

## ORGANOGERMANIUM COMPOUNDS. XVI.\*

THE EFFECT OF STRUCTURE ON THE PROPERTIES  
OF SOME TRIMETHYLGERMYL-SUBSTITUTED ALCOHOLS  
AND THEIR CARBON ANALOGUES

M. KRUMPOLC, V. BAŽANT and V. CHVALOVSKÝ

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

Received November 23rd, 1971

The properties of model alcohols  $(\text{CH}_3)_3\text{M}(\text{CH}_2)_n\text{OH}$ , where  $\text{M}=\text{C}$  or  $\text{Ge}$  and  $n = 1$  to  $4$ , have been evaluated by the method of competitive reactions with phenyl isocyanate and ketene, and by infrared spectroscopy. The structure of these alcohols is discussed as a possible cause of the electronic and steric effects.

In studying the intereffects between silicon or germanium and the oxygenous functional groups in compounds  $\text{R}_3\text{M}(\text{CH}_2)_n\text{OX}$ , where  $\text{M}=\text{Si}$  or  $\text{Ge}$ , there were observed some facts that cannot be accounted for by a simple inductive effect of the  $\text{R}_3\text{M}$  groups. The anomalies have been interpreted by assuming the possibility of a coordination linkage of oxygen to the metal  $\text{M}$  through the  $d$ -orbitals of the latter. To cast some light on the question of whether an interaction of this nature might occur between silicon and oxygen in trialkyl-substituted alcohols we studied<sup>1</sup> the properties of compounds  $\text{R}_3\text{Si}(\text{CH}_2)_n\text{OH}$ . However, the existence of a  $(p \rightarrow d)_\sigma$  coordination linkage should be even more probable in the analogues of germanium, which forms the coordination compounds more readily than silicon does<sup>2-4</sup>. This question is the subject of the present paper.

We have studied the properties of the hydroxyl groups in compounds  $(\text{CH}_3)_3\text{Ge}(\text{CH}_2)_n\text{OH}$  ( $n = 1$  to  $4$ ) and for comparison, in their carbon analogues  $(\text{CH}_3)_3\text{C}(\text{CH}_2)_n\text{OH}$ , where the  $(p \rightarrow d)_\sigma$  interaction is not possible. The properties of the hydroxyl groups were investigated by the reactions of alcohols with phenyl isocyanate and ketene, and by determination of the hydrogen bonds between the alcohols studied and standard proton-donors or proton-acceptors. The methods based on the reactions with ketene and with phenyl isocyanate had been worked out with, and tested on, simple carbon alcohols.

The competitive reactions of a carbon alcohol and a silicon alcohol with phenyl isocyanate giving rise to urethanes, were employed in several studies<sup>5-8</sup> to determine the relative rate constants, calculated<sup>7</sup> from the content of silicon in the dry residue left after evaporation of the urethanes. As the analytical determination of germanium is not satisfactorily accurate, the calculated

\* Part XV: This Journal 37, 3762 (1972).

values of the relative rate constants would vary in a considerable range. For this reason we have worked out a different method for the determination of germanium, independent of chemical analysis.

## EXPERIMENTAL

*Phenyl isocyanate* (Lachema, Brno) was distilled before use over a column, the fraction boiling at 66°C/25 Torr,  $n_D^{20}$  1.5370 being collected (ref.<sup>9</sup> b.p. 165.5°C,  $n_D^{19.6}$  1.53684).

*Model alcohols.* The synthesis and physical constants of trimethylgermyl-substituted alcohols were described earlier<sup>10,11</sup>. The alcohols were freed from the last traces of hydrogen chloride by shaking with distilled water until the aqueous layer gave no response to silver nitrate. The alcohols were then dried with a molecular sieve 4A to a water content 0.001 to 0.01% (determined by the Fischer method).

*2,2-Dimethyl-1-propanol*<sup>12</sup> was synthesized by introducing gaseous formaldehyde into tert-butylmagnesium chloride in a yield of 23%. B.p. 113°C (ref.<sup>12</sup> 111°C/730 Torr),  $n_D^{20}$  1.4140 (ref.<sup>14</sup> 1.4150),  $d_4^{25}$  0.8025.

*3,3-Dimethyl-1-butanol.* Dry O<sub>2</sub> was introduced into a Grignard agent prepared from 300 g of 3,3-dimethyl-1-chlorobutane<sup>13</sup> until the reaction mixture had ceased boiling. The mixture was decomposed with water and worked up in the usual manner. Distillation over a column afforded 90 g (35%) of 3,3-dimethyl-1-butanol, b.p. 143–144°C (ref.<sup>14</sup> 139–143°C),  $n_D^{20}$  1.4200 (ref.<sup>20</sup> 1.4202),  $d_4^{20}$  0.8216 (ref.<sup>20</sup> 0.815).

