the equilibration of V with VI and III with IV is the 1,2-eclipsing interactions (VII) in VI and IV that are absent in II.

Acknowledgment. We thank the Petroleum Research Fund (692-A4) and the National Science Foundation (GP-3343) for financial support of the work performed at Michigan State University.

(6) Fellow of the Alfred P. Sloan Foundation.

Gerasimos J. Karabatsos,[6] Nelson Hsi
Department of Chemistry, Michigan State University
East Lansing, Michigan

Seymour Meyerson
Research and Development Department
American Oil Company, Whiting, Indiana

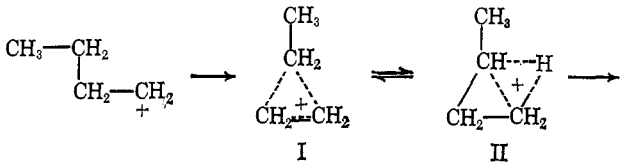
Received August 12, 1966

Carbonium Ions. IX. The Deamination of Isotopically Labeled 1-Butylamines

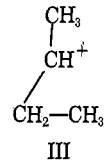
Sir:

We have commented[1] on the effect that alkyl substitution at C-2 of the 1-propyl system has on the relative stability and detectability of alkyl-bridged ions and edge-protonated cyclopropanes. We wish now to discuss the effect of alkyl substitution at C-3.

Formation of methylcyclopropane in the deamination of 1-butylamine[2] has implicated I and/or II and raised the question[2a] of the intermediacy of path II → III.



I II



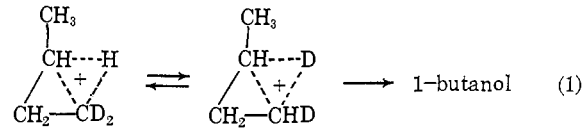
III

Mass spectral analysis of the trimethylsilyl ether of 1-butanol obtained from the deamination[3] of 1-butylamine-1,1-d_2 gave 99.5% d_2 and 0.5% d_1 (P − CH_3); 97.7% d_2 and 2.3% d_1 (P − C_3H_7). That of 1-butanol obtained from lithium aluminum deuteride reduction of the corresponding acid gave 98.5% d_2 and 1.5% d_1 (P − CH_3); 96.7% d_2 and 3.3% d_1 (P − C_3H_7).

From the deamination of 1-butylamine-2,2-d_2 the corresponding values were 96.3% d_2 and 3.7% d_1 (P − CH_3); 0.8% d_2, 7.0% d_1, and 92.2% d_0 (P − C_3H_7). From authentic 1-butanol-2,2-d_2 the values were 97.3% d_2 and 2.7% d_1 (P − CH_3); 0.8% d_2, 7.2% d_1, and 92.0% d_0 (P − C_3H_7).

From the deamination of 1-butylamine-3,3-d_2 the values were 96.3% d_2 and 3.7% d_1 (P − CH_3); 0.2% d_2, 0.4% d_1, and 99.4% d_0 (P − C_3H_7). From authentic 1-butanol-3,3-d_2 the values were 96.5% d_2 and 3.5% d_1 (P − CH_3); 0.3% d_2, 0.5% d_1, and 99.2% d_0 (P − C_3H_7). In all reported cases duplicate experiments gave identical results.

Since the 1-butanol obtained is less than 0.1% isotopically rearranged, both I and sequence 1 are excluded from the paths leading to 1-butanol. Further-

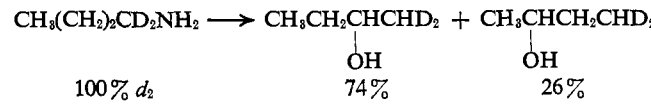


(1)

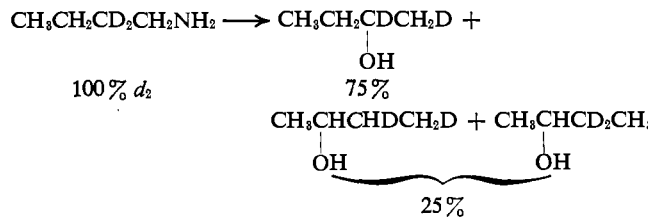
more, 1,4-hydride and 1,2- and 1,3-alkyl shifts are also excluded.

We now examine sequence II → III, *i.e.*, the question of a nominally 1,3-hydride shift.

