thracene. Mass spectral analysis gave biphenyl (78% d_2, 20% d_1, 2% d_0), dihydroanthracene (2% d_2, 9% d_1, 89% d_0), and anthracene (0% d_2, 1% d_1, 99% d_0); the starting material had 92% d_2, 6% d_1, 2% d_0. The percentage of deuterium loss from **9**-d_2 was equivalent to the level of deuterium incorporation in anthracene, indicative of essentially quantitative hydride transfer.

(b) **Monanion from Biphenyl-d_2.** Lithium–ammonia reduction of 4,4′-dideuteriobiphenyl and treatment of the product with anthracene by the same method employed with unlabeled biphenyl afforded quantitatively biphenyl, dihydroanthracene, and recovered excess anthracene. Deuterium distribution matched closely (±1%) that observed in a.

Equilibration of 1-d_2. Treatment of the deuterium-labeled 1-methyl derivative of dihydrobiphenyl (**1**-d_2) (0.88 mmol) with lithium amide (4.9 mmol) for 30 min at −33° in liquid ammonia (150 ml) in the absence of a cosolvent led to recovery of **1**-d_2 with ≤2% loss of deuterium by nmr analysis.

Analogous reaction with sodamide proceeded similarly to furnish **1**-d_2 with *ca.* 12% deuterium loss.

Attempted Methylation of the Radical Anion of Biphenyl-d_2. Reaction of biphenyl-d_2 (5 mmol) with lithium (5.5 g-atom) and methyl bromide under the usual conditions for reductive methylation led to recovery of biphenyl-d_2 (87%) and the mono- and dimethyl compounds **1**-d_2 (11%) and **2**-d_2 (1%). The latter two components apparently arise *via* dianion formation with the excess lithium (10 ± 2%). Net loss of deuterium was <2%, ruling out a mobile equilibrium involving protonation of **4**.

Acknowledgment. This investigation was supported in part by U. S. Public Health Service Research Grants CA-11,968 and CA-05246 from the National Cancer Institute and by the Louis Block Fund, The University of Chicago.

Metal–Ammonia Reduction. XIII. Regiospecificity of Reduction and Reductive Methylation in the Terphenyl Series[1]

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Abstract: Interaction of alkali metals with *p*-terphenyl in liquid ammonia affords both the theoretically predicted *cis*- and *trans*-1′,4′-dihydro-*p*-terphenyl (**2**) and the outer ring dihydro isomer, 1,4-dihydro-*p*-terphenyl (**1**). The relative ratios of **1** and **2** are dependent upon reaction variables, *e.g.*, metal, temperature, solvent, quenching agent (NH_4Cl or H_2O), etc., and under appropriate conditions product distribution may be shifted to favor exclusively the outer ring dihydro product **1**. This discrepancy from HMO theoretically predicted regiospecific reduction, the first encountered to date, may be rationalized in terms of an equilibrium between associated and free forms of a dianionic intermediate, protonation of which leads to **1** and **2**, respectively. Analogous reductive methylation of *p*-terphenyl furnishes products of both inner and outer ring attack. In contrast, metal–ammonia reduction and reductive alkylation of both *m*- and *o*-terphenyl proceeds regiospecifically in accord with theory in the central ring. The site of initial protonation of the *o*-terphenyl dianion appears nonregiospecific, occurring in both the 1′ and 4′ positions, while initial proton addition to the *m*-terphenyl dianion takes place exclusively in the 4′ position. Evidence is presented concerning the stability of the intermediate anionic species, their extent of association with the counterion, the relative importance of possible reaction pathways, and the stereochemistry of the 1,4-cyclohexadiene products.

According to Hückel molecular orbital theory,[2] reduction of polycyclic aromatic hydrocarbons (PAH) by alkali metals in liquid ammonia is predicted to occur at the regions of highest electron density in the intermediate anionic species, independent of the pathway. Careful reinvestigation of earlier work employing improved techniques of reaction, product characterization, and analysis has revealed a remarkable regiospecificity (*i.e.*, only a single dihydro isomer formed) for these reactions. Of the PAH investigated to date, which include biphenyl,[1] naphthalene,[3] anthracene,[4] phenanthrene,[5,6] chrysene,[7] benz[*a*]anthracene,[4,8] tetracene,[4] dibenz[*a*,*h*]anthracene,[4] pyrene,[9] and numerous alkyl derivatives of these, the only discrepancy between theory and experimental finding was detected with pyrene. The later compound, upon treatment with lithium in liquid ammonia, afforded, contrary to earlier claims, 1,9-dihydropyrene as the primary reduction product: the latter isomer is only one of at least five theoretically predicted equivalent structures.

We now wish to report studies on reduction and reductive methylation in the terphenyl series, including the first example of reduction nonregiospecific and partially contrary to theoretical prediction, and evidence for ion pair formation as an important factor in the determination of product structure.

In the only previous investigation of terphenyl, Hückel and Bretschneider reported[10] transformation of *p*-terphenyl upon treatment with sodium or calcium in liquid ammonia to a 2:1 mixture of a dihydroter-

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(1) Part XII: D. F. Lindow, C. N. Cortez, and R. G. Harvey, *J. Amer. Chem. Soc.*, **94**, 5406 (1972). For review on metal–ammonia reduction of aromatic molecules *cf.* R. G. Harvey, *Synthesis*, 161 (1970).

(2) A. Streitwieser, Jr., and S. Suzuki, *Tetrahedron*, 16, 153 (1961); A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, p 425.

(3) P. W. Rabideau and R. G. Harvey, *Tetrahedron Lett.*, 4139 (1970).

(4) R. G. Harvey, L. Arzadon, J. Grant, and K. Urberg, *J. Amer. Chem. Soc.*, 91, 4535 (1969).

(5) P. W. Rabideau, R. G. Harvey, and J. B. Stothers, *Chem. Commun.*, 1005 (1969).

(6) P. W. Rabideau and R. G. Harvey, *J. Org. Chem.*, **35**, 25 (1970).

(7) R. G. Harvey, *ibid.*, **36**, 3306 (1971).

(8) R. G. Harvey and K. Urberg, *ibid.*, 33, 2206 (1968).

(9) R. G. Harvey and P. W. Rabideau, *Tetrahedron Lett.*, 3695 (1970).

(10) W. Hückel and H. Bretschneider, *Justus Liebigs Ann. Chem.*, **540**, 157 (1939).

Table I. Thermal Dehydrogenation of Dihydro-*p*-terphenyl

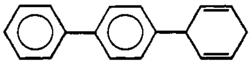
Temp, °C	Time, min	Product composition, % Cis-2	Trans-2	1	*p*-Terphenyl	Other
25		20	27	39	10	4
225	200	16	27	38	16	3
260–265	25	13	26	36	22	3
260–265	75	7	26	33	30	4
260–265	250	0	20	16	54	10
360–365[a]	10	0	8	0	80	12

[a] A quartz tube was employed in all experiments except this, in which a Pyrex tube was used.

phenyl (mp 70°) and an unidentified hydrocarbon (mp 150–153°), incorrectly assumed to be a terphenyl. Catalytic hydrogenation of the dihydro compound afforded 4-cyclohexylbiphenyl, indicating initial reduction in an outer ring. Hückel MO calculations,[2,11] on the other hand, predict the primary product from *o*-, *m*-, and *p*-terphenyl to be 1′,4′-dihydroterphenyl, arising from initial reduction of the inner ring.

