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Identification of Alkylbenzenes. II. Identification of the Eight Amylbenzenes and Cyclopentylbenzene by Means of Their Mono- and Diacetamino and Monobenzamino Derivatives

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In a previous paper[1] it was shown that monoalkylbenzenes may be identified by means of the acetamino derivatives which are obtained by the nitration of the hydrocarbon, followed by reduction of the nitro compound and subsequent acetylation of the amine. It was shown that by proper choice of nitrating mixture either the mono- or the dinitro compound can be made to predominate and that a quantitative separation of the monoaminoalkylbenzene from the diamino compound can be made by taking advantage of the fact that the monoamine–tin chloride–hydrogen chloride complex is soluble in ether.

In the present paper the characterization of the eight amylbenzenes and cyclopentylbenzene is described.

The properties of the amylbenzenes and the cyclopentylbenzene which were used in this investigation are given in Table I together with what appear to be the most reliable data given in the literature. In Table II are tabulated the melting points and the crystalline appearance of the mono- and the diacetamino and the monobenzamino derivatives. The "mixed melting points" are included for those melting points which lie closely together.

The monobenzamino derivatives were prepared in the usual manner by the reaction of the amine and benzoyl chloride in the presence of dilute alkali. They serve as a means of confirming the information obtained by preparing the two acetamino derivatives.

In this connection it should be stated that in all cases the use of the mild nitrating mixture yielded more or less of the dinitroalkylbenzene along with the mononitro compound. This made possible the preparation not only of the monoacetamino and the monobenzamino derivatives but also of the diacetamino derivative from the same initial 0.5–1.0 cc. of the hydrocarbon. The pure monoamine, which was obtained by way of ether extraction of the tin salt complex, was divided into two portions, one of which was acetylated and the other benzoylated. The pure diaminoamylbenzene was isolated from the aqueous solution which had been ether extracted. Acetylation yielded the expected derivative. The dibenzamino compounds were found to possess too high melting points to be desirable for purposes of characterization.

Only three of the monoacetamino- and three of the monobenzaminoamylbenzenes had been reported previously. All of the diacetamino compounds are new.

In the preparation of the monobenzamino derivatives it was observed that certain of the products apparently were mixtures of two isomeric compounds. These were found to be the *o*- and *p*-isomers. Fortunately for the purpose of characterization of the amylbenzenes, the *o*-acetamino derivatives are so soluble in dilute acetic acid and dilute alcohol that they do not contaminate the *p*-isomers.[2] On the other hand, the difference in solubility of the two benzamino derivatives is much smaller and the purification of the *p*-benzaminoalkylbenzene is more difficult. Nevertheless, there was no serious difficulty except with the derivative for isoamylbenzene, which could not be resolved into its pure components.

It is interesting to note that the only cases in which the formation of *o*-benzaminoalkylbenzene was observed were those in which the alkyl group is attached to the benzene nucleus by means of a secondary carbon atom: *n*-, iso-, and neopentylbenzene, and 2-methyl-1-phenylbutane.

The benzamino derivative obtained from *t*-amylbenzene melted at 113° whereas Anschütz and Beckerhoff[3] report that the melting point of *p*-benzamino-*t*-amylbenzene is 158°. However, the *p*-amino-*t*-amylbenzene obtained according to their directions yielded a benzoyl compound which melted at 112–113°.

The diacetamino derivative of *t*-amylbenzene was found to exist both in an anhydrous form and as an hemihydrate of 10° lower melting point. A similar hydrate was observed with the analogous derivative of 2-methyl-3-phenylbutane.

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[1] Ipatieff and Schmerling, THIS JOURNAL, **59**, 1056 (1937).

[2] Except in the case of *n*-amylbenzene, no attempt was made to isolate the *o*-acetamino derivatives of the hydrocarbons studied in this or the previous publication.[1]

[3] Anschütz and Beckerhoff, *Ann.*, **327**, 218 (1903).

In order to establish the relationship between the mono- and the diacetamino derivatives more definitely, *p*-aminoisoamylbenzene was synthesized and then nitrated. Reduction followed by acetylation yielded a diacetamino derivative identical with that obtained from the hydrocarbon.

