moved and the residual viscous red oil treated with 5 cc. of boiling petroleum ether (b. p. 60–110°). The insoluble dark gum was removed from the solution by decantation of the latter. On cooling, the petroleum ether deposited an orange-colored solid which weighed 235 mg. By concentrating the mother liquors, carefully discarding the red gum which formed regularly, another 540 mg. of this solid was obtained. The total yield was 775 mg. (26%). A sample was recrystallized from petroleum ether (Darco) to constant melting point; tiny needles, m. p. 146° (cor.).

Anal. Calcd. for $C_{21}H_{26}O_4$: C, 72.85; H, 7.89. Found: C, 73.55; H, 7.82.

1-Hydroxy-3-*n*-amyl-9-methyl-6-dibenzopyrone.—A mixture of 235 mg. of 2,6-dimethoxy-4-*n*-amyl-5'-methyl-2'-carboxybiphenyl, 0.6 cc. of 48% hydrobromic acid, 1 cc. of glacial acetic acid, and 0.5 cc. of acetic anhydride was heated to reflux to dissolve the solid acid, and heating continued for four hours. After pouring into 20 cc. of water, the reaction mixture was extracted three times with ether and the organic layer washed thoroughly with saturated aqueous sodium bicarbonate and dried over magnesium sulfate. The solvent was removed and the oily residue was treated with boiling petroleum ether (b. p. 60–110°) for five minutes. The solid material insoluble in this boiling solvent weighed 50 mg. After recrystallization from ethyl acetate, it melted at 183–185° (cor.), and a mixture of this material and an authentic specimen of 1-hydroxy-3-*n*-amyl-9-methyl-6-dibenzopyrone[8] showed no melting point depression.

The petroleum ether extract deposited another 50 mg. of the dibenzopyrone on standing. Concentration of the mother liquors showed that the remainder of the starting material had been essentially unchanged in the reaction.

Summary

1. Treatment of the lithium derivative of orcinol dimethyl ether with N-methylformanilide produced orsellinaldehyde dimethyl ether, which was converted to the corresponding 2,6-dimethoxy-4-methylcinnamic acid by means of malonic acid and pyridine. Addition to this acid of 2,3-dimethyl-1,3-butadiene gave 1,2-dimethyl-4-(2,6-dimethoxy-4-methylphenyl)-1-cyclohexene-5-carboxylic acid.

2. In a similar manner, 2,6-dimethoxy-4-*n*-amylcinnamic acid was synthesized from olivetol dimethyl ether. This cinnamic acid added isoprene to give 1-methyl-5-(2,6-dimethoxy-4-*n*-amylphenyl)-1-cyclohexene-4-carboxylic acid. In one instance, which could not be repeated, an isomer of this latter compound was formed.

3. That the adduct mentioned in 2 had a methyl group in the 1- rather than the 2-position, was proved by converting it to 1-hydroxy-3-*n*-amyl-9-methyl-6-dibenzopyrone, which had been synthesized by a method leaving no doubt of its structure. This was accomplished by conversion of the adduct to its methyl ester, dehydrogenation of the ester to 2,6-dimethoxy-4-*n*-amyl-5'-methyl-2'-carbomethoxybiphenyl which was saponified to the corresponding acid. Demethylation of this acid gave the pyrone.

Urbana, Illinois Received October 31, 1942

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[8] Adams and Baker, This Journal, 62, 2401 (1940).

[Contribution from the Chemical Laboratory of Trinity College]

A New Modification of the Ullmann Synthesis of Fluorene Derivatives

By Warren C. Lothrop and Paul A. Goodwin

The present paper describes preliminary investigation of a previously unexplored modification of the method of arriving at substituted *o*-aminobenzophenones, which as Ullmann[1] discovered react with nitrous acid to yield the corresponding fluorenones. The new method avoids the necessity of using *p*-toluenesulfonyl chloride to protect the amino group of anthranilic acid from the subsequent reactions with thionyl chloride and aluminum chloride, and therefore the frequent difficulty met with in removing this large and relatively inert group by hydrolysis afterwards.

