Low-Pressure Hydrogenation of Some Benzenepolycarboxylic Acids with Rhodium Catalyst

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Received May 2, 1966

In the procedure of Longone[1] tetrasodium pyromellitate is hydrogenated in aqueous solution for 3 days at 150° (200 atm) in the presence of Raney nickel. In our experiments the use of a very high catalyst ratio (70%) decreased the time considerably but the difficulty in removing inorganic salt after acidification of the reduction solution with mineral acid made us abandon this method.

In this laboratory cyclohexane-1,2,4,5-tetracarboxylic acid was readily obtained, in high yield, by reduction of pyromellitic acid in water in the presence of rhodium-on-carbon catalyst at room temperature to 60° and at less than 3 atm. The ease with which this reduction took place suggested application to the conversion of the isomeric benzenedicarboxylic acids. Cyclohexanedicarboxylic acids have been obtained by catalytic hydrogenation of the appropriate aromatic acids in acetic acid solution with platinum oxide[2] or under more vigorous conditions in aqueous alkaline solution.[3]

In the only reported hydrogenation of the free acids in aqueous solution the reaction was carried out at elevated temperature and rather high pressures (330–400 atm). Good yields were obtained under the described conditions with palladium and ruthenium catalysts, but the use of rhodium gave poor results.[4]

In the present study, when phthalic, isophthalic, and terephthalic acids were reduced under the same mild conditions used for the conversion of pyromellitic acid, excellent yields of the corresponding cyclohexanedicarboxylic acids were obtained. It was necessary to maintain a reaction temperature of 60–70°. At this temperature sufficient starting acid dissolved to allow uptake of hydrogen to proceed at a good rate. It is of interest that under these conditions the 1,2- and 1,4-dicarboxylic acids were obtained in essentially the *cis* form, while the 1,3-dicarboxylic acid was obtained as a 60:40 *cis–trans* mixture.

The results of these reductions make it appear that the procedure could be useful in the hydrogenation of other aromatic acids. There is some indication from this study that the success of the reaction may be more dependent on the water solubility of the reduction product than that of the starting acid.

Experimental Section[5]

All melting points were taken on a Thomas–Hoover apparatus which had been calibrated against known standards up to 200°. Melting points above this are considered uncorrected.

Cyclohexane-1,2,4,5-tetracarboxylic Acid.—A mixture of 12.7 g (0.05 mole) of pyromellitic acid, 5.0 g of 5% rhodium-on-carbon catalyst, and 200 ml of water was hydrogenated at 60° and 2.7 atm. Uptake was complete in 1.5 hr. The heated solution was filtered from the catalyst and the filtrate was concentrated to the beginning of crystallization. The mixture was cooled thoroughly and the product filtered and dried, mp 270–271° dec (lit.[1] mp 274–275° dec).

Anal. Calcd for $C_{10}H_{12}O_8$: C, 46.15; H, 4.64. Found: C, 46.14; H, 4.72.

Additional material melting at 269° was obtained on concentration of the filtrate to dryness; total yield was 75%. Infrared examination showed that the two crops were identical and that there was complete absence of aromatic bands.

In a second experiment (0.1 mole in 250 ml of water and 10.0 g of catalyst) the reduction solution, after removal of catalyst, was concentrated to complete dryness under reduced pressure, yield, 91%. Its infrared spectrum and melting point were identical with those of the analytical sample.

When pyromellitic acid was hydrogenated at room temperature, the reaction period was increased but the cyclohexanetetracarboxylic acid obtained was similar in all respects to the previous products.

The conversions of phthalic, isophthalic, and terephthalic acids to the corresponding cyclic structures were carried out at 60–70° in the presence of 4.0 g of 5% rhodium on alumina per 8.3 g (0.05 mole) of acid in 200 ml of water. In some instances 2.0 g of 2.5% rhodium on alumina[6] was used for the same amount of material.

Cyclohexane-1,2-dicarboxylic Acid.—After hydrogen uptake was complete the hot mixture containing a considerable amount of solid was filtered and the filtrate was cooled. The first crop yielded 1.6 g of material melting at 191–192°. The filter cake containing the catalyst was extracted thoroughly with hot water and the filtrate was concentrated to the beginning of crystallization. After cooling 2.9 g of acid was obtained, mp 194–195°. The two crops were identical as shown by their infrared spectra (no aromatic bands). A composite sample was submitted for analysis.

