maintained. After work-up, simple distillation gave product, bp 62–72° (0.07 mm), which was pure to glpc. The nmr spectrum (neat) was consistent with the structure of 2-methyl-4-pentenophenone wherein the α position was completely deuterated: δ 1.2 (s, $-CH_3$, 3 H), 2.4 (m, $-CH_2-$, 2 H), 5.0 (m, $=CH_2$, 2 H), 5.7 (m, $-CH=$, 1 H), 7.4 and 7.9 ppm (2 m, H_{arom}, 5 H). The ir spectrum contained strong absorptions at 1690, 990, 920, and 700 cm^{-1}.

Registry No.—4-Pentenophinone-*2*-d_2, 35666-59-2; 4′-chloro-4-pentenophenone-*2*-d_2, 35666-62-7; 2-methyl-4-pentenophenone-*2*-*d*, 35666-63-8.

The Reaction of Atomic Nitrogen with Propene

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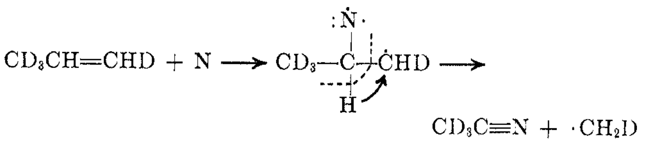
The reaction of atomic nitrogen with propene was first reported by Winkler and Trick.[2] Later work on this reaction in the gas[3–6] and solution[7] phases has shown widely differing results. We report here the solution phase reaction of propene with atomic nitrogen. The atomic nitrogen of this study was generated by a microwave discharge through molecular nitrogen. This is a conventional source of nitrogen atoms.

The major nitrogen-containing product of the reaction of atomic nitrogen with all hydrocarbons is HCN. Lichtin[6] has reported that the nitrogenous products from the propene reaction ($[C_3H_6]/[N] = 2.7$) in the gas phase are HCN (30% yield), acetonitrile (10% yield), and acrylonitrile (2% yield).

Lichtin, Shinozaki, and Shaw[3] have also used carbon-14 labeling to follow the fate of each of the three carbons in propene (labeled $^1CH_2{=}^2CH{-}^3CH_2$). Hydrogen cyanide arises slightly more extensively from C-3 than from C-1 or C-2. The acetonitrile contains one carbon from C-2 and another carbon from either C-1 or C-3. This result indicates that acetonitrile is formed from an intermediate in which C-1 and C-3 are equivalent.

Oka, Suda, and Sato[7] have studied the γ-radiolysis of liquid nitrogen containing a small amount of propene. Under these conditions, the only nitrogenous product was acetonitrile (12% yield). They propose that ground state (^4S) atomic nitrogen is the precursor of the acetonitrile. This result is in contrast to that previously reported for atomic nitrogen reactions with hydrocarbons, where HCN is the major product.

Oka, Suda, and Sato have also investigated the reaction of a 1:1 mixture of propene-d_0 and propene-d_6 and the reaction of $CD_3CH{=}CHD$. The acetonitrile from the propene-d_0–propene-d_6 mixture was mainly d_0 and d_3, while the acetonitrile from $CD_3CH{=}CHD$ was mainly d_3. They conclude that the key intermediate in acetonitrile formation is made by nitrogen atom addition to C-2 to make a primary radical. This radical makes acetonitrile by simultaneously cleaving away the hydrogen atom on C-2 and the CH_2 group.



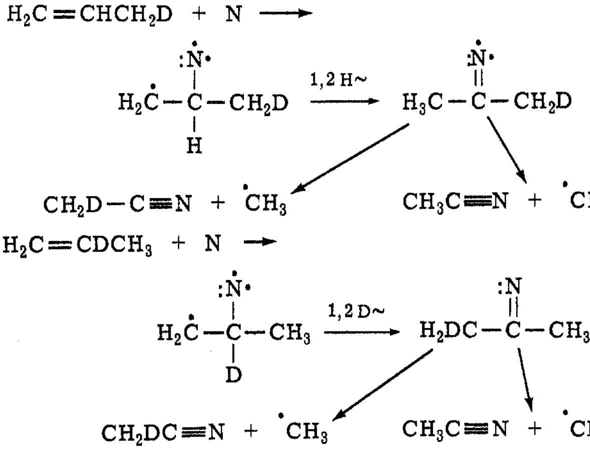
$$CD_3CH{=}CHD + N \longrightarrow CD_3{-}\overset{:\dot{N}\cdot}{\underset{H}{C}}{-}CHD \longrightarrow CD_3C{\equiv}N + \cdot CH_2D$$

In their pathway, acetonitrile is formed from C-2 and C-3; C-1 and C-3 never become equivalent as in the gas phase study of Lichtin.