Results

***p*-Terphenyl.** Interaction of lithium metal with *p*-terphenyl in liquid ammonia led to formation of 1,4-dihydro-*p*-terphenyl (**1**), *cis*- and *trans*-1′,4′-dihydro-*p*-terphenyl (**2**) and 1,4,1′′,4′′-tetrahydro-*p*-terphenyl (**3**),



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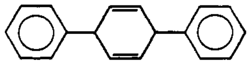

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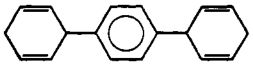

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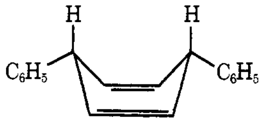
the relative proportions of which were dependent upon reaction conditions.

Compound **1**, a white crystalline solid (mp 69–70°), is apparently the dihydroterphenyl (mp 70°) obtained by Hückel and Bretschneider.[10] The 1,4-dihydro-*p*-terphenyl structure assigned by these workers on the basis of chemical evidence is supported by the presence in the nmr spectrum of a characteristic single benzylic proton (δ 3.90) in addition to the expected number of aryl, vinyl, and allylic protons (see Experimental Section); chemical shifts and splitting patterns closely resembled those of 1,4-dihydrobiphenyl. In addition, the ultraviolet spectrum exhibitied λ_{max} 254 mμ (ϵ 22,400), indicating the presence of the biphenyl chromophore. The tetrahydro compound **3** was generally a minor product (<5%) except with employment of large lithium excess. Its nmr spectrum differed from that of **1** essentially only in the relative ratios of protons.

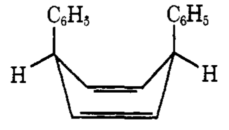
The *cis*- and *trans*-1′,4′-dihydro structures (**2**) were assigned the remaining dihydroterphenyl isomers on the basis of spectral data. The nmr spectra, which were closely similar in all respects, showed aryl, vinyl, and benzylic protons in the ratio of 5:2:1. In the ultraviolet region, both substances exhibited only weak absorption, indicating the absence of the biphenyl or styrene chromophores. The isomer melting at 157–158° is presumably the product, mp 150–153°, erroneously identified as a terphenyl isomer by Hückel and Bretschneider.[10] The second isomer was obtained only as an oil.

In principle, the cis–trans stereoisomers should be distinguishable by nmr spectroscopy, if we assume nonplanarity of the central 1,4-cyclohexadiene ring.[12] Trans-**2** may be expected to invert rapidly between equivalent conformers having one phenyl substituent pseudoaxial and the other pseudoequatorial, while cis-**2** should invert between diaxial and diequatorial conformations. However, the nmr spectra of both isomers proved temperature independent down to −80°, indicative of either inversion too rapid on the nmr time scale (*i.e.*, $\gtrsim$ 50 sec^{-1}) to detect, or planarity of the central ring.

trans



cis-diequatorial



cis-diaxial

Stereochemical assignment was achieved, however, by comparison of the relative rates of dehydrogenation in both chemical and thermal processes. Thermal decomposition of *cis*-1,4-cyclohexadienes proceeds, according to Frey, *et al.*,[13] by molecular elimination of hydrogen in a concerted process allowed by the Woodward–Hoffman rules:[14] in contrast, pyrolysis of trans isomers requires higher temperatures, furnishes products arising *via* carbon–carbon cleavage, and is thought to proceed by a radical-chain process. Competitive thermal dehydrogenation[15] of mixtures of **1** and **2** gave selective conversion of the outer ring isomer **1** and one of the inner ring isomers to *p*-terphenyl at temperatures >200°; reaction of the remaining isomer required temperatures >300° (Table I). The less reactive isomer was the higher melting one, which on this basis is assigned the trans-**2** structure.

This conclusion was supported by the results of chemical dehydrogenation with several different reagents (palladium-on-charcoal, DDQ, *o*-chloranil, basic

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(11) Calculations by the Dewar SCF–MO method, however, predict reduction in the outer ring; M. J. S. Dewar, J. A. Hashmall, and N. Trinajstić, *J. Amer. Chem. Soc.*, **92**, 5555 (1970). This is one of the few discrepancies between predictions by the two methods.

(12) A. W. Brinkmann, M. Gordon, R. G. Harvey, P. W. Rabideau, J. B. Stothers, and A. L. Ternay, *ibid.*, **92**, 5912 (1970).

(13) H. M. Frey, A. Krantz, and I. Stevens, *J. Chem. Soc. A*, 1734 (1969).

(14) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970, p 141.

(15) Reactions were conducted in the melt rather than in the gas phase, the method employed by Frey, *et al.*;[13] it is uncertain what difference, if any, this may make in the mechanism.

Al_2O_3). Reactions were generally clean, and in each case the isomer assigned the trans structure proved most resistant to transformation (Table II). Comparison of *o*-chloranil and DDQ is interesting, since concerted transfer of two hydrogen atoms to the former, but not the latter, reagent is symmetry allowed.[14] Indeed, *o*-chloranil proved highly selective at 25°, while DDQ exhibited the least selectivity of the methods employed (Table II); apparently even nonconcerted hydrogen transfer is relatively facile. Titration of the mixed dihydroterphenyl isomers with a solution of DDQ in benzene at ~75° was quantitative. Catalytic dehydrogenation, usually considered predominantly cis stereoselective, exhibited steric preference similar to that of the other reagents. Attempted dehydrogenation over Pd/C in refluxing benzene gave, in addition to *p*-terphenyl, unidentified products (33%) presumably arising through isomerization or disproportionation of the dihydro compounds; analogous reaction at higher temperature in *p*-cymene furnished a much smaller proportion of secondary products.

Table II. Chemical Dehydrogenation of Dihydro-*p*-terphenyl[a]

Reagent	Product composition, %				
	Cis-**2**	Trans-**2**	**1**	*p*-Terphenyl	Other
None	32	39	26	2	1
Pd/C	0	24	0	68	8
DDQ	12	20	2	64	2
o-Chloranil	0	27	0	71	2
Al_2O_3	3	42	0	55	0

[a] See Experimental Section for procedural details.

Reduction of *p*-terphenyl to afford both outer and inner ring dihydro derivatives is unique, representing the first clearly documented example of reduction nonregiospecific and partially contrary to theoretical prediction. Accordingly, we undertook to study this reaction in greater detail, with particular emphasis on whether ion-pair association, a factor neglected in the theoretical treatment but implicated in recent studies,[1,3,7] might be involved.

The nature of the metal employed markedly influenced the ratio of outer to inner ring reduction (Table III) with the ratio decreasing in the sequence Ca > K ≳ Na > Li. Thus, use of lithium permitted preferential inner ring reduction, while employment of calcium had a contrary effect, promoting outer ring attack. The observed cis/trans ratio appeared to deviate little from a value indicating a slight preference for trans independent of the metal cation. Concentration in the range 3.3×10^{-2}–1.67×10^{-3} had little effect on either the outer/inner ratio or the stereoselectivity of inner ring reduction. Equilibration of the pure trans isomer with 1 or 2 equiv of $LiNH_2$ in ammonia led to a mixture of isomers containing 45% cis, in close agreement with the ratio for reduction. Variation of solvent polarity through addition of cosolvents of increasing polarity (hexane, ether, dimethoxyethane, THF, TMEDA) tended to slightly alter the proportion of outer ring attack (Table III), without affecting the nonstereoselectivity of inner ring reduction.

