

ARTE OF ALKALINE HYDROLYSIS OF N-ALKYL ACETATES
AND THEIR ω -TERT-BUTYL, ω -TRIMETHYLSILYL
AND ω -TRIMETHYLGGERMYL DERIVATIVES*

J. POLA and V. CHVALOVSKÝ

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchbát*

Received November 9th, 1973

Rates of alkaline hydrolysis of n-alkyl acetates $\text{CH}_3(\text{CH}_2)_n\text{OCOCH}_3$ ($n = 2-8, 11$), their tert-butyl derivatives $(\text{CH}_3)_3\text{C}(\text{CH}_2)_n\text{OCOCH}_3$ ($n = 1-4$), trimethylsilyl derivatives $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OCOCH}_3$ ($n = 1-6$), and trimethylgermyl derivatives $(\text{CH}_3)_3\text{Ge}(\text{CH}_2)_n\text{OCOCH}_3$ ($n = 1-4$) were measured. Kinetic data were interpreted in terms of predominant steric effect of the alkoxy group.

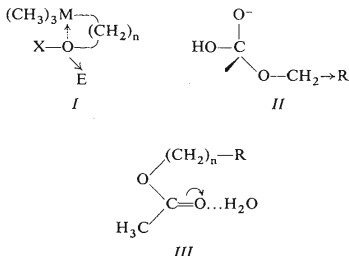
This work is a part of systematic study of the effect of substitution in linear aliphatic oxygen-containing compounds with $(\text{CH}_3)_3\text{M}$ group ($\text{M} = \text{Si}, \text{Ge}$). Carbofunctional silicon and germanium compounds of the type $(\text{CH}_3)_3\text{M}(\text{CH}_2)_n\text{OX}$ (M is Group IV element) are interesting from theoretical viewpoint, since intramolecular $(p-d)_\sigma$ coordinative interaction of the oxygen with silicon or germanium might occur in these compounds. From reactivities of the compounds $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OH}$ (ref.¹) and $(\text{CH}_3)_3\text{Ge}(\text{CH}_2)_n\text{OH}$ (ref.²) ($n = 1-4$) with electrophiles and from relative basicities of the oxygen (the measure of interaction with proton donor) of the compounds $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OX}$ ($\text{X} = \text{H}, \text{Si}(\text{CH}_3)_3$ (ref.³), $(\text{CH}_2)_n\text{Si}(\text{CH}_3)_3$ (ref.⁴) ($n = 1-4$) it followed that this coordinative interaction, if any, is for $n > 2$ very weak. In these cases we attempted to detect $(p-d)_\sigma$ interaction by comparing nucleophilicities and basicities of the oxygen of these compounds with the same properties of carbon analogues. It is however possible that a weak coordination bond could not be detected by means of interaction of oxygen with electron-deficient centre of electrophile due to stronger and competing requirements of electrophile (E) (see structure I). More sensitive means for indication of $(p-d)_\sigma$ interaction of the type $\text{O} \rightarrow \text{M}$ could be then nucleophilic attack of group X which is taking place in the rate determining step of alkaline hydrolysis of primary esters, where formation of transition state requires nucleophilic attack on hydroxyl ion on carbonyl group carbon. In ω -acetoxylalkyltrimethylsilanes or -germanes chosen for the study of

* Part CXIX in the series Organosilicon Compounds; Part CXVIII: This Journal 39, 1880 (1974).

(*p-d*)_s intramolecular interaction in this work, the *sp*² carbonyl oxygen could be suited better for this interaction than the oxygen in *sp*³ state.

EXPERIMENTAL

Preparation of acetates. All acetates, except (CH₃)₃Si(CH₂)_nOCOCH₃ (*n* = 1–4) (ref.¹), C₂H₅(CH₃)₂SiCH₂OCOCH₃ (ref.¹) reported earlier, and ethyl acetate (analytical purity grade, Lachema, Brno), were prepared from appropriate alcohols by reaction with acetyl chloride in the presence of stoichiometric amount of dry pyridine in dried diethyl ether. The acetates were obtained in 75–90% yield by fractional distillation or by preparative gas chromatography. The purity of all acetates was checked by gas chromatography and their structure was confirmed by IR and NMR spectroscopy. Physical constants of known alkyl acetates agreed with reported



