separated from the boiling solution.[17] The flask was cooled after a total refluxing time of three hours and the hydrocarbon was filtered. Recrystallized from alcohol and little benzene, it forms yellow crystals, often described in the literature.[18] The melting point was 182.8–183.8°. The picrate forms dark brown needles of the melting point 179–180°. The physical constants of the other ketones and hydrocarbons are listed in Table II.

TABLE II

KETONE (I)

R	B. p. °C.	B. p. Mm.	Calcd., % C	Calcd., % H	Found, % C	Found, % H
Ethyl	189–190	16–17	85.67	7.61	85.24	7.32
n-Propyl	194–197	14–15	85.67	7.99	85.29	8.21
n-Butyl	205–206	17–18	85.67	8.33	85.34	8.04
n-Pentyl	209–212	15–16	85.67	8.63	85.46	8.31
n-Hexyl	217–219	14–15	85.66	8.9	85.31	8.61
Phenyl[23]	216–219	7–8	88.08	6.34	87.62	6.08
Benzyl	195–197	1–2	87.96	6.71	87.61	6.34

HYDROCARBON (III)

R	M. p., °C.	Solvent	Form	Calcd., % C	Calcd., % H	Found, % C	Found, % H	Picrates[20] M. p., °C.	Picrates[20] Nitrogen, % Calcd.	Picrates[20] Nitrogen, % Found
Ethyl	143.2–144	Alcohol	Yellow needles	92.68	7.32	92.58	7.41	137.8–138.4	9.35	9.26
n-Propyl	97.8–98.6	Alcohol	Orange plates	92.11	8.04	92.26	7.74	125.5–126.2	9.06	8.57
n-Butyl	78.2–78.8	Alcohol	Long yellow needles	91.88	8.11	91.73	8.05	91.8–92.8	8.8	8.46
n-Pentyl	71–71.8	Alcohol	Long yellow needles	91.55	8.45	91.72	8.68	85.4–86.2	8.55	8.10
n-Hexyl	65.8–66.5	Alcohol	Long yellow needles	91.25	8.75	91.43	8.83	78.2–79.2[21]	5.38	5.13
Phenyl	113.5–114.5[19]	Benzene/ligr.	Yellow prisms					125.2–126	8.64	8.46
Benzyl[22]	167.8–168.6	Alcohol/benz.	Long yellow needles	95.58	6.42	95.78	6.76			

Summary

The rate of the cyclization of different ketones to 9,10-disubstituted anthracenes has been measured and found to decrease as the number of carbon atoms on the alkyl groups increases. The decrease in rate can best be explained in terms of the inductive effect of alkyl groups. A number of 9-alkyl-10-methylanthracenes has been prepared and the physical constants are described.

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[17] The cyclization of the ketone which leads to 9-methylanthracene is reported to take place in four days (Bradsher, ref. 6a).

[18] Bachman and Chemerda, *J. Org. Chem.*, **4**, 583 (1939); Barnett and Matthews, *Ber.*, **59**, 1437 (1926); J. E. Jones, Thesis, Harvard University, 1941.

[19] Barnett and Matthews, *Ber.*, **59**, 1437 (1926), report a melting point of 112°.

[20] All picrates form dark brown crystals and decompose when recrystallized from alcohol, benzene or ligroin. They are best recrystallized from methyl alcohol in the presence of some excess picric acid.

[21] 9-Hexyl-10-methylanthracene forms a picrate which contains two molecules of hydrocarbon. The same is reported for 9-butylanthracene (Stieglitz and Marx, *Ber.*, **56**, 1619 (1923)).

[22] This hydrocarbon did not form a picrate.

[23] This ketone solidified after long standing and had a crude melting point of 47–48°.

