Ultraviolet absorption, $\lambda_{\max}$ 226 mμ, log ϵ 4.00 and $\lambda_{\max}$ 381 mμ, log ϵ 4.76 with a minimum at 283 mμ, log ϵ 1.78.

Butyl α-Cyano-3-amino-2-cyclohexene-$\Delta^{1,\alpha}$-acetate.—The *n*-butyl ester was obtained in the same manner, m.p. 142–143° after recrystallization from benzene–ethanol.

Anal. Calcd. for $C_{13}H_{18}N_2O_2$: C, 66.64; H, 7.74. Found: C, 66.65; H, 7.63.

Ethyl α-Cyano-3-(N-benzylamino)-2-cyclohexene-$\Delta^{1,\alpha}$-acetate (III).—When a mixture of the monoketal, ethyl cyanoacetate and benzylamine was allowed to stand at 40° for 6 days, the N-benzyl derivative crystallized upon cooling the solution, m.p. 135–137°. An analytical sample was obtained by two crystallizations from 95% ethanol, m.p. 139–139.5°.

Anal. Calcd. for $C_{18}H_{20}N_2O_2$: C, 72.95; H, 6.80; N, 9.46. Found: C, 72.81; H, 7.07; N, 9.73.

Ultraviolet absorption, $\lambda_{\max}$ 386 mμ, log ϵ 4.80; $\lambda_{\max}$ 227 mμ, log ϵ 4.04.

Ethyl α-Cyano-3-hydroxy-2-cyclohexene-$\Delta^{1,\alpha}$-acetate (IV). **a. By Alkaline Hydrolysis.**—The eneamine ester (II) (2.08 g., 0.01 mole) was heated for 3.5 hr. in 100 ml. of refluxing 1 *N* alcoholic potassium hydroxide. The ammonia evolved was absorbed in 0.1 *N* hydrochloric acid; titration showed 0.93 mole equivalent of ammonia absorbed. A small amount of unreacted starting material was removed by filtration and the solution was concentrated *in vacuo* and acidified. There was obtained 1.4 g. (67%) of the light tan crystalline acid, m.p. 139–141°. An analytical sample was obtained by crystallization from cyclohexane–ethyl acetate, m.p. 142–143.5°; ultraviolet absorption, $\lambda_{\max}$ 343 mμ, log ϵ 4.44.

Anal. Calcd. for $C_{11}H_{13}NO_3$: C, 63.75; H, 6.32; N, 6.76; neut. equiv., 207. Found: C, 64.01; H, 6.37; N, 6.57; neut. equiv., 209.

b. By Acid Hydrolysis (4.5 Hr.).—A solution of 4 g. of (II) in 20 ml. of water and 20 ml. of ethanol with 7 ml. of concentrated sulfuric acid was allowed to reflux for 4.5 hr. The solution was filtered, concentrated and diluted with 30 ml. of water. After recrystallization of the product from ethanol there was obtained 1.4 g. of material melting at 139–141° and with no depression in melting point when mixed with a sample obtained by alkaline hydrolysis.

c. Acid Hydrolysis (24 Hr.).—A solution of 4 g. of the eneamine ester (II) was heated for 24 hr. in 20 ml. of 50% ethanol and 5 ml. of concentrated sulfuric acid. The alcohol was removed, the solution was diluted with water and it was then extracted with chloroform. From the chloroform there was obtained 0.4 g. of 3-methyl-2-cyclohexene-1-one, b.p. 60–61° at 4 mm., $n^{25}\mathrm{D}$ 1.4915. The 2,4-dinitrophenylhydrazone, m.p. 175–177° after crystallization from ethanol–ethyl acetate, gave no depression in m.p. when mixed with the 2,4-dinitrophenylhydrazone of an authentic sample.[1]

Knoevenagel Reaction with the Monoketal (I).—The ketal (7.7 g., 0.05 mole), ethyl cyanoacetate (11.3 g., 0.1 mole), acetic acid (4.8 g.), and 50 ml. of chloroform were heated under a soxhlet extractor containing anhydrous magnesium sulfate in the thimble. One-half gram portions of ammonium acetate were added after 5 min., 1 hr., 3 hr. and 5 hr. After 6 hr. the solution was washed with water and 8% bicarbonate. Removal of the volatile material by distillation *in vacuo* followed by distillation of the residue at 215–230° (3 mm.) gave a solid which was recrystallized from methylcyclohexane–ethyl acetate to give 3.4 g. (27%) of **ethyl α-cyano-3-(β-hydroxyethyl)-2-cyclohexene-$\Delta^{1,\alpha}$-acetate**, m.p. 105–108°. Recrystallization from benzene–petroleum ether gave an analytical sample, m.p. 112–112.5°; ultraviolet absorption, $\lambda_{\max}$ 339 mμ, log ϵ 4.24.

