

THE SOLVOLYSIS OF 1- AND 3-HOMOADAMANTYL-P-NITROBENZOATES IN ACETONITRILE-
WATER (70:30 by weight)*)

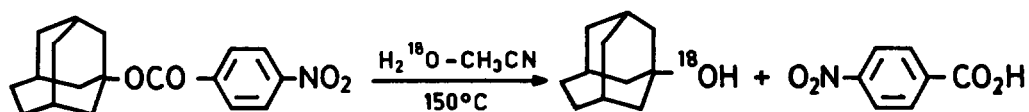
Ingrid Mergelsberg and Christoph Rüchardt⁺)

Chemisches Laboratorium der Universität Freiburg, Albertstr. 21, 7800 Frei-
burg (Germany)

Abstract The solvolysis rates of t.butyl, 1-adamantyl, 3- and 1-homoadaman-
tyl-p-nitrobenzoates in acetonitrile-water (70:30 by weight) are
reported and the relative rates are discussed. These are the first
solvolysis constants for 1- or 3-homoadamantyl esters of definite-
ly known structure.

The investigation of the solvolytic reactivity of polycyclic bridgehead
halides and tosylates has contributed much to the understanding of carbenium
ion chemistry¹⁾. Schleyer has shown that a linear relationship exists bet-
ween log k of solvolysis of a series of bridgehead bromides or tosylates²⁾
and the increase in strain on ionisation²⁾. This change in strain energy
 ΔH_{sp} was estimated by force field calculations as the difference in strain
of the polycyclic hydrocarbons and the bridgehead carbenium ions derived
from them²⁾. It proved to be impossible, however, to interpret the diffe-
rences in solvolytic reactivity of t.butyl and 1-adamantyl halides quanti-
tatively on the simple basis of strain arguments²⁾. The situation is better
understood since it has been shown that the ratio of t.butylchloride/1-ada-
mantyl chloride solvolysis rates, which varies between $10^{0.4}$ - $10^{3.7}$, is sol-
vent dependent owing to solvent participation in t.butyl chloride solvolyses.³⁾
To make the situation even more complex, it has been shown that in the gas
phase 1-adamantyl carbenium ions are $\sim 4 \text{ kcal}\cdot\text{mol}^{-1}$ more stable than t.butyl
carbenium ions owing to β -branching and CC-hyperconjugation in the bridge-
head cations^{4,5)} (vertical stabilisation⁶⁾). Only little reliable infor-
mation of this type is available for solvolysis reactions of the isomeric
homoadamantane bridgehead esters¹⁾. The kinetic data reported by Stetter⁷⁾

and by Stepanov⁸⁾ for the solvolysis of 1-homoadamantyl- and 3-homoadamantyl bromides and chlorides were obtained at a time when reliable structure information about this polycyclic system and its position isomers was not yet available^{9,10)}. Even the adamantyl carbinyl isomers could not be distinguished routinely then¹¹⁾. Our attempts to prepare pure 1- or 3-homoadamantyl bromides starting from the easily accessible corresponding carboxylic acids via Hunsdiecker procedures or via Baeyer-Villiger degradation to the corresponding alcohols and their transformation to the bromides were unsuccessful¹²⁾. We therefore decided to study the kinetics of hydrolysis of 1- and 3-homoadamantyl-p-nitrobenzoates in acetonitrile-water (70:30 by weight) with $\sim 10^{-3}$ mol \cdot l $^{-1}$ KOAC added¹³⁾ at 150°C using the ampule technique. The concentration of the esters was monitored by HPLC (25 cm column, Ø 4.6 mm; LiChrosorb Reversed Phase Merck RP-18 and RP-8, 30°C). For comparison t.butyl and 1-adamantyl p-nitrobenzoates were also studied. After 10 half times 94-98% of the corresponding bridgehead carbinols was formed (GC). 1-Hydroxy-homoadamantane isolated from a solvolysis reaction in H₂¹⁸O-CH₃CN (68% ¹⁸O-enrichment) had the same ¹⁸O-enrichment as the solvent according to MS-analysis. This excludes an acyl-oxygen cleavage mechanism and strongly supports the S_N1-path.



The relative solvolysis rates are recorded in the table together with literature data^{7,8)} and steric substituent constants φ_f ^{14,15)} of the groups R. There is qualitative agreement between the solvolytic reactivity of the bridgehead p-nitrobenzoates and the earlier kinetic data for the bromides and chlorides. The spread of the reactivity difference in the p-nitrobenzoate series is, however, smaller than for the halides. This may partly be due to the difference in reaction temperature. In agreement with Schleyer's analysis^{1,2)}, the rates of solvolysis in this series of bridgehead p-nitro-

benzoates decrease almost linearly with increasing change of strain enthalpy ΔH_{sp} in the ionisation process, as discussed above.

Table Relative Rates of Solvolysis of tertiary Esters R-X

R	RBr-EtOH-H ₂ O (80:20Vol.%) 25°C	RCI-EtOH-H ₂ O (80:20Vol.%) 25°C	ROpNb ^{b)} -CH ₃ CN-H ₂ O (70:30 by weight) 150°C	$\varphi_f^{c)}$
	k_1 (sec ⁻¹)	k_1 (sec ⁻¹)	k_1 (sec ⁻¹) ^{12b)}	
1-Adamantyl-	$\equiv 1.0^{16)}$	$\equiv 1.0^{16)}$	$\equiv 1.0$	4.08
1-Homoadamantyl-	7.5 ^{a,8)}	-	1.3	4.28
3-Homoadamantyl-	373 ⁷⁾	454 ⁷⁾	28.8	4.91
t-Butyl	814 ¹⁷⁾	1215 ¹⁸⁾	6.0	3.82

a) Relative rate at 50°C

b) pNb=p-nitrobenzoate

c) Steric substituent constants^{14,15)}

The conclusion that the 1-homoadamantyl cation has a lower thermodynamic stability than the 3-homoadamantyl cation is supported by the observation¹⁹⁾ that only the 3-homoadamantyl carbenium ion is observable under super acid conditions even if 1-homoadamantyl precursors are used²⁰⁾.

Quite exceptionally, however, the t.butyl p-nitrobenzoate hydrolyzes more slowly than the 3-homoadamantyl analogue, in contrast to the halide solvolysis reactions. We assume that this is the expression of steric acceleration (f-strain)²¹⁾ of the solvolysis of the 3-homoadamantyl ester. Similar rate enhancements are known for p-nitrobenzoate solvolysis reactions of other cyclic alcohols²¹⁾. The steric substituent constant $\varphi_f^{14,15)}$ in the table is largest for the 3-homoadamantyl group.

Acknowledgement Financial support by the Fonds der Chemischen Industrie is gratefully acknowledged. Particular thanks are due to Dr.H.Langhals for providing samples of the p-nitrobenzoates used in this work.

References and Notes

*) *Dedicated to Prof.H.Stetter on the occasion of his 65th birthday.*

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(Received in Germany 5 February 1982)