ever, ultimate analysis for carbon and hydrogen indicated the correct composition.

Anal. Calcd. for $C_{28}H_{18}O$: C, 90.8; H, 4.9. Found: C, 90.5; H, 4.9.

In one run a small amount (0.5 g.) of a crystalline material was obtained on concentrating the original alkali-insoluble ether extract of the reaction mixture. This melted at 279–281° (uncor.). It started to sublime below the melting point. Its structure is still unknown.

Anal. Found: C, 80.96; H, 4.14. Qualitative test for nitrogen was negative.

The yields of identifiable products from 18.0 g. of fluorenone originally present are:

Phenanthrone (9-hydroxyphenanthrene)	1.0 g. or 5%
9-Methoxyphenanthrene (calcd. from picrate)	6.2 g. or 30%
Di-9-phenanthryl ether	0.5 g. or 1.5%
Unchanged fluorenone (calcd. from phenylhydrazone)	5.4 g. or 30%
Total	66.5%

The yield of 9-phenanthrol, 9-methoxyphenanthrene, and di-9-phenanthryl ether, based on fluorenone consumed, is 51% and is largely 9-methoxyphenanthrene.

In one of the earlier runs the total crude product was oxidized with an excess of chromic anhydride dissolved in glacial acetic acid, yielding 3.58 g. of phenanthrenequinone, m. p. 198–200° (uncor.) (reported m. p. 201°) and 4.0 g. of *o,o'*-diphenic acid, m. p. 228–230° (reported m. p. 229°) from further oxidation of some of the quinone. This represented a 34% yield of phenanthrene derivatives, based on total fluorenone initially present.

Summary

The diazomethane ring enlargement of cyclic ketones has been applied to fluorenone to produce 9-phenanthrol, 9-methoxyphenanthrene, and di-9-phenanthryl ether.

The yield of 9-phenanthrol derivatives is 51% based on fluorenone consumed.

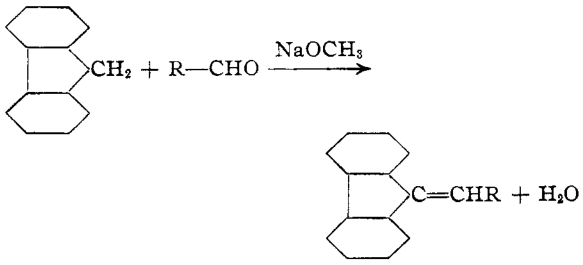
BETHLEHEM, PA. RECEIVED AUGUST 6, 1940

[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMICAL LABORATORY, LEHIGH UNIVERSITY]

Preparation of Alkylidene Fluorenes from Fluorene with Aliphatic Aldehydes

BY RAYMOND F. SCHULTZ AND CHARLES F. SMULLIN[1]

A large number of products have been made by the condensation of fluorene with aromatic aldehydes in the presence of a catalyst like sodium methylate.[2]



However, so far as we could ascertain, no similar reaction has been successful with aliphatic aldehydes.

Almost without exception the work with aromatic aldehydes was carried out in boiling alcoholic solution, under which conditions aliphatic aldehydes fail to react and often condense with themselves to form aldehyde resins.[3]

This paper describes the preparation of condensation products of fluorene with typical aliphatic aldehydes like propionaldehyde, *n*-butyraldehyde and isobutyraldehyde in xylene using potassium ethylate as condensing agent. Only in the case of *n*-butyraldehyde was it possible to isolate the pure alkylidene fluorene. It was a yellow solid melting at 55°. Isobutylidene fluorene and propylidene fluorene were isolated as crystalline dibromides which formed readily and were easily purified.

Attempts to debrominate the dibromides with zinc and acetic acid, in alcoholic solution,[4] gave highly unsaturated oils which could not be crystallized. On distillation at reduced pressure light yellow oils were obtained which were strongly unsaturated. However, estimation of the degree of unsaturation by means of an iodine chloride reagent (Wijs) indicated that the products were impure.

This work is being extended to the reaction of other aliphatic aldehydes and of nuclear substituted fluorenes.

Experimental Part

Procedure.—The apparatus consisted in all cases of a 1-liter three-necked flask fitted with a reflux condenser, a mercury-sealed stirrer, a dropping funnel, and a dry nitrogen inlet. In the flask were placed 3.9 g. potassium (0.1

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[1] Part of this material was taken from a thesis presented by C. F. Smullin in partial fulfillment of the requirements for the Master of Science degree at Lehigh University.

[2] Rieveschl and Ray, *Chem. Rev.*, **23**, 313 (1938).

[3] Thiele and Henle, *Ann.*, **347**, 291 (1906).