The simplest illustration of this method is given below in which anthranilic acid is refluxed with acetic anhydride and thus converted into 2-methyl-3,1,4-benzoxaz-4-one (I). The latter when treated with phenylmagnesium bromide by the inverse method yields the acetyl derivative of *o*-aminobenzophenone into which it can be readily converted by hydrolysis with dilute hydrochloric acid, as shown in the equations

The importance of carrying out the reaction by the inverse procedure was made evident when an experiment was performed adding I to a solution of the Grignard reagent. In this case none of the desired product resulted and only 2-acetamidophenyldiphenylcarbinol (II) was formed, even when equimolecular quantities were employed.

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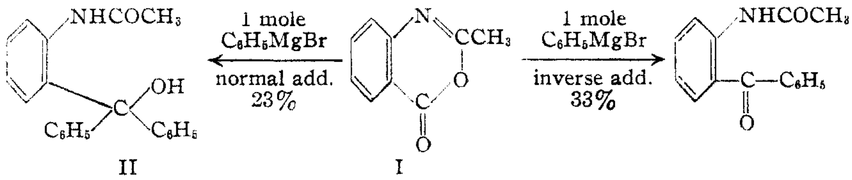
[1] Ullmann and Mallet, *Ber.*, 31, 1694 (1898).

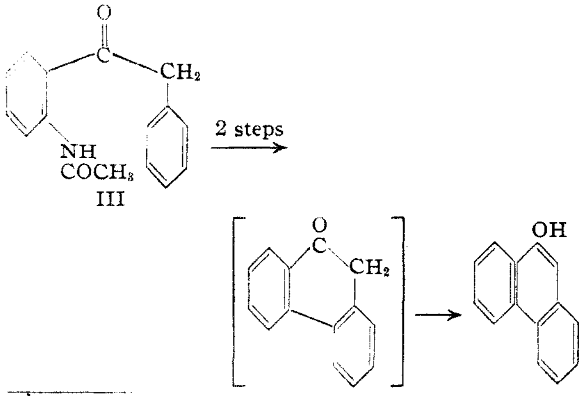


II I

The identity of this compound was easily proved by comparison with authentic samples of the whole series prepared by Baeyer and Villiger[2] directly from methyl anthranilate.

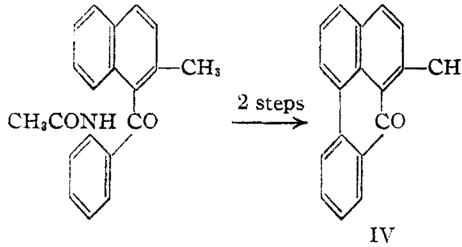
While compound I somewhat resembles a cyclic anhydride and is reported to enter into a Friedel–Crafts reaction,[3] it is probably more correctly considered as a lactone involving the enol form of acetylanthranilic acid. So far as the authors are aware no comprehensive study has been made of the reaction between Grignard reagents and this class of compound and scattered references in the literature such as that on coumarin by Heilbron and Hill[4] are not strictly analogous. It is interesting that in the latter case at least the carbinol is the sole product even by the inverse method.

With the above as a working basis seven representative aromatic halides were converted into Grignard reagents and reacted with I with results which were somewhat disappointing. Moderate success was met using *o*-bromotoluene, α-bromonaphthalene and 1-bromo-2-methylnaphthalene, but in the cases of *m*-bromotoluene, 2,4-dimethyliodobenzene, β-bromonaphthalene and benzyl chloride the products were extremely impure or formed only in negligible amounts. The failure with benzylmagnesium chloride was especially disappointing since it had been hoped that 2-acetamidophenyl benzyl ketone (III) which would be expected to result might then be converted into 9-phenanthrol