A pronounced time effect was also evident (Table IV), with increase in the time interval before quenching leading to higher proportion of **1** at the expense of **2**. Lower reaction temperature had a similar effect (Table V).

Table III. Reduction of *p*-Terphenyl: Effect of Metal, Cosolvent, and Concentration[a]

Metal	Cosolvent	Product composition, %[b]				
		Cis-**2**	Trans-**2**	**1**	Outer	Cis
	A. *p*-Terphenyl = 3.33×10^{-2} *M*					
Ca		12	15	67	71	45
K		19	25	42	49	43
Na		20	27	30	39	43
Li		33	38	26	27	47
Ca	THF	19	20	42	52	49
K	THF	34	39	23	24	47
Na	THF	29	33	31	33	47
Li	THF	33	31	34	35	52
Li	Hexane	34	37	28	28	48
Li	Ether	33	36	30	30	48
Li	DME	32	32	33	34	50
Li	TMEDA	26	30	44	44	46
	B. *p*-Terphenyl = 1.67×10^{-3} *M*					
Ca		6	7	36	74	46
K		19	25	48	52	43
Na		23	28	46	47	45
Li		22	31	35	40	42

[a] Conditions described in Experimental Section. [b] Values for Ca and Li are the average of four and five separate experiments, respectively. Yields were measured by peak area on glpc on a 6 or 8 ft × 0.25 in. 20% DEGS on Chromosorb W column at 200°; although cis-**2** and **3** were not separable under these conditions, nmr analysis of this peak collected off the glpc column indicated generally <3% **3** present. Aside from *p*-terphenyl, no significant products were encountered other than those indicated.

Table IV. Reduction of *p*-Terphenyl with Lithium: Effect of Time[a]

p-Terphenyl, mmol/l.	Time, min	Product composition, %				
		Cis-**2**	Trans-**2**	**1**	Outer	Cis
33.3	5	35	42	19	20	45
33.3	30	33	38	26	27	47
33.3	180	17	23	46	53	43
1.67	7	32	44	21	22	42
1.67	30	22	31	35	40	42
1.67	240	17	26	51	54	40

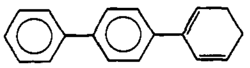
[a] Conditions were the same as Table III.

Table V. Reduction of *p*-Terphenyl: Effect of Temperature

Metal	Temp, °C	Product composition, %				
		Cis-**2**	Trans-**2**	**1**	Outer	Cis
Li	−33	33	38	26	27	47
Li	−78	26	33	37	39	56
Ca	−33	12	15	67	71	45
Ca	−78	9	11	77	79	45
Li[a]	−33	22	31	35	40	42
Li[a]	−78	23	31	44	45	43

[a] These reactions were conducted in dilute solution (*p*-terpheny = 1.67×10^{-3} *M*); for all others *p*-terphenyl = 3.33×10^{-2} *M*.

Substitution of water for NH_4Cl as the quenching agent completely and dramatically repressed inner ring reduction. Although a portion of the outer ring product (~30%) was recovered in the form of its conjugated isomer **4**, this isomerization was effectively excluded



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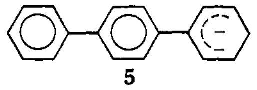
by half-quenching the reaction by dropwise addition of sufficient water (diluted with THF) to consume all but 1 equiv of added metal. The resulting monoanion, presumably **5**, could then be efficiently protonated with NH_4Cl to afford **1**, or alkylated with methyl bromide to give the related 1-methyl derivative **6**.



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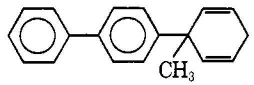

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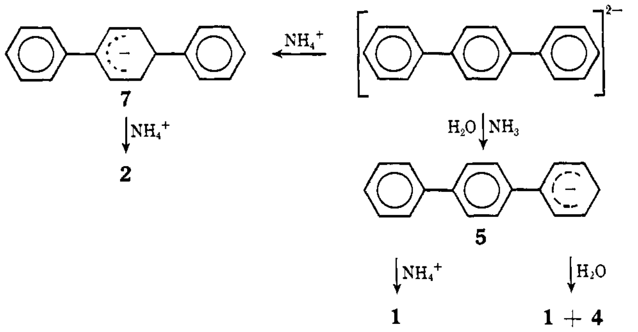
All the foregoing observations are consistent with the following tentative hypothesis (Scheme I). Interaction of *p*-terphenyl with alkali metals in liquid ammonia leads to formation of a relatively stable dianion, protonation of which may be either kinetically or thermodynamically controlled, depending upon the kinetic acidity of the proton source. Ammonia, a relatively weak acid ($pK_a \sim 34$), protonates slowly at the terminal position to afford the thermodynamically more stable monoanion, **5**. Water, though a considerably stronger acid, reacts at the same site.[16] Ammonium chloride, the strongest available acid, rapidly transfers a proton to the 1′- position, the most basic center in the *p*-terphenyl dianion, to furnish **7**, the monoanion predicted on purely kinetic grounds; the latter, like the parent biphenyl monoanion,[1] undergoes a second fast protonation at the benzylic 4′ position to afford **2**. Similar considerations determine the structures of the products from **5**, ammonium chloride providing the kinetic product **1**, and water the thermodynamic product **4** as well as **1**.

Scheme I



Increased outer ring reduction with longer time and greater dilution is obviously consistent with this scheme. However, the nature of the observed metal effect on the outer/inner ratio appears more complex. It is not simply related to the solubility of the corresponding amides (Ca < Li < Na), but parallels instead the expected degree of association of the respective cations (Ca > K > Na > Li). On this basis, the metal effect may be rationalized in terms of equilibria between associated and free forms of the dianion, protonation of which leads to **1** and **2**, respectively. Ion pair association localized in the positions of maximum electron density in the central ring may be expected to distort the charge distribution toward this region and markedly diminish the kinetic basicity of the entire ring system. As a consequence, the thermodynamic factor may be expected to exert major control over product structure, directing protonation to the outer ring. Alternatively, it is conceivable that association occurs preferentially on the outer ring as a consequence of the steric demands of the metal cations and their accompanying solvent shells. Charge distribution may be expected to be altered to favor this region, leading to protonation preferentially in the outer ring. Distinction between these two alternatives is not possible on the basis of the available evidence.

In either interpretation, the position of the association equilibrium might be expected to be dependent upon the solvating ability of added cosolvents. In agreement, reductions conducted in the presence of THF show markedly diminished proportion of outer ring product with Ca and K, a smaller decrease with Na, and essentially no change with Li (Table III). While these observations are compatible with competitive solvation of the cations by THF, this explanation is contrary to expectation based on the relative dielectric constants of THF (ϵ (25°) 7.6) and ammonia (ϵ (−33°) 22). Also, the influence of other factors (*e.g.*, amide solubility,[17] quenching time,[18] and the state of aggregation of the ammonia) is not readily evaluated, making uncertain the significance of this cosolvent effect at the present time.

If protonation of a dianion by ammonia accounts for a major portion of the outer ring product, this reaction should be suppressed in the presence of added amide ion. Although reduction of *p*-terphenyl (3.33×10^{-2} *M*) carried out in the presence of amide ion generated *in situ* failed to reveal any significant difference whether Li, Na, or K were used, analogous reaction at lower concentration (1.67×10^{-2} *M* in^{-1} *p*-terphenyl) exhibited appreciable inhibition of outer ring attack (Table VI). Control reactions demonstrated that sodium bromide, also present in these reactions, was not responsible for this effect.