Experimental[4]

General Procedure.—The method employed in the preparation of the mono- and diacetamino derivatives of the amylbenzenes and the cyclopentylbenzene was essentially the same as that discussed in the previous paper.[1] The nitration and the reduction were carried out in the manner there described. The reduction mixture was then extracted two or three times with ether and an excess of alkali was added to the aqueous solution, liberating the diamino derivative which was acetylated as usual. The ether solution was evaporated, the residue taken up in water and made alkaline to free the monoamine.

The benzoyl derivative of the monoamine was prepared by the Schotten–Baumann procedure.

In the previous paper it was stated that the ether solution of the mono- or diamine was dried over potassium carbonate before evaporating the ether. It has been found since that the drying is unnecessary since water does not interfere with the acetylation.

Dilute alcohol was usually very suitable as the solvent for recrystallizing the monoacetamino and monobenzamino-alkylbenzenes. By "dilute alcohol" is meant an aqueous solution containing just enough ethanol to keep the derivative in solution when hot. The lower melting crystals occasionally tended to come out as an oil, in which case more alcohol was added. In some cases it was found that hexane and heptane had certain advantages over the dilute alcohol as solvents for recrystallizing the monoacetamino and monobenzamino derivatives. There was less tendency for the derivative to be deposited as an oil and the rate of crystallization was more rapid. The diacetamino derivatives (except that of *t*-amylbenzene) are practically insoluble in the paraffinic hydrocarbons as well as in ether. They were recrystallized from dilute alcohol.

***n*-Amylbenzene.**—Benzoylation of the monoamine obtained from *n*-amylbenzene yielded two compounds, which were studied in a large scale preparation. *n*-Amylbenzene (15 g.) was shaken with 40 cc. of the mild (1:1 H_2SO_4–HNO_3) nitrating solution, the mixture being cooled in ice water. The product was poured on ice, ether extracted, and the extract washed and dried. The ether was evaporated and the extract shaken with tin and hydrochloric acid, sufficient alcohol being added to give a clear solution. The monoamine–tin chloride salt was extracted with ether and the free amine obtained by the usual procedure. A quantitative yield (16 g.) of the product was obtained; it was used as the source material for the experiments described below.

Four grams of the amine was shaken with excess benzoyl chloride and alkali until solidification of the derivative occurred. Fractional crystallization from hexane yielded 1.6 g. of less soluble pearly flakes, m. p. 120–128° (raised to 128–129° by recrystallization from dilute alcohol) and 1.2 g. of more soluble very small white needles, m. p. 96–99°. Recrystallization of the latter yielded crystals melting at 98–99° which analyzed correctly for benzamino-*n*-amylbenzene (see Table II).

Having determined that the benzamino derivative was a mixture of *o*- and *p*-isomers, *o*-acetamino-*n*-amylbenzene was sought for and found in the acetic acid filtrate from the acetylation of the amine as well as in the mother liquor from the recrystallization of the *p*-compound. Fractional crystallization from hexane followed by recrystallization from dilute alcohol of the product obtained by acetylating 1.0 g. of the amino-*n*-amylbenzene yielded 0.43 g. of pearly flakes, m. p. 101–102°,[5] and 0.15 g. of very soluble fine needles, m. p. 79–80°. The latter came out of solution very slowly, the recrystallization sometimes requiring twenty-four hours.

In order to establish the relationship between the two benzamino and the two acetamino derivatives the former were hydrolyzed and the liberated amines isolated and acetylated. The benzamino compound melting at 128–129° yielded pure *p*-acetamino-*n*-amylbenzene, m. p. 101–102°, thus confirming the assumed structure. From a sample of the other benzamino derivative melting at 97–101° there was obtained the *o*-acetamino compound melting at 78–79° as well as traces of the *p*-derivative, indicating that the benzamino compound contained a small amount of the higher melting isomer.

Isoamylbenzene.—The monoacetamino derivative of isoamylbenzene melted at 114–115°, which is in agreement with the melting point observed by Hickinbottom[6] for *p*-acetaminoisoamylbenzene. The monobenzamino derivative, however, appeared to be a mixture and various fractions obtained by recrystallization melted at 118–122°, 132–136° and intermediate temperatures. The values given in the literature for *p*-benzaminoisoamylbenzene are 147°,[7] and 151–153°,[6].

