

layer weighed 18 g. Besides unreacted benzene, the upper layer contained alkylbenzenes, which distilled as follows: Cut 1, 184–188°, 2.0 g.,  $n_{D}^{20}$  1.4901; 2, 188–193°, 2.4, 1.4911; 3, 193–195°, 1.9, 1.4915.

*Cut 1* consisted of 2-methyl-3-phenylbutane. Diacetamino derivative, m. p. 187–189°, no depression in m. p. with the same derivative of authentic 2-methyl-3-phenylbutane (m. p. 189°).

*Cut 3*, Monoacetamino derivative, m. p. 142–143°. The mixed m. p. with the same derivative of authentic 2-methyl-3-phenylbutane (m. p. 147°) was 143–145°; with that of *t*-amylbenzene (m. p. 140°) was 130–133°.

Mono benzamino derivative, m. p. 137–138°. The mixed melting point with the same derivative of authentic 2-methyl-3-phenylbutane (m. p. 141°) was 138–139°.

Diacetamino derivative, m. p. 183–184°. A more soluble fraction, m. p. 175–178°, was also obtained, indicating a mixture.

### Summary

The alkylation of benzene with neopentyl alcohol gives *t*-amylbenzene (30% yield) when sulfuric acid is used as catalyst and neopentylbenzene (9% yield) when aluminum chloride is used.

Neopentyl chloride and benzene react in the presence of aluminum chloride to form 2-methyl-3-phenylbutane (24% yield).

RIVERSIDE, ILLINOIS

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

## The Reaction of Fluorenone and Diazomethane—A New Route to 9-Phenanthrol Derivatives

BY RAYMOND F. SCHULTZ, EMMA DIETZ SCHULTZ AND JOHN COCHRAN<sup>1</sup>

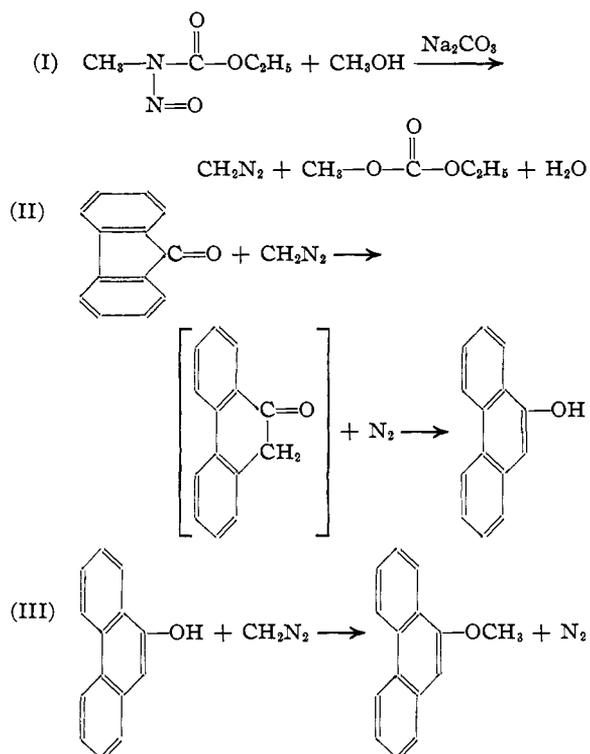
Cyclic aliphatic ketones react with diazomethane in methanol to form ketones with larger rings.<sup>2</sup> We have carried out an analogous reaction between fluorenone, an aromatic cyclic ketone, and diazomethane, and obtained a 50% yield of 9-methoxyphenanthrene. This provides a new route to 9-phenanthrol derivatives which are difficult to prepare in good yields. The best reported method is that of Fieser, Jacobsen and Price<sup>3</sup> involving the reaction of phenanthrene and methyl alcoholic bromine in which was obtained a 28–30% yield of 9-phenanthrol, based on phenanthrene consumed.