Table VI. Reduction of *p*-Terphenyl: Effect of Sodamide[a]

Concn, $M \times 10^{-2}$		Product composition, %				
$NaNH_2$	NaBr	Cis-2	Trans-2	1	Outer	Cis
0	0	23	28	46	47	45
0	4.0	21	29	39	44	42
1.5	2.5	37	41	21	21	47

[a] Conditions described in Experimental Section; concentration of *p*-terphenyl = 1.67×10^{-3} *M*.

According to the proposed mechanism, reductive methylation of *p*-terphenyl would be expected to furnish products of reaction in both outer and inner rings, namely 1-methyl-1,4-dihydro-*p*-terphenyl (**6**) and *cis*- and *trans*-1′,4′-dimethyl-1′,4′-dihydro-*p*-terphenyl (**8**). Indeed, these are the major products, (Table VII),

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[16] Water presumably reacts indirectly through relatively slow interaction with ammonia to generate the ammonium ion.

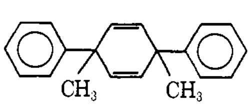
[17] Although the observed order of outer/inner reduction in the presence of THF (Ca, 1 > Li, 0.53 ≥ Na, 0.50 > K, 0.32) reflects the order of metal amide solubility, it would appear more significant that the proportion of outer ring attack is generally decreased rather than increased in the presence of THF.

[18] Considerably longer periods were required for decolorization by NH_4Cl of reactions conducted in the presence of THF (Ca, 3.5 > Li, 1.5 > Na, 1.0 > K, 0.3 min) than in its absence (all essentially instantaneous); however, these differences do not parallel variation in the outer/inner ratio nor relate to the proportion of outer ring attack.

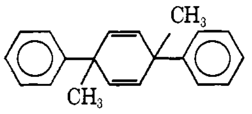
Table VII. Reductive Methylation of *p*-Terphenyl[a]

				Product composition, %					
Metal	RX	Time, min	Temp, °C	6	Cis-8	Trans-8	9	*p*-Terphenyl	Other
Li	CH_3Br	3.5	−33	1	22	15	9	51	2
Li	CH_3Br	30	−33	8	19	13	9	49	2
Li[b]	CH_3Br	5	−33	5	11	6	9	67	2
Li[c]	CH_3Br	7	−33	13	21	15	11	39	1
Li	CH_3Br	10	−78	3	30	23	9	31	4
Li[c]	CH_3Br	10	−78	10	33	31	9	16	1
Li	CH_3Cl	5	−33	4	38	24	7	26	1
Li	CH_3Cl	10	−78	1	51	32	4	12	0
Na	CH_3Br	30	−33	4	7	5	4	80	1
Na[c]	CH_3Br	10	−78	6	28	25	10	28	3
Ca	CH_3Br	30	−33	2	10	7	20	57	4

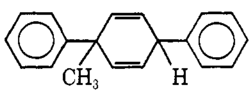
[a] Conditions were the same as employed as for reduction, method A, Table III. [b] Ether (75 ml) was employed as cosolvent; similar results were obtained with THF or TMEDA as cosolvent. [c] Twentyfold dilution, method B, Table III.



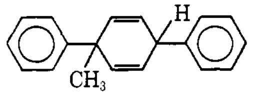
cis-**8**



trans-**8**



cis-**10**



trans-**10**

along with 1,4-dimethyl-**1** (**9**) and recovered *p*-terphenyl. Dimethylated products predominate, with the proportion of the monomethyl derivative directly related to reaction time (30 min > 3.5 min), and inversely related to concentration. The nature of the metal influences both conversion (Li > Ca > Na) and the outer/inner ratio (Ca, 1.2 > Na, 0.39 > Li, 0.24); the latter order parallels that observed for reduction, although the ratios are somewhat lower. The cis/trans ratio proved independent of the metal, but did vary somewhat with cosolvent, alkyl halide, and temperature.

Attempted analogous reaction in the presence of a catalytic proportion of colloidal iron (generated *in situ* from ferric chloride by reaction with lithium metal) dramatically repressed the "normal" reaction, providing as products only *p*-terphenyl and a small amount of **6**. All the foregoing observations are consistent with intermediacy of an associated *p*-terphenyl dianion slowly protonated by ammonia in the 4 position. In particular, formation of **8** and nonformation of the related inner ring monomethyl compound provide strong evidence *for* a stable dianion and *against* a protonated inner ring monoanion, such as **7**. Also, the iron effect is most simply interpreted in terms of reversal of dianion formation through iron-catalyzed reaction of the metal with ammonia.[19] The high proportion of *p*-terphenyl found on reductive methylation (*vs.* reduction) undoubtedly arises *via* competitive electron transfer between the dianion and the alkyl halide, particularly methyl bromide.

$$[p\text{-terphenyl}]^{2-} + CH_3X \xrightarrow{NH_3} p\text{-terphenyl} + CH_4 + X^- + H_2N^-$$

Incidentally, the inner ring monomethyl compounds *cis*- and *trans*-1′-methyl-1′,4′-dihydro-*p*-terphenyl (**10**), though not formed in reductive methylation, may be efficiently synthesized through methylation of the related monoanion **7**, generated *via* interaction of $LiNH_2$ with trans-**2**.

Assignment of the structures and stereochemistry of the *cis*- and *trans*-1′,4′-dimethyl and 1′-monomethyl-1′,4′-dihydro-*p*-terphenyl (**8** and **10**) is dependent primarily upon nmr spectral data supported by mass spectra and uv analysis. Thus, reaction in the central ring to form a 1,4-cyclohexadiene unconjugated with either aromatic ring is clearly indicated by the absence of the relatively intense biphenyl or styrene chromophores[21] in the uv spectra. The integrated proton ratios in the nmr proved equally consistent with this formulation; also, the methyl groups appeared as singlets, confirming their location in the benzylic position. The cis–trans assignments are tentative, based on the conformational properties of the 2,5-diphenyl-1,4-cyclohexadienyl ring system in relation to the nmr spectral data. If we assume rapidly equilibrating boat conformations,[25] the trans stereoisomers are distinguished by one phenyl substituent in both axial and equatorial orientations (Chart I) independent of ring inversion or the nature of R or R′; the cis isomers may be expected to exist as an equilibrium mixture of conformers bearing either diaxial (a, a′) or diequatorial (e, e′) phenyl groups, with the latter predominating to a decreasing extent as R and R′ increase in size. The methyl group in trans-**10** may be expected to favor the pseudoequatorial orientation in order to minimize transannular steric interaction, while the methyl group in the cis isomer should, for the same reason, exhibit axial preference. It is significant, therefore, that the methyl singlet of the cis isomer appears at

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(19) Iron-catalyzed consumption of alkali metals by reaction with ammonia is now a well-documented reaction;[1] failure of early workers to remove ferrous metal salts normally present in commercial ammonia undoubtedly accounts for the unsatisfactory results, particularly the recovery of large proportions of unreacted hydrocarbon, frequently reported in the older literature. The effect is sometimes useful in limiting reduction beyond a desired stage.[6,8,20]

(20) R. G. Harvey and K. Urberg, *J. Org. Chem.*, 33, 2570 (1968).

