from acetic acid: mp 161–62 °C; IR 2630 cm^{-1} (brd, OH); ^{1}H NMR 11.22 (brd s, 1 H, OH), 7.72 (m, 2 H) and 7.47 (m, 3 H) (C_6H_5), 2.10 (s, 3 H, CH_3).

Anal. Calcd for $C_{10}H_9N_2OCl$: C, 57.57; H, 4.35; N, 13.42; Cl, 16.99. Found: C, 57.84; H, 4.43; N, 13.26; Cl, 17.02.

Vilsmeier Reaction of 1a. Reaction of **1a** under the conditions above gave, from the ether extract, 27% of **4a**, mp 210–11 °C,[12] which was identical with a sample prepared by chlorination of 3,5-diphenylpyrazole with SO_2Cl_2.[5]

Neutralization of the basic aqueous solution gave 48% of **3a**: mp 191–93 °C (from acetic acid); IR 2650 cm^{-1} (brd, OH), ^{1}H NMR 8.50 (brd, 1 H, OH), 7.15–7.60 (m, 10 H, C_6H_5).

Anal. Calcd for $C_{15}H_{11}N_2OCl$: C, 66.55; H, 4.10; N, 10.35. Found: C, 66.67; H, 3.84; N, 10.28.

Vilsmeier Reaction of 2b. A solution of 1.7 g (11 mmol) of $POCl_3$ in 10 mL of DMF was cooled below 10 °C and treated with 1.74 g (10 mmol) of **2b**. The solution was stirred at room temperature for 150 min, poured into 100 mL of ice–water, and neutralized with $NaHCO_3$. The solid was collected, washed with water, and dried to give 1.49 g (77%) of **4b**.

Vilsmeier Reaction of 2a. Reaction using the same method as for **2b** gave 96% of **4a**.

4-Chloro-3,5-diphenyl-4-methyl-4*H*-pyrazole 1-Oxide (9). A solution of 0.85 g (5.5 mmol) of $POCl_3$ in 10 mL of DMF was cooled below 10 °C and treated in portions with 1.31 g (5 mmol) of **8**. After 60 min at 0–10 °C the solution was poured into 50 mL of ice–water and extracted with three 50-mL portions of ether. The ether solution was washed with saturated NaCl, dried (Na_2SO_4), and evaporated under reduced pressure without heating. The residue was crystallized from CH_2Cl_2 without heating to yield 0.41 g (29%) of **9**.[8]

Reaction of 1b with Acetyl Chloride. A mixture of 0.95 g (5 mmol) of **1b** in 25 mL of dry benzene was treated over 30 min with 0.4 g (5 mmol) of acetyl chloride in 5 mL of benzene. After 2 h at room temperature, the solution was washed with water, dried (Na_2SO_4), and evaporated. Recrystallization from ethanol gave 0.57 g (55%) of **3b**.

Acknowledgment. Y.I.K. wishes to acknowledge the support of Hong-Ik University and the Ministry of Education of the Republic of Korea during the course of this work.

Registry No. 1a, 59434-82-1; **1b**, 55026-66-9; **2a**, 59434-85-4; **2b**, 59434-84-3; **3a**, 71582-22-4; **3b**, 71549-27-4; **4a**, 71549-28-5; **4b**, 71549-29-6; **6b**, 71549-30-9; **8**, 17953-33-2; **9**, 61355-02-0; 3,5-diphenylpyrazole, 1145-01-3.

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[12] A melting point of 179–80 °C for this compound has been reported: Grandberg, I. I.; Kost, A. N. *J. Gen. Chem. USSR (Engl. Transl.)* **1961**, *31*, 3454.

