this synthesis gave a product, m.p. 68.5–70° (reported m.p. 67°), which when mixed with I showed no depression of melting point. The infrared spectrum of the substance was identical with that of I.

I is therefore properly formulated as 4-pentyl-1,3-cyclohexanedione.

EXPERIMENTAL

Ethyl acrylate was commercial grade used without purification. Methyl *n*-hexyl ketone was freed of capryl alcohol by refluxing for 28 hr. with 1.5% of its weight of boric acid and removing the water produced. It was then carefully distilled, b.p. 83° at 30 mm.

Product I from ethyl acrylate and methyl hexyl ketone. To a suspension of sodium ethoxide in xylene, prepared by addition of absolute ethanol (17.4 g.) to a suspension of sodium (6.90 g., 0.3 g. atom) in xylene (200 cc.) was added ethyl acrylate (40 g., 0.4 mole). The mixture was cooled in an ice bath and methyl *n*-hexyl ketone (20 g., 0.15 mole) was added dropwise. Heat was evolved and the mixture became viscous. As the mixture was stirred at 0° for 0.5 hr., the solution became less viscous. Stirring was continued overnight (17 hr.) at room temperature and 100 cc. of water was introduced. After the mixture had been stirred for another hour, the aqueous and xylene layers were separated and the aqueous layer was acidified with glacial acetic acid. The oil which separated on acidification crystallized while standing in the refrigerator. Recrystallization of the gummy yellow solid from ethyl acetate gave 8 g. (27%) I, colorless crystals, m.p. 69–70°.

Anal., Calcd. for $C_{11}H_{18}O_2$: C, 72.5; H, 10.0. Found: C, 72.6; H, 10.1.

Hydrolysis of I. A suspension of $Ba(OH)_2 \cdot 8H_2O$ (34.7 g., 0.11 mole) and I, (4 g., 0.022 mole) in 100 ml. of water was heated at reflux for 28 hr. Solid carbon dioxide was introduced until the mixture was neutral to *p*H paper. The precipitated barium carbonate was removed by filtration. The mixture was heated to reflux again and the hot solution was filtered. When the filtrate was treated with 20 ml. of 2*N* hydrochloric acid, a clear oil separated. The oil was extracted with ether and the ethereal solution was dried over magnesium sulfate. Evaporation of the ether left an oil which resisted attempts at crystallization. Some iodoform was obtained in the iodoform test on this oil. Treatment of it with 2,4-dinitrophenylhydrazine gave an oil which could not be crystallized.

4-n-amyl-1,3-cyclohexanedione (III). 4-Pentylresorcinol was prepared by the method of Dohme, Cox, and Miller.[6] The procedure of Adams and Baker[5] was followed in the reduction to III. The product was obtained in 88% yield, m.p. after recrystallization from pentane, 68.5–70°, mixture m.p. with I, 68.5–70°.

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Formylation of Furans

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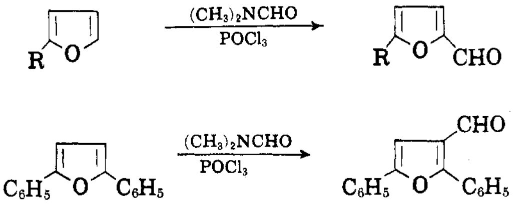
In recent years the use of dimethylformamide and phosphorus oxychloride as a formylating agent has found many applications in the heterocyclic series. The systems studied contained sulfur[1] and nitrogen[2] heteroatoms. In this report the authors wish to extend the scope of this reaction to the oxygen systems, namely furan and its derivatives.



R = H, CH_3, C_2H_5

The formylation of furan, 2-methylfuran, and 2-ethylfuran proceeded under mild conditions and gave furfural (64%), 5-methyl-2-furaldehyde (76%) and 5-ethyl-2-furaldehyde (80%), respectively. These aldehydes were identified by physical constants, solid derivatives, and, in the case of furfural, by comparison of the infrared spectrum with that of an authentic sample (experimental section).

