further development until methanol was used. In that solvent all of the remaining colored material was eluted, and the spectral data determined from the yellow solid (mp 78–80°) obtained on evaporation of the eluate were consistent with the alcohol, **2,2-diferrocenyl-1,2-diphenylethanol** (9): ir (CH_2Cl_2), 3590, 3510, 3420 (O–H), 3090, 3045, 3025 (aromatic C–H), 1600, 1575, 1500, 1450 (phenyl), 1100, 995 cm^{-1} (ferrocenyl); nmr ($CDCl_3$), δ 7.5–6.9 (complex multiplet, two, phenyl), 5.23 (s, one, CH–O or OH), 4.10 (s, ten, unsubstituted ferrocenyl rings), 4.18–3.70 (complex multiplet, nine, α and β ferrocenyl and CH–O or OH).

Registry No.—Lithium aluminum hydride, 1302-30-3; **8,** 12258-13-8; **9,** 12258-14-9.

Metal–Ammonia Reduction. II. Apparent Inhibition by Ferrous Metals[1]

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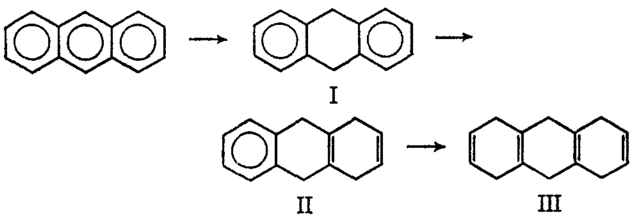
Conditions have recently been devised in this laboratory permitting the controlled, stepwise reduction of polycyclic aromatic hydrocarbons[2] by alkali metals dissolved in liquid ammonia.[3,4] A preliminary report[5] described procedures for the efficient conversion of 9,10-dihydroanthracene (I) into either 1,4,9,10-tetrahydroanthracene or 1,4,5,8,9,10-hexahydroanthracene (III), and also reported inhibition of this reduction by impurities in commercial ammonia or by iron salts. The essential features of the method are utilization of low lithium/hydrocarbon ratios and addition of the necessary proton source (*i.e.*, alcohol) late in the reaction period.



The inhibitory effects of trace metals and their salts which have been noted in scattered reports throughout the literature[4,6,7] have been the subject of speculation. However, aside from a study of the effect of colloidal iron on the Birch reduction of estradiol methyl ether,[8] the nature of the phenomenon has not been investigated. Dryden, Webber, Burtner, and Cella[8] conclude that iron interferes mainly by catalysis of the reaction between alcohol and alkali metal. Although this mechanism is probably valid when normal Birch conditions are employed (*i.e.*, alcohol present initially, generally in excess), it appears less certain for reactions conducted under other conditions.

TABLE I

REDUCTION OF ANTHRACENE (A) BY LITHIUM in AMMONIA[a]

Expt no.	Lithium, equiv	Metal salt added (1 equiv)	Product Composition,[b] %			
			A	I	II	III
1	2.5	. . .	0	90	10	0
2	5.0	. . .	0	15	68	17
3	10.0	. . .	0	0	32	68
4	2.5	$FeCl_3$	0	100	0	0
5	5.0	$FeCl_3$	0	100	0	0
6	10.0	$FeCl_3$	0	100	0	0
7	5.0	$CoCl_2$	0	100	0	0
8	5.0	Nickel acetyl acetonate	0	100	0	0
9	2.5	Commercial ammonia	0	100	0	0
10	5.0	Commercial ammonia	0	85	15	0
11	10.0	$FeCl_3$[c]	0	0	41	59
12	10.0	$FeCl_3$[d]	0	100	0	0
13	10.0	$FeCl_3$[e]	100	0	0	0

[a] Lithium wire was added to a solution of 900 mg of the hydrocarbon in 75 ml of dry THF and 150 ml of distilled ammonia, and the solution was maintained at reflux (−33°) for 2 hr, then quenched by rapid addition of alcohol. [b] Percentages were determined from the integrated peak values in the proton nmr spectra of the product.[5] [c] Ferric chloride was added 2 hr after lithium, and 5 min before alcohol. [d] Ferric chloride was added 2 hr after lithium, and 2 hr before alcohol. [e] Anthracene was added 2 hr after other components, and 2 hr before alcohol.

