and 0.72 g of a mixture of the two compounds, the relative amounts being determined by NMR. The total yield of compound **10** was 0.147 g (60%) and of acetanilide 0.033 g (24%).

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE 7925017). Partial financial support (to L.E.) from Stiftelsen Blanceflor-Boncompagnie-Ludovisi and Signeuls Fond is also gratefully acknowledged.

---

(43) A. Darapsky, *J. Prakt. Chem.*, **96**, 251 (1917).

(44) L. Engman and M. P. Cava, *Organometallics*, 1, 470 (1982).

Registry No. 1, 82093-37-6; **2**, 66697-24-3; **3**, 7475-56-1; **4**, 82093-38-7; **5**, 16222-10-9; **7**, 5326-87-4; **8**, 82093-39-8; **11**, 94-41-7; **12**, 4198-15-6; $NaBH_4$, 16940-66-2; 4-bromophenacyl bromide, 99-73-0; 2-bromocholestan-3-one, 22164-15-4; α-bromophenylacetic acid, 4870-65-9; sodium 2-thiophenetellurolate, 82093-40-1; thiophene, 110-02-1; butyllithium, 109-72-8; tellurium, 13494-80-9; phenacyl chloride, 532-27-4; phenacyl bromide, 70-11-1; phenacyl iodide, 4636-16-2; phenacyl acetate, 2243-35-8; phenacyl mesylate, 20187-61-5; desyl chloride, 447-31-4; α-bromo-1-naphthylacetic acid, 72191-56-1; acetophenone, 98-86-2; *p*-bromoacetophenone, 99-90-1; desoxybenzoin, 451-40-1; cholestan-3-one, 15600-08-5; 3-methyl-1-indanone, 6072-57-7; acetanilide, 103-84-4; phenylacetic acid, 103-82-2; 1-naphthylacetic acid, 86-87-3; diphenylacetic acid, 117-34-0; benzaldehyde, 100-52-7.

Arenes Disubstituted with Primary Alkyl Groups from Xylylene Dianions

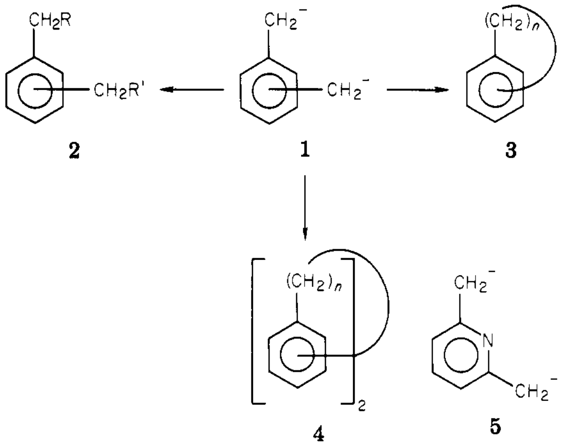
Robert B. Bates* and Craig A. Ogle

Department of Chemistry, University of Arizona, Tucson, Arizona 85721

Received February 8, 1982

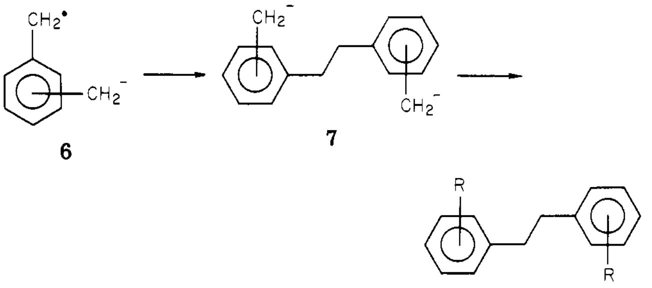
Xylenes were converted into dianions 1. Reaction of dianions 1 with dialkyl sulfates gave symmetrical dialkylbenzenes 2 ($R = R'$), while methyl iodide caused oxidative coupling followed by alkylation to give 8. Unsymmetrical dialkylbenzenes 2 ($R \neq R'$) were made by an indirect route involving monoanions 9 and 11. Reactions of dianions 1 with dihalides gave [*n*]cyclophanes *o*-3 (*n* = 5, 6, 9), *m*-3 (*n* = 8–10), and *p*-3 (*n* = 9–11) and [*n.n*]cyclophanes *o*-4 (*n* = 2, 5, 7, 9) and *m*-4 (*n* = 2, 6, 7). Dianion 5 from 2,6-lutidine was used to prepare nitrogen analogues of 2 ($R = R'$) and *m*-3 (*n* = 8–10).

Benzenes **2–4**, disubstituted with primary alkyl groups, are quite difficult to prepare due to limitations in the Friedel–Crafts alkylation with primary halides.[1] We report simple preparations of many such compounds in two steps from the corresponding xylene via the readily prepared[2] dianions **1**. Some analogous reactions of new pyridine-containing dianion **5** are also presented.



