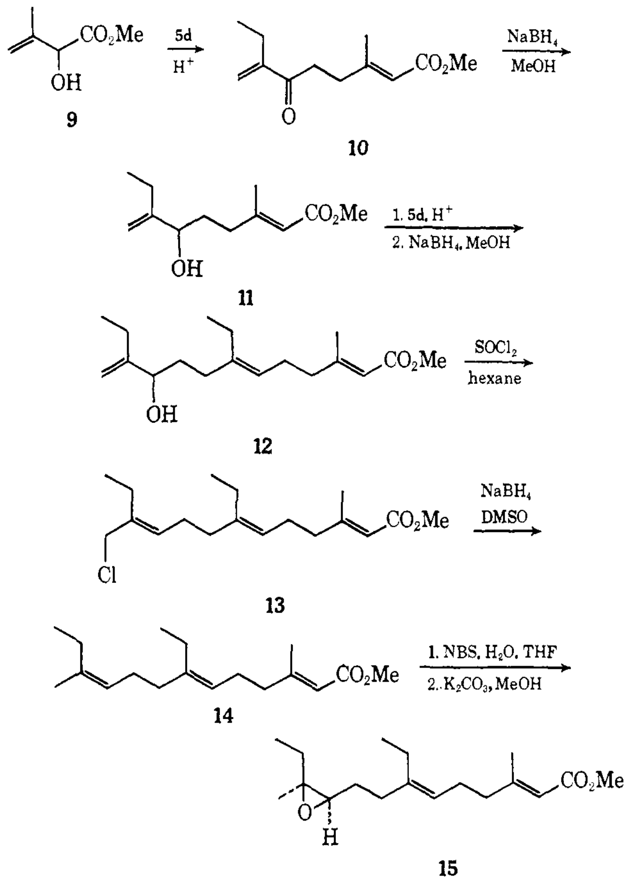

The olefinic ketal Claisen reaction has been employed in a facile stereoselective synthesis of the juvenile hormone **15**. The hydroxy ester **9**,[9] on treatment with ketal **5d** as described above, gave after chromatography on Florisil the keto ester **10** which was then reduced with sodium borohydride in methanol at 0°. The product, after chromatography on silica gel, was obtained in 51% yield and consisted of the *trans* hydroxy ester **11** contaminated with 13% of the *cis* isomer as estimated by vpc. The loss of high stereoselectivity here represents a unique case. Fortunately, the *cis* isomer is relatively volatile and could be easily removed by distilling it away from the *trans* isomer using a moderately efficient fractionating column. The residue (mass spectrum of purified material *m/e* 212, M+), on retreatment by the Claisen-reduction sequence, was transformed into the hydroxy ester **12**. After chromatography on silica gel the yield was 70% of material (*m/e* 294, M+) containing (as shown by vpc analysis) none of the *cis,trans* isomer. (Authentic *cis,trans* isomer was produced for comparison by applying the Claisen-reduction sequence to the pure *cis* form of **11**.) It is noteworthy, however, that extensive isomerization about the double bond conjugated with the ester was observed when carboxylic acid catalysis[5] was employed. The hydroxy ester **12** was submitted to conditions (thionyl chloride in hexane at 0° for 17 hr) for the S_Ni' reaction,[10] to give in 85% yield the chloride **13** contaminated, as shown by vpc, with 12% of an impurity containing what appeared to be the secondary chloride **12** (Cl in place of OH). This mixture (*m/e* 312, M+) was reduced at 50° with 1 equiv of sodium borohydride in DMSO containing 1,5-hexadiyne as a borane trapping agent. Under these conditions the reduction was selective giving predominantly the known[11] *trans,trans,cis*-trienic ester **14** contaminated (as shown by vpc) with a mixture rich in the aforementioned impurity. The known conversion of **14** into juvenile hormone **15**[11] was performed with our material. Reaction with N-bromosuccinimide in aqueous THF gave a bromohydrin which was readily separated from the chloride impurities (see above) by chromatography on silica gel. The bromohydrin, on treatment with potassium carbonate in methanol, afforded after distillation[7] at 85° (0.02 mm) *dl*-juvenile hormone (**15**) in 35% overall yield from **13**, identified with authentic material[12] by vpc, ir, nmr, and mass spectroscopy. By vpc and nmr analysis of the trienic ester,[13] as well as the juvenile hormone, it was possible to demonstrate that none of the small amounts of detectable impurities in our final product were stereoisomers of the juvenile hormone. Although the yields and purifications have not been optimized, this synthesis in its present state represents a short, highly stereoselective route to the hormone.[14]

Acknowledgment. We wish to thank the U. S. Public Health Service and the National Science Foundation for support of this research.