Conversion of the above furans to the corresponding aldehydes by the Gatterman reaction has been reported by Reichstein;[3] however, the dimethylformamide-phosphorus oxychloride method gives better yields by 15 to 30%. In view of the commercial availability of 2-methylfuran, this reaction presents an excellent procedure for the preparation of 5-methyl-2-furaldehyde.

When two substituents are introduced into the α positions of the furan nucleus, the formylation with dimethylformamide and phosphorus oxychloride becomes more difficult. In the case of 2,5-dimethylfuran resinification took place; however, 2,5-diphenylfuran gave 2,5-diphenyl-3-furaldehyde (40%) m.p. 89–90°, oxime, m.p. 170–171° (reported[4] m.p. of aldehyde 90–92°, m.p. of oxime 171–173°) and starting material (39%). This reaction presents an example of direct formylation in the β-position of the furan ring. Generally these aldehydes are prepared by conversion of some functional group in the β-position to an aldehyde.

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EXPERIMENTAL

2-Ethylfuran. 2-Acetylfuran, b.p. 70° (14 mm.), prepared in 65% yield using the procedure of Hartough and Kosak,[5] was converted to 2-ethylfuran, b.p. 90–91°, n_D^{20} 1.4400, in 17% yield by a Wolf-Kishner reduction according to the directions of Reichstein.[3]

2,5-Diphenylfuran. The procedure of Lutz and Rowlett[6] was used to prepare 2,5-diphenylfuran, m.p. 88–89°, in 84% yield from dibenzoylethylene.

Furfural. Phosphorus oxychloride (115 g., 0.75 mole) was added with constant stirring to dimethylformamide (54.8 g., 0.75 mole) in a flask fitted with a thermometer, dropping funnel, condenser, and stirrer. The addition, carried out at ice bath temperatures, required 30 min. and the reaction mixture was then kept at 0–5° for 40 min. Freshly distilled furan, b.p. 31–32°, n_D^{20} 1.4211 (45 g., 0.66 mole) was added with stirring over a period of 15 min. The ice bath was removed and the mixture heated. At 30° an exothermic reaction commenced with the evolution of hydrogen chloride. The ice bath was returned and after the reaction subsided, the mixture was heated at approximately 100° for 0.5 hr., cooled, and poured into ice water. A solution of potassium carbonate (132 g., 0.80 mole) in 200 ml. of water was added slowly and the mixture was steam distilled. The distillate was saturated with potassium carbonate and extracted with ether. After the extract was dried over sodium sulfate and ether was removed and the residue was distilled. The yield of pure furfural, b.p. 62–63° (19 mm.), n_D^{20} 1.5252 (lit.,[7] b.p. 63° (19 mm.), n_D^{20} 1.52608), was 40.3 g. (64%). The infrared spectra of the above and an authentic sample were identical.

The *oxime* was prepared in the usual way and after recrystallization from water melted at 89–90° (lit.,[8] m.p. 91–92°).

The *semicarbazone* was prepared and after recrystallization from 50% aqueous ethanol melted at 201–202° (lit.,[9] m.p. 202–203°).

5-Methyl-2-furaldehyde.[10] The above procedure was followed with some minor modifications. To a mixture of dimethylformamide (51 g., 0.70 mole) and phosphorus oxychloride (107 g., 0.70 mole) which was kept at 0.5° for 20 min. was added freshly distilled 2-methylfuran, b.p. 64°, n_D^{20} 1.4338 (50.5 g., 0.70 mole) at a rate such that the temperature of the reaction mixture did not rise above 20°. After the addition was completed, the mixture was kept at 0.5° for 1 hr. and then at room temperature for 1 hr. The mixture was poured into 600 ml. of cracked ice and water, neutralized with sodium carbonate (185 g., 1.75 mole) and allowed to stand overnight. The organic layer was separated and the aqueous phase extracted 3 times with 200-ml. portions of ether. The extracts and organic liquid were combined and dried over sodium sulfate, and the ether was removed. Distillation gave 41.7 g. (76%) of 5-methyl-2-furaldehyde, b.p. 72–73° (11 mm.), n_D^{20} 1.5283 [lit.,[11] b.p. 75–76° (13 mm.), n_D^{20} 1.53049].

