181. Polar Substituent Effects in the Solvolysis of Acyclic Tertiary Chlorides

Polar Effects VI

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Dedicated to Professor Dr. *Edgardo Giovannini* on the occasion of his 70th birthday

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Summary

The influence of twenty substituents R on the solvolysis rates and products of tertiary chlorides $R-CH_2CH_2C(CH_3)_2Cl$ (**7**) has been studied. H, CH_3, $(CH_3)_2NCH_2$, $ClCH_2$, Cl, CN and NO_2 exert an inductive effect only, as the good correlation of the rates with the corresponding inductive substituent constants σ_I^q shows. Bulkier alkyl groups, *i.e.* isopropyl and *t*-butyl, lower the rate due to a *Baker-Nathan* effect, while the *n*-electron donors CH_3S, CH_3O, HO and $(CH_3)_2N$ and the σ-electron donors $(CH_3)_3Sn$ and $HOCH_2$ cause rate increases based on σ_I^q constants. These accelerations are attributed to C,C-hyperconjugative and inductomeric effects which arise in the transition state for ionization. A comparison of the reactivity of the acyclic chlorides **7** and the corresponding 1-R-substituted 3-bromoadamantanes **1a** shows that polar substituent effects are more strongly transmitted in the rigid bicyclic compounds **1a** than in the flexible acyclic compounds **7**.

Introduction. As recently reported [1] several kinds of polar substituent effects are observable in the solvolysis of 1-R-substituted 3-bromoadamantanes **1a** in 80% (vol.-%) ethanol. When R was a hydrogen atom, an alkyl or an electron withdrawing substituent such as $BrCH_2$, HOOC, Br or CN, the logarithms of the respective first order rate constants ($\log k$) correlated well with the inductive substituent constants σ_I^q of R, as derived from the pK_a values of the corresponding 4-R-substituted quinuclidinium perchlorates **2** [2]. Ionization to adamantyl cations **3**, the precursors of adamantanols **1b** and their ethyl ethers **1c**, is therefore controlled by the inductive effect of R only in these cases.

On the other hand solvolysis rates were higher than calculated on the basis of the respective σ_I^q values when R was a *n*-electron donor (+*M*-substituent) such as HO, CH_3O and CH_3S, or a π-electron-donor such as C_6H_5 and $CH_3C{=}CH_2$. Surprisingly, rate increases were also observed when R was an electrofugal group [3], *i.e.* a σ-electron donor such as H_2NCH_2, $HOCH_2$, $H_2NC{=}O$ and $(CH_3)_3Sn$, despite the strong $-I$-effect of some of these groups [2]. These rate enhance-

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ments were ascribed to C,C-hyperconjugative or inductomeric [4] relay of positive charge from the incipient cationic center C(3) to the substituent at C(1), as depicted in **4** and **5**. Finally, when R was a powerful *n*-electron donor such as O^-, S^- and $(CH_3)_2N$, solvolytic fragmentation occurred yielding **6** with R = O, S and $(CH_3)_2N^+$, respectively. In the latter cases, then, the $-I$-effect of the substituents is partly or entirely compensated by an additional effect which is called into play in the transition state.

The bromoadamantanes **1a** were chosen for study because of the rigidly antiplanar orientation of the C(1),C(2)- and C(3),Br-bonds, which favors concerted fragmentation [5] and, by inference, also C,C-hyperconjugation. However, the question remained whether polar effects would be observable in similar, freely rotating acyclic models, such as **7**. These compounds are derived from adamantyl derivatives by omitting half of the carbon atoms, as indicated by the broken line in **1**. Furthermore, it was expedient to substitute Cl- for Br-atom as the leaving group in order to ensure conveniently measurable reaction rates. Consequently, the solvolyses of the γ-substituted tertiary chlorides **7** in *Table 1* were studied in 70% (vol.-%) dioxane, as described in the subsequent paper [6]. The present paper is concerned with the polar effects of the substituents R on reaction rates. However, it had also to be taken into account that substituents possessing a nucleophilic center as in **7f**, **7o**, **7q** and **7r**, might exert an accelerating neighboring group effect leading to cyclization, notwithstanding that such participation is usually not observed with leaving groups bonded to a tertiary carbon atom [7].