Our procedure is essentially that employed by Kohler, Tishler, Potter and Thompson,<sup>2e</sup> except that we use a solvent mixture of diethyl ether and methanol instead of methanol alone, in which fluorenone is not too soluble. As products we isolated the following: 5% of 9-phenanthrol, 30% of 9-methoxyphenanthrene, 1.5% di-9-phenanthryl ether, 0.5 g. of an unknown substance, m. p. 279–281°, and 30% unchanged fluorenone. This corresponds to a 51% yield of 9-phenanthrol derivatives based on fluorenone consumed. The main reactions concerned probably are:

(1) Part of this work was carried out by John Cochran in part fulfillment of the requirements for the degree of B. S. in Chemical Engineering, Lehigh University.

(2) (a) Mosettig and Burger, *THIS JOURNAL*, **52**, 3456 (1930); (b) Meerwein, *Chem. Zentr.*, **104**, I, 1758 (1933), German Patent 579,309; (c) Robinson and Smith, *J. Chem. Soc.*, 371 (1937); (d) Giraitis and Bullock, *THIS JOURNAL*, **59**, 951 (1937); (e) Kohler, Tishler, Potter and Thompson, *ibid.*, **61**, 1057 (1939).

(3) Fieser, Jacobsen and Price, *ibid.*, **58**, 2163 (1936).



Two equivalents of diazomethane, introduced as ethyl-N-methyl-N-nitrosocarbamate, were always added since the 9-phenanthrol first formed competed with fluorenone for the diazomethane.

9-Phenanthrol was isolated by extraction of an ether solution of the product with 10% sodium hydroxide<sup>3</sup> and subsequent acidification of the

alkaline extract. 9-Methoxyphenanthrene was separated as the picrate (m. p. 157–158.5° (uncor.)) and was recovered by decomposing the picrate with aqueous alcoholic ammonia. The small amount of 9-diphenanthryl ether was found in the crude 9-methoxyphenanthrene obtained from the picrate. The high-melting unknown product precipitated out on concentration of the original reaction mixture. The identity of 9-methoxyphenanthrene was checked by conversion to 9-phenanthrol which, in turn, was changed to the benzoate.

The reactions were all carried out at room temperature, hence it is difficult to account for the formation of di-9-phenanthryl ether which ordinarily is made by the high temperature dehydration of 9-phenanthrol.

The possibility of forming larger rings in this reaction is practically excluded because of the fact that the phenanthrone, theoretically first formed, is not known to react as a ketone but only as the enol, 9-phenanthrol.

The authors are extending this reaction to the preparation of substituted 9-phenanthrols of interest to theoretical and natural products chemistry.

### Experimental Part

**Procedure.**—The apparatus for a typical run consisted of a 500-cc. three-necked flask fitted with a stirrer, a dropping funnel, and a thermometer dipping into the liquid reaction mixture. In the flask were placed 18 g. (0.1 mole) of fluorenone, 50 cc. of pure diethyl ether, 100 cc. of methanol, and 1–2 g. of finely powdered sodium carbonate. Stirring was begun and 30 g. (0.21 mole) of ethyl N-methyl-N-nitrosocarbamate diluted with 20 cc. of methanol was added slowly over a period of about two hours. The reaction started after an induction period of about one-half hour and evolved heat. External cooling was used to keep the temperature below 30° in order to minimize loss of diazomethane. The mixture was allowed to stand at room temperature overnight and then concentrated at reduced pressures to remove all of the methanol. The crude product, an orange sirup, weighed 26.1 g. This was dissolved in ether and washed with water, followed by dilute hydrochloric acid to remove all of the sodium carbonate, and extracted three times with 25-cc. portions of 10% sodium hydroxide to remove phenanthrone. The alkaline extract on acidification, extraction with ether, and concentration yielded 1.0 g. of crude 9-phenanthrol (identified by recrystallization from benzene and mixed melting point with a known sample).

The ether solution of alkali-insoluble material was dried and concentrated but no crystalline substance separated out. Addition of a hot solution of 15 g. of picric acid in 100 cc. of 95% ethanol to the concentrate caused the formation of 13 g. of a picrate (with the evolution of heat). The

crude picrate melted at 145–147° (uncor.), after washing with saturated picric acid and with petroleum ether (b. p. 20–40°). It was largely the picrate of 9-methoxyphenanthrene.

