7. A. S. Atavin, A. N. Mirskova, and É. F. Zorina, Inventor's Certificate No. 420621 (1974); Byull. Izobr., No. 11 (1974).
8. U. E. Matter, C. Pascual, E. Pretsch, A. Pross, W. Simon, and S. Sternhell, Tetrahedron, 25, 693 (1969).
9. J. F. Arens, Adv. Org. Chem., 2, 117 (1960).
10. E. Fromm, H. Benzinger, and F. Schafer, Liebigs Ann. Chem., 394, 325 (1912).
11. E. Fromm and E. Siebert, Ber., 55, 1014 (1922).
12. H. J. Backer and J. Strating, Rec. Trav. Chim. Pays-Bas, 73, 565 (1954).
13. J. Nooi and J. F. Arens, Rec. Trav. Chim. Pays-Bas, 80, 244 (1961).

REACTION OF α- AND β-(TRIALKYLSILYL)ACROLEINS WITH A GRIGNARD REAGENT

M. G. Voronkov, S. V. Kirpichenko
V. V. Keiko, V. A. Pestunovich,
and O. I. Randin

UDC 542.91:547.1'128

The reaction of Grignard reagents with α,β-unsaturated aldehydes can proceed as 1,2- or 1,3-addition, depending on the structure of the aldehyde and the organomagnesium compound [1-4].

We have shown that the main pathway for the reaction of CH_3MgI with isomeric α- and β-(trialkylsilyl) acroleins is 1,2-addition, which forms the corresponding secondary organosilicon alcohols

$$\underset{\text{(Ia, b)}}{CH_2{=}C(SiR_3)CHO} + CH_3MgI \rightarrow \underset{\text{(IIa, b)}}{CH_2{=}C(SiR_3)CHOHCH_3}$$

$$\underset{\text{(IIIa, b)}}{R_3SiCH{=}CHCHO} + CH_3MgI \rightarrow \underset{\text{(IVa, b)}}{R_3SiCH{=}CHCHOHCH_3}$$

$R = C_2H_5$ (Ia)—(IVa); CH_3 (Ib) — (IVb)

We verified the structures of compounds (IIa, b) and (IVa, b), isolated by preparative gas chromatography (PGC), from their IR and PMR parameters.

The side reactions of α- and of β-(trialkylsilyl)acroleins are not identical. The α isomers to a considerable extent undergo cleavage of the Si — C bond, giving the decomposition product, hexaalkyldisiloxane. This is due to the instability of α-(trialkylsilyl)acroleins, which have the carbonyl group β to the silicon. Cleavage of the Si — C bond does not occur with the more stable β-(trialkylsilyl)acroleins. In this case the byproducts are primary γ-(trialkylsilyl)allyl alcohols, $R_3SiCH{=}CHCH_2OH$ (Va, b), and 1-trialkylsilyl-1-buten-3-ones, $R_3SiCH{=}CHCOCH_3$ (VIa, b). We deduced the structures of compounds (Va, b) and (VIa, b) from their PMR parameters.

The presence of γ-(trialkylsilyl)allyl alcohols in the reaction mixtures cannot be considered the result of the reducing action of the Grignard reagent, since CH_3MgI lacks the β hydrogen that is capable of giving the hydride ion [1]. The simultaneous presence of the primary alcohol and the ketone among the reaction products suggests the following scheme for their formation. The reaction of alkylmagnesium halides with carbonyl compounds proceeds via the alcoholate

$$R_3SiCH{=}CHCHO + CH_3MgI \rightarrow R_3SiCH{=}CHCH(CH_3)OMgI$$

which is then oxidized by another molecule of the starting aldehyde to the ketone with the concomitant formation of the reduction product of the aldehyde, the primary alcohol

$$R_3SiCH{=}CHCHO + R_3SiCH{=}CHCH(CH_3)OMgI \rightarrow$$
$$\rightarrow \underset{\text{(Va, b)}}{R_3SiCH{=}CHCH_2OH} + \underset{\text{(VIa, b)}}{R_3SiCH{=}CHCOCH_3}$$

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 431-433, February, 1978. Original article submitted October 26, 1976.

 0568-5230/78/2702-0372$07.50

These oxidation – reduction reactions have been described for aliphatic and aromatic aldehydes [1], but have not been reported for α, β-unsaturated aldehydes.

Thus, although the reaction of CH_3MgI with α- and β-(trialkylsilyl)acroleins is mainly 1,2-addition, the presence of the trialkylsilyl group in the aldehyde molecule causes side reactions not peculiar to acrolein and its analogs.

EXPERIMENTAL

All GLC analyses and preparative separations were carried out on a Khrom-3 instrument [katharometer, 4.6 m ×10 mm column, 20% polyphenyl ether on Chromaton N-AW-HMDC (0.25-0.5 mm)]. The column temperature was 110°C for trimethylsilyl derivatives and 140-150°C for triethylsilyl derivatives.