2 **1** **3** **4** **5**

Symmetrical Dialkylation Products 2 (R = R′). Reaction of the disodium salt of *m*-**1** with excess methyl iodide was reported to give *m*-diethylbenzene (*m*-**2**, $R = R' = Me$) as the major product by GC and NMR analyses.[2a] With the more ionic dipotassium salt of *p*-**1** and excess methyl iodide, we obtained almost none of the desired *p*-diethylbenzene (*p*-**2**, $R = R' = Me$) but instead a 72% yield (based on *p*-xylene, thus nearly quantitative based on dianion *p*-**1**[3]) of *p*-**8** (R = Et), presumably formed by a one-electron oxidation (to *p*-**6**)–dimerization (to *p*-**7**)–dialkylation sequence.[4] *o*-Xylene and *m*-xylene gave the analogous dimeric products *o*-**8** (R = Et, 53%) and *m*-**8** (R = Et, 41%), along with the corresponding diethylbenzenes *o*-**2** ($R = R' = Me$, 42%) and *m*-**2** ($R = R' = Me$, 55%). Such electron transfers to methyl iodide have been previously observed with carbanions which are sufficiently good reducing agents;[5] apparently *p*-**1**, with the lowest calculated resonance energy of the three isomeric dianions,[2b–d] is also the best reducing agent.[6]



6 **7** **8**

Dimeric products **8** were avoided by using dialkyl sulfates as the alkylating agents. With dimethyl sulfate, *p*-xylene was converted into *p*-diethylbenzene (*p*-**2**, $R = R' = Me$) in 63% yield and with diethyl sulfate into *p*-di-*n*-propylbenzene (*p*-**2**, $R = R' = Et$) in 65% yield.

---

(1) Price, C. *Org. React.* **1946**, *3*, 1.

(2) (a) Trimitsis, G. B.; Tuncay, A.; Beyer, R. D.; Ketterman, K. J. *J. Org. Chem.* **1973**, *38*, 1491. (b) Klein, J.; Medlik, A.; Meyer, A. Y. *Tetrahedron* **1976**, *32*, 51. (c) Klein, J.; Medlik-Balan, A. *J. Am. Chem. Soc.* **1977**, *99*, 1473. (d) Bates, R. B.; Hess, B. A., Jr.; Ogle, C. A.; Schaad, L. *Ibid.* **1981**, *103*, 5052.

(3) While *o*-1 and *m*-1 are produced essentially quantitatively from the corresponding xylenes, the *p*-1 used in this work was formed in about 70% yield from *p*-xylene.[2d]

(4) An alternate route to *p*-7 involving addition of dianion *p*-1 to *p*-xylene is rendered less likely by the finding that *m*-xylene, whose intermediate *m*-xylylene is *much* less stable (Pollack, S.; Raine, B.; Hemre, W. *J. Am. Chem. Soc.* **1981**, *103*, 6308) and would presumably give other products, goes to *m*-8 in only slightly diminished yield.

(5) Bahl, J.; et al. *J. Am. Chem. Soc.* **1977**, *99*, 6126.

(6) Bordwell, F.; Clemens, A. *J. Org. Chem.* **1981**, *46*, 1035.

0022-3263/82/1947-3949$01.25/0

Table I. Yields (in Percent) of 3 and 4

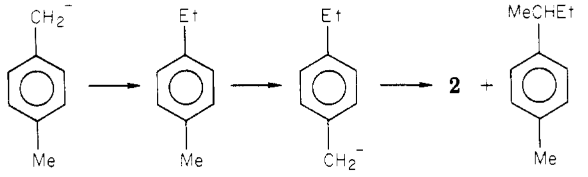
	o		*m*		*p*	
n	3	4	3	4	3	4
2[a]	0	40		25		0
3	0					
4[b]	0					
5	11	6	0	0		
6	7	0	0	8		
7	0	3	trace	2		
8	0	0	10		0	
9	7	9	26		5	
10			27		7	
11					7	

[a] I_2 used as dihalide. [b] Ethylene dibenzenesulfonate instead of dihalide.

Dianion **5** was formed in at least 85% yield by dimetalation of 2,6-lutidine, on the basis of its reaction with dimethyl sulfate which gave 2,6-diethylpyridine in 85% overall yield. Other lutidines were not investigated.

Unsymmetrical Dialkylation Products 2 (R ≠ R′). Attempts to sequentially alkylate *p*-**1** with two different alkylating agents failed to give unsymmetrical products **2** (R ≠ R′) but instead gave mixtures of the symmetrical products **2** (R = R′). We think the problem to be the very low solubility of the dipotassium salt of the dianion **1** relative to the monoanion intermediate; even though the dipotassium salt **1** is more reactive, it does not compete successfully for alkylating agent with the much more soluble monoanion intermediate.

