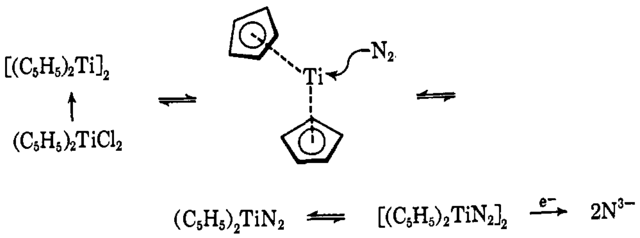

Acknowledgment. The authors are grateful to the National Institutes of Health (Grant No. GM 13797) for financial support.

(9) In the pictorial presentation of titanocene monomer, the structure featuring noncoplanar C_5H_5 units is used, as suggested by Hückel calculations of Brintzinger and Bartell.[8]

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Received May 7, 1970

Utilization of Molecular Nitrogen in the Synthesis of Organic Amines and Nitriles

Sir:

Past efforts in this laboratory have led to the discovery of the first identifiable transition metal species bearing a nitrogen (N_2) ligand capable of chemical modification: $[(C_5H_5)_2TiN_2]_2$, stable in benzene solution under N_2, is quantitatively reducible to the ammonia level ($2NH_3/Ti$).[1] In the similar titanium alkoxide series, reduction of N_2 to hydrazine has been achieved.[2] We now wish to describe a reaction system, utilizing dicyclopentadienyltitanium chloride and magnesium metal as starting materials, which permits in one laboratory operation the incorporation of nitrogen from N_2 into various organic carbonyl compounds by means of an overall reductive deoxygenation process.[3]

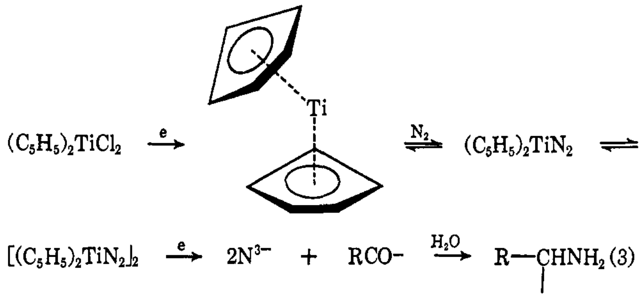
In a typical experiment, a solution of Cp_2TiCl_2 (2.5 g, 10^{-2} mol) in anhydrous, oxygen-free THF (80 ml) is added portionwise to magnesium powder (1 g) in THF (10 ml), all under dry N_2. After a few minutes, the first portion of Cp_2TiCl_2 solution turns first green and then black while N_2 uptake begins. During 1 hr, about 60 ml of N_2 at 23° is absorbed. An excess (1.5 g) of diethyl ketone is added to the black solution, and the reactants are stirred at room temperature for 5 days. Water is added and the mixture extracted with Et_2O. The ethereal solution of amine is treated with aqueous acid; the acidic solution is then washed with Et_2O, made basic, and amine is extracted with Et_2O. A mixture of 3-pentylamine and di(3-pentyl)amine (2:1 ratio) is obtained in about 25–50% yield (based on fixed N_2). When the amination reaction is carried out at a higher temperature for a shorter period of time, a somewhat lower yield is observed. A similar result can be obtained using sodium naphthalide as the reducing agent with extra sodium being added after the addition of the ketone.

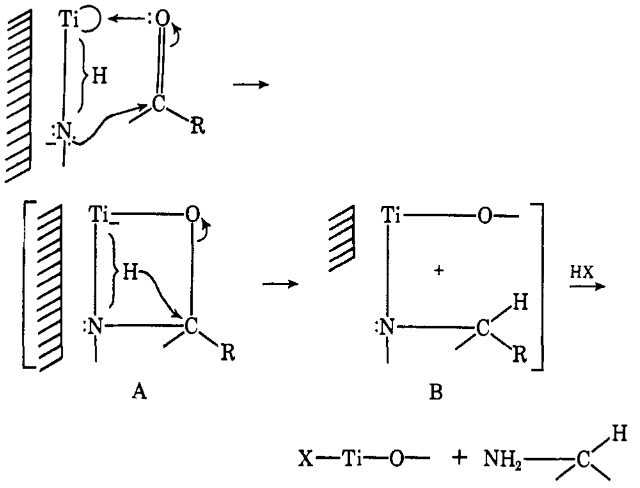
By means of reactions (eq 1) similar to that described above, di-*n*-butyl ketone is transformed into 5-nonyl- and di(5-nonyl)amines, and cyclohexanone can be converted to cyclohexylamine and dicyclohexylamine. In the aromatic series, benzaldehyde gives rise to benzylamine and some dibenzylamine, while benzophenone generates a poor yield (~5%) of benzhydrylamine. As an example of the acid chloride case, benzoyl chloride undergoes deoxygenation with incorporation of nitrogen, forming benzonitrile (eq 2). Low ester reactivity is revealed in the behavior of ethyl benzoate, which is minutely transformed into benzylamine. Product identification and yields are based on vpc and tlc data, including comparison with authentic samples.

