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CHARACTERIZATION OF ALKYLBENZENES AND RELATED HYDROCARBONS, FRIEDEL-CRAFTS ACETYLATION AND THE PREPARATION OF 2,4-DINITROPHENYLHYDRAZONES AND SEMICARBAZONES

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Although many derivatives of aromatic hydrocarbons have been reported in the literature (1) there are few only which appear to be applicable to their identification. The identification of monoalkylbenzenes by means of the monoacetamino, diacetamino, and benzamino derivatives has been reported (2). Recently the utility of 2,4-dinitrobenzenesulfenyl chloride as a reagent for the identification of aromatic systems has been pointed out (3) and in addition the *o*-aroylbenzoic acid derivatives of Underwood and Walsh (4) have been reinvestigated and extended to include the *o*-aroyltetrachlorobenzoic acids (5). The use of aroylpropionic acids prepared by the method of Friedel and Crafts has recently been suggested as suitable derivatives for the identification of many aromatic hydrocarbons (6). Sulfonation of aromatic hydrocarbons and the subsequent conversion of the sulfonic acid to a sulfonamide or substituted amide is well known (1) and the nitration of aromatic hydrocarbons has been used for identification purposes to a limited extent (7). Picric acid derivatives are frequently unstable and explosive (8); styphnic acid and 2,4,7-trinitrofluroenone derivatives have been used to some extent (9, 10).

The procedure used in this laboratory for the preparation of derivatives of many alkylbenzenes consists in the acetylation of the alkylbenzene by an adaptation of the Perrier procedure (11) whereby free aluminum chloride is prevented from coming into contact with the hydrocarbon thus minimizing the possibility of isomerization and transalkylation. The crude-acetylation product can be divided into a number of portions and each portion subsequently can be dissolved in alcohol and the ordinary carbonyl type derivatives can be prepared by standard procedures.

DISCUSSION OF RESULTS

The accompanying table illustrates the applicability of this procedure to the characterization of many aromatic systems. However this procedure is subject to certain limitations. It was observed that in the case of dialkylbenzenes having a tertiary alkyl group in the *para* position, such as in *para-tert*-butyltoluene, *para-tert*-amyltoluene, and *para-tert*-butylethylbenzene the tertiary alkyl group seems to be either partially or totally replaced by the acetyl groups. The *para-tert*-alkyltoluenes formed *p*-acetyltoluene and the *para-tert*-butylethylbenzenes yielded a mixture of acetylated hydrocarbons.

It was found that the acetylated 2-methyl-2-phenyl- and 2-methyl-3-phenyl-

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TABLE I

Dinitrophenylhydrazones and Semicarbazones of Acetylated Aromatic Hydrocarbons

Hydrocarbon	Reference	2,4-dinitrophenylhydrazone			Semicarbazone		
			N			N	
		M.P., °C	Found	Calc'd (See Table II)	M.P., °C.	Found	Calc'd (See Table II)
Benzene	(13)	250			198		
Methylbenzene	(13)	260			205		
Ethylbenzene		208–209^{a}	16.46	I			
1,2-Dimethylbenzene		254.5–256^{a}	17.09	I			
1,3-Dimethylbenzene		174.5–176^{a}	17.16	I	192–194^{a}	20.77	I
1,4-Dimethylbenzene		174–175$^{a, b}$	17.20	I	168–170^{a}	20.96	I
n-Propylbenzene	(14)	163–164^{a}	16.72	II	181–181.5		
Isopropylbenzene	(16)	185–186	16.62	II	199–200	18.22	II
n-Butylbenzene	(14)	160			180		
sec-Butylbenzene		145–146^{a}	15.36	III			
Isobutylbenzene	(16)	206.5–209.5^{a}	15.70	III			
tert-Butylbenzene		212.5–213.5^{a}	16.13	III			
1-Methyl-2-*n*-propylbenzene^{f}		147–149^{a}	15.90	III			
1-Methyl-3-*n*-propylbenzene^{f}		119–122^{a}	15.79	III			
1-Methyl-4-*n*-propylbenzene	(14)				161–162		
1-Methyl-2-isopropylbenzene		^{d}	15.42	III	^{d}	18.34	III
1-Methyl-3-isopropylbenzene		131–132^{a}	15.94	III			
1-Methyl-4-isopropylbenzene		^{e}	16.10	III	146–147.5^{a}	18.36	III
1,2-Dimethyl-3-ethylbenzene^{f}		222–224^{a}	15.35	III			
1,2-Dimethyl-4-ethylbenzene^{f}		166–168^{a}	14.90	III			
1,3-Dimethyl-2-ethylbenzene^{f}		218–220$^{a, g}$	15.37	III			
1,3-Dimethyl-4-ethylbenzene^{f}		197–198^{a}	15.91	III			
1,4-Dimethyl-2-ethylbenzene^{f}		180–181^{a}	16.15	III			
n-Amylbenzene	(15)	152.5–153			181–181.5		
2-Phenylpentane	(15)	149–149.5			172.5–173.5		
3-Phenylpentane	(15)	155.5–156.5			164.5–165		
2-Methyl-1-phenylbutane	(15)	147–148			196.5–197		
3-Methyl-1-phenylbutane	(16)	151.5–152	15.41	IV	203–204	16.54	IV
2-Methyl-2-phenylbutane		179.5–181^{a}	15.59	IV	209^{a}	17.20	IV
2-Methyl-3-phenylbutane	(16)	177–178$^{a, h}$	15.34	IV	201–203$^{a, i}$	17.02	IV
2,2-Dimethyl-1-phenylpropane	(16)	194–195	15.33	IV	227–228	17.10	IV
1-Methyl-4-isobutylbenzene	(17)				141–142^{c}		
1-Methyl-2-*tert*-butylbenzene^{j}		212–215^{a}	14.82	IV			
1-Methyl-3-*tert*-butylbenzene^{j}		^{e}		IV			
1-Methyl-4-*tert*-butylbenzene^{j}		260–262$^{a, k}$	17.90	V			
2-Phenylhexane	(16)	136–137	14.58	VI	162–163	16.07	VI
2-Methyl-2-phenylpentane		162–163^{a}	14.07	VI			
3-Methyl-3-phenylpentane	(16)	176–177	14.44	VI	191–192	15.60	VI
3-Methyl-2-phenylpentane	(16)	171–172^{a}	14.32	VI			
2,2-Dimethyl-3-phenylbutane	(12)	178–179			225–226		
2,3-Dimethyl-2-phenylbutane	(12)	184–185			209–210		
3,3-Dimethyl-1-phenylbutane^{j}		198.5–199.5^{a}	14.65	VI	222–223.5^{a}	16.56	VI
3-*tert*-Butylethylbenzene^{j}		166.5–167.5^{a}	14.72	VI	195–197^{a}	16.60	VI

