Determination of Solubility.—The purified cyclohexane was placed in a flask attached to the vacuum system by a ground glass joint, thoroughly degassed, and distilled into the ampoules containing aluminum bromide. Each ampoule was sealed off from the vacuum line when it was estimated that it would be nearly full of solution upon reaching the solution temperature. Solution temperatures were determined as described by Heldman and Thurmond.[3] All the solutions were clear and colorless. Samples were analyzed as follows: The aluminum bromide was precipitated in finely divided form[2] and the ampoule placed tip down in a long narrow flask equipped with standard taper joint and glass stopper. The flask and contents were weighed, and the flask shaken to break open the ampoule. The flask was then connected to a trap by all-glass connections using unlubricated standard taper joints. The trap was in turn connected to a vacuum pump. The vacuum pump was turned on and the flask cooled by immersion in a slurry of dry ice, chloroform, and carbon tetrachloride. After the system was evacuated, the dry ice slurry was removed and pumping continued until some time after the flask had reached room temperature. The cyclohexane was condensed in the trap. The aluminum bromide remained behind as a finely divided, white powder. The flask and contents were weighed and the cyclohexane calculated by difference. The aluminum bromide was removed by washing successively with nitrobenzene, water, and acetone. The flask and glass parts were weighed and the aluminum bromide calculated by difference.

TABLE I

SOLUTION TEMPERATURES OF ALUMINUM BROMIDE-CYCLOHEXANE MIXTURES

	Al_2Br_6			Al_2Br_6	
t, °C.	Mole fract.	Wt. % liq. phase	*t*, °C.	Mole fract.	Wt. % liq. phase
6.2	0.0503	25.1	38.7	0.178	57.9
8.8	.0568	27.6	39.8	.183	59.4
17.2	.0788	35.2	44.5	.220	64.2
26.4	.115	45.1	57.0	.333	76.0
28.5	.124	47.4	60.3	.380	79.5
36.0	.162	55.0	61.7	.393	80.4
37.6	.169	56.4	97.5	1.000	100.0

Results

The solution temperatures and compositions of the solutions examined are given in Table I. The moles of aluminum bromide are calculated on the basis of the formula Al_2Br_6. No correction was made for the cyclohexane in the vapor phase because of the comparatively low vapor pressure of cyclohexane and the small vapor volume present in the ampoules. The results show that aluminum bromide is appreciably more soluble in cyclohexane than in *n*-butane[2] or *n*-hexane[4] when calculated on a mole fraction basis. On a weight basis aluminum bromide is more soluble in cyclohexane than in *n*-hexane throughout the temperature range for which data are available and is more soluble in cyclohexane than in *n*-butane throughout much of the lower temperature range.

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(3) Heldman and Thurmond, *ibid.*, **66**, 427 (1944).

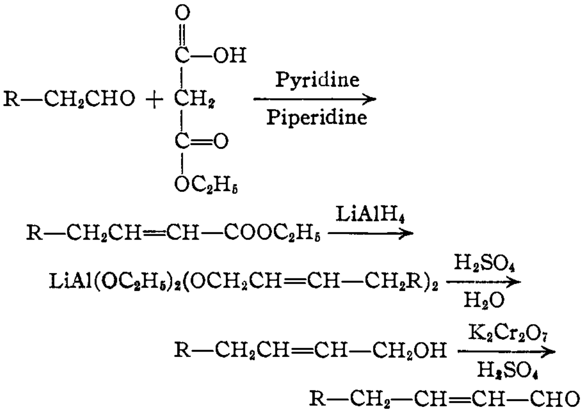
(4) Boedeker and Oblad, *ibid.*, **69**, 2036 (1947).

The Preparation of 2-Heptenal and 2-Nonenal

BY C. J. MARTIN, A. I. SCHEPARTZ AND B. F. DAUBERT[1]

Recent work in this Laboratory on the isolation and identification of flavor components in "reverted" soybean oil has necessitated the preparation of a number of α,β-unsaturated aldehydes of a high degree of purity. The recent availability of lithium aluminum hydride as a reducing agent[2] led to the development of a suitable method for the preparation of such aldehydes free of their saturated isomers.

