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THE SYNTHESSES OF 2-TRIFLUOROACETO
(ACETYL-1-C¹⁴) THIOPHENE AND
2-(HEPADECYL-1-C¹⁴)-IMIDAZOLINE

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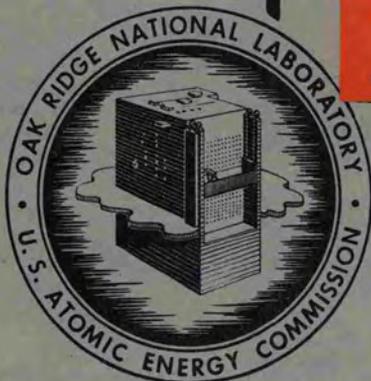
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CHEMISTRY DIVISION

THE SYNTHESSES OF 2-TRIFLUOROACETO(ACETYL-1-C¹⁴)-THIOPHENE

AND

2-(HEPTADECYL-1-C¹⁴)-IMIDAZOLINE

Part I

Vernon F. Raaen and Gus A. Ropp

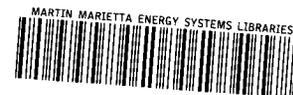
Part II

Vernon F. Raaen, O. Kenton Neville and Gus A. Ropp

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PART I

The Preparation of 2-Trifluoroaceto(acetyl-1-C¹⁴)-thiophene

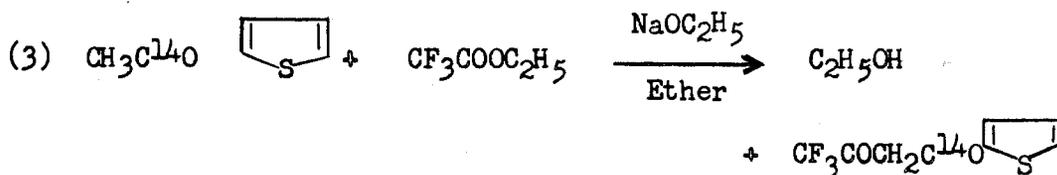
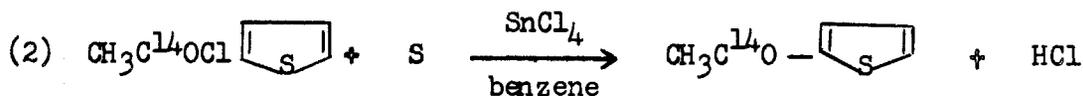
Vernon F. Raaen and Gus A. Ropp

Abstract

2-Trifluoroaceto(acetyl-1-C¹⁴)-thiophene has been prepared in 67% yield from sodium acetate-1-C¹⁴.

Introduction

Thenoyltrifluoroacetone (TTA), labeled with carbon-14 in the carbonyl group alpha to the ring, was prepared in 67% over-all yield from sodium acetate-1-C¹⁴ by the following series of reactions⁽¹⁾⁽²⁾:



-
- (2) J. R. Johnson and G. E. May, "Organic Syntheses", Coll. Vol. II, John Wiley & Sons, New York, N. Y., 1943, p. 8.
 (3) J. C. Reid and M. Calvin, University of California AEC MDDC-1405 August 13, 1947; J. Am. Chem. Soc., 70, 2949(1950).

The product, which had a millimolar activity of 800 μ c., was found to be 98% pure chemically by dilution technique.

Experimental

Acetyl-1-C¹⁴ chloride

Sodium acetate-1-C¹⁴ (2.72 g., 33 mmols., ca. 1 mc./mmol.) which had been dried over phosphorus pentoxide was stirred vigorously with 10.2 g. of freshly distilled phosphorus oxychloride and 30 ml. of dry benzene. The suspension in benzene was stirred with a bar magnet and heated at a rate sufficient to cause distillation over a two hour period through a short Vigreux column. The distilled acid chloride solution in benzene was collected in a 100 ml. receiver containing 40 ml. of dry benzene and 4.21 g. (50 mmols.) of thiophene which was used for the acylation. The receiver (Figure 1) was equipped with a stopcock in such a position that the bulb could be used either as the reaction vessel with a magnetic stirring bar or as a separatory funnel for washing the product. The use of this flask prevented escape of volatile radioactive compounds.

