when a product solution showing absorption both at 221 and 260 mμ is diluted and made slightly alkaline with NH_3, the band at 221 mμ rises and that at 260 mμ decreases. The interconversion takes place also in acidic solution but less rapidly. Solid material separated from a solution containing a large proportion of the 260-mμ species showed only weak infrared absorption at ~2130 cm^{-1}, but it did liberate N_2 on being oxidized by Ce(IV). Work on these reactions is continuing.

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D. E. Harrison, H. Taube
Department of Chemistry, Stanford University
Stanford, California 94305
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Direct Ammonia Formation under Mild Conditions by Molecular Nitrogen Reducing Systems Based on Organic Titanium Species

Sir:

Within the area of nitrogen fixation research, earlier investigators have reported the generation of ammonia after acidification of μ-ammino-metal species prepared by room temperature chemical reduction of metal salts of complexes in the presence of molecular nitrogen under generally high pressures.[1] Also, stable coordination compounds carrying N_2 ligands have been identified,[2] and an organic species which captures N_2 has been described.[3] In this communication we report a different mode of molecular nitrogen fixation: the direct formation of volatile ammonia, carried out at room temperature and under atmospheric pressure and brought about by the combined action of a low-valent organic titanium species[4] and an electron source.

Experiments were designed to involve titanium(II).[4] In a typical case, titanium tetrachloride (0.5 mole equiv) was added to a suspension of potassium *t*-butoxide[5] (1.0 mole equiv) in diglyme[6] at 0° under an atmosphere of nitrogen. The suspension of dialkoxytitanium dichloride was allowed to warm to room temperature, and potassium metal (1.0 equiv) was added. Reduction of the Ti(IV) species was evident by the change in color from off-white to intense black and by the disappearance of potassium metal within 12–24 hr. Throughout these operations, purified nitrogen was allowed to bubble through the reaction mixture and into a trap that contained a dilute aqueous solution of either boric or sulfuric acid. Within 48 hr after addition of potassium, ammonia was detected in the exit traps. Identification and analysis of ammonia was achieved by vpc,[7] by mass spectrometry,[8] and by titration.[9]

Ammonia production continued for at least several weeks. When volatile ammonia ceased to evolve,[10] addition of further amounts of potassium metal produced more volatile ammonia. Moreover, when the reduction of titanium(IV) was carried out in a stepwise manner, ammonia was not generated after the first equivalent of potassium had been consumed, but only after the second equivalent had been added. Yields of volatile ammonia on the order of 10–15% (based on titanium) have been realized. Ammonium ion has also usually been detected when reaction mixtures were subjected to hydrolysis with dilute sulfuric acid.

When argon was substituted for nitrogen in the above experiment, no ammonia was produced. Ammonia (or an ionic counterpart, *e.g.*, amide or nitride) has not been detected in any ingredient of the reactions. Alkali metal, alkali metal alcoholate, and titanium tetrachloride are all necessary materials for the production of volatile ammonia; when any one was omitted from the reaction mixture, no ammonia was detected in the exit gases.

Alkoxide anions other than *t*-butoxide have been utilized with success in that experiments in which potassium *t*-butoxide was replaced with the potassium salts of methanol, 1-hexanol, and phenol all produced volatile ammonia. Experiments of the above type, but involving sodium ethoxide coupled with potassium reduction or potassium *t*-butoxide coupled with sodium reduction, have also produced ammonia. Reduction of dicyclopentadienyltitanium dichloride with sodium naphthalide in THF[11] or diglyme under an atmosphere of nitrogen generated volatile ammonia as well.

On the basis of the following observations, we regard ethereal solvent as the most likely source of hydrogen in the processes leading to volatile ammonia. In experiments in which attempts were made to rigorously exclude water, the yields of volatile ammonia did not observably differ from those characteristic of runs in which no such precautions were taken. Also, the yields of ammonia were not notably affected by changing the nature of the organic unit in the titanium alkoxide. On the other hand, when the reaction was performed in xylene, ammonia was less abundant by an order of magnitude than in the experiments involving ethereal solvents.

We are investigating the mechanism and scope of these reactions.