Table 1. *Reaction products (in %) from $R-CH_2CH_2C(CH_3)_2Cl$ (7) in 70% dioxane [6]*

Starting material		Products			
7	R	Alcohols **8**	Olefins **9**	Olefins **10**	Cyclization products
a	H	71		29[a]	
e	$(CH_3)_3C$	41	35	24	
f[b]	$(CH_3)_2NCH_2$	42	23	14	**11**: 21
g[c]	$ClCH_2$	72[d]	21	7	
h	EtOOC	55[d]	21	24	
i	Cl	45	20[e]	35	
j[f]	NC	52	24	24	
k	O_2N	43	19[e]	38	
l[g]	CH_3S	46	26	28	
m	CH_3O	58	12	30	
n	HO	49	5	46	
o[b]	$(CH_3)_2N$	27[h]		37	**12**: 1
p	$(CH_3)_3Sn$				**13**: 100
q[c][f]	$HOCH_2$	49	30	12	**14**: 9
r	HOOC		3	2	**15**: 95
s[f]	OOC^-		6	5	**15**: 89
t	$(CH_3)_3N^+$	48	30	22	

[a] Mixture of **9** and **10** not separable by GLC. [b] 3 equiv. of NaOH added. [c] In 70% aqueous acetone. [d] The alcohol undergoes a secondary reaction [6]. [e] Determined as secondary product [6]. [f] With 3 equiv. Et_3N. [g] With 2 equiv. Et_3N. [h] Beside 35% fragmentation.

Table 2. *First order rate constants* k a) *for* 10^{-3}M *4-substituted 2-chloro-2-methylbutanes* 7 *in 80% ethanol*

Nr.	R	T [°]	k [s^{-1}]	$H^{\ddagger}$ [kcal/mol]	$S^{\ddagger}$ [cal/mol · degree]
7a	H	40.13	$1.04 \cdot 10^{-4}$	21.96 ± 0.22	− 6.78 ± 0.68
		49.86	$3.05 \cdot 10^{-4}$		
		59.57	$8.69 \cdot 10^{-4}$		
		60.00	$9.02 \cdot 10^{-4}$ b)		
7b	CH_3	52.05	$3.56 \cdot 10^{-4}$	21.83 ± 0.30	− 7.35 ± 0.90
		60.00	$8.20 \cdot 10^{-4}$ b)		
		66.00	$1.52 \cdot 10^{-3}$		
		71.90	$2.62 \cdot 10^{-3}$		
7c	CH_3CH_2	40.00	$8.75 \cdot 10^{-5}$	22.04 ± 0.04	− 6.84 ± 0.14
		56.25	$5.25 \cdot 10^{-4}$		
		60.00	$7.79 \cdot 10^{-4}$ b)		
		71.75	$2.51 \cdot 10^{-3}$		
7d	$(CH_3)_2CH$	56.00	$4.72 \cdot 10^{-4}$	21.77 ± 0.04	− 7.81 ± 0.12
		60.00	$7.12 \cdot 10^{-4}$ b)		
		76.00	$3.37 \cdot 10^{-3}$		
7e	$(CH_3)_3C$	50.00	$2.12 \cdot 10^{-4}$	21.84 ± 0.01	− 7.93 ± 0.04
		60.00	$6.08 \cdot 10^{-4}$		
		70.00	$1.64 \cdot 10^{-3}$		
7f	$(CH_3)_2NCH_2$	50.00	$1.87 \cdot 10^{-4}$ c)	22.79 ± 0.33	− 5.25 ± 0.98
		60.00	$5.45 \cdot 10^{-4}$ c)		
		60.00	$5.54 \cdot 10^{-4}$ b)		
		70.01	$1.57 \cdot 10^{-3}$ c)		
7g	$ClCH_2$	59.94	$2.14 \cdot 10^{-4}$ d)	19.41 ± 0.18	− 17.25 ± 0.52
		60.00	$2.16 \cdot 10^{-4}$ b)		
		69.95	$5.26 \cdot 10^{-4}$ d)		
		79.77	$1.18 \cdot 10^{-3}$ d)		
7h	EtOOC	60.00	$8.41 \cdot 10^{-5}$ b)	22.57 ± 0.19	− 9.67 ± 0.55
		69.97	$2.32 \cdot 10^{-4}$ e)		
		79.97	$6.18 \cdot 10^{-4}$ e)		
		90.02	$1.53 \cdot 10^{-3}$ e)		
7i	Cl	60.00	$2.20 \cdot 10^{-5}$ b)	22.89 ± 0.16	− 11.36 ± 0.44
		70.01	$6.18 \cdot 10^{-5}$		
		79.97	$1.66 \cdot 10^{-4}$		
		90.00	$4.15 \cdot 10^{-4}$		
7j	CN	60.00	$8.38 \cdot 10^{-6}$ b)	22.79 ± 0.15	− 13.59 ± 0.39
		100.07	$3.77 \cdot 10^{-4}$		
		110.00	$8.65 \cdot 10^{-4}$		
		119.55	$1.82 \cdot 10^{-3}$		
7k	NO_2	60.00	$2.42 \cdot 10^{-6}$ b)	26.83 ± 0.26	− 3.93 ± 0.70
		90.37	$7.84 \cdot 10^{-5}$		
		99.80	$2.02 \cdot 10^{-4}$		
		110.15	$5.62 \cdot 10^{-4}$		