*4,4-Dimethyl-1-pentanol.* Dry depolymerized formaldehyde was introduced into a Grignard agent prepared from 387 g of 3,3-dimethyl-1-chlorobutane until the reaction mixture had ceased boiling. After working up the mixture in the usual way there was obtained by distillation 189 g (51%) of 4,4-dimethyl-1-pentanol, b.p. 162°C (ref.<sup>15</sup> 160°C/720 Torr),  $n_D^{20}$  1.4262,  $d_4^{20}$  0.8221.

*5,5-Dimethyl-1-hexanol.* Dry ethylene oxide (181 g) was introduced into a Grignard agent, prepared from 483 g of 3,3-dimethyl-1-chlorobutane, stirred under a jet of nitrogen. Then the ether was gradually replaced by benzene until the temperature raised to 70°C. The mixture was kept boiling for 1 h and decomposed with water. Distillation gave 198 g (38%) of 5,5-dimethyl-1-hexanol, b.p. 181°C.

*The competitive reactions of alcohols with phenyl isocyanate.* A 50-ml flask was charged with weighed quantities of the two alcohols (1 to 3 g), 20 ml of benzene and the corresponding amount of phenyl isocyanate. The molar ratio of the alcohols was so chosen as to be approximately equal to the reciprocal ratio of their reactivities and the reaction mixture was left standing for 48 h at 20°C. The bulk of benzene and the unreacted alcohols was then evaporated with a jet of dry nitrogen at 40 to 50°C. The oily residue was evaporated at 20°C and 1 Torr to a constant weight. The higher-boiling alcohols [4,4-dimethyl-1-pentanol, 5,5-dimethyl-1-hexanol, (3-hydroxypropyl)-trimethylgermane, (4-hydroxybutyl)trimethylgermane] had to be evaporated from a thermostated glycerine bath at 40°C. The evaporation was ended when it was found that the sample weight had not changed by even 0.1 mg in the course of the last 10 to 15 h. The total time of evaporation was 150 to 300 h. The weight of the two dry urethanes was given by the ratio of reactivities of the two starting alcohols. Consequently, it applies that

$$x + y = m_1, \quad (1)$$

$$g = g_1 + xM_1 + yM_2, \quad (2)$$

TABLE I

Relative Rate Constants of Competitive Additions of Alcohols to Phenyl isocyanate (in Benzene) and Ketene at 20°C

Alcohols	Phenyl isocyanate		Ketene	
	measured	calculated	measured	calculated
CH <sub>3</sub> OH		1.38		2.38
C <sub>2</sub> H <sub>5</sub> OH	1.45 ± 0.02	1.46	—	2.47
CH <sub>3</sub> OH		1.66		2.19
n-C <sub>3</sub> H <sub>7</sub> OH	1.62 ± 0.01	1.70	2.24 ± 0.08	—
CH <sub>3</sub> OH		1.45		2.20
n-C <sub>4</sub> H <sub>9</sub> OH	1.48 ± 0.02	1.46	2.15 ± 0.13	—
C <sub>2</sub> H <sub>5</sub> OH		1.11		0.89
n-C <sub>3</sub> H <sub>7</sub> OH	1.17 ± 0.03	1.13	0.94 ± 0.03	—
C <sub>2</sub> H <sub>5</sub> OH		1.01		0.92
n-C <sub>4</sub> H <sub>9</sub> OH	1.01 ± 0.03	1.04	0.87 ± 0.02	—
n-C <sub>3</sub> H <sub>7</sub> OH		0.86		0.92
n-C <sub>4</sub> H <sub>9</sub> OH	0.89 ± 0.01	0.91	0.98 ± 0.03	0.96

where  $x$  and  $y$  are the numbers of the reacted mol of the alcohols (of the formed urethanes),  $m_1$  the number of mol of phenyl isocyanate,  $g$  the weight of the dry residue,  $g_1$  the weight of phenyl isocyanate, and  $M_1, M_2$  the molecular weights of the competing alcohols. Equations (1) and (2) imply

$$x = \frac{g - g_1 - M_2 m_1}{M_1 - M_2} \quad (3)$$

By combining these equations with equation<sup>16</sup> (4), wherein  $a$  and  $b$  designate the starting concentrations of the alcohols, the rate constants  $k_{rel}$  were calculated.

$$k_{rel} = k_1/k_2 = [\log(1 - x/a)] [\log(1 - y/b)]^{-1} \quad (4)$$

*The competitive reactions of alcohols with ketone.* About 2-ml test-tubes were charged with 400 to 600 mg of each alcohol and immersed into a bath kept at 20°C. Ketene, generated by pyrolysis of acetone vapour, was bubbled in for 1 to 2 min. The reaction mixture was analysed in a gas chromatograph Griffin and George, London (model D 6). The values of  $k_{rel}$  were calculated from the relation<sup>16,17</sup>

$$k_{rel} = k_1/k_2 \doteq (x/b)/(y/a), \quad (5)$$

where the symbols  $x, y, a, b$  represent the same quantities as in equation (4). To maintain validity of the approximative equation (5), the conversions of the alcohols were so chosen (according to the relative rate constants) that they did not exceed the tabulated critical values for a 3% relative error<sup>17</sup>. The values of  $k_{rel}$  for the additions of the alcohols to phenyl isocyanate and ketene, given in Tables I and II, are arithmetic means of at least three kinetic measurements.