Anal. Calcd. for $C_{12}H_{17}NO_4$: C, 62.03; H, 6.84; N, 5.58. Found: C, 61.74; H, 6.85; N, 5.77.

Fractionation of the product from another experiment starting with 15 g. of the ketal (I) gave 3.2 g. of a fraction, b.p. 174° (0.2 mm.), $n^{25}\mathrm{D}$ 1.4901, and a higher boiling fraction, 1.2 g. at 200–210°. The 200–210° fraction solidified immediately upon cooling while the 174° fraction solidified slowly after several weeks.

One gram of the ketal (174° fraction) dissolved in 5 ml. of 95% ethanol and 5 ml. of 6 *N* hydrochloric acid gave upon standing 0.6 g. of light tan solid, m.p. 134–136°. Recrystallization from methylcyclohexane–ethyl acetate gave material melting at 142–143° and unchanged when mixed with the enol (IV). The same procedure applied to the solid (V), gave 0.54 g. of the enol, m.p. 141–142°; a mixed melting point with IV was undepressed.

Reaction of V with Ammonia to Give II.—Five hundred milligrams of crude V dissolved in 10 ml. of methanol and 10 ml. of aqueous ammonia gave, after 15 min., 350 mg. of yellow crystals, m.p. 231–232° with no depression when mixed with a sample of II.

Ethylene Ketal of 3-Oxo-1-cyclohexene-1-acetonitrile.—The monoketal (I) (15.6 g.), cyanoacetic acid (9.5 g.) and ammonium acetate (0.45 g.) were heated in 50 ml. of refluxing benzene under a constant water separator for 2 hr., another portion of 0.15 g. of ammonium acetate was added and the heating was continued for 6 hr. Removal of the solvent and distillation of the residue up to 180° and 1 mm. gave 9.4 g. of crude material which was fractionated to give 4.5 g. (25%) of a light yellow oil, b.p. 122–127° at 2 mm., $n^{22}\mathrm{D}$ 1.5002. The 2,4-dinitrophenylhydrazone was recrystallized from ethanol–ethyl acetate to give small red prisms, m.p. 187–188.5°.

Anal. Calcd. for $C_{14}H_{13}N_5O_4$: C, 53.33; H, 4.16; N, 22.23. Found: C, 53.50; H, 3.90; N, 22.45.

Ethylene Ketal of Ethyl α-Cyano-3-oxo-cyclohexane-1-acetate.—A solution of 7.7 g. (0.05 mole) of I and 11.3 g. (0.1 mole) of ethyl cyanoacetate in 20 ml. of absolute ethanol was shaken for 20 hr. under 35 lb. hydrogen pressure with 0.2 g. of 5% palladium–charcoal catalyst.[9] Fractionation of the product gave 7.4 g. (58%) with a b.p. of 151–152° at 0.8 mm. and $n^{23}\mathrm{D}$ 1.4722.

Anal. Calcd. for $C_{13}H_{19}NO_4$: C, 61.64; H, 7.56; N, 5.53. Found: C, 61.86; H, 7.64; N, 5.26.

3-Oxo-cyclohexaneacetic Acid.—The crude ketal prepared as described above was hydrolyzed by heating in 30 ml. of acetic acid and 20 ml. of concentrated hydrochloric acid for 16 hr. Crystallization of the crude product from benzene gave 1.3 g. of acid, m.p. 79.5–81° (lit. 81–82°).[10]

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(9) American Platinum Works, Newark, N. J.

(10) P. D. Bartlett and G. F. Woods, THIS JOURNAL, **62**, 2933 (1940).

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Some Ethers of Pentaerythritol and Their Nitrate Esters[1]

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The allylation of pentaerythritol to form a mixture of monoallyl and diallyl ethers as the principal products has been accomplished by a modification of the method of Nichols and Yanovsky[2] for the partial allylation of pentaerythritol.