CAMBRIDGE, MASS. RECEIVED DECEMBER 18, 1943

[CONTRIBUTION FROM THE CENTRAL EXPERIMENT STATION, BUREAU OF MINES]

Hydrogenation of Anthracene by Tetralin[1]

BY MILTON ORCHIN[2]

Examination of some of the high-boiling liquid products obtained by hydrogenation of coal at the Bureau of Mines Central Experiment Station involved attempts at dehydrogenation. The physical properties of these oils indicated a large percentage of hydroaromatic compounds, yet catalytic liquid-phase dehydrogenation gave only small quantities of evolved hydrogen. To understand better the reactions that may occur when mixtures of aromatics and hydroaromatics such as are found in the products from the hydrogenation of coal are heated in the liquid phase in the presence of a catalyst, a study of the mixture anthracene and tetralin was undertaken.

The literature reveals that under the conditions necessary for liquid-phase dehydrogenation, the hydrogen is often utilized in what may be regarded as a sort of internal oxidation–reduction process. This transfer of hydrogen can be either intramolecular or intermolecular. Examples of the former are the conversion of methyl 2-(5,6,7,8-tetrahydro)-naphthyl ketone to 2-ethylnaphthalene[3]; and 1-hydroxy-1-allyl-1,2,3,4-tetrahydrophenanthrene to 1-*n*-propylphenanthrene.[4,5] Examples of the intermolecular transfer of hydrogen are the conversion of 2,3-naphthalic anhydride to 2,3-dimethylnaphthalene in small yield by means of *p*-cyclohexylphenol[6]; the disproportionation reactions in the terpene series[7]; the incomplete dehydrogenation of tetralin due to the equilibrium tetralin $\leftrightarrows$ naphthalene + $2H_2$[8]; and the work of Adkins and coworkers, who dehydrogenated many compounds by heating in a steel bomb with benzene as a hydrogen acceptor.[9]

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[1] Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Not copyrighted.

[2] Organic chemist, Central Experiment Station, Bureau of Mines, Pittsburgh, Pa.

[3] Newman and Zahm, THIS JOURNAL, **65**, 1097 (1943). Barbot, *Bull. soc. chim.*, [4] **47**, 1314 (1930), dehydrogenated the same ketone with sulfur at 220° and obtained a 71% yield of methyl 2-naphthyl ketone. Apparently, under these conditions the ketone group is not attacked.

[4] Bachmann and Wilds, THIS JOURNAL, **60**, 624 (1938).

[5] See also (a) Ruzicka, *Helv. Chim. Acta*, **19**, 419 (1936); (b) Fieser and Joshel, THIS JOURNAL, **61**, 2958 (1939); and (c) Mosettig and Duval, *ibid.*, **59**, 367 (1937); (d) for a recent complete review of the subject of dehydrogenation, see Plattner, *Die Chemie*, **55**, 131 (1942).

[6] Windaus and Thiele, *Ann.*, **521**, 163 (1935).

[7] Linstead, Michaelis and Thomas, *J. Chem. Soc.*, 1139 (1940).

[8] Linstead and Michaelis, *ibid.*, 1134 (1940).

[9] Adkins and Reid, THIS JOURNAL, **63**, 741 (1941), and Adkins, Richards and Davis, *ibid.*, **63**, 1320 (1941).

When tetralin and anthracene were heated together at one atmosphere pressure in the presence of a palladium catalyst, some of the hydrogen was transferred from the tetralin to the anthracene with the formation of naphthalene and hydroanthracenes. The extent of the reaction was influenced by the temperature, as indicated by the table in the experimental part. When the temperature was such that about 24% of the theoretical quantity of hydrogen was evolved, a 30% yield of 1,2,3,4-tetrahydroanthracene was obtained.

When tetralin and anthracene were heated in a sealed tube, a 60% yield of 1,2,3,4-tetrahydroanthracene was obtained. In addition, small quantities of 9,10-dihydroanthracene and 1,2,3,4,5,6,7,8-octahydroanthracene were formed. The reaction apparently resembles the catalytic hydrogenation of anthracene.[10]

In an extension of this method of hydrogenation, 2-cyclohexenone was used as a hydrogen donor in place of tetralin. 2-Cyclohexenone in its enolic form is a dihydrobenzene derivative, and its preparation by vapor-phase dehydration of 2-hydroxycyclohexanone gives considerable phenol.[11] The reaction between cyclohexenone and anthracene resulted in a 30% yield of 1,2,3,4-tetrahydroanthracene.