1,2:6,7-Dibenzo-1,7-homotropylium Cation. Examination of Steric Effects Operating in Homoaromatic Overlap

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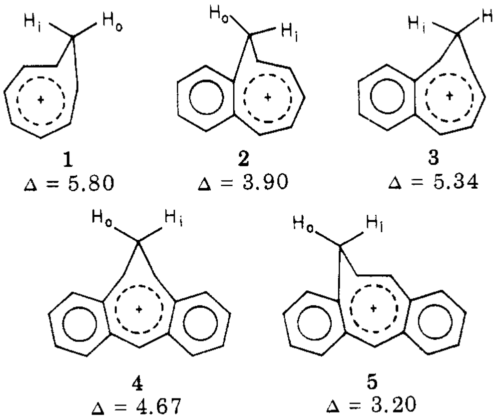
Received April 17, 1979

Monohomoaromatic systems include an sp^3-hybridized carbon inserted into a cyclic framework of pπ orbitals containing 4n + 2 π electrons, with the result that the topology of the system is no longer planar.[1,2] The influence of benzene annelation on homoaromatic systems seems to be of interest. In order to achieve maximum overlap of the pπ orbitals in these systems, the benzene rings must tilt to enable homoaromatic delocalization and at the same time the aromatic delocalization in the benzene rings must also be maintained. This distortion and the requirement to share common π bonds between benzenoid and homoaromatic components may introduce difficulties in achieving homoaromatic overlap followed by a depression of the homoaromatic character.

Chart I



The homotropylium cation (**1**) represents the most widely investigated system in this series.[3] The different environment of the protons attached to the sp^3-hybridized carbon bridge (H_i, H_o) in **1** results in a difference (Δ) of the chemical shifts of these two protons ($\Delta = \delta_{H_o} - \delta_{H_i}$).[1,2] Several mono- and dibenzannelated homotropylium cations (**2**–**5**) have been investigated in recent years.[4–7] In these cations, the comparison of the Δ values (ppm) of the bridgehead protons showed decreased values attributed to benzene annelation (Chart I). However, inspection of the magnetic characteristics of the benzannelated homoaromatic species **2**–**5** reveals two significant phenomena: (a) When benzene annelation is adjacent to the bridge, as in **2** and **5**, Δ is significantly decreased relative to Δ for **1**.[4,7] On the other hand, a remote benzene annelation with respect to the bridge, as in **3**[5] and **4**,[6] decreases the magnitude of Δ to a lesser extent relative to Δ for **1**. (b) In homotropylium cations where benzene annelation is remote with respect to the sp^3 bridge, the protons attached at the α position to the bridge show an upfield shift relative to the shift of the other peripheral protons (δ_{H_α} is 5.5 and 4.2 ppm in **3** and **4**, respectively). It therefore seems that the location of the benzannelation relative to the bridge rather than the extent of benzannelation influences the homoaromatic overlap.

Results and Discussion

To gain insight into the parameters operative in achieving homoaromatic overlap in benzannelated homotropylium species we studied the 1,2:6,7-dibenzo-1,7-homotropylium cation (**6**). This system includes a double ben-

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[1] For general reviews see: (a) Winstein, S. *Chem. Soc., Spec. Publ.* **1967**, *No. 21*, 5. (b) Haywood-Farmer, J. *Chem. Rev.* **1974**, *74*, 315. (c) Story, P. R.; Clark, Jr., B. C. *Carbonium Ions* **1972**, *3*, 1007. (d) Paquette, L. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 106.

[2] (a) Haddon, R. C. *J. Am. Chem. Soc.* **1975**, *97*, 3608. *Tetrahedron Lett.* **1974**, 2797. (b) Goldstein, M. J. *J. Am. Chem. Soc.* **1967**, *89*, 6357. (c) Bischof, P.; Gleiter, R.; Heilbronner, E. *Helv. Chim. Acta* **1970**, *53*, 1425. (d) Hehre, W. J. *J. Am. Chem. Soc.* **1972**, *94*, 8908; **1973**, *95*, 5807; **1974**, *96*, 5207.

[3] v. Rosenberg, J. L.; Mahler, J. E.; Pettit, R. *J. Am. Chem. Soc.* **1962**, *84*, 2842.

[4] Merk, W.; Pettit, R. *J. Am. Chem. Soc.* **1968**, *90*, 814.

[5] Corver, H. A.; Childs, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 6201.

[6] Childs, R. F.; Winstein, S. *J. Am. Chem. Soc.* **1967**, *89*, 6348.