data. *n*-Propyl acetate, b.p. 101°C, n_D^{20} 1.3824; *n*-butyl acetate, b.p. 126°C, n_D^{20} 1.3925; *n*-pentyl acetate, b.p. 149°C, n_D^{20} 1.3998; *n*-hexyl acetate, b.p. 169°C, n_D^{20} 1.4082; *n*-heptyl acetate, b.p. 191°C, n_D^{20} 1.4134; *n*-octyl acetate, b.p. 100°C/18 Torr; *n*-nonyl acetate, b.p. 236°C, n_D^{20} 1.4222; lauryl acetate, b.p. 149°C/15 Torr, n_D^{20} 1.4308; 2,2-dimethylpropyl acetate, b.p. 128°C, n_D^{20} 1.3923 (ref.⁵ 127°C, n_D^{20} 1.3893); 3,3-dimethylbutyl acetate, b.p. 155°C, n_D^{20} 1.4052 (ref.⁶ b.p. 156–157°C/741 Torr, n_D^{25} 1.4038); 4,4-dimethylpentyl acetate, b.p. 180.5°C, n_D^{20} 1.4109, for C₉H₁₈O₂ (158.2) calculated: 68.31% C, 11.47% H; found: 68.54% C, 11.62% H; 5,5-dimethylhexyl acetate, b.p. 201°C, n_D^{20} 1.4157, for C₁₀H₂₀O₂ (172.3) calculated: 69.73% C, 11.70% H; found: 69.61% C, 11.62% H; 5-trimethylsilylpentyl acetate, b.p. 132°C/29 Torr, n_D^{20} 1.4290, for C₁₀H₂₂O₂Si (202.4) calculated: 59.35% C, 10.96% H; found: 59.65% C, 11.12% H; 6-trimethylsilylhexyl acetate, b.p. 111°C/17 Torr, n_D^{20} 1.4248, for C₁₁H₂₄O₂Si (216.4) calculated: 61.05% C, 11.18% H; found: 61.10% C, 11.20% H; phenyldimethylsilylmethyl acetate, b.p. 96°C/5 Torr, n_D^{20} 1.4963 (ref.⁷ b.p. 91–105°C/3 Torr, n_D^{24} 1.5087); trimethylgermylmethyl acetate, b.p. 88°C/160 Torr, n_D^{20} 1.4270 (ref.⁸ b.p. 45–47°C/22 Torr, n_D^{20} 1.4283); 2-trimethylgermylethyl acetate, b.p. 118°C/110 Torr, n_D^{20} 1.4141, for GeC₇H₁₆O₂ (204.8) calculated: 41.05% C, 7.87% H; found: 40.90% C, 7.95% H; 3-trimethylgermylpropyl acetate, b.p. 118°C/60 Torr, n_D^{20} 1.4355, for C₈H₁₈GeO₂ (218.8) calculated: 43.91% C, 8.29% H; found: 43.67% C, 8.30% H; 4-trimethylgermylbutyl acetate, b.p. 100°C/14 Torr, n_D^{20} 1.4377, for C₉H₂₀GeO₂ (232.9) calculated: 46.24% C, 8.66% H; found: 45.78% C, 8.63% H.

Preparation of alcohols. 5-Trimethylsilylpentanol was prepared⁵ by reaction of 3-trimethylsilylpropylmagnesium bromide with ethylene oxide in diethyl ether, followed by hydrolysis. The

product was obtained as fraction of b.p. 145°C/85 Torr, n_D^{20} 1.4352 (ref.⁹ b.p. 85°C/8 Torr, n_D^{20} 1.4371) in 60% yield. 6-Trimethylsilylhexyl chloride was prepared by reaction of 6-chlorohexanol with trimethylchlorosilane in the presence of stoichiometric amount of dry pyridine in dry petroleum ether and obtained as fraction of b.p. 127°C/30 Torr in 42% yield. Its reaction with activated magnesium gave the Grignard reagent which was reacted with trimethylchlorosilane. The ether was partially replaced by dry benzene and the reaction mixture was stirred at 60°C for 2 days. The ether layer was separated and dried by magnesium sulphate. 6-Trimethylsilylhexanol was obtained as fraction of b.p. 124°C/16 Torr, n_D^{20} 1.4384, in 45% yield. For $\text{SiC}_{11}\text{H}_{23}\text{O}_2$ (215.4) calculated: 61.34% C, 10.76% H; found: 61.31% C, 10.73% H. The alcohols $(\text{CH}_3)_3\text{C}(\text{CH}_2)_n\text{OH}$ ($n = 1-4$), $(\text{CH}_3)_3\text{Ge}(\text{CH}_2)_n\text{OH}$ ($n = 1-4$) (ref.¹⁰), and phenyldimethylsilylmethanol¹¹ were prepared by reported procedures.