$$R_2CO \longrightarrow R_2CHNH_2 + (R_2CH)_2NH \qquad (1)$$

$$RCOCl \longrightarrow RCN \qquad (2)$$

In view of prior studies on the course of titanium-based nitrogen fixation reactions[1,4] and the chronology of the presently described nitrogen incorporation, it seems likely that sequence 3 is operative.[3] Although the exact structural nature of the nitride intermediate is obscure,[1] a titanium–nitrogen(III) bond may be presumed available at this stage.[5] In that case there exists opportunity for an initial interaction with a carbonyl group in which an unshared electron pair on oxygen is accommodated by empty titanium orbitals while anionic nitrogen attacks carbon. In somewhat





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(1) E. E. van Tamelen, R. B. Fechter, S. W. Schneller, G. Boche, R. H. Greeley, and B. Åkermark, *J. Amer. Chem. Soc.*, **91**, 1551 (1969).

(2) E. E. van Tamelen, R. B. Fechter, and S. W. Schneller, *ibid.*, **91**, 7196 (1969).

(3) M. E. Vol'pin, V. B. Shur, R. V. Kudryavtsev, and L. A. Prodayco, *Chem. Commun.*, 1038 (1969), have reported the formation of aniline in 3% yield as a result of treatment of a mixture of dicyclopentadienyl titanium dichloride and phenyllithium with N_2.

(4) E. E. van Tamelen, D. Seeley, S. Schneller, H. Rudler, and W. Cretney, *J. Amer. Chem. Soc.*, **92**, 5251 (1970).

(5) The nonplanar representation of monomeric titanocene, proposed by H. H. Brintzinger and L. S. Bartell, *ibid.*, **92**, 1105 (1970), is used herein.

the same way as the Wittig reaction progresses, a titanaceous intermediate of type A may form and then ring open with retention of titanium–oxygen and carbon–nitrogen bonds (B). Since, as discussed elsewhere,[4] one titanocene hydrogen seems to be available at the termination of a nitrogen fixation–reduction reaction, it is possible that such hydrogen may be transferred (possibly *via* nitrogen) to α carbon in the amine, as shown. The role of titanium in this overall process may be crucial, as intimated by the above, since other metal nitrides apparently do not undergo C-amination reactions of any kind. Investigations into the scope and mechanism of the above reaction type are being pursued in this laboratory.

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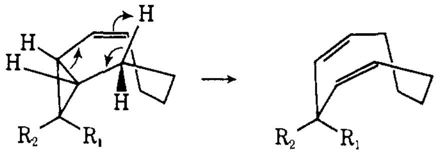
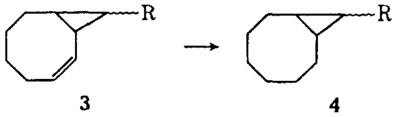
Stereoselective 1,5-Hydrogen Migration in 9-Hydroxymethylbicyclo[6.1.0]non-2-ene[1]

Sir:

The 1,5-hydrogen migration of bicyclo[6.1.0]non-2-ene (**1**, R_1, R_2 = H) to give *cis,cis*-1,4-cyclononadiene (**2**, R_1, R_2 = H) has been suggested to proceed through the unfavorable "saddle" conformation.[2] Where this conformation is not possible due to steric hindrance, the rearrangement is not expected to occur; *e.g.*, where R_1, R_2 = Br a complicated reaction ensues and the 1,5-hydrogen migration product is not observed, although it could be an intermediate.[3] In the corresponding monosubstituted compounds, the conformation necessary for rearrangement is possible where R_1 = H but not where R_1 = a bulky substituent. In support of this theory we have observed the selective rearrangement of the exo isomer of 9-hydroxymethylbicyclo[6.1.0]non-2-ene (**1**, R_1 = H, R_2 = CH_2OH) to 3-hydroxymethyl-*cis,cis*-1,4-cyclononadiene (**2**, R_1, R_2 = H, CH_2OH) under conditions that do not affect the corresponding endo isomer (**1**, R_1 = CH_2OH, R_2 = H).



