scribed previously and would appear to be quite difficult to obtain by any other means. It seems clear that we have available an excellent method for preparing certain substituted naphthalene compounds from selected β,γ-unsaturated lactones. The scope and limitations of the method are being explored further.

Other striking differences in chemical behavior between I and II have been observed and these will be discussed in a forthcoming paper.

EXPERIMENTAL[8]

Reaction of α-benzylidene-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide (II) with benzene. In a 2-l., round bottomed flask, fitted with a mechanical stirrer, dropping funnel, and reflux condenser, were placed 19.8 g. (0.15 mol.) of anhydrous aluminum chloride in 250 ml. of dry, thiophene-free benzene. The mixture was cooled to 10–20° and stirred for 1 hr. To this mixture was added dropwise with stirring a solution containing 12.4 g. (0.05 mol.) of II in 250 ml. of dry benzene, the temperature being maintained at 10–20° during the addition. The mixture turned brick-red. When all of the butenolide had been added, the mixture was stirred for an additional 3 hr. at room temperature. The complex was decomposed with dilute hydrochloric acid and the resulting mixture extracted with ether. The ether layer was washed with dilute sodium bicarbonate solution and water and then dried over anhydrous magnesium sulfate. Upon evaporation of the solvent on steam bath, a yellowish white solid was obtained. Crystallization from 95% ethanol gave 8.5 g. (70.8%) of white needles of 4-phenyl-2-naphthoic acid (III), m.p. 262.5–263.5°.

Anal. Calcd. for $C_{17}H_{12}O_2$: C, 82.24; H, 4.83. Found: C, 82.52; H, 4.81. Mol. wt. calcd.: 248. Found: 248 (neut. equiv.).

$\lambda_{\max}^{\mathrm{EtOH}}$ 245 mμ (ϵ 31,000), 290 mμ (ϵ 7990). Infrared absorption at 1695 cm.$^{-1}$ (s) and 2600 cm.$^{-1}$ (w).

Reaction of II with anisole. In a 500-ml. round bottomed flask, fitted with a mechanical stirrer, dropping funnel, and reflux condenser, were placed 4.7 g. (0.036 mol.) of anhydrous aluminum chloride and 3.8 g. (0.036 mol.) of anisole in 65 ml. of methylene chloride. The mixture was stirred for 1 hr. at 10°. To this mixture was added dropwise with stirring a solution containing 3 g. (0.012 mol.) of II in 100 ml. methylene chloride, the temperature being maintained at 10–20° during the addition. When all of the butenolide had been added, the mixture was stirred for an additional 3 hr. at room temperature. The complex was decomposed with 250 ml. of dilute (1:15) hydrochloric acid and the two layers which formed were separated, the water layer was washed with methylene chloride and the combined extracts were washed with dilute acid and water until neutral to litmus. Excess methylene chloride was removed by evaporation on a steam bath. The product was crystallized from 95% ethanol to give 1.5 g. (50%) of white needles, m.p. 258–260°.

Anal. Calcd. for $C_{17}H_{12}O_2$: C, 82.24; H, 4.83. Found: C, 82.57; H, 5.17.

Mixed melting point with the product obtained with benzene showed no depression. The ultraviolet and infrared spectra were also identical.

Decarboxylation of 4-phenyl-2-naphthoic acid (III). III [8.13 g. (0.033 mol.)] and 0.648 g. (0.0028 mol.) of copper chromite in 10 ml. of quinoline were heated under slow reflux for 7 hr. The mixture was treated with 100 ml. of ether and washed with several portions of dilute hydrochloric acid followed by sodium bicarbonate solution and water. The ether layer was dried over anhydrous magnesium sulfate.

The ether was removed by evaporation and 1-phenylnaphthalene was obtained as a viscous oil, b.p. 333–335° at 748 mm., $n_{\mathrm{D}}^{23.4}$ 1.6654 (reported b.p. 334–336°,[9] n_{D}^{18} 1.6692[10]).

