

complex in CH_2Cl_2 were added during 3 h 0.5 g (1.9 mmol) of 11 in 8 mL of CH_2Cl_2 with stirring. The reaction mixture was then added to 100 mL of saturated bicarbonate and filtered with Celite. The organic layer was washed with dilute HCl and water, dried, and evaporated. The oily product was recrystallized from petroleum ether (bp 80–100 °C). Yellow crystals of 12 slowly precipitated: 0.35 g (78%); mp 88–90 °C; IR (neat) 3080, 3020, 2920, 2860, 1650, 1600, 1500, 1450, 1030, 750 cm^{-1} ; $^1\text{H NMR}$ (100 MHz, CDCl_3) 7.81 (s, 1 H), 7.2 (m, 8 H), (s, 2 H), 4.0 ppm.

Anal. Calcd for $\text{C}_{19}\text{H}_{11}\text{ClO}$: C, 75.44; H, 4.32; Cl, 13.95. Found: C, 75.6; H, 4.3; Cl, 13.3.

This oxidation was also carried out with active MnO_2 . A yield of 61% for 12 was obtained.

7-Chloro-1,2,4,5-dibenzocyclooctadien-6-one (13). Ketone 12 (0.75 g) was hydrogenated catalytically in ethyl acetate (60 mL), 1 mL of AcOH, and 0.2 g of Pd/C (5%), at 70 psi for 2 h. After filtration the solution was washed with 5% bicarbonate, dried, and evaporated. The resulting oil (0.75 g, 98%) did not crystallize: IR (neat) 3010, 2970, 1700, 1600, 1500, 1450, 925, 810, 750, 630 cm^{-1} ; $^1\text{H NMR}$ (100 MHz, CCl_4) 7.2 (m, 8 H), 5.30 (d, 1 H, $J = 9$ Hz), 3.30 (dd, 2 H, $J_1 = 9$ Hz, $J_2 = 4$ Hz), 4.2 (s, 2 H) ppm.

Anal. Calcd for $\text{C}_{19}\text{H}_{13}\text{ClO}$: C, 74.85; H, 5.07; Cl, 13.84. Found: C, 74.4; H, 5.2; Cl, 14.0.

1,2,4,5-Dibenzocyclooctatrien-6-one (14). In a three-necked flask were placed under N_2 , 6.5 g of anhydrous LiCl (200 mmol), 100 mL of dry DMF, and 1 g of 13. The mixture was refluxed with stirring for 15 h. The solvent was then pumped off and the residue was extracted with CH_2Cl_2 , washed with dilute HCl, dried, and evaporated. The resulting oily product slowly crystallized out from petroleum ether (80–100 °C). The product 14 was obtained in 53% yield (0.41 g): mp 83 °C; IR (Nujol) 1670, 1620, 1460, 1270, 1030, 800, 710, 630 cm^{-1} ; $^1\text{H NMR}$ (100 MHz, CDCl_3) 7.2 (m, 9 H), 6.55 (d, 1 H, $J = 14$ Hz), 4.06 (d, 1 H, $J = 13$ Hz), 3.90 (d, 1 H, $J = 13$ Hz) ppm; $^1\text{H NMR}$ (270 MHz, CDCl_3) 7.3 (m, 8 H), 7.04 (d, 1 H, $J = 13.6$ Hz), 6.64 (d, 1 H, $J = 13.6$ Hz), 4.06 (d, 1 H, $J = 12.8$ Hz), 3.75 (d, 1 H, $J = 12.8$ Hz) ppm (upon radiation at 6.64 ppm the doublet at 7.04 ppm collapses into a singlet and vice versa).

Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{O}$: C, 87.21; H, 5.45. Found: C, 87.0; H, 5.5.

