

Oxidation of Substituted Benzyl Alcohols by Quinoxalinium Dichromate. A Kinetic Study

Beytiye Özgün* and Nebahat Değirmenbaşı

Gazi Üniversitesi, Fen-Edebiyat Fakültesi, Kimya Bölümü, Teknikokullar,
06500 Ankara, Turkey

Received October 17, 2003; accepted (revised) October 24, 2003

Published online April 9, 2004 © Springer-Verlag 2004

Summary. Quinoxalinium dichromate (*QxDC*) oxidizes benzyl alcohol and substituted benzyl alcohols smoothly in dimethyl sulfoxide (*DMSO*) and in the presence of acid to the corresponding aldehydes. The reaction has unit dependence on each of the alcohol, *QxDC*, and acid concentrations. Electron-releasing substituents accelerate the reaction, whereas electron-withdrawing groups retard the reaction, and the rate data obey *Hammett's* relationship. The reaction constant ρ was -1.09 ± 0.01 at 303 K. Oxidation of α,α -dideuteriobenzyl alcohol indicated the presence of a substantial primary kinetic isotope effect ($k_H/k_D = 6.78$ at 303 K). The reaction failed to induce the polymerization of acrylonitrile. The rates of oxidation were determined at different temperatures and the activation parameters were evaluated. The analysis of the dependence of the kinetic isotope effect on temperature indicated that the reaction involves a symmetrical cyclic transition state. A suitable mechanism is proposed.

Keywords. Quinoxalinium dichromate; Oxidation; Kinetics; Mechanism.

Introduction

The major use of Cr(VI) reagents in synthetic chemistry is to oxidize alcohols to carbonyl compounds. As a result, alcohol oxidation with these was extensively investigated. A number of new Cr(VI) reagents together with special reaction conditions have been developed. Anhydrous conditions are more conducive to complexation of substrates with Cr(VI) species and therefore to mild oxidation. The most significant recent Cr(VI) oxidants are quinolinium fluorochromate [1], pyridinium chlorochromate [2], pyridinium dichromate [3], pyridinium fluorochromate [4], and quinolinium chlorochromate [5]. We have been interested in the synthesis and kinetics of reactions of complexed Cr(VI) species [6] and have reported the kinetics and mechanism of oxidation of benzyl alcohol by potassium

* Corresponding author. E-mail: beytiye@gazi.edu.tr

chlorochromate [7] and quinolinium chlorochromate [8]. Recently we prepared quinoxalinium dichromate (*QxDC*) [9], which in dichloromethane readily oxidizes primary and secondary alcohols to the corresponding carbonyl compounds. Here, we examine the kinetics and mechanism of this oxidation of eleven primary benzylic alcohols with *QxDC* in *DMSO*.

Results and Discussion

Since the results for all alcohols studied were similar with regard to the rate laws and other experimental data, only representative data are reproduced for benzyl alcohol (*BA*). The oxidation of the alcohols by *QxDC* led to the formation of the corresponding aldehydes.

Rate Laws

Under pseudo-first-order conditions the pseudo-first order plots of $\log[QxDC]$ vs. time at different initial concentrations of *QxDC* (0.001 to 0.009 mol dm⁻³) are all linear with nearly the same slope indicating a first-order dependence of the rate on the *QxDC* concentration (Table 1). Further, the pseudo-first-order rate constants were independent of the initial concentration of *QxDC* at constant substrate concentration. In order to know the effect of the concentration of the alcohol on the rate of oxidation, the k_{obs} values were determined at different concentrations of alcohols in the range 0.04 to 0.50 mol dm⁻³ (Table 1). The reaction rate increases linearly with an increase in the concentration of alcohol (Table 1). Thus, the

Table 1. Rate constants for the oxidation of *BA* by *QxDC* in the presence of acid at 303 K

[<i>BA</i>]/ <i>M</i>	10 ³ [<i>QxDC</i>]/ <i>M</i>	10 ⁴ k_1 /s ⁻¹	10 ³ k_2 /s ⁻¹ <i>M</i> ⁻¹
0.04	3.0	7.49	18.73
0.06	3.0	11.25	18.75
0.08	3.0	15.12	18.90
0.10	3.0	19.08	19.08
0.12	3.0	23.09	19.24
0.15	3.0	29.02	19.35
0.20	3.0	38.48	19.24
0.50	3.0	95.59	19.11
0.06	1.0	11.48	
0.06	2.0	11.24	
0.06*	3.0	11.51	
0.06	4.0	11.41	
0.06	5.0	11.45	
0.06	6.0	11.03	
0.06	7.0	11.37	
0.06	8.0	11.58	
0.06	9.0	11.45	