Kinetic measurements. Measurements of rate constants of alkaline hydrolysis of acetates in 70% aqueous dioxane at 20°C were carried out by the method reported by Sarel and coworkers¹². Rate constants were calculated from the relation derived by the same authors from integrated form of the equation for the rate constant of second order reaction. The confidence interval for the probability equaling 0.95 was taken as a measure of reproducibility. Rate constants, along with their confidence intervals, are shown in Fig. 1.

RESULTS AND DISCUSSION

Three values of the rate constants of alkaline hydrolysis of acetates (Fig. 1) can be compared with the values obtained by Sarel and coworkers¹² (for $\text{C}_2\text{H}_5\text{OCOCH}_3$ $35 \cdot 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$, for $(\text{CH}_3)_3\text{CCH}_2\text{OCOCH}_3$ $8.6 \cdot 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$, and for

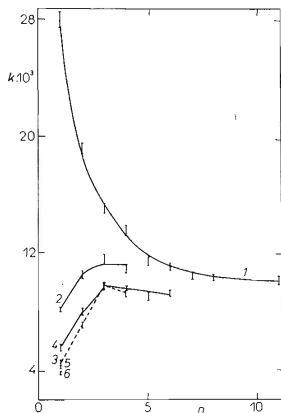


FIG. 1

Dependence of Rate Constants of Alkaline Hydrolysis of the Compounds 1 $\text{CH}_3(\text{CH}_2)_n\text{OCOCH}_3$, 2 $(\text{CH}_3)_3\text{C}(\text{CH}_2)_n\text{OCOCH}_3$, 3 $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OCOCH}_3$, 4 $(\text{CH}_3)_3\text{Ge}(\text{CH}_2)_n\text{OCOCH}_3$ on Number n of Methylene Groups 5 $\text{C}_6\text{H}_5(\text{CH}_3)_2\text{SiCH}_2\text{OCOCH}_3$, 6 $\text{C}_2\text{H}_5(\text{CH}_3)_2\text{SiCH}_2\text{OCOCH}_3$; (for $\text{CH}_3\text{OCOCH}_3$ $k(1 \text{ mol}^{-1} \text{ s}^{-1}) = 54 \cdot 10^3$) (ref.¹²)

$(\text{CH}_3)_3\text{C}(\text{CH}_2)_2\text{OCOCH}_3$ $21 \cdot 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$). The values determined in this work are always somewhat lower, and are at variance with reported data in the case of 3,3-dimethylbutyl acetate.

The rate determining step of alkaline hydrolysis of primary alkyl esters is assumed to be the attack of hydroxyl ion on carbonyl carbon of the ester. The ease of formation of transition state should be dependent on the extent of electron deficiency and on the steric shielding of the reaction centre. The initial great decrease of reaction rate in the series $\text{CH}_3(\text{CH}_2)_n\text{OCOCH}_3$ from $n = 0$ to $n = 2$ is not obviously due to different electronic effects of CH_3 , C_2H_5 , and $n\text{-C}_3\text{H}_7$ groups. It has recently been shown that alkyl groups, when attached to saturated skeleton, exert $-I$ effect (*cf.*^{13,14}). Such effect should lead to a decrease in the energy content of transition state of the reaction under study (see *II*). It seems likely that this and also subsequent, slower rate decrease is due to enveloping of the carbonyl group by the alkoxy group which results both in steric shielding of the reaction centre and in steric hinderance toward solvation of the carbonyl by water molecules. It is this solvation, whose effectiveness decreases with increasing n , which should lead to an increase of electron deficiency on the carbonyl carbon (*III*). From Stewart models of n -alkyl acetates it is evident that the alkoxy group can influence the carbonyl carbon by its steric effect already when $n = 1$, while the oxygen of the carbonyl group can be shielded only when $n = 6$. The steric shielding of the carbonyl carbon seems to be the factor responsible for decrease of rate constants in the series $\text{CH}_3(\text{CH}_2)_n\text{OCOCH}_3$. Steric effect of $(\text{CH}_3)_3\text{C}$ group may be similarly responsible for relatively lower reactivity of the series $(\text{CH}_3)_3\text{C}(\text{CH}_2)_n\text{OCOCH}_3$, which is lowest for $n = 1$. From differences between rate constants of respective members of homologous series $(\text{CH}_3)_3\text{C}(\text{CH}_2)_n\text{OCOCH}_3$ and $\text{CH}_3(\text{CH}_2)_n\text{OCOCH}_3$ it follows further that tert-butyl group, when compared to methyl group, exerts greater steric effect also in positions two or more carbons away from the reaction centre ($n = 2, 3, 4$).

