249. *The Preparation of Unsymmetrical Diphenyl Derivatives.*

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The symmetrical derivatives of diphenyl are readily obtainable by Ullmann's copper-powder method (*Annalen*, 1904, **332**, 38). The processes yielding unsymmetrical derivatives (Mayer and Freitag, *Ber.*, 1921, **54**, 347; Gull and Turner, J., 1929, 491; Lesslie and Turner, J., 1930, 1758; Späth and Gibian, *Monatsh.*, 1930, **55**, 342; Bamberger, *Ber.*, 1896, **29**, 446; Gomberg and Pernert, *J. Amer. Chem. Soc.*, 1926, **48**, 1373; Kenner and Shaw, J., 1931, 769; Hinkel and Hey, J., 1928, 1200) are often unsatisfactory.

The method now to be described is an extension of a recent synthesis of diphenyl (this vol., p. 1641) and is carried out in the following stages: (1) preparation of a tertiary alcohol (yield, 40—70%) from an arylmagnesium halide and a *cyclo*hexanone or *cyclo*hexenone; (2) dehydrogenation of the alcohol with sulphur, either directly or after dehydration (yield, at least 70%). The method is limited to the preparation of diphenyl derivatives which do not react with sulphur, and the presence of a methoxyl group introduces no complications. If, however, a hydroxyphenyl*cyclo*hexene is dehydrogenated with selenium, the product is usually a mixture of a hydroxydiphenyl with the corresponding hydrocarbon and as much as 30% of the phenol is sometimes dehydroxylated in this way. The behaviour of other substituents is under investigation.

The method is especially suitable for the preparation of alkyldiphenyls, since *cyclo*hexanone, the methyl*cyclo*hexanones, piperitone, and menthone are available commercially and other alkyl*cyclo*hexanones may be readily obtained by the Haller–Cornubert method of alkylation. The scope of the method may be extended by preparing an aryl*cyclo*hexane, either by the Friedel–Crafts synthesis or by the method of Meyer and Bernhauer (*Monatsh.*, 1929, **53** and **54**, 721), and submitting it to sulphur dehydrogenation.

The usual procedure for the preparation of the Grignard reagents was adopted: in difficult cases reaction was initiated by the addition of 0·1 mol. of ethyl bromide or methyl iodide, and an equivalent excess of the ketone was used in the subsequent stage. The tertiary alcohols were occasionally accompanied by the corresponding hydrocarbon, owing to partial dehydration during distillation. Slightly higher yields of diphenyl derivatives were obtained when the tertiary alcohols were dehydrated before dehydrogenation. Dehydration was best effected by concentrated formic acid; the solution of the alcohol in this acid became turbid in a few minutes, and the hydrocarbon separated in quantitative yield. Dehydrogenation was effected with the theoretical quantity of sulphur (1 to 3 atoms according to the number of hydrogen atoms to be removed) and was complete in 3·5—5 hours at 180—250°. In several instances the sulphur behaved as a dehydration catalyst, water being evolved during the dehydrogenation at a temperature far below that at which the tertiary alcohol undergoes thermal decomposition. The alkyldiphenyls were all purified by distillation from sodium.

o-Tolylmagnesium bromide and *cyclo*hexanone afforded 1-*o*-

tolyl*cyclo*hexanol (b. p. 149—151°/14 mm.; 50% yield), which was dehydrogenated to 2-methyldiphenyl (b. p. 130—136°/27 mm.). Oxidation with potassium permanganate (Jacobson, *Ber.*, 1895, **28**, 2547) yielded 2-phenylbenzoic acid, m. p. 113°.

1-*m*-Tolyl*cyclo*hexanol, b. p. 162°/19 mm., obtained in 45% yield from *m*-tolylmagnesium bromide and *cyclo*hexanone, furnished 3-methyldiphenyl in 70% yield on dehydrogenation; b. p. 148—150°/20 mm., $d_{4°}^{22°}$ 1·010, $n_{D}^{22°}$ 1·5916, $[R_L]_D$ 56·31 (calc., 55·03). Oxidation with 2% potassium permanganate gave 3-phenylbenzoic acid, m. p. 162°.