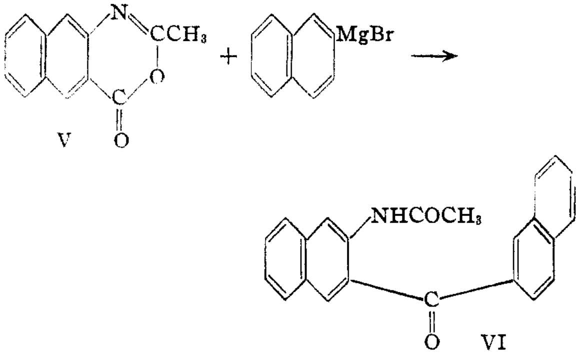
III

The products obtained from *o*-bromotoluene and α-bromonaphthalene were successfully carried through the reaction series yielding 1-methylfluorenone and 1,2-benzofluorenone, both of which were further reduced to the corresponding fluorene derivatives. In the case of 1-bromo-2-methylnaphthalene the usual condensation was blocked by the methyl group and a small quantity of 6-methyl-7-*m*-benzanthrone (IV) was obtained, thus indicating that the Ullmann reaction can occur in a peri position and result in the formation of a six-membered ring.



IV

In a recent article Martin[5] has described the synthesis of six of the seven possible dibenzofluorenes, but he was unable by this method to obtain 2,3,5,6-dibenzofluorene and assumed that its previous report[6] as a byproduct of the preparation of di-2-naphthylcarbinol must be correct. It was evident that the method set forth in this paper might yield this missing member of the series. Starting with 2-methyl-4-naphth-(2,3-d)-1,3-oxazin-4-one (V) and β-bromonaphthalene



V VI

2-acetamido-3-naphthyl-2′-naphthyl ketone was obtained and this on hydrolysis and ring-closure gave a substance which was evidently 2,3,5,6-dibenzofluorenone since its method of synthesis was quite unambiguous. This compound, however,

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[2] Baeyer and Villiger, *Ber.*, **37**, 3192 (1904).

[3] Hayashi and co-workers, *J. Chem. Soc. Japan*, **56**, 1102 (1935).

[4] Heilbron and Hill, *J. Chem. Soc.*, 2005 (1927).

[5] Martin, *ibid.*, 679 (1941).

[6] Schmidlin and Huber, *Ber.*, **43**, 2824 (1910).

melted at 184–185°, whereas the oxidation product of the "2,3,5,6-dibenzofluorene" of Schmidlin and Huber melted at 163–165°. Their hydrocarbon melted at 190.5°. It seems probable that their compound was in reality 2,2′-binaphthyl, m. p. 187–188°, the result of coupling two molecules of the Grignard reagent, and that their oxidation product was an impure sample of 2-(2′-naphthyl)-naphthoquinone(1,4) m. p. 177°.

Unfortunately an attempt to prove this by reducing the product from our series of reactions failed and we were not able, therefore, to obtain a complete synthesis of the fluorene.

The starting material for this latter part of the work V has been previously described[7]; its reactions with phenylmagnesium bromide and benzylmagnesium chloride were explored but only with the former was a pure product obtained: 2,3-benzofluorenone.

Experimental Part

2-Methyl-3,1,4-benzoxaz-4-one (I) was obtained in 55% yield by following the literature procedure[8] and purified by crystallization from benzene–ligroin.

When a solution of 30 g. of I in 125 cc. of dry benzene was added dropwise with vigorous stirring to the Grignard reagent formed from 32.3 g. of bromobenzene and 5.0 g. of magnesium in 125 cc. of absolute ether, a solid complex separated. This, after hydrolysis with dilute hydrochloric acid and steam-distillation to remove the solvent, gave a white solid, which recrystallized from dilute alcohol (m. p. 192–195°). The yield was 10.0 g. or 23%. A small sample crystallized from alcohol in small white plates, m. p. 197–198°. Baeyer and Villiger[2] give 192° as the melting point of **2-acetamidophenyldiphenylcarbinol** (II). The value for the free amine is given by these authors as 121.5° while our sample, formed by the hydrolysis of II with alcoholic hydrochloric acid, melted at 119°. Additional confirmation was given by the conversion of this amine by the action of acetic anhydride and sodium acetate into **2-methyl-4,4-diphenyl-3,1,4-benzoxazine**, m. p. 137–139° (lit. 135–137°).

All subsequent reactions were performed by the inverse method in which the Grignard reagent was formed in one three-necked flask equipped with stirrer and forced by nitrogen into a dropping funnel mounted in a second three-necked flask. The latter was equipped with a mechanical stirrer and condenser and mounted so that it could be warmed by steam or cooled by ice. It contained a solution of the oxazone in dry benzene and to it the reagent was added dropwise with vigorous stirring to prevent caking. This was done at 0° and followed by stirring at 30° for an hour before the products were worked up by standard procedures.

