[Contribution from the General Electric Research Laboratory]

ORGANOSILICON ALDEHYDES

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The reaction of carbon monoxide and hydrogen with olefins in the presence of a metal carbonyl catalyst, a process commonly referred to as the *Oxo Synthesis*, yields, in general, two theoretically possible isomeric aldehydes together with ketones, aldols, and other related products (1).

We have investigated the preparation of organosilicon aldehydes by the reaction of *allyl-* and *vinyl-silanes* with carbon monoxide and hydrogen under the usual conditions of the "Oxo" reaction. Under these conditions, the alkenyl silanes react to form aldehydes together with considerable amounts of higher molecular weight products which appear to be aldol condensation products. The various reaction products have been characterized in part by elemental analysis, by their reactions with the Fuchsin-aldehyde reagent, and by elemental analysis of their 2,4-dinitrophenylhydrazone derivatives.

Allyltrimethylsilane reacts with carbon monoxide and hydrogen in the presence of cobalt carbonyl to form a silicon-containing aldehyde and a material which we believe to be a dehydrated silicon-containing aldol; hexamethyldisiloxane and *n*-butyraldehyde also are formed in some quantity. *Trimethylvinylsilane*, on the other hand, appears to form two silicon-containing aldehydes and a silicon-containing aldol condensation product; no propionaldehyde or hexamethyldisiloxane are observed in this synthesis. We feel that the observed difference in behavior between the allyl and vinyl silane derivatives may be indicative of the relative degree of ease with which different organic side groups are cleaved from silicon by electrophilic reagents.

EXPERIMENTAL

All of the high pressure syntheses were conducted with reaction vessels, shakers, and auxiliary equipment obtained from the American Instrument Co.

(*a*). *Preparation of cobalt carbonyl.* The cobalt carbonyl used as the catalyst in the carbonylation reactions was prepared according to directions from Professor Homer Adkins (2). A 40-g. sample of Harshaw Cobalt Catalyst Co-D101P was reduced in hydrogen for 5 hours at 450°, cooled in hydrogen, and dumped directly into 150 ml. of dry benzene in a 300-ml. autoclave. The autoclave then was pressurized with 600 p.s.i. of hydrogen and 1900 p.s.i. of carbon monoxide to a total pressure of 2500 p.s.i. The autoclave was heated for 12 hours at 150°, then was cooled to room temperature and the excess gases were vented. The dark red reaction mixture was filtered into a brown glass bottle and kept under refrigeration to be used as a stock solution of cobalt carbonyl for the synthetic work.

(*b*). *Carbonylation of trimethylvinylsilane.* A 40-g. sample of trimethylvinylsilane (b.p. 54–55°) was placed in the 300-ml. autoclave together with 120 ml. of anhydrous ether and 12 ml. of the benzene stock solution of cobalt carbonyl. The autoclave then was pressurized with 1800 p.s.i. of carbon monoxide and 1200 p.s.i. of hydrogen (total pressure 3000 p.s.i.), and heated at 115° for 3 hours. During this reaction time the pressure dropped so that when the vessel was cooled the residual pressure was *ca* 1000 p.s.i. (It might be pointed out that carbon monoxide is quite soluble in ether; part of the pressure drop occurs immediately as soon as agitation of the pressurized vessel is begun.) After cooling the reaction vessel and venting the excess gas, the pale green reaction mixture was filtered into a distillation flask. The reaction products were then distilled rapidly to make certain that any residual cobalt carbonyl was thermally decomposed. This rapid preliminary distillation was found to be necessary to prevent excessive polymerization of the reaction products.

The product of the preliminary distillation then was redistilled in a Claisen flask. The ether, benzene, and unreacted trimethylvinylsilane were removed by gently heating the flask so that the liquid temperature did not exceed 90° and the vapor temperature did not exceed 80°. The distillate so obtained gave a negative test with the Fuchsin-aldehyde reagent. The remainder of the liquid was fractionated under a vacuum in a small distillation column (efficiency about 20 plates), and the following liquid fractions were obtained: (I) 4.2 g. boiling at 61–64° at 25 mm.; (II) 4.5 g. boiling at 62–65° at 10 mm.; and (III) 7.1 g. boiling at 194–209° at 8 mm. No residue remained in the distillation flask. All three of these fractions gave strong positive tests with the Fuchsin-aldehyde reagent. Densities and indices of refraction were measured:

n_D^{20} (I) 1.4238, (II) 1.4252, (III) 1.4549
d_4^{20} (I) 0.8347, (II) 0.8364

and molar refractivities were calculated and compared with the expected value, MR_D 39.4, for an aldehyde of the composition $C_6H_{14}OSi$: Found, MR_D (I) 39.8, (II) 39.8.