A series of experiments with anthracene carried out under our standard conditions[5] (Table I) provides new insight into inhibition by metallic salts. In the absence of added salts, I–III are the sole products, and their ratio is highly dependent upon the number of equivalents of lithium present (expt 1–3). Ferric chloride, cobaltous chloride, nickel acetylacetonate, or impurities in ammonia powerfully inhibit reduction beyond the dihydro stage (expt 4–9), and relatively large excesses of lithium are insufficient to counteract this effect. In contrast, transformation of anthracene itself to I remains entirely unaffected. This apparent relative rapidity of anthracene 9,10-dianion formation is supported by additional experiments. Thus, rapidly quenched reactions (1–2 min) analogous to expt 3 and 6 exhibited essentially the same product distribution as the former experiment. That ammonia ($pK_a \sim 34$)[4] is ineffective as a protonating agent compared to alcohol ($pK_a = 16–18$) may be deduced from the failure of conversion of I into II or III, despite a 2-hr delay before addition of ferric chloride (expt 3 *vs.* 12).

Salts of ferrous metals are readily reduced to the metallic state by alkali metals in liquid ammonia,[9] and the free metals are catalysts for reaction of lithium with both ammonia[9,10] (eq 1) and alcohol[7] (eq 2).

$$e^- + NH_3 \longrightarrow NH_2^- + {}^1/_2H_2 \qquad (1)$$

$$e^- + ROH \longrightarrow RO^- + {}^1/_2H_2 \qquad (2)$$

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(1) This investigation was supported in part by Public Health Service Research Grant CA-08674 from the National Cancer Institute.

(2) Stepwise reduction of benz[*a*]anthracene through the dodecahydro stage is reported in paper III: R. G. Harvey and K. Urberg, *J. Org. Chem.*, **33**, 2206 (1968). Efficient single-stage transformation of a large number of polycyclic aromatic compounds will be reported shortly.

(3) A. J. Birch, *Quart. Rev.* (London), **4**, 69 (1950).

(4) H. Smith, "Organic Reactions in Liquid Ammonia," John Wiley and Sons, Inc., New York, N. Y., 1963.

(5) R. G. Harvey, *J. Org. Chem.*, **32**, 238 (1967).

(6) A. J. Birch, *J. Chem. Soc.*, 430 (1944).

(7) W. Hückel, B. Graf, and D. Münkner, *Ann.*, **614**, 47 (1958).

(8) H. L. Dryden, Jr., G. M. Webber, R. R. Burtner, and J. A. Cella, *J. Org. Chem.*, **26**, 3237 (1961).

(9) K. W. Greenlee and A. L. Henne, *Inorg. Syn.*, **2**, 128 (1946), and references therein.

(10) W. L. Jolly, University of California Radiation Laboratory Report UCRL-16046, 1965; W. L. Jolly and C. J. Hallada in "Solvent Systems," T. C. Waddington, Ed., Academic Press Inc., New York, N. Y., 1965; E. J. Kirschke and W. L. Jolly, *Science*, **147**, 45 (1965).

That the iron-catalyzed[11] side reaction of importance is with ammonia rather than with alcohol is clear from the dramatic difference between a 5-min delay and a 2-hr delay before addition of alcohol (expt 11 *vs.* 12). This view is also supported by an experiment in which anthracene added to a solution of lithium in ammonia 2 hr after addition of ferric chloride was recovered unchanged (expt 13).

The experimental findings suggest the following interpretation: (1) initial rapid transfer of two electrons to anthracene with formation of its 9,10 dianion, further transformation of which fails to take place in the absence of an added proton source; (2) slower iron-catalyzed consumption of lithium by interaction with ammonia, complete in less than 2 hr; then (3) rapid protonation of dianion I on addition of alcohol, followed by further reduction by alternate acquisition of single electrons and protons until excess lithium is consumed. Failure of I to undergo further transformation in the absence of an added proton source is in accord with the results of kinetic studies on simple benzenoid compounds.[12]

The colloidal metal effect has already found useful application in this laboratory for selective single-stage reduction of compounds capable of forming stable dianions in liquid ammonia.[2]

Registry No.—Anthracene, 120-12-7; lithium, 7439-93-2; ammonia, 7664-41-7.

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[11] Less finely divided iron than that prepared *in situ* (*i.e.*, commercial iron powder) is ineffective as a catalyst.

[12] A. P. Krapcho and A. A. Bothner-By, *J. Amer. Chem. Soc.*, **81**, 3658 (1959); O. J. Jacobus and J. F. Eastham, *ibid.*, **87**, 5799 (1965).

