A Synthesis of *m*-Terphenyls

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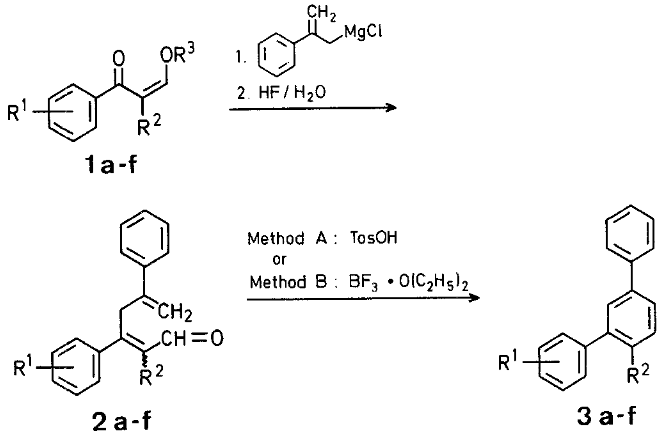
In earlier work, we have disclosed methods for cationic cyclizations to form unsymmetrical biphenyls[1] and aromatic rings[2]. We now describe a simple method for the preparation of *m*-terphenyls.

Most syntheses of terphenyls rely upon multistep procedures in which a dehydrogenation[3] or a radical coupling step is utilized[4]. The advantage of our method lies in the ease with which the aromatic system is assembled from readily available starting materials. Our starting material in each case was the hydroxymethylene derivative of a phenone **1** ($R^3 = H$)[5]. Addition of 2-phenallylmagnesium chloride to the *O*-trimethylsilyl derivative **1** [$R^3 = (CH_3)_3Si$] in ether at 0 °C, followed by immediate hydrolysis with aqueous hydrofluoric acid produced unsaturated aldehydes **2** as mixtures of (*E*)- and (*Z*)-isomers. In the absence of fluoride ion, a slower reaction takes place and some isomerization to an $\alpha,\beta,\gamma,\delta$-unsaturated aldehyde is observed. The products were stable to purification by flash chromatography[6] on silica gel. Alternatively, the crude products could be cyclized to the terphenyls **3** directly by treatment with *p*-toluenesulphonic acid in refluxing benzene (Method A) or by treatment at 23 °C in benzene with boron trifluoride etherate (Method B). Pure products were obtained by flash chromatography on silica gel. Analytically pure products were obtained by recrystallization from pentane or hexane.



Subsequent to the completion of our work, a preparation of 2-phenallylmagnesium chloride has been described in which an active form of magnesium was generated by condensation of the metal vapor into cold tetrahydrofuran[7]. Although we can attest to the propensity for allylic coupling during the preparation of this Grignard reagent, we feel that the alternative method using ultrasonic irradiation[8] is more convenient. A 240 W/40 kHz ultrasonic laboratory cleaner allowed us to prepare the Grignard reagent contaminated by a small amount (<5%) of the coupling product.

Our results are summarized in the Table. Compounds **3c**, **3d**, and **3f** appear to be new. Quaterphenyl **3e** has been prepared by an alkylation-dehydrogenation sequence[9]. Methylterphenyl **3b** was formed as a minor byproduct during the photolysis of *endo*-2-methylene-4,6-diphenylbicyclo[2.1.0]hex-3-ene[10]. The simplicity of our method and the ease with which it can be applied to the preparation of unsymmetrically substituted terphenyls suggests that it will be the method of choice for preparing such compounds.

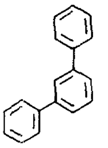
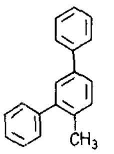
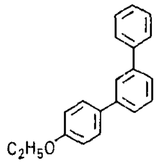
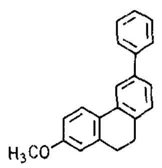
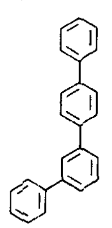
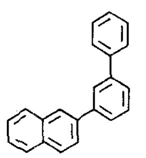
2-Phenallylmagnesium Chloride:

Several drops of dibromoethane were added to dry magnesium turnings (2.4 g, 0.1 mol) in anhydrous ether (15 ml). The mixture is stirred for 5 min at room temperature. The reaction flask is submerged in a sonicating bath (240 W/40 kHz) for an additional 5 min. A solution of 2-phenallyl chloride[12] (0.3 g, 2 mmol) in ether (5 ml) is added to the reaction flask during 20 min via cannula. Formation of the Grignard reagent is completed by sonicating for an additional 40 min.

3,5-Diphenyl-2-methylhexa-2,5-dienal (2b); Typical Procedure:

A solution of 3-hydroxy-2-methyl-1-oxo-1-phenylprop-2-ene (**1b**; $R^1 = R^3 = H$, $R^2 = CH_3$; 81 mg, 0.5 mmol) in anhydrous ether (15 ml) is treated at room temperature with a mixture (0.14 ml, 0.5 mmol) of