In order to determine whether the literature value could be checked, *p*-aminoisoamylbenzene was synthesized[7] and the acetyl and benzoyl derivatives found to melt at 113–114° and 151°, respectively. The latter crystallized from dilute alcohol in the form of pearly flakes, whereas the derivative obtained from isoamylbenzene separated as fine needles or an amorphous powder. It is apparent, therefore, that the values in the literature are correct and that the monobenzamino derivative prepared from the hydrocarbon is impure and is a mixture of the *o*- and *p*-isomers. In the case of the monoacetamino derivative the *o*-isomer is relatively more soluble and is removed readily on recrystallization, so that pure *p*-acetaminoisoamylbenzene is obtained.

2-Nitro-4-amino-isoamylbenzene was prepared by the nitration of the synthetic *p*-aminoisoamylbenzene. After some preliminary attempts (involving the use of glacial acetic acid as solvent) it was found that the nitration could be carried out most satisfactorily by adding 1.0 cc. of the amine to 2 cc. of concentrated sulfuric acid at 0° to get a

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(4) All melting points are uncorrected. The corrections to be applied (determined by means of a thermocouple) are 0.8 at 100°, 1.5 at 125°, 2.5 at 150°, 3.8 at 175°, 5.0 at 200°, and 6.0 at 225°.

(5) Hickinbottom, *J. Chem. Soc.*, 1119 (1937), reports 101° as the melting point of *p*-acetamino-*n*-amylbenzene.

(6) Hickinbottom, *ibid.*, 2396 (1932), reports 115–115.5°.

(7) Willgerodt and Dammann, *Ber.*, **34**, 3678 (1901).

TABLE I

THE ALKYLBENZENES: C_6H_5R

R	Literature values[j]			Present investigation		
	B. p., °C. 760 mm. (corr.)	n^{20}_D	d^{20}_4	B. p., °C. 760 mm. (corr.)	n^{20}_D	d^{20}_4
—$CH_2CH_2CH_2CH_2CH_3$[a]	205.3[k]	1.4885[k]	0.8587[k]	205	1.4883	0.8577
—$CH_2CH_2CH(CH_3)_2$[b]	198–199[l]	1.4845[l]	.8586[l]	197–199	1.4835	....
—$CH_2CH(CH_3)CH_2CH_3$[c]	194[m]	1.4875[m]	.859[m]	194–195	1.4873	.8584
—$CH(CH_3)CH_2CH_2CH_3$[d]	191–193	1.4880	.8602	192–193	1.4852	.8576
—$CH(CH_3)CH(CH_3)_2$[e]	188–189	1.4953	.8642	186	1.4882	.8795
—$CH(C_2H_5)CH_2CH_3$[f]	187	1.4969	.8717	190–191	1.4880	.8649
—$CH_2C(CH_3)_3$[g]	185.6–186	1.4876	.8565	185–186	1.4885	.8583
—$C(CH_3)_2CH_2CH_3$[h]	190[n]	1.4929[n]	.8669[n]	190–191	1.4934	.8737
Cyclo-C_5H_9[i]	217[o]	1.5280[o]	.9474[o]	219	1.5290	.926

[a] Obtained from the University of Illinois. [b] Prepared by the method of Fittig and Tollens [*Ann.*, **131**, 313 (1864)]. [c] Prepared by the reaction of benzylmagnesium chloride and *s*-butyl bromide [Glattfeld and Cameron, THIS JOURNAL, **49**, 1043 (1927)]. [d] Prepared by a modification of the method of Klages [*Ber.*, **35**, 3509 (1902); *cf.* ref. 9]. [e] Prepared by a modification of the method of Klages (ref. 9). [f] Prepared by a modification of the method of Klages [*Ber.*, **36**, 3692 (1903); *cf.* ref. 9]. [g] Prepared according to the method of Bygden [*Ber.*, **45**, 3482 (1912)]. [h] Ref. 9. [i] Prepared by Dr. B. B. Corson by the alkylation of benzene with cyclopentene in the presence of sulfuric acid [Ipatieff and Corson, unpublished results]. [j] For a complete summary, see Egloff and Grosse, "Physical Constants of Mononuclear Aromatic Hydrocarbons," U. O. P. Booklet No. 217, Universal Oil Products Company, Chicago, Illinois, 1938, pp. 19–20]. [k] Simon, *Bull. soc. chim. Belg.*, **38**, 47 (1929). [l] Klages, *Ber.*, **37**, 2317 (1904). [m] Levene and Kuna, *J. Biol. Chem.*, **110**, 323 (1935), for dextro form. [n] Gleditsch, *Bull. soc. chim.*, [3] **35**, 1095 (1906). [o] Zelinsky and Titz, *Ber.*, **64**, 183 (1931).

white precipitate which dissolved on stirring; 3 cc. of cold 2:1 H_2SO_4:HNO_3 was then added gradually. A dark red solution was obtained which yielded an orange precipitate when it was diluted with ice water. The addition of alkali resulted in the formation of a golden brown precipitate. Filtration followed by recrystallization of the precipitate from hexane yielded 2-nitro-4-aminoisoamylbenzene, yellow flakes, m. p. 90°.