Spectra were recorded with: IR: a UR-20 spectrophotometer, in a thin layer; PMR: a Tesla BS 487B spectrometer (80 MHz), as solutions in CCl_4 (5-10%) with hexamethyldisiloxane as internal standard.

Reaction of α-(Triethylsilyl)acrolein (Ia) with CH_3MgI. To the Grignard reagent prepared from Mg (0.66 g) and CH_3I (3.9 g) in ether (10 ml) was added (Ia) (4.25 g) in ether (5 ml) (0°C). The reaction mixture was stirred at 20°C for 2 h and worked up with saturated NH_4Cl solution at 0°C. The usual treatment and vacuum distillation gave a fraction (3.06 g) with bp 73-84°C (1.5 mm), consisting of hexaethyldisiloxane (26.5%) (yield 26%), (IIa) (62.5%) (yield 41%), and impurities (11%).

2-(Triethylsilyl)-1-buten-3-ol (IIa), isolated by PGC, and n_D^{20} 1.4687; d_4^{20} 0.8912. Found: C 64.51; H 11.90; Si 15.08%; MR 58.14. $C_{10}H_{22}OSi$. Calculated: C 64.43; H 11.90; Si 15.07%; MR 58.76. IR spectrum (ν, cm^{-1}): 1600 (C=C), 930 (=CH_2), 3350 (OH). PMR spectrum (δ, ppm): 0.04 m (6H, CH_2Si); 0.64 m (9H, CH_3CSi); 1.22 d (3H, CH_3, ^3J=6.5Hz); 2.53 s (1H, OH); 4.35 m (1H, CH); 5.29 dd (1H, = CH, ^2J = 2.75, ^4J=1 Hz); 5.85 dd (1H, =CH, ^4J=1.5 Hz).

2-(Trimethylsilyl)-1-buten-3-ol (IIb) was prepared similarly from (Ib) (2.85 g) in 45% yield; n_D^{20} 1.4483; d_4^{20} 0.8602. Found: C 58.35; H 11.20; Si 19.52%; MR 44.93. $C_7H_{10}OSi$. Calculated: C 58.27; H 11.18; Si 19.46%; MR 45.23. IR spectrum (ν, cm^{-1}): 1600 (C=C), 3350 (OH).

Reaction of β-(Triethylsilyl)acrolein (IIIa) with CH_3MgI. The reaction was carried out under conditions described above. Compound (IIIa) (6.15 g) after treatment with CH_3MgI gave a fraction (5.01 g) with bp 85-87°C (3 mm), containing 1-triethylsilyl-1-buten-3-ol (IVa) (83.7%) (yield 60%), γ-(triethylsilyl)allyl alcohol (Va) (5.7%), 1-triethylsilyl-1-buten-3-one (VIa) (3.3%), and impurities (2.3%).

The compounds, isolated by PGC, had the following properties.

Compound (IVa), $(C_2H_5)_3SiCH=CHCHOHCH_3$: n_D^{20} 1.4620; d_4^{20} 0.8713. Found: C 64.69; H 11.87; Si 14.95%; MR 58.82. $C_{10}H_{22}OSi$. Calculated: C 64.43; H 11.90; Si 15.07%; MR 58.76. IR spectrum (ν, cm^{-1}): 1620 (C=C), 3350 (OH). PMR spectrum (δ, ppm): 0.59 m (6H, CH_2Si); 0.95 m (9H, CH_3CSi); 1.20 d (3H, CH_3, ^3J=6.75 Hz); 3.40 s (1H, OH); 4.19 dd (1H, CH, ^3J=4.6, ^4J=0.8 Hz), 5.67 dd (1H, SiCH-, ^3J = 19.0 Hz); 6.04 dd (1H, CCH=).

Compound (Va), $(C_2H_5)_3SiCH=CHCH_2OH$, was identical (GLC, PMR) to a sample prepared earlier by hydrosilylation of propargyl alcohol [5].

Compound (VIa), $(C_2H_5)_3SiCH=CHCOCH_3$, n_D^{20} 1.4448, was identical (GLC) to 1-triethylsilyl-2-buten-3-one prepared by oxidation of (IVa) with a solution of CrO_3 in H_2SO_4. Compound (VIa) had n_D^{20} 1.4653; d_4^{20} 0.8760. Found: C 64.76; H 10.80; Si 15.34%; MR 58.14. $C_{10}H_{20}OSi$. Calculated: C 65.24; H 10.93; Si 15.33%; MR 57.37. Its PMR spectrum was identical to that quoted in [6]. Reaction of β-(trimethylsilyl)acrolein (IIIb) (5.64 g) with CH_3MgI [from Mg (1.08 g)] gave a fraction (4.54 g) with bp 75-83°C (20 mm), consisting of 1-trimethylsilyl-1-buten-3-ol (IVb) (97.4%) (yield 70%), γ-(trimethylsilyl)allyl alcohol (Vb) (0.7%), and 1-trimethylsilyl-1-buten-3-one (VIb) (1.9%).