Experimental

Preparation of Mono- and Diallyl Pentaerythritol Ethers.—A suspension consisting of 273 g. of pentaerythritol and 300 g. of *p*-dioxane was placed in a three-necked flask equipped with a mercury-sealed stirrer, a dropping funnel and a reflux condenser. A mixture of 80 g. of sodium hydroxide and 36 g. of water was slowly added to the suspension with vigorous stirring. The temperature of the reaction mixture was ncreased to 45°, 153 g. of allyl chloride was added, and the temperature was maintained at 45° for an additional nine hours. The cooled mixture was filtered to remove sodium chloride and unreacted pentaerythritol and concentrated. The residual mixture of allyl pentaerythritol ethers was fractionated at 1 mm. pressure.

Diallyl pentaerythritol ether, b.p. 120° (1 mm.), $n^{20}\mathrm{D}$ 1.4729, d^{20}_{20} 1.046, was obtained in a yield of 35% based on the allyl chloride. *Anal.* Calcd. for $C_{11}H_{20}O_4$: C, 61.08; H, 9.32. Found: C, 61.25; H, 9.09.

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(1) Publication approved by the Bureau of Ordnance, Navy Department.

(2) P. L. Nichols, Jr., and E. Yanovsky, THIS JOURNAL, **67**, 46 (1945).

Dinitrate Ester: $n^{20}\mathrm{D}$ 1.4688, $d^{20}{}_{20}$ 1.191. *Anal.* Calcd. for $C_{11}H_{18}N_2O_8$: C, 43.14; H, 5.92; N, 9.15. Found: C, 42.95; H, 6.08; N, 8.82.

Monoallyl Pentaerythritol Ether: b.p. 148–150° (1 mm.), $n^{20}\mathrm{D}$ 1.4843, $d^{20}{}_{20}$ 1.135, was obtained in 35% yield. *Anal.* Calcd. for $C_8H_{16}O_4$: C, 54.53; H, 9.15. Found: C, 54.50; H, 9.12.

Trinitrate Ester: $n^{20}\mathrm{D}$ 1.4797, $d^{20}{}_{20}$ 1.373. *Anal.* Calcd. for $C_8H_{13}N_3O_{10}$: C, 30.87; H, 4.21; N, 13.50. Found: C, 31.01; H, 3.93; N, 13.53.

Monopropyl Pentaerythritol Ether.—A solution of 35.2 g. of monoallyl pentaerythritol ether in 400 ml. of 95% ethanol was hydrogenated at room temperature and atmospheric pressure, using 0.2 g. of platinum oxide. The product was distilled at 125° (1 mm.), $n^{20}\mathrm{D}$ 1.4662, $d^{20}{}_{20}$ 1.096. *Anal.* Calcd. for $C_8H_{18}O_4$: C, 53.91; H, 10.18. Found: C, 53.57; H, 10.25.

Trinitrate Ester: $n^{20}\mathrm{D}$ 1.4654, $d^{20}{}_{20}$ 1.332. *Anal.* Calcd. for $C_8H_{15}N_3O_{10}$: C, 30.67; H, 4.83; N, 13.42. Found: C, 30.67; H, 4.77; N, 13.65.

Dipropyl Pentaerythritol Ether.—A solution of 25 g. of diallyl pentaerythritol in 175 ml. of 95% ethanol was hydrogenated at room temperature and atmospheric pressure, using 0.2 g. of platinum oxide. The product was distilled at 115° (1 mm.), $n^{20}\mathrm{D}$ 1.4461, $d^{20}{}_{20}$ 0.993. *Anal.* Calcd. for $C_{11}H_{24}O_4$: C, 59.97; H, 10.98. Found: C, 59.83; H, 11.06.

Dinitrate Ester: $n^{20}\mathrm{D}$ 1.4470, $d^{20}{}_{20}$ 1.144. *Anal.* Calcd. for $C_{11}H_{22}N_2O_8$: C, 42.57; H, 7.15; N, 9.03. Found: C, 42.59; H, 7.15; N, 9.15.

Monoglycerol Pentaerythritol Ether.—A mixture of 15 g. of monoallyl pentaerythritol ether, 100 ml. of 95% ethanol and 0.015 g. of osmium tetroxide dissolved in 5 ml. of water was placed in a three-necked flask equipped with a stirrer and dropping funnel. The temperature of the mixture was adjusted to 20° and 100 g. of cold 3% hydrogen peroxide was added dropwise with slow stirring. The reaction mixture was maintained at 0° overnight, then concentrated and subjected to molecular distillation. The distillate formed sugar-like crystals which softened at 55° and melted at 59–61°. *Anal.* Calcd. for $C_8H_{18}O_6$: C, 45.71; H, 8.64. Found: C, 45.91; H, 8.63.