[7] Mattescu, G. D.; Nenitzescu, C. D.; Olah, G. A. *J. Am. Chem. Soc.* **1968**, *90*, 6235.

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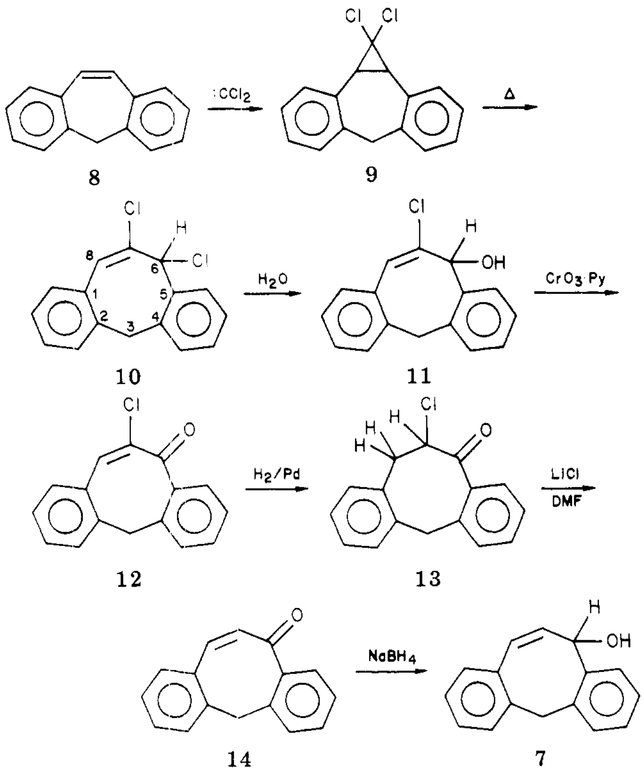
Table I. Chemical Shifts^a of 7 and the Homotropylium Cation 6[9,11]

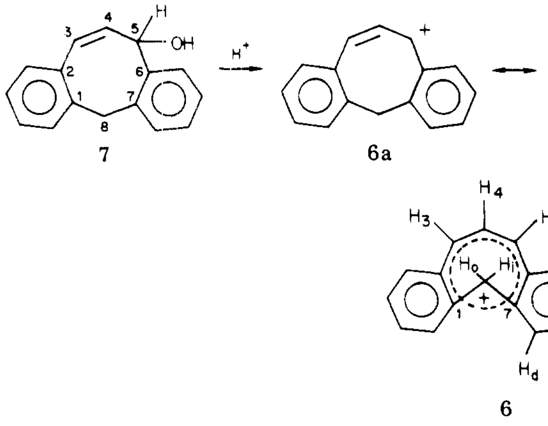
	H_3	H_4	H_5	H_a, H_d	H_b, H_c	H_o	H_i
7	6.80	5.70	4.95	7.10^b		3.95	3.90
6	9.18	8.05	9.18	8.14, 8.05	7.70, 8.31	4.83	2.52
$\Delta(\delta_{H_i})^c$	2.38	2.35	4.23	1.04, 0.95	0.60, 1.21	0.88	-1.38

^{a} Relative to Me_4Si (external, capillary). ^{b} Center of multiplet. ^{c} $\Delta(\delta_{H_i}) = \delta_{H_i}(6) - \delta_{H_i}(7)$.

zannelation adjacent to the homotropylium bridge and may shed light on the influence of benzannelation upon homoaromatic character.

Scheme I

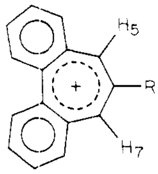




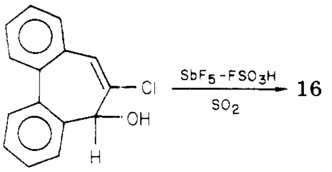
The synthesis of 7 is outlined in Scheme I. Treatment of 7 in a mixture of SO_2ClF and CD_2Cl_2 (1:1) with FSO_3H afforded 1,2:6,7-dibenzo-1,7-homotropylium cation (6). The ^1H NMR spectrum[9,11] of 6 reveals an ABCD pattern for the benzene ring protons, an A_2B pattern of the peripheral homoaromatic protons H_3, H_4, and H_5, and an AB pattern, assigned to the bridgehead of protons H_i and H_o (inner and outer protons) (Table I).