Compound (IVb), $(CH_3)_3SiCH=CHCHOHCH_3$, isolated by PGC, had n_D^{20} 1.4440; d_4^{20} 0.8396. Found: C 58.37; H 11.25; Si 19.55%; MR 45.65. $C_7H_{16}OSi$. Calculated: C 58.27; H 11.18; Si 19.46%; MR 45.23. IR spectrum (ν, cm^{-1}): 1610 (C=C), 3350 (OH).

Compound (Vb) was identical to $(CH_3)_3SiCH=CHCH_2OH$ prepared by hydrosilylation of propargyl alcohol;* n_D^{20} 1.4498; d_4^{20} 0.8636. Found: C 55.41; H 10.90; Si 21.61%; MR 40.52. $C_6H_{14}OSi$. Calculated: C 55.32; H

*Passage of $(CH_3)_3Si$ into propargyl alcohol in the presence of H_2PtCl_6 forms a mixture of the gem- and trans-isomeric alcohols in the ratio 46:54, which can be separated by PGC. The constants of $CH_2=C[Si(CH_3)_3]-CH_2OH$ are: n_D^{20} 1.4663; d_4^{20} 0.8648.

10.83; Si 21.56%; MR 40.58. PMR spectrum (δ, ppm): 0.09 s (9H, CH_3Si); 3.59 s (1H, OH); 4.06 dd (2H, CH_2, $^3J = 3.5$, $^4J = 0.9$ Hz); 5.85 dt (1H, SiCH, $^3J = 18.8$ Hz); 6.08 dt (1H, =CH).

Compound (VIb), $(CH_3)_3SiCH=CHCOCH_3$, had n_D^{20} 1.4480 [7]. The same ketone was prepared by oxidation of (IVb) with CrO_3 in H_2SO_4. The PMR spectrum was identical to that described in [7].

CONCLUSIONS

Reaction of α- and β-(trialkylsilyl)acroleins with methylmagnesium iodide forms the corresponding secondary unsaturated organosilicon alcohols. The reactions of α-(trialkylsilyl)acroleins are accompanied by cleavage of the Si—C bond. The byproducts from β-(trialkylsilyl)acroleins are primary unsaturated alcohols and α, β-unsaturated organosilicon ketones.

LITERATURE CITED

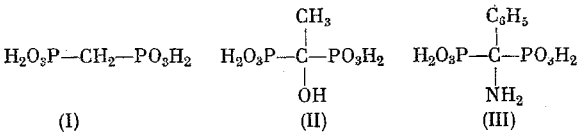
1. S. Patai (editor), The Chemistry of the Carbonyl Group, Interscience, New York (1966), p. 638.
2. R. Miravalles and A. J. Guillarmod, Helv. Chim. Acta, 49, 2313 (1966).
3. N. Boccara and R. Maitte, Bull. Soc. Chim. France, 1972, 1448.
4. B. Cheminat, Bull. Soc. Chim. France, 1972, 3415.
5. M. G. Voronkov, S. V. Kirpichenko, V. V. Keiko, L. V. Sherstyannikova, V. A. Pestunovich, and E. O. Tsetlina, Izv. Akad. Nauk SSSR, Ser. Khim., 1975, 390.
6. G. Stork and B. Ganem, J. Am. Chem. Soc., 95, 6152 (1973).
7. A. G. Brook and J. M. Duff, Can. J. Chem., 51, 2024 (1973).

SYNTHESIS AND ACID—BASE AND COMPLEXING PROPERTIES OF AMINO-SUBSTITUTED α-HYDROXYALKYLIDENEDIPHOSPHONIC ACIDS

M. I. Kabachnik, T. Ya. Medved',
N. M. Dyaglova, Yu. M. Polikarpov,
B. K. Shcherbakov, and F. I. Bel'skii

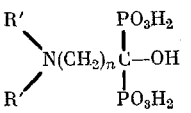
UDC 542.91:547.1'118

Methylenediphosphonic acid (I) and its derivatives, notably hydroxyethylenediphosphonic acid (II), because of their accessibility [1] and ability to form stable complexes with a series of metal cations, find various uses [2, 3]. We have made detailed studies of the complexing properties of (II) [4] and of aminobenzylidenediphosphonic acid (III) [5] and have measured the stability constants of metal complexes with these ligands by potentiometric titration



(I) (II) (III)

These acids in some cases display greater complexing ability than polyaminopolyphosphonic acids [2]. We decided to synthesize and study the properties of acids containing together with the hydroxymethylenediphosphonic acid grouping an additional coordination site, an amino group. Hence we prepared amino-substituted α-hydroxyalkylidenediphosphonic acids (IV)-(VII)



R=R'=H, $n=2$ (IV); R=R'=H, $n=3$ (V); R=H, R'=C_2H_5, $n=2$ (VI); R=R'=C_2H_5, $n=2$ (VII) R=R'=CH_3, $n=2$ (VIII)

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow.

Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 433-437, February, 1978. Original article submitted November 4, 1976.

0568-5230/78/2702-0374$07.50