rated as colorless crystals, which were removed by filtration. These were washed with water and dried; yield 1.1 g. After recrystallization from dilute methanol the compound melted at 128°.

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.32; H, 5.40. Found: C, 80.16; H, 5.46.

2-Acetoxyfluorenone.—One gram of 2-fluorenonediazonium chloride in 5 cc. of glacial acetic acid was heated gently until the evolution of nitrogen began. After the initial reaction subsided, the solution was again heated carefully until the evolution of nitrogen ceased and then boiled for five minutes. Fifteen cubic centimeters of ethanol was then added and the solution chilled in ice. The product which separated consisted of large yellow plates; yield 0.6 g.; m. p. 154°. After recrystallization from 95% ethanol, it melted at 157°. The compound was identified as 2-acetoxyfluorenone by a mixed melting point determination with an authentic sample of 2-acetoxyfluorenone. The latter was obtained by acetylation of 2-hydroxyfluorenone (1 g.) according to the method described for the preparation of 2-acetoxyfluorene. The yield was 1.15 g. On recrystallization from 95% ethanol it melted at 157°.

Anal. Calcd. for $C_{15}H_{10}O_3$: C, 75.60; H, 4.23. Found: C, 75.43; H, 4.28.

On saponification with 5% potassium hydroxide solution 2-acetoxyfluorenone (1.9 g.) was converted into 2-hydroxyfluorenone (1.5 g.), which after recrystallization from 50% acetic acid melted at 204°. Diels[1] reports this compound as sintering at 200° and melting at 206.7°.

Summary

The interaction of 2-fluorenediazonium chloride and acetic acid gives three compounds in the following yields: 2-chlorofluorene, 10%; 2-acetoxyfluorene, 46.7%; and 2-hydroxyfluorene, 11%.

From 2-fluorenonediazonium chloride and acetic acid there was obtained a 60% yield of 2-acetoxyfluorenone.

WASHINGTON, D. C.

RECEIVED MARCH 20, 1937

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Identification of Alkylbenzenes. I. Identification of Monoalkylbenzenes by Means of the Acetamino Derivative[1]

BY V. N. IPATIEFF AND LOUIS SCHMERLING

In the course of the study of the alkylation,[2] depolyalkylation,[3] and destructive alkylation[4] of aromatic hydrocarbons, the need for a simple method for the identification of alkylbenzenes became apparent. The boiling points and other physical constants are fairly satisfactory for distinguishing the homologous compounds but are inadequate in the case of isomers. Oxidation to benzoic acid or to one of the phthalic acids may be used to differentiate between mono- and dialkylbenzenes but is of no aid in the determination of the structure of the alkyl groups.

In the present investigation, the characterization of monoalkylbenzenes by means of their mono- and diacetamino derivatives was studied. Although there was nothing inherently new in the preparation of such derivatives by nitration, followed by reduction of the nitro compound and subsequent acetylation of the amine, there had been no previous study of the nitration of a series of alkylbenzenes under a single set of conditions; furthermore, it was not possible to predict whether the solid derivative would be a single compound or a mixture. If the nitration yielded a mixture of ortho and para isomers, the reaction would not be applicable. On the other hand, the preparation of a dinitro derivative would eliminate this difficulty since there is ample evidence[5] to show that only the 2,4-dinitro compound would be obtained.

The problem, then, consisted essentially in determining the conditions necessary for the formation either of a mononitro derivative, unadmixed with isomers, or of the dinitro derivative. This was less difficult than had been anticipated, and a procedure was developed by means of which monoalkylbenzenes may be identified easily and quickly using small amounts of material. It was found that under the prescribed conditions pure 4-nitroalkylbenzenes may be obtained by use of a nitrating mixture consisting of equal volumes of concentrated nitric and sulfuric acids. The ortho-substituted isomers are present in such small amount, if at all, that they do not interfere. It

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(1) Presented before the Division of Organic Chemistry at the Chapel Hill meeting of the American Chemical Society, April, 1937.

(2) Ipatieff, Corson and Pines, THIS JOURNAL, 58, 919 (1936).

(3) Ipatieff and Pines, *ibid.*, 58, 1056 (1936).

(4) Grosse and Ipatieff, *ibid.*, 57, 2415 (1935); Ipatieff, Komarewsky and Pines, *ibid.*, 58, 918 (1936).