* Containing 10⁻³ *M* acrylonitrile

Table 2. Dependence of the reaction rate on acidity^a

$[TsOH]/M$	0.05	0.07	0.10	0.20	0.25
$10^4 k_1/s^{-1}$	11.25	15.83	22.48	44.67	56.33

^a $[BA] = 0.06 M$, $[QxDC] = 0.003 M$, $T = 303 K$

reaction is first order with respect to the alcohol too. The plot of $1/k_1$ vs. $1/[BA]$ at $30^\circ C$ is linear with no intercept on the $1/k_1$ axis. This indicates the absence of a preformed complex or a complex whose formation constant is too low to be kinetically determined.

The oxidation was found to be acid-catalyzed. The k_{obs} values determined at increasing concentrations of $TsOH$ in the range 0.05 – 0.25 mol dm^{-3} increase (Table 2). The linear increase in the oxidation rate with acidity suggests the involvement of a protonated $Cr(VI)$ species in the rate determining step, which is a stronger oxidant and electrophile than an unprotonated $Cr(VI)$ species. There have been earlier reports suggesting the involvement of such $Cr(VI)$ species in chromic acid oxidation [10], and protonated $Cr(VI)$ species have been observed in the presence of $TsOH$ acid in nitrobenzene–dichloromethane mixtures [11].

Effect of Solvent Composition

The acid-catalyzed oxidation of BA was studied in solutions containing varying proportions of $DMSO$ and CH_2Cl_2 (Table 3). Permittivity (D) values for $DMSO$ – CH_2Cl_2 were estimated from the dielectric constants of the pure solvents [12] and are recorded in Table 3. It can be seen that the solvent effect on reactivity is quite significant. A plot of $\log k_1$ against the inverse of permittivity is linear ($r = 0.9618$) with a positive slope. This suggests an ion-dipole interaction in agreement [13] with the observation that in the presence of an acid, the rate-determining step involves a protonated $Cr(VI)$ species. The oxidation of BA was studied in eight organic solvents. The solubility of the reactants and the reaction of $QxDC$ with primary and secondary alcohols limited the choice of solvents. The values of the rate constant, k_{obs} , are recorded in Table 4. The increase in rate caused by the decrease in solvent polarity was attributed to an equilibrium shift favoring the formation of chromate ester [14].

Effect of Temperature

The catalyzed oxidation of the substituted benzyl alcohols was studied at different temperatures and it was observed that the rate increased with an increase in

Table 3. Dependence of the reaction rate on solvent composition^a

$DMSO:CH_2Cl_2 (v/v)$	70:30	60:40	50:50	40:60	30:70
D	35.40	31.60	27.80	24.00	20.24
$10^4 k_1/s^{-1}$	12.32	17.08	23.58	30.32	39.73

^a $[QxDC] = 0.003 M$, $[BA] = 0.06 M$, $[TsOH] = 0.05 M$; $T = 303 K$

Table 4. Effect of solvent on the oxidation of *BA* by *QxDC* at 303 K^a

Solvent	$10^4 k_1/s^{-1}$
<i>DMSO</i>	11.25
Dimethylformamide	13.01
Acetone	24.13
Dichloromethane	49.40
Tetrahydrofuran	57.49
Chloroform	86.54
Toluene	151.68
Benzene	160.15

^a [*QxDC*] = 0.003 M, [*BA*] = 0.06 M, [*TSOH*] = 0.05 M

Table 5. Temperature dependence of the oxidation of substituted benzyl alcohols by *QxDC*

No.	Substituents	$10^4 k_1/s^{-1}$			
		298 K	303 K	308 K	313 K
1	<i>p</i> -OMe	14.12	23.99	27.54	48.98
2	<i>p</i> -Me	13.59	23.18	26.57	45.52
3	<i>m</i> -Me	10.12	14.87	21.56	32.34
4	H	8.38	11.25	15.99	21.55
5	<i>m</i> -OMe	7.65	9.75	14.24	17.60
6	<i>p</i> -Cl	5.78	8.51	10.91	15.40
7	<i>p</i> -Br	5.41	7.86	9.55	12.44
8	<i>m</i> -Cl	4.15	6.72	8.58	10.92
9	<i>m</i> -Br	3.22	4.64	6.14	8.83
10	<i>p</i> -NO ₂	2.80	4.01	5.42	7.95
11	<i>PhCD</i> ₂ OH	1.17	1.66	2.35	3.33

[*QxDC*] = 0.003 M, [Alcohol] = 0.06 M, [*TSOH*] = 0.05 M

temperature (Table 5). From the linear plots of $\log k$ against the reciprocal of temperature, the activation energy was calculated. The activation parameters were calculated (Table 6) using the *Eyring* equation and the *Gibbs* equation [15].

