

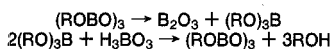
Experimental Section

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.

References and Notes

- (1) C. Walling, "Free Radicals in Solution", Wiley, New York, N.Y., 1957.
- (2) W. A. Pryor, "Free Radicals", McGraw-Hill, New York, N.Y., 1966.
- (3) G. A. Russell, *J. Chem. Educ.*, **36**, 111 (1959).
- (4) N. M. Emanuel, E. T. Denison, and Z. K. Maizus, "Liquid Phase Oxidation of Hydrocarbons", Plenum Press, New York, N.Y., 1967.
- (5) Reference 4, p 344.
- (6) Boric acid exists as metaboric acid at 140–170 °C under the conditions of most air oxidations.
- (7) A. N. Bashkurov, *Khim. Nauka Promst.*, **1**, 273 (1956).
- (8) Y. B. Cherkov, *Zh. Prikl. Khim.*, **32**, 363 (1959).
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- (10) D. Dimitrov, S. Voynova, and N. Pencev, *C. R. Acad. Bulg. Sci.*, **19**, 811 (1966).
- (11) P. Z. Bedoukian, *Am. Perfum. Cosmet.*, **80**, 23 (1965).
- (12) F. Broich and H. Grasmann, *Erdöl Kohle*, **18**, 360 (1965).
- (13) G. L. O'Conner and H. L. Nace, *J. Am. Chem. Soc.*, **77**, 1578 (1955).
- (14) A reviewer has suggested that the following reactions may occur on the VPC column:



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 olefin¹³ should be observed, lowering the yield of the alcohol. Cyclopentadecene was not observed as a significant product.

- (15) P. F. Wolf and R. K. Barnes, *J. Org. Chem.*, **34**, 3441 (1969).
- (16) N. P. Nies and G. W. Cambell in "Boron, Metallo-Boron Compounds and Boranes", R. M. Adams, Ed., Interscience, New York, N.Y., 1964.
- (17) See review for discussion of various suggested mechanisms: W. G. Woods and R. J. Brotherton, *Prog. Boron Chem.*, **3**, 1 (1970).

Synthesis of Authentic Tri-*O*-benzylphloroglucinol

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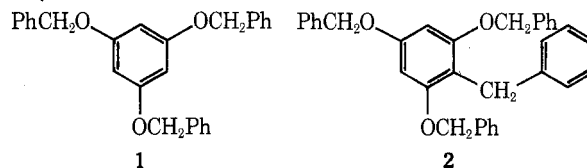
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It is surprising that such a simple compound as the tri-*O*-benzyl ether of phloroglucinol, allegedly prepared first in 1900, has actually been synthesized as a pure, individual compound only in the present work.

The tribenzylphloroglucinol (mp 39–41 °C) reported by Kaufler¹ and quoted in the literature as such^{2,3} is a mixture of several components as shown by repetition of the description¹ 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-tribenzoyldiphenylmethane) (2), has been achieved by TLC and column chromatography.

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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

Benylation 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*-benzyltri-*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.

$\text{C}_{27}\text{H}_{24}\text{O}_3$ (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).

$\text{C}_{34}\text{H}_{30}\text{O}_3$ (486) (compound 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 Debnylation 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.

References and Notes

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- (2) "Beilsteins Handbuch der Organischen Chemie", Vol. 6, 1923, p 1103.
- (3) I. Heilbron et al., Ed., "Dictionary of Organic Compounds", Vol. 5, 4th ed., Eyre and Spottiswoode, London, 1965, p 2737.

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 synthetic⁴ and qualitative analytical procedure.⁵