*The basicities and proton-donating capacities* of the alcohols were measured by infrared spectroscopy<sup>1</sup>.

## RESULTS AND DISCUSSION

The chosen reference alcohol was butanol. The method was tested on a series of *n*-alcohols (methanol to butanol): two values of  $k_{rel}$  were measured with two pairs of alcohols, and from these a third constant was calculated and then measured. The calculated and the measured values are given in Table I; comparison shows that the measurement of  $k_{rel}$  for the addition of alcohols to phenyl isocyanate is charged with an average relative error of 1 to 2%; in the additions to ketene 4 to 5%. The values of  $k_{rel}$  of all the alcohols measured are listed in Table II. The relative basicities of the alcohols, determined by infrared spectroscopy as a frequency shift  $\Delta\nu(\text{OH})$  of the proton donor between phenol and the alcohols (here proton acceptors) and between tetrahydrofuran and the alcohols (proton donors), are included in Table II.

With prolongation of the methylene chains in the two model series the differences associated with steric and polar factors tend to be obliterated and the reactivities of the alcohols become similar to those of non-branched aliphatic alcohols. Also the ratios of the relative reactivities of the alcohols with phenyl isocyanate and ketene tend to reach constant values. These facts reveal that in the transition state the steric

TABLE II

Relative Rate Constants of Competitive Additions of Alcohols to Phenyl isocyanate (in Benzene) and Ketene at 20°C and Values of  $\Delta\nu^a$

Alcohol	$k_{rel}$ ( $\text{CH}_3\text{OH} = 1$ )		$k_{rel}$ ( $n\text{-C}_4\text{H}_9\text{OH} = 1$ )		$\Delta\nu, \text{cm}^{-1}$	
	phenyl isocyanate	ketene	phenyl isocyanate	ketene	phenol <sup>a</sup>	tetrahydrofuran <sup>b</sup>
$\text{CH}_3\text{OH}$	1.00	1.00	1.48	2.15	—	—
$\text{C}_2\text{H}_5\text{OH}$	0.69	0.40	1.01	0.87	—	—
$n\text{-C}_3\text{H}_7\text{OH}$	0.62	0.45	0.89	0.98	—	—
$n\text{-C}_4\text{H}_9\text{OH}$	0.68	0.46	1.00	1.00	—	—
$(\text{CH}_3)_2\text{CHOH}$	0.24	0.23	0.35	0.49	—	—
$(\text{CH}_3)_3\text{CCH}_2\text{OH}$	0.35	0.27	0.52	0.58	228	154
$(\text{CH}_3)_3\text{C}(\text{CH}_2)_2\text{OH}$	0.68	0.45	1.00	0.96	236	151
$(\text{CH}_3)_3\text{C}(\text{CH}_2)_3\text{OH}$	0.66	0.46	0.97	0.98	234	155
$(\text{CH}_3)_3\text{C}(\text{CH}_2)_4\text{OH}$	0.68	0.44	1.00	0.94	233	157
$(\text{CH}_3)_3\text{GeCH}_2\text{OH}$	2.12	1.03	3.14	2.22	243	150
$(\text{CH}_3)_3\text{Ge}(\text{CH}_2)_2\text{OH}$	0.96	0.72	1.42	1.55	240	151
$(\text{CH}_3)_3\text{Ge}(\text{CH}_2)_3\text{OH}$	0.68	0.45	1.00	0.97	231	153
$(\text{CH}_3)_3\text{Ge}(\text{CH}_2)_4\text{OH}$	0.70	0.43	1.03	0.92	232	153

Accuracy <sup>a</sup>  $\pm 3 \text{ cm}^{-1}$ , <sup>b</sup>  $\pm 4 \text{ cm}^{-1}$ .

requirements are approximately the same in the two cases. Out of the model alcohols of carbon, only the first member of the series, *viz.* 2,2-dimethyl-1-propanol, exhibits a markedly lower reactivity. Its low reactivity is generally ascribed to the considerable steric hindrance of the oxygen atom by the bulky tert-butyl group, which strongly outweighs the positive inductive effects of the methyl groups. The reactivities of the other three carbon alcohols with a tert-butyl group at  $\beta, \gamma$  and  $\delta$  position are approximately the same, and equal to the reactivity of the reference butanol. A moderately higher reactivity, caused by the positive inductive effect of the tert-butyl group, would be expected with the  $\beta$  derivative. The fact that its reactivity is not higher might, perhaps, be interpreted with the aid of the steric "rule of six"<sup>18</sup>.