(21) Biphenyl and styrene exhibit λ_{max} 251.5 (ϵ 18,300)[22] and 248 mμ (ϵ 14,000),[23] respectively, whereas 1,4-dihydrobiphenyl[1,24] displays λ_{max} 262 mμ (ϵ 465).

(22) H. H. Jaffe and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, p 273.

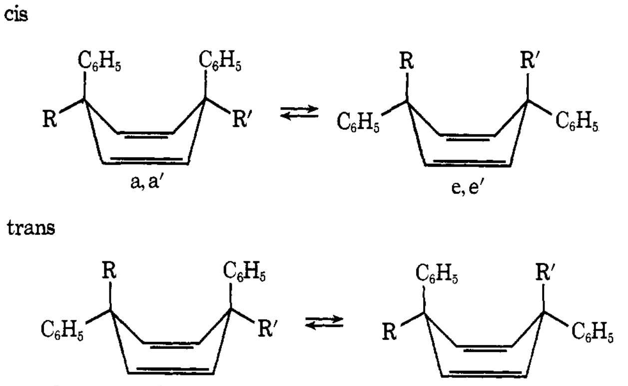
(23) A. Scott, "Interpretation of Ultraviolet Spectra of Natural Products," Pergamon Press, Oxford, 1964, p 98.

(24) P. J. Grisdale, T. H. Regan, J. C. Doty, J. Figueras, and J. L. Williams, *J. Org. Chem.*, 33, 1116 (1968).

(25) The related 9,10-dihydroanthracene and 1,4-dihydronaphthalene ring systems bearing substituent groups in the allyl position exist as boat structures in which the attached group exhibits strong preference for the pseudoaxial orientation.[4,12,26]

(26) J. L. Marshall and T. K. Folsom, *J. Org. Chem.*, 36, 2011 (1971).

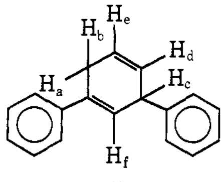
Chart I



8, R = R′ = CH_3
10, R = CH_3; R′ = H

higher field (δ 1.53) than that of the trans isomer (δ 1.59). Since axial groups lie in the positive shielding region over the 1,4-cyclohexadiene ring, their appearance at higher field than their equatorial counterparts, which do not experience this effect, is in agreement with expectation.[27] Similarly, the methyl protons of the dimethyl homolog cis-**8** appear at δ 1.53, confirming their expected diaxial orientation, while the methyl singlet of trans-**8** exhibits the intermediate value of δ 1.56 in agreement with expectation of a time-average resonance signal due to the equivalency of axial and equatorial contributions in this symmetrical molecule.[28] Other features of the nmr spectra are consistent with these assignments.[29] Equally consistent are the physical properties of the cis–trans pairs. Thus, the trans compounds are all crystalline solids, while the cis isomers are all oils at room temperature. Also, the cis isomer has the shortest retention time on a DEGS glpc column for each isomer pair.

m-**Terphenyl.** *m*-Terphenyl underwent regiospecific reduction with lithium in ammonia to furnish the predicted dihydro isomer, 1′,4′-dihydro-*m*-terphenyl (**11**). The yield proved dependent upon whether the quenching agent employed was water (45%) or ammonium chloride (~100%).



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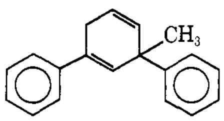
The 1′,4′-dihydro structure, **11**, was assigned and alternative structures such as the 1′,2′-, 2′,5′-, 1,4-, or 3,4-dihydro structures were excluded on the basis of the uv spectrum and the integrated proton ratios and characteristic splitting pattern in the 100-MHz nmr spectrum. Thus, **11** exhibited an aromatic multiplet at δ 7.2 (10 H), a vinyl multiplet at 6.1 (1 H), another vinyl multiplet at 5.85 (2 H), the methine signal at 4.1 (1 H), and the methylene as a broadened doublet at 3.1 (2 H). Saturation of the methylene doublet (H_a and H_b) resulted in the sharpening of the low field half of the vinyl AB system to two sharp lines (J = 10 Hz), allowing assignment of this resonance to H_e. The higher field half of this pattern is then assigned to H_d. Saturation of H_c removed the major coupling from the remaining vinyl multiplet assigned as H_f and collapsed the methylene doublet. In addition, under these conditions, the two members of the low field AB system appeared as triplets with a value of J = 2.5 Hz for the coupling of the methylene protons with H_e. Also, the higher field segment of this system and H_f appeared as narrow triplets with $J \approx 1.5$ Hz for their respective couplings with the methylene protons.

Reductive methylation of *m*-terphenyl, like reduction of this isomer, furnished a single product. This was identified as the related 1′-methyl-1′,4′-dihydro-*m*-terphenyl (**12**) in agreement with expectation.



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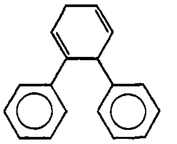
o-**Terphenyl.** Reduction of *o*-terphenyl paralleled that of the meta isomer furnishing the product of inner ring reduction 1′,4′-dihydro-*o*-terphenyl (**13**). The yield was essentially quantitative with ammonium chloride as quenching agent and somewhat lower (83%) with use of water for this purpose. Reductive methylation, although less satisfactory in that a mixture of products was provided, proved more revealing regarding the regioselectivity of initial attack. The major product component (45%) from reaction with methyl bromide at −33° under standard conditions proved to be the 1′-monomethyl derivative of **13**, 1′-methyl-1′,4′-dihydro-*o*-terphenyl (**14**). This was accompanied



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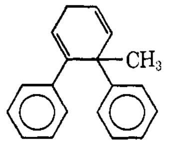

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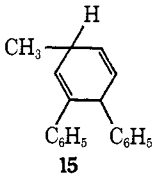
by the related 4′-methyl isomer **15** (24%), a third monomethyl isomer tentatively assigned the unusual



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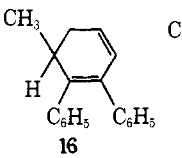

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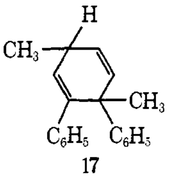

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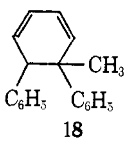

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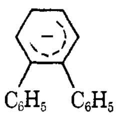
[27] This effect has recently been observed in the nmr spectra of the related 9,10-dihydroanthracene and 1,4-dihydronaphthalene ring systems.[4,12,26] While both these systems are known to be nonplanar, the conformation of the parent 1,4-cyclohexadiene system is not established. It should be emphasized that the foregoing arguments are based on the assumption of a preferred nonplanar conformation of the substituted 1,4-cyclohexadiene ring.

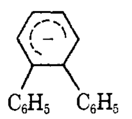
[28] When both methyl and phenyl are pseudoaxial (trans-**8** or trans-**10**) restricted rotation of the phenyl group should result in shielding of the methyl group and be reflected in a higher field methyl resonance for trans-**8** than for trans-**10**.