Pentanitrate Ester: m.p. 54.5–55.0°; $n^{31}\mathrm{D}$ 1.531, 1.520; $d^{20}{}_{20}$ 1.57. *Anal.* Calcd. for $C_8H_{13}N_5O_{16}$: C, 22.03; H, 3.00; N, 16.09. Found: C, 22.15; H, 2.97; N, 15.92.

Diglycerol Pentaerythritol Ether.—Diglycerol pentaerythritol ether was prepared by hydroxylating diallyl pentaerythritol ether. The method of preparation was similar to that used for the preparation of monoglycerol pentaerythritol ether from monoallyl pentaerythritol ether. The product crystallized after molecular distillation, m.p. 72.5–74.0°, softening at 69°, when heated rapidly (Fisher-Johns melting point apparatus). *Anal.* Calcd. for $C_{11}H_{24}O_8$: C, 46.47; H, 8.51. Found: C, 46.67; H, 8.43.

Hexanitrate Ester: $n^{20}\mathrm{D}$ 1.4878, $d^{20}{}_{20}$ 1.540. *Anal.* Calcd. for $C_{11}H_{18}N_6O_{20}$: C, 23.83; H, 3.27; N, 15.16. Found: C, 23.96; H, 3.08; N, 14.87.

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Functional Aromatic Silanes

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The preparation of aromatic silane derivatives containing nuclear substituted functional groups has been the subject of a series of recent investigations.[1–6]

Roberts, McElhill and Armstrong[1] described the preparation of *m*- and *p*-trimethylsilylbenzoic acid (I) *via* the Grignard reaction as well as by means of the corresponding lithium derivative.

In the present investigation the preparation of the *p*-trimethylsilylbenzoyl chloride (II) and the corresponding amide (III) was undertaken. The synthesis of the *p*-trimethylsilylbenzoyl chloride presented somewhat of a problem because of the well-known tendency of silyl groups connected to an aromatic ring to undergo cleavage in acid medium particularly at elevated temperatures. It therefore became necessary to adopt a procedure using mild conditions and working if possible at low temperatures. This was accomplished by using thionyl chloride in the presence of pyridine as a hydrohalogen acceptor

$$\underset{\text{I}}{(CH_3)_3SiC_6H_4COOH} + SOCl_2 \xrightarrow{\text{pyridine}} \underset{\text{II}}{(CH_3)_3SiC_6H_4COCl}$$

The above reaction required less than ten minutes and the resulting acid chloride reacted with an excess of cold concd. ammonium hydroxide which yielded instantly the corresponding amide (III).

$$\underset{\text{II}}{(CH_3)_3SiC_6H_4COCl} + NH_4OH \longrightarrow \underset{\text{III}}{(CH_3)_3SiC_6H_4CONH_2}$$

Silicon-containing aromatic aldehydes have hitherto not been reported in literature. *p*-Trimethylsilylbenzaldehyde (VI) was prepared by reaction of *p*-trimethylsilylphenylmagnesium bromide (IV) with ethyl orthoformate followed by hydrolysis of the resulting acetal (V)

$$\underset{\text{IV}}{(CH_3)_3SiC_6H_4MgBr} + HC(OC_2H_5)_3 \longrightarrow \underset{\text{V}}{(CH_3)_3SiC_6H_4CH(OC_2H_5)_2} \longrightarrow \underset{\text{VI}}{(CH_3)_3SiC_6H_4CHO}$$

The acetal was not isolated in pure form but was used directly in the hydrolysis step to yield the aldehyde (VI). Remarkable is the fact that *p*-trimethylsilylbenzaldehyde can be steam distilled from an acid solution without undergoing cleavage of the C (phenyl)–Si bond.

The synthesis of silicon-containing phenols is of very recent origin. Gilman and Nobis[7] in 1950 reported several unsuccessful attempts to prepare *o*- and *m*-trimethylsilylphenol by various methods and concluded that such phenols were unstable structures.

Sunthankar and Gilman,[8] however, succeeded in preparing trimethyl- and triphenylsilylnaphthols by the reaction of chlorosilanes with the corresponding naphthyllithium compounds.

After the present work was completed Speier[2] reported the successful synthesis of *o*- and *p*-trimethylsilylphenol by the reaction of *o*- and *p*-chlorophenoxytrimethylsilane with sodium and trimethylchlorosilane. The same investigator also reported that magnesium could not be used in place of sodium when used with *p*-bromophenoxytrimethylsilane.

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