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A New Synthesis of Tris(triphenylsilyl) Vanadate

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In 1958 Orlov *et al.*[1] reported the preparation of tris(triphenylsilyl) vanadate (III) by the reaction of tri-*n*-butyl vanadate and triphenylsilanol.

Chamberlain *et al.*[2] later reported the preparation of the title compound by the reaction of triphenylsilanol and vanadium oxytrichloride in the presence of ammonia.

The present authors have now found that the title compound can be synthesized by transesterification between triphenylacetoxysilane (I) and triisopropyl vanadate (II):

$$\underset{\text{I}}{3CH_3COOSiPh_3} + \underset{\text{II}}{OV\{OCH(CH_3)_2\}_3} \rightleftharpoons$$

$$\underset{\text{III}}{OV(OSiPh_3)_3} + 3CH_3COOCH(CH_3)_2 \qquad (1)$$

As part of our work on the preparation of metal alkoxides as polymerization catalysts, we will report

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[1] N. F. Orlov, B. N. Dolgov and M. G. Voronkov, *Doklady Akad. Nauk S. S. S. R.*, **122**, 246 (1958).

[2] M. M. Chamberlain, G. A. Jobs and B. B. Wayland, *J. Org. Chem.*, **27**, 3321 (1962).

on this new synthesis of this compound.

Experimental

Preparation of Triphenylacetoxysilane (I). Triphenylacetoxysilane was prepared by the reaction of triphenylchlorosilane and acetic anhydride.[3]

In a typical experiment, 20.0 g (0.067 mol) of triphenylchlorosilane was added to 34.2 g (0.335 mol) of acetic anhydride. After the triphenylchlorosilane had been dissolved in acetic anhydride upon heating, the mixture was refluxed for 4 hrs, then it was concentrated by distilling the excess acetic anhydride and allowed to stand at about −20°C in a dry ice-acetone bath. The crude product was precipitated, filtered, washed with cooled ether, and recrystallized from dry ether; mp 96—97°C (lit.[3] mp 97°C) The yield was 17.2 g (79%) based upon the triphenylchlorosilane.

Preparation of Triisopropyl Vanadate (II). The vanadate was prepared from 30.0 g of commercial ammonium metavanadate and isopropyl alcohol in a large excess by the procedure described by Cartan and Caughlan,[4] using the following reaction:

$$NH_4VO_3 + 3(CH_3)_2CHOH \rightleftharpoons \{(CH_3)_2CHO\}_3VO + NH_3 + 2H_2O \qquad (2)$$

The azeotrope was removed as it was formed. After several days, the majority of the excess alcohol was distilled. The contents in the flash were then centrifuged to remove the unreacted solids and the decomposition products. Repeated vacuum distillation gave 32.1 g (51.1%) of II; bp 75°C/2 mmHg and n_D^{25} 1.4782 (lit.[4] n_{15}^{D} 1.478).

Preparation of Tris(triphenylsilyl) Vanadate (III). This vanadate was prepared by Eq. (1). Nine grams (0.028 mol) of I and 2.1 g (0.009 mol) of II were dissolved in 100 m*l* of benzene. The mixture was refluxed for 90 hr and washed with water several times; the benzene layer was then separated and dried over anhydrous sodium sulfate overnight.

The crude product was precipitated, filtered, and recrystallized from benzene. The yield was 3.9 g (51%); mp 223—234°C (lit.[2] mp 225—226°C).

Found: C, 72.83; H, 5.29; V, 5.66; Si, 9.26%. Calcd for $C_{54}H_{45}O_4Si_3V$: C, 72.62; H, 5.08; V, 5.70; Si, 9.43%.

The NMR spectrum (60 Mc, room temperature) of this compound showed only the signals at τ near 2.75 assignable to the protons of the phenyl group and no signal characteristic for the isopropyl group.

The infrared spectrum indicated the characteristic bands of the phenyl group at 3060, 3025 (ν_{C-H}), and 1529 cm^{-1} ($\nu_{C=C}$).

In contrast, no band characteristic of the isopropyl group appeared. The strong absorption bands at 1430 and 1120 cm^{-1} are associated with the Si-phenyl group, while that at 1005 cm^{-1} can be attributed to the vanadyl group (V=O).

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3) N. S. Nametkin, A. V. Topchiev and F. F. Machus, *Doklady Akad. Nauk SSSR*, **87**, 233 (1952); *Chem. Abst.*, **47**, 12281 (1953).

4) F. Cartan and C. N. Caughlan, *J. Phys. Chem.*, **64**, 1756 (1960).