Experimental Section

A 100-ml resin flask was fitted with a heated water condenser (~65 °C), a mechanical stirrer (600 rpm), a fritted glass gas addition tube (25–50 μ pore size), and a thermometer. Cyclopentadecane (99%, 52.6 g, 0.25 mol) and 2.5 g of boric acid were placed in the flask and the reaction mixture heated slowly to 150–155 °C. The water present was driven off with the aid of air or nitrogen. The mixture was then heated to a given temperature (±2 °C) and air bubbled through the molten hydrocarbon for the required time. The reaction mixture was then cooled to ~95 °C and 25 ml of water added. (For the experiments in Table II only hexane was added.) After stirring at 95 °C for 1 h, the reaction mixture was cooled and hexane added. The mixture was transferred to a separatory funnel and the aqueous and organic layers separated. The organic phase was washed with water once more, weighed, and analyzed by VPC according to the conditions given in footnote *c*, Table I.

Registry No.—Cyclopentadecane, 295-48-7; cyclopentadecanone, 502-72-7; cyclopentadecanol, 4727-17-7.

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(14) A reviewer has suggested that the following reactions may occur on the VPC column:

$$(ROBO)_3 \rightarrow B_2O_3 + (RO)_3B$$
$$2(RO)_3B + H_3BO_3 \rightarrow (ROBO)_3 + 3ROH$$

We feel that these reactions are not significant here for the following reasons: (a) The metaboric acid (expt 1, Table II) was filtered before analysis. (b) No significant tailing of the alcohol peak was observed (which should occur if the above reactions take place on the column). (c) In the presence of boric acid, significant quantities of the olefin[13] should be observed, lowering the yield of the alcohol. Cyclopentadecene was not observed as a significant product.
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Synthesis of Authentic Tri-*O*-benzylphloroglucinol

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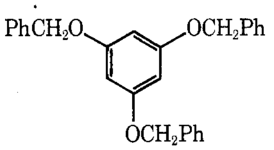
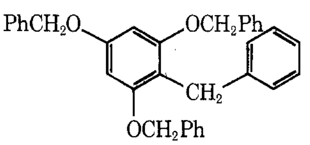
It is surprising that such a simple compound as the tri-*O*-benzyl ether of phloroglucinol, allegedly prepared first in 1900, has actually been synthesized as a pure, individual compound only in the present work.

The tribenzylphloroglucinol (mp 39–41 °C) reported by Kaufler[1] and quoted in the literature as such[2,3] is a mixture of several components as shown by repetition of the description[1] and TLC of the product.

Tri-*O*-benzylphloroglucinol (**1**), which is a promising intermediate in the synthesis of specially substituted flavonoids and *C*-methyl flavonoids, is obtainable by benzylation of phloroglucinol in the presence of sodium hydride. Separation from the by-product, *C*-benzyltri-*O*-benzylphloroglucinol (2,4,6-tribenzyloxydiphenylmethane) (**2**), has been achieved by TLC and column chromatography.



1



2

Rather simple spectra were obtained by NMR as evidence for the structures of **1** and **2**. These were verified by MS data.

Hydrogenation of the compound **1** in the presence of 10% Pd on carbon in glacial acetic acid yielded the starting material (phloroglucinol) which proved to be identical according to ir, TLC, and melting point with the authentic phloroglucinol.

Experimental Section

Benzylation of Phloroglucinol in the Presence of NaH. A 50% dispersion of sodium hydride in oil (1.44 g, 720 mg of NaH, 30 mmol) was gradually added to a stirred solution of anhydrous phloroglucinol (1.26 g, 10 mmol) in dimethyl sulfoxide (40 ml). After the evolution of hydrogen had ceased, benzyl chloride (3.6 ml, 30 mmol) was added to the reaction mixture. The temperature rose to about 50 °C. After stirring for about 40 min, the greenish suspension was then poured on ice (400 g), and allowed to stand overnight. The yellow powder (1.06 g) which precipitated was recrystallized from ethanol to give white needles (300 mg), mp 76–78 °C. This product was a mixture of two compounds (**1** and **2**) as shown by TLC in a 60:40 benzene–petroleum ether (bp 60–80 °C) mixture (R_f 0.6 and 0.7). Separation of this mixture by preparative TLC yielded pure tribenzylphloroglucinol, mp 96–97 °C (from ethanol), R_f 0.6, and *C*-benzyl-tri-*O*-benzylphloroglucinol, mp 101–103 °C (from ethanol), R_f 0.7. The two compounds were also separated on a silica gel column (0.05–0.20 mm) with the above solvent mixture.

$C_{27}H_{24}O_3$ (396) (compound **1**): *m/e* 396 (M^+), 91 (base); NMR ($CDCl_3$, Me_4Si) δ 5.13 (s, 6, OCH_2), 6.43 (s, 3, ArH), 7.57 (s, 15, ArH).

$C_{34}H_{30}O_3$ (486) (cmmpound **2**): *m/e* 486 (M^+), 91 (base); NMR ($CDCl_3$, Me_4Si) δ 4.21 (s, 2, $ArCH_2$), 5.16 (s, 2, OCH_2), 5.18 (s, 4, OCH_2), 6.49 (s, 2, ArH), 7.37–7.57 (m, 20, ArH).