(5) Shoesmith and Mackie, *J. Chem. Soc.*, 2334 (1928); Brady and Cunningham, *ibid.*, 121 (1934).

was found further that by use of more vigorous nitrating solution (namely, one composed of two volumes of sulfuric acid to one of nitric acid) it is the 2,4-dinitroalkylbenzenes[6] which are formed.

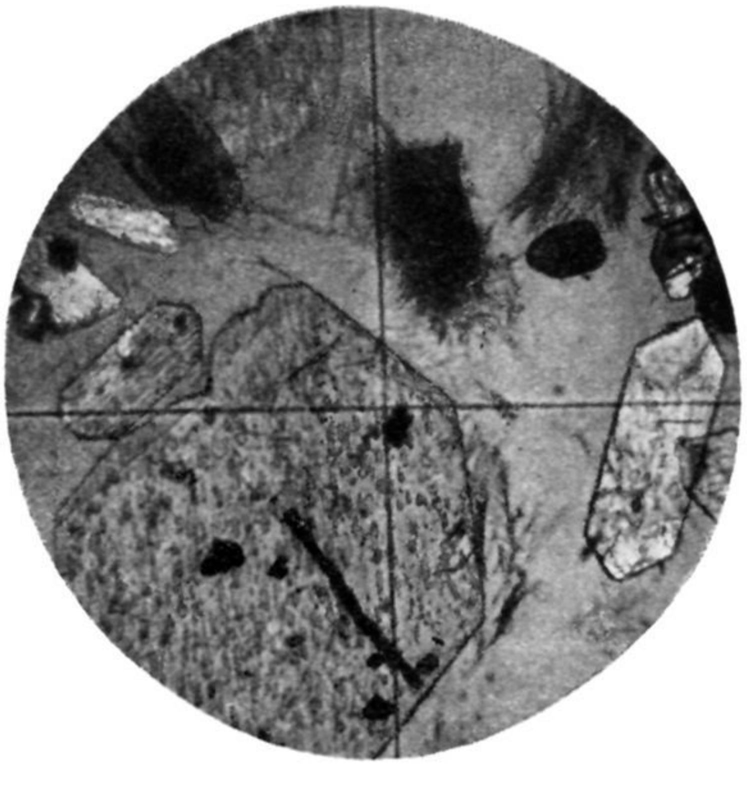
It is thus possible to obtain either the 4-acetamino- or the 2,4-diacetaminoalkylbenzenes as desired. The first are more suitable in the characterization of pure hydrocarbons; the second, because of solubility and other physical properties, in the identification of the components of aromatic mixtures. An important application of the latter consists of distinguishing between *n*- and isopropylbenzene when they occur separately or in a mixture with each other. Such an analysis is, of course, very desirable since the boiling points of the hydrocarbons are too close together to permit of their separation or definite identification. Although their diacetamino derivatives melt only 8° apart, there is little danger of confusing the derivatives since they crystallize in markedly different form and can be distinguished easily with the aid of a polarizing microscope.

In some cases, the mononitro compound may be contaminated with a small amount of the dinitrated hydrocarbon, and *vice versa*. Fortunately, the two may readily be separated by means of an ether extraction of the solution obtained on reducing the compounds with tin and hydrochloric acid. The monoamino compound forms an ether-soluble salt (presumably, $2RC_6H_4NH_2 \cdot SnCl_2 \cdot 2HCl$) with tin chloride in the presence of hydrogen chloride, whereas the analogous salt of the diaminoalkylbenzene is ether-insoluble. The material obtained from the ether extract is worked up separately from the other, and both the mono- and the diacetaminoalkylbenzenes may thus be obtained in a pure state from a single nitration product, giving a check on the identity of the hydrocarbon.

This method has been applied successfully by us in the determination of the structure of the different amylbenzenes obtained by the alkylation of benzene with cyclopentane and with methylcyclobutane, full details of which will be given in a forthcoming publication by Grosse and Ipatieff.