Nitration of 1-phenylnaphthalene. To 3 ml. of a 50-50 mixture of fuming nitric acid and glacial acetic acid, cooled in an ice bath, was added dropwise 0.25 ml. of 1-phenylnaphthalene. The solution was mixed and poured over ice. The 4-nitro-1-phenylnaphthalene thus obtained was crystallized from petroleum ether to give yellow crystals melting at 129–130° (reported[11] m.p. 129–130°).

Spectral measurements and analyses. Infrared spectra were obtained on a Perkin-Elmer 21 spectrophotometer, using chloroform as solvent. Ultraviolet spectra were measured in 95% ethanol using a Beckman DK-2 spectrophotometer. Microanalyses were conducted by Micro-Tech Laboratories, Skokie, Ill.

Acknowledgment. The authors gratefully acknowledge the financial assistance of the Research Corp. and the Philip D. Armour Cancer Fund.

DEPARTMENT OF CHEMISTRY
ILLINOIS INSTITUTE OF TECHNOLOGY
CHICAGO 16, ILL.

---

[8] M.p.'s are corrected.

(9) R. Weiss and K. Woidich, *Monatsh.*, **46**, 455 (1925).

(10) W. Davies, N. W. Gamble, aud W. E. Savage, *J. Chem. Soc.*, 4678 (1952).

(11) R. T. Arnold, C. Collins, and W. Zenk, *J. Am. Chem. Soc.*, **62**, 983 (1940).

Aluminum Iodide as a Friedel-Crafts Catalyst[1]

ERNEST R. KLINE, BRUCE N. CAMPBELL, JR.,[2]
AND EARL C. SPAETH[3]

Received April 1, 1959

A comparison of aluminum iodide with aluminum chloride and aluminum bromide as catalysts in typical Friedel-Crafts alkylations and acylations seems not to have been reported. The absence of such an investigation may be due, in part, to the well known sensitivity of aluminum iodide to air and moisture.[4]

Aluminum iodide was prepared by two methods which minimize contact with air and moisture. Comparisons have been made with aluminum chloride and aluminum bromide as catalysts in the isopropylation, succinoylation, and benzoylation of benzene. The results of these experiments are summarized in Table I. The reactions using aluminum chloride reported in this table are each the best of several made to determine conditions which give moderately good yields. The alkylations with aluminum bromide and aluminum iodide (Method B) represent the average of two runs. Although aluminum iodide acts as a catalyst in all these reactions,

---

(1) Based on part of the Ph.D. thesis of B.N.C., University of Connecticut, 1958.

(2) To whom inquiries should be sent. Present address: Department of Chemistry, MacMurray College, Jacksonville, Ill.

(3) Present address: Apt. 203, 1600 N. Quinn St., Arlington, Va.

(4) G. W. Watt and J. L. Hall, *Inorganic Syntheses*, McGraw-Hill Book Company, Inc., New York, N. Y., 1953, Vol. IV, p. 119.

only in the case of isopropylation does it appear to have a possible advantage over the other two catalysts. Since in this case aluminum iodide causes a greater total isopropylation it may well prove to be a useful catalyst for compounds which are diffiult to alkylate. The products obtained with aluminum iodide in the other two reactions were distinctly more difficult to purify than those obtained with the other two catalysts due to difficulties in freeing from iodine.

TABLE I

RESULTS OF COMPARISON REACTIONS WITH BENZENE AS THE SUBSTRATE

Substituting Reagent	Catalyst	Products Yields, %	
		Isopropylbenzene	Diisopropylbenzene
Isopropyl chloride	$AlCl_3$	49.0	10.4
Isopropyl chloride	$AlBr_3$	59.0	8.4
Isopropyl chloride	AlI_3[a]	48.5	25.7
Isopropyl chloride	AlI_3[b]	62.5	13.7
		β-Benzoylpropionic acid	
Succinic anhydride	$AlCl_3$	55.0	
Succinic anhydride	$AlBr_3$	78.5	
Succinic anhydride	AlI_3[b]	43.2	
		Benzophenone	
Benzoyl chloride	$AlCl_3$	69.5	
Benzoyl chloride	$AlBr_3$	71.5	
Benzoyl chloride	AlI_3[b]	19.5	

[a] Method A. [b] Method B.

