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.); $n^{20}D$ 1.4241.

Anal. Calcd. for $C_{13}H_{25}O_2N$: 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 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.); $n^{25}D$ 1.4642; yield, 92%.

Anal. Calcd. for $C_9H_{19}O_2N$: 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.—A solution 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 $C_9H_{20}ON_2$: N, 16.3. Found: N, 15.9.[2]

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

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Ethyl 3-Halocoumarin-4-carboxylates

Ethyl 3-Chlorocoumarin-4-carboxylate.—Phenol (1.74 g., 0.0185 mole) and diethyl oxalochloroacetate[1] (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 $C_{12}H_9O_4Cl$: Cl, 14.06. Found: Cl, 14.2.

Ethyl 3-Bromocoumarin-4-carboxylate.—Phenol (4.32 g., 0.046 mole) and diethyl oxalobromoacetate[2] (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 $C_{12}H_9O_4Br$: Br, 26.91. Found: Br, 26.8, 26.9.

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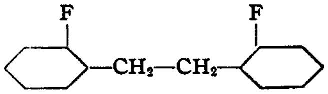
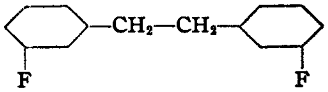
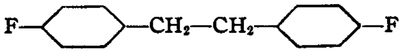
[1] Cope, THIS JOURNAL, **58**, 572 (1936).

[2] Brühl, *Ber.*, **36**, 1732 (1903).

The Di-fluorobibenzyls

The first stage in the pyrolysis of toluene was shown[1] 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 fluorotoluenes[2] 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.

Compound	M. p., °C.	B. p., °C.	%C	%H	%F	Mol. wt.
	40–41	270–271	77.7	5.7	17.2	205
	34–35	267–268	76.7	5.5	16.6	173
	90	269	77.1	5.7	17.1	175
$(C_{14}H_{12}F_2)$, theoretical			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.[3] 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.

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[1] M. Szwarc, *J. Chem. Phys.*, **16**, 128 (1948).

[2] M. Szwarc and J. S. Roberts, *ibid.*, **16**, 609 (1948).

[3] A. Siwoloboff, *Ber.*, **19**, 795 (1886).