The reaction between tetralin and anthracene to give naphthalene, dihydroanthracene and tetrahydroanthracene may be represented stoichiometrically by the equations

$$(1)\quad C_{10}H_{12} + 2C_{14}H_{10} \leftrightarrows C_{10}H_8 + 2C_{14}H_{12}$$

$$(2)\quad 2C_{14}H_{12} \leftrightarrows C_{14}H_{10} + C_{14}H_{14}$$

Reaction (1) can proceed to a limited extent in the absence of a catalyst, as indicated by experiments 8 and 9. The disproportionation reaction (2) apparently requires a catalyst, as no 1,2,3,4-tetrahydroanthracene could be found in the same reactions. The isolation of some tetrahydroanthracene when dihydroanthracene was dehydrogenated is evidence for reaction (2).[12]

In one attempt to elucidate the steps of the reaction, 9,10-dihydroanthracene was refluxed in ethanol solution with Raney nickel. The reaction mixture gave a good yield of 1,2,3,4-tetrahydroanthracene. Anthracene was found to behave similarly. Apparently, the hydrogen adsorbed on the surface of Raney nickel can be utilized for the hydrogenation reactions, and this constitutes a novel method for the preparation of small quantities of tetrahydroanthracene.

When the tetralin–anthracene reaction is accompanied by the evolution of hydrogen, the origin of the hydrogen, of course, is tetralin. As the temperature is increased, the hydrogen may also result from dehydrogenation of the hydroanthracenes. Undoubtedly other equilibria are present in the system at different times, but the mechanism of the reaction remains speculative.

The results support the theory that one of the steps in the hydrogenation of coal is the transfer of hydrogen from a reactive hydrogen donor to a molecule that can act as a hydrogen acceptor.[13] The ease of transfer of hydrogen also suggests that considerable discretion must be exercised in determining "primary" products of the hydrogenation of coal.

Experimental[14]

The apparatus used in the open-tube experiments consisted simply of a test-tube containing the reactants connected to a reflux condenser by either a rubber stopper or a ground-glass joint. A piece of rubber tubing led from the top of the condenser to an inverted cylinder of water standing in a water-bath. The catalyst used in each experiment (except 8 and 9) was a mixture of palladium and charcoal containing approximately 30% palladium.[15]

Materials

Tetralin.—A good grade of commercial tetralin, obtained by the hydrogenation of naphthalene, was distilled twice from sodium and the middle cut of the second distillation used.

Anthracene.—Commercial anthracene was purified by two distillations with ethylene glycol[16] and twice recrystallized from benzene, melting point 215.2–217.2°. For purposes of comparison, samples of 9,10-dihydroanthracene, 1,2,3,4-tetrahydroanthracene and 1,2,3,4,5,6,7,8-octahydroanthracene were prepared.

9,10-Dihydroanthracene.[17]—Sodium reduction of an amyl alcohol solution of anthracene gave 84% of 9,10-dihydroanthracene, m. p. 108.0–109.8°.

1,2,3,4-Tetrahydroanthracene prepared from the reaction between anthracene and tetralin was purified through the picrate,[18] and after two recrystallizations from alcohol, the hydrocarbon was obtained as colorless plates, m. p. 100.5–101.5°. The trinitrobenzene complex also was prepared, yellow needles, m. p. 133.2–133.8°, from alcohol. *Anal.*[19] Calcd. for $C_{20}H_{17}N_3O_6$: N, 10.63. Found: N, 10.43.

Subsequently, tetrahydroanthracene was prepared from 9,10-dihydroanthracene and from anthracene. To 0.5449 g. of 9,10-dihydroanthracene in 25 ml. of ethanol there was added about 8 g. of Raney nickel.[20] After the mixture was refluxed for two and one-half hours in a nitrogen atmosphere, it was filtered, and the filtrate was concentrated. On cooling, 0.3326 g. of 1,2,3,4-tetrahydroanthracene, m. p. 98.0–100.2°, was obtained. The mother liquor was treated with 0.3 g. of *s*-trinitrobenzene and 0.245 g. of the 1,2,3,4-tetrahydroanthracene trinitrobenzene complex, m. p. 132.8–133.4°, was obtained, making a total yield of 81%. When 0.3377 g. of anthracene in 50 ml. of ethanol was treated with about 10 g. of Raney nickel, a 71% yield of 1,2,3,4-tetrahydroanthracene was obtained.

