mation is to be entrusted entirely to machines, they will have to be instructed not only how to examine ligands in order to determine the sense of chirality[2] but also how to decide when such an examination is appropriate and whether, for example, a sinister sense of chirality is to be expressed as *S* or as *s*. These additional problems also call for precise definitions and alone provide sufficient practical justification for an inquiry as to what constitutes a chiral or a prochiral element. We faced no arbitrary choices in formulating relevant criteria and are presenting these tests with the expectation that they can serve their stated objectives. However, we found that an appropriate definition of a chiral element can be based on the outcome of either one or both of two distinct reflection tests. Our decision to use both tests in the definition of a chiral element was prompted by the realization that only this choice provided a classification that would be compatible with the Cahn–Ingold–Prelog system which, in turn, is firmly based on tradition. We present this choice not as the necessarily best solution, but rather as a point of departure for a fuller discussion which might concern itself more with the tasks of the future than with preserving the concepts of the past. Unfortunately we see no *single* answer as to what would be the most useful definition of a chiral element; those who are cataloguing and comparing stereoisomers will have to identify the partial structures that can only be described in chiral terms and these structures are not necessarily the same entities that enter the equations of those who calculate such chiral properties as optical rotation.

In factorizing a structure into the components relevant to the distinction of stereoisomers we have adhered, as far as possible, to the categories set forth by Cahn, *et al.*[2] These classes may allow alternative ways of factorizing a structure. We observed, however, that as long as the assembly of differentiated atoms met our definition of an element of stereoisomerism[26] the use of alternative classifications did not change the nature of either the *f*-ligands or of the framework to which they are attached. Moreover, only two basic types of the elemental assembly are needed to describe all forms of stereoisomerism that we have considered: (1) the assembly of the proper center and (2) the assembly of the line of torsion (B.3). Although the traditional geometric concepts (center, axis, plane, helix,[2] cis–trans isomerism[10]) are serving well as a basis of a comprehensive nomenclature of stereoisomerism, it remains an aim of fundamental stereochemistry to provide a unique mode of factorization for any stereoisomer. The two elemental assemblies of the center and of torsional isomerism appear to meet this objective for any compound that has a fully defined pattern of connectedness[28] between its constituent atoms.

Acknowledgment.—The authors wish to express their indebtedness to all colleagues who commented on drafts of this paper. Particular thanks are due to Dr. R. S. Cahn, who also called our attention to the interesting group of compounds comprised of 22 and its isomers; also to Professors D. Arigoni, A. Dreiding, W. Klyne, K. Mislow, V. Prelog, and H. Z. Sable.

Metal-Ammonia Reduction. XI. Regiospecific and Stereoselective Reduction in the Chrysene Series

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Metal-ammonia reduction of chrysene through the hexahydro stage proceeds regiospecifically *via* 5,6-dihydro- (**1**) and 4b,5,6,12-tetrahydro- (**2**) to 4b,5,6,10b,11,12-hexahydrochrysene (**3**). Existence in liquid ammonia of stable monoanionic intermediates related to **1** and **2**, but not **3**, is demonstrated by reductive methylation. Cis stereoselectivity observed in reduction of both **2** and 5,6,11,12-tetrahydrochrysene to **3** is dependent upon olefin structure. Conformational analysis of **3** indicates three possible conformations of *trans*-**3**, a boat–boat, a boat–chair, and a chair–chair form, and two sets of three similar configurations for *cis*-**3**, a "folded" set and a "twisted" set. The relative importance of thermodynamic, steric, and ion-pair factors in determining product stereochemistry is discussed.

In the previous papers of this series,[1,2] methods for the efficient, controlled reduction of representative polycyclic aromatic hydrocarbons by means of solutions of alkali metals in liquid ammonia were described. These transformations proved uniquely regiospecific (*i.e.*, only a single dihydro isomer formed at each stage), uncomplicated by secondary processes (*e.g.*, isomerization, disproportionation, dimerization, etc.) and frequently also stereospecific;[3-5] moreover, the sites of reduction were in general accord with predictions of molecular orbital theory.[6,7] Analogous reductive alkylations of polycyclic aromatic carbanions in liquid ammonia were found to exhibit similar regiospecificity but generally contrary stereoselectivity.[8-10]

We report now extension of these studies to the chry-

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[1] Paper X: R. G. Harvey and P. W. Rabideau, *Tetrahedron Lett.*, 3695 (1970).

[2] *Cf.* review: R. G. Harvey, *Syn.*, 161 (1970).

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

[4] P. W. Rabideau, R. G. Harvey, and J. B. Stothers, *Chem. Commun.*, 1005 (1969); P. W. Rabideau and R. G. Harvey, *J. Org. Chem.*, **35**, 25 (1970).

[5] A. W. Brinkmann, M. Gordon, R. G. Harvey, P. W. Rabideau, J. B. Stothers, and A. L. Ternay, Jr., *J. Amer. Chem. Soc.*, **92**, 5912 (1970).