We have examined the liquid phase reaction of propene with atomic nitrogen at −160°. The nitrogenous products from this reaction are HCN (55.4% yield), acetonitrile (4.9%), and acrylonitrile (0.17%). The mechanism of formation of acetonitrile and acrylonitrile was studied by reaction of 2-deuteriopropene and 3-deuteriopropene. Hydrogen cyanide from these reactions was not analyzed for deuterium content, because the proton of HCN readily exchanges with protons adsorbed on glass.

Acetonitrile from the reaction of 3-deuteriopropene was 55% undeuterated and 45% monodeuterated by mass spectrometric analysis at 15 eV. The acetonitrile formed from 2-deuteriopropene was 61% undeuterated and 39% monodeuterated. These results are consistent with an intermediate for acetonitrile formation in which C-1 and C-3 become equivalent by a 1,2-hydrogen (or deuterium) shift from C-2 to C-1. It is proposed that the intermediate preceding nitrile formation from atomic nitrogen–alkene reactions is the imino radical. Independently generated imino radicals are reported to β cleave to product nitriles and other radicals (Scheme I).[8]

SCHEME I



These results cannot be explained by the mechanism of Sato, Oka, and Suda,[7] which postulates a nearly simultaneous cleavage of the carbon–hydrogen bond on C-2 and the C-1 to C-2 bond.

Hydrogen cyanide, the major product of the propene–atomic nitrogen reaction, may be formed by the pre-

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[2] C. A. Winkler and G. S. Trick, *Can. J. Chem.*, **30**, 915 (1952).

[3] Y. Shinozaki, R. Shaw, and N. N. Lichtin, *J. Amer. Chem. Soc.*, **86**, 341 (1964).

[4] P. T. Hinde, Y. Titani, and N. N. Lichtin, *ibid.*, **89**, 1411 (1967).

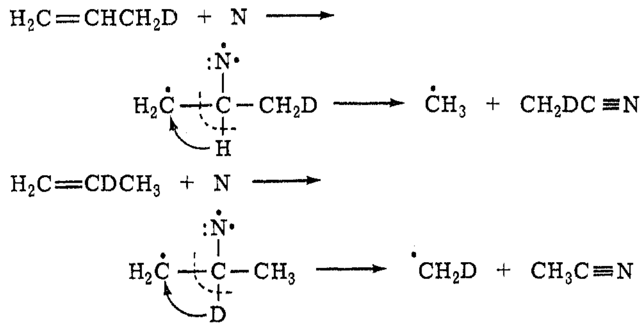
[5] Y. Titani and N. N. Lichtin, *J. Phys. Chem.*, **72**, 526 (1968).

[6] N. N. Lichtin, "The Chemistry of Ionization and Excitation," G. R. A. Johnson and G. Scholes, Ed., Taylor and Francis, London, 1967, p 181.

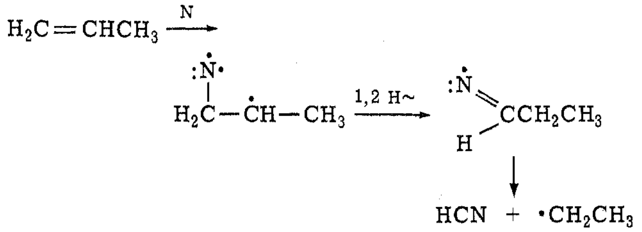
[7] T. Oka, Y. Suda, and S. Sato, *Bull. Chem. Soc. Jap.*, **42**, 3083 (1969).

[8] M. L. Poutsma and P. A. Ibarbia, *J. Org. Chem.*, **34**, 2848 (1969).

Oka, Suda, Sato Proposal



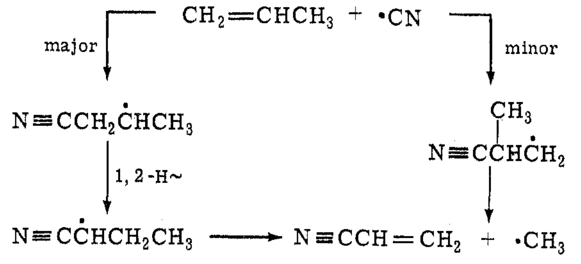
ferred addition of nitrogen atoms to the terminal olefinic carbon of propene.