EXPERIMENTAL

The two methods used to prepare aluminum iodide are like many previously reported in that they are based on elemental combination. They differ in the apparatus and manipulations needed for the preparation and use of this catalyst.

Method A. Several small, sealed, glass tubes, closed at one end with a fragile glass membrane and containing 5 g. of iodine and 1 g. of aluminum, were heated gradually in a small, improvised, electric furnace to 300°, and this temperature was maintained overnight. Cooling was completed by rolling the tubes just as the product was solidifying. An attempt to prepare larger amounts of aluminum iodide by this method resulted in an explosion. A special reaction flask with a test tube-like appendage was used to allow the catalyst tube to be opened beneath the surface of the reaction solvent.

Method B. This method used a two compartment apparatus for the preparation of aluminum iodide. Compartment *A* was about 100 mm. long and 40 mm. in diameter and was joined to a standard-taper joint through a thin septum *C*. Compartment *B*, initially about 200 mm. long and 25 mm. in diameter, was joined at its midpoint to *A* by a 7-cm. length of 16-mm. tubing. The middle third of this connecting tube was thickened to facilitate sealing later. The open end *D* was stoppered and a vacuum applied through *E* before introducing the reactants. This operation tested the strength of the septum.

The weighed quantity of iodine was introduced into *A* through *D* and *F*. The aluminum was introduced into *B* through *D*. It is important that no iodine remain in *B* when the aluminum is introduced. The open end of *B* was sealed off below *D*, and a vacuum was applied at *E*. During this operation, the mechanical pump should be protected with a NaOH trap. Tube *E* was sealed off under vacuum. Both chambers were heated gently until some iodine distilled, and a visible amount of aluminum iodide had formed. Heating was then continued and intensified until all the iodine had reacted. When the reaction was complete, the aluminum iodide was distilled away from the excess aluminum and sealed in the larger chamber by collapsing the connecting tube at *F* and removing the smaller chamber. About 0.1 mol. of aluminum iodide was usually made in each apparatus. There would seem to be no limitation on the amount of catalyst which could be made by this method if sufficient care is taken during the initial stages of this preparation. Before the solid aluminum iodide was used it was pulverized by loosening large pieces from the walls with gentle heating and shaking when again cool. This enabled the catalyst to pass more easily and completely through the neck of the large chamber into a reaction flask when the glass septum was opened.

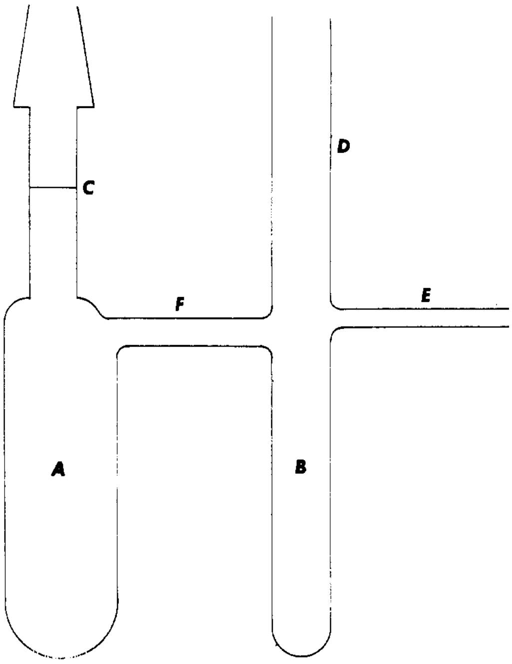


Figure 1

Isopropylation. This method was developed along the lines suggested by Spaeth and Germain.[5] In the present work the benzene (1.6 mol.), which also served as the solvent, and the catalyst (0.01 mol.) were combined, and isopropyl chloride (0.4 mol.) was added at room temperature. Ice and hydrochloric acid were used for hydrolysis. The product layer was extracted once with 10% sodium hydroxide and twice with water before it was dried and an aliquot was fractionally distilled.