Catalytic Debenzylation of Tri-*O*-benzylphloroglucinol. Pd/carbon (10%, 114 mg) in glacial acetic acid (20 ml) was prehydrogenated, then a solution of tribenzylphloroglucinol (63 mg, 0.16 mmol) in glacial acetic acid (10 ml) was added and the hydrogenation was continued at room temperature; 11 ml of hydrogen was absorbed (theoretical 11.5 ml). The catalyst was removed and the solution evaporated to dryness to obtain a product (18 mg), mp (after drying at 110 °C) 211–216 °C (lit. 219 °C) (anhydrous phloroglucinol), which proved to be identical with authentic phloroglucinol (TLC, ir).

Registry No.—**1**, 59434-20-7; **2**, 59434-21-8; phloroglucinol, 2041-15-8.

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A Simple Method for Converting Nitriles to Amides. Hydrolysis with Potassium Hydroxide in *tert*-Butyl Alcohol

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Many years ago it was reported that nitriles could easily be converted into amides by heating them in weakly basic medium in the presence of hydrogen peroxide.[1–3] Treatment of a nitrile with sodium hydroxide and hydrogen peroxide in aqueous ethanol has become a standard synthetic[4] and qualitative analytical procedure.[5]

Table I. Conversion of Nitriles to Amides

Nitrile	g	Registry no.	Base	g	Solvent	ml	Reaction time, min	Yield of amide, %		Registry no.
								Crude	Pure	
Phenylacetonitrile	5	140-29-4	KOH	10	*tert*-Butyl alcohol	50	30	93.6	90.1[a]	103-81-1
Butyronitrile	5	109-74-0	KOH	10	*tert*-Butyl alcohol	50	30		53.9	541-35-5
Capronitrile	5	628-73-9	KOH	10	*tert*-Butyl alcohol	50	60	89.5	84.4[a]	628-02-4
Benzonitrile	5	100-47-0	KOH	10	*tert*-Butyl alcohol	50	20		90.3	55-21-0
3-Nicotinonitrile	5	100-54-9	KOH	10	*tert*-Butyl alcohol	50	40		51.1	98-92-0
Butyronitrile	5		KOH	10	Butyronitrile	18.5	30	42.8	25.3[b]	
Benzonitrile	5		KOH	10	Benzene	50	30		3.4	
Benzonitrile	10		KOH	10	Methyl alcohol	50	60	78.3	51.1[a]	
Benzonitrile	10		NaOH	6	Methyl alcohol	50	120	71.6	55.4[a]	
Benzonitrile	10		NaOH	12	Methyl alcohol	50	15		77.5	
Benzonitrile	5		NaOH	8	*tert*-Butyl alcohol	50	60	95.4	90.2[a]	

[a] The crude amide was washed with a few milliliters of cold petroleum ether. [b] Recrystallized from benzene.

Our interest in this reaction was stimulated when we observed that benzamide was not hydrolyzed when refluxed in *tert*-butyl alcohol containing powdered solid potassium hydroxide. Subsequently, we found that benzonitrile, when refluxed for 20 min in *tert*-butyl alcohol containing powdered potassium hydroxide, gave a 94% yield of benzamide.

Several other nitriles were also converted into amides. The data are given in Table I. In those cases where the amide was relatively water insoluble (workup was in aqueous media) yields of 85–95% were realized.

Since the potassium hydroxide is insoluble in *tert*-butyl alcohol we also tried potassium hydroxide in methyl alcohol. However, going to homogeneous solutions gave lower yields of amides and more hydrolysis to the carboxylic acid. Potassium hydroxide in benzene gave little amide. Sodium hydroxide in methanol gave moderate yields, but sodium hydroxide in *tert*-butyl alcohol proved as effective as potassium hydroxide in *tert*-butyl alcohol, giving a 95% yield of benzamide.

It is clear from this work that the addition of hydrogen peroxide to the reaction is not necessary for high yields. Although some participation of peroxide as an impurity in our potassium or sodium hydroxide cannot be excluded, the stoichiometry of the reaction precludes this being a major pathway.

Roberts and Whitney, who did a brief kinetic study on the basic hydrolysis of benzonitrile in dimethyl sulfoxide, reported that benzamide was the only product. They suggested that the reaction might be made synthetic by using massive amounts of sodium or potassium hydroxide.[6] In our work, we used a four- to fivefold excess of base, in order to increase the surface area and reduce reaction time.

The most likely explanation as to why the hydrolysis stops at the amide stage in the *tert*-butyl alcohol is that the amide is tied up at the end of the reaction as the insoluble sodium or potassium salt, precluding further nucleophilic attack.

Experimental Section

General Procedure for Hydrolysis of Nitriles. To a stirred solution of 5 g (0.0485 mol) of benzonitrile in 50 ml of *tert*-butyl alcohol was added 10 g of finely powdered potassium hydroxide. The reaction mixture was refluxed for 20 min while stirring. The mixture was cooled and poured into 100 ml of an aqueous sodium chloride solution. The mixture was extracted three times with chloroform (total volume 200 ml). The chloroform solution was dried over magnesium sulfate. Removal of the solvents under vacuum gave 5.3 g (90.3%) of pure benzamide, mp 132 °C.

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