1.0 mole. The ozonide was decomposed with 20 ml. of solution consisting of equal volumes of 30% hydrogen peroxide and 10% sodium carbonate; these were heated for 3 hours at 60°. Acetone (0.4 g.) b.p. 55–57°, semicarbazone, m.p. 183°, 2-thiophenealdehyde (3.3 g.) and 2-thiophenecarboxylic acid, 1.6 g., were isolated from the reaction product.

The liquid corresponding to 2-thiophenealdehyde boiled at 69° at 8 mm. The phenylhydrazone of the aldehyde melted at 135–136° after recrystallizing once from ethanol; the melting point of the phenylhydrazone was in agreement with the phenylhydrazone of 2-thiophenealdehyde reported in the literature.[10]

The isolated acid, after sublimation, had a neutral equivalent of 128.8 and melted at 129°, corresponding to 2-thiophenecarboxylic acid.[11]

Hydrogenation.—Ten grams of the pentenylthiophene was hydrogenated in the presence of 3 g. of palladized alumina (0.5% palladium) under conditions described for the hydrogenation of butenylthiophene. The pentylthiophene obtained distilled at 42–44° at 2 mm., $n^{20}\text{D}$ 1.5011.

The chloromercury derivative of the pentenylthiophene after crystallization from absolute ethanol melted at 168°. It showed no depression in melting point when mixed with a known sample of 2-isopentyl-5-chloromercurithiophene.

Anal. Calcd. for $C_9H_{13}SHgCl$: S, 8.23. Found: S, 8.37.

IV. Synthesis of 2-Isopentylthiophene. 2-Isovalerylthiophene.—The synthesis was made according to the method of Hartough and Kosak[12] using 200 ml. of thiophene, 42.6 g. of phosphorus pentoxide and 30.6 g. of isovaleric acid. Thirty-four grams (67% yield) of 2-isovalerylthiophene boiling at 77–79° at 2.0 mm., $n^{20}\text{D}$ 1.5329, was obtained. The semicarbazone melted at 165–166°.

Anal. Calcd. for $C_{10}H_{15}N_3SO$: N, 18.67. Found: 18.63.

2-Isopentylthiophene.—2-Isovalerylthiophene (12 g.) was reduced by a modified Wolff–Kishner reduction.[13] The 2-isopentylthiophene (3 g.) was distilled from sodium. It boiled at 65–66° at 8.5 mm., $n^{20}\text{D}$ 1.4981, yield 25%. Its 2-isopentyl-5-thiophenemercurichloride melted at 168°, reported,[6] 171.5–172°, after recrystallization from absolute ethanol.

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(10) A. Hantzsch, *Ber.*, **22**, 2827 (1889).

(11) C. Paal and J. Tafel, *ibid.*, **18**, 456 (1885).

(12) H. D. Hartough and A. I. Kosak, THIS JOURNAL, **69**, 3098 (1947).

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RIVERSIDE, ILLINOIS RECEIVED JANUARY 15, 1951

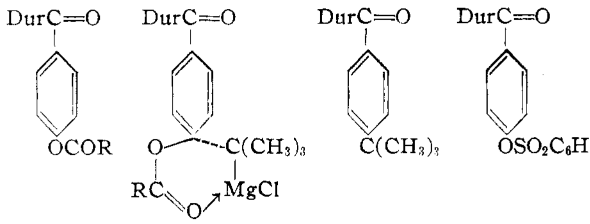
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Replacement of Nuclear Acyloxyl Groups by the Action of a Grignard Reagent

BY REYNOLD C. FUSON AND WILLIAM D. EMMONS[1]

Acetic, benzoic, mesitoic and benzenesulfonic esters of duryl *p*-hydroxyphenyl ketone react with *t*-butylmagnesium chloride to yield *p*-*t*-butylphenyl duryl ketone.

The discovery that certain Grignard reagents are capable of displacing the cyano group in *p*-cyanophenyl duryl ketone[2] suggested that other groups which could be detached as stable ions might behave in a similar manner. The mesitoxy radical seemed particularly attractive since its carbonyl group is known to be resistant to attack. Moreover, by coördination with the magnesium atom of the Grignard reagent it could conceivably serve to facilitate attack of the nucleus by making the essential step intramolecular.



