a small amount of *p*-toluenesulfonic acid. It was considered to be a linear polysalicylide with *p*-toluenesulfonate as terminal group: IR (KBr) 1726, 1596, 1480, 1447, 1372, 1283, 1246, 1197, 1156, 1121, 1045, 744, 686 cm^{-1}. Some other polysalicylides seemed to be present, but only small impure samples could be obtained. Very similar results were obtained after refluxing a sample of **3c** in diglyme for 19 h.

(b) The mass spectrum of **3c** introduced at 300 °C (probe temperature) showed, in agreement with the preceding results, the following peaks: *m/e* (rel abundance) 515 (1), 480 (1), 396 (4), 395 (12), 361 (4), 360 (13), 277 (8), 276 (16), 275 (88), 248 (10), 242 (4), 241 (16), 240 (83), 197 (9), 196 (18), 169 (11), 168 (18), 157 (11), 156 (10), 155 (100), 139 (16), 121 (28), 120 (91), 92 (98), 91 (99), 77 (12), 76 (11), 65 (59), 64 (79), 63 (73).

Attempted Esterification of 2-Furoic Acid with Phenyl *p*-Toluenesulfonate. 2-Furoic acid (0.5 g, 4.46 mmol) and phenyl *p*-toluenesulfonate were mixed and heated under nitrogen at 250 °C for 4 h. After that period, both starting materials were recovered unchanged and the formation of phenyl furoate could not be detected.

Thermolysis of Trisalicylide in the Presence of 2-Furoic Acid. Trisalicylide (0.8 g, 2.2 mmol) and 2-furoic acid (1 g, 8.9 mmol) were mixed and heated under nitrogen at 250 °C for 15 min. The resulting mixture was dissolved in benzene and subjected to column chromatography on silica to give 0.11 g (0.6 mmol, 27%) of phenyl furoate.

The Metal-Ammonia Reduction of Mono- and Dinaphthylbenzenes

Zbigniew Marcinow and Peter W. Rabideau*

Department of Chemistry, Indiana University-Purdue University at Indianapolis, Indianapolis, Indiana 46205

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The metal-ammonia reduction of 1- and 2-phenylnaphthalene (**9** and **10**, respectively), 1,3-bis(1-naphthyl)benzene (**5**), 1,3-bis(2-naphthyl)benzene (**6**), 1,4-bis(1-naphthyl)benzene (**7**), and *m*-quinquephenyl (**8**) has been investigated. **9** affords a mixture of isomeric dihydro products together with 1-phenyl-1,2,3,4-tetrahydronaphthalene, and the effect of metal, temperature, and quenching methods on the product distribution is reported. **10** provided only a single dihydro (1,4-) isomer plus a tetrahydro product. Both **5** and **7** provided a number of dihydro, tetrahydro, hexahydro, and octahydro products. On the other hand, **6** afforded high yields of a single tetrahydro product with lithium, and exclusively an octahydro product when 5–7 mol of sodium was used. In contrast to the terphenyls, which seem to have a propensity for inner-ring reduction, none of the naphthyl benzenes showed any tendency to reduce in the central benzene ring. *m*-Quinquephenyl reduced in two rings with no evidence for reduction in the central or outer rings.

Although the metal-ammonia reduction behavior of a large number of benzene and polynuclear aromatic compounds has been investigated,[1,2] relatively little attention has focused on compounds with multiple aromatic rings connected by active (π) or inactive (CH_2) spacers. One exception is a report on the isomeric terphenyls.[3] *p*-Terphenyl reacts with alkali metals in anhydrous ammonia to provide both central-ring reduction (**1**), and outer-ring reduction (**2**) products. The yield of **1** ranges from ca. 25 to 75% and is largely a function of the particular metal used with the ratio of outer- to inner-ring reduction decreasing in the series Ca > K > Na > Li. On the other hand, the isomeric *m*-terphenyl and *o*-terphenyl provide only central-ring reduction (**3** and **4**, respectively).

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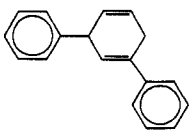

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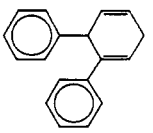

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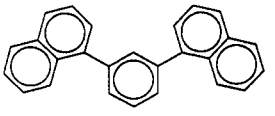
An aim of this study was to learn if the tendency for central-ring reduction, as observed with the terphenyls, would also prevail in multiple ring systems where (a) the outer rings have greater electron affinity (e.g. **5**–**7**) or (b) there are more than three rings (e.g. **8**). However, the investigation of **5**–**7** required a thorough understanding of the reduction behavior of the simpler cases, the isomeric phenylnaphthalenes.

