comparison column versus the S_N2 versus E2 column (Table 3).

In comparing S_N2 versus E2, nine texts[6-9,11,14,15,17,18] consider all four reaction mechanism determinants: base strength, temperature, steric effects, and nucleophilicity. Six texts[10,13,16,19,21,22] elaborate upon three of the four characteristics; one[22] excludes basicity, two[13,16] omits temperature, two[10,21] exclude steric requirements, and one[19] omits nucleophilicity.

In comparing S_N1 versus E1, only two texts[7,9] use all four factors. Most texts[8,13,16,17,19,21,22] use three of the four above factors, one[22] of these omits base strength, three[8,13,21] omit temperature, one[16] omits steric requirements, and two texts[17,19] omit nucleophile strength. One text[12] relies on base strength and nucleophile strength, and one[20] uses reaction temperature and nucleophile strength. Surprisingly, in some texts, only one factor is used to compare S_N1 versus E1; three[10,15,18] discuss only base strength, while two[6,11] consider reaction temperature and nucleophile strength only, respectively.

3. Zaitsev and Hofmann Elimination.

Zaitsev rules and Hofmann rules predict the regio- and stereochemistry of the new double bond resulting from E2 elimination. Both Zaitsev elimination and Hofmann elimination should be discussed as parts of E2 elimination, because they include concepts critical to predicting the elimination products. The Zaitsev elimination should be discussed first

Table 4. Zaitsev vs. Hoffman Elimination on Presentation in Comprehensive Introductory Organic Chemistry Textbooks.

	Zaitsev Elim.	Hofmann Elim.	Zaitsev vs. Hofmann				
			Regiochemical Determinants				
	Rationale Included	Presented w/E2	Steric Effects	Carbanion Stability	Proton Acidity	LG Basicity	
Preferred Entries →	y	y	y	y	y	y	Ref
1	y	y	n	y	n	n	6
2	n	n	y	y	n	n	7
3	y	n	y	n	n	n	8
4	y	y	y	y	y	n	9
5	n	n	y	n	n	n	10
6	y	y	y	y	n	y	11
7	y	n	n	n	n	y	12
8	y	n	y	n	n	n	13
9	n	y	y	n	y	n	14
10	y	y	y	y	n	n	15
11	n	y	y	n	n	n	16
12	n	n	y	n	n	n	17
13	n	n	y	n	n	y	18
14	y	n	n	n	n	n	19
15	y	y	y	n	n	n	20
16	y	y	y	n	n	n	21
17	n	n	n	n	n	n	22

due to its straightforward general mechanism, followed by the Hofmann elimination, which applies in specific cases. The rationale for the Zaitsev elimination is included only in some texts.[6,8,9,11-13,15,19-21] Some textbooks[6,9,11,14-16,20,21] present the Hofmann elimination alongside the E2 elimination, while others[7,8,10,12,13,17,18] present it independently (Table 4). Two texts,[19,22] omit the Hofmann elimination entirely.

Comparing the Zaitsev and the Hofmann eliminations uses substrate steric requirements, carbanion stability, proton acidity, and leaving group basicity as regiochemical determinants (Table 4). However, no text uses all four criteria. Although one text[9] considers steric effects, carbanion stability, and proton acidity, it omits basicity; another text[11] omits proton acidity, but considers the other three factors. Carbanion stability, proton acidity, or leaving group basicity are discussed in a few texts; some[6,7,9,11,15] utilize carbanion stability, others concentrate on proton acidity[9,14] or basicity[11,12,18] only. Most texts[7-11,13-18,20] present steric hindrance as a regiochemical determinant. It is preferable that all four determinants indicated be used in comparing the Zaitsev elimination versus the Hofmann elimination, in order to help students better understand the underlying principles and how to apply them.

Conclusion

Pertinent sections of 17 comprehensive and recently used introductory organic chemistry textbooks dealing with nucleophilic substitution versus elimination reactions were canvassed. These textbooks have many variations and differences in content and presentation of nucleophilic substitution versus elimination reactions. Comparing the texts will reduce confusion in students, especially those who consult multiple texts for alternate or multiple explanations and guide modifications to later editions.

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