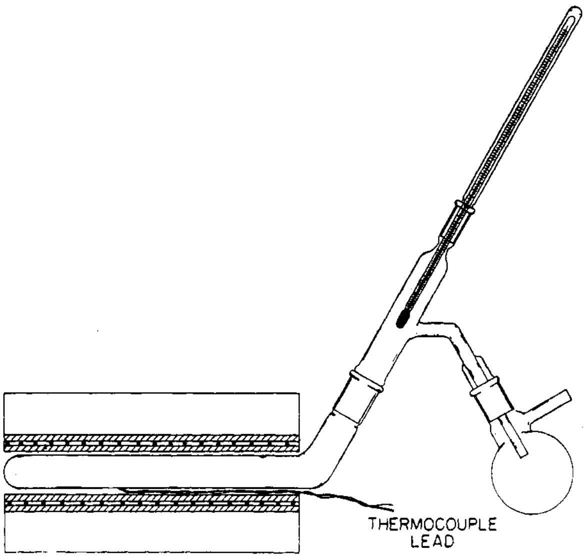

Fig. 1. Pyrolysis apparatus

p-Vinylacetophenone. Into the pyrolysis tube illustrated in Fig. 1 was charged 35 g. of polyvinylacetophenone. The tube, with a thermocouple attached, was placed in a stationary combustion furnace inclined about 30° upward toward the opening. The heating zone of the furnace was 12 in. long and extended an inch beyond the polymer charge at the outlet end of the tube. The thermocouple output activated a regulator which registered and controlled the furnace temperature. The furnace was heated to 200° to soften the polymer, vacuum was applied, and the temperature was raised to 400° for depolymerization. The temperature of the distilling product was in the vicinity of 100° at 1–2 mm. The receiver was cooled in ice. When the pyrolysis was completed (60–90 min.), the tube was removed from the furnace, cooled, and recharged. This process was repeated several times before the accumulation of nonvolatile pyrolysis products had to be removed. A total of 110 g. of polymer was pyrolyzed to give 70 g. of crude distillate. The oil was redistilled, in the presence of a small amount of hydroquinone, at 75–80° (0.3 mm.). The 48 g. of crystalline distillate was recrystallized from 40 ml. of *n*-heptane at 0°. The yield was 33 g. (30%); m.p. 34–35°.

If desired, the pyrolysis can be conducted in a flask immersed in a molten metal or salt bath at 400° with a somewhat reduced yield.

p-Vinylbenzoic Acid.[7] To 31 g. (0.21 mole) of *p*-vinylacetophenone in 150 ml. of dioxane was added dropwise, with stirring, 530 ml. (0.63 mole) of a $1.19M$ solution of potassium hypochlorite[8] over a 45-min. period. The temperature was maintained at 35° with slight cooling. The mixture was stirred an additional 30 min. at 35°. The small amount of excess hypochlorite was discharged by the addition of 1 ml. of acetone as indicated by acidic iodide solution. The mixture was cooled, extracted with one portion of ether, and the aqueous phase was added to 75 ml. of concentrated hydrochloric acid mixed with ice. The product was recovered by filtration and washed with cold water. The damp cake was dissolved in 150 ml. of warm ethanol containing a little hydroquinone, and hot water was added to incipient crystallization. Crystallization was completed at 5°. The acid was dried *in vacuo* at room temperature; yield, 27 g.

This acid was warmed in 150 ml. of ethyl ether to dissolve the monomeric acid. Filtration through Perlite removed the polymeric material, and 600 ml. of petroleum ether was added to the filtrate. Crystallization was completed at 5°. The product was collected and washed with the same mixed solvent. Bromine titration of the double bond[9] indicated 100.0% vinylbenzoic acid. The melting point was 138–141°; yield, 21 g. (67%).

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(7) The hypochlorite oxidation of *p*-vinylacetophenone was mentioned by W. J. Dale and B. D. Vineyard before the Division of Organic Chemistry at the 137th Meeting, ACS, Cleveland, Ohio, April 1960.