Acknowledgment. The authors are grateful to the National Institutes of Health (Grant GM 13797) for

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[1] M. E. Vol'pin and V. B. Shur, *Nature*, **209**, 1236 (1966), and references cited therein. See also H. Brintzinger, *J. Am. Chem. Soc.*, **88**, 4305 (1966); **88**, 4307 (1966).

[2] A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1965); J. P. Collman and J. W. Kang, *J. Am. Chem. Soc.*, **88**, 3459 (1966). For the direct incorporation of N_2, see: A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *Chem. Commun.*, 79 (1967); A. Sacco and M. Rossi, *ibid.*, 316 (1967); A. Misono, Y. Uchida, T. Saito, and K. M. Song, *ibid.*, 419 (1967); A. Yamamoto, L. S. Pu, S. Kitazume, and S. Ikeda, *J. Am. Chem. Soc.*, **89**, 3071 (1967); D. E. Harrison and H. Taube, *ibid.*, **89**, 5706 (1967).

[3] D. C. Owsley and G. K. Helmkamp, *ibid.*, **89**, 4558 (1967).

[4] E. E. van Tamelen and M. A. Schwartz, *ibid.*, **87**, 3277 (1965).

[5] The metal alkoxide either was prepared *in situ* from alcohol and alkali metal, or (more conveniently) commercially available reagent was used.

[6] Distilled from sodium metal into the reaction vessel.

[7] Column (6 ft × 0.25 in.) of 20% Carbowax 20M on Porapak Q.

[8] Performed on an Associated Electrical Industries MS-9 high-resolution mass spectrometer. We thank Dr. Alan Duffield for this determination.

[9] N. H. Furman, Ed., "Scott's Standard Methods of Chemical Analysis," Vol. 1, 6th ed, D. Van Nostrand Co. Inc., Princeton, N. J., 1962, p 745.

[10] Completion of ammonia evolution was usually accomplished by warming the reaction mixture.

[11] G. W. Watt, L. J. Baye, and F. O. Drummond, Jr., *J. Am. Chem. Soc.*, **88**, 1138 (1966).

financial support and to Professor H. Taube, Stanford University, for encouragement.

[12] Max Kade Foundation, Inc., Research Fellow, 1967–1968.
[13] National Science Foundation Postdoctoral Fellow, 1966–1967.
[14] National Institutes of Health Postdoctoral Fellow, 1966–1967.

E. E. van Tamelen, Gernot Boche,[12] S. W. Ela,[13] R. B. Fechter[14]
Department of Chemistry, Stanford University
Stanford, California 94305

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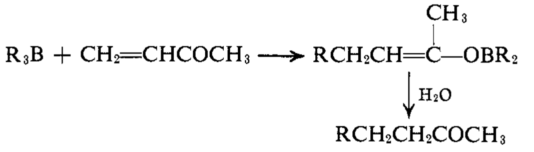
A Facile Reaction of Organoboranes with Methyl Vinyl Ketone. A Convenient New Ketone Synthesis *via* Hydroboration

Sir:

We wish to report that trialkylboranes, readily available *via* hydroboration,[1] undergo a remarkably fast 1,4 addition to methyl vinyl ketone. Hydrolysis of the initially formed intermediate produces the corresponding methyl ketone I.



$$R_3B + CH_2{=}CHCOCH_3 \longrightarrow RCH_2CH{=}\overset{CH_3}{\overset{|}{C}}{-}OBR_2 \xrightarrow{H_2O} RCH_2CH_2COCH_3$$

I

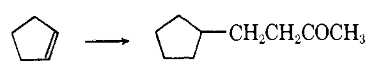
Indeed, both the addition and hydrolysis can be made to occur concurrently in a few minutes at 25°, providing a remarkably simple conversion of a large variety of olefins into the corresponding ketones II–VIII. Since methyl ketones are readily converted into the corresponding acids by the haloform reaction,[2] this likewise provides a simple synthesis of the corresponding carboxylic acids involving a lengthening of the chain by three carbon atoms.