Anal. Calcd for $C_8H_{12}O_4$: C, 55.80; H, 7.02. Found: C, 55.94; H, 6.76.

The melting points of the two crops (lit.[7] mp 191.5–192.5°) and gas–liquid partition chromatography (glpc)[8] of the composite sample indicated that the composite represented good quality *cis* isomer (>95%). Third and fourth crops melting at 189–194° and 174–184° were obtained by further concentration of the filtrates giving a total yield of 93%. Glpc[8] showed that the third crop material was mainly the *cis* isomer (93.4%) while the last portion was a mixture of 55% *cis* and 30% *trans* acids.

In subsequent experiments after reduction was complete sufficient hot water was added to dissolve the crystalline material. The whole was concentrated dryness, mp 178–182°; the yield was 91% from three runs.

Glpc[8] indicated that the product contained 86% *cis* and 13% *trans* acids.

Cyclohexane-1,3-dicarboxylic Acid.—A total yield of 96% (mp 112–134°) was obtained from three 0.5-mole runs. Infrared examination showed absence of aromatic bands. The dried material was analyzed without further purification.

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[1] D. T. Longone, *J. Org. Chem.*, **28**, 1770 (1963).

[2] H. A. Smith and F. P. Byrne, *J. Am. Chem. Soc.*, **72**, 4406 (1950).

[3] L. L. Ferstandig and W. A. Pryor [U. S. Patent 2,828,335 (1958)] describe the reduction of the salts of the acids at 116° (40–90 atm) with ruthenium dioxide. B. J. Armitage, G. W. Kenner, and M. J. T. Robinson [*Tetrahedron*, **20**, 723 (1964)] hydrogenated a solution of sodium isophthalate for 4 days at 180° (200 atm) in the presence of freshly prepared Raney nickel.

[4] H. C. Dehm and L. G. Maury [U. S. Patent 2,888,484 (1959)] obtained 38% yield cyclohexane-1,4-dicarboxylic acid from the rhodium on carbon catalyzed reduction of terephthalic acid at 300° (330 atm). Under less drastic conditions the yield was lower.

[5] Microanalyses were conducted by O. Kolsto and his associates; thin layer chromatography was performed by Mrs. Karen Gibson and gas–liquid partition chromatography was performed by D. Nelson; infrared examination was conducted by A. Kammer and W. Washburn. The authors gratefully acknowledge the help of these people.

[6] Rhodium on carbon or on alumina could be used interchangeably. The rhodium catalysts were purchased from Engelhard Industries, Newark, N. J.

[7] R. P. Linstead, S. B. Davis, and R. Whetstone, *J. Am. Chem. Soc.*, **64**, 2093 (1942).

[8] The samples were converted to the dimethyl esters with diazomethane by the method of H. Schlenk and J. L. Gellerman, *J. Anal. Chem.*, **32**, 1412 (1960). Chromatography was carried out in a Barber–Coleman Model 10 unit with a thermal conductivity detector: stationary phase, 20% Apiezon L; support, Chromosorb W; column dimensions, 8 ft × 0.25 in.; temperature, 150°; pressure, 22 psi (helium).

Anal. Calcd for $C_8H_{12}O_4$: C, 55.80; H, 7.02. Found: C, 56.05; H, 7.08.

In one run it was possible to get some *cis* acid by fractional crystallization (for use as a standard) but the procedure of Skita and Rossler[9] gave far better separation. From 20 g of the mixture of isomers, shown by glpc to be 60% *cis* and 40% *trans*, 9.9 g of *cis* acid, mp 164–167° (lit.[9] mp 167.5°), and 7.0 g of *trans* acid, mp 147–150° (lit.[9] mp 150.5°), were obtained. Each was shown by glpc to be a single component.