Table I. Metal-Ammonia Reduction of 1-Phenylnaphthalene (9)[a]

			% composition[c]		
entry	metal (mmol)[b]	temp, °C	11	12	13
1	Li (2.5)	-78	34	58	7
2	Li (5)	-78	31	-	69
3	Li (10)	-78	30	-	70
4	Li (10)	-33	30	-	69
5	Na (2.5)	-78	25	69	6
6	Na (5)	-78	28	48	24
7	Na (2.5)	-33	25	53	5
8	Na (10)	-33	26	16	58
9[d]	Na (2.0)	-33	10	30	30

[a] Reactions inverse quenched after 1 h by pumping into aqueous ammonium chloride. [b] Millimoles of metal per millimole of hydrocarbon. [c] By GC; difference from 100% represents unreacted starting material. [d] Results from ref 4.



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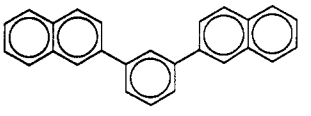

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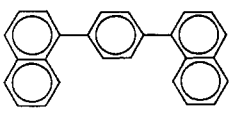

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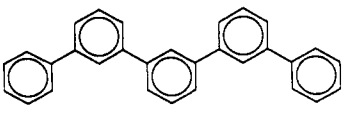

8

(1) Harvey, R. G. *Synthesis* **1970**, *4*, 161.
(2) Rabideau, P. W. *Tetrahedron* **1989**, *45*, 1579.
(3) Harvey, R. G.; Lindow, D. F.; Rabideau, P. W. *J. Am. Chem. Soc.* **1972**, *94*, 5412.

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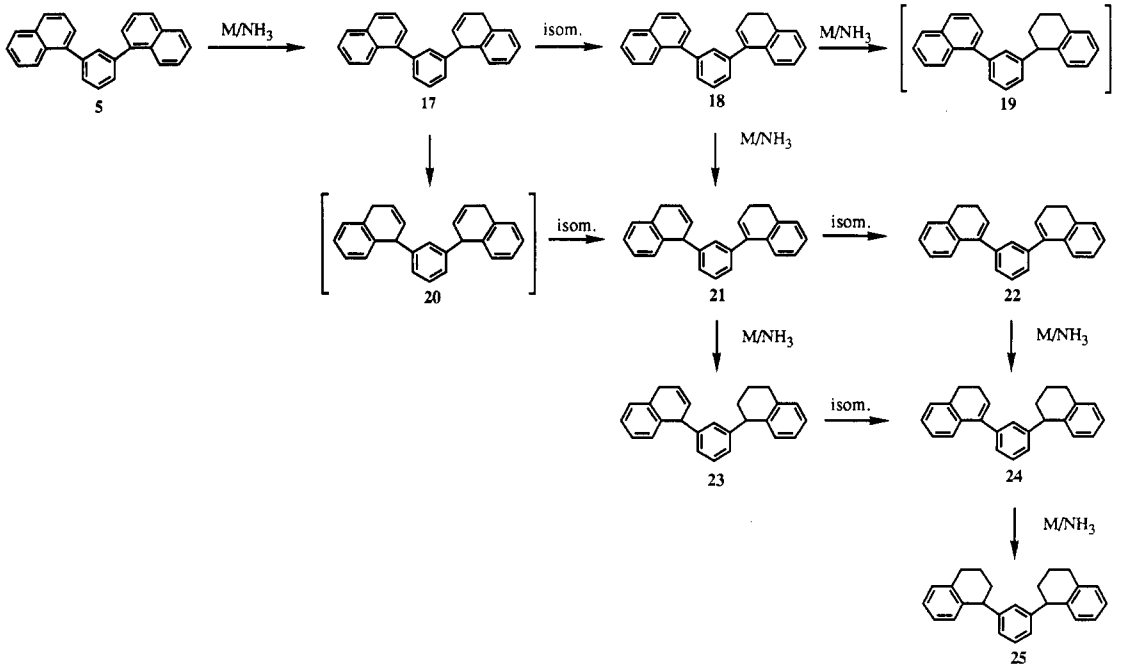
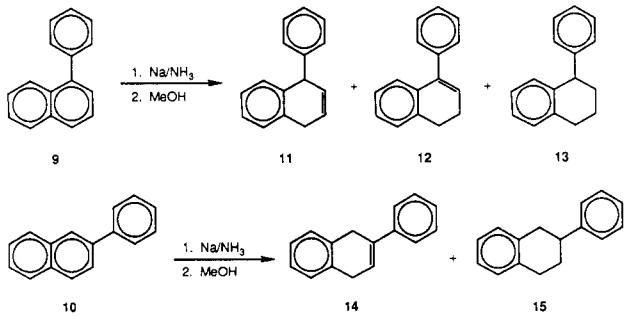
Scheme I