An indirect approach to unsymmetrical products **2** (R ≠ R′), involving two monoanion intermediates rather than a dianion intermediate, was found to be feasible. Thus, *p*-xylene was converted into *p*-propylethylbenzene (*p*-**2**; R = Me, R′ = Et) by monometalation to **9** followed by methylation to **10** (80%), selective metalation on the methyl group to **11**, and ethylation to *p*-**2** (R = Me, R′ = Et;[7] 92%, accompanied by 2% of **12**).

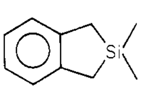


9 **10** **11** **12**

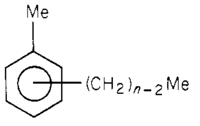
[*n*]Cyclophanes (3) and [*n*.*n*]Cyclophanes (4). The reactions of dianions **1** with α,ω-dihalides provide obvious routes to cyclophanes **3** and **4** which are in most cases simpler than previously used methods.[8-10] As we could not find a nonreacting solvent for the dianion salts, a solution containing the dihalide (dibromide except where noted) was added slowly to a stirred suspension of the dianion salt; the very low solubility of the dianion salt compared to the monoanion salt formed on initial reaction with the dihalide presumably helped to reduce polymer formation.

Table I shows yields of cyclophanes **3** and **4** by this route. For the *n* = 2 cases, the dihalide was simply iodine, and the reactions provide excellent routes to [2.2]orthocyclophane (*o*-**4**, *n* = 2) and [2.2]metacyclophane (*m*-**4**, *n* = 2). Attempts to obtain the corresponding para isomer (*p*-**4**, *n* = 2) gave only polymer, and no benzocyclobutene (*o*-**3**, *n* = 2), *o*-xylylene, or *p*-xylylene was found either in these iodine oxidations or in oxidations with ethylene dibromide.

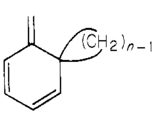
Methylene iodide gave no indan (*o*-**3**, *n* = 3) when reacted with *o*-**1**,[11] but dimethyldichlorosilane gave a 70% yield of the analogous product **13**.[12] Since ethylene dibromide acts as an oxidant in reactions with easily oxidized dianions such as **1**,[13] ethylene dibenzenesulfonate was tried instead with *o*-**1**, but no tetralin (*o*-**3**, *n* = 4) was observed.



13



14



15

The [*n*]orthocyclophanes (*o*-**3**)[8] with *n* = 5, 6, and 9 were prepared in 7–11% yield by this approach, but surprisingly none of the corresponding products with *n* = 7 and 8 were found. The [*n*]metacyclophanes (*m*-**3**)[9] with *n* = 5 and 6 were not found although they are known,[9d,f] but with *n* = 7 ~1% was formed, and with *n* = 8–10, the yields were much better. None of the [*n*]paracyclophane (*p*-**3**)[10] with *n* = 8 was observed, but with *n* = 9–11 the compounds were readily prepared by this route. Though the yields of these [*n*]cyclophanes are low, these are the shortest routes to them.

A type of byproduct observed to accompany the [*n*]ortho- and [*n*]paracyclophanes **3** but not the corresponding meta isomers was the reduction product **14**. Its failure to form in the meta case could be due to the inability of the meta isomers to form spiro structures such as **15**, which may thermally decompose to diradicals which abstract two hydrogen atoms, giving **14**.

The [*n*.*n*]orthocyclophanes (*o*-**4**) with *n* = 5, 7, and 9 and the corresponding meta isomers with *n* = 6 and 7 were obtained as crystalline substances in the indicated yields. These dimeric substances were not looked for in the higher meta cases or in the para cases (except for *n* = 2 [10b,e,h]) but were probably present. These are the shortest synthetic routes to the [*n*.*n*]cyclophanes.

Reaction of 2,6-lutidine-derived dianion **5** with iodine or ethylene dibromide failed to produce observable amounts of [2.2](2,6)-pyridinophane **16**.[14] This dianion reacted as expected with the appropriate α,ω-dihalides to produce **17** (*n* = 8–10; 5%, 9%, and 9% yields).[9e]

Attempts were also made to make [2.*n*]paracyclophanes from dianion *p*-**7**, in which a two-carbon bridge is already present. We were unable to generate dianion *p*-**7** in high concentration by reaction of *p*-**1** with an appropriate amount of oxidant, so we attempted its preparation by

---

(7) Pines, H.; Schaap, L. *J. Am. Chem. Soc.* **1958**, *80*, 3076.