TABLE I—*Continued*

Hydrocarbon	Reference	2,4-dinitrophenylhydrazone			Semicarbazone		
			N			N	
		M.P., °C	Found	Calc'd (See Table II)	M.P., °C.	Found	Calc'd (See Table II)
4-*tert*-Butylethylbenzene[j]		[d]					
p-*tert*-Amyltoluene[j]		145–147[a, m]	14.93	VI	145–146[a, n]		
1-Methyl-1-phenylcyclopentane	(16)	174–175	14.65	VII			
Benzylcyclopentane	(16)	168–169	14.56	VII			
Phenylcyclohexane	(16)	201–203					
1-Methyl-2-phenylcyclohexane	(19)	191.8–192.8					
1-Methyl-3-phenylcyclohexane	(19)	182.2–182.9					
1-Methyl-4-phenylcyclohexane	(19)	182–183.8					
1-Methyl-1-phenylcyclohexane	(20)	181					
p-Tolylcyclohexane	(16)	165.5					
1-Phenyl-1-cyclohexylethane	(16)	167–169					
1-Methyl-4-isopropyl-1-phenylcyclohexane	(21)	202–203					
1-Methyl-1-(2,5-dimethylphenyl)-cyclohexane	(22)	172–174					
1-Methyl-1-(2-methyl-5-ethylphenyl)cyclohexane	(22)	179–181					
1-Methyl-2-isopropyl-x-cyclohexylbenzene	(18)	185–187					
1-Methyl-1-(2-methyl-5-*n*-propylphenyl)cyclohexane	(22)	230–233					
1-Methyl-1-(2-methyl-5-isobutylphenyl)cyclohexane	(17)	220–222					
1-(2-Methyl-5-isopropyl phenyl)-cyclohexane	(23)	169–170					
3-Ethylindan	(24)	150					
1,3,3,5-Tetramethylindan	(18)	170–171					
4-Methylbiphenyl	(21)	230–232					
4-Ethylbiphenyl	(21)	227–229					
4-Isopropylbiphenyl	(16)	224–225					
Bicyclo[3.2.1]-2,6-dimethyl-2-phenyloctane	(26)	177–180					

