1,2,3,4-tetrahydrophenanthrene. After twenty-four hours of refluxing, the mixture was diluted, the organic layer separated, and the aqueous layer extracted with benzene. The residue remaining after removal of solvent from the combined extracts was distilled at 160° and 0.5 mm. The colorless distillate crystallized on cooling, weight 0.59 g. (63%); m. p. 54.5–55.5°. A sample recrystallized from alcohol gave fine, colorless prisms; m. p. 55.5–56.5°.

Anal. Calcd. for $C_{15}H_{14}$: C, 92.7; H, 7.3. Found: C, 92.5; H, 7.2.

The **picrate** crystallized from alcohol as orange-red needles; m. p. 159–160°.

Anal. Calcd. for $C_{21}H_{17}O_7N_3$: N, 9.9. Found: N, 9.8.

Summary

A method has been devised for the preparation of 4,5-methylenephenanthrene from acenaphthene.

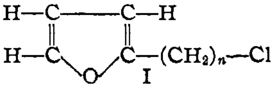
ANN ARBOR, MICHIGAN RECEIVED OCTOBER 21, 1940

[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY, LEHIGH UNIVERSITY]

2-α-Furylethanol and 2-α-Furylethyl Chloride

BY E. D. AMSTUTZ AND JULIUS PLUCKER, III

In recent years furfuryl alcohol has become one of the most readily available of furan derivatives. Its higher homolog, 3-α-furylpropanol, is also easily obtained[1] by catalytic reduction of furylacrolein. These compounds may be converted into the corresponding chlorides in satisfactory yield by the method of Kirner.[2]



I

Furfuryl chloride (I, n = 1) when treated with magnesium in ether has been reported[3] to yield, as one of the products, *sym*-difurylethane. The formation of this compound indicates rather strongly that a Grignard reagent was actually formed. Its further reaction with furfuryl chloride is understandable in view of the reactive halogen in that compound. Nevertheless, it would appear that conditions have not been found under which the Grignard reagent is of use synthetically in reactions other than the one mentioned. Unsuccessful attempts to prepare the Grignard reagent from 3-α-furylpropyl chloride (I, n = 3) also have been reported,[4] although it is probable that failure in this case was not due to great reactivity of the halogen.

It has recently been found that ethyl 2-furanacetate on reduction with sodium and alcohol gives 2-α-furylethanol.[5] This alcohol, which is produced in yields of about 32% of the theoretical, is a water-white liquid of stability comparable to that of the propanol. The synthesis of 2-α-furylethyl chloride (I, n = 2) was accomplished in the usual manner by treatment of the alcohol with thionyl chloride in the presence of ether and pyridine. Like the propyl chloride, the ethyl chloride is somewhat unstable, turning dark and depositing a black oil after standing several days at room temperature. In contrast to its adjacent compounds in the homologous series it reacts with magnesium to give a stable and usable Grignard reagent.

Experimental

2-α-Furylethanol.—A solution of 32.8 g. (0.213 mole) of ethyl 2-furanacetate in 360 cc. (7.83 moles) of absolute ethyl alcohol was dropped during the course of twenty minutes onto 31.2 g. (1.36 g. atoms) of sodium metal in a one-liter flask in an oil-bath heated to 145°. Heating was continued for twenty minutes after the addition and a further 60 cc. of absolute alcohol was added. The addition of 60 cc. of alcohol was repeated fifteen minutes later. Heating was then continued until all the sodium had dissolved. The dark red solution was cooled slightly and rapidly steam distilled until about 350 g. of distillate had been collected. The residue remaining in the flask was then saturated with salt and extracted with seven 50-cc. portions of ether. The ether extracts were combined, dried over anhydrous magnesium sulfate and distilled: 2-α-Furylethanol (7.8 g., 32% of the theoretical), b. p. 86–88° at 21 mm., 96–97° at 42 mm., n^{25}_{D} 1.4788, d^{25}_{4} 1.0705, MR_D (calcd.) 29.94, MR_D (obsd.) 29.66.

Anal. Calcd. for $C_6H_8O_2$: C, 64.23; H, 7.19. Found: C, 64.26; H, 6.92.

α-Naphthylurethan of 2-α-furylethanol, m. p. 85.2–86° (from ligroin).

Anal. Calcd. for $C_{17}H_{15}O_3N$: C, 72.57; H, 5.38. Found: C, 72.85; H, 5.72.

2-α-Furylethyl Chloride.—Into a solution of 7.8 g. (0.067 mole) of furylethanol and 6.6 g. (0.084 mole) of pyridine and 25 cc. of dry ether in a 200-cc. 3-necked flask provided with a mechanical stirrer, reflux condenser and dropping funnel was added dropwise over a period of forty-five

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(1) Bray and Adams, THIS JOURNAL, **49**, 2101 (1927).

(2) Kirner, *ibid.*, **51**, 3131 (1929).

(3) Gilman and Hewlett, *Rec. trav. chim.*, [4] **51**, 93 (1932).

(4) Ref. 3 and Hewlett, *Iowa State Col., J. Sci.*, **6**, 439 (1935).