In 6 proton H_i is shifted paratropically (-1.38 ppm), and the two protons H_i and H_o differ in their chemical shifts (Δ = 2.4 ppm) (Table I). These phenomena are rationalized by the induced diamagnetic ring current resulting from a homoaromatic overlap of 6π electrons. It should be noted that the value for Δ of 6 is the lowest observed in the benzannelated homotropylium cations and is in line with the suggestion that adjacent benzannelation to the aromatic bridge reduces this value significantly. Furthermore, it should be noted that this reduced value originates mainly from a reduced paratropic shift of H_i (δ_{H_i} is 2.52 ppm in 6, as compared with 1.50 and 0.55 ppm in 5 and 4, respectively). On the other hand, the peripheral protons H_3, H_4, and H_5 as well as the benzene ring protons (H_a–H_d) are significantly shifted to lower field (Table I).

To evaluate the effect of the developed induced ring current resulting from homoaromatic overlap on the chemical shifts in 6, we compared its chemical shifts with those of the Hückeloid cation 15. This ion schematically represents an abstraction of the homoaromatic bridge from 6 and is related to it in the same sense as the tropylium cation is related to the homotropylium cation (1). Thus, the comparison between the peripheral protons (H_3, H_4, H_5) of 6 and the respective protons of 15 may reveal the effect of the induced ring current on the chemical shifts of the homoaromatic species. 6-Chloro-1,2:3,4-dibenzotropylium cation (16[12]), a closely related derivative of 15, was prepared by treatment of 17[13] in SO_2 with FSO_3H.



15, R = H
16, R = Cl



17

Comparison of the shifts of protons H_3 and H_5 of 6 (9.18 ppm) with the corresponding protons H_5 and H_7 of the aromatic cation 16 and of the benzo protons of the two systems (7.60–8.40 ppm) reveals a diamagnetic shift of a similar magnitude. The chloro-substituted tropylium cat-

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[8] All compounds gave satisfactory microanalyses and mass spectra.

[9] Chemical shifts (δ) are given in parts per million relative to Me_4Si, recorded on a Varian HA 100-D apparatus at 100 MHz. The assignments were assisted by double-resonance experiments with a Hewlett-Packard 4204A oscillator.

[10] Without use of a catalytic amount of AcOH, hydrogeneolysis of the chlorine atom of 12 was concomitant.

[11] Recorded on a Bruker WH 270 instrument at 270 MHz.

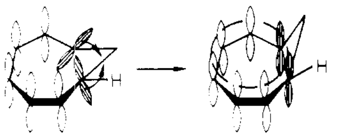
[12] Joshi, G.; Singh, N.; Pande, L. *Synthesis* **1972**, 317.

[13] Coburn, T. T.; Jones, W. M. *J. Am. Chem. Soc.* **1974**, *96*, 5218.

ion **16** was chosen as a reference system because of its convenient synthesis. However, unsubstituted benzotropylium cations reveal similar enhanced shifts.[14] Therefore, the chemical shifts of the peripheral protons of **6** point to an effective ring current as the consequence of an efficient homoaromatic overlap and contradict the poor overlap which would have been deduced merely from the value of Δ.

Additional support for the homoaromaticity of **6** comes from the comparison of the total proton diamagnetic shift of **6** with that of the homoaromatic cations **4** and **5**. It is well established[15] that one positive charge delocalized over a conjugated system results in a total deshielding of 10.7 ppm. It has also been shown that an excessive diamagnetic shift is indicative of an induced diamagnetic ring current in the system.[16] The formation of the charged systems **4** and **5** from the parent alcohols was followed by a total diamagnetic shift of 15.1 ppm and 17.0 ppm, respectively. The ionization of **7** to form **6** showed a total diamagnetic shift of 16.6 ppm. Therefore it has to be concluded that **6** is diatropic in the same sense as the homoaromatic ions **4** and **5**.