(8) M. S. Newman and H. L. Holmes, *Org. Syntheses*, Coll. Vol. II, 428 (1943).

(9) This analysis was a "dead-stop" end-point titration with pyridinium bromide perbromide as titrant and mercuric acetate as catalyst, developed and performed by E. P. Przybylowicz and A. D. Baitsholts, of these Laboratories.

The Reaction of 9,10-Dihydro-9,10-ethano-9-anthranol and 2,6-Di-*t*-butylphenol with Lithium Aluminum Hydride

John S. Meek and Constantine Bouboulis

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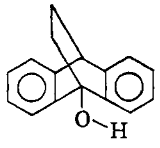
Lithium aluminum hydride when treated with excess methyl, ethyl or isopropyl alcohol liberates four equivalents of hydrogen while *t*-butyl and *t*-amyl alcohols liberate but three equivalents.[1] Two compounds which might liberate only two equivalents of hydrogen are the bridgehead alcohol (I) prepared in these laboratories and 2,6-di-*t*-butylphenol.[2] These compounds were tested and it was found that compound I was comparable with *t*-butyl alcohol and liberated three equivalents of hydrogen. However, 2,6-di-*t*-butylphenol was found to be of the next order of hindrance and it liberated only two equivalents of hydrogen.



As no precipitate was formed, it is likely that the evolution of only two equivalents of hydrogen is due to the inability of three 2,6-di-*t*-butylphenoxide groups to fit around an aluminum atom rather than to insolubility of the complex causing precipitation before a third equivalent of the phenol could react.

Aqueous sodium hydroxide solutions do not dissolve 2,6-di-*t*-butylphenol, but it seems doubtful that the lowered acidity of this hindered phenol would cause it to be unreactive with the bis-2,6-

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(1) H. C. Brown and R. F. McFarlin, *J. Am. Chem. Soc.*, 80, 5372 (1958).

(2) During the course of a visit at Colorado, Professor H. C. Brown suggested that compound I would be considerably more hindered than *t*-butyl alcohol in its reaction with lithium aluminum hydride.

di-*t*-butylphenoxyaluminohydride ion rather than a steric factor. After this complex with the phenol had been formed, the addition of compound I did not liberate a third equivalent of hydrogen. This showed that I does not exchange with the phenol in the complex ion as such an exchange would lead to the tris-9,10-dihydro-9,10-ethano-9-anthroxyaluminohydride ion as was formed with I acting directly on lithium aluminum hydride.

Methanol liberated hydrogen slowly from the bis-2,6-di-*t*-butylphenoxyaluminohydride ion and, while not quite two equivalents of hydrogen were evolved, no further hydrogen was released upon the addition of hydrochloric acid. This evolution of hydrogen by methanol may be due to exchange or two methoxide ions may be small enough to fit around the aluminum atom together with the 2,6-di-*t*-butylphenoxide ions.

The next stage of hindrance where an excess of a hydroxyl compound would liberate only one equivalent of hydrogen from lithium hydride might be found with an alcohol such as I if substituents were in the 1,8-positions. If bulky enough presumably they could even completely shield the hydroxyl group.

EXPERIMENTAL

Starting materials. The 2,6-di-*t*-butylphenol was a gift of the Ethyl Corporation. The 9,10-dihydro-9,10-ethano-9-anthrol was prepared by condensing anthrone dissolved in pyridine with ethylene at 180° under pressure of about 1500 to 3000 p.s.i. This solvent seems more satisfactory than aqueous sodium hydroxide and dioxane, which were used in our original procedure.[3]

Measurement of hydrogen evolution. A quantitative hydrogenation apparatus was used and solutions were injected with graduated hypodermic syringes. One milliliter of $0.78M$ solution of lithium aluminum hydride in tetrahydrofuran was added to an excess of methanol and 89 ml. of hydrogen was evolved at 25° and 630 mm. When the bridgehead alcohol was used, 66.2 ml. of hydrogen was evolved. A second solution gave 94 ml. of hydrogen with excess methanol and 49 ml. with excess hindered phenol. The values reported are the averages of three runs. No precipitate was observed on mixing either the phenol or the alcohols with the lithium aluminum hydride.

