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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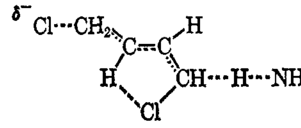
Recently it has been shown that cyclopropene[1] and 1-methylcyclopropene[2] can be synthesized by addition of the appropriate allylic chloride to a suspension of sodium amide in an inert solvent. A carbene intermediate seems to be involved in these reactions. We were interested in determining whether 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).

TABLE I

DATA FOR *cis*- AND *trans*-1-CHLORO-1,3-BUTADIENE

Chloride	$n^{20}D$	Ultraviolet[a] λ_{max}, mμ (ε)	Retention times,[b] min	Bp, °C	Yield, %
cis-1-Chloro-1,3-butadiene[c]	1.4707	233 (26,900)	136	66.5–68	72
trans-1-Chloro-1,3-butadiene[d]	1.4696	228 (18,700)	141	66–67.5	52

[a] The solvent was cyclohexane. [b] The flow rate (He) was 213 ml/min. [c] Contained 10% *trans* isomer. [d] Contained 15% *cis* isomer.

On the other hand, in the elimination with *cis*-1,4-dichloro-2-butene, hydrogen–chlorine bonding, leading to *cis*-diene, would be impossible since the extended π bonding in this transition state would prevent rotation of the 2,3-carbon bond. Steric hindrance between the chlorine atoms in the transition state would cause these atoms to lie away from each other and, hence, elimination would lead to the *trans* diene.

Experimental Section[10]

Reaction of *cis*- and *trans*-1,4-Dichloro-2-butene with Sodium Amide.—To a 500-ml, five-neck, round-bottom flask, equipped with a dropping funnel, fritted-glass nitrogen inlet, thermometer, mechanical stirrer, and outlet to a Dry Ice trap, and containing 20 g (0.51 mol) of sodium amide in 250 ml of mineral oil at 80°, was added, dropwise, 25 g (0.20 mol) of the dichloride in 135 ml of mineral oil. When the addition was complete, the trap was removed from the Dry Ice bath, and the ammonia was allowed to evaporate. The remaining liquid was distilled.

Identification and Analysis of the Products.—*cis*-1-Chloro-1,3-butadiene was confirmed as the principal product from *trans*-1,4-dichloro-2-butene on the basis of its boiling point, and infrared, ultraviolet, and nmr spectra. These spectra were all essentially identical with those of commercial 1-chloro-1,3-butadiene, obtained from Aldrich Chemical Co., Inc. Vpc analysis indicated that the commercial 1-chloro-1,3-butadiene contained approximately 85% *cis* isomer and 15% *trans* isomer.

trans-1-Chloro-1,3-butadiene was confirmed as the principal product from *cis*-1,4-dichloro-2-butene on the basis of the following observations: its nmr spectra showed only vinyl hydrogen absorption, the boiling point and the nmr, infrared, and ultraviolet spectra were very similar to those of *cis*-1-chloro-1,3-butadiene, and *trans*-1-chloro-1,3-butadiene rearranged with iodine to a *cis–trans* mixture, as described by Viehe.[6,11]

The 1-chloro-1,3-butadienes were analyzed by vpc according to the procedure of Viehe.[6] Peak enhancement studies confirmed that the products from *cis*- and *trans*-1,4-dichloro-2-butene were composed of the same compounds, but in different quantities.

Preparations and Purities of *cis*- and *trans*-1,4-Dichloro-2-butene.—*cis*-1,4-Dichloro-2-butene was synthesized according to the procedure of Babbit, Amundsen, and Steiner.[12] *trans*-1,4-Dichloro-2-butene was obtained from Eastman Organic Chemicals Department. Vpc analysis showed that the *cis* isomer was contaminated with approximately 5% of an unknown impurity, and a trace of the *trans* isomer. *trans*-1,4-Dichloro-2-butene contained only a trace of the *cis* isomer and no other impurities. The conditions for analysis on an Aerograph 90 P-3 chromatograph were as follows: flow rate (He), 323 ml/min; column length and diameter, 6 ft × 0.25 in.; column temperature, 29°; column composition, 2.5% SE-30 on 60–80 mesh DMCS Chromosorb W. Under these conditions the retention times of *cis*- and *trans*-1,4-dichloro-2-butene, are, respectively, 3.2 and 4.0 min.

Registry No.—*cis*-1,4-Dichloro-2-butene, 1476-11-5: *trans*-1,4-dichloro-2-butene, 110-57-6; sodium amide, 12125-45-0; *cis*-1-chloro-1,3-butadiene, 10033-99-5; *trans*-1-chloro-1,3-butadiene, 16503-25-6.

Acknowledgment.—Acknowledgment is made to the Research Corporation for support of this research. We are indebted to Mr. Gerald Oliver of the Jet Propulsion Laboratory, Pasadena, Calif., for the nmr spectra.

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[10] Boiling points are uncorrected.

[11] Viehe reports that heating a mixture of *cis*-1-chloro-1,3-butadiene and a solution of 1% iodine in benzene at 100° gives an equilibrium mixture of 70 ± 5% *cis* isomer and 30 ± 5% *trans* isomer. We confirmed this using the *cis*-1-chloro-1,3-butadiene from *trans*-1,4-dichloro-2-butene. Heating the *trans*-1-chloro-1,3-butadiene with iodine–benzene solution gave a mixture of 60% *cis* isomer and 40% *trans* isomer. The rearrangment undoubtedly would have gone to equilibrium if the decomposition products had been removed and the iodine replenished. We found that disappearance of iodine was rapid, and if more iodine was added, the rearrangement continued.

[12] J. Babbit, L. Amundsen, and R. Steiner, *J. Org. Chem.*, **26**, 2231 (1960).

A Conformational Analysis of Some 2-Alkoxytetrahydropyrans

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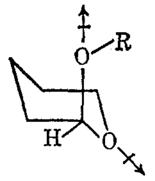
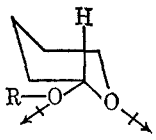
Oxane rings substituted in the 2 position by electronegative groups are generally more stable with the 2 substituent in an axial conformation. The interactions which cause the observed destabilization of the equatorial conformation in these compounds are commonly referred to as the anomeric effect, a term first used by Lemieux and Chu.[1] Examples of the anomeric effect are to be found in certain 1-substituted D-glucopyranosides,[2] 2-substituted tetrahydropyrans,[3,4] and substituted dioxanes.[5] Edward[6] has explained the anomeric effect in terms of a dipole–dipole interaction between the lone electron pairs of the ring oxygen and the substituent bond. Because of the angles between the dipoles, this interaction would be much smaller for an axial substituent (A) than for an equatorial substituent (B).



A



B

As would be expected in a dipole–dipole interaction, the magnitude of the anomeric effect is dependent on the dielectric constant of the solvent. A solvent of high

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[1] R. U. Lemieux and N. J. Chu, Abstracts, 133rd National Meeting of the American Chemical Society, San Francisco, Calif., April 1958, p 31N.

[2] For examples, see E. L. Eliel, N. J. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," John Wiley and Sons, Inc., New York, N. Y., 1965, pp 375–377.

[3] G. E. Booth and R. J. Ouelette, *J. Org. Chem.*, **31**, 544 (1966).

[4] C. B. Anderson and D. T. Sepp, *Chem. Ind.* (London), 2054 (1964).

[5] C. Altona, C. Romers, and E. Havinga, *Tetrahedron Lett.*, No. 10, 16 (1959).

[6] J. T. Edward, *Chem. Ind.* (London), 1102 (1955).