

lithium aluminum hydride (7.4 g., 14% excess) to yield 60 g. (97.7%) of 2-nonenol. The product, after low-temperature oxidation, was fractionally distilled by the same procedure as for 2-heptanal. The fraction (12.2 g.) boiling at 119.5–126.5° at 21 mm. and n_D^{20} 1.4426 was stabilized with hydroquinone and identified by preparation of the following derivatives: semicarbazone, m. p. 164–165° (Delaby, *et al.*,⁴ 160–161°; von Braun and Rudolph,⁵ 163°); *p*-nitrophenylhydrazone, m. p. 109.6–110.8° (Delaby, *et al.*,⁴ 113°; von Braun and Rudolph,⁵ 109°); 2,4-dinitrophenylhydrazone, m. p. 124.4–125°.

Anal. Calcd. for $C_{18}H_{20}N_4O_4$: C, 56.24; H, 6.30; N, 17.49. Found: C, 56.08; H, 6.03; N, 17.62.

(5) von Braun and Rudolph, *Ber.*, **67**, 269 (1934).

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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF PITTSBURGH
PITTSBURGH, PENNSYLVANIA

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The Vapor Phase Fluorination of Acetyl Fluoride¹

BY WILLIAM T. MILLER, JR., AND MAURICE PROBER²

In the direct fluorination of aliphatic acids and their derivatives, Bockemüller³ observed β - and γ - but no α -substitution. It was of interest to determine if hydrogen substitution occurred in the direct fluorination of acetyl fluoride, where only α -replacement was possible.

Equivalent quantities of fluorine and acetyl fluoride, both diluted with nitrogen, were passed into a steam-jacketed copper reactor, which was packed with copper gauze.⁴ The products were condensed, caused to react with ethyl alcohol, and the resulting esters fractionally distilled. The fluorinated esters comprised approximately 50% by weight of the total esters plus some unreacted alcohol. The isolation of appreciable unreacted ethyl acetate was consistent with Bockemüller's observation on the low reactivity of the α -hydrogen. All of the possible substitution products were formed. Ethyl fluoroacetate and ethyl difluoroacetate were isolated in approximately 6:1 ratio. Only trace amounts of ethyl trifluoroacetate were isolated.

Experimental

Acetyl fluoride was prepared according to the procedures of Calloway⁵ and Nesmejanov and Kahn.⁶ Fractional distillation from antimony trifluoride and treatment with sodium fluoride yielded a product free of acetyl chloride and hydrogen fluoride, b. p. 18.0–18.2° at 734 mm.

The reaction was carried out in a steam-jacketed copper tube, 75 × 3.5 cm., packed with a roll of 40-mesh copper wire gauze. Fluorine diluted with dry, oxygen-free nitrogen, and acetyl fluoride carried by a stream of nitrogen,

were passed into the reactor in an equal molar ratio. The molar ratio of nitrogen to fluorine varied from 2:1 to 3:1. The reactants were condensed in ice, Dry Ice, and liquid air traps, arranged in series. The hydrogen fluoride was removed by sodium fluoride which preceded the Dry Ice trap. The condensates were combined and the theoretical amount of absolute ethyl alcohol added at Dry Ice temperature. The reaction product was allowed to warm up to room temperature, kept at room temperature for a day, and refluxed for three hours. It was diluted with ether, and washed with cold, saturated solutions of potassium fluoride, potassium carbonate and calcium chloride. The reaction mixture was fractionally distilled at an atmospheric pressure of 740 mm.

In a typical run, 500 g. (0.804 mole) of acetyl fluoride was passed into the reactor, and 48.0 g. of organic products were condensed in the traps, with a 16.5 g. weight increase of the sodium fluoride. After distilling off the ether, the following fractions were obtained: 0.2 g., b. p. 37–68°; 15.4 g., b. p. 68–78° (ethyl acetate and ethyl alcohol-ethyl acetate azeotrope); 1.0 g., b. p. 78–96°; 0.5 g., b. p. 96–103°; 3.4 g., b. p. 103–114°; 6.4 g., b. p. 114–115°; 2.2 g. residue. Fluorinated compounds were present in all but the 68–78° b. p. fraction.

In order to obtain sufficient product to permit isolation of pure reaction products, six runs were made, and the appropriate fractions combined and distilled. A fraction boiling fairly sharply at 115–116° reacted with excess liquid ammonia at room temperature to form an amide, m. p. 107.5–108.0°. The earlier reported boiling points of ethyl fluoroacetate, 121.6°⁷ and 126°⁸ are higher than the value observed in the present work, but the m. p. of the amide is in excellent agreement with the literature value of 108°.⁹ Recently a boiling point of 117–118° has been reported¹⁰ which is in better agreement with our value. A second fraction, ethyl difluoroacetate, boiled at 98.2–99.2°, reported¹¹ 99.2°, and gave an amide m. p. 51.0–51.9°⁹ reported⁹ 51.8°. A small amount of a low-boiling fraction gave a plateau at 53°, and yielded a fluorine containing amide, m. p. 72.7–74.0°. An azeotrope of ethyl alcohol and ethyl trifluoroacetate was reported to boil at 56°¹² and the melting point of trifluoroacetamide was reported to be 74.8°.¹³ A trace amount of high boiling ester was obtained in one run, and it was hydrolyzed with 10% hydrochloric acid to yield an impure fluorine containing acid (or mixture) of m. p. 187–205°. All of the fluoroacetic acids are liquids, and the isolation of a solid acid indicated that coupling reactions had occurred during fluorination.

(7) Swarts, *J. chim. phys.*, **28**, 634 (1931).

(8) Ray and Ray, *J. Ind. Chem. Soc.*, **13**, 427 (1936).

(9) Swarts, *Bull. classe sci., Acad. roy. Belg.*, **28** (1909).

(10) Gryszkiewicz-Trochimowski, Sporzyński and Wnuk, *Rec. trav. chim.*, **66**, 413–418 (1947).

(11) Swarts, *Bull. classe sci., Acad. roy. Belg.*, **41**, 628 (1903).

(12) Bigelow and Fukuhara, *THIS JOURNAL*, **63**, 788 (1941).

(13) Swarts, *Bull. classe sci., Acad. roy. Belg.*, **8**, 343 (1922).

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1-(β -Carboxyethyl)-3,4,7-trimethoxydibenzofuran

BY PAUL E. FANTA

The attempted preparation of acid IV by a crossed Ullmann reaction¹ of methyl β -(2-iodo-3,4,5-trimethoxyphenyl)-propionate and methyl 2-iodo-5-methoxybenzoate was described in an earlier paper.² This note concerns an alternative synthetic approach which was also unsuccessful.

(1) For a survey of the Ullmann reaction see Fanta, *Chem. Rev.*, **38**, 139 (1946).

(2) Frank, Fanta and Tarbell, *THIS JOURNAL*, **70**, (1948).

(1) Taken from the thesis presented by Maurice Prober to the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of Master of Science, January, 1943. Work on this problem was interrupted in 1941 because of the war research program.

(2) Present address: General Electric Co., Schenectady, N. Y.

(3) Bockemüller, *Ann.*, **506**, 20 (1933).

(4) Compare: Miller, Calfee and Bigelow, *THIS JOURNAL*, **59**, 198 (1937); Calfee and Bigelow, *ibid.*, **59**, 2072 (1937), and following papers by Bigelow, *et al.*

(5) Calloway, *THIS JOURNAL*, **59**, 1476 (1937).

(6) Nesmejanov and Kahn, *Ber.*, **67**, 370 (1934).