1,2,3,4,5,6,7,8-Octahydroanthracene.—β-2-(5,6,7,8-Tetrahydronaphthoyl)-propionic acid was prepared in 70% yield by the Friedel–Crafts reaction between tetralin and succinic anhydride in nitrobenzene at 0°. Benzene also

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[10] Fries and Schilling, *Ber.*, **65**, 1494 (1932).

[11] Bartlett and Woods, THIS JOURNAL, **62**, 2933 (1940).

[12] In this connection, it is interesting to note that Fries and Schilling (ref.10) obtained some anthracene when they hydrogenated dihydroanthracene at room conditions. Wieland, *Ber.*, **45**, 485 (1912), also obtained anthracene from dihydroanthracene by shaking a benzene solution of the latter with a special palladium black catalyst.

[13] Storch, *Chem. Rev.*, **29**, 483 (1941).

[14] All melting points corrected.

[15] Zelinsky and Turowa-Pollak, *Ber.*, **58**, 1295 (1925).

[16] Fieser, "Experiments in Organic Chemistry," 2d ed., D. C. Heath Co., Boston, Mass.

[17] Bamberger, *Ber.*, **20**, 3075 (1887).

[18] Schroeter, *ibid.*, **57**, 2014 (1924).

[19] Dr. T. S. Ma, University of Chicago.

[20] Prepared by Mary E. Montague and E. H. Kaplan, of this Laboratory, according to "Organic Syntheses," **21**, 15 (1941).

TABLE I

REACTIONS BETWEEN TETRALIN AND ANTHRACENE

Reactions 1 to 4, inclusive, were open-tube reactions; all others were sealed-tube reactions.

	Starting materials, g.						Per cent. products[a]					
Expt.	$C_{10}H_{12}$[b]	$C_{14}H_{10}$[c]	Pd-C	Bath temp., °C.	Time, hours	% H_2 evolved[d]	$C_{10}H_{12}$[b]	$C_{10}H_8$[e]	$C_{14}H_{10}$[c]	$C_{14}H_{12}$[f]	$C_{14}H_{14}$[g]	$C_{14}H_{18}$[h]
1	0.462	None	0.137	225–230	7	83	+[i]	+	–[j]	–	–	–
2	0.458	1.001	0.131	225–230	7	0	+	+	93	+	+	–
3	0.59	0.531	0.100	270–290[k]	7	65	–	+	79	–	+	–
4	1.01	0.75	0.100	220–260[l]	6.5	24	42	44	44	1	30	–
5	1.98	5.00	0.100	300–315	5	–	+	+	83	–	–	–
6	4.98	3.56	0.100	300–330	6	–	16	54	+	+	41	–
7	5.4	6.20	0.500	340	7	–	14.8	69.3	9.0	3.5	61.3	0.8
8	1.98	2.686	None	290 350	8 6	–	+	–	87	4	0	–
9	1.98	2.607	None	390–420	1	–	+	–	88	5	0	–

[a] The percentage figures are yields based upon starting tetralin (in the case of naphthalene) and anthracene (in the case of hydroanthracenes). The figures represent the minimum amount present. [b] Tetralin. [c] Anthracene. [d] These figures are based upon the theoretical yield of 44.8 ml. hydrogen per millimole of tetralin. [e] Naphthalene. [f] 9,10-Dihydroanthracene. [g] 1,2,3,4-Tetrahydroanthracene. [h] 1,2,3,4,5,6,7,8-Octahydroanthracene. [i] + means isolated and identified but not determined quantitatively. [j] – means not isolated; may or may not be present. [k] Inside temperature 230–250°. [l] Inside temperature 230–235°.

can be used as the solvent.[8,21a] Clemmensen reduction of the keto acid gave γ-2-(5,6,7,8-tetrahydronaphthyl)-butyric acid in 94% yield.[8] The acid was converted to the acid chloride at room temperature with thionyl chloride. In the hope of minimizing the formation of 4-keto-1,2,3,4,-5,6,7,8-octahydrophenanthrene, the acid chloride was cyclized in carbon disulfide at 0° with stannic chloride. However, cyclization took place in both directions.[21b] The mixture of ketones (11.7 g. from 15.0 g. of the tetralylbutyric acid) was reduced by the Clemmensen procedure[16] and gave 4.72 g. of 1,2,3,4,5,6,7,8-octahydroanthracene, m. p. 71–72°, recrystallized from alcohol, melting point 72.0–73.0°.