[29] All compounds assigned trans stereochemistry show aromatic singlets at 7.22 ppm when phenyl is attached to carbon bearing hydrogen and aromatic multiplets at 7.30 ppm when phenyl is attached to carbon bearing methyl. The compounds assigned cis stereochemistry, however, show an upfield shift of 0.05 and 0.04 ppm with each additional methyl group. Introduction of methyl groups into the allylic positions of 1,4-cyclohexadiene so as to not disturb the relative proportion of conformers results in a 0.07 ppm upfield shift in vinyl resonance per methyl; trans-**2** *vs.* trans-**8** shows an upfield shift of 0.14 ppm, whereas those compounds assigned cis stereochemistry show a uniform upfield shift of only 0.04 ppm per methyl (compare Stadtler File 5677M, 1,4-cyclohexadiene, *vs.* 2912M, 2,2,5,5-tetramethyl-1,4-cyclohexadiene, and 1-methyl- *vs.* 1,4,4-trimethyl-1,4-dihydrobiphenyl[1]).

structure[30] **16** (10%), and minor amounts of at least three additional components (21% total) incompletely separated on the glpc column. Two compounds of similar retention time were isolated from subsequent related reactions and identified as the 1′,4′-dimethyl analog of 1′,4′-dihydro-*o*-terphenyl (**17**) and a new monomethyl isomer, most probably **18**. Within the limits of experimental detection, therefore, all products of both reduction and reductive methylation appear to derive from exclusive inner ring attack. Analogous reaction with CH$_3$Cl at −78° afforded the dimethyl compound **17** (67%) and recovered *o*-terphenyl (21%) as major products along with small amounts of **16** (4%) and **14** (5%). Additional evidence with regard to the mechanism of these transformations was obtained from "back reaction" of the dihydro compound **13** with LiNH$_2$ in ammonia followed by methyl bromide. The 4′-methyl compound **15** was the major product (~30%) along with **18** (12%), **14** (9%), *o*-terphenyl (~15%), and recovered **13**.

Taken together, the foregoing results support (1) existence of a relatively stable *o*-terphenyl dianion in ammonia at −78°; (2) existence of two related monoanions at −33° protonated at C-4′ and C-1′, respectively with the former predominating; (3) methylation of the latter monoanion to afford **15** and **18**; and (4) proton abstraction from the dihydro compound **13** to form the same two monoanions, with the C-4′ monoanion predominating under the conditions of the experiment. The most significant feature of these results is the indication that, despite the overall regiospecificity of reduction of *o*-terphenyl, the protonation appears to be nonregiospecific occurring in both the 1′ and the 4′ positions, the relative ratio of which is dependent upon reaction conditions.





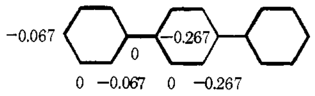
Discussion

According to HMO theory,[2] initial protonation of the intermediate anions derived from addition of one or two electrons to PAH is expected at the sites of maximum electron density as determined by the coefficients (c_r^2) of the lowest vacant MOs (Table VIII); for *o*-, *m*-, and *p*-terphenyl these are the 1′,4′, and 1′ positions, respectively. The monoprotonated dianion of *p*-terphenyl contains three positions (2′, 4′, 6′) of equivalent highest electron density according to simple Hückel calculations. The perturbation introduced by the 1′-methine may be expected to diminish electron density at the adjacent 2′ and 6′ positions, leading to maximum density at the 4′ position and prediction of net overall 1′,4′ reduction. Similar considerations predict net overall 1′,4′ reduction of both *o*- and *m*-terphenyl with initial protonation at the 1′ and 4′ positions, respectively.

Table VIII. Coefficients (c_r^2) of Lowest Vacant MOs of Terphenyl[a]

Position	Ortho	Meta	Para
1	0.059	0.056	0.054
2	0.061	0.047	0.060
3	0.008	0.008	0.008
4	0.092	0.077	0.088
1′	*0.119*	0.077	*0.124*
2′		0	0.049
3′	0.012	0.077	
4′	0.078	*0.180*	
5′		0	

[a] Values are omitted for symmetrically equivalent positions.



Departure from predicted regiospecificity by *p*-terphenyl was related in the preceding section to ion-pair association[31] coupled with low kinetic acidity of the proton source (H$_2$O) in relation to the kinetic basicity of the *p*-terphenyl dianion. Contradiction of prediction is only apparent, however, since the theory is applicable only in the absence of counterion and solvation effects and assumes a kinetic mode of protonation. Indeed, conditions which favor either dissociation of ion pairs or kinetic protonation tend to promote attack on the central ring of the *p*-terphenyl dianion, in accord with prediction.

The relative stability of the dianion of *p*-terphenyl in liquid ammonia is surprising in view of demonstration in the preceding paper[1] of facile protonation of even the dianion of anthracene, previously considered stable in this medium. The symmetry of the *p*-terphenyl ring system which effectively delocalizes the charge fairly over a large number of carbon atoms is undoubtedly a significant factor contributing to the relatively low kinetic basicity of any free dianion present. Ion-pair association may be expected to diminish the reactivity of the associated portion of the dianion; contact ion pairs are generally markedly less reactive than their less tightly associated counterparts.[32,33] In this regard, it is pertinent that treatment of 1′,4′-dihydro-*p*-terphenyl (**2**) with excess amide ion under the conditions of reduction yields only products of inner ring attack on protonation or methylation. Thus, dianion formation fails to occur to any significant extent through back reaction, indicating that the equilibrium between the dianion and its monoprotonated form lies far to the side of the latter. The apparent

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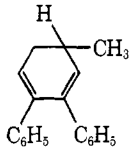
(30) It should be pointed out that, although structures **14–18** are entirely consistent with their integrated proton nmr spectra and mass spectra, structure 16 is not unequivocally established by this means. Alternative structures, *e.g.*, 19 and 20, equally compatible with the physical data, are considered less probable on the grounds that reaction conditions tending to favor formation of **16** also favor formation of 4′-protonated products.



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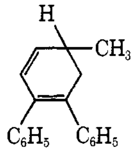

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(31) More detailed examination of these phenomena will be required to distinguish possible equilibria between associated (2 Li$^+$, Ar^{2-}), partially associated (Li$^+$||Ar^{2-}, Li$^+$), and solvent-separated (2 Li$^+$||Ar^{2-}) ion pairs and free ions.

(32) T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **90**, 4654 (1968); N. H. Velthorst and G. J. Hoijtink, *ibid.*, **87**, 4529 (1965).

(33) The inverse relative reactivity has been reported for tight *vs.* solvent-separated ion pairs of sodium naphthalene; *cf.* S. Bank and B. Bockrath, *ibid.*, **93**, 430 (1971).

relative stability of the *p*-terphenyl dianion in ammonia, therefore, appears to reflect the slow rate of protonation of the associated form of the dianion rather than its thermodynamic stability.

Reduction of *o*-terphenyl in apparent accord with theoretical prediction is more remarkable than the contrary might have been, since application of molecular orbital theory to this molecule is questionable, due to the virtual impossibility of attainment of planarity by the hydrocarbon or its anionic intermediates. Indeed, the ultraviolet spectrum of *o*-terphenyl indicates it to be more properly considered a 2-phenylbiphenyl.[22] Therefore, electron distribution within the corresponding dianion may be expected to be considerably closer to equivalence at the 1′ and 4′ positions than calculated, so that competitive initial protonation at both sites (as determined by methylation) is not an unreasonable expectation. Association of ion pairs and solvation may also be contributory factors; however, distinction between free, solvent-separated and/or contact ion pairs and determination of their relative influence on product structure are beyond the scope of the present inquiry.