$CH_3CH_2CH{=}CH_2 \longrightarrow CH_3(CH_2)_5COCH_3$
II

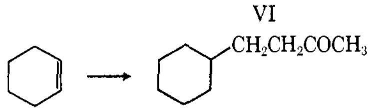
$CH_3CH{=}CHCH_3 \longrightarrow CH_3CH_2CH(CH_3)CH_2CH_2COCH_3$
III

$(CH_3)_2C{=}CH_2 \longrightarrow (CH_3)_2CH(CH_2)_3COCH_3$
IV

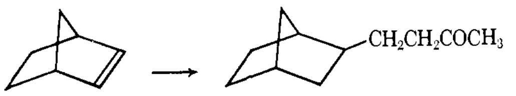
$CH_3(CH_2)_5CH{=}CH_2 \longrightarrow CH_3(CH_2)_9COCH_3$
V



VI



VII



VIII

There is a disadvantage in that only one of the three groups on boron participates in the reaction under these mild conditions. However, this is compensated for by the remarkable speed with which the reaction occurs and the mildness of the conditions which promise to make the synthesis broadly applicable to a wide variety of structures and derivatives.

We have utilized two general procedures.

Procedure A. In a 200-ml flask was placed 11.2 g (100 mmoles) of 1-octene and 30 ml of tetrahydrofuran. The flask was flushed with nitrogen and 3.3 ml of a 1.00 *M* solution of borane in tetrahydrofuran was injected with a hypodermic syringe to achieve hydroboration.[3] After 1 hr, 3.5 g (50 mmoles) of methyl vinyl ketone in 15 ml of tetrahydrofuran was added and the reaction mixture was maintained at 40° for 2 hr. Then 15 ml of water was added and the solution was heated at 40° for 1 hr to hydrolyze the enol dialkylborinite intermediate. The solution was dried over magnesium sulfate. Glpc analysis indicated the formation of 31 moles of ketone, a yield of 93%, containing 2-decanone and 5-methyl-2-undecanone in an 86:14 ratio.[4]

Procedure B. Hydroboration was carried out as above, using 120 mmoles of 1-octene, to form 40 mmoles of the organoborane. Then 1.8 ml (100 mmoles) of water was added, followed by 4.4 g (60 mmoles) of methyl vinyl ketone. The reaction mixture was allowed to stir for 1 hr at 25°.[5] Glpc analysis indicated the presence of 39.5 mmoles of the dodecanones, a yield of 99%, in a molar ratio of 85:15.

The ketones were isolated by removal of the tetrahydrofuran under vacuum followed by a simple distillation of the reaction mixture. No difficulty was encountered in the separation from the much higher boiling boron-containing side products.

The experimental results are summarized in Table I.

Table I. Conversion of Olefins into 4-Alkyl-2-butanones by Reaction of the Corresponding Organoboranes with Methyl Vinyl Ketone

Olefin	Product,[a] %	Yield,[c,d] % Procedure A	Yield,[c,d] % Procedure B
Ethylene	2-Hexanone	99	
Propylene	2-Heptanone[b]	100	
1-Butene	2-Octanone, 85 5-Methyl-2-heptanone, 15		99 (86)
2-Butene	5-Methyl-2-heptanone		80 (70)
Isobutylene	6-Methyl-2-heptanone		65 (50)[e]
1-Octene	2-Dodecanone, 85 5-Methyl-2-undecanone, 15	93 (85.5)	99 (83)
Styrene	6-Phenyl-2-butanone, 57 5-Methyl-5-phenyl-2-pentanone, 43	93	
Cyclopentene	4-Cyclopentyl-2-butanone		99 (86)
Cyclohexene	4-Cyclohexyl-2-butanone	100	95 (80)
Norbornene	4-(*exo*-Norbornyl)-2-butanone		99 (80)

[a] All products were either compared with authentic samples or exhibited analytical data and spectra in accordance with the assigned structures. [b] Analysis for the two isomers was not made. [c] By glpc analysis. [d] Numbers in parentheses are isolated yields. [e] Reaction relatively slow; yield increased with additional time.

Hydroboration of a 1-alkene produces approximately 6% of the secondary alkyl derivative.[1] Hydroboration

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[1] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.
[2] R. C. Fuson and B. A. Bull. *Chem. Rev.*, 15, 275 (1934).
[3] G. Zweifel and H. C. Brown, *Org. Reactions*, 13, 1 (1963).
[4] Clathration with urea provides a simple means of separating the major product from the branched-chain impurity.
[5] Actually, glpc examination indicated that the reaction was essentially complete in 10 min.