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

[7] Pyrene, however, provided only one of five theoretically predicted equivalent structures.

[8] R. G. Harvey and L. Arzadon, *Tetrahedron*, **25**, 4887 (1969).

[9] R. G. Harvey and C. C. Davis, *J. Org. Chem.*, **34**, 3607 (1969).

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

sene ring system, in an attempt to further probe the limits of controllability and stereospecificity. Evidence will be presented relating to the nature of the intermediate anionic species, the extent of protonation by the medium, the conformational properties of intermediates, and the relative importance of ion-pair association[10] and other factors in the determination of product stereochemistry. Surprisingly, metal–ammonia reduction of chrysene has not previously been reported[2] and reduction by other means, including catalytic hydrogenation[11] and lithium in ethylenediamine[12] affords highly reduced products, primarily dodecahydrochrysenes.

Results

According to HMO theory,[6] initial reduction of chrysene is expected at the 5,6 bond. Experimentally, reduction of chrysene with lithium in ammonia tended to proceed beyond the dihydro stage to the tetrahydro level. The conditions successfully employed to limit or prevent excessive reduction of other polycyclic hydrocarbons[2] (*i.e.*, low metal–hydrocarbon ratios, rapid quenching with an external proton source, colloidal iron) were relatively ineffectual. A brief investigation (Table I) implicated two factors as primarily responsible: the relative insolubility of chrysene, and the facile protonation of the initial intermediate by ammonia[13] to provide the more soluble and readily reducible 5,6-dihydrochrysene (**1**). These factors were effectively counteracted by use of the most efficient cosolvent (THF > DME > ether), by addition of the metal in portions (method B) rather than all at once (method A), and by use of sodium,[14] rather than lithium or calcium. Yields of **1** under optimum conditions were in the range of 80–85%.

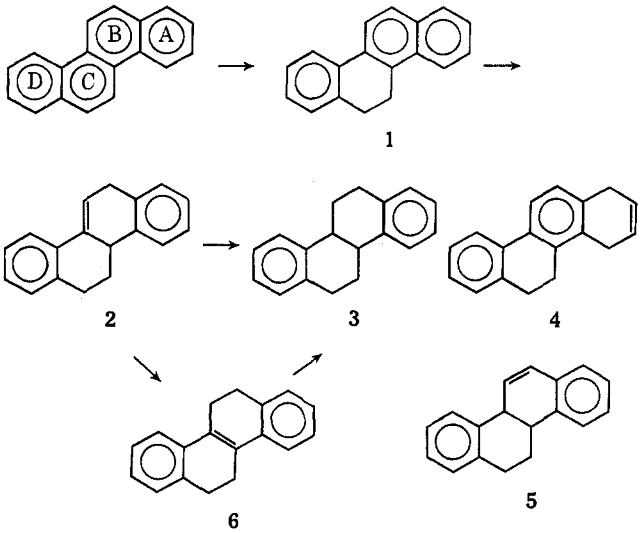
TABLE I
REDUCTION OF CHRYSENE BY ALKALI METALS IN LIQUID AMMONIA[a]

Expt	Metal (equiv)	Cosolvent (ml)	Method[b]	Product composition, %[c] Chrysene	Dihydro	Tetrahydro
1	Li (2.2)	None	A	30	9	61
2	Li (2.2)	THF (75)	A	19	38	43
3	Li (2.2)	THF (150)	A[d]	24	35	42
4	Na (2.2)	THF (75)	A	20	45	35
5	Ca (2.2)	THF (75)	A	38	10	52
6	Na (2.2)	DME (75)	A	50	18	31
7	Na (2.2)	THF (75)	B	25	69	7
8	Li (2.2)	THF (75)	B	25	50	24
9	Na (2.5)	THF (100)	B	9	82	9

[a] Reaction conditions are described in the Experimental Section. [b] The metal was added as a single piece in method A, and in four equal portions at 3-min intervals in method B. [c] Percentages refer to integrated peak values from glpc. [d] The amount of hydrocarbon was decreased from 5 to 2 mmol in this experiment only.

The nmr spectrum of the dihydro compound matched that of authentic 5,6-dihydrochrysene (**1**) prepared by ethanolysis of the chrysene–sodium adduct formed in dimethoxyethane according to the method of Hunt and Lindsey.[15] Samples of pure **1**, independent of their chemical origin, melted in a similar range (161.5–163°), 10° lower than reported[15] (171–173°); the discrepancy is apparently due to the presence of residual chrysene (detected by glpc) in samples purified by recrystallization from alcohol, the method employed by the earlier workers.