When 10.0 g. of I in 125 cc. of dry benzene was thus treated with the Grignard reagent formed from 9.7 g. of bromobenzene and 1.5 g. of magnesium a product was obtained which crystallized from dilute alcohol in small white plates, m. p. 88°, while Auwers[9] gives 89° for **2-acetamidobenzophenone.** The yield was 5.2 g. or 33%.

Hydrolysis of the above was accomplished by refluxing with concentrated hydrochloric acid in alcohol. The resulting **2-aminobenzophenone** crystallized from alcohol in small yellow needles in 83% yield (m. p. 103°).[10]

2-Methyl-2′-acetamidobenzophenone was formed by the action of *o*-tolylmagnesium bromide according to the above-described procedure. The product was obtained in 43% yield after crystallization from dilute alcohol (m. p. 104°).

Anal. Calcd. for $C_{16}H_{15}O_2N$: C, 75.90; H, 5.93; N, 5.53. Found: C, 76.27; H, 6.19; N, 5.46.

When 10.1 g. of the above amide was refluxed with 13 cc. of concentrated hydrochloric acid in 80 cc. of alcohol, made alkaline with ammonia, treated with Norite, diluted and allowed to cool **2-methyl-2′-aminobenzophenone** separated in bright yellow needles, m. p 84°. The yield was 6.5 g. or 77%.

Anal. Calcd. for $C_{14}H_{13}ON$: C, 79.62; H, 6.16; N, 6.63. Found: C, 79.87; H, 6.16; N, 6.33.

1-Methylfluorenone was formed in 49% yield by the diazotization of the above amine (3.6 g.) in 500 cc. of 5 *N* hydrochloric acid with 1.4 g. of sodium nitrite. The orange product which separated on warming this solution on the steam-bath for two and one-half hours was thrice extracted with hot 3 *N* potassium hydroxide and the residue crystallized from dilute alcohol, yielding 1.6 g. of bright yellow needles, m. p. 98°.

Anal. Calcd. for $C_{14}H_{11}O$: C, 86.60; H, 5.19. Found: C, 86.80; H, 5.39.

The identity of this compound was confirmed by its conversion into fluorenone-1-carboxylic acid[11] by the action of alkaline potassium permanganate. The alkaline extracts of the product resulting from the ring closure on acidification yielded **2-methyl-2′-hydroxybenzophenone** which crystallized from dilute alcohol in small, cream-colored plates, m. p. 65–67°. The yield was 0.12 g.

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.26; H, 5.70. Found: C, 79.56; H, 5.88.

1-Methylfluorene.—Reduction of the fluorenone (0.5 g.) was accomplished with difficulty by refluxing for fifty-two hours in 9 cc. of acetic acid with 3.6 cc. of 47% hydriodic acid and 0.1 g. of red phosphorus. Crystallization from alcohol yielded 0.1 g. of white leaflets, m. p. 87°, and 0.1 g. of unchanged starting material was obtained from the mother liquors.

Anal. Calcd. for $C_{14}H_{12}$: C, 93.32; H, 6.70. Found: C, 93.82; H, 6.84.

2-Acetamido-3′-methylbenzophenone.—When the same quantities and procedure used above with *o*-bromotoluene were tried with *m*-bromotoluene, 3.9 g. of impure, oily crystals was obtained. These could not be purified and were accordingly hydrolyzed by refluxing with a solution of 20 cc. of concentrated hydrochloric acid, 100 cc. of water

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(7) Fries, Walter and Schilling, *Ann.*, **516**, 248 (1935).

(8) Bogert, Gortner and Amend, This Journal, **33**, 951 (1911).

(9) Auwers, *Ber.*, **29**, 1263 (1896).

(10) Gabriel and Stelzner, *ibid.*, **29**, 1303 (1896).

(11) Fieser and Seligman, This Journal, **57**, 2174 (1935).

and 50 cc. of alcohol. The clear solution was separated from tars and made alkaline with ammonia yielding **2-amino-3′-methylbenzophenone.** This crystallized from dilute methanol in long yellow needles, m. p. 57°, and weighed 1.91 g. representing a 10% over-all yield.

