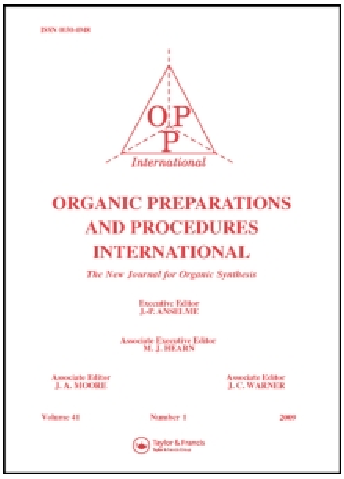

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A CONVENIENT ONE-POT SYNTHESIS OF NOVEL FUNCTIONALIZED TERPHENYLS

V. V. Suresh[ab]; H. M. Chawla[ac]

[a] Department of Chemistry, Indian Institute of Technology, New Delhi, India [b] M. Tech. Thesis, Indian Institute of Technology, New Delhi, India [c] Department of Chemistry, University of Victoria, Victoria, Canada

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A CONVENIENT ONE-POT SYNTHESIS OF NOVEL FUNCTIONALIZED TERPHENYLS

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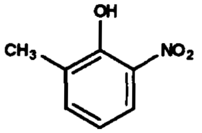
V. V. Suresh[†] and H. M. Chawla[*††]

Department of Chemistry
Indian Institute of Technology
New Delhi-110016, INDIA

Recent successes in chemical and enantiomeric separations[1] by inclusion complexation, developments in the chemistry of organic clathrates such as tri-o-thymotide[2] and chirality transfer in photooxygenation reactions[3] have prompted vigorous efforts in the design and synthesis of new phenolic hosts.[4] Functionalized terphenyl derivatives **3**, **4** and **7** are attractive synthons for this purpose as well as for the development of new chromogenic ionophores.[5] A survey of literature indicates that these molecules (except **7**) have not been synthesized and in principle, may be obtained only by multi-step procedures with low net yields. We now report a one-pot procedure for the preparation of terphenyls **3**, **4** and **7** from *o*- and *p*-cresols by reaction with cerium (IV) ammonium nitrate (CAN)



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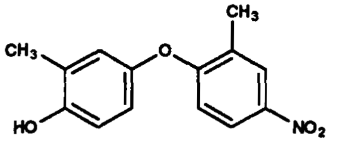

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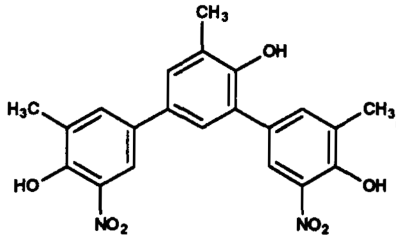

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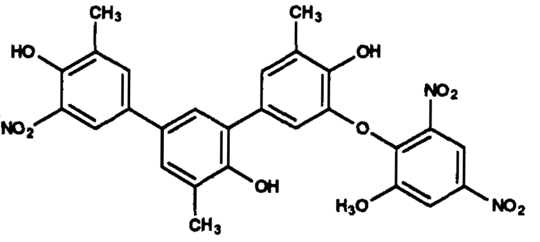

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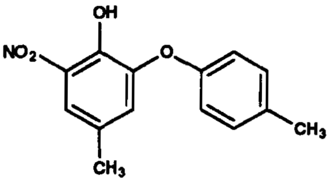

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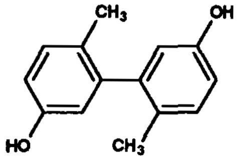

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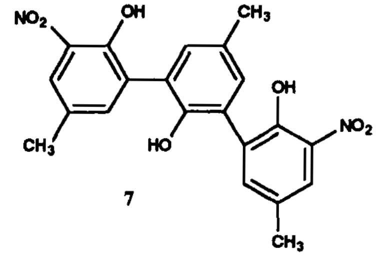

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and hydrogen peroxide. Although the net yields are not high (30-40%), it is noteworthy that the possible alternative methods involve costly reagents, several steps[5] and do not give better yields.

Though the exact role of hydrogen peroxide is a subject of further study, [6] the reaction in the absence of hydrogen peroxide gave a tarry unresolvable mixture. When the amount of hydrogen peroxide was in excess of 7-8 equivalents, the reaction was very sluggish and did not yield terphenyl derivatives. Decreased amounts of hydrogen peroxide resulted in the formation of numerous by-products[8] (TLC) and hence defeated the purpose of devising a convenient procedure for obtaining **3**, **4** and **7**.