I II III IV

Experiments with duryl *p*-mesitoxyphenyl ketone (I, R = Mes) and *t*-butylmagnesium chloride bear out this speculation. *p*-*t*-Butylphenyl duryl ketone (III) is produced in a 74% yield, and 65% of the mesitoxy moiety is accounted for as mesitoic acid. The hypothetical coördination complex is represented by II (R = Mes). Further study showed, however, that the displacement could be effected with unhindered acyloxy groups. The acetoxy (I, R = CH_3) and benzoxy (II, R = C_6H_5) derivatives were converted to *p*-*t*-butylphenyl duryl ketone (III) in yields of 70 and 43%, respectively. In the experiment with the benzoxy compound benzoic acid was isolated in a 25% yield.

It is of especial interest that the same type of change can be effected with sulfonic esters. The benzenesulfonate (IV) derived from duryl *p*-hydroxyphenyl ketone yields the *p*-*t*-butyl ketone (III) in 17% yield when treated with the *t*-butyl reagent.

The duryl *p*-hydroxyphenyl ketone, from which all the esters were derived, is readily obtained by treatment of *p*-anisyl duryl ketone with a mixture of hydrobromic and acetic acids. A much better method is the Friedel–Crafts condensation of *p*-acetoxybenzoyl chloride and durene. During the reaction the acetate group is hydrolyzed and the product, obtained in 76% yield, is duryl *p*-hydroxyphenyl ketone. The cleavage of the ester group is not surprising since *p*-acetoxyphenyl duryl ketone is a vinylog of an acid anhydride.

Experimental

Duryl *p*-Hydroxyphenyl Ketone.—To a solution of 90.0 g. of *p*-acetoxybenzoyl chloride, 61.7 g. of durene and 300 ml. of carbon disulfide was added over a 30-minute period 122.1 g. of aluminum chloride. The solution was stirred and heated under reflux for 90 minutes and poured into a mixture of ice and dilute hydrochloric acid. The carbon disulfide was distilled and the residue steam distilled to remove impurities. The residual oil crystallized when cooled and was recrystallized from benzene (Darco); m.p. 202.0–202.5°; yield 88 g. (76%).

Anal.[3] Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.28; H, 7.39.

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[2] R. C. Fuson, W. D. Emmons and R. Tull, *J. Org. Chem.*, **16**, 648 (1951).

[3] The microanalyses were performed by Miss Emily Davis and Miss Rachel Kopel.

TABLE I

ESTERS

Ester	Yield, %	M.p., °C	Solvent	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
p-MesCO$_2$C$_6$H$_4$CODur	86	181.0–183.0	Ethyl acetate	80.97	80.83	7.05	7.28
p-CH$_3$CO$_2$C$_6$H$_4$CODur	84	103.5–104.5	Ethanol	77.00	76.95	6.83	7.02
p-C$_6$H$_5$CO$_2$C$_6$H$_4$CODur	60	188.0–189.0	Ethyl acetate	80.42	80.29	6.18	6.33
p-C$_6$H$_5$SO$_2$OC$_6$H$_4$CODur	58	133.5–134.5	Ethanol	70.02	69.75	5.62	5.76

The phenol was also prepared by hydrolysis of duryl p-methoxyphenyl ketone. To 3.0 g. of this compound was added 6 ml. of 48% hydrobromic acid and 8 ml. of glacial acetic acid. The solution was boiled overnight and poured into water. The product was recrystallized from benzene; yield 1.8 g. (62%).

Synthesis of Esters.—All the esters were prepared by standard methods and are listed in Table I together with melting points, yield, solvents and analytical data.

Reaction of the Esters with t-Butylmagnesium Chloride.—The procedure was substantially the same in every case and is illustrated by that employed with the acetate which is described below.

p-Acetoxyphenyl Duryl Ketone and t-Butylmagnesium Chloride.—A Grignard reagent was prepared from 4.8 g. of magnesium, 20.2 g. of t-butyl chloride and 150 ml. of ether. To this solution was added 11.8 g. of p-acetoxyphenyl duryl ketone in 150 ml. of dry benzene. The solution turned reddish-brown and was stirred under reflux overnight. The mixture was poured into a mixture of ice and dilute hydrochloric acid. The ether layer was washed with water and dried with sodium sulfate. Evaporation of the solvent left an oil which crystallized when cooled. The ketone was recrystallized from ethanol (Darco); yield 7.8 g. (70%); m.p. 126.0–127.0°. A mixture melting point with an authentic sample of p-t-butylphenyl duryl ketone showed no depression.