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[9] The acetoxy methyl ester (**9**, OAc in place of OH) was prepared by a method analogous to that for formation of the acetoxy ethyl ester (see footnote 9 of R. J. Anderson, C. A. Henrick, and J. B. Siddall, *J. Amer. Chem. Soc.*, **92**, 735 (1970)). Methanolysis of the acetate in the presence of anhydrous potassium carbonate at 0° for 1 min afforded the hydroxy ester **9** (mass spectrum *m/e* 130, M+) in 81% yield. We wish to thank Dr. John Siddall and Mr. Richard Anderson of Zoecon Corp. for providing us with samples and information regarding the preparation of the acetoxy ethyl ester.

[10] W. S. Johnson, T. Li, C. A. Harbert, W. R. Bartlett, T. R. Herrin, B. Staskun, and D. H. Rich, *J. Amer. Chem. Soc.*, **92**, 4461 (1970).

[11] K. H. Dahm, B. M. Trost, and H. Röller, *ibid.*, **89**, 5292 (1967).

[12] W. S. Johnson, T.-t. Li, D. J. Faulkner, and S. F. Campbell, *ibid.*, **90**, 6225 (1968).

[13] We wish to thank Dr. J. B. Siddall of Zoecon Corp. for providing us with an authentic mixture of the *trans,trans,cis-*, *trans,trans,trans-*, *cis,trans,trans-*, and *cis,trans,cis*-trienic ester isomers which are all resolvable by vpc.

[14] All new compounds reported in this paper have been fully characterized by ir, nmr, and mass spectrometry. Satisfactory combustion analyses were obtained for all of these substances except for some of the α,β-unsaturated ketone intermediates which have not yet been obtained completely pure.

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Stoichiometric Reduction of Molecular Nitrogen by Iron Complexes

Sir:

A fair number of stoichiometric[1-3] or even catalytic[4,5] reductions of molecular nitrogen with group IV to VI transition metal systems have been described in the

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[1] M. E. Volpin and V. B. Shur, *Nature*, **209**, 1236 (1966), and earlier references quoted there.

[2] E. E. Van Tamelen, R. B. Fechter, S. W. Schneller, G. Boche, R. H. Greeley, and B. Akermark, *J. Amer. Chem. Soc.*, **91**, 1551 (1969), and earlier references quoted there.

[3] G. Henrici-Olive and S. Olive, *Angew. Chem., Int. Ed. Engl.*, **8**, 650 (1969), and earlier references quoted there.

[4] M. E. Volpin, M. A. Ilatovskaya, L. V. Kosyakova, and V. B. Shur, *Chem. Commun.*, 1074 (1968).

[5] E. E. Van Tamelen and D. A. Seeley, *J. Amer. Chem. Soc.*, **91**, 5194 (1969).

literature. Surprisingly enough, however, no comparable stoichiometric N_2 reduction has been reported yet for complexes of iron, which is such a prominent constituent of both enzymatic and heterogeneous N_2-reduction catalysts.[6] A number of complexes have been found which contain N_2 coordinated to an iron atom,[7-9] but these complexes do not appear to be susceptible to reductive cleavage of the N≡N bond. In this communication we describe conditions for a clean, stoichiometric reduction of N_2 to NH_3 by iron compounds.

Whereas reaction systems derived from alkali naphthalides (Napht^-) and several titanium, vanadium, or chromium compounds bring about efficient reduction of N_2,[2,3] we find that the potential of $\text{Napht}^- \rightleftarrows \text{Napht}^0 + e^-$ is not quite reducing enough to promote this reaction efficiently in the presence of the corresponding iron compounds. Observed yields do not exceed *ca.* 0.5 mmol of NH_3 per mmol of $FeCl_3$ employed, even in the presence of a 25-fold excess of lithium naphthalide, and they are drastically diminished by the addition of free naphthalene (for experimental conditions see footnote 10). In keeping with this view, a large increase in N_2 reduction is observed when the more strongly reducing naphthalene dianion[11] (Napht^{2-}) is used as a reductant. With 8 mmol of Napht^{2-} per mmol of $FeCl_3$ (so that no free napth^0 is formed and the potential of the final reaction mixture is still governed by the equilibrium $\text{Napht}^{2-} \rightleftarrows \text{Napth}^- + e^-$) a yield of 0.82 mmol of NH_3/mmol of Fe is observed (Figure 1a). Stoichiometric yields (0.98 mmol of NH_3/mmol of Fe) are obtained when 2,6-dimethylnaphthalene dianion (DMNpht^{2-}) is employed as a reductant instead of Napht^{2-}. The electron-releasing methyl substituents undoubtedly make the aromatic dianion even more reducing.

The same stoichiometric yields are obtained with reaction systems containing naphthalene, if the concentration of Napht^{2-} is kept at the attainable maximum by an excess of metallic lithium (20 mmol per mmol of $FeCl_3$).[12] For this reduction four naphthalene moieties per iron appear to be required in the critical reaction step, as indicated by the sharp drop-off of reaction yields when less than 4 mmol of naphthalene/mmol of $FeCl_3$ is present in the reaction mixture (Figure 1b).