Anal. Calcd. for $C_5H_{11}C_6H_3NH_2NO_2$: N, 13.46. Found: N, 13.51.

Reduction of the nitroaminoisoamylbenzene was carried out by dissolving 1.0 g. of the compound in excess hydrochloric acid and ethanol and shaking the solution with 3 g. of granulated tin. The mixture was warmed for a few minutes to complete the reaction, the product was decanted from the unreacted tin, and the diamine was isolated in the usual manner. Acetylation yielded the diacetaminoisoamylbenzene, m. p. 215–216°. The melting point was not depressed when the material was mixed with the diacetamino derivative obtained from isoamylbenzene.

2-Methyl-1-phenylbutane.—The mono- and diacetamino derivatives of this hydrocarbon were obtained in pure state without difficulty. The monobenzamino derivative consisted chiefly of crystals melting at 126°. A small amount of material melting at 118–121° was isolated from the more soluble fractions. Glattfeld and Cameron[8] report 118° as the melting point of *p*-benzaminobenzylbutane.

***t*-Amylbenzene.**—The carefully purified monoacetamino derivative of this hydrocarbon melted at 141–142°. The melting point of *p*-acetamino-*t*-amylbenzene has been reported as 138–139°,[3] and, more recently, as 140–141°.[6] On the other hand, the pure monobenzamino derivative melted at 113° whereas Anschütz and Beckerhoff[3] found 158° to be the melting point of *p*-benzamino-*t*-amylbenzene. However, the reaction of *t*-amyl alcohol with aniline according to their directions yielded an amine, the acetyl and benzoyl derivatives of which melted at 140–141° and 112–113°, respectively. Mixed melting point determinations with the analogous compounds obtained from *t*-amylbenzene showed no depression.

As additional evidence that the reduction product of the nitroamylbenzene was actually *p*-amino-*t*-amylbenzene, the purified amine (isolated via the tin salt) was[9] diazotized and converted to *p*-*t*-amylphenol: m. p. and "mixed m. p.," 95°.

Diacetamino-*t*-amylbenzene had the most unusual set of properties of all the derivatives studied. When water was added to the acetic anhydride solution of the derivative to hydrolyze the excess anhydride, a viscous oil was obtained. After standing for twenty-four hours, this crystallized yielding large transparent flattened prisms (as large as 3 mm. on a side), which crushed to a white powder melting at 169–170°; the resolidified melt melted at 179–180°, indicating, as was confirmed by analysis, that the lower melting crystals were hydrated.

Recrystallization of the derivative from dilute alcohol took place very slowly, the material usually separating as small flattened prisms, occasionally as long, white, soft needles, m. p. 179–180°. The latter were the more unstable for if they were allowed to remain in contact with the solvent for several hours they gradually changed over into the prisms. In the dry state the needles apparently retain their form permanently.

Although the melting point of either form was 179–180°, the derivative immediately liquefied and appeared to boil when placed in a bath at 150°. It then resolidified and melted at 179–180°. A fresh sample placed in a cold bath and slowly heated melted at 179–180°. It appears probable that the crystals gradually lost their water of solvation

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(8) Glattfeld and Cameron, THIS JOURNAL, **49**, 1043 (1927).

(9) Ipatieff, Pines and Schmerling, *ibid.*, **60**, 353 (1938).