[a] Corrected melting point. [b] Mixture m.p. with the 2,4-dinitrophenylhydrazone obtained from the acetylated 1,3-dimethylbenzene was 152°. [c] *Anal.* Calc'd for $C_{14}H_{21}N_3O$: C, 67.98; H, 8.56. Found: C, 67.83; H, 8.72. [d] No definite melting point. [e] Melts to a turbid viscous liquid at 152°, then becomes clear and less viscous at 158–159°. Compare reference (25). [f] Hydrocarbon obtained from R. W. Schiessler. [g] Mixture m.p. with the 2,4-dinitrophenylhydrazone obtained from the acetylated, 1,2-dimethyl-3-ethylbenzene was 190–192°. [h] Mixture m.p. with the 2,4-dinitrophenylhydrazone obtained from the acetylated 2-methyl-2-phenylbutane was 177–179°. [i] Mixture m.p. with the semicarbazone obtained from the acetylated 2-methyl-2-phenylbutane was 203–204°. [j] Hydrocarbon obtained from M. J. Schlatter. [k] Dark red precipitate, very slightly soluble in ethanol, no depression of the m.p. when mixed with toluene derivative. [l] Hydrocarbon obtained from L. Schmerling. [m] Also isolated a small amount of a dark red precipitate m.p. 259–261°. Mixture m.p with the 2,4-dinitrophenylhydrazone obtained from the acetylated toluene showed no depression. [n] *Anal.* Calc'd for $C_{15}H_{23}N_3O$: C, 68.9; H, 8.9. Found: C, 69.23; H, 8.78. [o] Two easily isolated derivatives: (i) orange-colored, slightly soluble in 95% ethanol, m.p. 165–166°, [a] N found: 15.31. (ii) Yellow-colored, soluble in 95% ethanol, m.p. 145–146, [a] N found: 15.39.

TABLE II

CALCULATED VALUES FOR NITROGEN OF DINITROPHENYLHYDRAZONES AND SEMICARBAZONES

	Calculated for:			
	Dinitrophenylhydrazone		Semicarbazone	
I	$C_{16}H_{16}N_4O_4$	17.06	$C_{11}H_{15}N_3O$	20.47
II	$C_{17}H_{18}N_4O_4$	16.36	$C_{12}H_{17}N_3O$	19.12
III	$C_{18}H_{20}N_4O_4$	15.72	$C_{13}H_{19}N_3O$	18.02
IV	$C_{19}H_{22}N_4O_4$	15.12	$C_{14}H_{21}N_3O$	16.96
V	$C_{15}H_{14}N_4O_4$	17.81	$C_{10}H_{13}N_3O$	21.97
VI	$C_{20}H_{24}N_4O_4$	14.57	$C_{15}H_{23}N_3O$	16.07
VII	$C_{20}H_{22}N_4O_4$	14.6	$C_{15}H_{21}N_3O$	16.2

butane form semicarbazones and 2,4-dinitrophenylhydrazones having similar melting points and their mixture melting points do not show any depression. It was not established whether isomerization of the amyl groups might have occurred during the acetylation.

The necessity for first complexing the aluminum chloride with acetyl chloride was shown by reversing the order of addition of reagents in the acetylation of *para*-cymene. Anhydrous aluminum chloride was added to the *para*-cymene and followed after 15–20 minutes by acètyl chloride in carbon disulfide. The only derivatives isolated were found to arise from toluene and *meta*-cymene. No derivative obtained from *para*-cymene was isolated. If, however, the acetyl chloride was added immediately to the *para*-cymene containing the aluminum chloride then the isomerization and transalkylation did not occur.

The advantage of preparing more than one type of derivative from a single acetylation mixture was shown in the case of *meta*- and *para*-xylene. The 2,4-dinitrophenylhydrazones of the acetylated hydrocarbons have similar melting points (mixture m.p. shows a 20° depression); however their semicarbazones have quite different melting points.

EXPERIMENTAL

Standard acetylation procedure. In a 50-cc. conical flask, fitted with a calcium chloride drying tube, were placed 1.4 g. of anhydrous powdered aluminum chloride, 5 cc. of carbon disulfide, and 0.8 cc. of acetyl chloride. After five minutes 2 cc. of the hydrocarbon dissolved in 5 cc. of carbon disulfide was added to the flask with swirling. Similar experiments have shown that as little as 0.3 to 0.4 cc. of hydrocarbon, with proportional amounts of the other reagents, may be used. The mixture was allowed to stand at room temperature until all the aluminum chloride dissolved (10–15 minutes). The mixture was poured onto ice and 5 cc. of concentrated hydrochloric acid. An additional 5 cc. of carbon disulfide was added and the organic layer was separated. This layer was washed successively with 3 cc. of 10% hydrochloric acid, water, 5% sodium bicarbonate and water, until washings were neutral to litmus. The organic layer was dried over calcium chloride and the carbon disulfide was evaporated. The residue was dissolved in alcohol and 2,4-dinitrophenylhydrazones and semicarbazones were prepared according to Shriner and Fuson (13).

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SUMMARY

The characterization of aromatic hydrocarbons by means of the modified Perrier procedure of the Friedel-Crafts acetylation reaction is discussed. A tabulation is included of sixty-nine aromatic hydrocarbons which can be characterized in this manner.

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