Dehydrogenation of 1-*p*-tolyl*cyclo*hexanol (Sabatier and Mailhe, *Compt. rend.*, 1904, **138**, 1321) similarly afforded 4-methyldiphenyl (b. p. 134—136°/15 mm., m. p. 47·5°), which was oxidised to 4-phenylbenzoic acid, m. p. 219—220° (methyl ester, m. p. 115°).

3-Phenyl-$\Delta^{1:3}$-menthadiene, b. p. 153°/18 mm., obtained in 70% yield by the method of Read and Watters (J., 1929, 2170), afforded 5-methyl-2-*iso*propyldiphenyl (80% yield) on dehydrogenation; b. p. 158°/19·5 mm., $[R_L]_D$ 70·25. The molecular exaltation (1·36 units) is therefore of the same order as that of the isomeric 2-methyl-5-*iso*propyldiphenyl (Rupe and Tomi, *Ber.*, 1914, **47**, 3070).

1-*p*-Anisyl*cyclo*hexanol, obtained (44% yield) from *p*-anisylmagnesium bromide and *cyclo*hexanone, had b. p. 167°/20 mm. and, after recrystallisation from alcohol, m. p. 38°. Dehydrogenation furnished 4-methoxydiphenyl (b. p. 174°/18 mm., m. p. 189°; 90% yield), which was identified by conversion into 3 : 4′-dinitro-4-methoxydiphenyl, m. p. 170° (Bell and Kenyon, J., 1926, 3048).

2-*Methoxy*-5-*methyldiphenyl.*—To the well-cooled Grignard reagent prepared from 3-bromo-*p*-tolyl methyl ether (Zincke and Wiederhold, *Annalen*, 1902, **320**, 202) (32 g.), magnesium (3·6 g.), and ether (150 c.c.), was added gradually *cyclo*hexanone (16 g.) diluted with an equal volume of ether. The mixture was finally boiled for ½ hour and worked up in the usual way. The 1-(4′-*methoxy*-m-*tolyl*)cyclo*hexanol* had b. p. 182/19 mm. (16 g.; 36%) and, after recrystallisation from alcohol, m. p. 77° (Found: C, 76·8; H, 9·0. $C_{14}H_{20}O_2$ requires C, 76·4; H, 9·1%). Dehydrogenation furnished 2-*methoxy*-5-*methyldiphenyl* as a pale yellow oil, b. p. 170—175°/20 mm. The ether (2·8 g.) was demethylated by heating at 150° for 8 hours with hydriodic acid (*d* 1·7; 15 g.) and red phosphorus (0·5 g.), and the resulting 2-*hydroxy*-5-*methyldiphenyl*, m. p. 68°, recrystallised from light petroleum (b. p. 40—50°) (Found: C, 84·6; H, 6·6. $C_{13}H_{12}O$ requires C, 84·8; H, 6·5%).

1-*Phenylnaphthalene.*—α-Naphthylmagnesium bromide and *cyclo*hexanone furnished a mixture (*ca.* 50% yield) of 1-α-naphthyl*cyclo*hexanol with the corresponding hydrocarbon, which on dehydrogenation afforded 1-phenylnaphthalene, b. p. 190°/12 mm., in 70% yield. Oxidation with potassium permanganate yielded 2-benzoylbenzoic acid, m. p. 92°, or 124° after dehydration (Mohlau and Berger, *Ber.*, 1893, **26**, 1199).

Diphenyl.—Crude *cyclo*hexylbenzene, prepared from *cyclo*hexanol and benzene (Meyer and Bernhauer, *Monatsh.*, 1929, **53** and **54**, 721), gave a lower yield of diphenyl (m. p. and mixed m. p. 70°) than is obtained by the dehydrogenation of 1-phenyl-Δ^1-*cyclo*hexene (this vol., p. 1641).

One of us (I. R. S.) gratefully acknowledges the award of a National Research Scholarship by the New Zealand Department of Scientific and Industrial Research.

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[*Received, May 9th,* 1932.]