Table 2 (continued)

Nr.	R	T [°]	k [s^{-1}]	$H^{\ddagger}$ [kcal/mol]	$S^{\ddagger}$ [cal/mol · degree]
7l	CH_3S	56.00	$7.55\cdot10^{-5}$	22.77±0.04	− 8.43±0.01
		60.00	$1.16\cdot10^{-4}$[b]		
		66.00	$2.17\cdot10^{-4}$		
		76.00	$5.88\cdot10^{-4}$		
7m	CH_3O	56.00	$1.04\cdot10^{-4}$[f]	23.41±0.12	− 5.85±0.36
		60.00	$1.61\cdot10^{-4}$[b]		
		66.00	$3.05\cdot10^{-4}$[f]		
		76.00	$8.57\cdot10^{-4}$[f]		
7n	HO	52.05	$1.64\cdot10^{-4}$	23.50±0.31	− 3.79±0.91
		60.00	$3.97\cdot10^{-4}$[b]		
		62.00	$4.86\cdot10^{-4}$		
		71.90	$1.41\cdot10^{-3}$		
7o	$(CH_3)_2N$	56.00	$3.57\cdot10^{-4}$	23.79±0.05	− 2.45±0.15
		60.00	$5.59\cdot10^{-4}$[b]		
		76.00	$3.04\cdot10^{-3}$		
7p	$(CH_3)_3Sn$	40.00	$1.13\cdot10^{-3}$[e]	18.93±0.09	−11.68±0.29
		50.00	$3.01\cdot10^{-3}$[e]		
		59.98	$7.45\cdot10^{-3}$[e]		
		60.00	$7.48\cdot10^{-3}$[b]		
7q	$HOCH_2$	50.10	$3.47\cdot10^{-4}$	21.29±0.04	− 8.68±0.11
		59.94	$9.49\cdot10^{-4}$		
		60.00	$9.57\cdot10^{-4}$[b]		
		70.00	$2.52\cdot10^{-3}$		
7r	HOOC	60.00	$1.37\cdot10^{-4}$[b]	20.88±0.01	−13.75±0.04
		69.87	$3.50\cdot10^{-4}$[g]		
		79.93	$8.62\cdot10^{-4}$[g]		
		89.95	$2.02\cdot10^{-3}$[g]		
7s	^{-}OOC	49.96	$1.66\cdot10^{-3}$[c]	19.13±0.27	−12.21±0.83
		59.98	$4.29\cdot10^{-3}$[c]		
		60.00	$4.24\cdot10^{-3}$[b]		
		69.91	$9.98\cdot10^{-3}$[c]		
7t	$(CH_3)_3N^+$	60.00	$6.65\cdot10^{-6}$[b]	23.64±0.02	−11.49±0.06
		80.08	$5.37\cdot10^{-5}$		
		90.08	$1.39\cdot10^{-4}$		
		110.35	$8.32\cdot10^{-4}$		