2-Cyclohexenone.—After several unsuccessful attempts to prepare this ketone by selenium dioxide oxidation of cyclohexene (mole for mole in ethanol solution), it was prepared in poor yield (10%) by the chromic oxide oxidation of cyclohexene,[22] $n^{24}\mathrm{D}$ 1.483; compound with 2,4-dinitrophenylhydrazine, m. p. 171.5°, after sintering at 163°.[22a] *Anal.*[19] Calcd. for $C_{12}H_{12}N_4O_4$: N, 20.28. Found: N, 20.02.

Reactions between Tetralin and Anthracene.—The conditions and results of the various experiments are summarized in the table. In working up the mixtures resulting from the reactions between anthracene and tetralin the problem in the most extreme case was one of separating and identifying tetralin, naphthalene, anthracene, 9,10-dihydroanthracene, 1,2,3,4-tetrahydroanthracene, and 1,2,3,4,5,6,7,8-octahydroanthracene. The reaction mixtures were not worked up in the same fashion each time, but characteristic differences in properties of these six substances were utilized to advantage. These differences may be summarized briefly. Tetralin and naphthalene sublime and steam-distil more readily than the other substances and, of these, only naphthalene forms a picrate. Anthracene alone of all these substances forms an adduct with maleic anhydride.[23] The adsorption of the anthracenes on a column of activated alumina in increasing strength of adsorption is octahydroanthracene, 1,2,3,4-tetrahydroanthracene, 9,10-dihydroanthracene, and anthracene (see below). 1,2,3,4-Tetrahydroanthracene forms a picrate, whereas 9,10-dihydroanthracene does not. The former also readily forms a complex with *s*-trinitrobenzene.[24]

Experiment 7 will be described in detail, as it illustrates all the techniques used in separating and identifying products.

Experiment 7.—A mixture of 6.2 g. of powdered anthracene, 0.5 g. of palladium-charcoal, and 5.5 cc. of tetralin was heated in a sealed tube in a nitrogen atmosphere at 340° for seven hours. The tube was cooled and opened (no pressure), the contents were dissolved in benzene, filtered, and distilled at the vacuum of the water pump. A high-boiling fraction of 4.6 g. was collected at a bath temperature of 170° and a residue (A) was retained in the flask.

The distillate consisted of naphthalene and tetralin, separated by precipitation of naphthalene as the picrate and estimation of the tetralin content of the oily hydrocarbon residue by comparison of its refractive index with that of a synthetic mixture of known composition.

Residue A yielded anthracene in the form of its maleic anhydride adduct. The filtrate from that afforded 1,2,3,4-tetrahydroanthracene, crystallizing from alcohol. Trinitrobenzene was now added to the solution, precipitating a mixture of the complexes of naphthalene and tetrahydroanthracene. The hydrocarbons were regenerated by passage of the complexes through alumina and separated by steam-distillation.

The material in the mother liquor from the complex precipitation was recovered, dissolved in benzene–petroleum ether and separated into 9,10-dihydro- and 1,2,3,4,-5,6,7,8-octahydro-anthracene by chromatographic adsorption on a column of alumina.

The isolated products were identified by their melting points and mixed melting points. The yields of purified products obtained are recorded in the table.