Further transformation to the tetrahydro stage, less obviously predictable, also proceeded regiospecifically to afford a tetrahydrochrysene. The latter was assigned the 4b,5,6,12-tetrahydrochrysene structure **2** on the basis of the nmr spectrum, the integrated proton ratios of which were inconsistent with the alternative structures, 1,4,5,6- and 4b,5,6,10b-tetrahydrochrysene[16] (**4** and **5**). Also, isomerization of **2** with dilute methanolic HCl afforded the symmetrical isomer 5,6,11,12-tetrahydrochrysene (**6**), the structure of which was confirmed by independent synthesis.[17] The nmr spectrum of **6** exhibited a characteristic A_2B_2 pattern for 8 protons in the benzylic region in addition to an aromatic multiplet (8 H).



Preparatively, **2** was most conveniently obtained directly from chrysene *via* reduction with the calculated proportion of sodium or lithium. Concurrent reduction beyond this stage, though generally detected, was minimal in the absence of excess metal; with employment of even a large excess of sodium (8 equiv) in the presence of colloidal iron, less than 2% hexahydrochrysene was formed. The utility of iron in limiting reduction of certain hydrocarbons was noted earlier.[3,4]

A moderately stable tetrahydro anionic intermediate is suggested by the relative resistance of **2** to further reduction following its formation from **1**. This was confirmed by analogous reductive methylation with lithium and methyl bromide in ammonia. Glpc analysis of the product revealed three major compo-

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(11) E. Clar, "Polycyclic Hydrocarbons," Vol. I, Academic Press, New York, N. Y., 1964, p 249; S. Friedman, M. L. Kaufman, and I. Wender, *J. Org. Chem.*, **36**, 694 (1971).

(12) J. D. Brooks, R. A. Durie, and H. Silberman, *Aust. J. Chem.*, **17**, 55 (1964).

(13) The closely related 9,10-dihydrophenanthrene dianion and/or radical anion was earlier demonstrated[4] to undergo rapid protonation by ammonia.

(14) Not only is the oxidation potential of Na lower than that of Li or Ca, but the solubility of the corresponding amide is considerably greater than those of $LiNH_2$ or $Ca(NH_2)_2$ [important in the protonation equilibrium: $(Ar^-M^+) + NH_3 \rightleftharpoons ArH + (M^+NH_2^-)$].

(15) S. E. Hunt and A. S. Lindsey, *J. Chem. Soc.*, 2227 (1958).

(16) In contrast, reductive methylation of 2-phenylnaphthalene with lithium in ammonia and methyl bromide furnished as the major product, 2-methyl-2-phenyl-1,2-dihydronaphthalene, analogous to **5**: unpublished results.

(17) E. Cahana, G. Schmidt, and K. Shah, *J. Org. Chem.*, **24**, 557 (1959).

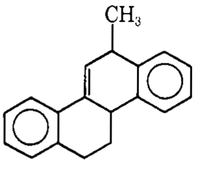
TABLE II

REDUCTION OF TETRAHYDROCHRYSENE[a]

Isomer	Metal	Cosolvent	Temp, °C	Method[b]	Quench	Time, min	Product composition, %[c] cis-3	trans-3	2 or 6
2	Na	THF[d]	−33	B	NH_4Cl	20	66	33	
2	Li	THF[d]	−33	B	NH_4Cl	20	64	34	2
2	Na	ether[e]	−33	B	NH_4Cl	20	64	34	2
2	Li	ether[e]	−33	B	NH_4Cl	20	65	34	1
2	Na	ether[e]	−33	A	NH_4Cl	20	66	33	
2	Na	ether[e]	−78	A	NH_4Cl	20	66	33	
2	Na	ether[e]	−78	A	H_2O	20	80	20	
2	Li	ether[e]	−78	A	H_2O	20	76	24	
2	Na	ether[e]	−33	A	*tert*-BuOH	20	75	24	
6	Na	ether[e]	−33	A	NH_4Cl	5	82	16	2
6	Li	THF[e]	−33	A	NH_4Cl	5	76	24	
6	Li	THF[e]	−33	A	H_2O	60	82	16	1
6	Li	THF[e]	−33	A	H_2O	5	79	18	
6	Na	THF[e]	−33	C	EtOH	3	49	36	13
Chrysene	Na	THF[d]	−33	B	NH_4Cl	20	66	33	1

[a] Reaction conditions are described in the Experimental Section. [b] The metal was added as a single piece in methods A and C, and in four equal portions at 3-min intervals in method B; alcohol (1 ml) was added to the solution before the metal in method C. [c] Percentages refer to integrated peak values from glpc. [d] Volume of cosolvent = 100 ml. [e] Volume of cosolvent = 70 ml.

nents characterized as 12-methyl-4b,5,6,12-tetrahydrochrysene (**7**, 48%), 10b-methyl-4b,5,6,10b-tetrahydrochrysene (**8**, 21%), and 5,6-dimethyl-5,6,11,-12-tetrahydrochrysene (**9**, 15%) by nmr analysis of samples trapped off the glpc column. The predominance of monomethylated derivatives is consistent with existence of a monoanion of **2** as the major stable intermediate species in ammonia (see Discussion). The dimethylated produce **9** may arise from a dianion or from **7** through abstraction of the proton at the 4b position by amide ion and methylation of the resulting allylic anion at the more accessible 11 position.