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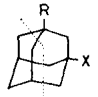
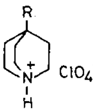
[a] Average of three runs, maximum deviation from mean value 3.8%. [b] Extrapolated. [c] With 3 or 5 equiv. Et_3N. [d] Calculated from the first half life. [e] With or without 3 equiv. of Et_3N. [f] In agreement with previous measurements [12]. [g] With 3 equiv. of *p*-toluenesulfonic acid.



1a X = Br
b X = OH
c X = OEt



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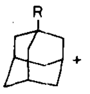

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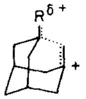

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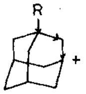

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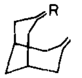

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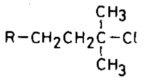

$R{-}CH_2CH_2\overset{CH_3}{\underset{CH_3}{C}}{-}Cl$

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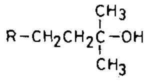

$R{-}CH_2CH_2\overset{CH_3}{\underset{CH_3}{C}}{-}OH$

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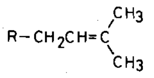

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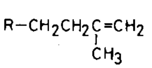

$R{-}CH_2CH_2\underset{CH_3}{C}{=}CH_2$

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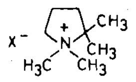

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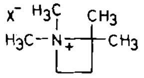

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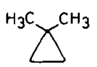

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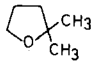

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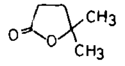

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Results. Reaction of the chlorides **7a** and **7e–7t** in aqueous dioxane led to the corresponding alcohols **8** and olefins **9** and **10** which, in the case of **7f** and **7o–7s**, were accompanied by the cyclized products **11–15**, respectively [6]. The products and their yields are summarized in *Table 1.*

The rate constants, which were measured conductometrically in 80% ethanol [1], obeyed the first order rate law. They are listed in *Table 2.* In the case of **7g** the rate constant was calculated from the conductivity change during the first half life because formation of the alcohol **8** (R = $ClCH_2$) is followed by its cyclization to the ether **14** in a secondary reaction which is about three times slower than the initial reaction.

The only products obtained from the trimethyltin derivative **7p** were 1,1-dimethylcyclopropane (**13**) and trimethyltinhydroxide *(Table 1).* At first it was not clear whether the former was formed in a concerted 1,3-elimination reaction according to **16** or by way of the carbenium ion **17**. A decision was reached by comparing the solvent sensitivity factor *m* in the *Grunwald-Winstein* equation [8] for **7p** in 70, 80 and 90% ethanol with the *m*-value for the 'homomorph' **7e** in the same solvents *(Table 3).* The *m*-values for **7p** and **7e** of 0.71 and 0.78, respectively, lie in the range which is characteristic of limiting (S_N1) solvolyses[1]. A two-step process involving the cationic intermediate **17** is thus indicated for **7p**.

Discussion. As noted in the introduction the question is whether the inductive effect, as measured by σ_I^q, accounts for the total polar effect of the substituents R

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[1] *m*-Values between 0.2 and 0.4 are typical of displacement reactions such as the one shown in **16** [8].