Succinoylation. The method used was an adaptation of that described by Sommerville and Allen and modified by Martin and Fieser.[6] In the present investigation the relative amounts of catalyst, succinic anhydride, and benzene were 0.1 mol., 0.05 mol., and 50 ml. (0.565 mol.) respectively, and the reflux time was about 0.5 hr. The solid product was collected in a manner similar to that suggested by these authors.

Benzoylation. These reactions were carried out by a modification of the method of Minnis.[7] The mole ratio of benzoyl chloride to catalyst was 1/1.5. An excess of benzene was used, and carbon disulfide was the solvent. The reaction mixture was stirred at room temperature for about 18 hr. and

---

(5) E. C. Spaeth and C. B. Germain, *J. Am. Chem. Soc.,* **77,** 4066 (1955).

(6) L. F. Sommerville and C. F. H. Allen, *Org. Syntheses,* **Coll. Vol. II,** 81 (1943). E. L. Martin and L. F. Fieser, *Org. Syntheses,* **Coll. Vol. II,** 82 (1943).

(7) W. Minnis, *Org. Syntheses,* **Coll. Vol. II,** 520 (1943).

refluxed for 4 hr. The products were isolated by distillation at reduced pressure and allowed to crystallize.

Acknowledgment. The authors are grateful to the Research Corporation for a Frederick Gardner Cottrell grant in support of this work.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CONNECTICUT
STORRS, CONN.

Studies in the Hydroxyanthracene Series, II.[1] Synthesis of Some Heterocyclic Compounds from 2-Anthrol

N. H. SHAH AND SURESH SETHNA

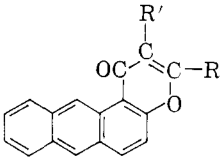
Received April 22, 1959

The present work deals with the synthesis of pyrone and furan derivatives from 2-anthrol.

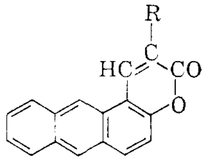
In the Pechmann condensation of 2-anthrol with ethyl acetoacetate in presence of either concentrated or 80% sulfuric acid, a pure condensation product could not be obtained. However, in the presence of phosphorus pentoxide (Simonis reaction) 2′-methyl-2,1-anthra-γ-pyrone (Ia) was obtained. This gave a styryl derivative with benzaldehyde and on hydrolysis gave 1-acetyl-2-anthrol. A similar reaction with ethyl benzoylacetate gave 2′-phenyl-2,1-anthra-γ-pyrone(Ib). On condensation with malic acid in presence of concentrated sulfuric acid, 2-anthrol gave an unworkable mass, but the desired 2,1-anthra-α-pyrone(IIa) was synthesised by the Perkin acetylation of 1-formyl-2-anthrol, as well as by the Knoevanagel condensation of malonic ester with 1-formyl-2-anthrol and subsequent hydrolysis and decarboxylation of ethyl-2,1-anthra-α-pyrone-3′-carboxylate (IIb) formed.

1-Acetyl-2-anthrol on Kostanecki-Robinson acetylation gave 2′-methyl-3′-acetyl-2,1-anthra-γ-pyrone (Ic), which on heating with dilute alcoholic sodium carbonate solution gave 2′-methyl-2,1-anthra-γ-pyrone (Ia) described above. The same ketone on Kostanecki-Robinson benzoylation gave 2′ - phenyl - 3′ - benzoyl - 2, 1 - anthra - γ - pyrone (Id) which on heating with dilute alcoholic sodium hydroxide on a steam bath gave 2′-phenyl-2,1-anthra-γ-pyrone (Ib) described before. 1-Acetyl-2-anthrol required for this work was prepared by the Friedel-Crafts acetylation of 2-anthrol, and also by the Fries rearrangement of 2-anthrolacetate at room temperature in nitrobenzene solution. Its structure was proved by oxidation of its methyl ether with sodium hypochlorite solution to 2-methoxyanthraquinone - 1 - carboxylic acid, previously prepared by Ch. Marschalk[2] by the nuclear methylation of 2-hydroxyanthraquinone to 1-methyl-2-hydroxyanthraquinone and subsequent oxidation of its methyl ether.