Anal. Calcd. for $C_{14}H_{13}ON$: C, 79.62; H, 6.16; N, 6.63. Found: C, 79.83; H, 6.52; N, 6.94.

2-Methylfluorenone.—Ring-closure of 0.49 g. of the above amine in the usual manner followed by five fractional crystallizations gave a few milligrams of product (m. p. 89°) and considerable by product but none of the usually accompanying phenol. Kruber[12] has reported 92° as the m. p. of the pure compound.

An attempt to form **2-acetamidophenyl benzyl ketone** (III) by the action of benzylmagnesium chloride on I yielded a yellow-brown oil which could not be crystallized, appeared to distil unchanged *in vacuo* and was completely unaffected by attempted hydrolyses.

2-Acetamidophenyl 1′-naphthyl ketone resulted when the Grignard reagent formed from 17.7 g. of α-bromonaphthalene, 2.26 g. of magnesium and 50 cc. of dry ether was added in the usual manner to a solution of 15 g. of I. The product weighed 11.6 g. (47%) and was thus obtained as small, tan crystals, m. p. 123–125°. An analytical sample crystallized white from alcohol, m. p. 125°.

Anal. Calcd. for $C_{19}H_{15}O_2N$: C, 78.88; H, 5.19; N, 4.84. Found: C, 78.77; H, 5.28; N, 4.79.

The above ketone also resulted when the reaction was carried out in the normal rather than in the inverse manner employed above. The yield was only 2.4 g., however, and there was also formed 1.2 g. of a product crystallizing from glacial acetic acid in small white needles, m. p. 209–211°. This was assumed to be **di-(1-naphthyl)-2′-acetamidophenylcarbinol.**

Anal. Calcd. for $C_{29}H_{18}O_2N$: C, 83.45; H, 5.51; N, 3.35. Found: C, 83.50; H, 5.55; N, 3.39.

Hydrolysis of 1.19 g. of this carbinol in the usual way gave 0.69 g. of fine white needles crystallizing from acetone-alcohol (m. p. 206°, dec.) and which were evidently crystals of **di-(1-naphthyl)-2′-aminophenylcarbinol.**

Anal. Calcd. for $C_{27}H_{21}ON$: C, 86.37; H, 5.64; N, 3.73. Found: C, 86.70; H, 5.37; N, 3.49.

1-Naphthyl 2′-Aminophenyl Ketone.—When 11.3 g. of the above described 1-naphthyl 2′-acetamidophenyl ketone was hydrolyzed 7.5 g. (78%) of a product was obtained from alcohol as small, yellow prisms (m. p. 138°). A m. p. of 140° has been reported.[1]

1,2-Benzofluorenone was obtained from the above amine in 25% yield as dark orange needles, m. p. 133°, in agreement with Graebe.[13] It was reduced (53%) to **1,2-benzofluorene** (chrysofluorene) by refluxing for one week in acetic acid with red phosphorus and hydriodic acid. The product recrystallized from acetic acid in white plates of m. p. 182° in close agreement with the literature values.[14] It seemed desirable to carry through these last two steps, for, although both compounds were previously known, no direct conversion of the fluorenone had been made, and both compounds are thus shown to have been correctly described.

2-Methyl-1-naphthyl 2′-Acetamidophenyl Ketone.—Using 19.6 g. of freshly prepared 1-bromo-2-methylnaphthalene[15] and the usual procedure modified by the necessary addition of 100 cc. of dry benzene to keep the Grignard reagent in solution, 9.5 g. (34%) of product was obtained. It crystallized from dilute alcohol in small tan crystals m. p. 132°.

Anal. Calcd. for $C_{20}H_{17}O_2N$: C, 79.18; H, 5.65; N, 4.62. Found: C, 79.61; H, 6.10; N, 4.54.

Hydrolysis of the above amide was accomplished in 68% yield giving 5.6 g. of small yellow crystals m. p. 111°. An analytical sample on recrystallization melted at 114°.

Anal. Calcd. for $C_{18}H_{15}ON$: C, 82.76; H, 5.75; N, 5.36. Found: C, 82.51; H, 5.73; N, 5.25.