Kinetic Isotope Effect

To ascertain the importance of the cleavage of the α -C–H bond in the rate-determining step, the oxidation of α,α -dideuteriobenzyl alcohol was studied at four different temperatures (*cf.* Table 5). The reaction exhibited the presence of a substantial primary kinetic isotope effect ($k_H/k_D = 6.78$ at 303 K).

Induced Polymerization of Acrylonitrile

The oxidation of *BA* under a nitrogen atmosphere failed to induce polymerization of acrylonitrile. Further addition of acrylonitrile had no effect on the rate (Table 1). Thus, a one-electron oxidation giving rise to free radicals is unlikely.

Table 6. Activation parameters of the oxidation of substituted benzyl alcohols by *QxDC*

Substituent	ΔH^\ddagger kJ mol ⁻¹	$-\Delta S^\ddagger$ J mol ⁻¹ K ⁻¹	ΔG_{298}^\ddagger kJ mol ⁻¹
<i>p</i> -OMe	58.2 ± 0.3	104 ± 1.0	88.9 ± 0.4
<i>p</i> -Me	56.6 ± 0.5	109 ± 1.5	89.1 ± 0.7
<i>m</i> -Me	57.8 ± 0.1	108 ± 0.5	89.9 ± 0.2
H	47.3 ± 0.8	145 ± 2.5	90.5 ± 1.1
<i>m</i> -OMe	41.1 ± 0.8	166 ± 2.5	90.6 ± 1.1
<i>p</i> -Cl	47.5 ± 0.4	147 ± 1.5	91.3 ± 0.6
<i>p</i> -Br	39.9 ± 0.7	173 ± 2.5	91.5 ± 1.0
<i>m</i> -Cl	47.2 ± 0.4	151 ± 1.0	92.2 ± 0.5
<i>m</i> -Br	49.2 ± 0.8	146 ± 2.5	92.7 ± 1.1
<i>p</i> -NO ₂	54.4 ± 1.0	131 ± 3.0	93.4 ± 1.3
PhCD ₂ OH	52.1 ± 1.1	144 ± 3.5	95.0 ± 1.5

Correlation Analysis of Reactivity

A Hammett plot [16] of $\log k_1$ vs. σ was drawn (Fig. 1) to correlate structure-reactivity for these reactions. The rate increased with electron-donating groups and decreased with respect to electron-withdrawing groups (Table 5). Electron-donating substituents stabilize a transition state having a carbocation centre by resonance. This facilitates the bond-breaking process in the transition state. On the other hand, an electron-withdrawing substituent increases the capacity of the carbocation centre, suggesting the development of a loose or partial positive charge at the transition state, which in turn helps the bond-making process, thus leading to a decrease in rate. The negative ρ values indicate an electron-deficient transition state and increase with increase in temperature. The ρ values at temperatures 298, 303, 308, and 313 K are -1.05 , -1.09 , -1.10 and -1.25 . Such values are not uncommon in hydride ion transfer mechanism [17]. The similarity of ΔG^\ddagger values

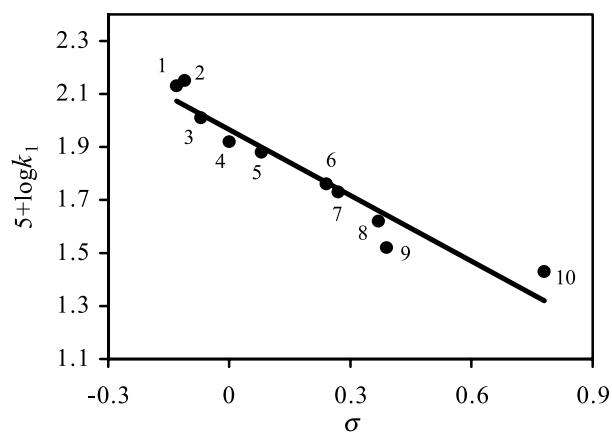
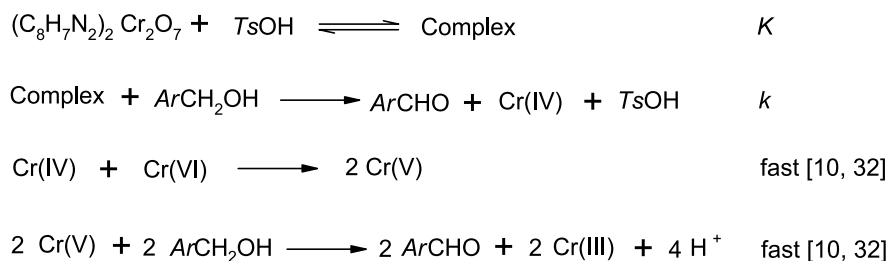