In an earlier study, Eisenbraun et al.[4] reduced 1-phenylnaphthalene (**9**) and 2-phenylnaphthalene (**10**) with 2 mol of Na in ammonia at −33 °C for 45 min followed by a methanol quench. The reduction of **9** produced very little (10%) of the primary product **11**, but rather gave **12**, which results from isomerization (see below) and **13** as the major products (30% each). We repeated this experiment, but with an increase in the amount of metal from 2.0 to 2.5 mol, and with an ammonium chloride quench. This led to increased yields of both **11** and **12** as shown in Table I. However, further increases in the amount of metal produced overreduction, affording **13** as the major product. The reduction of **9** was not sensitive to changes in temperature and metal (sodium or lithium), and this is in contrast to the behavior of naphthalene itself.[5]

The rapid quenching with ammonium chloride employed in this study may be expected to produce somewhat different results from those of the earlier work using methanol. The use of large amounts of metal with a methanol quench would no doubt lead to some reduction in the two remaining aromatic rings, since isolated benzene rings may be reduced during alcohol quenching. However, this is generally not true with ammonium chloride, especially with inverse quenching.



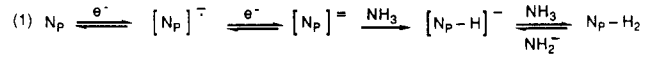
Using the same conditions as for **9**, Eisenbraun et al.[4] found poorer results with the isomeric 2-phenylnaphthalene (**10**); 10% of the tetrahydro isomer **15** was obtained with 90% unreacted **10**. When we repeated this experiment with an increase in metal and an ammonium chloride quench, reasonable yields (up to 76%) of the expected, primary reduction product **14** were obtained. However, in contrast to **11**, **14** may be reduced directly without prior rearrangement if it is formed in the reaction mixture as the neutral hydrocarbon.

Table II. Metal-Ammonia Reduction of 2-Phenylnaphthalene (10)[a]

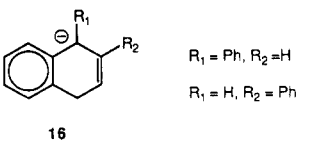
			% composition[c]	
entry	metal (mmol)[b]	temp, °C	14	15
1	Li (5)	−78	59	37
2	Li (10)	−78	31	66
3	Li (10)	−33	2	98
4	Na (2.8)	−33	76	–
5	Na (3.8)	−33	65	29
6[d]	Na (2.0)	−33	–	10

[a] Reactions inverse quenched after 1 h by pumping into aqueous ammonium chloride. [b] Millimoles of metal per millimole of hydrocarbon. [c] By GC; difference from 100% represents unreacted starting material. [d] Results from ref 4.

As illustrated in eq 1, the reduction of naphthalenes[5] (Np) proceeds through a radical anion to a dianion that is too basic to persist in ammonia solution. Protonation of the dianion by ammonia produces a monoanion, **16**, which may also be protonated by ammonia (albeit more slowly) to establish the final equilibrium shown in eq 1.



However, this latter protonation produces a small amount (1–2%) of the 1,2-dihydro product, and in some cases this regioisomer may build up since it is generally not deprotonated under these conditions, i.e., the last step is usually not reversible for this regioisomer. Furthermore, the protonation of **16** is very sensitive to conditions. It has