Table. *m*-Terphenyls **3a-f** prepared

Product		Yield [%]^a (Method)	m.p. [°C]^b (Lit. m.p.)	^{1}H-N.M.R. ($CDCl_3$)^c δ [ppm]	M.S.^{d} m/e
3a		41 (B)	see experimental		
3b		58 (A)	see experimental		
3c		90 (A)	131–132$^{\circ e}$	1.44 (t, 3 H, J=7 Hz); 4.08 (q, 2 H, J=7 Hz); 6.9–7.8 (m, 13 H)	274 (M^+), 246, 217, 202, 189; calc. for $C_{20}H_{18}O$: 274.1359; observed: 274.1345
3d		93 (A)	87–88$^{\circ f}$	2.88 (s, 3 H); 3.83 (br. s, 4 H); 6.8–7.8 (m, 11 H)	286 (M^+), 270, 250, 194; calc. for $C_{21}H_{18}O$: 286.1357; observed: 286.1339
3e		55 (B)	162–163° (156–166°)[9]	7.3–7.8 (m)	306 (M^+), 218, 202, 175; calc. for $C_{24}H_{18}$: 306.1408; observed: 306.1407
3f		45 (A)	67$^{\circ g}$	7.1–8.0 (m)	280 (M^+), 255, 220; calc. for $C_{22}H_{16}$: 280.1252; observed: 280.1249

[a] Yield of pure, isolated product based on **1** (R^3=H).

[b] Not corrected.

[c] Varian XL-100 spectrometer.

[d] Varian MAT-311 mass spectrometer.

[e] $C_{20}H_{18}O$ (274.3) calc. C 87.56 H 6.61; found 87.43 6.40

[f] $C_{21}H_{18}O$ (286.4) calc. C 88.08 H 6.34; found 88.26 6.63

[g] Not analysed.

equal volumes of triethylamine and chlorotrimethylsilane. A thick white precipitate appears. The heterogeneous mixture is stirred for 15 min at room temperature, then cooled to 0 °C. The solution of 2-phenallylmagnesium chloride in ether (~2 mmol) is transferred to the reaction mixture at 0 °C. Stirring is continued for an additional 30 min at 0 °C. The reaction is quenched by pouring the mixture into 1 normal hydrochloric acid (50 ml) containing sodium fluoride (0.42 g, 10 mmol). The two phase mixture is stirred for 1 h and is partitioned between ether (50 ml) and water (50 ml). The organic layer is washed with water (50 ml), then brine (50 ml), and dried with magnesium sulphate. Evaporation of the solvent provides the crude product which is purified on a small column of silica gel. Elution with hexane removes the styrene and a trace of the dimer; elution with 15% ethylacetate in hexane produces the desired aldehyde **2b** as a mixture of (*E*)- and (*Z*)-isomers (1.5 : 1); yield: 119 mg (90%).

(*E*)-isomer:
^{1}H-N.M.R. ($CDCl_3$): δ=1.94 (s, 3 H); 3.78 (s, 2 H); 4.98 (d, 1 H, J=1 Hz); 5.32 (d, 1 H, J=1 Hz); 7.22 (m, 10 H); 9.49 ppm (s, 1 H).

(*Z*)-isomer:
^{1}H-N.M.R. ($CDCl_3$): δ=1.65 (s, 3 H); 3.90 (s, 2 H); 5.02 (d, 1 H, J=1 Hz); 5.40 (d, 1 H, J=1 Hz); 7.22 (m, 10 H); 10.2 ppm (s, 1 H).

4'-Methyl-1,1':3',1''-terphenyl (3b); Typical Procedure for Method A:
A solution of the isomeric mixture of aldehyde **2b** (119 mg, 0.45 mmol) in benzene (0.5 ml) is transferred to a refluxing solution of *p*-toluenesulphonic acid (26 mg, 0.14 mmol) in benzene (4 ml). After 10 min, the heating bath is removed and the reaction mixture is treated with saturated aqueous sodium hydrogen carbonate solution (10 ml). Evaporation of the benzene is followed by extraction with dichloromethane (3 × 20 ml). The organic layer is washed with water (1 × 50 ml), brine (1 × 50 ml), and dried with magnesium sulphate. Evaporation of the solvent followed by flash chromatography on silica gel (hexane elution) furnishes the terphenyl **3b**; yield: 71 mg (64%); oil (Ref.[10], no melting point given).

^{1}H-N.M.R. ($CDCl_3$): δ=2.10 (s, 3 H); 7.20 ppm (m, 13 H).

I.R. (CH_2Cl_2): ν=3050, 1600, 1470, 1440, 1390, 810, 755, 695 cm^{-1}.

M.S.: m/e=244 (M^+); 229 (M^+-CH_3); calculated for $C_{19}H_{16}$: 244.1252; observed: 244.1243.

1,1':3',1''-Terphenyl (3a); Typical Procedure for Method B:
A solution of aldehyde **2a** (211 mg, 0.85 mmol) in benzene (4 ml) is added at room temperature to a solution of boron trifluoride etherate

(0.315 ml, 2.5 mmol) in benzene (4 ml). The purple solution is stirred for 30 min, then poured into saturated aqueous sodium hydrogen carbonate solution (20 ml). Evaporation of the benzene is followed by extraction with dichloromethane (3 x 20 ml). The organic layer is washed first with water (1 x 50 ml), then brine (1 x 50 ml), and dried with potassium carbonate. Evaporation of the solvent followed by flash chromatography on silica gel (hexane elution) furnishes terphenyl **3a**; yield: 95 mg (48%); m.p. 83–84 °C (Ref.[11], m.p. 89 °C).

^{1}H-N.M.R. ($CDCl_3$): $\delta = 7.20$ (m, 14H).

I.R. (CH_2Cl_2): $\nu = 3040$, 1600, 1575, 1475, 1405, 1070, 800 cm^{-1}.

M.S.: $m/e = 230$ (M^+); calculated for $C_{18}H_{14}$: 230.1095; observed: 230.1085.

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