The possibility of a coordination bond of the hydroxyl oxygen to the germanium atom by the  $(p-d)_\sigma$  interaction can be assessed from the values of  $k_{rel}$  of the germlyl-substituted alcohols. A coordination bond would be expected to cause a marked decrease in the electron density of the oxygen atom and a consequential suppression of its reactivity in the reactions employed, whose rate-determining step is a nucleophilic attack on the electronically deficient central carbon in the groupings  $C=C=O$  or  $N=C=O$ . Table II reveals, however, that the values of  $k_{rel}$  of the addition reactions of trimethylgermyl-substituted alcohols invariably decrease with the increasing number of methylene groups, which can be explained by predominance of the inductive effect of the trimethylgermyl group. The insignificant role of the steric effect is best seen in the reactivity of hydroxymethyltrimethylgermane. Compared to its carbon analogue it is extraordinarily reactive, which is evidently due to the strong +I effect of the trimethylgermyl group (the electronegativities<sup>19</sup> of germanium and carbon are 1.7 and 2.5, respectively) and to the greater atom radius of germanium (Ge 1.22 Å, C 0.77 Å), which suppresses the steric hindrance of the hydroxyl group by the three methyl groups. The +I effect of the group  $(CH_3)_3Ge$  is appreciable even at the  $\beta$  position. The reactivities of the other homologous alcohols of germanium are practically identical with the reactivity of butanol, which accords with the idea that the +I effect can be transferred along the carbon chain.

Quantitatively the same, though less precise, conclusions can be drawn from the measurement of the frequency shift  $\Delta\nu$  of phenol as proton donor in the formation of hydrogen bonds with the model alcohols as proton acceptors (Table II). The greatest shift, approximately  $10\text{ cm}^{-1}$ , has been observed with the  $\alpha$  and  $\beta$  derivatives of germanium. Within the range of experimental error, the frequency shifts of the hydroxyl groups of the other alcohols are mutually identical. The hydroxyl groups have also been studied spectroscopically by investigating the hydrogen bonds of the alcohols, as proton donors, to tetrahydrofuran, as a proton acceptor. However, the differences in the frequency shifts of the hydroxyl groups were so small as to be obliterated by the experimental error.

## REFERENCES

1. Pola J., Bažant V., Chvalovský V.: This Journal 37, 3885 (1972).
2. Muettterties E. L.: J. Am. Chem. Soc. 82, 1082 (1960).
3. Aggarwall R. C., Onyszuchuk M.: Proc. Chem. Soc. 20 (1962).
4. Beattie I. R.: Quart. Revs. (London) 17, 382 (1963).
5. Davis T. L., McFarnum J.: J. Am. Chem. Soc. 56, 883 (1934).
6. Spier J. L., Daubert B. F., McGregor R. R.: J. Am. Chem. Soc. 70, 1117 (1948).
7. Mironov V. F., Pogonkina N. A.: Izv. Akad. Nauk U.S.S.R, Otd. Chim. Nauk 1960, 1998.
8. Mironov V. F., Kravčenko A. L., Petrov A. D.: Izv. Akad. Nauk SSSR, Otd. Chim. Nauk 1964, 1209.
9. *Handbook of Chemistry and Physics*. Chemical Rubber Publishing Co., Cleveland, Ohio 1961.
10. Krumpolc M., Chvalovský V.: Synth. Inorg. Metalorg. Chem. 1, 51 (1971).
11. Krumpolc M., Chvalovský V.: This Journal 37, 1392 (1972).
12. Sommer L. H., Blankham H. D., Miller P. C.: J. Am. Chem. Soc. 76, 803 (1954).
13. Schmerling L.: J. Am. Chem. Soc. 67, 1152 (1945).
14. Whitmore F. C., Heyd J. W.: J. Am. Chem. Soc. 60, 2030 (1938).
15. Whitmore F. C., Karnatz F. A., Popkin A. H.: J. Am. Chem. Soc. 60, 2540 (1938).
16. Jungers J. C.: *Chemická kinetika*, p. 188. Published by Nakladatelství ČSAV, Prague 1963.
17. Krumpolc M.: This Journal 36, 3013 (1971).
18. Newman M. S.: *Prostranstvennyje Effekty v Organičeskoj Chimii*, p. 216. Izd. Inostr. Lit., Moscow 1960.
19. Pauling L.: *The Nature of the Chemical Bond*, 6th Ed. Cornell Univ. Press, Ithaca 1948.
20. Whitmore F. C., Homeyer A. H.: J. Am. Chem. Soc. 55, 4555 (1933).

Translated by J. Salák.