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# The Dimerization of Substituted 3-TMSO-1-alkynes with $(\phi_3P)_3RhCl$

THOMAS RÜPING and HELLMUT SINGER*

*Universität Mainz, FB Chemie, J. J. Becher-Weg 34, D-6500 Mainz, F.R.G.*

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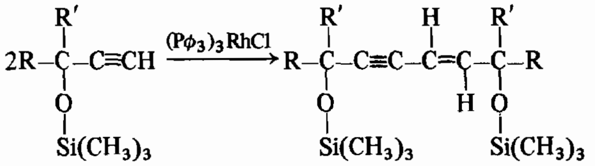
## Abstract

3-Trimethylsilyloxy-1-alkynes were prepared from 3-hydroxy-1-alkynes and dimerized with $(\phi_3P)_3RhCl$ as a catalyst. The influence of a steric effect on the rates of dimerization is demonstrated.

## Introduction

The dimerization of α-hydroxyacetylenes using $(\phi_3P)_3RhCl$ as catalyst is well known [1]. The formation of 1,4-disubstituted *trans*-vinylacetylenes (eqn. (1)) as a function of substituents on the monomer [2] and of different phosphorus ligands [3] has been studied. We have now investigated the steric influence upon the dimerization using a selected group of monomers.



$$2\mathrm{R}-\overset{\mathrm{R'}}{\underset{\mathrm{OSi(CH_3)_3}}{\mathrm{C}}}-\mathrm{C{\equiv}CH}\xrightarrow{(P\phi_3)_3RhCl}\mathrm{R}-\overset{\mathrm{R'}}{\underset{\mathrm{OSi(CH_3)_3}}{\mathrm{C}}}-\mathrm{C{\equiv}C}-\overset{\mathrm{H}}{\mathrm{C}}=\underset{\mathrm{H}}{\mathrm{C}}-\overset{\mathrm{R'}}{\underset{\mathrm{OSi(CH_3)_3}}{\mathrm{C}}}-\mathrm{R} \qquad (1)$$

## Experiments

### *3-TMSO-1-alkynes*

These were prepared according to the literature [4] from 0.12 mol $(CH_3)_3SiCl$, 0.1 mol α-hydroxyacetylene and 0.25 mol triethylamine using 50 ml DMF as solvent. The products were distilled using a teflon spinning band column (Normag). Yields and some data of the 3-TMSO-1-alkynes are given in Table I.

### *Dimerization*

0.5 ml 3-TMSO-1-alkyne, 88 mg $\phi_3P$ and 20 mg $[(C_8H_{12})_2RhCl]_2$ [5] (P:Rh = 6:1) were added under an atmosphere of argon in a 10 ml flask to 5 ml toluene and heated for about 8 h to 110 °C. After distillation of the solvent brown oils remained, which were sublimed in a high vacuum (heating temperature 80–130 °C). The products were yellow, viscous, pleasant-smelling oils. Some elementary analyses are given in Table II. The yields of isolated products varied from 20% to 70% depending mainly on the efficiency of the separation with the sublimation.

### *Kinetic Experiments*

0.5 ml 3-TMSO-1-alkyne, 88 mg $\phi_3P$ and 20 mg $[(C_8H_{12})_2RhCl]_2$ were added under an atmosphere of argon in a 10 ml flask to 5 ml solvent (depending on the monomer, toluene or *o*-xylene) and 0.5 g of