Cyclohexane-1,4-dicarboxylic Acid.—Hydrogenation of terephthalic acid gave essentially *cis* acid. In one reduction the solution was filtered hot and the catalyst cake was washed with 50 ml of hot water. The well-cooled mixture yielded less than 0.5 g of material, mp 280–295° (impure *trans* acid). The filtrate was concentrated to dryness. The residue (6.8 g) was extracted with 1000 ml of analytical grade chloroform. The extract on concentration under reduced pressure yielded 6.5 g (75.7% of *cis* acid), mp 170–171° (lit.[10] mp 166–167°). Glpc showed it to be of high purity (99.6–99.8%). The portion, insoluble in chloroform, after recrystallization from water melted at 310° (lit.[10] mp 312–313°, *trans* acid.)

In other runs, after reduction was complete the mixture was filtered hot, the catalyst cake was washed thoroughly with hot water, and the combined filtrates were concentrated to dryness. Yields were over 90% and the products after isolation melted in the range of 160–172°.[11] None showed any aromatic bands in their infrared spectra. One lot melting at 158–164° was found by glpc to be a mixture of 80% *cis* and 20% *trans* isomers.

(9) A. Skita and R. Rossler, *Ber.*, **72**, 265 (1939).

(10) R. Malachowski and J. Jankiewiczowna, *ibid.*, **67**, 1783 (1934).

(11) One of the referees called Japanese Patent 27245 (1964) to our attention. It described the hydrogenation of aromatic dicarboxylic acids with rhodium oxide at 60–70° (100 atm). *cis*-1,4-Cyclohexanedicarboxylic acid was obtained in 88% yield.

Thionoacyloxysilanes

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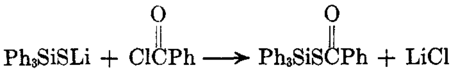
Received May 5, 1966

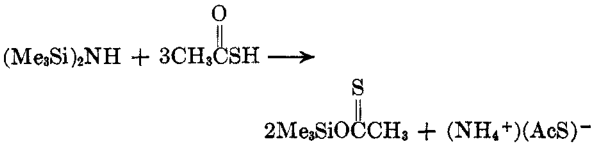
The preparation of only one thiolacyloxysilane has appeared in the literature.[1] Apparently no thiono-



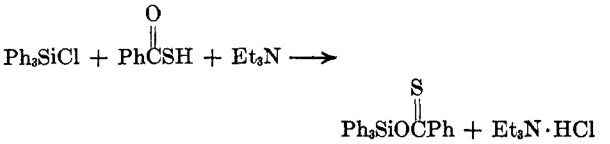
$$\mathrm{Ph_3SiSLi + Cl\overset{O}{\overset{\|}{C}}Ph \longrightarrow Ph_3SiS\overset{O}{\overset{\|}{C}}Ph + LiCl}$$

acyloxysilanes have been reported. This Note describes the preparation and some properties of this new type of compound.

Two methods were used to prepare thionoacyloxysilanes (eq 1 and 2).



$$\mathrm{(Me_3Si)_2NH + 3CH_3\overset{O}{\overset{\|}{C}}SH \longrightarrow 2Me_3SiO\overset{S}{\overset{\|}{C}}CH_3 + (NH_4^+)(AcS)^-} \quad (1)$$

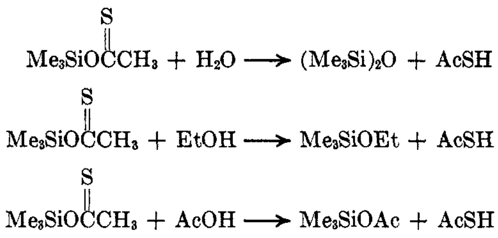


$$\mathrm{Ph_3SiCl + Ph\overset{O}{\overset{\|}{C}}SH + Et_3N \longrightarrow Ph_3SiO\overset{S}{\overset{\|}{C}}Ph + Et_3N{\cdot}HCl} \quad (2)$$

Thionoacyloxysilanes prepared in these ways have a bright yellow color. These new compounds possess infrared spectra showing no normal carbonyl absorptions as reported by Gilman and Lichtenwalter[1] for thiolbenzoxytriphenylsilane. In agreement with West's theory,[2] the ultraviolet spectra of thionoacetoxysilanes are similar to the spectra of O-alkyl thioacetates. The ultraviolet spectra of thionoacetoxytrimethylsilane and dithionoacetoxydimethylsilane showed absorption peaks at 245 mμ (ε 4570) and 243 mμ (ε 4400), respectively. Janssen[3] reported an absorption peak at 241 mμ (ε 9600) for O-ethyl thioacetate.