(8) (a) Plattner, P. *Helv. Chim. Acta* **1944**, *27*, 801. (b) Cope, A.; Fenton, S. *J. Am. Chem. Soc.* **1951**, *73*, 1668. (c) Cram, D.; Allinger, N. *Ibid.* **1956**, *78*, 2518. (d) Dale, J.; Hubert, A.; King, G. *J. Chem. Soc.* **1963**, 73. (e) Markl, G.; Fuchs, R. *Tetrahedron Lett.* **1972**, 4695. (f) Anastassiou, A.; Libsch, S.; Griffith, R. *Ibid.* **1973**, 3103. (g) Hiyama, T.; Ozaki, Y.; Nozaki, H. *Tetrahedron* **1974**, *30*, 2661.

(9) (a) Lindsay, W.; et al. *J. Am. Chem. Soc.* **1961**, *83*, 943. (b) Marchesini, A.; et al. *Tetrahedron Lett.* **1971**, 671. (c) Fujita, S.; Hirano, S.; Nozaki, H. *Ibid.* **1972**, 403. (d) Hirano, S.; et al. *Tetrahedron* **1975**, *31*, 2219. (e) Tamao, K.; et al. *J. Am. Chem. Soc.* **1975**, *97*, 4405. (f) van Straten, J.; de Wolf, W.; Bickelhaupt, F. *Tetrahedron Lett.* **1977**, 4667. (g) Otsubo, T.; Misumi, S. *Synth. Commun.* **1978**, *8*, 285. (h) Turkenburg, L.; et al. *J. Am. Chem. Soc.* **1980**, *102*, 3256.

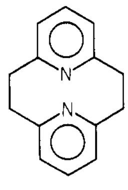
(10) (a) Cram, D.; Goldstein, M. *J. Am. Chem. Soc.* **1963**, *85*, 1063. (b) Cram, D.; Cram, J. *Acc. Chem. Res.* **1971**, *4*, 204. (c) Wolf, A.; et al. *J. Am. Chem. Soc.* **1973**, *95*, 1680. (d) Kane, V.; Wolf, A.; Jones, M. *J. Am. Chem. Soc.* **1974**, *96*, 2643. (e) Kaplan, M.; Truesdale, E. *Tetrahedron Lett.* **1976**, 3665. (f) Kammula, S.; et al. *J. Am. Chem. Soc.* **1977**, *99*, 5815. (g) Gassman, P.; Bailey, T.; Hoye, R. *J. Org. Chem.* **1980**, *45*, 2923. (h) Boekelheide, V. *Acc. Chem. Res.* **1980**, *13*, 65. (i) Kaneda, T.; et al. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1015.

(11) Small amounts of oxidation product *o*-4 (*n* = 2) were obtained in this reaction.

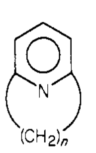
(12) Vdovin, V.; et al. *Dokl. Akad. Nauk SSSR* **1964**, *154*, 383. Eismont, M.; Traven, V.; Stepanov, B. *Zh. Obshch. Khim.* **1979**, *49*, 950.

(13) Bahl, J.; et al. *J. Org. Chem.* **1976**, *41*, 1620.

(14) Baker, W.; et al. *J. Chem. Soc.* **1958**, 3594.

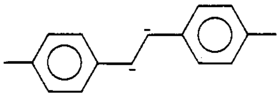


16

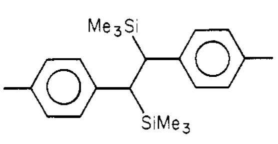


17

dimetalation of *p*-8 (R = Me). This dimetalation went in 67% yield based on quenching with trimethylsilyl chloride to *p*-8 (R = Me_3SiCH_2); also formed (9%) is the stilbene-type dianion 18, as indicated by the 19 obtained in the



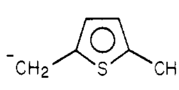
18



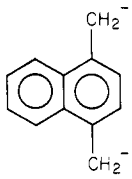
19

quench. Oxidation of the mixture of dianions *p*-7 and 18 produced none of the desired [2.2]paracyclophane (*p*-4, *n* = 2) but instead polymer and (*Z*)- and (*E*)-4,4′-dimethylstilbenes. With trimethylene dibromide, the dianion mixture gave none of the desired [2.5]paracyclophane.

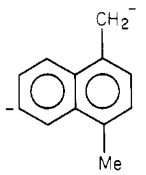
Attempts to extend this method of dianion preparation to the previously unprepared 20[15] and 21[2a] failed. In the



20



21



22

case of 20, ring opening appeared to be occurring,[15b] and in the case of 21, monometalation was the major reaction (~70%), with 22 (~15%) being the only dimetalation product observed (D_2O quench).