Experimental

Procedure.—A mixture of 0.5–1.0 cc. of the aromatic hydrocarbon and 5 cc. of a nitrating mixture was shaken for three to five minutes. The nitrating mixture consisted of equal volumes of sulfuric acid (d. 1.84) and nitric acid (d. 1.42), when the mononitro compound was desired as the chief product (Note 1), or of two volumes of the sulfuric acid to one of the nitric when it was the disubstituted derivative which was to be obtained. No attempt was made to cool the reaction mixture. When the evolution of heat had ceased, the mixture was poured upon a small amount of cracked ice; the oily nitro layer was taken up in ether, washed twice with water, and the ether was evaporated on a water-bath. To the residue was added 5 g. of granulated tin, 5 cc. of concentrated hydrochloric acid, and sufficient ethyl alcohol to bring all, or nearly all, of the nitrocompound into solution. The mixture was shaken until reduction was complete as was shown by the absence of marked turbidity on pouring a test portion into water (Note 2). This usually required less than ten minutes. In those cases in which the reduction took place more slowly, the reaction was hastened by heating the mixture on the water-bath; usually, however, the reduction was very exothermic and did not require the application of external heat. When reduction was complete, the aqueous alcoholic solution was decanted from the excess tin into about 20 cc. of water. The solution was extracted with ether and sufficient concentrated alkali was added to the aqueous solution to dissolve most of the precipitate of tin hydroxide which formed at first. The amino compound was extracted with ether, washed with water, dried by shaking for a few minutes with potassium carbonate, and the ether removed by evaporation. To the residue there was added 1 cc. of acetic anhydride. The derivative usually crystallized almost immediately. The material was warmed with 5 cc. of water to hydrolyze the excess anhydride. Since some of the acetamino derivatives are quite soluble in dilute acetic acid, it was occasionally necessary to evaporate almost to



100 ×.

Fig. 1.—Mixture of the diacetamino derivatives of *n*- and isopropylbenzene.

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[6] The orientation of the nitro groups has been proved for toluene, ethylbenzene, *n*-propylbenzene, and *t*-butylbenzene (*cf.* references in preceding footnote). It is presumably the same in the case of all the disubstituted monoalkylbenzenes prepared by the procedure described in this paper.

dryness the aqueous solution containing the hydrolyzed acetic anhydride. The crude derivative was filtered and then recrystallized from hot water or dilute alcohol, yield 40–70%.

The ether extract of the reduction solution was tested in order to determine whether it consisted of traces of unreduced nitro compound or of an amine–tin chloride complex. In the latter case the amine was liberated by the addition of alkali and worked up separately from the main batch of derivative. Although the amount of material thus received was often only a small portion of the total, this was well worthwhile since it was the monoacetaminoalkylbenzene only which was obtained, even when the derivative prepared from the major portion was the diacetamino compound. When the chief or only product was the monosubstituted derivative, two alternatives were possible: either part of the compound could be obtained from the ether extract and the remainder from the aqueous solution, or the ether extraction could be made complete and all the monoamine isolated therefrom. The latter procedure gave the more satisfactory results, especially when small amounts of diaminoalkylbenzene were present.

The time required for the preparation of the derivative, exclusive of the recrystallization of the product, was about thirty minutes.

NOTE 1.—Both toluene and ethylbenzene yielded practically only the 2,4-dinitroalkylbenzene regardless of which nitrating mixture was used. For neither hydrocarbon could more than traces of the monosubstituted derivative be isolated. The *n*-alkylbenzenes showed a marked tendency to yield dinitro derivatives even with the milder nitrating solution. In the case of *n*-propylbenzene and of *n*-butylbenzene the formation of the dinitrated by-product could be greatly diminished by cooling the reaction mixture.

TABLE I

p-$RC_6H_4NHCOCH_3$

Mixed m. p. (1:1 mixture) of *n*-C_3H_7 with iso-C_3H_7, 90–92°. Mixed m. p. of *i*-C_3H_7 with *n*-C_4H_9, 83–87°. Mixed m. p. of *s*-C_4H_9 with cyc-C_6H_{11}, 109–111°.