2-(Acetyl-1-C¹⁴)-thiophene

The procedure used for the acylation was essentially that described in Organic Syntheses⁽²⁾ with some modifications of the apparatus to insure against loss of the labeled compounds. To the prepared benzene solution vigorously stirring in the reaction bulb at 0°, 14.0 g. (40 mmols.) of stannic chloride in 15 ml. of dry benzene was added over a thirty minute period from the attached dropping funnel. A tan addition product separated from the solution. The batch was kept twelve hours at 5° and then one hour at room temperature. The

addition product was decomposed with hydrochloric acid solution, and the product was washed in ether and dried over anhydrous magnesium sulfate.

2-Trifluoroaceto(acetyl-1-C¹⁴)-thiophene

The dry ether solution of 2-(acetyl-1-C¹⁴)-thiophene was run through a sintered glass filter disc into a cold stirred solution of ethyl trifluoroacetate (4.75 g., 35 mmols.), sodium methoxide (1.89 g., 35 mmole) and 5 ml. of anhydrous ether. The mixture was stirred two days at room temperature in a nitrogen atmosphere. The solvents were distilled in vacuo, and the residue was decomposed by addition of excess 10% sulfuric acid. The oil was extracted with ether, the ether solution was treated with 35 ml. of 1 M. magnesium acetate, and the pH was brought to 6.5 by the addition of aqueous ammonia. The mixture containing the precipitated magnesium chelate of thenoyltrifluoroacetone was stirred thoroughly and excess solvent was drawn off through a filter stick. Seventy milliliters of 10% sulfuric acid was added and the batch was subjected to steam distribution. The yellow oily thenoyltrifluoroacetone was collected in a water separator. The solidified product was dried over phosphorus pentoxide to give 4.82 g. (67% yield based on sodium acetate), m. p. 40-41°. The millimolar activity was determined after Van Slyke combustion⁽⁴⁾ to be 800 uc. (3.7 μ c. per mg.). In preliminary runs the product was found at times to crystallize in a second form, m. p. 75-80°. This form was converted to the lower melting form by heating above 80°.

(4) O. K. Neville, ibid, 70, 3501 (1948).

Dioxime of 2-Trifluoroaceto(acetyl-1-C¹⁴)-thiophene

A sample of labeled thenoyltrifluoroacetone was diluted 595-fold with pure inactive thenoyltrifluoroacetone. The mixture was dissolved in ether and the dioxime⁽³⁾ was prepared and purified, m.p. 133-134°. The millimolar activity was shown to be equivalent to 780 μ c. before dilution. Hence the chemical purity of the product, 2-trifluoroaceto(acetyl-1-C¹⁴)-thiophene, was $780/800 = 98\%$.