Experimental Section

NMR spectra were recorded at 60 MHz on a Varian EM-360L spectrometer and at 250 MHz on a Bruker WM-250 spectrometer. Chemical shifts are reported in parts per million downfield from tetramethylsilane. Mass spectra were recorded on a Varian MAT 311A spectrometer equipped with a Varian SS 200 data system. Melting points were uncorrected. Elemental analyses of liquids were performed by Industrial Testing Laboratories, Inc., St. Louis, MO, and of solids by the University of Arizona Analytical Center, Tucson, AZ.

Volatile products were isolated and purified by gas chromatography with a Varian Aerograph Model 700, equipped with a 6 ft × 0.25 in. column packed with either 10% UCON LB550X or 10% Se-30 on Chromosorb P.

Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone. Pentane and hexane were washed with sulfuric acid, distilled from $LiAlH_4$, and stored over CaH_2. A solution of *n*-butyllithium in hexane (1.4–2.4 M) was used as received from the Alfa Division of Ventron Corp.; potassium *tert*-butoxide was used as received from Aldrich Chemical Co.; all other reagents were purified by standard methods. All glassware used in anion preparation was dried for several h at 200 °C before use. Anion preparation and reaction were carried out under positive argon pressure. All carbanion transfers were done via syringe or cannula.

Dianions 1 and 5. In a 250-mL round-bottomed flask with a serum-capped side arm, 2.4 g (22 mmol) of potassium *tert*-butoxide and 1.2 mL (10 mmol) of *o*-xylene were added to 50 mL of hexane. The system was equipped with a condenser and magnetic stir bar and serum capped. On addition of 9.2 mL of 2.4 M *n*-butyllithium (22 mmol), a red-orange precipitate formed immediately. The suspension was allowed to reflux under argon for 1 h and was cooled to room temperature before the anion (*o*-1, 100% yield) was filtered and rinsed with pentane. *m*-1 (bright yellow, 100% yield), *p*-1 (dark red, 70% yield), and 5 (olive green, 85% yield) were prepared analogously.

Reactions of Dianions 1 with Methyl Iodide. *p*-Xylylene dianion (*p*-1, 10 mmol) was suspended in 50 mL of pentane and cooled to 0 °C. To the vigorously stirred suspension was slowly added 5.0 mL (40 mmol) of methyl iodide. The solution was washed several times with water and dried over magnesium sulfate, the solvent was evaporated and the residue was distilled (bulb to bulb). The product (*p*-8, R = Et: mp 60 °C, 72% yield) was recrystallized from low-boiling petroleum ether: ^1H NMR ($CDCl_3$) δ 1.25 (*t*, 6 H), 2.65 (q, 4 H), 2.9 (s, 4 H), 7.2 (s, 8 H). Anal. Calcd for $C_{18}H_{22}$: C, 90.7; H, 9.3. Found: C, 90.1; H, 9.2.

Dianion *o*-1 similarly gave *o*-8 (R = Et): mp 28–29 °C; 53%; ^1H NMR (CCl_4) δ 1.23 (t, 6 H), 2.63 (q, 4 H), 2.84 (s, 4 H), 7.05 (s, 8 H). Anal. Calcd for $C_{18}H_{22}$: C, 90.7; H, 9.3. Found: C, 90.5; H, 9.6.

Dianion *m*-1 gave *m*-8 (R = Et): mp 29–31 °C; 41%; ^1H NMR (CCl_4) δ 1.23 (t, 6 H), 2.63 (q, 4 H), 2.84 (s, 4 H), 7.05 (s, 8 H). Anal. Calcd for $C_{18}H_{22}$: C, 90.7; H, 9.3. Found: C, 90.5; H, 9.5.

Reactions of Dianions 1 and 5 with Dimethyl Sulfate and Diethyl Sulfate. To a suspension of dianion *p*-1 (10 mmol) in 50 mL of hexane was added excess dimethyl sulfate (4 mL). The suspension was then refluxed under argon until the anion color disappeared. Excess dimethyl sulfate was destroyed by adding 50 mL of 20% NaOH/ethanol solution and refluxing for 3 h. The solution was washed with water and dried over magnesium sulfate, the solvent was fractionally distilled off, and the residue was bulb to bulb distilled. *p*-Diethylbenzene (63% yield) was separated from *p*-ethyltoluene (27% yield) by GC.

Reaction of dianion *p*-1 with diethyl sulfate was done analogously, giving *p*-dipropylbenzene in 61% yield.

Dianion 5 with dimethyl sulfate gave 2,6-diethylpyridine (85% yield).