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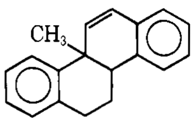

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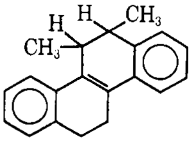

9

The stereochemical course of reduction of the tetrahydro isomers **2** and **6** is of particular interest. Although numerous examples of metal–ammonia reduction of cyclic styrenoid and stilbenoid olefins are found in the literature,[18] the majority involve natural products or related molecules of complex structure for which the observed steric course is variable and the factors controlling the stereochemistry are poorly understood. Reduction of both **2** and **6** with lithium or sodium proceeded smoothly and quantitatively to afford *cis*- and *trans*-4b,5,6,10b,11,12-hexahydrochrysene (**3**). A marked preference for one stereoisomer was observed under all conditions (Table II). The predominant isomer was assigned the cis structure on the basis of its lower melting point [69–70° (lit.[19] 75°)] compared with that of the trans isomer [114–115° (lit.[19,20] 112–114°, 115°)]. In the nmr spectra, deshielding due to steric crowding between the C-4 and equatorial C-5 protons, expected to be greater in the trans than the cis isomer,[21] was evident in the aromatic region of only the higher melting isomer, further confirming the structural assignment. Interestingly, reaction of the styrenoid structure **2** under a variety of conditions (quenched with ammonium chloride) afforded a lower cis–trans ratio (2:1) than analogous transformation of **6** for which the cis–trans ratio ranged from 3:1 to 5:1. With less efficient quenching agents, water or *tert*-butyl alcohol, **2** gave cis–trans ratios in the higher range. In contrast, reduction of **6** under Birch conditions (*i.e.*, alcohol present initially) resulted in markedly diminished cis steric preference (Table II).

Variation of solvent, metal, or temperature had no significant effect on these ratios, indicating ion pairing to be of little importance in determining product stereochemistry. Equilibration of the trans isomer with sodamide in refluxing ammonia afforded 86% *cis*-**3** and 14% *trans*-**3** at equilibrium (25 hr required). Insofar as the observed cis–trans ratios differ from this thermodynamic equilibrium proportion, they would appear to be kinetically determined (see Discussion).

Direct conversion of chrysene to **3** was possible with employment of large excess of sodium metal (10 g-atoms); the yield was virtually quantitative, with the only other discernible product being **2** (1%). By comparison, reduction of chrysene with a large excess of sodium in refluxing isoamyl alcohol furnished *cis*-**3** (22%), *trans*-**3** (38%), and tetrahydro isomers **2** plus **6** (40%). Further treatment with more sodium in fresh isoamyl alcohol failed to very appreciably alter these percentages. It appears, therefore, that the cis–trans ratio is altered to favor the trans isomer at elevated temperature and that complete conversion to the hexahydro level is not favored under these conditions.

Discussion

Thus chrysene, like all other polycyclic aromatic hydrocarbons investigated to date (naphthalene,[10] anthracene,[3,22] phenanthrene,[4] benz[*a*]anthracene,[3] tet-

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[18] H. Smith, "Organic Reactions in Liquid Ammonia," Vol. I, part 2, Wiley, New York, N. Y., 1963.

[19] A. D. Jarrett and J. D. Loudon, *J. Chem. Soc.*, 4052 (1955).

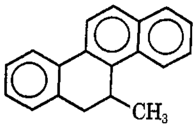
[20] G. Ramage and R. Robinson, *ibid.*, 607 (1933).

[21] W. Nagata, T. Terasawa and K. Tori, *J. Amer. Chem. Soc.*, **86**, 3746 (1964).

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

racene,[3] dibenz[*a,h*]anthracene,[3] pyrene,[1] and numerous alkyl derivatives), undergoes metal–ammonia reduction regiospecifically at each stage. Preferential reduction of the B ring rather than the A ring of **1** at the second stage is somewhat surprising. However, dihydrochrysene is essentially a bridged 2-phenylnaphthalene, and influence of the D ring is sufficient, apparently, to overcome the counter effect of alkyl substitution in the B ring.

Facile protonation of the dihydrochrysene radical anion and/or dianion by ammonia, as indicated by the observed ease of reduction beyond this stage, is consistent with the pK_a of the benzylic anion ($pK_a \sim 37$) relative to that of ammonia ($pK_a \sim 34$). The related 9,10-dihydrophenanthrene intermediate was earlier demonstrated to be rapidly protonated by ammonia.[4] Principal evidence for this was the failure to undergo alkylation under conditions wherein other benzylic anions undergo efficient reaction. Analogous treatment of the dilithiochrysene adduct in ammonia with methyl bromide led, unexpectedly, to formation of a methylated derivative of dihydrochrysene (60%). The nmr spectrum exhibited a single methyl doublet (3 H) at δ 1.13 (J = 7 Hz) in addition to the appropriate number of benzylic and aromatic protons (3 H and 10 H, respectively) for a monomethyldihydrochrysene. The latter was assigned the 5-methyl structure **10** on the basis of its dehydrogenation with trityl fluoroborate[23] in acetic acid to 5-methylchrysene.