1,2,4,5-Dibenzocyclooctatrien-6-ol (7). The ketone 14 (0.4 g, 1.9 mmol) was reduced with NaBH_4 (1 g) in ethanol (70 mL) for 5 h and then added to 200 mL of water and extracted with CH_2Cl_2 . The organic layer was dried and evaporated. The oily product (0.36 g) did not crystallize: IR (neat) 3400, 3080, 3020, 2920, 1490, 1450, 1250, 1050, 750, 720, 630 cm^{-1} ; $^1\text{H NMR}$ (270 MHz, CDCl_3) 7.1 (m, 8 H), 6.80 (d, 1 H, $J = 10.8$ Hz), 5.70 (dd, 1 H, $J_1 = 10.8$, $J_2 = 6.8$ Hz), 4.95 (d, 1 H, $J = 6.8$ Hz), 3.95 (d, 1 H, $J = 14.1$ Hz), 3.90 (d, 1 H, $J = 14.1$ Hz), 2.30 (s, 1 H, br, exchanges with D_2O) ppm.

Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{O}$: C, 86.48; H, 6.31. Found: C, 86.0; H, 6.5.

1,2,6,7-Dibenzo-1,7-homotropylium Cation (6). Into a NMR tube were introduced 10 mg (0.045 mmoles) of 7 and 0.2 mL of dichloromethane- d_2 . The solution was cooled to -70 °C and 0.2 mL of SO_2ClF was added. Then FSO_3H (0.2 mL) (Cationics Inc.) was added and a dark red solution was formed. A capillary of Me_4Si was introduced and the tube was sealed. The spectrum was recorded at 30 °C: $^1\text{H NMR}$ (270 MHz, CD_2Cl_2 , SO_2ClF , HSO_3F) 9.18 (d, 2 H, $J = 11.5$ Hz), 8.31 (t, 2 H, $J = 9.1$ Hz), 8.14 (d, 2 H, $J = 7$ Hz), 8.11 (t, 1 H, $J = 11.5$ Hz), 8.05 (d, 2 H, $J = 9.1$ Hz), 7.70 (t, 2 H, $J = 7$ Hz), 4.83 (d, 1 H, $J = 11.4$ Hz), 2.52 (d, 1 H, $J = 11.4$ Hz) ppm.

6-Chloro-1,2,3,4-dibenzotropylium Cation (16). In a NMR tube were introduced 30 mg (0.2 mmol) of 17¹³ and 0.4 mL of SO_2 (-70 °C). To a cooled mixture was added $\text{SbF}_5\text{-FSO}_3\text{H}$ (1:1) (magic acid) (Cationics Inc.). A clear red solution was formed and then a capillary of Me_4Si was introduced into the NMR tube followed by sealing of the tube. The spectrum was recorded at -25 °C: $^1\text{H NMR}$ (100 MHz, SO_2 , $\text{FSO}_3\text{H-SbF}_5$) 9.83 (s, 2 H), 8.1–8.4 (m, 8 H) ppm.

Acknowledgment. $^1\text{H NMR}$ spectra at 270 MHz were

recorded on the Bruker WH-270 spectrometer of the Weizmann Institute of Science, Rehovoth, Israel.

Registry No. 6, 71606-71-8; 7, 71516-25-1; 8, 256-81-5; 9, 67464-66-8; 11, 71516-26-2; 12, 71516-25-1; 13, 71516-27-3; 14, 71516-28-4; 16, 71516-18-2; 17, 53137-48-7.

Alumina-Assisted Aryl Cyanation¹

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We wish to report an improved procedure for aryl cyanation using tetrakis(triphenylphosphine)palladium(0) (1).² Our method is based on the use of neutral alumina either as a support for sodium cyanide or as a cocatalyst.^{3,4}

Current methods for converting aryl halides into their corresponding nitriles are based on (1) stoichiometric reaction with copper(I) cyanide (150–240 °C) and (2) catalytic displacement by cyanide ion employing group 8 metal complexes (30–100 °C).^{2,5–8} Although both nickel- and palladium-based catalysts have proven useful, in practice, the latter are simpler to prepare, purify, handle, and store. Procedures described herein extend the synthetic utility of palladium to aryl bromides without requiring the use of HMPA as solvent and also improve displacement on aryl iodides.^{2,8}

