none (I, R = C_6H_5). It was recrystallized from glacial acetic acid, xylene or butanol and melted at 158°.

Anal. Calcd. for $C_{25}H_{16}O$: C, 90.4; H, 4.8. Found: C, 90.2; H, 4.8.

The yellow **phenylhydrazone**, recrystallized from xylene, melted at 236°.

Anal. Calcd. for $C_{31}H_{22}N_2$: N, 6.6. Found: N, 7.0.

(d) **β-Acetylnaphthalene.**—Analogously, 3.4 g. of β-acetylnaphthalene gave an almost quantitative yield of the yellow α-(2-naphthoyl)-β-(3′-pyrenyl)-ethylene (I, R = β-naphthyl). Recrystallization from xylene or glacial acetic acid gave crystals, melting at 184°.

Anal. Calcd. for $C_{29}H_{18}O$: C, 91.1; H, 4.7. Found: C, 90.9; H, 4.6.

The orange-colored **phenylhydrazone** crystallized from xylene, and melted at 246°.

Anal. Calcd. for $C_{35}H_{24}N_2$: N, 5.9. Found: N, 6.2.

9-(3′-Pyrenylidene)-fluorene—The condensation of 4.6 g. of the aldehyde with 3.3 g. of fluorene was carried out, using sodium ethoxide as catalyst.[3] The yellow-orange fulvene (II) separated spontaneously from the solution, and melted after recrystallization from xylene, butanol or glacial acetic acid at 210°.

Anal. Calcd. for $C_{30}H_{18}$: C, 95.2; H, 4.8. Found: C, 94.9; H, 5.0.

α-Phenyl-β-(3-pyrenyl)-acrylic Acid (III, R = C_6H_5).—One mole each of pyrene-3-aldehyde and sodium phenylacetate was heated in boiling acetic anhydride (1.5 to 2 moles) for two hours. After cooling, the reaction mixture was diluted with water, and the solid residue filtered and washed with alcohol. From glacial acetic acid, the acid was obtained in yellow needles of m. p. 259°; yield, 30%.

Anal. Calcd. for $C_{25}H_{16}O_2$: C, 86.2; H, 4.6. Found: C, 86.5; H, 4.9.

α-(1-Naphthyl)-β-(3′-pyrenyl)-acrylic acid (III, R = 1-naphthyl) was obtained analogously from pyrene-3-aldehyde and sodium 1-naphthylacetate; yellow needles of m. p. 290° (from nitrobenzene).

Anal. Calcd. for $C_{29}H_{18}O_2$: C, 87.4; H, 4.5. Found: C, 87.1; H, 4.7.

α-(3-Pyrenyl)-β-(2′-pyridyl)-ethylene Methiodide (IV).—To a solution of pyrene-3-aldehyde (4 g.) and α-picoline methiodide (4 g.) in a small quantity of absolute alcohol, 10 to 15 drops of piperidine was added at 180°. Heating was continued for thirty minutes; then the red precipitate was filtered, washed with alcohol, dried, and recrystallized from nitrobenzene: m. p. 295°; yield, 65%.

Anal. Calcd. for $C_{24}H_{18}IN$: C, 64.4; H, 4.0; N, 3.1. Found: C, 64.1; H, 4.0; N, 3.3.

α-(3-Pyrenyl)-β-(6′-methyl-pyridyl-2′)-ethylene methiodide was prepared in 70% yield from 2.3 g. of pyrene-3-aldehyde and 4 g. of 2,6-lutidine methiodide, as described above. It was recrystallized from nitrobenzene, and formed red shiny crystals of m. p. 275°.

Anal. Calcd. for $C_{25}H_{20}IN$: N, 3.0. Found: N, 3.1.

α-(3-Pyrenyl)-β-(2′-quinolyl)-ethylene methiodide was formed in 75% yield as a red-violet, insoluble substance from 2.3 g. of pyrene-3-aldehyde and 2.8 g. of quinaldine methiodide; m. p. 285°.

Anal. Calcd. for $C_{28}H_{20}IN$: N, 2.8. Found: N, 2.8.

sym-**Di-(3-pyrenyl)-ethylene (V).**—(a) 10 g. of pyrene-3-aldehyde was dissolved in 100 ml. of dry benzene. Dry hydrogen chloride and hydrogen sulfide were passed simultaneously through the cold solution. The yellow precipitate was filtered and washed with water, alcohol and ether. It could not be recrystallized, as it decomposed on heating in high-boiling solvents. In its crude state the polymeric pyrene-3-thioaldehyde melted at 260–270°.