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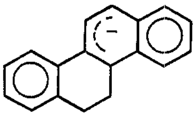
Apparently, therefore, the intermediate 5,6-dihydro-5-chrysenyl monoanion persists in liquid ammonia, and the protonation equilibrium ($ArH^- + NH_3 \rightleftharpoons ArH_2 + H_2N^-$) is readily shifted to the right by further reduction.

Although a moderately stable tetrahydro monoanionic intermediate such as **12** provides the simplest explanation for the origin of the monomethyl compounds **7** and **8**, a dianion mechanism may not be entirely rejected. Thus a dianion such as **13** may be considered to react rapidly at C-12 to furnish a monoalkyl monoanion, **14**, which either undergoes rapid protonation by the medium or is very much less reactive with respect to further alkylation and persists until reaction is quenched. Also, solvent-separated and/or contact ion pairs of differing reactivity may be involved, as suggested earlier for the naphthalene ring system.[10] Definitive answer to these questions lies beyond the scope of the present inquiry.



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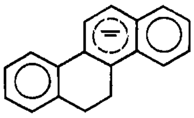

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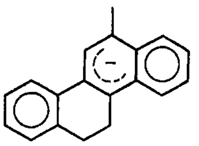

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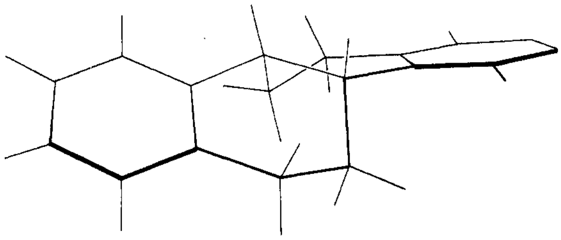
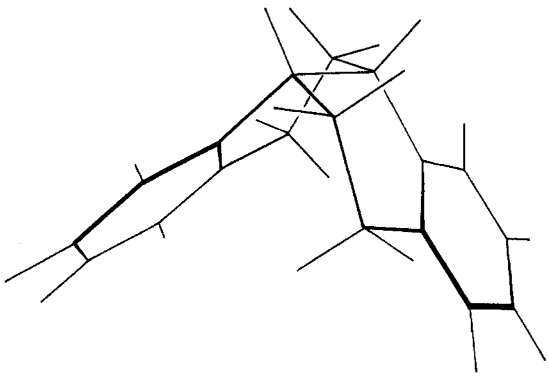
The observed cis stereoselectivity of reduction of **2** and **6** contrasts markedly with the reported nonstereoselective transformation of closely related compounds. The most relevant case is the reported nonstereoselective reduction of 1,8- and 2,8-dimethoxy-**2** with sodium and ethanol in ammonia by Birch and Smith.[24] Product stereochemistry is presumably determined during final protonation of the monoanion of **3**. According to Smith,[18] at least two factors may be considered to exert a controlling influence, a *conformational factor* involving the relative stabilities of the available conformations of the anion and a *steric approach factor* involving the relative accessibility of the anion to the proton donor in these conformations.

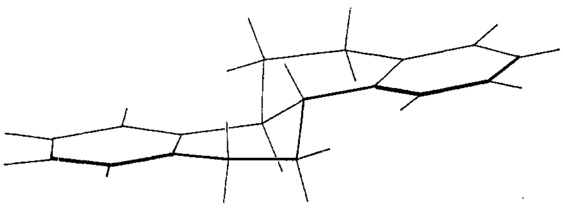
Consider first the conformational properties of hexahydrochrysene. Molecular models indicate three conformations for *trans*-**3**, a boat–boat, a boat–chair, and a chair–chair form, and two sets of three similar configurations for *cis*-**3**, a "folded" set and a "twisted" set. Steric interactions appear roughly comparable for the corresponding members of each of these three sets of conformers, and the chair–chair forms (**15**) represent energy minima in all cases. Therefore, on a simple statistical basis one might expect a cis–trans ratio of 2:1 at equilibrium; the observed proportion was 86% cis at −33°. The conformational preference of the monoanion will be a compromise between maximum overlap of the benzylic anion orbital with the aromatic π system and minimum steric interaction elsewhere. Since the geometry of the twisted chair–chair configuration **15a** appears to permit essentially zero overlap, this conformation may be eliminated from



15a, *cis* twisted



15b, *cis* folded



15c, *trans*

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[23] W. Bonthrone and D. H. Reid, *J. Chem. Soc.*, 2773 (1959).