Reaction of sodium cyanide with iodobenzene in toluene in the presence of 10 mol % of 1 at 80 °C for 2 h afforded a 5% yield of benzonitrile. In contrast, a similar reaction using the same quantity of sodium cyanide, which was first impregnated onto alumina, gave a quantitative conversion to the nitrile. When nonimpregnated alumina (~10% of that contained in the impregnated reagent) was used as a cocatalyst, a 20% yield of nitrile was obtained. Increasing the amount of alumina decreased the yield of nitrile. Aryl bromides were less reactive for cyanation and gave higher yields when alumina was present as a co-catalyst instead of as a support. As in the case of aryl iodides, increasing the amount of nonimpregnated alumina resulted in reduced yields. Catalyst 1 or an intermediate derived from 1 appears to undergo slow decomposition on the alumina surface. A similar situation is evident for cyanide-coated alumina; e.g., when the amount of 1 used for displacement on bromobenzene was increased from 10 to 20 mol %, the nitrile produced after 19 h at 80 °C rose from 3 to 99%. Decomposition appears to be faster on $\text{NaCN}/\text{Al}_2\text{O}_3$ than on nonimpregnated alumina and is of greater consequence for the less reactive halides. On the basis of the results obtained for the series of halides sum-

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Table I. Alumina-Assisted Aryl Cyanation^a

function of alumina	reactant	product	temp, °C	time, h	yield, % ^b
cocatalyst	chlorobenzene	benzonitrile	110	16	0.2 (0)
support	chlorobenzene	benzonitrile	80	16	0
cocatalyst	3-(chloromethyl)benzoate	3-(cyanomethyl)benzoate	100	20	5 (1)
cocatalyst	bromobenzene	benzonitrile	80	24	98 (20)
cocatalyst ^c	bromobenzene	benzonitrile	80	24	46
cocatalyst ^d	bromobenzene	benzonitrile	80	22	11
support	bromobenzene	benzonitrile	80	19	3
support ^e	bromobenzene	benzonitrile	80	19	99
catalyst	1-bromonaphthalene	1-cyanonaphthalene	100	40	90 (13)
support	iodobenzene	benzonitrile	80	2	98 (5)
support	iodobenzene	benzonitrile	80	2	75 ^f
cocatalyst	iodobenzene	benzonitrile	80	2	20
cocatalyst ^g	iodobenzene	benzonitrile	80	2	16
support	3-iodotoluene	3-cyanotoluene	80	3	95 (2)
support	3-iodotoluene	3-cyanotoluene	80	3	62 ^f

^a Unless noted otherwise, procedures used were similar to those described in the Experimental Section. ^b Yields were determined by GLC using internal standard techniques. Material balance was >95% in all cases. Numbers in parentheses refer to control experiments carried out in the absence of alumina. ^c Alumina used was 0.1 g. ^d KCN used. ^e A 20 mol % of 1 was used. ^f Isolated yield. ^g Alumina used was 0.5 g.

marized in Table I, it is recommended that alumina be used as a support for cyanation of aryl iodides and as a co-catalyst for aryl bromides.

The use of bis(triphenylphosphine)phenylpalladium(II) iodide as catalyst or potassium cyanide as the source of cyanide ion failed to improve yields. Aryl chlorides gave poor conversions under all conditions employed. Experimental details are described below.

Experimental Section

General Methods. Unless stated otherwise, all reagents and chemicals were obtained commercially and used without purification. Chlorobenzene, bromobenzene, iodobenzene, 1-bromonaphthalene, and 3-iodotoluene were purchased from Aldrich Chemical Co. The 3-chloromethyl benzoate was prepared from 3-chlorobenzoic acid (Aldrich Chemical Co.) by esterification with CH₃OH-concentrated H₂SO₄. Tetrakis(triphenylphosphine)palladium(0) was prepared using established procedures.⁹ The palladium complex was handled in air but stored under nitrogen. Toluene was dried by distillation from sodium and benzophenone under a nitrogen atmosphere. Neutral alumina was purchased from Bio-Rad Laboratories (AG-7, 100-200 mesh) and used as obtained. All ¹H, ¹³C, and IR spectra were recorded using Varian A-60, JOEL FX 60 QD, and Beckman Acculab 7 spectrometers, respectively. Product mixtures were analyzed by GLC on a Hewlett-Packard Model 5830 A flame ionization instrument using internal standards. Culture tubes were used as reaction vessels (25 × 150 mm Corning No. 9826 tubes) and were equipped with a No-Air stopper and a Teflon-coated stirring bar.