The general scheme of reaction may be outlined as follows



$$R{-}CH_2CHO + \begin{array}{c} O \\ \| \\ C{-}OH \\ | \\ CH_2 \\ | \\ C{=}O \\ | \\ OC_2H_5 \end{array} \xrightarrow[\text{Piperidine}]{\text{Pyridine}}$$

$$R{-}CH_2CH{=}CH{-}COOC_2H_5 \xrightarrow{LiAlH_4}$$

$$LiAl(OC_2H_5)_2(OCH_2CH{=}CH{-}CH_2R)_2 \xrightarrow[H_2O]{H_2SO_4}$$

$$R{-}CH_2CH{=}CH{-}CH_2OH \xrightarrow[H_2SO_4]{K_2Cr_2O_7}$$

$$R{-}CH_2{-}CH{=}CH{-}CHO$$

Experimental

Preparation of 2-Heptenal.—Ethyl hydrogen malonate (256 g.) was condensed with *n*-valeraldehyde (83.3 g.) in pyridine (469 g.) with piperidine (1.2 ml.) as a catalyst, according to the method of Galat.[3] After removal of the pyridine and piperidine, the ethyl 2-heptenoate was distilled *in vacuo* under nitrogen: yield, 118 g. (78.2%), b. p. 58–58.8° (3 mm.), $n^{25}D$ 1.4355.

To a solution of lithium aluminum hydride (10.9 g., 14% excess) in absolute ether (450 ml.) there was added ethyl 2-heptenoate (78 g.) according to the method of Nystrom and Brown.[2] Although the crude yield of 2-heptenol was 45 g. (79%), distillation, under nitrogen, through a Vigreux column, resulted in a loss of approximately 50% because of partial polymerization of the alcohol. The 2-heptenol had a boiling point of 75–75.5° at 15 mm.

The 2-heptenol (21.7 g.) was oxidized by the low-temperature oxidation procedure of Delaby and Guillot-Allègre,[4] yielding 2-heptenal, 15.9 g. (74.6%).

The product was stabilized with hydroquinone and distilled in a glass helix-packed column; b. p. 80–85° at 14 mm., $n^{20}D$ 1.4314. The aldehyde was identified by preparation of the following derivatives: semicarbazone, m. p. 168–168.4° (Delaby, *et al.*,[4] 169°); *p*-nitrophenylhydrazone, m. p. 115.5–116° (Delaby, *et al.*,[4] 110–112°); 2,4-dinitrophenylhydrazone, m. p. 131.5–132°.

Anal. Calcd. for $C_{13}H_{16}N_4O_4$: C, 53.41; H, 5.52; N, 19.17. Found: C, 53.17; H, 5.23; N, 19.03.

Preparation of 2-Nonenal.—Ethyl hydrogen malonate (143.6 g.) was condensed with heptaldehyde (63 g.) in the manner described above: yield of ethyl 2-nonenoate, 79.4 g. (78.2%); b. p. 104° at 8 mm.

The ethyl 2-nonenoate (79.4 g.) was reduced with

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(1) The financial assistance of the National Association of Margarine Manufacturers is gratefully acknowledged.

(2) Nystrom and Brown, THIS JOURNAL, **69**, 1197 (1947).

(3) Galat, *ibid.*, **68**, 376 (1946).

(4) Delaby and Guillot-Allègre, *Bull. soc. chim.*, **53**, 301 (1933).

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}_{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*-nitrophenylhydrazone, m. p. 109.6–110.3° (Delaby, *et al.*,[4] 113°; von Braun and Rudolph,[5] 109°); 2,4-dinitrophenylhydrazone, 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).

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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 interrnpted 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).

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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 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).