Table 3. *First order rate constants (s^{-1}) for $(CH_3)_3SnCH_2CH_2C(CH_3)_2Cl$* (**7p**) *and $(CH_3)_3CCH_2CH_2C(CH_3)_2Cl$* (**7e**) *in ethanol/water at 50.0°*

Solvent	**7p**	**7e**
70% ethanol	$7.75 \cdot 10^{-3}$	$6.31 \cdot 10^{-4}$
80% ethanol	$3.01 \cdot 10^{-3}$	$2.12 \cdot 10^{-4}$
90% ethanol	$8.68 \cdot 10^{-4}$	$5.57 \cdot 10^{-5}$

in the chlorides **7a**–**7t**. A plot of log*k* for these chlorides against σ_I^q shows *(Fig. 1)* that this does not apply to all the cases. In fact four kinds of substituent effects are discernible.

The first kind is observed with the substituents H, CH_3, $(CH_3)_2NCH_2$, $ClCH_2$, Cl, CN and NO_2. The log*k* values of these chlorides, *i.e.* **7a**, **7b** and **7f**–**k**, correlate well with the respective σ_I^q values (r = 0.9956). Ionization rates are therefore controlled by the inductive effect alone. The reaction constant ρ of -0.71 derived from the slope of the inductive regression line *(Fig. 1)* shows that the ionization rates are less affected by the substituents than are the pK_a values of 4-substituted quinuclidinium salts **2**, for which ρ is unity by definition [2]. The ρ value for the solvolysis of these chlorides is also considerably lower than for the corresponding bromoadamantanes **1a**, namely -1.14 [1]. Since the distances between the substituent and the reaction centers are approximately equal in both series it follows that the inductive effect is less strongly transmitted through the acyclic molecules **7** than through the bulkier and rigid bicyclic compounds **1a**. This could be due to a stereoelectronic factor or to better access of the solvent 80% ethanol (dielectric

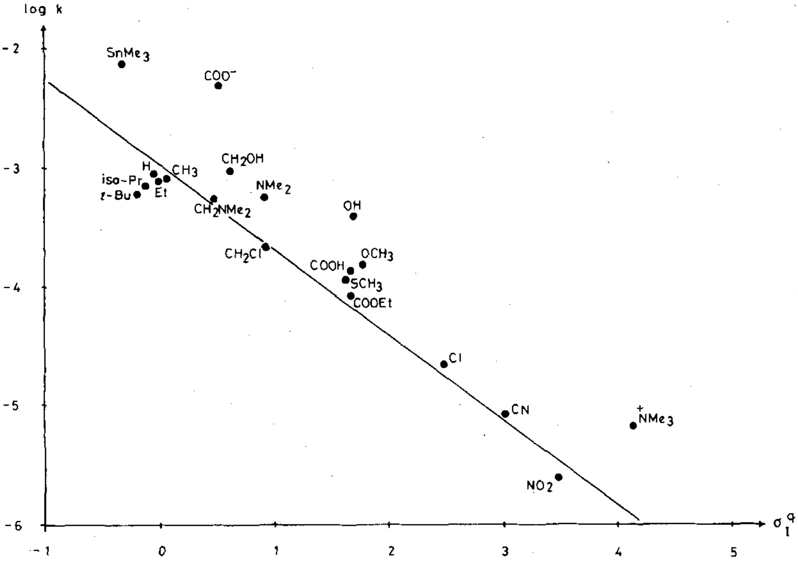

Fig. 1. *Relationship between log*k *for $R{-}CH_2CH_2C(CH_3)_2Cl$* (**7**) *in 80% ethanol and inductive substituent constants σ_I^q*

Table 4. *Relative rate constants for $R{-}CH_2CH_2C(CH_3)_2Cl$ (7) in 80% ethanol (60.0°), inductive substituent constants σ_I^q and deviation from the inductive regression line in* Figure 1