Impregnation of NaCN on Alumina. A NaCN/Al₂O₃ reagent was prepared using 5 mmol of NaCN per gram of alumina based on procedures similar to those previously described.^{3,10}

General Procedure for Small-Scale Reactions. Procedures similar to that described for the conversion of bromobenzene to benzonitrile were followed for all of the small-scale reactions described in Table I. Into an oven-dried 50-mL culture tube equipped with a stirring bar and a No-Air stopper was placed 0.045 g (0.04 mmol) of tetrakis(triphenylphosphine)palladium(0) along with 0.1 g (2.0 mmol) of sodium cyanide crushed together with 0.05 g of alumina (mortar and pestle). The tube was degassed under a stream of nitrogen and 4 mL of a degassed solution of bromobenzene in toluene (0.1 M, 0.4 mmol) containing 0.4 mmol of tridecane (internal standard) was added via syringe. The

mixture was heated to 80 °C for 24 h with vigorous stirring. Analysis of the product mixture (GLC) indicated complete conversion to the nitrile. Mass balance was 100%.

For reactions employing impregnated cyanide, 0.5 g of the NaCN/Al₂O₃ reagent was used.

Conversion of 3-Iodotoluene to 3-Cyanotoluene. A mixture of 30 g of NaCN/Al₂O₃, 5.5 g (25.0 mmol) of 3-iodotoluene, 2.9 g (2.5 mmol) of tetrakis(triphenylphosphine)palladium(0), and 100 mL of toluene was stirred for 3 h at 80 °C in a 250-mL round-bottom flask under a nitrogen atmosphere. Analysis of the product mixture by GLC indicated complete conversion to the nitrile. The mixture was filtered and the alumina was washed with ether. Solvent was then removed under reduced pressure yielding a yellow oil plus a precipitate. Petroleum ether was added to triturate the remaining palladium residue, and upon filtration and distillation 1.81 g (62%) of 3-cyanotoluene [bp 79–81 °C (6 mm)] was obtained having an IR and ¹³C NMR spectrum identical with an authentic sample.

Registry No. Chlorobenzene, 108-90-7; 3-(chloromethyl)benzoate, 31719-77-4; bromobenzene, 108-86-1; 1-bromonaphthalene, 90-11-9; iodobenzene, 591-50-4; 3-iodotoluene, 625-95-6; benzonitrile, 100-47-0; 3-(cyanomethyl)benzoate, 5689-33-8; 1-cyanonaphthalene, 86-53-3; 3-cyanotoluene, 620-22-4; alumina, 1344-28-1; sodium cyanide, 143-33-9.

Selective O-Demethylation of Catechol Ethers. Comparison of Boron Tribromide and Iodotrimethylsilane

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A variety of reagents are available for demethylation of mono- and polymethyl aryl ethers.^{1a-e} We sought a demethylating agent which would provide the maximum yield of **1b** rather than the 1:3:2 ratio of **1a**, **1b**, and **1c** obtained with 1.1 equiv of BBr₃ or heating in the presence

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(10) It has been found that for cyanide ion displacement on 1-bromooctane, a loading of 5 mmol of NaCN per gram of alumina produces the maximum amount of reactive cyanide: Quici, S., Regen, S. L., unpublished results. Interestingly, if one assumes a closely packed array of sodium and cyanide ions on the alumina surface (surface area equals 240 m² g⁻¹), this amount of salt corresponds approximately to that required for monolayer coverage.

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