10 ml each were collected and the major component was found in tubes 49–102. The fractions were combined, the solvents were evaporated, and the product was crystallized from aqueous ethanol to afford 0.8 g (86%) of colorless needles: mp 186–188°; $[\alpha]^{25}D$ 13.5° (*c* 0.4, 0.1 *N* HCl); uv max (0.01 *N* HCl) 253 mμ (ε 5300), 262 (5610), 268 (6580), and 274 (5560).

Anal. Calcd for $C_{19}H_{26}O_{10}N_2 \cdot H_2O$: C, 49.56; H, 6.13; N, 6.09. Found: C, 49.14; H, 6.24; N, 6.12.

1-β-Lactosylbenzimidazole (6).—The preparation of **6** followed the exact same procedure given above for the preparation of **5**. A picrate was obtained from cold methanol, the analytical sample of which had mp 219–222°.

Anal. Calcd for $C_{25}H_{29}N_5O_{17}$: C, 44.72; H, 4.35; N, 10.43. Found: C, 44.93; H, 4.59; N, 10.29.

Regeneration of the free nucleoside with an anion exchange resin as described above and chromatography on a cellulose column gave **6**, which resisted crystallization for many months. Therefore, it was lyophilized and dried further in a drying pistol (P_2O_5) under high vacuum at 40° for 48 hr and at 110° for 24 hr to afford 0.46 g of a fluffy, white powder which liquified slowly at temperatures above 170° to a viscous syrup: $[\alpha]^{25}D$ 4° (*c* 1.3, H_2O); uv max (0.01 *N* HCl) 253 mμ (ε 5095), 262 (5390), 268 (6230), and 275 (5325).

Anal. Calcd for $C_{19}H_{26}N_2O_{10} \cdot H_2O$: C, 49.56; H, 6.13; N, 6.09. Found: C, 49.77; H, 5.80; N, 6.00.

Picrate of 1-β-D-Glucopyranosylbenzimidazole (7). From 5.—A sample (0.2 g) of **5** was dissolved in 50 ml of methanol and the solution was saturated with dry hydrogen chloride gas at 0°, then kept at room temperature for 2 days in a pressure bottle. The solution was evaporated to dryness, the residue was dissolved in methanol, and the pH (moist pH paper) was adjusted to neutrality with a few drops of ammonium hydroxide. To this solution was added 1 ml of 10% methanolic picric acid and the flask was chilled in the refrigerator for several days. The crystals (mp 142–152°) were filtered off and recrystallized from water to give yellow needles, mp 146–149°, $[\alpha]^{25}D$ −19.4° (*c* 1, pyridine) [lit.[12] mp 145–148°, $[\alpha]^{15}D$ −18° (*c* 2, pyridine)].

From 6.—Application of the same procedure as above to **6** resulted in a product (mp 128–138°) which required two recrystallizations from water to give yellow needles whose melting point was not depressed upon admixture with the picrate of **7**.

Registry No.—**5**, 35672-33-4; **5** picrate, 35672-34-5; **6**, 35672-35-6; **6** picrate, 35737-07-6.

A Convenient Deuterium Exchange Technique

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During the course of our investigations of the enolene rearrangement,[1-3] a convenient and mild deuterium exchange technique was developed which we believe to be superior to presently used procedures. Our technique capitalizes on the elegant procedure of Pasto and Meyer,[4] which makes ethanol-*O*-d_1 easily and economically available as a source of exchangeable deuterium and incorporates a novel method of isolating the desired deuterated product from the reaction mixture.

The compound to be deuterated is dissolved in an appropriate excess of ethanol-*O*-d_1 and a catalytic amount of sodium metal is added. The resulting solution is stirred at room temperature overnight, the ethanol is removed *in vacuo*, and a second portion of ethanol-*O*-d_1, is added. After exchange with two or three portions of ethanol-*O*-d_1 has been carried out in this way, an amount of acetyl chloride just sufficient to destroy the sodium ethoxide present is added. The resulting ethyl acetate is removed along with ethanol-*O*-d_1 by flash distillation, and the remaining material is distilled to effect isolation of the desired deuterated product.

This method has been shown to be generally applicable to ketones which boil considerably higher than ethanol and ethyl acetate and it should also be suitable for the deuteration of other compounds which possess acidic hydrogens. Among the compounds which were successfully deuterated in the α position by this technique are 4-pentenophenone; 4′-R-4-pentenophenone where R = CH_3, CH_3O, Cl; 2-R-4-pentenophenone where R = CH_3, CH_2CH_3, $(CH_2)_2CH_3$, $CH(CH_3)_2$, $C(CH_3)_3$, and C_6H_5; 2-allyl-1-indanone; 2-allyl-1-tetralone; 3-methyl-4-pentenophenone; 2,3-dimethyl-4-pentenophenone; 2-ethyl-3-methyl-4-pentenophenone; 3-methyl-2-*m*-propyl-4-pentenophenone; and 2-α-methylallyl-1-tetralone.