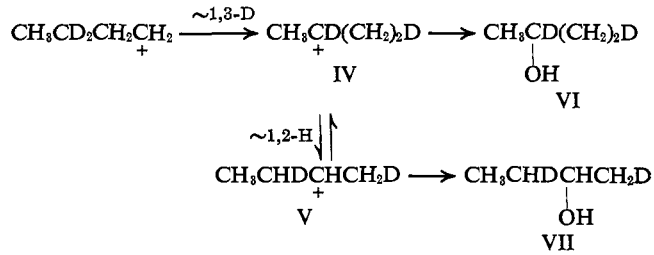
Mass spectral analysis of the trimethylsilyl ether of 2-butanol obtained from the deamination of 1-butylamine-1,1-d_2 (97.0% d_2 and 3.0% d_1) gave 82.3% d_2, 2.8% d_1, and 15.0% d_0 (P − CH_3); 71.8% d_2, 2.7% d_1, and 25.5% d_0 (P − C_2H_5). From the (P − C_2H_5) ion, after removing the contribution of the singly deuterated amine, the following may be written.[4]



From the deamination of 1-butylamine-2,2-d_2 (96.3% d_2 and 3.7% d_2) the values were 81.0% d_2 and 19.0% d_1 (P − CH_3); 72.0% d_2, 3.9% d_1, and 24.1% d_0 (P − C_2H_5). The data are consistent with



From the deamination of 1-butylamine-3,3-d_2 (96.3% d_2 and 3.7% d_1) the values were 96.5% d_2 and 3.5% d_1 (P − CH_3); 19.0% d_1 and 81.0% d_0 (P − C_2H_5). From these results an upper limit may now be calculated for the contribution of 1,3-hydride shifts. From the fact that the d_1 contribution (3.5%) to the (P − CH_3) ion is not larger than the d_1 already present in the starting material (3.7% d_1 amine), VII cannot comprise more than 0.5% of the alcohol. Taken in conjunction with conclusions based on nmr data, this places an upper limit of 2–3% on VI.



In Figure 1 the pertinent region of the nmr spectrum of the trimethylsilyl ether of 2-butanol obtained from the deamination of 1-butylamine-3,3-d_2 is shown.

(1) G. J. Karabatsos, N. Hsi, and S. Meyerson, *J. Am. Chem. Soc.*, **88**, 5649 (1966).

(2) (a) P. S. Skell and I. Starer, *ibid.*, **82**, 2971 (1960); (b) J. H. Bayless, F. D. Mendicino, and L. Friedman, *ibid.*, **87**, 5790 (1965).

(3) For reaction conditions see ref 1. All deuterated amines reported in this paper were prepared from the reduction of the corresponding nitriles with lithium aluminum hydride or deuteride.

(4) The (P − CH_3) ions arise 21% by loss from the 2-butyl group [15.0/(97.0 − 25.5) × 100 = 21.0%] and 79% by loss from the trimethylsilyl group. Details will appear in a full paper.

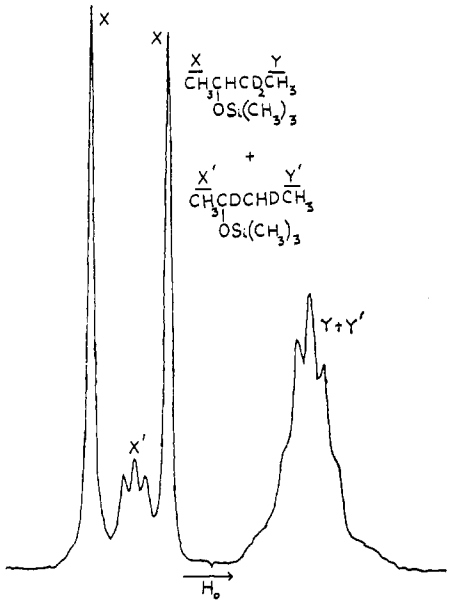


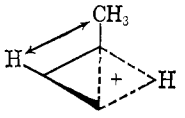
Figure 1.

The integrated area ratio of the signals from the 1-methyl and 4-methyl is 1.06:1.00. Since the corresponding ratio of the ether of unlabeled 2-butanol is 1.07:1.00 under our instrumental conditions, VI cannot be present in significant amount. From the ratio 83:17 of A:B, the following may be written.

$$CH_3CD_2CH_2CH_2NH_2 \longrightarrow \underset{\text{100\% } d_2}{} \quad \underset{\text{83\%}}{CH_3CD_2\underset{OH}{\underset{|}{C}}HCH_3} + \underset{\text{17\%}}{CH_3\underset{OH}{\underset{|}{C}}DCHDCH_3}$$

In turn, this product distribution accounts satisfactorily for the isotopic distribution of the (P − C_2H_5) ions in the mass spectrum of the derived trimethylsilyl ether.