Fig. 1. Hammett plot for the *QxDC* oxidation of substituted benzyl alcohols (for numbering see Table 5)



Scheme 1

arises from changes in ΔH^\ddagger and ΔS^\ddagger values and stresses the probability that these oxidation reactions involve similar rate determining steps (Table 6). The high negative values of activation entropies support the assumption of a highly solvated transition state due to its increased polarity. They are also indicative of the bimolecular rate-determining step [18] as shown in Scheme 1.

The correlation between activation enthalpies and entropies of oxidation of the eleven alcohols is fairly good ($r=0.9891$). The value of the isokinetic temperature is 267 K. However, according to *Exner* [15] an isokinetic relationship between the calculated values of activation enthalpies and entropies is often vitiated by random experimental errors. *Exner* suggested an alternative method for establishing the isokinetic relationship. *Exner's* plot between $\log k_1$ at 298 K and at 313 K was reasonably linear ($r=0.9732$, Fig. 2). The value of isokinetic temperature evaluated from *Exner's* plot is 186 K. The linear isokinetic correlation implies that all the alcohols are oxidized by the same mechanism and the changes in the rate are governed by changes in both the enthalpy and entropy of activation.

Mechanism

The oxidations have been studied in non-aqueous medium. Thus, hydrolysis of dichromate may safely be ruled out. *QxDC* shows stronger absorbance in the wave length region 375–320 nm than $\text{K}_2\text{Cr}_2\text{O}_7$. This indicates that in solution *QxDC* does not dissociate to any appreciable extent. The fact that only *TsOH* brings about

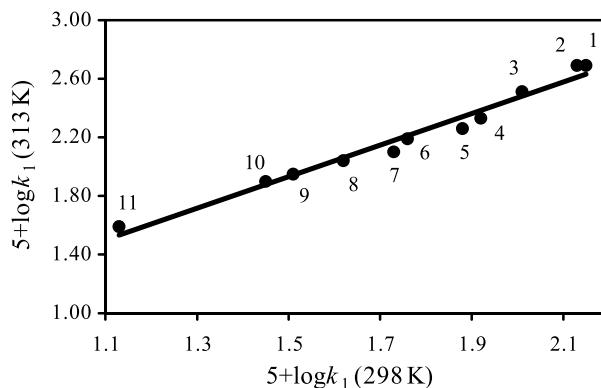


Fig. 2. *Exner* plot for the *QxDC* oxidation of substituted benzyl alcohols (for numbering see Table 5)

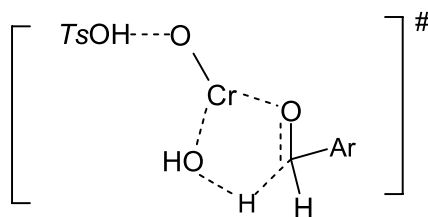
the oxidation points out an involvement of *TsOH* in the oxidation process. The UV-VIS spectrum clearly confirms the complex formation between oxidant and *TsOH*. Complex formation between imidazolium dichromate-*TsOH* [19], pyridinium dichromate-*TsOH* [20], *NDC-TsOH*, and *INDC-TsOH* [21] has already been reported. If the formation constant of the complex is small the oxidation is dependent on [*TsOH*]. The *QxDC-TsOH* complex is more reactive than other Cr(VI) species because the complexation makes the oxidant a better electrophile. It behaves like a protonated Cr(VI) species, which is a stronger oxidant and electrophile [10].

An examination of the kinetic data obtained in the present investigation showed that the rate of oxidation of the alcohols was dependent on the first powers of the concentrations for each reactant (substrate, oxidant, and acid) (Table 1) and *QxDC-TsOH* is the likely oxidizing species.