6-Methyl-7-meso-benzanthrone (IV).—An attempted ring-closure of the above amine (2 g.) in the usual manner gave 0.18 g. of material melting 111–120° and after three crystallizations a few milligrams of orange crystals (m. p. 125°) identical with that previously reported.[16]

2-Naphthyl 2′-Acetamidophenyl Ketone.—When the Grignard reagent prepared from 10 g. of 2-bromonaphthalene, 1.17 g. of magnesium, 60 cc. of dry ether diluted with 50 cc. of dry benzene was added to a solution of 7.8 g. of I in 75 cc. of dry benzene, a viscous reddish oil resulted which defied attempts at purification. It was accordingly hydrolyzed with dilute alcoholic hydrochloric acid and then freed from a considerable quantity of tar. There resulted 1.0 g. of **2-naphthyl 2′-aminophenyl ketone** which crystallized from methanol in small yellow needles m. p. 106°, representing a yield of 8.3% based on the bromonaphthalene used.

Anal. Calcd. for $C_{17}H_{13}ON$: C, 82.58; H, 5.26; N, 5.67. Found: C, 82.82; H, 5.46; N, 5.57.

3,4-Benzofluorenone was obtained by a ring-closure of the above amine but in traces only, in both an orange, stable form (m. p. 159°) and in an unstable yellow form. This phenomenon has already been described.[17]

2-Methyl-4-naphth-(2,3-d)-1,3-oxazin-4-one (V)[7] was obtained from 2-amino-3-naphthoic acid.[18] Reaction of 15 g. of this with phenylmagnesium bromide by the inverse procedure gave two products. One was presumably **2-acetamido-3-naphthyldiphenylcarbinol:** 1.2 g. of thin white needles crystallizing from acetone and alcohol and melting at 226° dec.

Anal. Calcd. for $C_{25}H_{21}O_2N$: C, 81.74; H, 5.72; N, 3.81. Found: C, 81.64; H, 5.93; N, 4.04.

The other compound crystallized from alcohol in small bright yellow plates, m. p. 141–145°. The yield was 8.0 g. or 39%. This **3-(2-acetamido)-naphthyl phenyl ketone** was hydrolyzed in the usual way yielding **3-(2-amino)-naphthyl phenyl ketone,** 39% of the theoretical. The product recrystallized from alcohol in fine, orange-yellow needles m. p. 114°.

Anal. Calcd. for $C_{17}H_{13}ON$: C, 82.59; H, 5.26; N, 5.67. Found: C, 82.50; H, 5.50; N, 5.95.

2,3-Benzofluorenone[19] resulted in 13% yield by the ring-closure of the above amine in the usual manner. It was

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[12] Kruber, *Ber.*, **65B**, 1382 (1932).

[13] Graebe, *ibid.*, **29**, 827 (1896).

[14] Cook and Hewett, *J. Chem. Soc.*, 369 (1934)

[15] Mayer and Sieglitz, *Ber.*, **55**, 1851 (1922).

[16] Charrier and Ghigi, *Gazz. chim. ital.*, **62**, 928 (1932).

[17] Schaarschmidt, *Ber.*, **50**, 293 (1917).

[18] Dutta, *ibid.*, **67**, 1321 (1934).

[19] Thiele and Wanscheidt, *Ann.*, **376**, 276 (1910).

found necessary for complete purification to boil the crude fluorenone with a trace of stannous chloride in hydrochloric acid. The product then crystallized from alcohol in small yellow plates, m. p. 150–152°. From the alkaline extracts a small quantity of **2-hydroxy-3-naphthyl phenyl ketone** separated on acidification. This crystallized from alcohol in golden yellow leaflets, m. p. 156°.

Anal. Calcd. for $C_{17}H_{13}O_2$: C, 81.91; H, 5.22. Found: C, 82.29; H, 5.05.

When the naphthoxazone V was treated with benzylmagnesium chloride none of the desired **2-acetamido-3-naphthylbenzyl ketone** was obtained. However a small yield of **2-acetamido-3-naphthyldibenzylcarbinol** did result and the product melting at 181° crystallized from acetone-alcohol in colorless prisms.