In order to achieve an efficient homoaromatic pπ overlap, the two π orbitals in the α-position to the bridge must tilt and the protons attached to the α-carbon atoms should be distorted relative to the homoaromatic delocalization periphery.[2a] Thus, they are no longer parallel to the diamagnetic anisotropic region as reflected by the paratropic shifts of these protons in cations **3** and **4**. Adjacent benzannelation to the bridge may hinder orbital overlap due to the rigidity of the benzene rings and result in the two alternative effects: either dampening of the homoaromatic overlap, which is not the case here, or another route which may become important in the achievement of this overlap.



In view of the experimental results we suggest that in homotropylium cations bearing adjacent benzannelation the bridge is distorted and tilted toward the conjugated periphery, relative to the respective angle in **1**. The proposed distortion of the bridge in the achievement of the pπ orbital overlap is accompanied by the concomitant removal of proton H_i from the paratropic region of the induced magnetic field. Hence, the reduced Δ value in homoaromatic systems bearing benzene annelation adjacent to the bridge originates from the change of chemical shift of the bridgehead proton H_i rather than from a poor overlap. The additional steric effect suggested to operate in gaining homoaromatic overlap correlates well with the gradual change of the spectral characteristics observed in the benzannelated homotropylium series **2**–**5**. While in **3** and **4** the sole mechanism operating in achieving the overlap[2a] is a distortion of the "α-carbons", systems **2** and **5** represent a case where the mutual operation of the two processes in gaining the overlap, i.e., tilting of the "free" α-carbon and a concomitant distortion of the bridge, occurs (diminution of Δ relative to **3** and **4**). In **6** the distortion of the sp^3 bridge seems to be the parameter responsible for the achievement of homoaromatic character and therefore shows the most significant diminution of the Δ value.[17]

This suggestion is also supported by the chemical shifts of H_α (adjacent to the bridge). As already mentioned for **3** and **4**, where the benzannelation is remote from the sp^3 bridge, these protons are shifted to higher field due to the unhindered tilting of the α-carbons. On the other hand, in **2** and **5** the H_α appear at low field. Further support for the distortion of the bridge comes from the geminal coupling constants of protons H_i and H_0 in **1** and **6**. In **1** J = 6.7 Hz, while in **6** J = 12.4 Hz. The increase of the coupling constants reflects the increase of the C_1–C_8–C_7 angle as a result of the "flattening" of the sp^3-hybridized bridge. This means that the Θ_c is closer to an octagonal angle and emphasizes the suggested "flattening" mechanism.

In view of these results we propose that the distortion of the homoaromatic bridge relative to the periphery represents an additional parameter operative in benzannelated homoaromatic species.

Experimental Section

General Procedures. Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Infrared spectra were recorded on Perkin-Elmer Model 137 and 337 spectrometers. Ultraviolet spectra were recorded with the aid of a Unicam SP-280 spectrometer. Mass spectra were determined on Varian MAT Model 311 and 111 instruments. ^{1}H NMR chemical shifts are reported in (δ) parts per million downfield relative to Me_4Si. In spectra run in FSO_3H the Me_4Si was placed in a concentered capillary (external standard). The spectra were recorded on a Varian HA-100D spectrometer (100 MHz) or on a Bruker WH-270 (270 MHz). The assignments were assisted by double-resonance experiments.

8,8-Dichlorodibenzobicyclo[5.1.0]octadiene (9). The reaction was carried out in a three-necked flask equipped with a mechanical stirrer. To a solution of 12.5 g (0.31 mol) of NaOH in 2.5 mL of water were added 2.5 g (13 mmol) of **8** dissolved in 50 mL of $CHCl_3$ and 0.35 g (1.54 mmol) of benzyltriethylammonium chloride. The solution was stirred vigorously and heated to 50 °C for 2 h. The two phases were then stirred at room temperature for an additional 12 h. Water (250 mL) was then added and the water layer was extracted with CH_2Cl_2. The organic layer was washed with 10% HCl and water, dried, and evaporated. The residue was recrystallized from ethanol to yield 2.6 g of **9** (70%): mp 116 °C; UV ($CHCl_3$) 270 (ϵ 700), 272 (850), 245 nm (11 000); IR (Nujol) 1500, 1980, 1050, 840, 820, 760, 750, 715, 625 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) 7.1 (m, 8 H), 4.52 (d, 1 H, J = 13 Hz), 3.31 (d, 1 H, J = 13 Hz), 3.31 (s, 2 H) ppm.