(5) Ryan. Plucker and Amstutz, THIS JOURNAL, **62**, 2037 (1940).

minutes a solution of 9.0 g. (0.076 mole) of thionyl chloride in 25 cc. of ether. The rate of addition was such as to cause the ether to reflux. When about two-thirds of the thionyl chloride had been added considerable white precipitate had formed and a bath was placed under the flask to keep the ether refluxing. Stirring and refluxing were continued for three hours more at which time the mixture had developed a deep brown color. The dark red supernatant liquid was then poured off and the residue extracted with four 25-cc. portions of ether. The ethereal solutions were combined, washed with several 50-cc. portions of water and small quantities of a saturated sodium bicarbonate solution until free of acid. The neutral ether solution was then dried over anhydrous magnesium sulfate and distilled.[6] There was obtained 5.1 g. (60.7% of the theoretical) of 2-α-furylethyl chloride, b. p. 70–71° at 42 mm., 63° at 26 mm., n^{25}_{D} 1.4788, d^{25}_{4} 1.1229, *MR*D (calcd.) 33.28, *MR*D (obsd.) 32.95.

Anal. Calcd. for C_6H_7OCl: C, 55.16; H, 5.41. Found: C, 55.27; H, 5.91.

2-α-Furylethylmagnesium Chloride and 3-α-Furylpropionic Acid.—In a 200-cc. 3-necked flask equipped with a mercury sealed stirrer, dropping funnel and reflux condenser was placed 30 cc. of dry ether, 0.6 g. (0.025 g. atom) of magnesium and 3 g. (0.023 mole) of α-furylethyl chloride. A small crystal of iodine was added and the mixture stirred and refluxed for several hours. At the end of this time a faint turbidity was apparent but the Gilman test for a Grignard reagent[7] was negative. After about twelve hours of standing, however, much magnesium had gone into solution and the reaction was completed by refluxing and stirring for several hours more. Gilman's test was then positive. The mixture was poured onto about 100 g. of crushed dry-ice in a beaker. On working up the product in the usual way there was obtained 0.8 g. (25%) of 3-α-furylpropionic acid, which, on recrystallization from ligroin, melted at 56.6–57.6°; reported,[3] 56.5–58°.

Anal. Calcd. for $C_7H_8O_3$: C, 59.97; H, 5.75. Found: C, 59.94; H, 6.05.

Summary

1. It has been shown that ethyl-2-furanacetate may be reduced by the method of Bouveault and Blanc to 2-α-furylethanol.

2. A procedure has been developed which gives improved yields of chlorides from such alcohols as 2-α-furylethanol and 3-α-furylpropanol.

3. It has been found that 2-α-furylethyl chloride, in contrast to its adjacent compounds in the homologous series, reacts with magnesium to yield a stable and synthetically valuable Grignard reagent.

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[6] Gilman and Hewlett, ref. 3, reported a yield of 20% of 3-α-furylpropyl chloride from the alcohol. The modification of Kirner's method given here consistently yields over 40% of the same chloride.

[7] Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Unsymmetrical Organobismuth Compounds

BY HENRY GILMAN AND H. L. YABLUNKY

The only unsymmetrical organobismuth compound which has been described in any detail is diphenyl-α-naphthylbismuth, which was prepared by Challenger and co-workers,[1]

$$(C_6H_5)_2BiBr + \alpha\text{-}C_{10}H_7MgBr \longrightarrow (C_6H_5)_2BiC_{10}H_7\text{-}\alpha + MgBr_2 \quad (1)$$

Incidental to studies concerned with optically active organobismuth compounds, these authors tried unsuccessfully to prepare other unsymmetrical organobismuth compounds. More recently, Norvick[2] reported the formation of diethylamylbismuth, together with triethylbismuth and triamylbismuth, from the reaction between amylbismuth dichloride and ethylmagnesium bromide, but has not yet provided physical data on the unsymmetrical compound.

On the basis of general observations concerned with the relative reactivities of organometallic compounds,[3] it appeared quite probable that a variety of unsymmetrical compounds could be made and would be found to be reasonably stable. This has been shown to be the case. Several procedures have been used, and these are illustrated in the following reactions for the synthesis of di-*p*-tolyl-α-naphthylbismuth.

$$(p\text{-}CH_3C_6H_4)_2BiX + \alpha\text{-}C_{10}H_7MgBr \longrightarrow (p\text{-}CH_3C_6H_4)_2BiC_{10}H_7\text{-}\alpha + MgXBr \quad (2)$$

$$2p\text{-}CH_3C_6H_4MgBr + \alpha\text{-}C_{10}H_7BiBr_2 \longrightarrow (p\text{-}CH_3C_6H_4)_2BiC_{10}H_7\text{-}\alpha + 2MgBr_2 \quad (3)$$

$$(p\text{-}CH_3C_6H_4)_2BiNa + \alpha\text{-}C_{10}H_7I \longrightarrow (p\text{-}CH_3C_6H_4)_2BiC_{10}H_7\text{-}\alpha + NaI \quad (4)$$

Acting on the observation of Challenger and

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[1] (a) Challenger, *Proc. Chem. Soc.*, **29**, 76 (1913); *J. Chem. Soc.*, **105**, 2210 (1914). (b) Challenger and Allpress, *Proc. Chem. Soc.*, **30**, 293 (1914); *J. Chem. Soc.*, **107**, 16 (1915). (c) Challenger, *ibid.*, **109**, 250 (1916). (d) Challenger and Goddard, *ibid.*, **117**, 762 (1920). (e) Challenger and Allpress, *ibid.*, **119**, 913 (1921). (f) Challenger and Ridgway, *ibid.*, **121**, 104 (1922).

[2] Norvick, *Nature*, **135**, 1038 (1935).

[3] Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, p. 482.