Chromatographic Separation of 9,10-Dihydroanthracene and 1,2,3,4-Tetrahydroanthracene.—A solution of 100 mg. of 9,10-dihydroanthracene and 100 mg. of 1,2,3,4-tetrahydroanthracene in 100 ml. of petroleum ether (b. p. 60–68°) was passed through a 9-inch column containing 65 g. of activated alumina. Following the 100 ml. of solution, an additional 125 ml. of petroleum ether, then 100 ml. of 20% benzene in petroleum ether, were passed through the column by gravity. The receivers were changed after

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(21)(a) Krollpfeiffer and Schafer, *Ber.*, **56**, 620 (1923).

(21)(b) These authors cyclized γ-2-tetralylbutyric acid by heating it with concentrated sulfuric acid and obtained a 75% yield of the ketoanthracene. No keto phenanthrene was isolated.

(22) Whitmore and Pedlow, THIS JOURNAL, **63**, 758 (1941).

(22)(a) Whitmore and Pedlow give the melting point of cyclohexenone 2,4-dinitrophenylhydrazone as 117°, while Bartlett and Woods (ref. 11) give the melting point as 163°. Although these discrepancies are not readily explained, it should be noted that the hydrazone can theoretically exist in stereoisomeric forms, and there is the additional possibility that the cyclohexene portion may undergo spontaneous aromatization.

(23) Bachmann and Kloetzel, *ibid.*, **60**, 481 (1938).

(24) Although 9,10-dihydroanthracene can also form a complex with trinitrobenzene (Sudborough, *J. Chem. Soc.*, 1339 (1916)), the complex dissociates readily and is difficult to obtain.

about every 50 ml. of solution had been collected. Six fractions were thus collected. Evaporation of fractions 1, 2, 3 and 6 gave no residue. The fourth fraction gave a mixture with m. p. 75–88°. The fifth fraction gave crystals, m. p. 104.5–108.5°, and after recrystallization there was obtained 25 mg., m. p. 108.0–109.8°, identical with 9,10-dihydroanthracene.

Dehydrogenation of 9,10-Dihydroanthracene.—In a test-tube connected to a reflux condenser were placed 1.00 g. of 9,10-dihydroanthracene and 100 mg. of palladium–charcoal catalyst. The tube was placed in a bath at 200° for a few minutes, during which time 6 ml. of gas was collected (blank). The temperature was raised to 300° and kept at 300–340° for three hours, during which time an additional 118 ml. of gas was collected (83%). The reaction mixture was cooled, dissolved in benzene, filtered, and the anthracene removed by means of maleic anhydride. There was obtained 1.24 g. of adduct equivalent to 0.8 g. of anthracene (80%). After the excess maleic anhydride had been removed, the remaining material was treated with trinitrobenzene; whereupon 70 mg. of the 1,2,3,4-tetrahydroanthracene complex, m. p. 128–131°, was obtained, mixed melting point, no depression.

Reaction between 2-Cyclohexenone and Anthracene.—In a preliminary experiment, cyclohexenone was refluxed with palladium–charcoal, but no hydrogen was evolved.[25] A mixture of 2.95 g. anthracene, 3.84 g. cyclohexenone, and 300 mg. of palladium–charcoal was heated in a sealed tube for seven and one-half hours at 295–325°. The tube was cooled in dry-ice, opened (pressure), and the contents dissolved in benzene and filtered. The benzene solution was extracted with 5% sodium hydroxide solution and the alkaline extract made to 500 ml. A 20-ml. aliquot was titrated with potassium bromate–potassium bromide solution.[26] The titration indicated 1.74 g. of phenol present in the total reaction mixture. The tribromophenol formed in the titration was filtered and recrystallized from ethanol, m. p. 91–92° (literature reports 95°). The benzene solution remaining after the alkaline extraction was treated with maleic anhydride and 1.64 g. endoanthracene maleic anhydride was precipitated and filtered. The excess maleic anhydride was extracted from the filtrate, the benzene was evaporated, and the residue was distilled. The distillate (2.45 g.) was dissolved in 20 ml. of ethanol and treated with 2 g. of picric acid. There was obtained 1.52 g. of orange-yellow crystals, m. p. 110–113°, identical with the picrate of 1,2,3,4-tetrahydroanthracene. The mother liquor was passed through a column of activated alumina. The first fraction gave 50 mg. of 1,2,3,4-tetrahydroanthracene. The second fraction contained some tetrahydroanthracene, some dihydroanthracene, and some other material that may have resulted from the polymerization of cyclohexenone. After removal of about 135 mg. of 9,10-dihydroanthracene, m. p. 107–109°, mixed melting point, no depression, the remaining material was treated with trinitrobenzene. There separated 0.386 g. of 1,2,3,4-tetrahydroanthracene trinitrobenzene complex, m. p. 128–130.5°, mixed melting point, no depression. The mother liquor was not investigated further.