[24] A. J. Birch and H. Smith, *ibid.*, 1882 (1951); 4909 (1956).

consideration. Although the remaining cis and trans chair–chair forms (**15b,c**) allow satisfactory orbital overlap, steric hindrance to approach of the proton donor is somewhat less to the folded cis conformer **15b** than to the more nearly planar trans conformer **15c**. Accordingly, a modest predominance of the former isomer may be predicted; experimentally 64–82% cis was observed.

The observed dependence of stereoselectivity on the structure of the olefin **2** or **6** and the efficiency of the quenching agent requires additional explanation. The latter effect may be rationalized as due to equilibration in the presence of the more strongly basic anions generated with employment of water or *tert*-BuOH as quenching agents. The former effect, however, cannot be accommodated in current concepts and involvement of an ion-pair factor seems likely. In this concept, the steric requirements of the counterions may be expected to dictate different structures for the respective intermediate dianions (from **2** and **6**), rapid protonation of which by ammonia[25] would lead to different stereoisomers. A cis-directing effect of ion pairing on the reduction of 1,3-dienes[26] and diphenylacetylene[27] has earlier been proposed.

Experimental Section

Physical Data.—Proton nmr spectra were obtained on a Varian A-60 spectrometer; chemical shifts are reported relative to TMS in $CDCl_3$ or CCl_4. Gas chromatographic analyses were performed on a F & M Model 500 chromatograph employing either a 4 ft × 0.25 in. 5% Apiezon L on 60–80 mesh Chromosorb W column (A) or a 6 ft × 0.25 in. 5% FFAP on 70–80 mesh Varaport 30 column (B) at 200° and 40-psi helium pressure. The latter column, employed in all the later work, afforded most efficient separations; retention times of **1**, **2**, *trans*-**3**, and *cis*-**3** were 17.8, 11.2, 7.1, and 5.4 min, respectively. Quantitative glpc data were verified by internal standard.

Metal–Ammonia Reduction.—Precautions for the exclusion of impurities (moisture, air, peroxides, ferrous metals) were scrupulously observed; all reductions with lithium were carried out under helium (passed through a drying tower containing Drierite and Ascarite) rather than nitrogen for reasons stated earlier.[2,3] Tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were freshly distilled from $LiAlH_4$ before use. Ammonia was distilled into the reaction vessel through a column of barium oxide (10–20 mesh). Lithium wire (Lithium Corp. of America) was wiped free of oil and washed with hexane immediately before use. All reductions were carried out in a Morton flask equipped with a Dry Ice condenser, employing the conditions described for reduction of chrysene to **1**, unless specified otherwise.

5,6-Dihydrochrysene (1).—A solution of chrysene (1.14 g, 5 mmol) in 100 ml of THF was added to 150 ml of refluxing ammonia. To the resulting suspension was added sodium metal (12.5 mg-atoms) in four approximately equal pieces at 3-min intervals. After a total reaction time of 20 min, the intense blue color was discharged by addition of excess NH_4Cl (20 g) as rapidly as possible. Glpc analysis (column A) of the crude product showed **1** (82%) along with chrysene (9%) and **2** (9%). Chromatography on alumina gave pure **1**, mp 161.5–163°; the nmr spectrum showed aryl and benzylic protons (A_2B_2 pattern at δ 3.13) in the expected ratio.

Authentic **1** was prepared *via* alcoholysis of the disodiochrysene adduct formed in DME by a modification of the procedure of Hunt and Lindsey.[15] Yields considerably higher (*ca.* 80%) than previously reported[15] (35%) were obtained from reactions conducted in minimum solvent volume. In a typical reaction, a chilled suspension of chrysene (2.28 g, 10 mmol) in DME (10 ml) was treated with sodium dispersion (40% in mineral oil, 0.50 g of Na, 22 mmol) under nitrogen. The resulting deep green solution was stirred at ambient temperature for 3 hr and then decomposed by the rapid addition of excess ethanol. Glpc analysis of the crude product gave chrysene (7%), **1** (81%), *trans*-**3** (5%), and *cis*-**3** (6%). Chromatography on alumina gave pure **1**, mp 161.5–163°, the nmr spectrum of which agreed with that of **1** obtained by reduction in ammonia. *Note:* the stabilized commercial sodium must be employed as supplied, since washing with organic solvents prior to use greatly diminishes activity.

4b,5,6,12-Tetrahydrochrysene (2). A. From Chrysene.—To a stirred solution of anhydrous $FeCl_3$ (40 mg) in 150 ml of refluxing ammonia was added a solution of chrysene (1.14 g, 5 mmol) in 100 ml of THF. Sodium (40 mg-atoms) was added to the resulting stirred suspension in four approximately equal pieces at 3-min intervals. The color of the ensuing solution became initially deep green, then blue, and finally a characteristic deep purple. Reaction was quenched with NH_4Cl (20 g) 20 min after addition of the first piece of metal. Partition of the product between water and ether, followed by conventional work-up procedures, afforded 1.03 g of a product containing **2** (80%), **1** (15%), **3** (1%), and chrysene (4%) by glpc analysis on column A. Recrystallization from alcohol furnished pure **2**, mp 79–80°. The nmr spectrum was complex, exhibiting aromatic, benzylic, vinyl, and aliphatic protons in the expected ratios; the vinyl protons appeared as a triplet at δ 6.4 (J = 3 Hz), and the benzylic protons occurred as multiplets centered at δ 2.6 (3 H) and 3.1 (2 H).