R =	M. p., °C. (uncorr.)	Crystalline form (macroscopic appearance)
CH_3[c]	(145)[e]	
C_2H_5[c]	(94)[f]	
n-C_3H_7[a]	96[g]	Pearly flakes
i-C_3H_7[b]	106[h]	Glistening flakes
n-C_4H_9[c]	105[i]	Pearly flakes
s-C_4H_9[b]	126[j]	Pearly flakes
t-C_4H_9[b]	170[k]	Pearly flakes
t-C_5H_{11}[b]	142[l]	Pearly flakes
cyc-C_6H_{11}[d]	130–131[m]	Glistening flakes

[a] Prepared by the hydrogenation of allylbenzene. [b] Prepared by the method of Ipatieff, Corson and Pines [THIS JOURNAL, **58**, 919 (1936)]. [c] Eastman product, purified and redistilled. [d] Prepared by the method of Corson and Ipatieff [THIS JOURNAL, **59**, 645 (1937)]. [e] Beilstein, 4th ed., Vol. XII, p. 920. This derivative is not usually obtained by this method. [f] *Ibid.*, p. 1090. This derivative is not usually obtained by this method. [g] Baddely and Kenner [*J. Chem. Soc.*, 307 (1935)] also report 96°; previous workers, 87°. [h] Constam and Goldschmidt [*Ber.*, **21**, 1159 (1888)] report 102–102.5°. [i] Reilly and Hickinbottom, *J. Chem. Soc.*, **117**, 111 (1920). [j] *Idem.*, p. 120. [k] Beilstein, 4th ed., Vol. XII, p. 1167; *cf.* Shoesmith and Mackie, *J. Chem. Soc.*, 2335 (1928). [l] Anschütz and Beckerhoff [*Ann.*, **327**, 222 (1903)] report 138–139°. [m] Kurssanov [*ibid.*, **318**, 324 (1901)] reports 128–129.5°,

TABLE II

$RC_6H_3(NHCOCH_3)_2$

Mixed m. p. of CH_3 with C_2H_5, 190–195°. Mixed m. p. of *n*-C_3H_7 with *i*-C_3H_7, 197–200°. Mixed m. p. of *i*-C_3H_7 with *n*-C_4H_9, 187–190°. Mixed m. p. of *n*-C_3H_7 with *t*-C_4H_9, 185–189°. Mixed m. p. of *n*-C_4H_9 with *t*-C_4H_9, 180–185°.

R =	M. p., °C. (uncorr.)	Crystalline form (microscopic appearance)	Nitrogen, %	
			Calcd.	Found
CH_3	221[a]	Small needles		
C_2H_5	223[b]	Small needles		
n-C_3H_7	208	Small feathery needles	11.96	11.73
iso-C_3H_7	216	Six-sided prisms	11.96	11.92
n-C_4H_9	214	Soft white needles	11.29	11.19
s-C_4H_9	192	Stout needles	11.29	11.03
t-C_4H_9	210	Rectangular prisms	11.29	11.00
t-C_5H_{11}	181	Needles or flattened prisms	10.69	10.75
cyc-C_6H_{11}	261–2[c]	Flattened prisms	10.21	10.11

[a] Beilstein, 4th ed., Vol. XIII, p. 133. [b] *Ibid.*, p. 177. [c] The diaminocyclohexylbenzene (presumably the 2,4-compound). recrystallized from water or heptane: m. p. 105–106°. Calcd.: N, 14.74. Found: N, 14.42.

NOTE 2.—In some cases the monoaminoalkylbenzene–tin chloride complex was quite insoluble in dilute acid solution and precipitated when the reduction solution was poured into water. In such cases, the precipitate could be differentiated from unreduced nitro compound by extracting with ether and testing with alkali.

Identification of *n*- and Isopropylbenzene in a Mixture with Each Other.—The diacetamino derivative of *n*-propylbenzene crystallizes from water or dilute alcohol in the form of soft, white, feathery aggregates (spherical clusters) which are seen to be made up of short thread-like crystals when viewed under high magnification. On filtering, the aggregates are easily broken up and a powdery material is obtained. The isomeric isopropyl derivative, on the other hand, crystallizes in the form of hard, glistening prisms which retain their shape even when filtered. These are anisotropic and show up beautifully in the polarizing microscope with crossed nicols, whereas under the same conditions the diacetamino-*n*-propylbenzene crystals are barely visible.

These rather surprisingly marked differences in the crystalline properties of the derivatives at once suggested a means for distinguishing each in a mixture of the two. Experiments which were made with synthetic mixtures gave very satisfactory results. The more vigorous nitrating mixture was used so as to lead eventually to the production of the diacetamino derivatives. The nitration and subsequent reduction proceeded smoothly. When acetic anhydride was added to the mixture of diamines, the acetamino derivatives crystallized out almost immediately. Water was added to hydrolyze the excess anhydride, and the mixture was heated until all of the derivative dissolved.