7	R	k_{rel}	σ_I^q	Deviations
a	H	1	0	
b	CH_3	0.91	0.11	
c	C_2H_5	0.86	0.03	
d	$(CH_3)_2CH$	0.79	−0.08	0.6
e	$(CH_3)_3C$	0.67	−0.15	0.4
f	$(CH_3)_2NCH_2$	0.61	0.52	
g	$ClCH_2$	0.24	1.02	
h	EtOOC	0.093	1.70	
i	Cl	0.024	2.51	
j	NC	0.0093	3.04	
k	O_2N	0.0027	3.52	
l	CH_3S	0.13	1.66	1.6
m	CH_3O	0.18	1.86	3
n	HO	0.44	1.74	6
o	$(CH_3)_2N$	0.62	1.05	2.5
p	$(CH_3)_3Sn$	8.3	−0.26	4
q	$HOCH_2$	1.1	0.66	2.5
r	HOOC	0.15	1.70	2
s	^{-}OOC	4.7	0.61	11
t	$(CH_3)_3N^+$	0.0074	4.15	(5.5)

constant 35) to the region between the substituent and the reaction center in the acyclic molecule. This should lead to an increase in the local effective dielectric constant and a concomitant attenuation of the polar effect.

The second group of substituents includes isopropyl and *t*-butyl, the corresponding chlorides **7d** and **7e** reacting 1.6–2.5 times, respectively, slower than expected (*Fig. 1* and *Table 4*)[2]. As the values of k_{rel} in *Table 4* show, the rates of the alkyl substituted chlorides decrease in the socalled *Baker-Nathan* order, *i.e.* $CH_3 > C_2H_5 > iso\text{-}C_3H_7 > t\text{-}C_4H_9$[3], which is now widely considered to result from the increase of steric hindrance to solvation of the incipient cation **18** which accompanies α-branching in the alkyl groups [9].

The chlorides **7l**–**7q** which form a third group react 1.6 to 6 times faster than predicted on the basis of the corresponding σ_I^q values (*Fig. 1* and *Table 4*). In this case the substituents are *n*-electron donors (+*M*-substituents), *i.e.* CH_3S, CH_3O, HO and $(CH_3)_2N$, as well as σ-electron donors (electrofugal groups), *i.e.* $(CH_3)_3Sn$ and $HOCH_2$. As observed with the corresponding bromoadamantanes **1a** [1] these substituents exert a special electron releasing effect which leads to rate enhancements. However, the latter are considerably smaller than in the adamantane series **1a**, where accelerations of 44 and 15,000 were observed for **1a** with R=OH and $(CH_3)_2N$, respectively [1]. The latter compound underwent concerted fragmentation to **6** ($R=(CH_3)_2N^+$), whereas the acyclic chloroamine **7o** fragmented by way of the cation **18** in 38% yield [11]. Nevertheless, it appears justifiable to explain the special substituent effects in the series **1a** and **7** in a like manner, namely by C, C-hyper-

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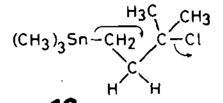
[2] The ethyl substituent is a borderline case.

[3] The electron donating effect of these alkyl groups increases in the reverse order [2] [10].



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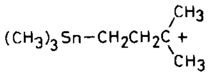

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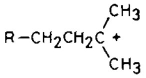
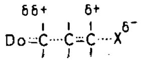
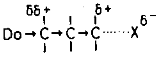


18



19



20

conjugation in the case of *n*-electron donors, and by the inductomeric effect in the case of σ-electron donors [4]. Both effects arise in the transition state for ionization, as illustrated by **19** and **20** (Do = donor).

However, these small accelerations could be also attributed to an anchimeric (neighboring group) effect in the cases in which R is nucleophilic, as when R = CH_3S, CH_3O, HO and $(CH_3)_2N$. However, it has been shown elsewhere4) that these chlorides react *via* carbenium ions **18** and that they do not undergo appreciable cyclization *(Table 1)*. Even the formation of 21% of the pyrrolidinium salt **11** from **7f** (R = $(CH_3)_2NCH_2$) and 9% of the cyclic ether **14** from **7q** (R = $HOCH_2$) show no clear evidence of being anchimerically assisted [14]. On the other hand the formation in all these cases of relatively large amounts of terminal olefins **10** (*Hofmann*-type elimination) points to the participation of sulfur, oxygen and nitrogen atoms during the proton abstraction in the intermediate cations **18**5). The behaviour of the third group of chlorides is therefore best explained by a mechanism involving intermediate carbenium ions of the type **18**–**20**.