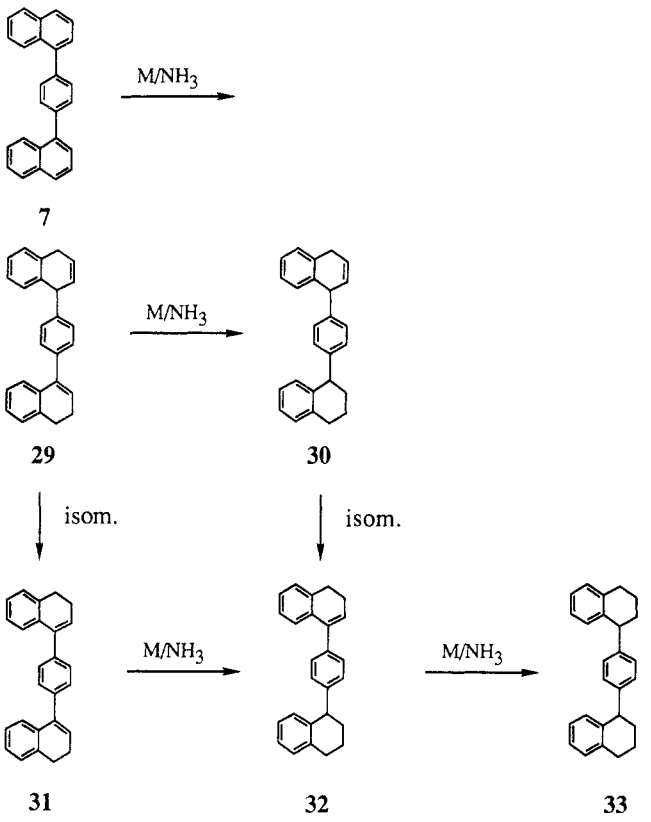
(4) Eisenbraun, E. J.; Melton, R. G.; Flanagan, P. W.; Hamming, M. C.; Keen, G. W. *Prepr. Div. Petrol. Chem., Am. Chem. Soc.* **1971**, *16*, B43.
(5) (a) Rabideau, P. W.; Burkholder, E. G. *J. Org. Chem.* **1978**, *43*, 4283. (b) Rabideau, P. W.; Huser, D. L. *J. Org. Chem.* **1983**, *48*, 4266.

Table III. Metal–Ammonia Reduction of 1,3-Bis(1-naphthyl)benzene (5)[a]

entry	metal (mmol)[b]	temp, °C	% composition[c]							
			17	18	21	22	23	24	25	unident
1	Na (2.5)	-78	18	5	7	6	1	2	2	6
2	Na (5)	-78	3	6	13	28	3	5	10	2
3	Na (2.5)	-33	10	14	1	1	-	1	2	-
4	Na (5)	-33	8	23	20	40	1	1	2	-
5	Na (10)	-33	2	4	14	17	11	30	14	8
6[d]	Na (5)	-33	6	18	21	32	2	7	6	3
7	Li (5)	-33	12	30	8	17	2	6	7	4
8	Li (10)	-33	-	-	-	-	18	46	26	10
9	Li (20)	-33	-	-	-	-	17	7	72	4
10	Li (10)	-78	4	7	22	21	9	17	12	7

[a] Reaction inverse quenched after 1 h by pumping into aqueous ammonium chloride. [b] Millimoles of metal per millimole of hydrocarbon. [c] By GC; difference from 100% represents unreacted starting material. [d] Reaction run for 20 min.

Scheme II

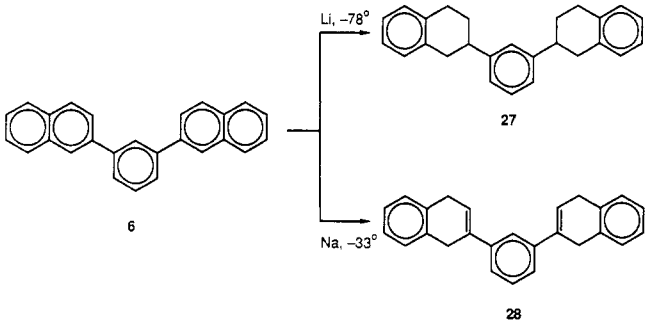


been shown to be favored by lithium over sodium, and by higher temperatures (-33 °C).[5b] Hence excess lithium in ammonia at reflux represents the best conditions for reduction beyond the initial stage, and 2-phenyl-1,2,3,4-tetrahydronaphthalene (**15**) can be produced in 98% yield in this way (Table II).