Anal. Calcd for $C_{17}H_{12}Cl_2$: C, 71.31; H, 5.19; Cl, 24.47. Found: C, 71.0; H, 4.2; Cl, 24.3.

7-Chloro-1,2:4,5-dibenzocyclooctatrien-6-ol (11). **9** (1.5 g) was heated to 200–210 °C for 45 min under N_2. The liquid was stirred with a magnetic stirrer and cooled. Acetonitrile (60 mL) and 75 mL of a saturated solution of sodium bicarbonate were added and the mixture was stirred for 2 h. Water (150 mL) was then added and the reaction mixture was extracted with CH_2Cl_2, dried, and evaporated to yield 1.48 g of **11** as a light yellow oil: UV (EtOH) 270^{s} (ϵ 10 000), 240 nm (40 000); IR (neat) 3300, 1200, 1120, 1090, 860, 840, 760, 730 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) 7.2 (m, 8 H), 6.75 (s, 1 H), 5.10 (s, 1 H), 3.91 (d, 1 H, J = 12 Hz), 3.86 (d, 1 H, J = 12 Hz), 3.1 (br s, exchanges with D_2O) ppm.

Anal. Calcd for $C_{16}H_{12}OCl$: C, 75.14; H, 4.69; Cl, 13.89. Found: C, 74.4; H, 4.4; Cl, 13.0.

7-Chloro-1,2:4,5-dibenzocyclooctatrien-6-one (12). The oxidation was carried out with a CrO_3/pyridine complex.[18] To the

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[14] For example see: Olah, G. A.; Liang, G. *J. Org. Chem.* **1975**, *40*, 2108 and references cited therein.

[15] Schaeffer, T. C.; Schneider, W. G. *Can. J. Chem.* **1963**, *41*, 966.

[16] Willner, I.; Becker, J. Y.; Rabinovitz, M. *J. Am. Chem. Soc.* **1979**, *101*, 335.

[17] Similar phenomena were observed in the homotropylium cation derived from **11** and in the protonation products of **12** and **14** in which a hydroxyhomotropylium cation form is significant. For the significance of the hydroxyhomotropylium species cf.: Chapman, O. L.; Fugiel, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 215. Brookhart, M.; Ogliaruzo, M.; Winstein, S. *Ibid.* **1967**, *89*, 1965. Holmes, J. D.; Pettit, R. *Ibid.* **1963**, *85*, 2531. See also ref 5.

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}; ^1H NMR (100 MHz, $CDCl_3$) 7.81 (s, 1 H), 7.2 (m, 8 H), (s, 2 H), 4.0 ppm.

Anal. Calcd for $C_{16}H_{11}ClO$: 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}; ^1H 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 $C_{16}H_{13}ClO$: 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}; ^1H 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; ^1H 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 $C_{16}H_{12}O$: 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}; ^1H 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 $C_{16}H_{14}O$: 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: ^1H 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 17[13] and 0.4 mL of SO_2 (−70 °C). To a cooled mixture was added SbF_5–FSO_2H (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: ^1H NMR (100 MHz, SO_2, FSO_3H-SbF_5) 9.83 (s, 2 H), 8.1–8.4 (m, 8 H) ppm.

Acknowledgment. ^1H 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.

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[18] Poss, G. I.; Arth, G. E.; Beyler, R. E.; Sarett, L. H. *J. Am. Chem. Soc.* **1953**, *75*, 422.

Alumina-Assisted Aryl Cyanation[1]

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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 $NaCN/Al_2O_3$ 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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