The product was fractionated through 0.8 × 25 cm. electrically heated column packed with 1/16-in. glass helices and equipped with a variable take-off head. Five center-cut fractions were collected, combined weight 34.6 g. (63%), b.p. 79° (15 mm.), which had a constant refractive index n_D^{20} 1.5310–1.5312.

The *oxime* was prepared and after recrystallization from water melted at 112–113° (lit.,[12] m.p. 110–112°).

The *semicarbazone* was prepared and after recrystallization from 50% ethanol melted at 197° (lit.,[3] m.p. 197°).

In another experiment the mixture of phosphorus oxychloride (123 g., 0.80 mole), dimethylformamide (58.5 g., 0.80 mole), and methylfuran (50.5 g., 0.70 mole) as prepared above was heated to 130° over a 2-hr. period. Evolution of hydrogen chloride was observed. The product was isolated by steam distillation and after distillation gave 51.8 g. (67%) of pure 5-methyl-2-furaldehyde, b.p. 82–84° (17 mm.), n_D^{20} 1.5312.

5-Ethyl-2-furaldehyde. The procedure described for 5-methyl-2-furaldehyde was employed to convert 2-ethylfuran (6.2 g., 0.065 mole) to 6.4 g. (80%) 5-ethyl-2-furaldehyde, b.p. 99° (24 mm.), n_D^{20} 1.5201 [lit.,[3] b.p. 79–81° (12 mm.)]. Fractionation through a Vigreux column gave the following constants, b.p. 82–83° (11 mm.), n_D^{20} 1.5220.

A *semicarbazone* was prepared and after recrystallization from 50% aqueous ethanol melted at 167–168° (lit.,[3] 176–177°).

5-Ethyl-2-furoic acid[13] was prepared by oxidation with silver oxide. Recrystallization from benzene gave the pure acid m.p. 93.5–94.5° (lit.,[13] 93–94°).

2,5-Diphenyl-3-furaldehyde. A mixture of 2,5-diphenylfuran (2.2 g., 0.010 mole), dimethylformamide (1.1 g., 0.015 mole), and phosphorus oxychloride (2.3 g., 0.015 mole) was heated on a steam bath for 3 hr. The reaction mixture was dissolved in 25 ml. of dimethylformamide and poured into 100 ml. of water. An oil separated, which solidified and gave 2.36 g. of a tan solid m.p. 54–64°.

This substance was heated on a steam bath with 100 ml. of 40% sodium bisulfite solution for 1 hr., cooled, filtered, and dried. The resulting solid was triturated with ether and filtered. Evaporation of the ether gave 1.08 g. of a pale yellow solid, m.p. 77–85°. This crude material was purified by chromatography on 75 g. of Merck acid-washed alumina. The fraction eluted with 20% benzene in pentane was 0.86 g. (39%) of 2,5-diphenylfuran m.p. 88–89°. It gave no depression in melting point when mixed with starting material.

The bisulfite addition product was decomposed with hydrochloric acid to give 1.20 g. of a brown solid, m.p. 85–87°. Recrystallization from ethanol after a charcoal treatment gave 1.0 g. (40%) of 2,5-diphenyl-3-furaldehyde m.p. 89–90° (lit.,[4] m.p. 90–92°).

The *oxime* was prepared and after recrystallization from ethanol melted at 170–171° (lit.,[4] 171–173°).

Attempts to formylate 2,5-dimethylfuran by the above procedures lead to resinification.

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