***p*-Methylbenzyl Anion 9.** In a 250-mL round-bottomed flask equipped a with serum-capped side arm and magnetic stir bar, 5.6 g (50 mmol) potassium *tert*-butoxide and 8 mL (67 mmol) *p*-xylene were added to 50 mL of pentane. The system was charged with argon and stirred while 21 mL of 2.4 M *n*-BuLi in hexane (50 mmol) was added. The red suspension was stirred for 1 h. The anion was filtered, rinsed with pentane, and dissolved in 100 mL of THF for further reaction.

***p*-Ethylbenzyl anion** 11 was prepared by dropwise addition of 4.5 mL of 2.4 M *n*-butyllithium (10.8 mmol) to 1.4 mL (10 mmol) *p*-ethyltoluene (**10**, obtained by quenching **9** with dimethyl sulfate) and 1.1 g potassium *tert*-butoxide in 50 mL of pentane, which was stirred at 0 °C under argon in a 250-mL round-bottomed flask equipped with a serum capped side arm. The orange-red precipitate darkened on stirring for 1 h at 25 °C. The anion was filtered and rinsed with pentane. The yield of anion was 92% based on quench products.

***p*-Propylethylbenzene (*p*-2; R = Me, R′ = Et).** Compound 11 (10 mmol) in 75 mL of THF was stirred at 0 °C while 2.2 mL (15 mmol) of diethyl sulfate was added. When the anion color was gone, 25 mL of 10% sodium hydroxide in ethanol was added and the solution refluxed for 3 h. After the mixture was washed with saturated ammonium chloride and dried over magnesium sulfate, the solvent was removed by distillation, and the residue was bulb to bulb distilled. The yield of *p*-(*n*-propyl)ethylbenzene was 92%.

Reactions of 1 and 5 with α,ω-Dihalides. The carbanion (10 mmol) after being rinsed with pentane, was suspended in 250 mL of THF at −78 °C. The dihalide was dissolved in 50 mL of THF and added dropwise at a rate of 15 mL/h to the rapidly stirred dianion. After addition was complete, the reaction was allowed to warm to room temperature. When the anion color disappeared, the solution was washed with saturated ammonium chloride and dried over magnesium sulfate, THF was removed by distillation, and the residue was dissolved in petroleum ether and the mixture cooled, causing the dimers to crystallize out. The ether was removed, the residue was bulb to bulb distilled, and the product was purified by GC.

---

[15] (a) Clarke, A.; McNamara, S.; Meth-Cohn, O. *Tetrahedron Lett.* **1974**, 2373. (b) Gronowitz, S.; Frejd, T. *Acta Chem. Scand., Ser. B* **1975**, *B29*, 818.

***o*-3 (*n* = 5):**[8a] ^{1}H NMR ($CDCl_3$) δ 1.4–1.9 (m, 6 H), 2.7–2.9 (m, 4 H), 7.1 (s, 4 H).

***o*-3 (*n* = 6):**[8c,e] ^{1}H NMR ($CDCl_3$) δ 1.2–1.9 (m, 8 H), 2.8 (t, 4 H), 7.1 (s, 4 H).

***o*-3 (*n* = 9):**[8g] ^{1}H NMR ($CDCl_3$) δ 1.1–2.0 (m, 14 H), 2.78 (t, 4 H), 7.2 (s, 4 H).

***o*-4 (*n* = 2):**[8b] mp 105–108 °C (lit.[8b] 109–110 °C); ^{1}H NMR ($CDCl_3$) δ 3.03 (s, 8 H), 6.92 (s, 8 H).

***o*-4 (*n* = 5):** mp 157–160 °C; mass spectrum, *m/e* 292.2183, calcd for $C_{22}H_{28}$ 292.2191; ^{1}H NMR ($CDCl_3$) δ 1.5–2.1 (m, 12 H), 2.4–2.9 (m, 8 H), 7.1 (s, 8 H).

***o*-4 (*n* = 7):** mp 111–114 °C: mass spectrum, *m/e* 348.2830, calcd for $C_{26}H_{36}$ 348.2817; ^{1}H NMR ($CDCl_3$) δ 1.2–1.9 (m, 20 H), 2.4–2.9 (m, 8 H), 7.2 (br s, 8 H).

***o*-4 (*n* = 9):** mp 89–91 °C: mass spectrum, *m/e* 404.3451, calcd for $C_{30}H_{44}$ 404.3443; ^{1}H NMR ($CDCl_3$) δ 1.2–1.9 (m, 28 H), 2.4–2.8 (8 H), 7.2 (s, 8 H).