The oxyalumino hydrides. A solution of lithium aluminum hydride in tetrahydrofuran was added to a solution of the alcohol until evolution of hydrogen ceased. Removal of the solvent under reduced pressure gave a white solid whose spectrum in a potassium bromide pellet showed a greatly reduced hydroxyl peak when compared with the starting alcohol. The complex with water gave the starting alcohol back quantitatively with the evolution of hydrogen. Methanol and ethanol also released hydrogen from the complex.

In a similar manner the phenol complex was isolated but on exposure to air quickly turned to a yellow oil. The complex on heating at 80° bubbled and became a yellow oil. The complex liberated hydrogen when treated with water or methanol.

In another experiment 0.80 ml. of a stock solution of lithium aluminum hydride (about 0.75 mmole) was added to a fifty fold excess of methanol and 80.4 ml. of hydrogen was liberated. Next 0.80 ml. of the stock solution was added to 1 g. of 2,6-di-*t*-butylphenol in 8 ml. of tetrahydrofuran and 62.6 ml. of hydrogen was evolved, partly because of drying the solvent and partly from reaction with the phenol. A second addition of 0.80 ml. of the stock solution then liberated 40.6 ml. of hydrogen from the dried solution of excess phenol. After this evolution of hydrogen had ceased, the addition of 1 ml. of methanol liberated an additional 41.4 ml. of hydrogen. This came off slowly over a period of 4 hr. A final addition of hydrochloric acid liberated no further hydrogen.

In a similar experiment the addition of 2 g. of the alcohol I to the phenol complex did not liberate any hydrogen while subsequent addition of methanol did.

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[3] J. S. Meek, V. C. Godefroi, and W. B. Evans, abstracts, 123rd meeting of the American Chemical Society 27M, 1953. See also M. Wilhelm and D. Y. Curtin, *Helv. Chim. Acta*, 40, 2129 (1957).

Some Alkoxyorganosilanes[1]

L. W. BREED, R. L. ELLIOTT, W. J. HAGGERTY, JR., AND F. BAIOCCHI

Received September 1, 1960

In the course of an investigation of organosilicon polymers containing bulky organic groups, we have prepared several organoalkoxysilanes whose synthesis and properties have not been reported elsewhere. Each of the compounds was obtained from the well known condensation of an aryl Grignard reagent with either an alkoxysilane or an alkoxychlorosilane.

Two of the new compounds, 4-chlorophenylethoxydiphenylsilane and 4-chlorophenylethoxydimethylsilane, were prepared for an investigation of the synthesis of monomers of the type $(C_2H_5OSiR_2C_6H_4)_4Si$, where R is methyl or phenyl. Treating either compound with silicon tetrachloride in the presence of sodium in diethyl ether failed to initiate a reaction. When boiling toluene was used as the solvent, considerable cleavage of the ethoxyl groups occurred and pure products could not be isolated from the reaction mixture.

The other new compounds—diethoxymethyl-1-naphthylsilane, diisopropoxymethyl-1-naphthylsilane, diethoxymethyl-2-naphthylsilane, and 2-biphenylyldiethoxymethylsilane—were prepared for an investigation of the effect of bulky pendant aromatic groups on the formation of siloxane chains. Also used in this investigation was 4-biphenylyldiethoxymethylsilane whose preparation has been described elsewhere.[2] An attempt to prepare 9-

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(1) This research was supported by the United States Air Force under Contract AF 33(616)-3675, monitored by the Materials Laboratory, Wright Air Development Division, Wright-Patterson Air Force Base, Ohio.

(2) L. W. Breed, *J. Org. Chem.*, 25, 1198 (1960).