The thiolacetate anion exists in both the thiol $[CH_3C(O)S^-]$ and thiono $[CH_3C(O^-){=}S]$ forms.[4] Therefore, either thiono- or thiolacetoxysilanes might have been expected. However, bond energies[5,6] indicate that a thionoacetoxysilane should be more stable than a thiolacetoxysilane by approximately 15 kcal.

Thionoacetoxytrimethylsilane reacts with compounds containing an hydroxyl group as summarized.



$$\mathrm{Me_3SiO\overset{S}{\overset{\|}{C}}CH_3 + H_2O \longrightarrow (Me_3Si)_2O + AcSH}$$

$$\mathrm{Me_3SiO\overset{S}{\overset{\|}{C}}CH_3 + EtOH \longrightarrow Me_3SiOEt + AcSH}$$

$$\mathrm{Me_3SiO\overset{S}{\overset{\|}{C}}CH_3 + AcOH \longrightarrow Me_3SiOAc + AcSH}$$

The products were identified by gas–liquid partition chromatography (glpc), by comparison of retention times with authentic standards, and by infrared analyses of the reaction mixtures. Reaction with water or ethanol is rapid at room temperature. The reaction with acetic acid is slow unless it is catalyzed with sodium acetate. These reactions are accompanied by a loss of the yellow color.

Experimental Section

Thiolacetic acid was prepared as described in the literature.[7] Thiolbenzoic acid was obtained from Evans Chemitics, Inc., and was freshly distilled. Triphenylchlorosilane (neut equiv 300, calcd 295), hexamethyldisilazane, and dimethyldichlorosilane were obtained from Dow Corning Corp.

Thionoacetoxytrimethylsilane was prepared by adding thiolacetic acid (20 ml, 0.279 mole) dropwise to a solution of hexamethyldisilazane (19.7 ml, 0.093 mole) in hexane (50 ml). After the mixture was cooled to room temperature, it was filtered free of ammonium thioacetate. After the salt was washed with five 10-ml portions of hexane and dried, it weighed 8.0 g (92% of theory). Distillation of the filtrate and washings gave 23.3 g (85% yield) of yellow liquid: bp 84–85° (160 mm); $n^{25}\mathrm{D}$ 1.4513; d^{25}_4 0.929; $\lambda_{\max}^{\text{hexane}}$ 207 mμ (ε 2730), 245 (4570), and 389 (11.5); $\lambda_{\max}^{\mathrm{CCl_4}}$ 3.35 (m), 3.44 (w), 5.82 (w), 5.92 (w), 7.36 (s), 16.7 (w), 20.7 (m), 28.6 (w), and 35 (m) μ; $\lambda_{\max}^{\mathrm{CS_2}}$ 7.84 (s), 8.00 (s), 8.20 (s), 9.90 (s), 11.8 (s), 14.3 (w), and 15.4 (m) μ. The nmr spectrum showed two absorptions in the ratio 3:1 at τ 9.62 (Si—Me) and 7.49 (C=SMe), respectively. τ values are relative to tetramethylsilane (τ 10).

Anal. Calcd for $C_5H_{12}OSSi$: Si, 18.9; S, 21.6; mol wt, 148. Found Si, 18.5; S, 21.1; mol wt, 163 (cryoscopically in benzene).

Di(thionoacetoxy)dimethylsilane was prepared by adding triethylamine (38.5 ml, 0.275 mole) to a solution of dimethyl-

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(1) H. Gilman and G. D. Lichtenwalter, *J. Org. Chem.*, **25**, 1064 (1960).

(2) R. West, *J. Organometal. Chem.*, **3**, 314 (1965).

(3) M. J. Janssen, *Rec. Trav. Chim.*, **79**, 454 (1960).

(4) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. 4, Chemical Publishing Co., Inc., New York, N. Y., 1965, p 18.

(5) C. Eaborn, "Organosilicon Compounds," Butterworth and Co. (Publishers) Ltd., London, 1960, p 90.

(6) L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, p 1157.

(7) E. K. Ellingboe, "Organic Syntheses," Coll. Vol. IV, N. Rabjohn, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, p 928.