Elemental analyses were made:[1]

Anal. Calc'd for $C_6H_{14}OSi$: C, 55.53; H, 10.84.
Found (I): C, 55.6; H, 11.2.
(II): C, 57.2; H, 10.5.
(III): C, 55.1; H, 10.8.

The molecular weight of (III) was determined as 371; its hydroxyl equivalent was 890.

The *2,4-dinitrophenylhydrazone* derivatives of (I) and (II) were prepared: m.p. of deriv. (I) 131–132°; m.p. of deriv. (II) 129–130°; mixture melting point of both derivatives 126–130°. These derivatives were analyzed for their nitrogen content:

Anal. Calc'd: N, 18.17. Found: (I) N, 18.1; (II) N, 18.9.

It may be seen from the above data that compound (I) is one of the aldehydes expected as a reaction product from the carbonylation reaction, and that (III) probably is a condensed aldol derivative. Considering the unexplainable divergence in the analytical data, the exact nature of compound (II) is somewhat in doubt. We feel, however, that it probably is an isomer of (I) since it is a silicon-containing aldehyde. All three of the products of this reaction were shown to contain silicon by the combustion tests.

(*c*). *Carbonylation of allyltrimethylsilane.* A 40-g. sample of allyltrimethylsilane in 80 ml. of anhydrous ether was placed in the 300-ml. autoclave together with 20 ml. of the benzene stock solution of cobalt carbonyl. The autoclave was pressurized with 1800 p.s.i. of carbon monoxide and 1400 p.s.i. of hydrogen, and then was heated with agitation at 125° for 4 hours. After cooling the vessel and venting the 900 p.s.i. of residual gas pressure, the almost colorless reaction mixture was filtered and subjected to the same distillation procedure used in the preceding reaction with trimethylvinylsilane. The fractional distillation of the stripped product yielded: 7.7 g. of *n*-butyraldehyde (characterized by its boiling point, index of refraction, and the m.p. of the 2,4-dinitrophenylhydrazone derivative); 6.6 g. of hexamethyldisiloxane (identified by its boiling point, index of refraction, and characteristic odor); (IV) 3.2 g. boiling at 73.5–74° at 22 mm.; (V) 7.3 g. boiling at 150–154° at 15 mm. There was a small amount of residue remaining in the still pot after the distillation. Densities and indices of refraction were measured:

n_D^{20} (IV) 1.4239, (V) 1.4550
d_4^{20} (IV) 0.8459, (V) 0.8910

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[1] Although quantitative analyses for silicon were not made, the substantial residues of silica left in the combustion analyses for carbon and hydrogen indicated the presence of silicon as an integral part of the various compounds. This also was true of the compounds derived from allyltrimethylsilane.

Calc'd MR_D for an aldehyde $C_7H_{16}OSi$: 43.8; Found (IV): 43.5.

Anal. Calc'd for $C_7H_{16}OSi$: C, 58.28; H, 11.18.

Found (IV): C, 58.7; H, 10.7.

A *2,4-dinitrophenylhydrazone* of (IV) was prepared. This compound melted at 108–109°.

Anal. Calc'd: C, 48.13; H, 6.21; N, 17.27.

Found: C, 47.9; H, 6.15; N, 17.55.

Compound (V), obviously an aldehyde by the Fuchsin test, and containing silicon, appeared to be somewhat impure as obtained:

Anal. Calc'd for $C_{14}H_{30}OSi_2$: C, 62.16; H, 11.18; Mol. Wt., 270.

Found (V): C, 60.4; H, 10.2; Mol. Wt., 280–285.

The *dinitrophenylhydrazone* of (V) was prepared; Calc'd: N, 12.46. Found: N, 13.5. The melting point of this derivative was 153°. The hydroxyl equivalent of fraction (V) appeared to be an infinite quantity.

It will be apparent that the carbonylation of allytrimethyl silane yielded only one monomeric aldehyde product; from the appearance of *n*-butyraldehyde as a cleavage product, we believe that this aldehyde is the *iso* compound. The nature of the condensed product is, considering the analytical data, somewhat in doubt.

The monomeric aldehydes, both from allyltrimethylsilane and from trimethylvinylsilane, could be condensed with resorcinol to form resinous materials.

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REFERENCES

(1) ADKINS AND KRSEK, *J. Am. Chem. Soc.*, **70**, 383 (1948); WENDER AND ORCHIN, R. I. 4270, U. S. Bureau of Mines, June 1948.

(2) Private communication, Prof. Adkins to D. T. Hurd.