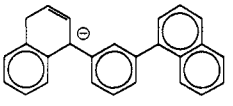
As shown in Scheme I, the reduction behavior of dinaphthylbenzene (**5**) is quite complex although reaction is confined to the naphthalene rings with no evidence of benzene ring reduction. An important question is whether or not the presence of charge in one ring lowers the reactivity of a second, nearby ring. When 5 mol of metal was used (4 mol is necessary for reduction of two rings), the amount of two-ring reduction products (**21–25**) ranged from a high of 87% (Na, -78 °C) to a low of 49% (Li, -33 °C) (see Table III). In fact, with only 2.5 mol of sodium at -78 °C, two-ring reduction amounts to 18% as compared to 23% for one-ring reduction (**17, 18**). Thus a second ring is not deactivated due to the presence of a nearby anion site, an observation consistent with the behavior of 1,2-bis(4-methyl-1-naphthyl)ethane.[6] This may, of course, be a matter of solubility, although enhanced reactivity due to intramolecular electron transfer cannot be ruled out.

Each of the products from **5** may be understood in terms of the observed behavior for 1-phenylnaphthalene; that is, reduction followed by isomerization and then a second reduction. This process appears to occur without synergism in each of the naphthalene rings to provide the array of products shown in Scheme I. As expected, the bistetrahydro product **25** ultimately prevails with Li at -33 °C, and the 72% yield could presumably be increased with more metal and increased reaction time.

The isomer **6**, with the naphthalenes attached through the β position, behaved quite differently, with 10 mol Li at -78 °C, **27** was formed as the exclusive product. This was also true with Na under the same conditions, but the yield was considerably lower (26%). With less Na (5–7 mol) at -33 °C, the bisdihydro product **28** was formed in about 80% yield. Hence **6** has a strong tendency to reduce in both rings.



Of course both **5** and **6** have meta substitution at the benzene ring and in the case of a monoanion such as **26**, this essentially insulates the neutral naphthalene ring from charge delocalization; for this reason, **7** was investigated.



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The behavior of **7** was rather similar to **5**, also an α-phenylnaphthalene, in that a number of double-ring reduced products were detected with various levels of reduction and rearrangement (Scheme II). In contrast to **5**, however, no single-ring reduced products were observed. Once again, an excess of Li at -33 °C produced the bistetrahydro product in good yield (see Table IV).

The reaction of quinquephenyl **8** with 5.5 mol Li at -33 °C produced a tetrahydro isomer ($C_{30}H_{26}$ by mass spec-

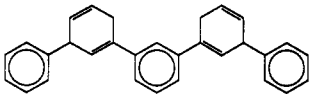
(6) Rabideau, P. W.; Marcinow, Z. *Fuel* **1985**, *64*, 872.

Table IV. Metal–Ammonia Reduction of 1,4-Bis(1-naphthyl)benzene (7)[a]

			% composition[c]				
entry	metal (mmol)[b]	temp, °C	29	30	31	32	33
1	Na (20)	−33	–	22	–	23	51
2	Li (20)	−33	–	16	–	–	84
3	Na (5)	−33	16	2	46	6	13
4	Na (5)	−78	30	1	40	2	6
5	Na (3)	−78	8	1	23	3	4

[a] Reactions inverse quenched after 1 h by pumping into aqueous ammonium chloride. [b] Millimoles of metal per millimole of hydrocarbon. [c] By GC; difference from 100% represents unreacted starting material.

troscopy and elemental analysis) as the major product (65%). Proton NMR showed that the reaction had occurred in a similar way to *m*-terphenyl with central-ring reduction in both *m*-terphenyl moieties, but distinction between isomers **34** and **35** could not be made. However, structure **34** was assigned on the basis of the UV spectrum since the extinction coefficient of $\epsilon = 1.09 \times 10^5$ ($\lambda = 248$ nm) is more consistent with a *m*-divinylbenzene than a styrene. Similar treatment of the isomer **36** did not lead to reduction products perhaps due to its very low solubility.



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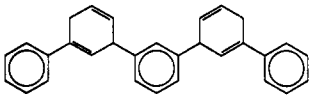

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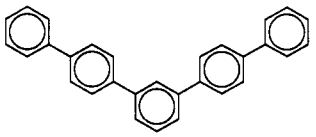

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Conclusion. The aim of this study was to learn if the propensity for inner (central) ring reduction observed for the terphenyls would carry over to other multiple-ring aromatics, and to investigate how reduction of one aromatic unit might affect the reactivity of a second unit in the same molecule. We observed no inner-ring reduction whatsoever in the dinaphthylbenzenes, and we may conclude that the behavior of the terphenyls is not to be expected when the outside rings have greater electron affinity. However, when this is not true (i.e., quinquephenyl), there does seem to be a tendency for products wherein the outer rings are not reduced. We may also conclude that electron addition to a second aromatic ring is not adversely affected by a neighboring anion. In fact, more often than not, both naphthalene rings of the dinaphthylbenzenes were reduced in preference to single-ring reduction. We had reported this earlier for naphthalenes separated by "inert" spacers (CH_2CH_2) as opposed to the active (π) spacers herein.[6]