TABLE I. The Preparation and Characterization of 3-TMSO-1-alkynes, R,R'C(OSiMe$_3$)–C≡CH

| Compound No. | Starting alkyne | | Yield (%) | Boiling point | | $n_D$ (°C) | C found | (calc.) | H found | (calc.) |
|---|---|---|---|---|---|---|---|---|---|---|
| | R | R' | | (°C) | (torr) | | | | | |
| 1 | Me | Me | 72 | 113–116 | (760) | 1.4007(19) | 60.8 | (61.48) | 10.4 | (10.32) |
| 2 | $\phi$ | H | 54 | 109 | (20) | 1.4908(20) | 70.8 | (70.53) | 7.9 | (7.89) |
| 3 | Et | Me | 55 | 134–138 | (760) | 1.4121(19) | 63.3 | (63.47) | 10.7 | (10.65) |
| 4 | Me | H | 20 | 112 | (760) | 1.4053(20) | 59.0 | (59.10) | 10.1 | (9.92) |
| 5 | $H_2C{=}CH$ | Me | 48 | 136 | (760) | 1.4164(21) | 64.6 | (64.23) | 9.7 | (9.58) |
| 6 | Cyclohexyl | | 78 | 78 | (18) | 1.4447(22) | 67.6 | (67.28) | 10.2 | (10.27) |
| 7 | Et | H | 59 | 120–125 | (760) | 1.4073(23) | 60.6 | (61.48) | 10.1 | (10.32) |
| 8 | iProp | Me | 73 | 81 | (63) | 1.4165(22) | 65.5 | (65.15) | 10.8 | (10.94) |
| 9 | Prop | H | 37 | 72 | (98) | 1.4173(20) | 62.6 | (63.47) | 10.5 | (10.65) |
| 10 | tBu | Me | 78 | 170 | (760) | – | | purity only about 95% | | |

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*Author to whom correspondence should be addressed.

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TABLE II. The Dimerization of the 3-TMSO-1-alkynes

| Compound no. | Starting alkyne | | C found | (calc.) | H found | (calc.) | Relative rates at 100 °C | The sum of the steric parameters of R and R′ |
|---|---|---|---|---|---|---|---|---|
| | R | R′ | | | | | | |
| 11 | Me | Me | | | | | 13500 | 0 |
| 12 | ϕ | H | | | | | 390 | 1.19 |
| 13 | Et | Me | 62.4 | (63.47) | 10.2 | (10.65) | 49 | 0.08 |
| 14 | Me | H | | | | | 91 | −1.12 |
| 15 | $H_2C$=CH | Me | | | | | 37 | 2.07 |
| 16 | Cyclohexyl | | 68.2 | (67.28) | 10.0 | (10.27) | 37 | ? |
| 17 | Et | H | 62.9 | (61.48) | 10.1 | (10.32) | 22 | −1.04 |
| 18 | iProp | Me | 63.7 | (65.15) | 10.8 | (10.94) | 26 | 0.48 |
| 19 | Prop | H | 65.2 | (63.47) | 10.1 | (10.65) | 24 | −0.81 |
| 20 | tBu | Me | 65.7 | (66.60) | 11.0 | (11.18) | 1 | 1.43 |

TABLE III. $^1$H NMR Spectra of the 3-TMSO-1-alkynes in $CDCl_3$[a]

| Compound no. | Acetylenic proton | TMSO-substituent | R | R′ |
|---|---|---|---|---|
| 1 | 2.57(s) | 0.42(s) | 1.69(s) | 1.69(s) |
| 2 | 2.46(d, 1.5 Hz) | 0.17(s) | 7.2(m) | 5.30 (d; 1.5 Hz) |
| 3 | 2.32(s) | 0.16(s) | 1.61(q; 6.5 Hz)<br>0.94 (t; 6.5 Hz) | 1.39(d) |
| 4 | 2.36(d, 1.5 Hz) | 0.16(s) | 1.41(d; 6.6 Hz) | 4.49(dq; 6.6 + 1.5 Hz) |
| 5 | 2.49(s) | 0.17(s) | 4.91(dd; 9.5 + 1.6 Hz)<br>5.25(dd; 16.5 + 1.6 Hz)<br>5.79 (dd; 16.5 + 9.5 Hz) | 1.47(s) |
| 6 | 2.38(s) | 0.16(s) | (R + R′): 1.63 (m; broad) | |
| 7 | 2.29 (d, 2.0 Hz) | 0.13(s) | 1.58(m; 2H)<br>0.92(t; 6.5 Hz) | 4.12(dt; 6.0 + 2.0 Hz) |
| 8 | 2.44(s) | 0.22(s) | 1.02(d; 9.8 Hz)<br>1.80(m; 1 H) | 1.45(s) |
| 9 | 2.3(d, 1.8 Hz) | 0.14(s) | 1.55(m; 4H)<br>0.93(t; 4.5 Hz) | 4.22(dt; 4.0 + 1.8 Hz) |
| 10 | 2.3(s) | 0.14(s) | 0.92(s) | 1.32(s) |