Experimental Section

Physical Data. Proton nmr spectra were obtained on a Varian A-60 spectrometer; chemical shifts are reported relative to TMS in CCl_4 or CS_2. Trace amounts of *p*-terphenyl in each of the samples derived from this compound allowed linear corrections of the chemical shifts against the sharp peak at δ 7.62. Each of the pairs of cis–trans isomers were also examined as a mixture to check the difference in chemical shifts between the corresponding peaks from each isomer. Integration was consistent with the assigned structures. Glpc analyses were performed on a F & M Model 500 chromatograph employing either a 6 ft × 0.25 in. or a 8 ft × 0.25 in. 20% DEGS column on 60–80 Chromosorb W at 200°. Calibration of the instrument with known mixtures gave a 10% greater response of the thermal conductivity detector to terphenyl; the reported product ratios are corrected by this factor. Glpc analysis of product ratios is supported in all cases by nmr analysis of total product mixtures. The reported yield data are considered to be accurate within reasonable limits of the methods employed (~5%). Retention times of compounds cited herein relative to *p*-terphenyl (1.00, 20 min) are cis-**8**, 0.25; cis-**10**, 0.28; trans-**8**, 0.31; cis-**2**, 0.32; trans-**10**, 0.34; trans-**2**, 0.35; **9**, 0.48; **6**, 0.55; and **1**, 0.57. All compounds trapped off the glpc column for characterization were verified not to be artifacts of thermal decomposition by comparison of their nmr spectra with those of the initially isolated crude products. Mass spectra were obtained on a Finnigan 1015 mass spectrometer at 70 eV except where indicated otherwise.

Reactions in Liquid Ammonia. Precautions for the exclusion of impurities (moisture, air, peroxides, and ferrous metal salts in commercial ammonia) were scrupulously observed, and the general procedure described in the preceding paper was followed. All reactions were conducted under helium in a three-neck flask fitted with a Dewar condenser. Products were isolated rapidly by partition between ether and water without waiting for evaporation of ammonia in order to minimize isomerization and other secondary processes. Nmr spectra were taken on crude products as soon as practicable after isolation and before glpc analysis in order to detect aromatization, isomerization, etc., occurring spontaneously or on the glpc column. This practice is recommended for all products of metal–ammonia reduction of hydrocarbons.

Reductive Methylation in Liquid Ammonia. Reaction was conducted in the manner described for reduction of *p*-terphenyl except that prior to quenching with NH_4Cl gaseous methyl bromide (or methyl chloride) was passed through a column of 50% silica gel (20–40 mesh)–sand into the reaction vessel until the color of the solution was discharged. Although a flow meter was not employed in early experiments, the gas was introduced relatively rapidly; a fast flow of ~60 mmol/min was employed in later experiments.

Reduction of *p*-Terphenyl. A solution of *p*-terphenyl (5 mmol, 1.15 g) in THF (75 ml) partially precipitated upon addition to refluxing ammonia (150 ml), but redissolved upon dissolution of lithium wire (11 g-atoms, 77 mg, 3 pieces) to furnish a deep blue solution. After 30 min, reaction was quenched by addition of solid NH_4Cl (20 g) all at once (1–2 sec); a large flask (1 l.) was necessary to accommodate the foaming occasioned by the rapid quenching technique. Products were isolated immediately by partition between water and ether followed by conventional work-up procedures, and analyzed by nmr and glpc.

The following modifications were also employed: (1) *water quench*, water (20 ml) was employed in place of NH_4Cl; (2) *half-quench*, a solution of water (6 mmol, 108 mg) in THF (75 ml) was added over a 10-min period to the product of lithium–*p*-terphenyl interaction (without cosolvent), and reaction quenched in the usual manner after an additional 5 min; (3) *dilute conditions*, *p*-terphenyl (1.6 mmol) followed by the metal (3.7 g-atoms) was added to 1 l. of refluxing ammonia; (4) *sodamide present*, amide ion was generated *in situ* by the dropwise addition of ethyl bromide to just decolorize a solution of the metal in ammonia, then reduction was carried out in the usual manner.

1,4-Dihydro-*p*-terphenyl (1). Reduction of *p*-terphenyl with lithium in ammonia half-quenched with water afforded a crude product containing **1** (87%) and **2** (5%). Recrystallization from methanol gave pure **1**: mp 69–70°; nmr (CCl_4) δ 7.39 (m, 9 aromatic), 5.76 (s, 4, vinylic), 3.95 (broad t, 1, CH, J = 8.5 Hz), and 2.76 ppm (broad d, 2, CH_2, J = 8.5 Hz); uv_{max} (95% ethanol) 254 mμ (ϵ 22,400).

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.85; H, 7.04.

***trans*-1′,4′-Dihydro-*p*-terphenyl (Trans-2).** The product of reduction of *p*-terphenyl with lithium in ammonia under dilute conditions afforded upon recrystallization twice from petroleum ether trans-**2**: white needles, mp 157–58°; nmr (CCl_4) δ 7.22 (s, 10, aromatic), 5.82 (s, 4, vinylic), and 3.99 ppm (m, 2, CH); uv_{max} (95% ethanol) 268 (ϵ 2,000), 263 (ϵ 2,000), and 257 mμ (ϵ 1,600).

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.96; H, 7.17.

***cis*-1′,4′-Dihydro-*p*-terphenyl (Cis-2).** A sample of cis-**2** trapped off the glpc column was an oil; nmr (CCl_4) δ 7.25 (s, 10, aromatic), 5.80 (m, 4, vinylic), and 3.99 ppm (m, 2, CH).

1′,4′,1′′,4′′-Tetrahydro-*p*-terphenyl (3). Reduction of *p*-terphenyl with 7.5 equiv of lithium under standard conditions furnished a crude product containing 30–40% of **3** by nmr. Recrystallization from 95% ethanol gave 0.2 g of pure **3** as needles: mp 108–110°; nmr (CCl_4) δ 7.05 (s, 4, aromatic), 5.7 (s, 8, vinylic), 3.85 (t, 2, J = 9 Hz, C*H*), and 2.7 ppm (d, 4, J = 9 Hz).

Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.50; H, 8.00.

Analogous reduction of **1** with 2.5 equiv of lithium also afforded **3** (>50%) together with an unidentified product.

1,4-Dihydro-1-methyl-*p*-terphenyl (6). The product of interaction of *p*-terphenyl with lithium in ammonia was half-quenched with water, then a stream of methyl bromide gas was passed through a column of 50% silica gel–sand into the reaction vessel until the color of the solution was discharged. Solid NH_4Cl (20 g) was added cautiously and the product worked up in the usual manner to afford **6** (91%). A sample trapped off the glpc column was obtained as an oil which solidified. Recrystallization from methanol gave **6**: mp 45.5–47°; nmr (CCl_4) δ 7.42 (m, 9, aromatic), 5.71 (s, 4, vinylic), 2.72 (m, 2, CH_2), and 1.47 ppm (s, 3, CH_3); uv_{max} (cyclohexane) 255 mμ (ϵ 18,000); mass spectrum *m/e* 246 (parent peak), 231 (parent − CH_3, base peak).

Anal. Calcd for $C_{19}H_{18}$: C, 92.63; H, 7.37. Found: C, 92.64; H, 7.35.