However, some neighboring O–C(5) participation [7] cannot be excluded in the cyclization of **7r** (R = COOH) and **7s** (R = COO^-), which form the lactone **15** in yields of 95 and 89%, respectively, at elevated rates *(Fig. 1, Table 4)*. A strong indication that a different mechanism obtains for these compounds comes from the plot of log*k* for the acyclic chlorides **7** against log*k* for the corresponding 3-bromoadamantanes **1a** *(Fig. 2)*. If both series of compounds reacted by the same mechanism the points should lie close to the regression line, as most of them do. However, the points for HOOC and OOC^- lie well above, which indicates a rate-enhancing effect for **7r** and **7s** which is not available to the corresponding bromoadamantanes **1a**. Anchimeric assistance to ionization is such an effect since it cannot operate in the bicyclic bromides **1a**. As anticipated the point for $(CH_3)_2N$ lies well below the line in *Figure 2* because the bromoadamantane **1a** with R = $(CH_3)_2N$ undergoes concerted fragmentation to **6** (R = $(CH_3)_2N^+$) [1], in contrast to the acyclic chloride **7o** which reacts by way of the cation **18** (R = $(CH_3)_2N$).

The trimethylammonium salt **7t** also yielded products derived from the cation **18**. But its rate constant failed to correlate with σ_I^q *(Fig. 1, Table 4)*, despite the exclusively electron withdrawing nature of the $(CH_3)_3N^+$ group. However, it is well known that salts often fail to fit linear free energy relationships [15].

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4) For **7l** in [12], for **7m** and **7n** in [13], and for **7o** in [11].

5) This has been studied more thoroughly in the cases where R = HO and CH_3O [13].

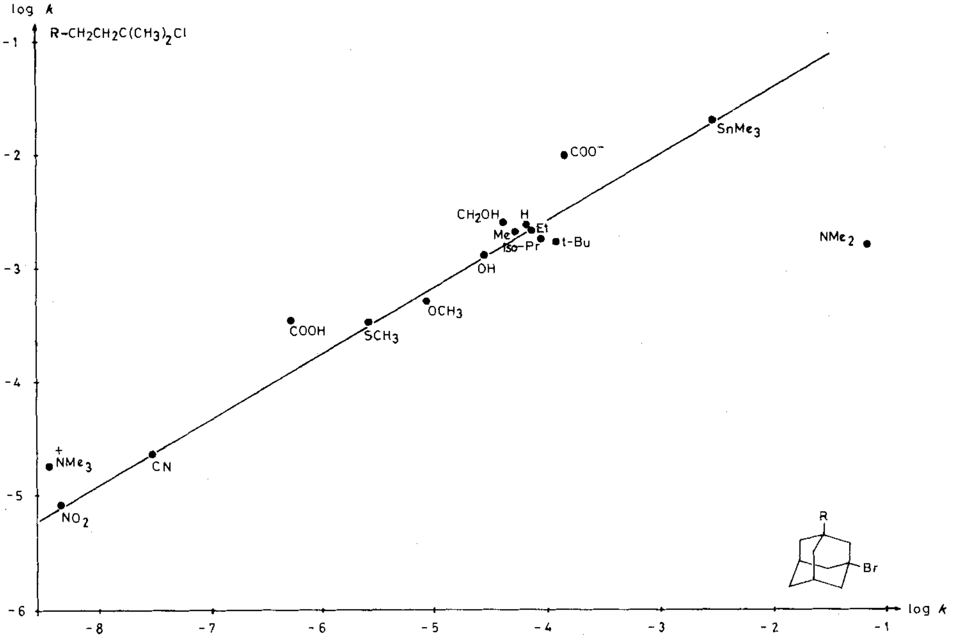

Fig. 2. *Relationship between* log k *for* $R-CH_2CH_2C(CH_3)_2Cl$ (7) *and* log k *for 1-R-3-bromoadamantanes* **1a** *in 80% ethanol*

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