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** $n^{20}\text{D}$ **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*-nitrophenyl**hydrazone,** m. p. **109.6–110.8° (Delaby,** *et al.*,[4] 113°; **von Braun and Rudolph,**[5] 109°); 2,4-dinitro**phenyl**hydrazone, m. p. 124.4–125°.

Anal. Calcd. for $C_{15}H_{20}N_4O_4$: C, 56.24; H, 6.30; N, 17.49. Found: C, 56.08; H, 6.03; N, 17.62.

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

CONTRIBUTION NO. 671
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The Vapor Phase Fluorination of Acetyl Fluoride[1]

BY WILLIAM T. MILLER, JR., AND MAURICE PROBER[2]

In the direct fluorination of aliphatic acids and their derivatives, Bockemüller[3] 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 Calloway[5] 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 reported[10] which is in better agreement with our value. A second fraction, ethyl difluoroacetate, boiled at 98.2–99.2°, reported[11] 99.2°, and gave an amide m. p. 51.0–51.9°,[9] reported[9] 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.

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[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).

[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).

RECEIVED MARCH 4, 1948

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

BY PAUL E. FANTA

The attempted preparation of acid IV by a crossed Ullmann reaction[1] 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.

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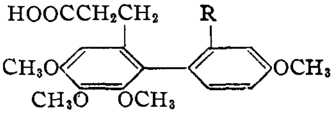
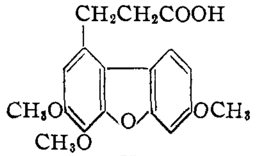
[1] For a survey of the Ullmann reaction see Fanta, *Chem. Rev.*, **38**, 139 (1946).

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



I, R = NO_2 II, R = NH_2
III, R = CN IV, R = COOH



V

A crossed Ullmann reaction of methyl β-(2-iodo-3,4,5-trimethoxyphenyl)-propionate and excess 4-bromo-3-nitroanisole yielded β-[2-(4,5-6,4′-tetramethoxy-2′-nitro)-biphenyl]-propionic acid (I), which was readily reduced to the corresponding amino compound (II). When II was diazotized and treated with cuprous cyanide under conditions calculated to yield the nitrile III, only 1-(β-carboxyethyl)-3,4,7-trimethoxydibenzofuran (V) was obtained. The formation of dibenzofuran from 2-amino-2′-methoxybiphenyl[3] and of 3,4,7-trimethoxydibenzofuran from 2,3,4,4′-tetramethoxy-2′-aminophenyl[4] under similar conditions has been reported.

The structure assigned to V is supported by a comparison of its absorption spectrum with that of 3,4,7-trimethoxydibenzofuran and compounds I and II as shown in Fig. 1. The spectrum of each dibenzofuran derivative exhibits a maximum near 300 mμ which has the same extinction coefficient as the corresponding maximum at 260 mμ. In the case of the biphenyl derivatives I and II, the extinction coefficients of the higher and lower wave length maxima differ greatly.

Experimental[5]

β-[2-(4,5,6,4′-Tetramethoxy-2′-nitro)-biphenyl]-propionic Acid (I).—A mixture of 7.60 g. (0.02 mole) of methyl β-(2-iodo-3,4,5-trimethoxyphenyl)-propionate and 27.8 g. (0.12 mole) of 4-bromo-3-nitroanisole was heated at 220–255° while 20 g. of electrolytic copper dust was added in small portions with stirring. The product was extracted with six 25-cc. portions of benzene. Evaporation of the benzene gave a red-brown tar which was refluxed for an hour with 25 cc. of Claisen alkali. Fifty cc. of water was added and the mixture was centrifuged to remove 4,4′-dimethoxy-2,2′-dinitrobiphenyl. Acidification of the aqueous solution with hydrochloric acid gave a dark oil which was purified by refluxing with Darco and Celite in aqueous methanol. Cooling and scratching gave a fine, yellow solid which was recrystallized from benzene with the addition of ligroin, when it formed granular, yellow crystals, yield 2.20 g. (28%), m. p. 100–102°.