In all cases encountered in our work, the reaction substrate was soluble in ethanol; however, in instances where the material to be deuterated is not ethanol soluble, an inert cosolvent such as dioxane may be added to maintain homogeneity.

Experimental Section

The following examples are representative of the technique.

4-Pentenophenone-2-d_2.—4-Pentenophenone[2] (8.0 g, 0.05 mol) was stirred with 59 ml (1.0 mol) of ethanol-*O*-d_1 and *ca.* 0.2 g of sodium metal for 24 hr, after which time the ethanol-*O*-d_1 was removed by the application of aspirator vacuum and a second 59-ml portion of ethanol-*O*-d_1 was added. After 24 hr this process was again repeated and, after the final period of stirring, the solution was neutralized by the addition of *ca.* 1 ml of acetyl chloride. The resulting mixture was concentrated and distilled *in vacuo* to obtain product, bp 58–65° (0.05 mm), $n^{25}D$ 1.5282. The yield was 6.5 g. The nmr spectrum (CCl_4) was consistent with the structure of 4-pentenophenone-2-d_2: δ 2.45 (d, $-CH_2-$, 2 H), 5.0 (m, $=CH_2$, 2 H), 5.9 (m, $-CH=$, 1 H), 7.4 and 7.9 ppm (2 m, H_{arom}, 5 H). The ir spectrum contained strong absorptions at 1690, 975, and 910 cm^{-1}.

Anal. Calcd for $C_{11}H_{10}D_2O$: C, 81.44; H + D, 8.69. Found: C, 81.27; H + D, 8.70.

4′-Chloro-4-pentenophenone-2-d_2.—The deutration procedure used was identical with that employed with 4-pentenophenone: 5.0 g (0.026 mol) of 4′-chloro-4-pentenophenone[5] was used and, after work-up, vacuum distillation gave water-clear distillate, bp 80–85° (0.06 mm). This product was further purified by column chromatography on silica gel [petroleum ether (bp 60–80°)–benzene] followed by micro vacuum distillation. The product thus obtained was pure to glpc analysis and the nmr spectrum (neat) was consistent with the structure of 4′-chloro-4-pentenophenone wherein the α position was 96.5% deuterated: δ 2.1 (d, $-CH_2-$, 2 H), 2.5 (m, $-CH_2-$, 0.07 H), 4.7 (m, $=CH_2$, 2 H), 5.5 (m, $-CH=$, 1 H), 6.9 (d, H_{arom}, 2 H), and 7.4 ppm (d, H_{arom}, 2 H). The ir spectrum contained strong absorptions at 1680, 1000, and 915 cm^{-1}.

Anal. Calcd for $C_{11}H_9D_2OCl$: C, 67.17; H + D, 6.66. Found: C, 67.31; H + 6.64.

2-Methyl-4-pentenophenone-2-d.—The deuteration applied to 2-methyl-4-pentenophenone[6] was identical with that employed with 4-pentenophenone with the exception that reflux was

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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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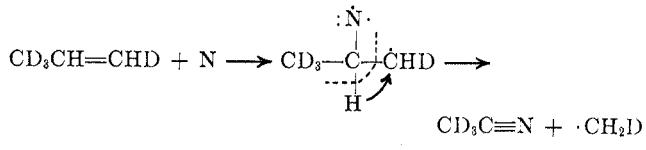
The reaction of atomic nitrogen with propene was first reported by Winkler and Trick.[2] Later work on this reaction in the gas[3-6] and solution[7] phases has shown widely differing results. We report here the solution phase reaction of propene with atomic nitrogen. The atomic nitrogen of this study 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.

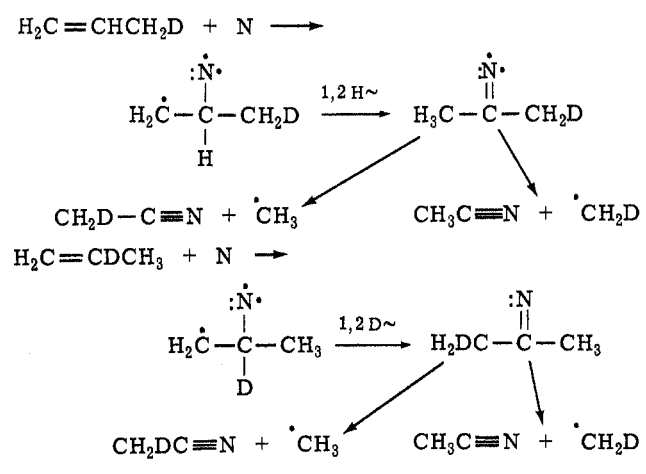


In their pathway, acetonitrile is formed from C-2 and C-3; C-1 and C-3 never become equivalent as in the gas phase study of Lichtin.

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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