Experimental Section

Proton NMR spectra were obtained at 90 Mz on a Varian EM-390 or at 300 MHz on a General Electric QE-300 spectrometer. Mass spectra were determined on a HP 5988A GC–MS at an ionization potential of 30 eV. Gas chromatographic analyses were done on a Varian 3700 (fid; split capillary injector) using a 25 m × 0.25 mm OV-17 column. Microanalyses were performed by Galbraith Laboratories, Inc. (although dihydroaromatics tend to be somewhat unstable). THF was distilled from benzophenone ketyl immediately prior to use. 1- and 2-phenylnaphthalene were purchased from Aldrich Chemical Co. 1,3-Bis(1-naphthyl)benzene (**5**), 1,3-bis(2-naphthyl)benzene (**6**), 1,4-bis(1-naphthyl)benzene (**7**) and quinquephenyls (**8**, **36**) were synthesized according to the previously described procedure,[7,8] based on aryl–aryl bond formation via Grignard generation and trapping of arynes.

General Procedures for Metal–Ammonia Reduction. All reactions were carried out under a slight pressure of dry argon. The metal was added in pieces to a solution of reduced compound (0.76 mmol) in 60 mL of ammonia/THF solution (2:1) at reflux (−33 °C) or at −78 °C. After the indicated reaction period, the reaction was quenched by pumping (argon pressure) through a glass tube into a large volume of saturated ammonium chloride. Products were isolated by ether extraction and purified by careful chromatography on 230–400-mesh silica gel (Merck) or (if necessary) silica gel impregnated with 2% THF, with hexane/ethyl acetate (100:1) as a solvent.

Reduction of 1- and 2-Phenylnaphthalene. The metal was added in pieces to a solution of the hydrocarbon (1.25 mmol) in 60 mL of ammonia/THF (2:1). After 1 h, the reaction was inverse quenched into aqueous ammonium chloride solution using argon pressure,[5] and the products were isolated by ether partition. Purification was accomplished by column chromatography, and identification was made by comparison with authentic spectral data.[9] Product analysis is provided in Tables I and II.

1,3-Bis(1-naphthyl)benzene (5) was reduced with lithium or sodium according to the general procedure (see Table III). Analytical samples of the reduction products were obtained by column chromatography.

1-(1-Naphthyl)-3-(3,4-dihydro-1-naphthyl)benzene (18): mp 139–140 °C; NMR (CCl_4) δ 2.38 (m, 2 H), 2.76 (m, 2 H), 6.03 (t, 1 H), 7.03 (s, 4 H), 7.35 (m, 8 H), 7.8 (m, 3 H); GC–MS *m/e* 332 (M^+). Anal. Calcd for $C_{26}H_{20}$: C, 93.94; H, 6.06. Found: C, 93.40; H, 6.05.

1-(1,4-Dihydro-1-naphthyl)-3-(3,4-dihydro-1-naphthyl)benzene (21): oil; NMR (CCl_4) δ 2.36 (m, 2 H), 2.75 (m, 2 H), 3.40 (m, 2 H), 4.53 (m, 1 H), 5.90 (m, 3 H), 7.0 (m, 12 H); GC–MS *m/e* 334 (M^+). Anal. Calcd for $C_{26}H_{22}$: C, 93.37; H, 6.63. Found: C, 93.64; H, 6.55.

1,3-Bis(3,4-dihydro-1-naphthyl)benzene (22): mp 68–70 °C; NMR (CCl_4) δ 2.30 (m, 4 H), 2.70 (m, 4 H), 5.97 (t, 2 H), 6.97–7.20 (m, 12 H); GC–MS *m/e* 334 (M^+). Anal. Calcd for $C_{26}H_{22}$: C, 93.37; H, 6.63. Found: C, 93.48; H, 6.71.

1-(1,4-Dihydro-1-naphthyl)-3-(1,2,3,4-tetrahydro-1-naphthyl)benzene (23): oil; NMR ($CDCl_3$) δ 1.56–2.15 (m, 4 H), 2.77 (t, 2 H), 3.40 (m, 2 H), 4.0 (M, 1 H), 4.50 (m, 1 H), 5.90 (br s, 2 H), 7.0 (m, 12 H); GC–MS *m/e* 336 (M^+). Anal. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19. Found: C, 92.95; H, 7.17.