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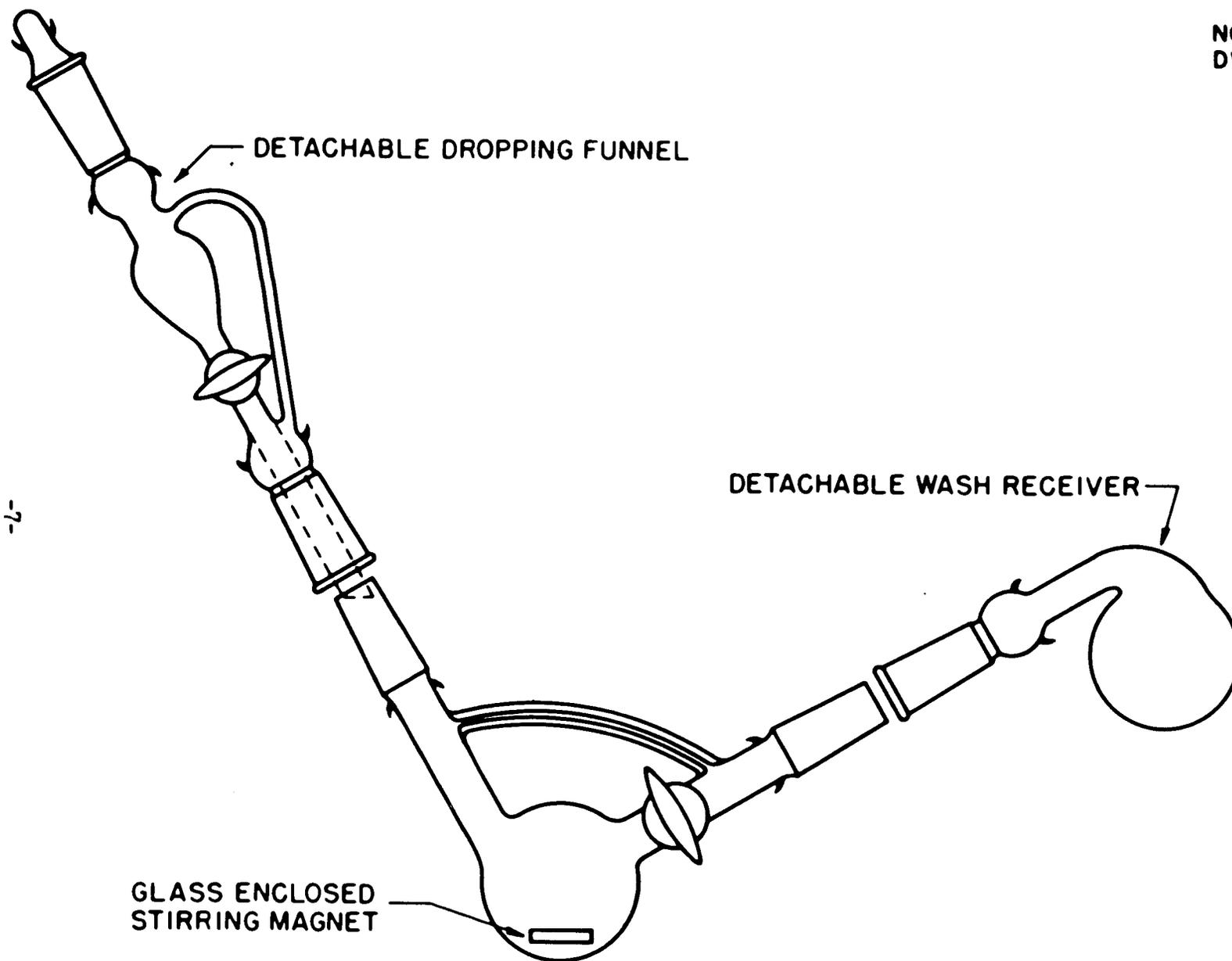


FIGURE 1

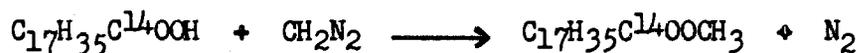
PART II

The Synthesis of 2-(Heptadecyl-1-C¹⁴)-imidazoline

Vernon F. Raaen, O. Kenton Neville and Gus A. Ropp

Abstract

2-(Heptadecyl-1-C¹⁴)-imidazoline [2-(heptadecyl-1-C¹⁴)-glyoxalidine] having a millimolar activity of 727 μ c. was prepared in 80% yield from stearic acid labeled with carbon-14 in the carboxyl group according to the following equations:



Experimental

Stearic-1-C¹⁴ acid⁽²⁾ (283 mg., ca. 1 mc.) in a small bulb with a 12/30 standard taper joint was methylated using diazomethane in ether solution. The excess reagent was decomposed with a drop of acetic acid, and the bulb was fitted to a short Vigreux column for distillation of the ether. Ethylene

(2) The labeled stearic acid was obtained from the United States Testing Co., Hoboken, N. J.

diamine (0.7, ml., 10 mmols.) was added and the reaction bulb was heated fifteen hours at 70°. The pressure was reduced to 15 mm., and the ethylene diamine distilled off leaving a crystalline residue in the still pot. The product was then distilled at 15-20 mm. pressure by heating the pot at 250° in a Woods metal bath. It was at times necessary to force the product along by heating with a direct flame. The 2-(heptadecyl-1-C¹⁴)-imidazoline(248 mg., m.p. 73-77°, 80.5% yield) was shown to have a millimolar activity of 727 uc. (2.35 μ c. per mg.) by Van Slyke combustion⁽³⁾ and assay⁽³⁾ using the vibrating reed electrometer of a sample diluted 300-fold with the unlabeled compound.

Acknowledgements

The authors wish to acknowledge the previous work of Drs. B. G. Wilkes, G. H. Law and R. H. Wellman on the synthesis of unlabeled 2-heptadecylimidazoline.

(3) O. Kenton Neville, J. Am. Chem. Soc., 70, 3501 (1948).