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Author(s): Edward J. Horning and Kenneth L. Marsi
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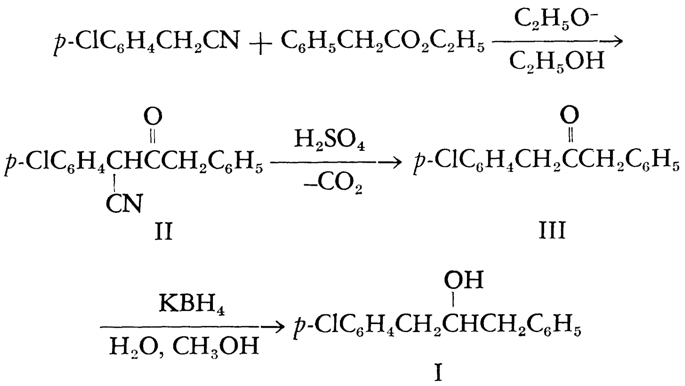
1-Phenyl-3-(p-chlorophenyl)-2-propanol and Derivatives

EDWARD J. HORNING and KENNETH L. MARSI[1]

A literature search for a synthetic route to mono *para*-substituted dibenzylcarbinols revealed that only one such compound, the methoxy derivative, has been prepared, and that by a rather difficult five-step synthesis (1). In the present study two attempts at better routes to compounds of this type have been made: (*a*) by a reaction between *p*-substituted benzylmagnesium halides and phenylacetaldehyde, and (*b*) by a Claisen condensation between *p*-substituted phenylacetonitrile and ethyl phenylacetate, followed by hydrolysis, decarboxylation, and reduction of the resulting ketone. The benzyl Grignard reagents reacted in an anomalous manner with phenylacetaldehyde, and no desired carbinol could be isolated. This reaction has received attention elsewhere (2). In a trial synthesis by route (*b*) we were able to prepare 1-phenyl-3-(*p*-chlorophenyl)-2-propanol (I) in moderate yields and without complication. The preparation of two derivatives of I is also described.



$$p\text{-}ClC_6H_4CH_2CN + C_6H_5CH_2CO_2C_2H_5 \xrightarrow[C_2H_5OH]{C_2H_5O^-}$$

$$p\text{-}ClC_6H_4\underset{\substack{|\\ CN}}{CH}\overset{\substack{O\\ \|}}{C}CH_2C_6H_5 \xrightarrow[-CO_2]{H_2SO_4} p\text{-}ClC_6H_4CH_2\overset{\substack{O\\ \|}}{C}CH_2C_6H_5$$

II III

$$\xrightarrow[H_2O,\ CH_3OH]{KBH_4} p\text{-}ClC_6H_4CH_2\overset{\substack{OH\\ |}}{C}HCH_2C_6H_5$$

I

Experimental[2]

α-(4-chlorophenyl)-γ-phenylacetoacetonitrile (II).—The synthesis of this compound was adapted from the procedure of Coan and Becker (3) and involved a sodium ethoxide catalyzed condensation of *p*-chlorophenylacetonitrile and ethyl phenylacetate to give a 58% yield of II, m.p. 128.5–129.5° (reported 131.0–131.2° (3)).

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[1] Present addresses, respectively: Phillips Petroleum Company, Phillips, Texas, and Department of Chemistry, Long Beach State College, Long Beach 4, California.

[2] Melting points are uncorrected. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside 77, N.Y.

1-Phenyl-3-(p-chlorophenyl)-2-propanone (III).—α-(4-chlorophenyl)-γ-phenylacetonitrile (II), 21.6 g. (0.08 mole), and 65 ml. of 60% sulfuric acid were stirred together at reflux until the evolution of carbon dioxide ceased (27 hrs.). The mixture was diluted with 200 ml. of ice water and extracted three times with 150 ml. portions of ether, and the ether layer washed successively with 100 ml. 10% sodium hydroxide and 100 ml. water. After drying over anhydrous sodium sulfate, filtering and distilling the ether, a dark oil remained, m.p. 25.5–38.5°. Recrystallization from petroleum ether yielded 15.9 g. of a white solid (81.2%) m.p. 40–42° (reported for 1-phenyl-3-(*p*-chlorophenyl)-2-propanone, 35.9–36.5° (3)); 2,4-dinitrophenylhydrazone, m.p. 118.5–120.5° (reported 124.5–125.0° (3)).

1-Phenyl-3-(p-chlorophenyl)-2-propanol (I).—A slurry of 2.29 g. (0.043 mole) of potassium borohydride, 10 ml. of water, and 25 ml. of methanol was prepared in a 300 ml. round bottom flask equipped with a magnetic stirrer and a reflux condenser. The 10.4 g. (0.043 mole) of 1-phenyl-3-(*p*-chlorophenyl)-2-propanone, m.p. 40–42°, dissolved in 30 ml. of methyl alcohol, was added through a dropping funnel over a period of 10 minutes at such a rate that a moderate reflux was maintained. The mixture was then allowed to reflux for 4 hours longer. Thirty-six ml. of 2 N sodium hydroxide solution was slowly added through the dropping funnel and the mixture refluxed for an additional 2 hours. Upon cooling, a yellow oil separated. The alkaline mixture was then extracted continuously with ether for 19 hours. After drying the ether layer over anhydrous sodium sulfate and distilling the solvent, 14.1 g. of yellow oil remained. Vacuum distillation through a Todd column yielded 6.5 g. (62%) of a colorless oil, b.p. 178–181°/1.5 mm., n_D^{21} 1.5785.

Anal. Calcd. for $C_{15}H_{15}ClO$: C, 73.01; H, 6.13; Cl, 14.37. Found: C, 73.26; H, 5.99; Cl, 14.01.

The 3,5-dinitrobenzoate of 1-phenyl-3-(p-chlorophenyl)-2-propanol (I) was prepared according to the general procedure given by Shriner, Fuson, and Curtin (4). The crude ester was recrystallized several times from ethyl acetate; m.p. 165.5–166.5°.

Anal. Calcd. for $C_{22}H_{17}ClN_2O_6$: C, 59.94; H, 3.89; Cl, 8.04; N, 6.35. Found: C, 60.05; H, 3.73; Cl, 7.97; N, 6.39.

The phenylurethan derivative of 1-phenyl-3-(p-chlorophenyl)-2-propanol (I) was prepared by adding 0.24 g. of phenylisocyanate to 0.5 g. of the carbinol, and heating the mixture on the water bath for five minutes. The syrupy material crystallized upon standing overnight in the cold. Several recrystallizations from petroleum ether gave 0.3 g. of white crystals, m.p. 69–70.5°.

Anal. Calcd. for $C_{22}H_{20}ClNO_2$: C, 72.22; H, 5.51; Cl, 9.69; N, 3.83. Found: C, 72.35; H, 5.59; Cl, 9.56; N, 4.06.

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—Department of Chemistry, Fort Hays Kansas State College, Hays