Anal. Calcd for $C_{18}H_{16}$: C, 93.05; H, 6.94. Found: C, 93.06; H, 6.83.

B. From Dihydrochrysene.—To 50 ml of refluxing ammonia was added consecutively a solution of **1** (2.5 mmol) in THF (25 ml), $FeCl_3$ (10 mg), and lithium metal (8.75 mg-atoms). The resulting purple solution was stirred at reflux for 1 hr, then decomposed with water, and worked up by the usual procedure to afford almost pure (by nmr) **2**, recrystallization of which from methanol gave **2**, mp 79–80°.

Isomerization of 2 to 6.—A solution of **2** (1.14 g) and *p*-toluensulfonic acid (200 mg) in ethanol (10 ml) was heated at reflux for 3 hr, then treated with 5% aqueous $NaHCO_3$, extracted with ether, dried, and evaporated to furnish 1.10 g of **6**. Recrystallization from methanol furnished pure **6**, mp 106–107° (lit.[15] 105°); the nmr spectrum displayed the expected aryl (8 H), benzylic (4 H), and allylic (4 H) protons, the latter as an A_2B_2 pattern centered at δ 2.8.

***cis*- and *trans*-4b,5,6,10b,11,12-Hexahydrochrysene (3). A. From 6.**—A solution of **6** (0.53 g, 2.4 mmol) in 35 ml of anhydrous ether was added to 75 ml of refluxing ammonia. To this was added sodium metal (0.14 g, 6 g-atoms) with efficient stirring. Reaction was quenched after 5 min with excess NH_4Cl (10 g). Work-up by the usual method provided *cis*- and *trans*-**3**, 82 and 16%, respectively. Samples trapped off the glpc column (B) melted at 69–70 and 114–115°, respectively (lit.[19,20] 75 and 112–114°, 115° for *cis*- and *trans*-**3**, respectively). The nmr spectra were complex, exhibiting aromatic, benzylic, and aliphatic protons in the expected ratios. Pure *cis*-**3** in larger quantity was conveniently obtained by recrystallization from alcohol; pure *trans*-**3** was isolated from chromatography of the mother liquors on alumina.

B. From 2.—Analogous reaction of **2** afforded *cis*- and *trans*-**3** in 2:1 ratio. See Table II for other examples.

C. From Chrysene.—Direct reduction of chrysene to the hexahydro stage was efficiently achieved with excess sodium (10 g-atoms) in ammonia. See Table II.

Reductive Methylation of Chrysene. A. 5-Methyl-5,6-dihydrochrysene (10).—The blue solution formed upon interaction of sodium with chrysene in THF–ammonia (by the method described for synthesis of **1**) was decolorized after 20 min with methyl bromide gas and then decomposed with excess NH_4Cl. Glpc analysis (column B) indicated **1** (23%) and **10** (65%) as the major product components. The 5-methyl-5,6-dihydro structure was assigned **10** on the basis of its conversion to 5-methylchrysene, mp 117–118° (lit.[28] 117.2–117.8°), with trityl fluoroborate in acetic acid.[23] 5-Methylchrysene was obtained free of chrysene by chromatography on alumina. The nmr spectrum of **10** exhibited a methyl doublet at δ 1.1 (J = 8 Hz); the methyl group of 5-methylchrysene appeared at δ 3.15.

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[25] Attempts to trap an intermediate dianion with methyl bromide afforded only **3**, indicating absence of any appreciable concentration of mono- or dinegative ions of hexahydrochrysene in ammonia after 20 min at −33°.

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B. Mono- and Dimethyltetrahydrochrysene (7, 8, and 9).—Reductive methylation of chrysene utilizing a procedure analogous to that employed for reduction to the tetrahydro stage afforded a complex product mixture. Major components **7** (48%), **8** (21%), and **9** (15%) were trapped off the glpc column and identified by nmr and mass spectrometry. The integrated proton nmr spectra were consistent with the assigned structures. In particular, the spectrum of **7** exhibited a methyl doublet at δ 1.33 (J = 7 Hz, 3 H) and a vinyl resonance at δ 6.30 (d, J = 4 Hz with fine splitting, 1 H); the spectrum of **8** had a methyl singlet at δ 0.95 (3 H) and vinyl protons as a pair of doublets (2 H) at δ 6.63 (J = 10 Hz) and 6.42 (J = 9 Hz), respectively; and the spectrum of **9** contained overlapping methyl doublets at δ 1.05 (J = 7 Hz, 3 H) and 1.18 (J = 7 Hz, 3 H). Alternative structures derived from **10**, *e.g.*, 5-methyl-4b,5,6,12-tetrahydrochrysene, were ruled out by the fact that analogous reductive methylation of **1** also provided the same three major products.