The only experimental evidence therefore for the intermediacy of I and II is the formation of methylcyclopropane. As only 2% of the hydrocarbon fraction is methylcyclopropane,[2a] and the hydrocarbon fraction comprises less than 30% of total product, I and II can be responsible for less than 0.6% of product. This should be contrasted with the 6% product—cyclopropane and isotopically rearranged 1-propanol—arising from the corresponding species in the deamination of 1-propylamine. Repulsive interactions in VIII, analogous to those suggested for the isobutyl and neopentyl systems,[1] can account for these differences.



VIII

Finally, we wish to point out that the rearrangement 2-butyl cation ⇌ 2-butyl cation is only slightly slower than its capture by water. Assuming capture by water to be diffusion controlled leads to the conclusion that the activation energy of this rearrangement is *ca.* 2 kcal/mole. Under the experimental conditions isotopically labeled 2-butanol did not undergo isotope position rearrangement.

Acknowledgment. We thank the Petroleum Research Fund (692-A4) and the National Science Foundation (GP-3343) for financial support of the work performed at Michigan State University.

(5) Fellow of the Alfred P. Sloan Foundation.

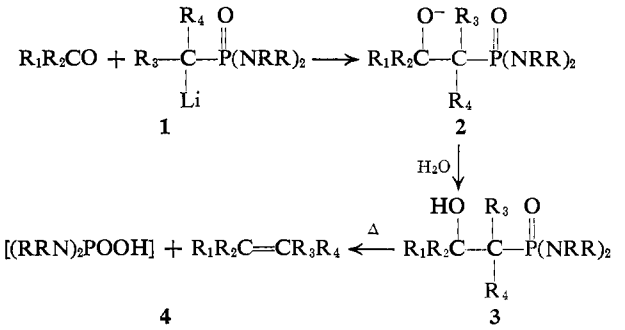
Gerasimos J. Karabatsos,[5] Ramon A. Mount, Donald O. Rickter
Department of Chemistry, Michigan State University
East Lansing, Michigan

Seymour Meyerson
Research and Development Department
American Oil Company, Whiting, Indiana
Received August 12, 1966

The Synthesis of Olefins from Carbonyl Compounds and Phosphonic Acid Bisamides

Sir:

We report herein a new and useful two-step synthesis of olefins from carbonyl compounds and α-lithiophosphonic acid bisamides (**1**) according to the sequence



The possibility that the key transformation of **3** to **4** might occur was indicated in part by the discovery that β-hydroxy sulfinamides undergo thermal decomposition to olefins, amines, and sulfur dioxide.[1]

The carbanionic reagents of type **1** are readily generated. Thus, treatment of methylphosphonic acid bis(dimethylamide)[2,3] in tetrahydrofuran at −78° under nitrogen with 1 equiv of *n*-butyllithium produces the α-lithio derivative **1** (R_3 = R_4 = H; R = CH_3) in high yield,[4] as shown by reaction with the carbonyl function of aldehydes and ketones to form β-hydroxyphosphonic acid bisamides of type **3**, R = CH_3, almost quantitatively. The lithio derivative **1** (R_3 = R_4 = H; R = CH_3) is quite stable even at 0° in tetrahydrofuran solution under nitrogen. The adducts of general type **3**, R_3 = R_4 = H, derived from ketones and aldehydes undergo elimination to form olefins **4**, R_3 = R_4 = H, upon heating at reflux in dry benzene or toluene solution in the presence of silica gel catalyst for 10–12 hr.[5] The intermediate *alkoxy* adducts **2**, in contrast to the *β-hydroxy* phosphonic acid amides **3** and in contrast

(1) E. J. Corey and T. Durst, *J. Am. Chem. Soc.*, 88, 5656 (1966).

(2) The phosphonyl amides used in this work were obtained from the corresponding phosphonyl dichlorides by a minor modification of the method of G. M. Kosolapoff and L. B. Payne, *J. Org. Chem.*, 21, 413 (1956). The dichlorides were prepared by the procedures of A. M. Kinnear and E. A. Perren, *J. Chem. Soc.*, 3437 (1952).

(3) New compounds prepared in this work have been characterized satisfactorily by elemental analysis and infrared and nmr spectroscopy.

(4) Metalation was complete after 15 min at −78°. The homologs **1** (R_3 = alkyl, R_4 = H, R = CH_3) require 2 hr at −50°, and **1** (R_3 = R_4 = R = CH_3) requires 5 hr at −40°.

(5) A solution of **3** in about 10 times the weight of benzene with 2–3 times the weight of silica gel ("Woelm") has generally been employed. The elimination also occurs if silica gel is not used as catalyst, but the rate is reduced roughly by a factor of 2. Olefin formation proceeds more rapidly with the adducts derived from ketones than with those derived from aldehydes.