EXPERIMENTAL SECTION

^1H NMR spectra were recorded on Nicolet-99.55 MHz Jeol-FT-NMR spectrometer using TMS, as the internal standard and values reported are in δ scale. IR spectra were obtained as KBr pellets on a SP-1200 Grating IR spectrophotometer and mass spectra were recorded on a JMS-D300 Jeol mass spectrometer at 70 ev. Melting points were determined in open capillaries on an electric melting point apparatus (Adair Dutt) and are uncorrected. The time allowed for completion of the reaction was monitored by TLC performed on silica gel (BDH, Bombay) plates using iodine for visualizing the spots. The purity of the compounds obtained was examined by TLC in at least three different solvents. Column chromatography was carried out on silica gel (60-120 mesh) and the organic solvent extracts were usually dried over anhydrous $MgSO_4$. *o*- and *p*-Cresols were purchased from BDH (Bombay). The solvents used were freshly distilled before use. Petroleum ether refers to the solvent with a boiling range of 60-80°.

Preparation of Terphenyl Derivatives (3, 4 and 7). General Procedure.- To a solution of cerium (IV) ammonium nitrate (50 g) in water (10-15 mL), a solution of hydrogen peroxide (30%, 10 mL) was added followed by the addition of freshly distilled cresol (10 mL, 100mM). The resultant solution was warmed on a water bath with continuous stirring (45 minutes to 1 hr.). When the reaction was complete, the mixture was cooled, extracted with chloroform (8 x 20 mL) and the combined $CHCl_3$ extract was concentrated *in vacuo* to give a gummy mass which was column chromatographed (SiO_2: 4 x 45 cm). Initial elution (for the reaction with *o*-cresol) with hexane gave **1** and **2** while subsequent elution with petroleum ether (1 L) gave **3**. Further elution with 1:1 petroleum ether-benzene afforded terphenyl **4**.

Similar elution of the *p*-cresol case gave **5** from the petroleum ether eluate (1 L), **6** from the 3:1 petroleum ether- benzene eluate (1 L) and terphenyl **7** from the 1:1 petroleum ether-benzene eluate (0.5 L). The physical and spectral data of compounds obtained is given below.

6-Methyl-2-nitrophenol (**1**, 28%) was obtained as yellow needles from hexane, mp. 71°, lit.[7] 71-72°. It gave positive Lassaigne's and ferric chloride tests. IR (KBr); 3140, 3300, 2900, 1600, 1580, 1450, 1300, 1230, 1150, 750 cm^{-1}.

^1H NMR ($CDCl_3$): δ 10.9 (s, 1H), 6.87-8.0 (m, 3H), 2.3 (s, 3H) MS (m/z, % abundance): 153 (30), 125 (15), 110 (20), 97 (25), 85 (33.3), 83 (28), 71 (18), 70 (15), 69 (12), 57 (60), 55 (30).

2-Methyl-4-nitrophenyl-4'-hydroxy-3'-methylphenyl Ether (**2**, 13%) was recrystallized from petroleum ether as thin yellow needles, mp. 57°, lit.[7] 58° and gave positive Lassaigne's and ferric chloride tests. IR (KBr): 3300, 2980, 2900, 1560, 1500, 1450, 1400, 1340, 1260, 1240, 1180, 750 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ 10.7 (s, IH) (, 7.1 (m, 6H), 2.31 (s, 3H), 2.23 (2, 3H), MS (m/z, % abundance): 259 (100), 242 (30), 229 (20), 213 (10), 197 (30), 183 (28), 153 (15), 141 (20), 113 (20), 107 (55.5), 91 (100), 77 (45), 79 (30), 65 (90), 56 (15), 55 (90), 53 (20).

4,5,'4"-Trimethyl-2,2"-dinitro-[1,1',3',1"-terphenyl]-3,4',3"-triol (**3**, 32%) was recrystallized from petroleum ether as yellow platelets; mp. 280°. It gave positive Lassaigne's and ferric chloride tests and was soluble in aqueous NaOH. IR (KBr): 3260, 1600, 1560, 1500, 1420, 1350, 1250, 1220, 1190, 1150, 950, 730 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ 11.3 (s, 2H), 11.2 (s, 1H), 8.8 (m, 3H), 8.3 (m, 3H), 2.4 (s, 6H), 2.3 (s, 3H); MS (m/z, % abundance): 410 (80), 365 (30), 304 (29), 259 (10), 199 (30), 198 (80), 168 (25), 152 (15), 120 (60), 107 (30), 106 (40), 105 (80).