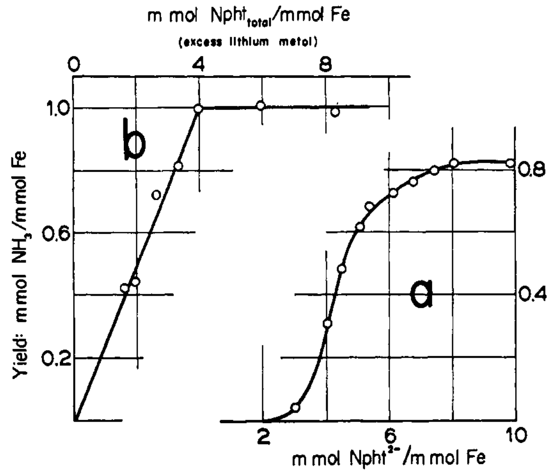

Figure 1. Requirements for iron-induced N_2 reduction: (a) dependence of NH_3 yields on the ratio of dilithium naphthalene/$FeCl_3$ employed, (b) effect of total naphthalene concentration (expressed as mmol of $\text{Napht}_{\text{total}}$/mmol of Fe) on the extent of N_2 reduction in the presence of 20 mmol of Li metal/mmol of $FeCl_3$. Experimental conditions are as follows. (a) A 0.05 *M* solution of $FeCl_3$ in THF (10 ml) was added, under Ar, to varying amounts of a solution of dilithium naphthalide in THF (0.16 *M* in naphthalene, 0.27 *M* in Li). The reaction flask was placed in an autoclave and heated, under 1600 psi of N_2, to 60° for 4 hr. NH_3 yields were determined by hydrolysis, removal of THF and naphthalene, and subsequent Kjeldahl distillation. (b) Metallic lithium (69 mg) was added to the reaction mixture under argon; otherwise the procedure is identical with the one given above.

The iron-containing N_2 reduction systems described above differ from related systems containing titanium, vanadium, or chromium compounds in that the reaction yields do not approach a limiting value of 2 mmol of NH_3/mmol of metal (see, *e.g.*, ref 3), but clearly have 1 mmol of NH_3/mmol of metal as their limit. This feature, as well as the considerably more negative potential required here to induce the reduction of N_2, will hopefully find its explanation in a more detailed mechanistic study of this reaction.

Of particular interest is the question of which kind of N_2 complexes are intermediates in this reaction and why interaction with the metal renders the N_2 molecule so much more susceptible to reduction in these species than in any of the known iron–N_2 complexes.

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(6) A. Sacco and M. Aresta, *Chem. Commun.*, 1223 (1968).

(7) C. H. Campbell, A. R. Dias, M. L. H. Green, T. Saito, and M. G. Swanwick, *J. Organometal. Chem.*, **14**, 349 (1968).

(8) G. M. Bancroft, M. J. Mays, and B. E. Prater, *Chem. Commun.*, 585 (1969).

(9) In reaction systems containing iron compounds and reductants such as Grignard reagents or lithium alkyl compounds, N_2 reduction has been observed, but these reactions yielded only on the order of 0.1 mmol of NH_3/mmol of iron complex: M. L. Khidekel and Y. B. Grebenschchikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 761 (1965). These low reduction yields and the concomitant dominance of side reactions would render mechanistic studies quite difficult.

(10) The reactions are carried out in tetrahydrofuran at 60° (see also the legend for Figure 1). Yields of NH_3, determined by hydrolysis and Kjeldahl distillation, initially increase with time, but level off after about 4 hr. The rate and extent of N_2 reduction are independent of N_2 pressure in the range of 30–100 atm; at atmospheric pressure, it is diminished to roughly one-third. N_2 reductions proceed also at room temperature; substantially longer times are required for completion, however.

(11) J. Smid, *J. Amer. Chem. Soc.*, **87**, 655 (1965).

(12) The possibility that the known reaction, $6Li + N_2 \rightarrow 2Li_3N$, is responsible for the observed N_2 reduction can be excluded. In the absence of $FeCl_3$, otherwise identical reaction systems yield only 0.02–0.03 mmol of NH_3, compared to 0.99 mmol in the presence of 1 mmol of $FeCl_3$.

Unusual Coordination in a Cobalt(II) Complex with the Tripod Ligand Tris(2-diphenylphosphinoethyl)amine

Sir:

The ligand tris(2-diphenylphosphinoethyl)amine, $(Ph_2PCH_2CH_2)_3N$, (NP_3), which contains both high-spin and low-spin stabilizing donor atoms (potential donor set 1N and 3P), has been used in order to obtain five-coordinate Ni(II) and Co(II) complexes