1-(3,4-Dihydro-1-naphthyl)-3-(1,2,3,4-tetrahydro-1-naphthyl)benzene (24): oil; NMR (CCl_4) δ 1.60–2.13 (m, 4 H), 2.30 (m, 2 H), 2.70 (m, 4 H), 4.00 (m, 1 H), 5.90 (m, 1 H), 6.97 (m, 12 H); GC–MS 336 (M^+). Anal. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19. Found: C, 92.68; H, 7.04.

1,3-Bis(1,2,3,4-tetrahydro-1-naphthyl)benzene (25): oil; NMR ($CDCl_3$) δ 1.60–2.20 (m, 8 H), 2.77 (m, 4 H), 4.0 (t, 2 H), 6.70–7.25 (m, 12 H); GC–MS *m/e* 338 (M^+). Anal. Calcd for $C_{26}H_{26}$: C, 92.26; H, 7.74. Found: C, 91.99; H, 7.97.

1-(1-Naphthyl)-3-(1,4-dihydro-1-naphthyl)benzene (17). This compound could not be obtained free from **5** and **21**. Column chromatography of the crude product (entry 1, Table III) on silica gel impregnated with 2% TNF provided substantial separation (80% by glpc) of **17**, and NMR spectra were determined: NMR (CCl_4) δ 3.40 (m, 2 H), 4.50 (m, 1 H), 5.90 (br s, 2 H), 6.95–7.90 (m, 15 H); GC–MS *m/e* 332 (M^+).

1,3-Bis(2-naphthyl)benzene (6) was reduced with 5 mol of sodium in refluxing ammonia according to general procedure to provide a tetrahydro product as a major compound (80% by GLPC). Chromatography on silica gel following by recrystallization from methanol gave pure **1,3-bis(1,4-dihydro-2-naphthyl)benzene (28)** in 48% yield as white needles: mp 92–93 °C; NMR ($CDCl_3$) δ 3.50 (t, 4 H), 3.72 (m, 4 H), 6.23 (m, 2 H), 7.1–7.5 (m, 12 H); GC–MS *m/e* 334 (M^+). Anal. Calcd for $C_{26}H_{22}$: C, 93.37; H, 6.63. Found: C, 93.53; H, 6.60.

With 10 mol of lithium at −78 °C compound **6** was reduced exclusively to **1,3-bis(1,2,3,4-tetrahydro-2-naphthyl)benzene (27)**: oil; NMR ($CDCl_3$) δ 1.70–2.30 (m, 4 H), 2.85 (m, 10 H), 7.10

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(m, 12 H); GC-MS m/e 338 (M^+). Anal. Calcd for $C_{26}H_{26}$: C, 92.26; H, 7.74. Found: C, 92.46; H, 7.92.

1,4-Bis(1-naphthyl)benzene (7) was reduced according to general procedure under a variety of conditions as described in Table IV. After two crystallizations of the crude product (entry 3) from benzene, **1,4-bis(3,4-dihydronaphthyl)benzene (31)** was isolated as white needles (25%): mp 222-224 °C; NMR ($CDCl_3$) δ 2.45 (m, 4 H), 2.85 (t, 4 H), 6.15 (t, 2 H), 7.15 (m, 8 H), 7.38 (s, 4 H); GC-MS m/e 334 (M^+). Anal. Calcd for $C_{26}H_{22}$: C, 93.37; H, 6.63. Found: C, 92.73; H, 6.58.

Chromatography on silica gel followed by recrystallization from hexane of the crude product (entry 2) provided pure **1,4-bis(1,2,3,4-tetrahydro-1-naphthyl)benzene (33)** (60%) as white needles: mp 127-129 °C; NMR ($CDCl_3$) δ 1.7-1.95 (m, 8 H), 2.15 (m, 2 H), 2.85 (m, 4 H), 4.08 (t, 2 H), 6.85-7.15 (m, 12 H); GC-MS m/e 338 (M^+). Anal. Calcd for $C_{26}H_{26}$: C, 92.26; H, 7.74. Found: C, 92.28; H, 7.87.

Substantial separation of three additional compounds was achieved by column chromatography (80-90% by GLPC). However, further purification by attempted crystallization failed; they are probably oils. On the basis of NMR data and mass spectra, these compounds were assigned as **29**, **30**, **32** (they show similarity in nonaromatic area to **21**, **23**, and **24**, respectively.