***m*-3 (*n* = 8):**[9e] ^{1}H NMR ($CDCl_3$) δ 0.45–0.90 (m, 4 H), 1.0–1.8 (m, 8 H), 2.62 (t, 4 H), 6.8–7.3 (m, 4 H).

***m*-3 (*n* = 9):**[9b,e] ^{1}H NMR ($CDCl_3$) δ 0.7–1.4 (m, 10 H), 1.4–1.9 (m, 4 H), 2.7 (t, 4 H), 6.8–7.3 (m, 4 H).

***m*-3 (*n* = 10):**[9d,e,g] ^{1}H NMR ($CDCl_3$) δ 0.93 (m, 4 H), 1.10 (m, 4 H), 1.18 (p, 4 H), 1.66 (p, 4 H), 2.64 (p, 4 H), 6.98 (d, 1 H), 7.11 (s, 2 H), 7.21 (t, 2 H).

***m*-4 (*n* = 2):**[9a] mp 131–132 °C (lit.[9a] mp 132.5–133 °C); ^{1}H NMR ($CDCl_3$) δ 1.95–3.25 (m, 8 H), 4.28 (m, 2 H), 6.9–7.3 (m, 6 H).

***m*-4 (*n* = 6):** mp 88–90 °C; mass spectrum, *m/e* 320.3; ^{1}H NMR ($CDCl_3$) δ 1.1–1.8 (m, 16 H), 2.58 (t, 8 H), 6.8–7.3 (m, 8 H). Anal. Calcd for $C_{24}H_{32}$: C, 89.94; H, 10.06. Found: C, 89.90; H, 10.10.

***m*-4 (*n* = 7):** mp 83–86 °C; mass spectrum, *m/e* 348.2834, calcd for $C_{26}H_{36}$ 348.2817; ^{1}H NMR ($CDCl_3$) δ 0.9–1.9 (m, 20 H), 2.53 (t, 8 H), 6.8–7.25 (m, 8 H).

***p*-3 (*n* = 9):**[9g,10a,i] ^{1}H NMR ($CDCl_3$) δ 0.31 (p, 4 H), 0.62 (p, 2 H), 0.95 (p, 4 H), 1.42 (p, 4 H), 2.59 (t, 4 H), 7.12 (s, 4 H).

***p*-3 (*n* = 10):**[9g,10a,i] ^{1}H NMR ($CDCl_3$) δ 0.52 (p, 4 H), 0.73 (p, 4 H), 1.12 (p, 4 H), 1.58 (p, 4 H), 2.63 (t, 4 H), 7.12 (s, 4 H).

***p*-3 (*n* = 11):**[9g,10i] ^{1}H NMR ($CDCl_3$) δ 0.55 (m, 2 H), 0.78 (m, 8 H), 1.15 (p, 4 H), 1.53 (p, 4 H), 2.60 (t, 4 H), 7.04 (s, 4 H).

17 (*n* = 8):[9e] ^{1}H NMR ($CDCl_3$) δ 1.01 (m, 4 H), 1.40 (m, 4H), 1.81 (p, 4 H), 2.86 (t, 4 H), 6.80 (d, 2 H), 7.48 (t, 1 H).

17 (*n* = 9):[9e] ^{1}H NMR ($CDCl_3$) δ 0.93 (p, 4 H), 1.26 (m, 6 H), 1.89 (p, 4 H), 2.83 (t, 4 H), 6.90 (d, 2 H), 7.44 (t, 1 H).

17 (*n* = 10):[9e] ^{1}H NMR ($CDCl_3$) δ 1.27 (br s, 8 H), 1.35 (t, 4 H), 1.82 (p, 4 H), 2.84 (t, 4 H), 6.92 (d, 2 H), 7.48 (t, 1 H).

1,1-Dimethyl-1-silabenzo[*c*]cyclopentene (13). To a 250-mL round-bottomed flask containing 10 mmol of *o*-xylene dianion (*o*-1) suspended in 150 mL of pentane was added 1.2 mL (10 mmol) dichlorodimethylsilane via syringe with stirring. When the anion color disappeared, the solution was washed with water and dried over magnesium sulfate. The pentane was removed by distillation, the residue was distilled (bulb to bulb), and the product was purified by GC. The liquid 13 was obtained: 70% yield; ^{1}H NMR ($CDCl_3$) δ 0.38 (s, 6 H), 2.15 (s, 4 H), 7.1–7.5 (m, 4 H). Anal. Calcd for $C_8H_{14}Si$: C, 74.07; H, 8.64. Found: C, 74.05; H, 8.50.

1,2-Di-*p*-tolylethane was prepared by adding with stirring 50 mmol of *p*-methylbenzyl anion 9 slurried in 100 mL of THF to 6.4 g (25 mmol) of iodine in 100 mL of THF in a 250-mL round-bottomed flask, serum capped under argon. Ether (50 mL) was added, the solution was washed with saturated ammonium chloride followed by saturated sodium bisulfite and dried over magnesium sulfate, and the solvent was evaporated. The product (70%), after bulb to bulb distillation (180 °C, 2 mm) and recrystallization from low-boiling ether, had the following: 77–79 °C; ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 6 H), 2.85 (s, 4 H), 7.12 (s, 8 H).