Anal. Calcd. for $C_{21}H_{18}N_2O_7$: C, 61.46; H, 4.39; N, 6.87. Found: C, 61.32; H, 4.34; N, 6.76

3,4',4"-Trihydroxy-4,5',5"-trimethyl-2-nitro[1,1',3',1"-terphenyl]-3"-[6"'-methyl-2"',4"'-dinitrophenyl] Ether (**4**, 16%) was recrystallized from petroleum ether-benzene mixture as yellow needles, mp. 303°. It gave positive Lassaigne's and ferric chloride tests and was soluble in aqueous NaOH. IR (KBr): 3200-3380, 1600, 1550, 1520, 1400, 1360, 1300, 1220, 1190, 1100, 750 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ 11.1 (s, ^{1}H), 8.0 (d, 2H), 7.9 (d, 2H), 6.8 (d, 2H), 6.24 (s, 2H), 2.37 (s, 3H), 2.3 (s, 3H), 2.1 (s, 6H). MS (m/z, % abundance): 560 (12), 515 (33), 410 (40), 304 (50), 259 (12), 214 (95), 198 (15), 181 (20), 169 (20), 165 (18), 154 (12), 115 (40), 108 (20), 96 (30), 90 (29), 77 (40), 69 (50), 65 (30), 63 (28), 53 (20).

Anal. Calcd. for $C_{28}H_{23}N_3O_{10}$: C, 59.89; H, 4.1; N, 7.48. Found: C, 59.74; H, 4.05; N, 7.42

2-Hydroxy-5-methyl-3-nitrophenyl-4'-methylphenyl ether (**5**, 37%) was crystallized as yellow needles, mp. 65°, lit.[7] 65- 67°. It gave positive Lassaigne's and ferric chloride tests. IR (KBr): 3200, 2990, 1600, 1500, 1450, 1410, 1330, 1250, 1190, 760 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ 10.4 (s, 1H), 7.8 (m, 2H), 7.4 (d, 2H), 7.0 (d, 2H), 2.3 (s, 6H). MS (m/z, % abundance): 259 (60), 213 (10), 198 (12), 153 (9), 12 (20), 108 (60), 106 (40), 91 (15), 77 (12), 65 (20), 28 (30).

2,2'-Dihydroxy-5,5'-dimethylbiphenyl (**6**, 19%) was crystallized from benzene as dark brown solid, mp. 153°, lit.[7] 153°. It gave a positive ferric chloride test for phenols. IR (KBr) 1390, 2980, 1600, 1500, 1320, 1300, 1220, 1200, 800, 760 cm^{-1}.

^{1}HNMR (CDCl$_3$); d 6.7 (t, 2H), 6.5 (d, 2H), 5.9 (d, 2H), 4.72 (s, 2H), 2.3 (s, 6H). MS (m/z, % abundance): 214 (98), 197 (80), 167 (40), 158 (43), 145 (35), 135 (30), 108 (29), 107 (20), 91 (30), 77 (40), 65 (20), 51 (23), 39 (20).

5,5',5"-Trimethyl-3,3"-dinitro-[1,1',3',1"-terphenyl]-2,2',2"-triol (**7**, 41%) was recrystallized as small platelets from petroleum ether-benzene, mp. 255°. It gave positive Lassaigne's and ferric chloride tests. IR (KBr); 3330, 1600, 1520, 1500, 1450, 1360, 760, 750 cm^{-1}.

^{1}HNMR (CDCl$_3$): δ 11.1 (s, 2H), 8.0 (s, 1H), 7.5 (d, 1H), 7.13 (d, 2H), 5.25 (s, 2H), 2.2 (s, 6H), 2.1 (s, 3H). MS (m/z, % abundance): 410 (100), 392 (10), 382 (25), 375 (35), 330 (19), 301 (12), 300 (10), 259 (10), 213 (12), 201 (10), 153 (8), 108 (20), 77 (98), 36 (40).

Anal. Calcd. for $C_{21}H_{18}N_7O_8$: C, 61.46; H, 4.39; N, 6.87. Found: C, 61.34; H, 4.35; N, 6.78

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† Abstracted from the M. Tech. Thesis, Indian Institute of Technology, New Delhi-110016, India.

* Present address: Department of Chemistry, University of Victoria, Victoria, V8W 3P6, Canada.

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