The presence of a substantial primary kinetic isotope effect indicates that the rupture of the C–H bond occurs after the O–H bond cleavage creating a carbocation centre or a positive character in the transition state. The ρ values higher than -3 generally suggest a fairly large degree of carbonium character in the transition state [22]. The ρ value of -1.09 found in the present study is indicative of a partial bonding. The negative value of the polar reaction constant together with the substantial deuterium isotope effect indicates that the transition state approaches a carbocation in character. Hence, the transfer of a hydride from the alcohol to the oxidant is suggested.

The hydride transfer may take place either by a cyclic process *via* an ester intermediate [23] or by an acyclic one-step bimolecular process [24]. *Kwart* and *Nickel* [23] have shown that the dependence of k_H/k_D on temperature can be successfully employed to determine whether the loss of hydrogen proceeds through a concerted cyclic process or by an acyclic one.

The data for protio- and deuterio-benzyl alcohols, fitted to the familiar expression, $k_H/k_D = A_H/A_D e^{-\Delta H^\ddagger/RT}$, show a direct correspondence with the properties of a symmetrical transition state in which activation-energy difference for protio- and deuterio-compounds are equal to the difference in the zero-point energy for the respective C–H and C–D bonds (ca. 4.5 kJ mol^{-1}) and the entropies of activation of the respective reactions are nearly equal [25, 26]. Evidence against a hydrogen transfer occurring by a concerted one-step bimolecular process has been well documented by *Bordwell* [27]. It is evident that in the present study also the hydrogen transfer does not occur by an acyclic bimolecular process. It is well established that intrinsically concerted sigmatropic reactions characterized by a transfer of a hydrogen in a cyclic transition state are the only truly symmetrical processes involving a linear hydrogen transfer [28]. Furthermore, a cyclic hydride transfer in the oxidation of alcohols by Cr(VI) involves six electrons and, being a *Hückel*-type system, is an allowed process [29]. Therefore, one can safely conclude that in the oxidation of benzyl alcohols by *QxDC*, the hydride transfer occurs *via* a chromate ester. Formation of ester intermediates in the oxidation of hydroxy compounds is well documented [10]. Further, an intermolecular hydride transfer should normally lead to a correlation with σ^+ values [30]. Good correlation with *Hammnett's* σ values is also in accordance with the ester mechanism. A mechanism depicted in Scheme 2 accounts for the experimental results. Thus, a transition state having a planar, cyclic symmetrical structure can be envisaged for the decomposition of the ester



Scheme 2

intermediate (Scheme 2). A linear transition state will certainly exhibit a larger isotope effect than a cyclic intermediate [31].

Experimental

Materials

All the alcohols were commercial products (Fluka or Aldrich) and purified by either recrystallization or distillation. *p*-Toluenesulphonic acid (*TsOH*) was used as a source of protons. *DMSO* and CH_2Cl_2 were purified by the usual methods [33]. α,α -Dideuteriobenzyl alcohol was purchased from Isotec Inc. (USA), its isotopic purity was $\geq 98\%$.

Product Analysis

The product analysis was carried out under kinetic conditions. In a typical experiment *BA* (0.51 cm^3 , 0.005 mol) and *QxDC* (0.48 g , 0.001 mol) were dissolved in 10 cm^3 of *DMSO* and the solution was allowed to stand for ca. 24 h to ensure completion of the reaction. Most of the solvent was removed by distillation under reduced pressure. The residue was then treated with an excess of a freshly prepared saturated solution of 2,4-dinitrophenylhydrazine in $1.5 \text{ M H}_2\text{SO}_4$ and kept overnight in a refrigerator. The precipitated 2,4-dinitrophenylhydrazone (*DNP*) was filtered off, dried, weighed, recrystallized from ethanol, and weighed again. The product was identical (mp and mixture mp) with an authentic sample of the *DNP* of benzaldehyde. The yields of *DNP* before and after recrystallization were 84% and 76%.

Kinetic Measurements

The pseudo-first-order conditions were attained by keeping a large excess (10-fold or greater) of the alcohols with respect to *QxDC*. The reactions were carried out at constant temperature ($\pm 0.3 \text{ K}$) and were followed up to 80% conversion by monitoring the decrease in $[\text{QxDC}]$ at 355 nm on a Shimadzu UV-160A double-beam spectrophotometer. The pseudo-first-order rate constant, k_1 , was evaluated from the linear plots of $\ln[\text{QxDC}]$ versus time. The values reported were the mean of at least duplicate runs and were reproducible to within $\pm 4\%$.