Anal. Calcd. for $C_{19}H_{21}O_8N$: C, 58.30; H, 5.41. Found: C, 58.31; H, 5.54.

β-[2-(2′-Amino-4,5,6,4′-tetramethoxy)-biphenyl]-propionic Acid (II).—A portion of the nitro compound in ethanol was shaken for one-half hour with Raney nickel and hydrogen at 1000 lb. and 155°. Evaporation of the solvent and crystallization of the residue from benzene–ligroin gave a light tan crystalline powder, yield 42%, m. p. 125.5–126°.

Anal. Calcd. for $C_{19}H_{23}O_6N$: C, 63.15; H, 6.41. Found: C, 64.95; H, 6.61.

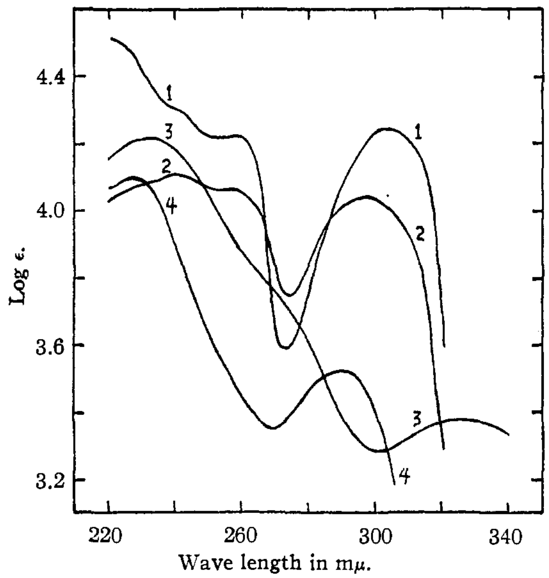


Fig. 1.—Molar extinction curves in ethanol: (1) 3,4,7-trimethoxydibenzofuran[4]; (2) dibenzofuran derivative, V; (3) nitrobiphenyl derivative, I; (4) aminobiphenyl derivative, II.

1-(β-Carboxyethyl)-3,4,7-trimethoxydibenzofuran (V).—A 360-mg. (0.001 mole) portion of the amino acid II was dissolved in a mixture of 10 cc. of water and 10 drops of sulfuric acid and diazotized at −5° by the addition of 74 mg. of solid sodium nitrite. Upon standing for an hour at room temperature gas was evolved and a flocculent orange precipitate separated. The yield of crude product melting at 132–145° was 76%. Crystallization from dilute methanol gave 191 mg. (58%) of tan needles, m. p. 146–148°. An analytical sample, m. p. 148°, was obtained by successive recrystallization from dilute methanol (Darco) and benzene.

Anal. Calcd. for $C_{18}H_{18}O_6$: C, 65.45; H, 5.49. Found: C, 65.16; H, 5.29.

The same product was obtained in lower yield when the diazonium solution was poured into a solution of cuprous cyanide in aqueous sodium cyanide.

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[3] Mascarelli and Pirona, *Gazz. chim. ital.*, **68**, 117 (1938); *C. A.*, **32**, 6235 (1938).

[4] Tarbell, Frank and Fanta, This Journal, **68**, 502 (1946).

[5] All melting points are corrected and were taken on the heated stage. The microanalyses are by C. W. Beazley, S. M. Nagy and Mrs. O. C. Sauvage. Absorption curves were determined with a Beckmann Spectrophotometer.

The Fluorination of Periodic Acid

By Gilson H. Rohrback and George H. Cady

As part of the research now under way to produce compounds in which the hydrogen atoms of acids have been replaced by fluorine, the study of the reaction of fluorine with periodic acid was undertaken. Fluorination of both solid $HIO_4 \cdot 2H_2O$ and KIO_4 as well as an aqueous or sulfuric acid solution of the acid were carried out, but the desired compound fluorine periodate was not obtained. The reaction of fluorine with $HIO_4 \cdot 2H_2O$