Equilibration of 3.—A solution of *trans*-**3** (200 mg) in 75 ml of THF was added to a solution of sodamide (from 980 mg of sodium and 40 mg of $FeCl_3$) in 120 ml of liquid ammonia and stirred at reflux for 3 hr. Conventional work-up provided recovered **3**. Repetition at various time intervals led to the following cis-trans ratios by glpc analysis.

Time, hr	% cis	% trans
3	20	80
8.5	50	50
15	75	25
21.5	85	15
25	86	14

Registry No.—**2**, 31570-60-2; *cis*-**3**, 31579-69-8; *trans*-**3**, 31579-70-1; **6**, 18930-97-7; chrysene, 218-01-9.

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Stereochemistry of the Addition of Methylzinc and -cadmium Reagents to Acyclic Aldehydes[1a]

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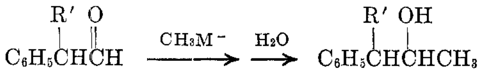
The reactivity and stereochemistry of addition of methyl Grignard and Cd and Zn reagents toward 2-phenylpropanal (**1**), 2-phenylbutanal (**2**), and 2-phenyl-3-methylbutanal (**3**) have been determined. The reactivity of *in situ* dimethylcadmium and -zinc reagents containing magnesium halide was comparable to that of the Grignards. The lower stereoselectivity observed with the cadmium and especially the zinc reagents toward **1** and **2** has been rationalized as resulting from a tight four-center transition state for such reactions. The anomalous results obtained for the addition of the methyl reagents to 2-phenyl-3-methylbutanal represent a violation of the postulates of Cram, Karabatsos, and Felkin.

In our continuing study of the addition reactions of *in situ* alkylzinc and -cadmium reagents, we have determined the stereochemistry of addition of various methyl reagents to a series of 2-phenylalkanals (**1**, **2**, and **3**). The stereochemistry of addition of isopropylmagnesium bromide to **3** has also been determined. The per cent stereoselectivity obtained with the various organometallic reagents was determined by glpc analysis with racemic reagents.



$$C_6H_5\overset{R'}{\overset{|}{C}}H\overset{O}{\overset{\|}{C}}H \xrightarrow{CH_3M^-} \xrightarrow{H_2O} C_6H_5\overset{R'}{\overset{|}{C}}H\overset{OH}{\overset{|}{C}}HCH_3$$

1, R′ = CH_3 **4a,b**, R′ = CH_3
2, R′ = C_2H_5 **5a,b**, R′ = C_2H_5
3, R′ = $i\text{-}C_3H_7$ **6a,b**, R′ = $i\text{-}C_3H_7$

$\binom{R,S}{S,R}$ threo; $\binom{S,S}{R,R}$ erythro
a **b**

The absolute configurations of threo and erythro isomers of **4** and **5**, as well as those obtained from the reaction of isopropylmagnesium bromide with **3**, are known.[2] The identification of *threo*- and *erythro*-3-phenyl-4-methyl-2-pentanols (**6**) resulting from addition of methylmagnesium iodide to **3** is based on their order of elution on STAP and FFAP, their relative rates of dehydration, and their characteristic infrared spectra (see Experimental Section).

From an inspection of Table I it is evident that, for all threo-erythro pairs, the threo isomer possesses the shorter retention time (entries 3, 5, and 8). On this basis entry 10 is assigned the threo configuration. Thermal dehydration (see Experimental Section) of all threo-erythro pairs in the presence of zinc bromide indicated that the alcohol of longer retention time (erythro) in each instance underwent dehydration at the faster rate. A study of the rate of solvolysis of *threo*- and *erythro*-3-phenyl-2-butanols (**4**) by Cram[3] has revealed that the erythro isomer reacts at a faster rate than the threo isomer. All the threo and erythro isomers obtained by preparative glpc are consistent with the above assignments.

Results

From the results compiled in Table II, certain general observations can be made.

(1) On the basis of unchanged aldehyde, the reactivity of $(CH_3)_2M$ (M = Zn, Cd) toward the various aldehydes is greater than that toward 4-*tert*-butylcyclohexanone,[4] and is essentially equivalent to that of the Grignard reagents. The reactivity of organozinc reagents prepared from methyllithium is extremely low.

(2) The stereochemistry of addition of Grignard reagents to acyclic aldehydes is independent of concentration (association). CH_3MgBr is more stereoselective than CH_3MgI. By contrast, the stereochemistry of addition of zinc and cadmium reagents,

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[1] (a) Taken in part from Ph.D. theses of E. J. G. and W. J. K., University of New Hampshire, 1969. (b) National Defense Education Act Fellow, 1966–1969. (c) Nationl Science Foundation Trainee, 1966–1969.

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