[4] Wieland, *et al.*, *Ber.*, **55**, 3313 (1922).

mole) and 150 cc. of xylene (distilled from sodium) to which 10 cc. (*ca.* 0.1 mole) of absolute ethanol was slowly added. After the reaction had moderated, 16.6 g. of recrystallized fluorene (0.1 mole) was added rapidly. The mixture was heated to boiling and then allowed to cool to room temperature, being stirred throughout the preparation. A small amount of potassium was still undissolved and was coated with a bright yellow solid (probably potassium fluorene) while the solution was deep green in color. Now 0.12 mole of the aldehyde, dissolved in 50 cc. of xylene, was slowly added while the solution was vigorously stirred. The aldehydes were all washed with cold sodium bicarbonate solution and water and dried over magnesium sulfate, then fractionated through a three-foot column packed with Fenske glass rings. Only materials boiling over a range of less than one-half degree centigrade were used in the experiments. Reaction took place immediately with evolution of heat and the deposition of a smeary solid on the walls of the flask. Generally the color changed from a deep green to a brown or red when all of the aldehyde had been added. The reaction mixture was stirred for about a half hour and then heated to the boiling point of xylene for a few minutes. On cooling it was treated with water and hydrochloric acid to remove potassium compounds and concentrated under reduced pressure to remove xylene. The residue was taken up in ether and crystallized when possible.

9-Propylidene Fluorene and Propylidene Fluorene Dibromide.—When propionaldehyde was used, the product yielded 4 g. of unchanged fluorene and some uncrystallizable oil. This oil was treated with 5 cc. of bromine dissolved in petroleum ether. Bromine was absorbed rapidly without evolution of hydrogen bromide and a red oil precipitated. This was extracted with petroleum ether (b. p. 20–40°), and 8 g. (29% yield based on unrecovered fluorene) of crude dibromide precipitated on cooling.

Recrystallization from ligroin (b. p. 60–100°) gave very compact pale yellow crystals of propylidene fluorene dibromide, m. p. 102–103°.

Anal.[5] Calcd. for $C_{16}H_{14}Br_2$: C, 52.5; H, 3.85. Found: C, 52.3; H, 3.98.

Four grams of the dibromide was dissolved in 75 cc. of absolute ethanol and treated with 10 g. of zinc dust and 6 cc. of glacial acetic acid. After reaction ceased another 10 g. of zinc dust and 6 cc. of glacial acetic acid were added. The mixture was then boiled for a few minutes, cooled, and diluted with 200 cc. of pure ether. The solution was then washed free of ethanol and acetic acid with water followed by aqueous sodium carbonate and dried over magnesium sulfate. On concentrating a small amount of an oil was formed which failed to crystallize. It boiled at 155–159° (3 mm.). The distillate was a light yellow oil which rapidly absorbed bromine. Unsaturation, as determined by iodine–chloride absorption (Wijs), was about one-half that required for propylidene fluorene. Apparently, some of the product decomposed on distillation.

9-*n*-Butylidene-fluorene.—After removing solvent from the *n*-butyraldehyde run, a thick oil resulted which deposited 14 g. (yield 63%) of a light yellow crystalline solid on prolonged cooling. Recrystallization from a little hot methanol gave a mass of yellow needles melting at 55°. No unchanged fluorene was isolated.

Anal. Calcd. for $C_{17}H_{16}$: C, 92.7; H, 7.3. Found: C, 92.7; H, 7.5.

The product on long standing in contact with the atmosphere liquefies and acquires a strong odor of butyraldehyde. Apparently, oxygen is absorbed, followed by cleavage to the components fluorene and *n*-butyraldehyde.

9-*n*-Butylidene-fluorene Dibromide.—Two grams of the purified hydrocarbon was dissolved in chloroform and treated with bromine in chloroform solution until a faint color persisted. The crude crystalline mass obtained on removing chloroform was recrystallized from ligroin (b. p. 90–120°). The compact pale yellow crystals melted at 93–94° with decomposition.

Anal. Calcd. for $C_{17}H_{16}Br_2$: C, 53.7; H, 4.24. Found: C, 54.1; H, 4.30.

9-Isobutylidene-fluorene and 9-Isobutylidene-fluorene Dibromide.—When isobutyraldehyde was used a thick oil was obtained which failed to crystallize on prolonged cooling. This oil was then treated with bromine in chloroform until a color persisted. On cooling, 25 g. of crude dibromide separated out (yield 66%). Recrystallization from ligroin (b. p. 60–100°) gave faintly yellow compact crystals melting at 131–132°.

Anal. Calcd. for $C_{17}H_{16}Br_2$: C, 53.7; H, 4.24. Found: C, 54.0; H, 4.43.

Four grams of the dibromide was treated with zinc and glacial acetic acid in absolute alcohol solution, as described in the propionaldehyde experiment. An oil was obtained which failed to crystallize (b. p. 157–159° (2 mm.)). It rapidly absorbed bromine but obviously was not pure 9-isobutylidene-fluorene, as judged by iodine–chloride absorption (Wijs). The substance absorbed about one-half of the calculated amount of iodine chloride.

Reaction of Acetaldehyde and Fluorene.—When acetaldehyde was used, under the same conditions, the only isolable products were fluorene and a thick red tar which was probably an aldehyde resin. Apparently, the acetaldehyde condensed with itself before reaction with fluorene was possible.

Summary

Propionaldehyde, *n*-butyraldehyde, and isobutyraldehyde were condensed with fluorene in the presence of potassium ethylate. *n*-Butylidene-fluorene was isolated as the olefin; propylidene-fluorene and isobutylidene fluorene were isolated as dibromides.

Bethlehem, Pa. Received August 6, 1940

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[5] The authors are indebted to Emma Dietz Schultz for the semimicro analyses. All melting points are uncorrected.