Still greater steric effect of $(\text{CH}_3)_3\text{M}$ groups seems to be responsible for the lower reactivity of all members of series $(\text{CH}_3)_3\text{M}(\text{CH}_2)_n\text{OCOCH}_3$, relative to their carbon analogues. In both series $(\text{CH}_3)_3\text{M}(\text{CH}_2)_n\text{OCOCH}_3$ the steric effect of $(\text{CH}_3)_3\text{M}$ groups is detectable not only for $n = 3, 4$, but also in the compounds $(\text{CH}_3)_3\text{Si}(\text{CH}_3)_n \cdot \text{OCOCH}_3$ with $n = 5, 6$. This fact is surprising, especially in that a similar steric shielding of the reaction centre by distant $(\text{CH}_3)_3\text{M}$ group was not observed in reactions of the compounds $(\text{CH}_3)_3\text{M}(\text{CH}_2)_n\text{OH}$ ($\text{M} = \text{Si}, \text{Ge}; n = 3, 4$) with electrophiles^{1,2}. This leads to the question whether the influencing of the reaction centre by distant $(\text{CH}_3)_3\text{M}$ groups during interaction of the compounds $(\text{CH}_3)_3 \cdot \text{M}(\text{CH}_2)_n\text{OCOCH}_3$ with nucleophiles is not due to the fact that their steric effect is primarily induced by weak $(p-d)_\sigma$ interaction of the $\text{O} \rightarrow \text{M}$ type. (The higher probability of detection of such an intramolecular interaction in reactions of $(\text{CH}_3)_3 \cdot \text{M}(\text{CH}_2)_n\text{OX}$ with nucleophiles was explained in the introduction.) The ether and carbonyl oxygen could both participate in the $\text{O} \rightarrow \text{M}$ interaction, and to dif-

ferentiate these two modes is difficult. Electronic interaction of the type $M \leftarrow OC(O)CH_3$ would decrease electron deficiency on the carbonyl carbon and thus also reactivity. The interaction of the type $-C=O \rightarrow M$ should result in a decrease of the energy content of transition state of the reaction and would lead to rate acceleration. However, it should also bring the bulky group to the vicinity of the reaction centre. Providing that the latter factor is prevailing, reaction rate would be sterically inhibited. This fact may indicate that $(CH_3)_3M$ group in the above compounds acts only as a weak electron acceptor, since electron density on the carbonyl oxygen substantially increases in transition state.