URBANA, ILLINOIS RECEIVED APRIL 2, 1951

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF THE OAK RIDGE NATIONAL LABORATORY]

Studies in the Wagner Rearrangement.[1,2,3] II. The Synthesis and Structure Determination of Benz[a]anthracene-5,6-C$_1^{14}$

BY CLAIR J. COLLINS, JOHN G. BURR, JR., AND DANIEL N. HESS

The synthesis of benz[a]anthracene-5,6-C$_1^{14}$ is reported in an over-all yield, from carbon-C^{14} dioxide, of 76%. Degradation of this labeled hydrocarbon indicates that the radioactivity is distributed between positions 5 and 6 of the benz[a]-anthracene structure in the ratio 48:52.

Introduction

The synthesis of phenanthrene-9-C^{14} through the Wagner rearrangement of 9-fluorene(methanol-C^{14}) has been reported.[1] In order to demonstrate the generality of the procedure as a synthetic process for introducing isotopic carbon into aromatic polynuclear hydrocarbons, and to study the directive influence of various substituents on the course of this reaction, the method has been applied to the preparation of unsymmetrically substituted derivatives of phenanthrene. The synthesis and structure determination of benz[a]anthracene-5,6-C$_1^{14}$ (VI), the first of these, is now reported.

11H-Benzo[b]fluorene-11-one[4] (I) was converted to the hydrocarbon (II) by hydrogenation in the presence of a large excess of 10% palladium-on-carbon catalyst. The hydrocarbon was then converted to benz[a]anthracene-5,6-C$_1^{14}$ (VI) through compounds III, IV and V by a series of reactions analogous to those described[1] for the synthesis of phenanthrene-9-C^{14}.

Since the structures for both the carbinol (V) and the hydrocarbon (VI) are unsymmetrical, the carbonium ion intermediate which may be written in the dehydration of 11H-benzo[b]fluorene-11-(methanol-C^{14}) (V) might conceivably rearrange in either one or both of two ways to produce benz[a]-anthracenes labeled in the 5-position, the 6-position, or in both of these positions. The degradative scheme shown in the reaction series VI → XI was employed to locate the radioactivity in structure VI.

The labeled benz[a]anthracene (VI) was oxidized to the dihydrodiol (VII) with osmium tetroxide.[5] Attempts to cleave VII with lead tetraacetate failed. Treatment with chromium trioxide in acetic acid yielded 5,6-benz[a]anthraquinone (VIII), however, which was converted to the dibasic acid (IX) with hydrogen peroxide. Although this acid, upon distillation at atmospheric pressure, was converted to a mixture of the keto-acid (X) and the ketone (XI), the acid (X) could be obtained in much higher yield from the dicarboxylic acid (IX) by cyclization with sulfuric acid.[6] Fieser and Dietz assigned X as the probable structure of this keto-acid. We have confirmed this structure by decarboxylation of X in quinoline with basic copper carbonate catalyst, to the known ketone XI, whose identity was demonstrated by comparison with an authentic sample.[7] The

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[1] Paper I in this series: C. J. Collins, THIS JOURNAL, **70**, 2418 (1948).

[2] This paper is based upon work performed under Contract Number W-7405, eng. 26 for the Atomic Energy Commission at the Oak Ridge National Laboratory.

[3] Presented before the Division of Organic Chemistry at the 118th Meeting of the American Chemical Society, Chicago, Illinois, September, 1950.

[4] J. Thiele and A. Wanscheidt, *Ann.*, **376**, 269 (1921).

[5] J. W. Cook and R. Schoental, *J. Chem. Soc.*, 172 (1948).

[6] L. F. Fieser and E. M. Dietz, THIS JOURNAL, **51**, 3143 (1929).

[7] M. Orchin and L. Reggel, *ibid.*, **73**, 439 (1951). These authors kindly furnished us with their experimental procedure for the synthesis of compound XI (not labeled) prior to publication of their paper. The Orchin–Reggel synthesis was performed in this Laboratory by Dr. A. Russell Jones.