Quinquephenyl (8) was treated with 5.5 mol of lithium at -33 °C according to the general procedure. Careful column chromatography of the crude mixture allowed isolation of tetrahydro isomer **34** as a major product (40%, 65% by GLPC): oil; NMR ($CDCl_3$) δ 3.06 (br s, 4 H), 4.06 (br s, 2 H), 5.73 (m, 2 H), 5.87 (m, 2 H), 6.07 (br s, 2 H), 7.10-7.26 (m, 14 H); λ_{max}^{MeOH} 205 (log ϵ = 4.99) 248 nm (log ϵ = 5.04); GC-MS m/e 386 (M^+). Anal. Calcd for $C_{30}H_{26}$: C, 93.22; H, 6.78. Found: C, 93.58; H, 6.61.

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Ozonolysis of Acenaphthylene and 1-Substituted Acenaphthylenes

Toshiya Sugimoto, Masatomo Nojima,* and Shigekazu Kusabayashi

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

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The ozonolysis of 1-methylacenaphthylene (**1b**) and acenaphthylene (**1c**) in carbon tetrachloride, acetonitrile, acetic acid, and trifluoroethanol revealed that the ozonide yield was much higher in reactions in protic solvents than in aprotic solvents. Such an assistance of the protic solvents on the ozonide formation was not observed in the case of the more bulky 1-phenylacenaphthylene (**1a**). In the ozonolysis of **1a-c** in methanol, capture of the ozonolysis intermediate by the solvent occurs significantly, affording in each case the corresponding naphthopyran derivative **3**. The structure of the methanol-derived product obtained from acenaphthylene (**1c**) is revised from the structure **14** reported by Callighan to the methoxynaphthopyran **3c**, based on NMR data and chemical transformations. The structure of the methanol-derived products **3a,b** demonstrates that fragmentation of the primary ozonide obtained from 1-methyl- and 1-phenylacenaphthylene occurs such that the hydroperoxide resides on the more substituted carbon. These data are compared with those of the ozonolysis of pyrene (**17**).

The ozonolysis of alkenes has attracted attention with regard to mechanism.[1] We were interested in the ozonlysis of 1-substituted acenaphthylenes **1a,b** for the following reasons. (a) The reaction of acenaphthylene (**1c**) in chloroform has been reported to afford exclusively the polymeric products, while in methanol a solvent-participated product is obtained in good yield.[2] Thus, it would be interesting to see if the phenyl and methyl substituent in **1a,b** could affect the course of the reaction, since these substituents are expected to exert a meaningful influence on the orientation of the carbonyl oxide and/or carbonyl moiety. (b) The structural assignment of the methanol-participated products from **1a,b** would provide information on the direction of cleavage of the corresponding primary ozonides.

Results and Discussion

Ozonolysis of 1-Phenylacenaphthylene (1a). Ozonolysis of **1a** in carbon tetrachloride or acetic acid gave the corresponding ozonide **2a** in around 55% yield (eq 1 and

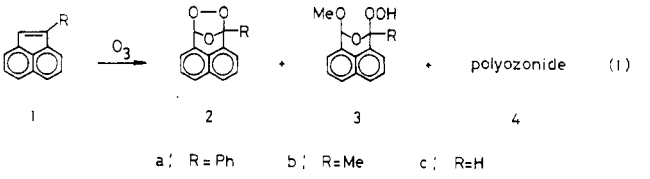
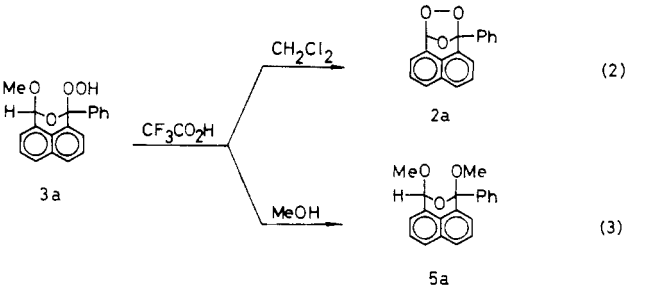


Table I). When the reaction was undertaken in methanol at -70 °C, however, the methanol-derived product **3a** was obtained in 30% yield, together with the ozonide **2a**. In accordance with the proposed structure, treatment of the methanol-derived product **3a** with trifluoroacetic acid in methylene chloride gave the ozonide **2a** quantitatively (eq 2) while the reaction in methanol resulted in exclusive



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