1 2



3 4

We attempted to synthesize the exo and endo isomers of 9-hydroxymethylbicyclo[6.1.0]non-2-ene (**3**, R = CH_2OH) *via* the addition of ethyl diazoacetate to 1,3-cyclooctadiene followed by lithium aluminum hydride reduction. Injection of the alcohol product mixture into a vapor-phase chromatograph at 200° with the injection port and detector heated to 230 and 240°, respectively, gave a chromatogram showing two peaks in the ratio of *ca.* 4:1. Samples of each product were collected from the vpc.[4] The nmr spectrum ($CDCl_3$) of the minor component, compatible with the expected endo isomer of **3**, R = CH_2OH, displays a hydroxymethylene doublet (J = 7 Hz) at τ 6.45 (2 H), two olefinic multiplets centered at 4.3 and 4.6, and absorptions to 9.0 ppm. The nmr spectrum of the major product consists of a four-proton multiplet extending from τ 4.1 to 4.9 and a multiplet at 6.35 that integrates for three protons suggesting that a rearrangement had occurred and 3-hydorxymethyl-1,4-cyclononadiene as a possible structure. The rearranged product analyzed for an isomeric structure. *Anal.* Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.84; H, 10.85. The gross structure was confirmed by hydrogenation followed by chromic acid oxidation to cyclononanecarboxylic acid identified as its carboxyanilide; mp 139–140.2°, lit.[5] mp 140–141°. A mixture melting point gave no depression. The position of the double bonds was confirmed by ozonolysis followed by hydrogen peroxide oxidation to give adipic acid.

The infrared spectrum of **2** displayed bands at 1637 (w), 1070 (s), 1060 (s), 1020 (s), 813 (m), 743 (s) cm^{-1}, a *cis*-olefinic C–H out-of-plane deformation band at 705 (s) cm^{-1}, and no bands corresponding to the C–H out-of-plane and in-plane deformation bands characteristic of *trans*-olefins, supporting the assigned cis,cis stereochemistry. Repeating the synthesis of **2** but reducing the ester with lithium aluminum deuteride followed by vpc collection gives the deuterated compound ($-CD_2OH$) whose nmr spectrum now clearly shows the bisallylic H_3 as a triplet (J = 7.5 Hz) at τ 6.1. The nmr spectrum of the liquid acetate of **2** (R_1 = CH_2OAc) gives a two-proton doublet (J = 2 Hz) at τ 5.9.

In order to confirm the identity of the starting alcohols (**3**, R = CH_2OH), exo and endo isomers of 9-carboethoxybicyclo[6.1.0]non-2-ene (**3**, R = CO_2Et) were separated and collected by preparative vpc.[4] Hydrogenation gave the corresponding dihydro exo and endo isomers (**4**, R = CO_2Et) which were, respectively, identical with the major and minor products from the copper-catalyzed addition of ethyl diazoacetate to cyclooctene,[6] a reaction which is expected to give a

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(1) Presented in part at the Midwest Regional American Chemical Society Meeting, Kansas City, Mo., Oct 1969.

(2) D. S. Glass, R. S. Boikess, and S. Winstein, *Tetrahedron Lett.*, 999 (1966). This article contains an excellent discussion and leading references. A heteroatom analog, 3,4-epoxycyclooctene, undergoes thermal rearrangement to *cis,cis*-3-oxa-1,4-cyclononadiene among other products (J. K. Crandall and R. J. Watkins, *ibid.*, 1717 (1967)).

(3) M. S. Baird, D. G. Lindsay, and C. B. Reese, *Chem. Commun.*, 784 (1968).

(4) Wilkens A-700 (Autoprep) instruments were used for vpc analyses and separations utilizing fluorosilicone (QF-1) as stationary-phase material. Typical retention times (minutes) for a 20 ft × $^3/_8$ in. 30% QF-1 column under a helium gas flow rate of 100 cc/min at 200° were: **1**, R_1 = CH_2OH, R_2 = H (19); **2**, R_1, R_2 = CH_2OH (15); *endo*-**3**, R = CO_2Et (22.5); *exo*-**3**, R = CO_2Et (25); *endo*-**4**, R = CO_2Et (22); *exo*-**4**, R = CO_2Et (30).

(5) C. D. Gutsche and T. D. Smith, *J. Amer. Chem. Soc.*, 82, 4067 (1960). We are indebted to Professor Gutsche for an authentic sample of the derivative.

(6) S. Akiyoshi and T. Matsuda, *ibid.*, 77, 2476 (1955). The formation of isomers is not discussed and the reported melting point of the hydrolysis product is probably that of an isomeric mixture of carboxylic acids.