The mother liquor after precipitation of the picrate was washed free of picric acid and concentrated to give 12 g. of an oily material. To this was added 50 cc. of alcohol, 12 g. of phenylhydrazine, and 1 cc. of glacial acetic acid, and the mixture was boiled for several minutes. On cooling, 8 g. of fluorenone phenylhydrazone precipitated as red crystals, melting at 144–147° (uncor.). This corresponds to 5.3 g. of fluorenone recovered.

**9-Methoxyphenanthrene from the Crude Picrate.**—The crude picrate was dissolved in warm 95% ethanol and treated with aqueous alcoholic ammonia until the red color of the picrate disappeared. The solution was then diluted with diethyl ether and washed three times with dilute aqueous ammonia, once with water, dried over magnesium sulfate, and concentrated. The residual ether was replaced by methanol as a better crystallizing solvent. The yield was 5.3 g. of crystalline 9-methoxyphenanthrene. On recrystallization from methanol, it formed long white needles melting at 95–96° (uncor.) (reported m. p. 96–97°).

**9-Phenanthrol from 9-Methoxyphenanthrene.**—In order to further identify 9-methoxyphenanthrene, it was converted to 9-phenanthrol by Fieser's<sup>3</sup> procedure, and finally 9-phenanthrol was converted to its benzoate.

Two grams of 9-methoxyphenanthrene was heated for two hours with 3.2 cc. of 40% hydrobromic acid, 4.2 cc. of acetic anhydride, and 10 cc. of glacial acetic acid. On cooling the product was diluted with water and filtered to obtain 1.8 g. of a crystalline product melting at 140–145°. Recrystallization from benzene and petroleum ether (b. p. 20–40°) gave tan needles melting at 153–155° (reported m. p. 152–153°).

**9-Phenanthryl Benzoate from 9-Phenanthrol.**—One gram of phenanthrone, 1.3 cc. of benzoyl chloride, and 3 cc. of pyridine were heated to boiling for several hours. On cooling the mixture was dissolved in diethyl ether, washed with aqueous sodium bicarbonate, dilute hydrochloric acid, and water. The ether solution was dried over magnesium sulfate, concentrated to dryness, and the residue crystallized out of methanol. The yield was 0.8 g. of white crystals melting at 99–100° (uncor.) (reported m. p. 96–97°).

**9-Methoxyphenanthrene Picrate from Pure 9-Methoxyphenanthrene.**—Rather than purify the crude picrate obtained from a reaction mixture, a pure picrate was made from recrystallized 9-methoxyphenanthrene. Two grams of 9-methoxyphenanthrene dissolved in hot 95% ethanol was treated with an excess of a warm saturated alcoholic picric acid solution and heated to boiling. On slowly cooling the solution deposited red needles of the picrate which were collected and washed first with alcoholic picric acid and finally with petroleum ether (m. p. 157–158.5° (uncor.)).

*Anal.* Calcd. for  $C_{21}H_{15}N_3O_5$ : N, 9.62. Found: N, 9.77.

Occasionally, a few tenths of a gram of di-9-phenanthryl ether was obtained along with the 9-methoxyphenanthrene on decomposition of the crude picrate. The melting point is 200–202° (reported m. p. 210°), which is rather low; how-

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.

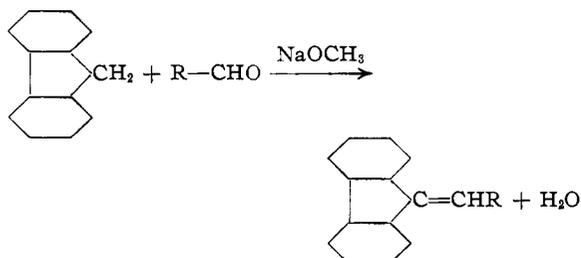
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[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMICAL LABORATORY, LEHIGH UNIVERSITY]

## Preparation of Alkylidene Fluorenes from Fluorene with Aliphatic Aldehydes

BY RAYMOND F. SCHULTZ AND CHARLES F. SMULLIN<sup>1</sup>

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.<sup>2</sup>



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.<sup>3</sup>

This paper describes the preparation of condensation products of fluorene with typical

(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).

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,<sup>4</sup> 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

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