Anal. Calcd. for $C_{27}H_{25}O_2N$: C, 82.03; H, 6.33; N, 3.54. Found: C, 81.97; H, 6.39; N, 3.22.

2-Acetamido-3-naphthyl 2′-naphthyl ketone (VI) was obtained in very impure condition by the action of 2-naphthylmagnesium bromide on V following the usual procedures. A small sample after repeated crystallizations from methanol was finally obtained as white needles, m. p. 169°.

Anal. Calcd. for $C_{20}H_{17}O_2N$: C, 81.37; H, 5.05; N, 4.12. Found: C, 81.80; H, 5.18; N, 3.98.

Hydrolysis of the bulk of the above amide effected the removal of a large quantity of tarry by-products and gave a 4% yield based on the 2-bromonaphthalene used. The **2-amino-3-naphthyl 2′-naphthyl ketone** formed crystallized from alcohol in fine orange-yellow needles; m. p. 154–156°.

Anal. Calcd. for $C_{21}H_{15}ON$: C, 84.83; H, 5.09; N, 4.71. Found: C, 84.91; H, 5.26; N, 4.72.

2,3,5,6-Dibenzofluorenone.—From 0.5 g. of the above amine by the usual diazotization procedure, a product (0.1 g.) was obtained which crystallized from glacial acetic acid in small orange-yellow leaflets, m. p. 185°.

Anal. Calcd. for $C_{21}H_{12}O$: C, 90.00; H, 4.32. Found: C, 90.10; H, 4.14.

As a by-product 25 mg. of alkali-soluble material resulted, which likewise crystallized from glacial acetic acid in small golden needles, m. p. 139°. This was evidently **2-hydroxy-3-naphthyl 2′-naphthyl ketone.**

Anal. Calcd. for $C_{21}H_{14}O_2$: C, 84.55; H, 4.73. Found: C, 84.30; H, 5.07.

The attempted reduction of the dibenzofluorenone by red phosphorus and hydriodic acid produced no results after over a week's refluxing.

In all of the described Grignard reactions varying amounts of the oxazone were recovered as the free acetyl amino acid. The yields have been calculated however on the basis of the original quantities used.

Summary

A new modification of the Ullmann synthesis of fluorene derivatives has been described. Three new fluorene derivatives: 1-methylfluorenone, 1-methylfluorene and 2,3,5,6-dibenzofluorenone have been described together with numerous intermediates. The synthesis has also been applied to the preparation of several previously reported compounds.

Although the yields are not high, the method is necessary for the synthesis of some compounds which were previously accessible only with difficulty.

HARTFORD, CONN.
WASHINGTON, D. C.

RECEIVED DECEMBER 8, 1942

[CONTRIBUTION FROM THE WM. H. CHANDLER CHEMISTRY LABORATORY, LEHIGH UNIVERSITY]

The Condensation of 2-Furanacetic Acid with o-Nitrobenzaldehyde

BY E. D. AMSTUTZ AND ERVIN R. SPITZMILLER

It has only been within the past several years that the substance 2-furanacetic acid (I) has been available in quantities sufficient to permit an investigation of its chemical behavior. It was to be expected that the methylene group would resemble that in phenylacetic acid and would be capable therefore of participating in a Perkin condensation with aromatic aldehydes. This paper reports optimum conditions for the reaction of 2-furanacetic acid with o-nitrobenzaldehyde and the nature of the products formed.

Preliminary experiments indicated that the customary method of condensation,[1] using acetic anhydride, zinc chloride and a temperature of 120° for a period of about five hours was not well suited to the present reactants. Much decomposition occurred as evidenced by the formation of dark red tar. The yield of product, compound (II) only, was low. Eventually it was found that

TABLE I

			Yields, %		
Run[a]	T, °C.	Time hr.	Crude	Compound (II)[b]	Compound III[b]
II	120– 5	6	59.2	17.8	16.8
III	60–70	6	69.7	25.1	17.5
	80–90	5			
IV	73– 5	12	100.7	42.6	23.2

[a] Run I was mentioned earlier and is not included here.
[b] Purified material.

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(1) Pschorr, *Ber.*, **29**, 496 (1896).