TABLE II

THE DERIVATIVES

	$RC_6H_4NHCOCH_3$[a]		$RC_6H_4NHCOC_6H_5$[b]		$RC_6H_3(NHCOCH_3)_2$		
R	M. p., °C. (uncorr.)	Nitrogen, % (Calcd.: 6.83)	M. p., °C. (uncorr.)	Nitrogen, % (Calcd.: 5.24)	M. p., °C. (uncorr.)	Crystalline appearance	Nitrogen, % (Calcd.: 10.69)
$—CH_2CH_2CH_2CH_2CH_3$	101–102[c]	6.97	128–129[i]	5.58	202[p]	White, soft needles	10.66
	(*o*-) 79–80	6.71	(*o*-) 99	5.43			
$—CH_2CH_2CH(CH_3)_2$	114[d]	6.84	(132–136)[j]	5.54	215–216	White powder	10.50
$—CH_2C(HCH_3)CH_2CH_3$	115–116[e]	6.90	126[k]	5.15	193–194[q]	Tiny white needles	10.56
$—CH(CH_3)CH_2CH_2CH_3$	107	7.03	127–128[l]	5.44	181–182[r]	Rectangular plates	10.71
$—CH(CH_3)CH(CH_3)_2$	147–148[f]	6.81	141–142	5.24	193[s]	Rectangular prisms	10.63
$—CH(C_2H_5)CH_2CH_3$	145–146[g]	6.94	154[m]	5.19	199–200[t]	Glistening needles	10.80
$—CH_2C(CH_3)_3$	164	6.85	164–165	5.21	240–241	Glistening flakes	10.58
$—C(CH_3)_2CH_2CH_3$	141–142[h]	6.93	112–113[n]	5.14	180–181[u]	Flattened prisms or needles	10.75
Cyclo-C_5H_9	134	6.80[v]	154[o]	5.58[w]	228	Needles or stout hexagonal prisms	10.67[x]

[a] Usually crystallize from dilute alcohol as pearly flakes; from hexane as flakes or needles.

[b] Crystallize from dilute alcohol or hexane as pearly flakes or needles.

[c] Hickinbottom, *J. Chem. Soc.*, 1119 (1937).

[d] *Idem.*, 2396 (1932). [h] *Idem.* [j] *Idem.* The m. p. of *p*-benzaminoisoamylbenzene is reported as 151–153°.

[k] Glattfeld and Cameron, THIS JOURNAL, **49**, 1043 (1927), give 118° as the m. p. of *p*-benzaminobenzylbutane.

[n] Anschütz and Beckerhoff, *Ann*, **327**, 218 (1903), report 158°. [v] Calcd., 6.90. [w] Calcd., 5.28.

[x] Calcd., 10.77.

"Mixed melting points" (approximately 1:1 mixtures): [d+e] 108–110°. [f+g] 137–139°. [g+h] 133–135°. [i+k] 107–111°. [k+l] 105–110°. [i+l] 100–105°. [m+o] 126–128°. [p+t] 168–171°. [q+s] 179–182°. [r+u] 153–165°.

[s] Hydrated form melts at 189°. [u] Hydrated form melts at 169–170°.

during the heating so that the observed melting point was that of the anhydrous derivative; the large prisms melting at 169–170° lost the water of solvation less readily and only on melting.

The following analyses confirm the above explanation of the two melting points.

(a) Sample melting at 170°. Dried in Abderhalden drier at 100° and 20 mm. before analysis. Calcd. for $C_{15}H_{22}O_2N_2$: N, 10.69. Found: N, 10.75.

(b) Sample melting at 170°. Not dried before analysis. Calcd. for $C_{15}H_{22}O_2N_2 \cdot H_2O$: N, 10.00; H_2O, 6.42. Calcd. for $C_{15}H_{22}O_2N_2 \cdot 0.5H_2O$: N, 10.33; H_2O, 3.32. Found: N, 10.44; H_2O, 3.01.

(c) Sample melting at 180–181°. Dried in Abderhalden drier at 100° and 20 mm. before analysis. Found: N, 10.90.

(d) Sample melting at 179–180°. Not dried before analysis. Found: H_2O, 3.19.

It may be concluded then that the derivative is the hemihydrate of diacetamino-*t*-amylbenzene.

2-Methyl-3-phenylbutane.—The diacetamino derivative of this hydrocarbon apparently crystallized both with and without water of solvation. The hydrated crystals melted at 189°. The melting point of the resolidified material was 193°. It was also found that crystals melting at the higher temperature could be obtained by recrystallization from water.

Summary

The eight amylbenzenes and cyclopentylbenzene have been characterized by the preparation of their mono- and diacetamino and monobenzamino derivatives. All three derivatives may be obtained from a single nitration product.

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