[CONTRIBUTION FROM THE NAVAL RESEARCH LABORATORY]

CATALYTIC HYDROGENATION OF SOME ARYL-SUBSTITUTED ALIPHATIC ACIDS

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In the course of an investigation of cyclohexyl-substituted aliphatic acids, the following were derived from the corresponding aryl derivative by catalytic reduction: cyclohexylstearic acid, *p*-cyclohexylcyclohexylstearic acid, *p*-dodecylcyclohexylstearic acid, and cyclohexylundecanoic acid. The arylstearic acids are a mixture of about equal parts of the 9- and 10-substituted acid prepared by the Friedel and Crafts reaction of the olefinic acid and an aromatic compound (1, 2, 3). The arylundecanoic acid is prepared by the same reaction and the product is a mixture of the 10- and 11-substituted acid (4). Aqueous potassium permanganate oxidation demonstrated the presence of para-oriented arylstearic acids (1).

Smith, Alderman, and Nadig (5) reduced phenyl-substituted aliphatic acids, with up to five carbon atoms in the chain, in a quantitative study of catalytic hydrogenation. This was an elaboration of the qualitative investigation of some of these compounds by Adams and Marshall (6). The hydrogenation of the benzene nucleus in these investigations was conducted in a solution of acetic acid with a platinum catalyst at room temperature (or slightly elevated) and a hydrogen pressure of several atmospheres. Baker and Schuetz (7) found that simple benzenoid hydrocarbons were reduced at high hydrogen pressure under the influence of Adams catalyst. The reduction proceeds readily at room temperature. Adkins (8) evaluated the reduction of the benzene ring with nickel catalysts.

The present work extends the investigation of the catalytic hydrogenation of the benzenoid structure in aralkyl acids with regard to compounds with greater length of aliphatic chain and more complex substitution on the aromatic ring. It was found that with increased molecular complexity larger amounts of catalysts, higher hydrogen pressure, and longer time favored complete reduction (6). Purified starting materials were necessary for successful hydrogenation of the aryl-substituted aliphatic acids. Purification of the acids was attained by refluxing an alcoholic solution of the starting materials with Raney nickel. It was recalled that in the preparation of these acids the aromatic component was usually a commercially available product frequently contaminated with difficultly removable organic sulfur impurities. The poisoning of hydrogenation catalysts from this and other causes has been previously reported and remedial methods devised (9, 10).

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TABLE I

Catalytic Hydrogenation of Aryl-substituted Aliphatic Acids

STARTING ACID[f]	MOLES	°C.	HRS.	CATALYST[a]	ACID PRODUCT[f]
Phenylstearic	0.57	165	5	Ni(R)	Cyclohexylstearic
Phenylstearic	.20	200	2	UOP	Cyclohexylstearic
Phenylstearic	.20	200	3	UOP[b]	Cyclohexylstearic
p-Xenylstearic	.10	165	5	Ni(R)	*p*-Cyclohexylcyclohexylstearic
p-Xenylstearic	.06	200	4	UOP	*p*-Cyclohexylcyclohexylstearic
p-Dodecylphenylstearic	.08	240	4	Ni(R)	*p*-Dodecylcyclohexylstearic
Phenylundecanoic	.05	85	18	PtO_2[c]	Cyclohexylundecanoic
Phenylundecanoic	.07	80	1	PtO_2[d]	Cyclohexylundecanoic
Phenylundecanoic	.38	230	5	Ni(R)	Cyclohexylundecanoic
Phenylundecanoic	.59	150	2	UOP[e]	Cyclohexylundecanoic

[a] Unless otherwise noted, the initial hydrogen pressure varied between 175 to 200 atmospheres. The UOP catalyst, which is essentially nickel on kieselguhr, was obtained from Universal Products Company, Riverside, Illinois.

[b] Dioxane was used as solvent.

[c] The hydrogenation was incomplete. In this reaction glacial acetic acid was used as solvent and the initial hydrogen pressure was four atmospheres.

[d] Glacial acetic acid was used as solvent.

[e] The UOP catalyst was pulverized before use; the unpulverized, ⅛″ pellets failed to catalyze this reaction.

[f] The substituted stearic acids are mixtures of the 9- and 10-isomers. The substituted undecanoic acids are mixtures of the 10- and 11-isomers.

TABLE II

Some Physical Constants of the Starting Materials and Hydrogenation Products

Aryl-substituted aliphatic acids[a, b]

	B.P., °C.	MM.	n_D^{20}	NEUTRALIZATION EQUIVALENT	
				Found	Theory
Phenylstearic	207–220	0.4	1.4881	356	360
p-Xenylstearic	258–278	1.2	1.5290	441	437
p-Dodecylphenylstearic	220–235	1.0	1.4980	540	529
Phenylundecanoic	165–173	0.5	1.4960	276	262
ALICYCLIC-SUBSTITUTED ALIPHATIC ACIDS[a, b]					
Cyclohexylstearic	201–205	0.1	1.4713	371	366
p-Cyclohexylcyclohexylstearic	209–228	0.3	1.4888	450	443
p-Dodecylcylohexylstearic	176–196	0.3	1.4787	540	535
Cyclohexylundecanoic	140–142	0.2	1.4768	270	268

Data are for the purified material.

[b] The substituted stearic acids are mixtures of 9- and 10-substituted acids. The substituted undecanoic acids are mixtures of 10- and 11-substituted acids.

EXPERIMENTAL

The general method adopted here for the preparation of the cyclohexyl-substituted aliphatic acids was as follows: An alcoholic solution of the aryl-substituted acid[2,3] was heated under reflux for six hours with approximately 20% (by weight) of Raney nickel. The catalyst was removed by sintered-glass filtration or centrifugation and the solvent distilled under water-pump vacuum. The resulting acid was then fractionated in vacuum.

High pressure hydrogenations were conducted in an electrically heated bomb (185 or 300 ml. capacity) mounted in a mechanical rocker (American Instrument Company). Glass liners for these bombs were omitted after preliminary runs indicated that a liner was not needed. Low pressure reactions were carried out in a conventional Parr shaking apparatus equipped with a heat-jacketed reaction bottle. Unless otherwise noted, no solvent was used. Approximately 10% of catalyst was employed throughout the investigation.

At the completion of the reaction the mixture was removed from the bomb with benzene. The catalyst was freed from the mixture and the solvent removed by water-pump vacuum. The reduced acid was then fractionated in vacuum.

Table I indicates the conditions for the hydrogenation of the aryl-substituted aliphatic acids. Table II shows some of the properties of the cyclohexyl-substituted aliphatic acids prepared in this investigation. Each compound is characterized by the boiling point, refractive index, and neutralization equivalent. The expected decreased values for refractive index and boiling point were observed in the hydrogenation products. The refractive index decrease for the reduced monobenzenoid structure is approximately .02 and for the dibenzenoid ring is .04. Apparently, the mixed isomers of the starting material hinder the formation of crystalline derivatives since no solid products were obtained. The yield in most cases was essentially quantitative.

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[2] The arylstearic acids were supplied by the Eastern Regional Research Laboratory of the Department of Agriculture and are described in publications by that Laboratory (1, 2, 11).

[3] The phenylundecanoic acid was an Eastman Kodak Company product.