Acknowledgment.—The author wishes to express his appreciation to Dr. H. H. Storch for his interest and suggestions throughout this work and to Dr. M. S. Newman for suggestions regarding the manuscript.

Summary

When anthracene and tetralin are heated together at 1 atmosphere pressure in the presence of a palladium catalyst, a 30% yield of 1,2,3,4-tetrahydroanthracene can be obtained.

When anthracene and tetralin are heated together in a sealed tube in the presence of a palladium catalyst, the reaction resembles a catalytic hydrogenation of anthracene and a 61% yield of 1,2,3,4-tetrahydroanthracene along with small amounts of 9,10-dihydroanthracene, and 1,2,3-4,5,6,7,8-octahydroanthracene are obtained. This type of hydrogenation of anthracene can also be achieved with 2-cyclohexenone.

The dehydrogenation of 9,10-dihydroanthracene in the liquid phase results in expulsion of less than the theoretical quantity of hydrogen and formation of some 1,2,3,4-tetrahydroanthracene.

1,2,3,4-Tetrahydroanthracene can be conveniently prepared in good yield by refluxing an ethanol solution of anthracene or 9,10-dihydroanthracene with Raney nickel.

PITTSBURGH, PA. RECEIVED DECEMBER 10, 1943

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(25) Compare Ruzicka, ref. 5a, who by heating 3-methylcyclohexene-2-one for two days with selenium at 260° obtained only a 15% yield of *m*-cresol.

(26) United States Pharmacopeia, X.

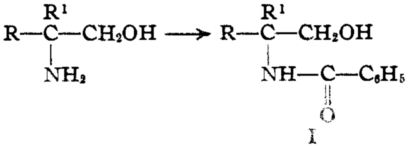
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF INDIANA UNIVERSITY]

Amino Acids. III. α-Amino-*n*-butyric Acid and α-Amino-isobutyric Acid

BY JOHN H. BILLMAN AND EARL E. PARKER

The method used for the synthesis of alanine[1] from 2-amino-*n*-propanol has now been extended to the preparation of α-amino-*n*-butyric acid and α-amino-isobutyric acid from 2-amino-*n*-butanol and 2-amino-2-methyl-*n*-propanol.

The amino alcohols were benzoylated with benzoyl chloride and anhydrous sodium carbonate in benzene to yield the N-benzoylamino alcohol I.

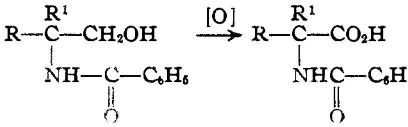


$$\mathrm{R{-}\overset{R^1}{\underset{NH_2}{C}}{-}CH_2OH \longrightarrow R{-}\overset{R^1}{\underset{NH-\overset{}{C}(=O)-C_6H_5}{C}}{-}CH_2OH} \qquad (1)$$

I

The yield of crude 2-benzoylamino-*n*-butanol was 89–91% while the yield of pure 2-benzoylamino-2-methyl-*n*-propanol was 78–79%.

A number of oxidizing agents were tried in order to ascertain whether any of them possessed advantages over alkaline permanganate for the oxidation of the benzoylated amino alcohols to the corresponding amino acids II. Among those examined and found to react were lead dioxide,



$$\mathrm{R{-}\overset{R^1}{\underset{NH-C(=O)-C_6H_5}{C}}{-}CH_2OH \xrightarrow{[O]} R{-}\overset{R^1}{\underset{NHC(=O)-C_6H_5}{C}}{-}CO_2H}$$

II

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[1] Billman and Parker, THIS JOURNAL, **65**, 2455 (1943).