Acknowledgements

The authors are grateful to the Research Foundation of Gazi University for supporting this study.

References

- [1] Murugesan V, Panduragan A (1992) *Indian J Chem* **31B**: 377
- [2] Corey EJ, Suggs JW (1975) *Tetrahedron Lett* **16**: 2647

- [3] Corey EJ, Schmidt G (1979) *Tetrahedron Lett* **20**: 399
- [4] Bhattacharjee MN, Chaudhuri MK, Dasgupta HS, Roy N (1982) *Synthesis* **7**: 588
- [5] Srinivasan R, Ramosh CV, Madhulatha W, Balasubramanian K (1996) *Indian J Chem* **35B**: 480
- [6] a) Özgün B, Değirmenbaşı N (1996) *Synth Commun* **26**: 3601; b) Özgün B, Değirmenbaşı N (1999) *Synth Commun* **29**: 763; c) Değirmenbaşı N, Özgün B (2002) *J Inst Sci Techn Gazi Univ* **15**: 657; d) Değirmenbaşı N, Özgün B (2003) *Monatsh Chem* **134**: 1565; e) Değirmenbaşı N, Özgün B (2003) *Monatsh Chem* (accepted for publication)
- [7] Özgün B, Pek A (1991) *React Kinet Catal Lett* **43**: 589
- [8] Özgün HB, Değirmenbaşı N (1997) *J Chem Res (S)* 32; (1997) *J Chem Res (M)* 220
- [9] Değirmenbaşı N, Özgün B (2002) *Monatsh Chem* **133**: 1417
- [10] Wiberg KB (1965) *Oxidation in Organic Chemistry*, part A. Academic Press, New York, p 69
- [11] a) Banerji KK (1978) *J Chem Res (M)* 2561; b) Banerji KK (1979) *Ind J Chem* **17A**: 300
- [12] Furniss BS, Hannaford AJ, Smith PWG, Tatchell AR (1989) *Vogel's Textbook of Practical Organic Chemistry*. John Wiley & Sons, New York, p 1442
- [13] Amis ES (1967) *Solvent Effects on Reaction Rates and Mechanisms*. Academic Press, New York, p 42
- [14] Westheimer FH (1949) *Chem Rev* **45**: 419
- [15] Frost AA, Pearson RG (1970) *Kinetics and Mechanism*. Wiley Eastern, New Delhi, p 144
- [16] Wiberg KB (1964) *Physical Organic Chemistry*. Wiley, New York, p 403
- [17] Harlan L, Goering & Robert RJ (1958) *J Am Chem Soc* **80**: 3277
- [18] Klumpp GW (1982) *Reactivity in Organic Chemistry*. Wiley, New York
- [19] Chidambaranathan V (1997) Ph.D. Thesis, Annamalai University, Annamalainagar
- [20] Amutha M (1999) Ph.D. Thesis, Annamalai University, Annamalainagar
- [21] Karunakaran C, Chidambaranathan V (1999) *Revue Roumaine de Chimie* **44**: 491
- [22] Freeman F, Yamachika NJ (1970) *J Am Chem Soc* **92**: 3730
- [23] Kwart H, Nickle JH (1973) *J Am Chem Soc* **95**: 3394
- [24] Rocek J, Westheimer FH, Eschenmoser A, Moldovanyi L, Schreiber J (1962) *Helv Chim Acta* **45**: 2554
- [25] Kwart H, Latimer HC (1971) *J Am Chem Soc* **93**: 3770
- [26] Kwart H, Slutsky J (1972) *J Chem Soc Chem Commun*: 1182
- [27] Bordwell FG (1972) *Acc Chem Res* **5**: 374
- [28] Woodward RB, Hoffmann R (1969) *Angew Chem* **8**: 781
- [29] Littler JS (1971) *Tetrahedron* **27**: 81
- [30] Wiberg KB (1963) *Physical Organic Chemistry*. John Wiley, New York, p 410
- [31] Scott SL, Bakac A, Espenson JH (1992) *J Am Chem Soc* **114**: 4205
- [32] Cainelli G, Cardillo G (1984) *Chromium Oxidation in Organic Chemistry*. Springer, Berlin
- [33] Perrin DD, Armarego WL, Perrin DR (1966) *Purification of Organic Compounds*. Pergamon Press, Oxford