***cis*- and *trans*-1′,4′-Dihydro-1′,4′-dimethyl-*p*-terphenyl (Cis- and Trans-8).** Reductive methylation of *p*-terphenyl with lithium and methyl chloride at −78° for 10 min furnished a product containing cis-**8** (51%), trans-**8** (32%), **9** (4%), and recovered *p*-terphenyl (12%) by glpc analysis (Table VII). A sample of cis-**8** trapped off the glpc column had nmr (CCl_4) δ 7.27 (m, 10, aromatic), 5.72 (s, 4, vinylic), and 1.53 ppm (s, 6, CH_3). Trans-**8**, similarly obtained, showed nmr (CCl_4) δ 7.30 (m, 10, aromatic), 5.68 (s, 4, vinylic), and 1.56 ppm (s, 6, CH_3); mass spectra *m/e* 260 (parent peak), 245 (parent − CH_3, base peak) for both isomers.

Equilibration of Trans-2. Anhydrous $FeCl_3$ (30 mg) was added to refluxing ammonia (150 ml) followed by lithium metal (5.55 g-atoms). When the blue color was discharged, indicative of complete conversion to lithium amide, a solution of trans-**2** (450 mg, 2 mmol) and *p*-terphenyl (15%) in THF (75 ml) was added. After 20 min, reaction was quenched with solid NH_4Cl (20 g), and worked up in the usual way. Glpc analysis gave cis-**2** (30%), trans-**2** (36%), and *p*-terphenyl (34%). Analogous reaction with only 1 equiv of lithium amide gave essentially the same result. In neither case were detected **1** or other products of outer ring attack.

***cis*- and *trans*-1′,4′-Dihydro-1′-methyl-*p*-terphenyl (Cis- and Trans-10).** A solution of trans-**2** (1.6 mmol) and *p*-terphenyl (18%) in THF was added to a solution of lithium amide (1.6 mmol) in ammonia generated as described in the previous experiment. After 20 min, gaseous methyl bromide was passed into the solution which was then quenched and worked up in the usual way. Glpc analysis of the crude product showed cis-**10** (42%), trans-**10** (28%), and *p*-terphenyl (27%). A sample of cis-**10** trapped off the glpc column had nmr (CCl_4) δ 7.31 (m, 5, aromatic), 7.20 (s, 5, aromatic), 5.76 (s, 4, vinylic), 3.94 (broad s, 1, CH), and 1.53 ppm (s, 3, CH_3). Trans-**10**, similarly obtained, showed nmr (CCl_4) δ 7.29 (m, 5, aromatic), 7.23 (s, 5, aromatic), 5.75 (s, 4, vinylic), 3.97 (broad s, 1, CH), and 1.59 ppm (s, 3, CH_3); mass spectra *m/e* 246 (parent peak), 231 (parent − CH_3, base peak) for both isomers.

Reduction of *m*-Terphenyl. Reaction was carried out exactly as with the para isomer. The only notable difference was development of an intense green rather than a blue color during reaction. The nmr spectrum of the crude material indicated quantitative conversion to **11**. Recrystallization from 95% ethanol furnished the analytical sample of **11** as small white needles (0.7 g, 63%): mp 75°; uv$_{max}$ (95% ethanol) 252 mμ (ϵ 15,000); nmr spectral data cited under Results.

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.15; H, 7.07.

Reductive Methylation of *m*-Terphenyl. The reaction was conducted in the manner described for the para isomer. Glpc analysis of the product on a 3 ft 5% DEGS column at 154° revealed the expected product **12** as the major component (90%, retention time 4.8 min); it was accompanied by two minor constituents (5% each) with retention times 3.1 and 9.1 min, respectively. The analytical sample of **12** (an oil) was trapped off the glpc column: nmr (CCl_4) δ 7.25 (m, 10, aromatic), 6.0 (m, 1, vinyl), 5.8 (m, 2, vinyl), 3.1 (broad s, 2, CH_2), and 1.55 ppm (s, 3, CH_3).

Anal. Calcd for $C_{19}H_{18}$: C, 92.64; H, 7.36. Found: C, 92.53; H, 7.43.

Reduction of *o*-Terphenyl. Interaction of *o*-terphenyl with lithium in ammonia according to the general procedure utilized for the other isomers afforded a brownish-red solution, conventional work-up of which furnished an oil containing **13** (98%) and *o*-terphenyl (2%). Chromatography on silica gel (hexane) afforded a pure sample of **13**: nmr δ 7.2 (broad s, 10, aromatic), 6.2 (m, 1, vinylic), 5.85 (m, 2, vinylic), 4.45 (m, 1, CH), and 3.0 ppm (m, 2, CH_2).

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.64; H, 7.35.

Reductive Methylation of *o*-Terphenyl. The major product from reductive methylation of *o*-terphenyl with lithium and methyl bromide at −33° under standard conditions was **14** (45%). A sample trapped off the glpc column was an oil having nmr (CCl_4) δ 7.23 (broad s, 5, aromatic), 7.0 (m, 3, aromatic), 6.6 (m, 2, aromatic), 5.7 (m, 3, vinylic), 2.95 (m, 2, CH_2), and 1.40 ppm (s, 3, CH_3); mass spectrum *m/e* 246 (parent equal to base peak), 231 (parent − CH_3, 70%). Lesser products were **15** (24%), **16** (10%), and three minor constituents (21% total) poorly separated; two of the latter were subsequently identified as **17** and **18**. A sample of **15** trapped off the glpc column was slightly contaminated with *o*-terphenyl which did not interfere with interpretation of the nmr spectrum: δ 7.04 (s, aromatic), 6.00 (m, 1, vinylic), 5.67 (m, 2, vinylic), 4.4 (m, 1, benzylic), 3.0 (m, 1, allylic), and 1.29 and 1.23 ppm (pair d, 3, CH_3, $J = 7.2$); two methyl doublets in the ratio of 8:2 indicate cis and trans isomers in similar ratio; mass spectrum *m/e* 246 (parent peak, 55%), 231 (parent − CH_3, 51%). A sample of **16** similarly obtained had nmr (CCl_4) δ 7.00 (s, aromatic), 5.7–6.3 (m, vinylic), 1.7–2.8 (m, allylic), and 1.03 ppm (d, CH_3, $J = 7$); mass spectrum *m/e* 246 (parent equal to base peak), 231 (parent − CH_3, 86%).

Analogous reaction with methyl chloride at −78° afforded the dimethyl compound **17** (67%), along with **16** (4%), **14** (5%), and recovered *o*-terphenyl. A sample of **17** trapped off the glpc column had nmr (CCl_4) δ 7.2 (broad s, 5, aromatic), 7.0 (m, 3, aromatic), 6.6 (m, 2, aromatic), 5.6 (m, 3, vinylic), 3.0 (m, 1, CH), 1.40 and 1.39 (pair s, 3, CH_3), and 1.28 and 1.21 ppm (pair d, 3, CH_3, $J = 7.2$); on the basis of the ratio of methyl peaks, cis–trans isomers were present in the ratio of 3:2, mass spectrum *m/e* 260 (parent peak, 65%), 245 (parent − CH_3, 62%).

Reductive methylation of *o*-terphenyl with lithium and methyl bromide at −33° half-quenched with water in the usual manner afforded a mixture of products rich in **18** (14%); also present were **16** (4.5%), **14** (14%), **15** + *o*-terphenyl (40%), and **13** (25%). A, sample of **18** trapped off the glpc column had nmr δ 7.0 (m, aromatic), 6.0 (m, vinylic), 3.60 (m, 1, benzylic), and 1.60 ppm (s, 3, CH_3); mass spectrum *m/e* 246 (parent, 27%), 231 (parent − CH_3, 11%).

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