On cooling, there crystallized white feathery crystals, having the physical appearance of the diacetamino-*n*-propylbenzene. When viewed under the microscope, it was chiefly the short needles of the *n*-propylbenzene derivative which were seen. The melting point of the material so obtained was 202–204°, indicating the presence of a small amount of the isomeric compound. The mother liquor from this first crystallization, then, contained the major portion of the more soluble isopropylbenzene derivative. Hence, it was evaporated to about 3 cc. and allowed to stand. Crystals soon appeared and even with the unaided eye the glistening flakes of diacetaminoisopropylbenzene could be discerned. When examined under the microscope, both the small needles of the *n*-propylbenzene derivative and the large prisms of the isomeric isopropyl derivative were observed. When the nicols were crossed, the former disappeared from view and the latter shone brilliantly in the dark field.

After several fractional crystallizations from hot water the isopropyl derivative was isolated in an almost pure state, m. p. 214°.

Acknowledgment.—We wish to thank Dr. J. D. Kurbatov for assistance in the study of the crystal forms and Mr. R. W. Moehl for taking the photomicrograph.

Summary

A simple, uniform procedure is described for the preparation of the mono- and the diacetamino derivatives of monoalkylbenzenes. The physical properties of a series of such compounds is given.

Nitration of the alkylbenzene is shown to yield either the mononitro or the dinitro derivative or a mixture of both depending upon (a) the nature of the side chain, and (b) the composition of the nitrating mixture.

Under the prescribed conditions the *p*-acetaminoalkylbenzene was obtained unadmixed with ortho or meta isomers.

A method is presented for separating monoaminoalkylbenzenes from diaminoalkylbenzenes, based on the solubility in ether of the monoamine–tin chloride–hydrogen chloride complex.

It is shown that by means of the diacetamino derivatives it is possible to distinguish between the two propylbenzenes, when they occur either separately or in a mixture with each other.

RIVERSIDE, ILLINOIS RECEIVED APRIL 14, 1937

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Studies in the Ketone Sugar Series. VII. The Action of Titanium Tetrachloride on the Methylfructoside Acetates

BY EUGENE PACSU AND FRANCIS B. CRAMER

It has been shown in a series of investigations[1] that titanium tetrachloride is capable of transforming the acetylated β-alkyl glycosides and the fully acetylated derivatives of the aldoses into the corresponding α-forms. A characteristic of the reaction appears to be the formation of halochromic addition compounds which do not occur when stannic chloride[2] is employed to promote the same transformation. It has also been shown that the α-acetates of the sugars undergo a secondary change and are smoothly transformed to the corresponding α-acetochloro compounds. In order to test the generality of the conversion it seemed necessary to submit a ketose derivative, tetraacetyl-β-methylfructoside <2,6>, to the action of titanium tetrachloride. A yellow halochromic salt was produced immediately when this reagent was added to the chloroform solution of the fructoside. Contrary to expectation, no conversion into the α-form could be detected after the mixture had been heated for four hours. Neither did the starting material undergo any secondary reaction, since only unchanged tetraacetyl-β-methylfructoside was recovered after the reaction mixture had been worked up in the usual way. Such behavior of the β-methylfructoside acetate might be compared with that of β-pentaacetylfructose <2,6> which has been shown in Part VI[3] to undergo isomerization into the α-form only to a very slight extent when treated with zinc chloride in acetic anhydride solution. Since α-pentaacetylfructose <2,6>, on the other hand, has been found to suffer a rapid and almost complete conversion into the β-pentaacetate of fructose in the presence of zinc chloride, it was thought that tetraacetyl-α-methylfructoside <2,6> might readily rearrange into the β-isomer when treated with titanium tetrachloride. The result of the experiment was an unexpected one. The reaction product

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[1] Pacsu, *Ber.*, **61**, 1508 (1928); THIS JOURNAL, **52**, 2563, 2568, 2571 (1930).

[2] Pacsu, *Ber.*, **61**, 137 (1928).

[3] Cramer and Pacsu, THIS JOURNAL, **59**, 711 (1937).