Anal. Calcd. for $(C_{17}H_{10}S)_x$: C, 82.9; H, 4.1. Found: C, 82.5; H, 4.4.

(b) A mixture of 2 g. of the thioaldehyde, 1 g. of Raney nickel and 20 g. of boiling naphthalene was heated for one hour. After removal of the naphthalene *in vacuo*, a brown-red residue was obtained, which was washed with alcohol and recrystallized from ethyl benzoate: m. p. 315°; yield, 75% (calculated on pyrene-3-aldehyde).

Anal. Calcd. for $C_{34}H_{20}$: C, 95.3; H, 4.7. Found: C, 95.1; H, 4.8.

DEPARTMENT OF ORGANIC CHEMISTRY
THE HEBREW UNIVERSITY, JERUSALEM

RECEIVED JANUARY 13, 1948

---

[3] Schlenk and Bergmann, *Ann.*, **479**, 56 (1930).

NEW COMPOUNDS

Hexahydrojulolidine

To a solution of julolidine,[1] 1,2,3,5,6,7-hexahydrobenzo-(i,j)-quinolizine (20 g., 0.115 mole), in alcohol (20 ml.) there was added Raney nickel (2 g.) and the mixture was shaken at 200° under a pressure of 2000 lb. of hydrogen. After removal of solvent and catalyst, the residue was distilled yielding 5 g. (low yield due to accidental loss) of a colorless oil: b. p. 76–80° at 3 mm.

Anal. Calcd. for $C_{12}H_{21}N$: C, 80.44; H, 11.73. Found: C, 80.55; H, 11.45.

The **picrate** of hexahydrojulolidine was readily prepared using an ethereal solution of picric acid. After recrystallization from hot water the picrate was obtained as an amorphous yellow solid, m. p. 165–167°.

Anal. Calcd. for $C_{18}H_{24}N_4O_7$: C, 52.94; H, 5.88. Found: C, 52.82; H, 5.69.

The **methiodide** of hexahydrojulolidine formed readily and could be recrystallized from a solution of alcohol and ether. It was obtained as an amorphous white solid, m. p. 294–298° with decomposition.

Anal. Calcd. for $C_{13}H_{24}IN$: C, 48.50; H, 7.47. Found: C, 48.51; H, 7.45.

Hexahydrojulolidine hydrochloride and also the quaternary methiodide derivative were found to be convulsants when tested intravenously in rabbits.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROCHESTER
ROCHESTER, NEW YORK
V. BOEKELHEIDE
G. P. QUINN[2]

RECEIVED APRIL 30, 1948

---

[1] Glass and Weissberger, "Organic Syntheses," **26**, 40 (1946).

[2] Aided by a grant from the National Foundation for Infantile Paralysis, Inc.

Some Derivatives of Levulinic Acid

Levulinic acid diethylamide was prepared (a) by heating 50 g. of levulinic acid with 50 g. of diethylamine at 250° for ten hours (autoclave), yield 60%; and (b) by adding 13.4 g. of γ-chlorovaleroactone[1] to a cold solution of 15 g. of diethylamine in 50 cc. of ether; the reaction was completed on the water-bath and the solution filtered from diethylamine hydrochloride and distilled, yield 70%. The amide is soluble in water and boils at 108° (0.9 mm.); $n^{22}D$ 1.457.

Anal. Calcd. for $C_9H_{17}O_2N$: C, 63.2; H, 10.0; N, 8.2. Found: C, 63.3; H, 10.2; N, 8.2.

---

[1] Clemo and Ramage, *J. Chem. Soc.*, 54 (1931).

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^{23}_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]

---

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

WEIZMANN INSTITUTE OF SCIENCE
DANIEL SIEFF RESEARCH INSTITUTE
REHOVOTH, ISRAEL L. HASKELBERG

RECEIVED JANUARY 2, 1947

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.

---

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

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

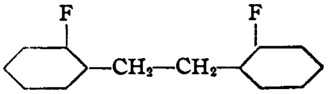
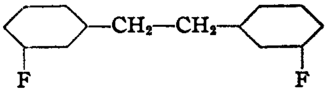
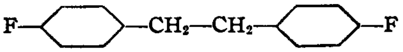
DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE 39, MASS. ERNEST H. HUNTRESS
CENTRAL RESEARCH LABORATORY
GENERAL ANILINE AND FILM CORPORATION
EASTON, PENNSYLVANIA ROBERT T. OLSEN

RECEIVED APRIL 8, 1948

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.

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY M. SZWARC
MANCHESTER 13, ENGLAND J. S. ROBERTS

RECEIVED MARCH 22, 1948

---

(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).