[a] Bruker 60 MHz; TMS as internal standard; compound number and substituent R, R′ as in Table I.

durene or mesitylene as an internal standard. The mixtures were heated for 6 h at a constant temperature between 50 and 130 °C. Samples were taken every 15 to 20 min; they were analysed by GLC (Carlo Erba Fractovap 2101; 2 m glass column with 10% OV-1 on chromosorb; Kipp & Zonen BD 12 recorder and integrator; column temperature 70–100 °C for the monomers and 250–280 °C for the dimers.) The decrease of the monomer was analysed according to a second order reaction.

## Results and Discussion

Alkynes with a secondary or tertiary hydroxy group in the α-position have been silylated using trimethylchlorosilane [4]; only sterically very demanding hydroxyacetylenes such as ethynylfluorenol and 3,3-diphenyl-1-propyne-3-ol could not be converted into their TMSO-derivatives by this or a similar method.

The 3-TMSO-1-alkynes were dimerized using $(\phi_3P)_3RhCl$ as a catalyst eqn. (1). The dimers as well as the monomers were characterized spectroscopically; their $^1$H NMR data are summarized in Tables III and IV.

The mass spectra of the 3-TMSO-1-alkynes gave no or very weak signals for the molecular ion, but the $(M\text{-}1)^+$-ions were pronounced. Essential fragments originated from α-fissions at silicon and carbon, from O–C and O–Si cleavages and, from these cleavages subsequent to an α-fission, eliminating an alkene or $(CH_3)_2Si{=}CH_2$.

The molecular ion for the dimers was more intense. The ion $(M\text{-}1)^+$ was always missing, because of the absence of an acetylenic proton. The Si–O

TABLE IV. $^1H$ NMR spectra of the (di-TMSO)alkene-ynes in $CDCl_3$[a]

| Compound no. | Olefinic protons | TMSO-groups | R | R′ |
|---|---|---|---|---|
| 11 | 6.43(d; 16.5 Hz) | 0.08(s) | 1.28(s) and | 1.48(s) |
| | 6.92(d; 16.5 Hz) | 0.14(s) | | |
| 12 | 5.89(d; 15 Hz) | 0.20(s) | 7.4(m) | 5.32(d; 5 Hz) |
| | 6.37(dd; 15 + 5 Hz) | 0.28(s) | | 5.68(s) |
| 13 | 5.59(d; 15 Hz) | 0.16(s) | 1.53(q; 7.5 Hz) | 1.45(s) |
| | 6.08(d; 15 Hz) | 0.21(s) | 0.97(t; 7.5 Hz) | 1.29(s) |
| | | | 0.95(t; 7.5 Hz) | |
| 15 | 5.57(d) | 0.13(s) | 4.87(dd; 9.2 + 1.5 Hz) | 1.55(s) |
| | 6.25(d) | 0.18(s) | 4.98(dd; 9.2 + 1.5 (Hz) | 1.40(s) |
| | | | 5.19(dd; 16.4 + 1.5 Hz) | |
| | | | 5.32(dd; 16.4 + 1.5 Hz) | |
| | | | 5.72(m) | |
| | | | 5.88(m) | |
| 16 | 5.61(d; 15 Hz) | 0.12(s) | 2.56(m, 20H) | |
| | 6.23(d; 15 Hz) | 0.19(s) | | |
| 17 | 5.53(d; 15 Hz) | 0.11(s) | 1.3 - 1.7(m, 4H) | 4.29(t) |
| | 6.05(dd; 15 + 1.5 Hz) | 0.18(s) | 0.87(t; 6 Hz) | 3.90(m, 1H) |
| | | | 0.76(t; 6 Hz) | |
| 18 | 5.54(d; 16 Hz) | 0.11(s) | 1.02(d; 6.5 Hz) | 1.40(s) |
| | 6.12(d; 16 Hz) | 0.18(s) | 0.90(d; 6.5 Hz) | 1.30(s) |
| | | | 1.65(m, 1 H) | |
| | | | 1.78(m, 1 H) | |
| 19 | 5.54(d; 15.5 Hz) | 0.11(s) | 0.97(t; 5.5 Hz) | 4.43(m, 1 H) |
| | 6.11 (dd; 15.5 + 2 Hz) | 0.17(s) | 0.88(t; 5.5 Hz) | 4.05(t) |
| | | | 1.2 - 1.7(m, 4H) | |
| 20 | 5.52(d; 15 Hz) | 0.10(s) | 0.98(s, 9 H) | 1.38(s, 3 H) |
| | 6.22(d; 15 Hz) | 0.14(s) | 0.87(s, 9 H) | 1.28(s, 3 H) |