The deuterium content of the acrylonitrile formed from propene was also studied. The acrylonitrile from 3-deuteriopropene was 97% undeuterated and 3% monodeuterated by mass spectrometric analysis at 14 eV. That formed from 2-deuteriopropene was 9% undeuterated and 91% monodeuterated. These results indicate selective elimination of the methyl group of propene. They can be explained by a mechanism involving cyanogen radicals, which are present in hydrocarbon–atomic nitrogen reactions to a small extent.[9]

Addition of cyanogen radicals to propene can occur in two ways (Scheme II). The major pathway includes a 1,2-hydrogen rearrangement, which is uncommon in low temperature condensed phase chemistry. It is possible that this major pathway does not lead to acrylonitrile, but to other products by addition of another molecule of propene (C_4 nitriles were not found). However, the minor pathway is a reasonable one to account for this product.

SCHEME II



The reaction of atomic nitrogen with liquid propene closely parallels the gas phase reaction. There is little resemblance between these reactions and the reactions of the reactive species produced by the γ-radiolysis of propene in liquid nitrogen. The active species in the latter reactions cannot be ground state atomic nitrogen.

Experimental Section

"Active" nitrogen, which is mainly ground state (quartet) atomic nitrogen, was generated by a 2450-Mc microwave discharge through molecular nitrogen. The molecular nitrogen (prepurified grade) was first passed over copper turnings at 500° to remove all but a few ppm of oxygen. Reaction with propene was accomplished by bubbling the atomic nitrogen stream through liquid olefin. Most reaction takes place in the condensed phase, since reaction flames[9] are not seen before the nitrogen reaches substrate, and the yellow nitrogen afterglow does not persist after contact with the substrate. The molar ratio of propene to atomic nitrogen was 120:1. The flow rate of atomic nitrogen (43.8 μmol/min) was determined by a calorimetric method[10] and by the nitric oxide titration method.[11]

2-Deuteriopropene and 3-deuteriopropene were made by D_2O hydrolysis of the corresponding Grignard reagents. Propene was purified by trap-to-trap distillation through a −131° trap. The isotopic purity of the deuterated propenes was determined by mass spectrometry at 11.2 eV. The infrared spectrum of 3-deuteriopropene showed a carbon–deuterium stretch at 2160 cm^{-1}; the carbon–deuterium stretch in 2-deuteriopropene was at 2225 cm^{-1}.

Nitrilic products from the atomic nitrogen reactions were separated from excess propene by trap-to-trap distillation and were analyzed by gas chromatography on a dinonylphthalate column and by comparison of the infrared and mass spectra to those of known samples.

Registry No.—Atomic nitrogen, 17778-88-0; propene, 115-07-1.

Acknowledgment.—The financial support of the Air Force Office of Scientific Research (Grant. No. 1983) is acknowledged with gratitude.

(9) A. N. Wright and C. A. Winkler, "Active Nitrogen," Academic Press, New York, N. Y., 1968.

(10) J. J. Havel and P. S. Skell, *J. Amer. Chem. Soc.*, **94**, 1792 (1972).

(11) P. Harteck, G. Mannella, and R. R. Reeves, *J. Chem. Phys.*, **29**, 608 (1958).

Benzyl Alcohol as Hydrogen Donor in Selective Transfer Hydrogenation of Unsaturated Steroids

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In a previous paper[1] we suggested transfer hydrogenation as the first step of the reaction of an α,β-unsaturated ketone with benzyl alcohol under conditions of homogeneous basic catalysis. This prompted us to investigate benzyl alcohol as donor in hydrogen transfer also under conditions of heterogeneous catalysis.[2] To our knowledge, these properties were still unexplored, although some alcohols had been occasionally used to reduce various acceptors in the presence of nickel or palladium.[3]

The present report deals with experiments performed on representative unsaturated steroids as acceptors in order to investigate the scope and limitations of this reaction.

The results obtained by heating solutions of the steroid in benzyl alcohol or other carbinol in the presence of Pd catalyst are summarized in Table I. Benzyl alcohol

(1) R. Vitali, G. Caccia, and P. P. Castelli, *Ann. Chim.* (*Rome*), **62**, 315 (1972).

(2) *Cf.* E. A. Braude and R. P. Linstead, *J. Chem. Soc.*, 3544 (1954).

(3) E. C. Kleiderer and E. C. Kornfeld, *J. Org. Chem.*, **13**, 455 (1948). For other references see E. A. Braude, R. P. Linstead, and P. D. W. Mitchel, *J. Chem. Soc.*, 3578 (1954).