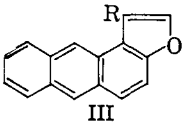
1-Formyl-2-anthrol condensed with ethyl bromoacetate to give ethyl-1-formyl-2-anthroxyacetate which on hydrolysis and ring closure gave anthra [2,1-b] furan (IIIa). Through the same series of reactions, 1-acetyl-2-anthrol furnished 1-methyl-anthra [2,1-b] furan (IIIb).



I



II



III

a. R = CH_3, R′ = H
b. R = C_6H_5, R′ = H
c. R = CH_3, R′ = $COCH_3$
d. R = C_6H_5, R′ = COC_6H_5

a. R = H
b. R = $COOC_2H_5$
c. R = COOH

a. R = H
b. R = CH_3

EXPERIMENTAL

All melting points are uncorrected.

2′-Methyl-2,1-anthra-γ-pyrone (Ia). To a mixture of 2-anthrol (1.94 g.) (prepared according to Perkin and Hall[3]) and ethyl acetoacetate (1.3 g.), phosphorus pentoxide (2.5 g.) was gradually added with stirring. The reaction mixture was heated on a steam bath for 1 hr. Crushed ice was then added and the residue taken up in ether. The ethereal layer was repeatedly washed with alkali (2%, 200 ml. in all) and then with water. The residue obtained on evaporating the ether, crystallized from dilute acetic acid (charcoal) in light brown needles, m.p. 173°. It gave a bluish green fluorescence with concentrated sulfuric acid.

Anal. Calcd. for $C_{18}H_{12}O_2$: C, 83.1; H, 4.6. Found: C, 82.9; H, 4.5.

This compound (0.5 g.) on heating with alcoholic potassium hydroxide (30%, 20 ml.) on a steam bath for 10 hr. gave 1-acetyl-2-anthrol described below.

2′-Styryl-2,1-anthra-γ-pyrone, prepared from the above pyrone, crystallized from absolute alcohol in long yellow needles, m.p. 237–238°.

Anal. Calcd. for $C_{25}H_{16}O_2$: C, 86.2; H, 4.6. Found: C, 86.1; H, 4.6.

2′-Phenyl-2,1-anthra-γ-pyrone (Ib). Obtained from 2-anthrol (1 g.), and ethyl benzoylacetate (0.65 g.) in dry ether (10 ml.) and phosphorus pentoxide (2 g.), crystallized from dilute acetic acid in pale yellow needles, m.p. 219°.

Anal. Calcd. for $C_{23}H_{14}O_2$: C, 85.7; H, 4.3. Found: C, 85.7; H, 4.8.

2,1-Anthra-α-pyrone (IIa). A mixture of 1-formyl-2-anthrol (prepared according to Jain and Seshadri[4]) (2.22 g.), acetic anhydride (2 g.) and fused sodium acetate (0.82 g.) to which a crystal of iodine was added, was refluxed in an

---

(1) Part I, S. S. Lele, N. H. Shah, and Suresh Sethna, *J. Org. Chem.*, **21**, 1293 (1956).

(2) Ch. Marschalk, *Bull. soc. chim.*, **6**, 655 (1939); [*Chem. Abstr.*, **33**, 5388 (1939)].

(3) J. Hall and A. G. Perkin, *J. Chem. Soc.*, 2031 (1923).

(4) A. C. Jain and T. R. Seshadri, *J. Sci. Industr. Res.*, **15B**, 61 (1956).