[a] Compound number and substituents R, R′ as in Table II.

cleavage dominated with the ion $(CH_3)_3Si^+$ representing the 100% peak for most dimers.

The dimerization of the 3-TMSO-1-alkynes was studied kinetically at different temperatures. The decrease of the monomer was measured by GLC; it followed a second order reaction leading to experimental rate constants. The reactivity of the TMSO-alkynes was lower than that of the corresponding α-hydroxyalkynes by a factor of about 10. Therefore higher reaction temperatures had to be used, from 50–80 °C for the most reactive TMSO-alkyne (no. 1) to 110–130 °C for the TMSO-alkyne no. 10. For a comparative interpretation, the rates at 100 °C were selected; therefore some of the values were the result of an extrapolation (Table II). This limitation and the absence of any knowledge concerning kinetic or thermodynamic data of single steps of the proposed mechanism [1, 2] restricted any correlation of the relative rates with steric or electronic data of the alkynes to a qualitative level.

Earlier studies of the codimerization of α-hydroxyacetylenes [2] indicated that the $\pi$-complexation of the acetylenes is markedly influenced by steric effects. On the other hand the oxidative addition of the 1-alkynes is not inhibited by bulky substituents at the alkyne [2, 6], but depends upon the acidity of the acetylene [6].

Using the chemical shifts of the acetylenic protons as an estimate for an electronic effect [6], no correlation was found with the relative rates of the dimerizations of the TMSO-alkynes. On the other hand a plot of the steric parameters of the substituents R + R′ [7] of the TMSO-alkynes *versus* the relative rates of their dimerization (Table II) indicated some regularities. The rates increased from TMSO-pentyne (no. 7) to TMSO-methylpentyne (no. 3) and decreased with the introduction of further methyl groups, that is from TMSO-dimethylpentyne (no. 8) to TMSO-trimethylpentyne (no. 10). An analogous gradation was observed for the rates of the equivalent hydroxyacetylenes [8]. Conforming to this result is the steep increase of the rate of dimerization from TMSO-butyne (no. 4) to TMSO-methylbutyne (no. 1) and a decrease when the methyl group is replaced by bulkier alkyl groups: an ethyl group (no. 3) and then, as above, isopropyl (no. 8) and tert.-butyl (no. 10).

These results can be used as an indication for a steric influence on the rate of the dimerization, which in the series of the TMSO-alkynes commences at a steric parameter for R + R′ equal to about zero represented by 3-TMSO-3-methyl-but-1-yne (no. 1) and within the series of α-hydroxyacetylenes it sets in with 3-methylpent-1-yn-3-ol [8].

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