Reactivity of trimethylsilyl- and trimethylgermylalkyl acetates decreases on going from γ to β , and to α -derivatives. The alkoxy oxygen of the ester in alkaline hydrolysis transfers well electronic effects of the substituents attached to the carbonyl carbon¹⁵. As $(CH_3)_3MCH_2$ ($M = Si, Ge$) groups are regarded as stronger electron donors than $(CH_3)_3CCH_2$ groups (*cf.*^{16,17}), it could reasonably be assumed that on going from β to α derivatives the reactivity in the series $(CH_3)_3M(CH_2)_nOCOCH_3$ ($M = Si, Ge$) would decrease more than in the series $(CH_3)_3C(CH_2)_nOCOCH_3$. Essentially the same decrease of reactivity when going from γ to α *via* β -derivative in all the series $(CH_3)_3M(CH_2)_nOCOCH_3$ ($M = C, Si, Ge$), along with comparatively lower reactivity of corresponding derivatives of series $(CH_3)_3M(CH_2)_nOCOCH_3$ ($M = Si, Ge$), indicate that electron donor ability of $(CH_3)_3MCH_2$ ($M = Si, Ge$) group is decreased in ground state and that the carboxylic carbon is more sterically hindered by $(CH_3)_3M$ ($M = Si, Ge$) group. Both these phenomena are in the case of the compounds $(CH_3)_3MCH_2OCOCH_3$ ($M = Si, Ge$) obviously due to the so called α -effect, *i.e.* intramolecular interaction of d orbitals of silicon or germanium with the σ_{C-O} or p orbital, since solely steric effects of $(CH_3)_3M$ ($M = C, Si, Ge$) groups on the carbonyl carbon in the β -position are undoubtedly comparable. The reactivity of the compounds $L(CH_3)_2SiCH_2OCOCH_3$ ($L = C_2H_5, C_6H_5$) can be explained similarly. Their lower reactivity in comparison with trimethylsilylmethyl acetate is obviously due to the bulkier C_2H_5 or C_6H_5 groups. The fact that $(CH_3)_3SiCH_2$ group exhibits in interaction of the compounds $(CH_3)_3SiCH_2O-X$ with nucleophiles weaker electron-donating character (if any) is not surprising, since from ¹³C and ²⁹Si NMR spectra of the compounds $(CH_3)_3SiCH_2OX$ it follows that electron-donating ability of $(CH_3)_3SiCH_2$ group is markedly decreased in the ground state of these molecules¹⁸. To date, $(CH_3)_3SiCH_2$ group has been considered as a strong electron donor (*e.g.*^{16,17}). The fact that the electron donor character of $(CH_3)_3SiCH_2$ group in the above compounds is in their reaction with electrophiles enforced by electrophile, owing to the strong polarisability of $(CH_3)_3SiCH_2$ group, and is connected with the α -effect, will be discussed in a subsequent paper¹⁹.

REFERENCES

1. Pola J., Bažant V., Chvalovský V.: *This Journal* 37, 3885 (1972).
2. Krumpolc M., Bažant V., Chvalovský V.: *This Journal* 38, 711 (1973).
3. Pola J., Chvalovský V.: *This Journal* 38, 1674 (1973).
4. Pola J., Schraml J., Chvalovský V.: *This Journal* 38, 3158 (1973).
5. Quayle O. R., Norton H. M.: *J. Am. Chem. Soc.* 62, 1170 (1940).
6. Sarel S., Newmann M. S.: *J. Am. Chem. Soc.* 78, 5416 (1956).
7. Fessenden R. J., Coon M. D.: *J. Med. Chem.* 9, 262 (1966).
8. Mironov V. F., Kravčenko A. L., Petrov A. D.: *Izv. Akad. Nauk SSSR* 1964, 1209.
9. Sommer J. H., van Strien R. E., Whitmore F. C.: *J. Am. Chem. Soc.* 71, 3056 (1949).
10. Krumpolc M., Chvalovský V.: *This Journal* 37, 1392 (1972).
11. Pola J., Papoušková Z., Chvalovský V.: *This Journal* 38, 1522 (1973).
12. Sarel S., Asšai L., Newmann M. S.: *J. Am. Chem. Soc.* 78, 5420 (1956).
13. McIver R. T., Scott J. A., Riveros J. M.: *J. Am. Chem. Soc.* 95, 2706 (1973).
14. Brauman N. I., Blair L. K.: *J. Am. Chem. Soc.* 92, 5986 (1970).
15. Tommila E., Hinshelwood C. N.: *J. Chem. Soc.* 1938, 1801.
16. Sommer L. H., Gold I. R., Goldberg G. M., Marans M. S.: *J. Am. Chem. Soc.* 71, 1509 (1949).
17. Cudlín J., Chvalovský V.: *This Journal* 27, 1658 (1962).
18. Pola J., Schraml J., Chvalovský V.: Unpublished results.
19. Pola J., Chvalovský V.: Unpublished results.

Translated by J. Hetflejš.