Levulinic acid dibutylamide was prepared similarly in 60% yield from 40 g. of γ -chlorovaleroactone and 80 g. of n-butylamine in 100 cc. of ether; b. p. 140° (2 mm.); n²⁰D 1.4241.

Anal. Calcd. for C₁₂H₂₅O₂N: C, 68.7; H, 11.0; N, 6.2. Found: C, 68.9; H, 11.4; N, 6.5.

γ-Hydroxy-n-valeroyl Diethylamide.—(a) Hydrogenation of 17.1 g. of levulinic acid diethylamide in 30 cc. of water with 2.3 g. of Raney nickel at room temperature

of water with 2.3 g. of Raney nickel at room temperature and 90 atmospheres gave the product boiling at 101° (0.1 mm.) in quantitative yield.

(b) The diethylamide (34.2 g.) was heated with aluminum isopropoxide (50 g.) and isopropyl alcohol (250 g.) under a column until no more acetone was formed (four hours). The product, isolated in the usual way, boiled at 90° (0.05 mm.); n²⁵D 1.4642; yield, 92%.

Anal. Calcd. for $C_0H_{19}O_2N$: C, 62.4; H, 11.0; N, 8.1. Found: C, 62.4; H, 10.9; N, 8.0.

γ-Amino-n-valeric Acid Diethylamide.of 17.1 g. of levulinic acid diethylamide in 120 cc. of 17% alcoholic ammonia was hydrogenated at 70° and under 40 atm. pressure in presence of 2 g. of Raney nickel. Hydrogen absorption ceased after three hours: b. p. 85-90° (0.1 mm.); yield, 17 g.

Anal. Calcd. for C9H20ON2: N, 16.3. Found: N, 15.9.3

(2) The free amino acid has been prepared similarly by Knoop and Oesterlin, Z. physiol. Chem., 148, 309 (1925).

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REHOVOTH, ISRAEL

L. HASKELBERG

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Compound	M. p., °C.
F	
	40-41
	34–35
F	
$F \longrightarrow CH_2 - CH_2 \longrightarrow -F$	90
(C ₁₄ H ₁₂ F ₂), theoretical	

Ethyl 3-Halocoumarin-4-carboxylates

Ethyl 3-Chlorocoumarin-4-carboxylate.—Phenol (1.74 0.0185 mole) and diethyl oxalochloroacetate¹ (4.0 g., 0.018 mole) in dioxane (4 ml.) slowly added to ice cold concentrated sulfuric acid (10 ml.), stood at room temperature for eight days and poured onto ice gave 0.7 g. (15.4% yield) of ethyl 3-chlorocoumarin-4-carboxylate. After recrystallization from 50% ethanol this product showed m. p. 116.3-116.6° uncor.; 118.1-118.4° cor.

Anal. Calcd. for C12H2O4C1: C1, 14.06. Found: C1, 14.2.

Ethyl 3-Bromocoumarin-4-carboxylate.—Phenol (4.32) , 0.046 mole) and diethyl oxalobromoacetate? (12.0 g., 0.045 mole) in dry ether (5 ml.) was slowly added to cold

concentrated sulfuric acid (30 ml.). The dark red solution stood at 0° for ninety-six hours, then at 25° for twenty hours. After pouring onto ice, extracting with ether (and removing from the resulting solution, some 29% of unreacted ester by alkaline extraction) there was obtained 1.40 g. (14.7% yield on unrecovered ester) of ethyl 3-bromocoumarin-4-carboxylate. Recrystallization from 70-80% ethanol gave yellow crystals, m. p. 120.7-121.3° uncor.; 122.2-122.8° cor.

Anal. Calcd. for C12H2O4Br: Br, 26.91. Found: Br, 26.8, 26.9.

DEPARTMENT OF CHEMISTRY

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

CAMBRIDGE 39, MASS.

ERNEST H. HUNTRESS

CENTRAL RESEARCH LABORATORY

GENERAL ANILINE AND FILM CORPORATION

EASTON, PENNSYLVANIA ROBERT T. OLSEN

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The Di-fluorobibenzyls

The first stage in the pyrolysis of toluene was shown1 to be the formation of the benzyl radical and a hydrogen atom. The benzyl radicals thus formed subsequently dimerized to bibenzyl.

Recent investigation of the pyrolysis of the fluorotoluenes2 showed the same type of decomposition. The fluorobenzyl radicals produced in this way dimerized to the corresponding di-fluorobibenzyls, isolated as previously described. 1.2 The melting points, boiling points and the results of analysis of di-fluorobenzyls thus obtained are summarized in the following Table.

B. p., °C.	%C	%н	%F	Mol. wt.
270-271	77.7	5.7	17.2	205
267–268	76.7	5.5	16.6	173
269	77.1	5.7	17.1	175
	77.0	5.5	17.5	218

All these compounds have a strong smell very similar to that of bibenzyl. Boiling points were determined by the micro-method of Siwoloboff. A correction of +4° was introduced by comparing the boiling point of bibenzyl actually determined in this way (280-281°) with that stated in the literature (284°). Molecular weights were estimated by the Rast method.

We are indebted to Professor M. Stacey of the University of Birmingham for the fluorine analyses.

DEPARTMENT OF CHEMISTRY

THE UNIVERSITY

M. SZWARC

Manchester 13, England

J. S. Roberts

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