Dianion *p*-7 was prepared by addition of 4.5 mL of 2.4 M *n*-butyllithium in hexane with stirring to 1,2-di-*p*-tolylethane (1 g, 4.76 mmol) and potassium *tert*-butoxide (1.1 g, 9.8 mmol) in 25 mL of pentane in a 250-mL round-bottomed flask equipped with a serum-capped side arm under argon at 0 °C. A dark red precipitate formed immediately. The reaction mixture was stirred at room temperature for 1 h, filtered, and rinsed with pentane. The dianion mixture was dissolved in 60 mL of THF for further reaction. The yields based on the quench products below were 67% for *p*-7 and 9% for 18.

Reaction of Dianion *p*-7 with Chlorotrimethylsilane. The above mixture of dianions *p*-7 and 18 in THF was stirred while excess chlorotrimethylsilane (2 mL) was added. The red anion color disappeared immediately. The solution was washed with saturated ammonium chloride and dried over magnesium sulfate. Volatiles were evaporated off, and the products were separated by fractional crystallization from ether.

p-8 (R = Me_3SiCH_2): mp 54–55 °C; ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 18 H), 2.13 (s, 4 H), 2.9 (s, 4 H), 7.05 (s, 8 H). Anal. Calcd for $C_{22}H_{34}Si_2$: C, 74.58; H, 9.60. Found: C, 74.30; H, 9.80.

19 (presumably meso from steric considerations): mp 210–212 °C; ^{1}H NMR ($CDCl_3$) δ −0.45 (s, 18 H), 2.30 (s, 6 H), 2.65 (s, 2 H), 7.05 (s, 8 H). Anal. Calcd for $C_{22}H_{34}Si_2$: C, 74.58; H, 9.60. Found: C, 74.90; H, 9.60.

Registry No. *o*-1, 59305-41-8; *m*-1, 59305-39-4; *p*-1, 59305-43-0; *o*-**3** (*n* = 5), 1075-16-7; *o*-**3** (*n* = 6), 1076-69-3; *o*-**3** (*n* = 9), 54537-92-7; *m*-**3** (*n* = 8), 7048-98-8; *m*-**3** (*n* = 9), 7198-61-0; *m*-**3** (*n* = 10), 7125-13-5; *p*-**3** (*n* = 9), 6787-60-6; *p*-**3** (*n* = 10), 5649-96-7; *p*-**3** (*n* = 11), 7125-19-1; *o*-**4** (*n* = 2), 82639-89-2; *o*-**4** (*n* = 5), 82639-90-5; *o*-**4** (*n* = 7), 82639-91-6; *o*-**4** (*n* = 9), 82639-92-7; *m*-**4** (*n* = 2), 82639-94-9; *m*-**4** (*n* = 6), 82639-95-0; *m*-**4** (*n* = 7), 82639-96-1; **5**, 82639-83-6; *p*-**7**, 82639-86-9; *p*-**8** (R = Et), 51526-06-8; *p*-**8** (R = Me_3SiCH_2), 18816-94-9; *o*-**8** (R = Et), 27499-60-1; *m*-**8** (R = Et), 82639-84-7; **9**, 59305-42-9; 11, 82639-85-8; **13**, 2764-87-6; **17** (*n* = 8), 56912-80-2; **17** (*n* = 9), 56929-81-8; **17** (*n* = 10), 4432-68-2; **18**, 82639-88-1; **19**, 82639-87-0; $Br(CH_2)_3Br$, 109-64-8; $Br(CH_2)_4Br$, 110-52-1; $Br(CH_2)_5Br$, 111-24-0; $Br(CH_2)_6Br$, 629-03-8; $Br(CH_2)_7Br$, 4549-31-9; $Br(CH_2)_8Br$, 4549-32-0; $Br(CH_2)_9Br$, 4549-33-1; $Br(CH_2)_{10}Br$, 4101-68-2; $Br(CH_2)_{11}Br$, 16696-65-4; *o*-xylene, 95-47-6; *m*-xylene, 108-48-5; *p*-xylene, 106-42-3; 2,6 dimethylpyridine, 108-48-5; methyl iodide, 74-88-4; dimethyl sulfate, 77-78-1; diethyl sulfate, 64-67-5; *p*-diethylbenzene, 105-05-5; *p*-diethyltoluene, 622-96-8; *p*-dipropylbenzene, 4815-57-0; 2,6-diethylpyridine, 935-28-4; propylethylbenzene, 20024-90-2; iodine, 7553-56-2; ethylene dibromide, 106-93-4; methylene diiodide, 75-11-6; dimethyldichlorosilane, 75-78-5; ethylene glycol dibenzenesulfonate, 116-50-7.