Reactions of *cis*- and *trans*-1,4-Dichloro-2-butene with Sodium Amide

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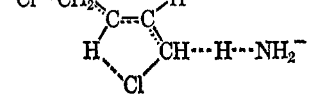
Recently it has been shown that cyclopropene[1] and 1-methylcyclopropene[2] can be synthesized by addition of the appropriate allylic chloride to a suspension of sodium amide in an inert solvent. A carbene intermediate seems to be involved in these reactions. We were interested in determining whether this procedure might be applicable to the synthesis of 3-chloromethylcyclopropene from *trans*- and/or *cis*-1,4-dichloro-2-butene and sodium amide. We recognized that both *cis*- and *trans*-1,4-dichloro-2-butene might react with sodium amide to give mainly 1-chloro-1,3-butadiene by 1,4 elimination, inasmuch as it has already been shown that *trans*-1,4-dichloro-2-butene reacts with potassium hydroxide to give 1-chloro-1,3-butadiene.[3] In the case of *cis*-1,4-dichloro-2-butene, additional reactions are possible, such as insertion on the 4-carbon atom to give 3-chlorocyclobutene, or attack of a carbanion precursor to the carbene on the 4-carbon atom to eliminate chloride and gave 3-chlorocyclobutene. Finally, unless 3-chloromethylcyclopropene were removed rapidly, further reaction with base could occur.

Results and Discussion

The allylic dichlorides were added to sodium amide in mineral oil through which a slow stream of nitrogen was passed, carrying any products to a Dry Ice trap. The products from *cis*- and *trans*-1,4-dichloro-2-butene were studied by nmr, ultraviolet, and infrared spectroscopy and vapor phase chromatography. The nmr spectra showed only vinyl hydrogen peaks (τ 5.2–4.9),[4] and thus suggested that *cis*- and *trans*-1,4-dichloro-2-butene both gave only 1-chloro-1,3-butadiene.[5] However, the nmr spectra of the two products were not identical, the spectrum of the compound from *trans*-1,4-dichloro-2-butene being more complex and shifted downfield. The infrared spectra were also very similar, but not identical. Using the vapor phase chromatographic method of Viehe[6] for the separation of *cis*- and *trans*-1-chloro-1,3-butadiene, the interesting observation was made that the product from *trans*-1,4-dichloro-2-butene consisted of mainly *cis*-1-chloro-1,3-butadiene, whereas the product from *cis*-1,4-dichloro-2-butene was primarily *trans*-1-chloro-1,3-butadiene.[7,8] The data for the *cis*- and *trans*-1-chloro-1,3-butadienes are listed in Table I.

To account for the differences in the direction of elimination for *cis*- and *trans*-1,4-dichloro-2-butene, we would like to suggest the following explanation. Viehe[9] has proposed that the higher concentration of *cis*-1-chloro-1,3-butadiene over *trans*-1-chloro-1,3-butadiene at equilibrium results from bonding between the chlorine atom and the 3-hydrogen atom in *cis*-1-chloro-1,3-butadiene. Perhaps this stabilizing, hydrogen–chlorine bonding, which would lead to *cis*-diene, is operative in the transition state in the elimination with *trans*-1,4-dichloro-2-butene, as shown.



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[1] G. L. Closs and K. D. Krantz, *J. Org. Chem.*, **31**, 638 (1966).

[2] F. Fisher and D. E. Applequist, *ibid.*, **30**, 2089 (1965).

[3] A. A. Petrov and N. P. Sopov, *J. Gen. Chem. USSR*, **15**, 981 (1945). These authors do not state that they used the *trans* isomer, but the method of synthesis is known to give only 3,4-dichloro-1-butene and *trans*-1,4-dichloro-2-butene.

[4] For a discussion on the position of absorption of vinyl hydrogens in the nmr spectrum, see J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. Y., 1965, pp 84, 85.

[5] The absence of all but some insignificant peaks in the neighborhood of τ 8.3–8.8 indicated that neither 3-chloromethylcyclopropene nor 3-chlorocyclobutene was formed. For a discussion on the postion of absorption of the methylene hydrogens of these compounds, see K. B. Wiberg and B. J. Nist, *J. Amer. Chem. Soc.*, **83**, 1226 (1961). Although 3-chloromethylcyclopropene could have decomposed during isolation of the product, and, hence, nmr analysis would have failed to indicate its formation, this seems unlikely since a negligible amount of residue remained after distillation.

[6] H. G. Viehe, *Ber.*, **97**, 598 (1964).

[7] For the exact compositions of the diene products, see Table I. Vpc analysis also indicated the presence of a small amount of an unidentified impurity.

[8] As far as we can determined, this is both the first report on the formation of 1-chloro-1,3-butadiene from *cis*-1,4-dichloro-2-butene, and the first report on the synthesis of reasonably high purity *trans*-1-chloro-1,3-butadiene.

[9] H. G. Viehe, *Angew. Chem.*, **75**, 793 (1963).