

Heptane dicarboxylic acid-1,5 has been obtained as a solid.

In the course of the synthesis, the following new compounds were prepared: ethyl δ -iodovalerate, triethyl ester of heptane tricarboxylic acid-1,5,5, heptane tricarboxylic acid-1,5,5 and the silver salt of heptane dicarboxylic acid-1,5.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

**THE USE OF PLATINUM-OXIDE PLATINUM BLACK IN THE
CATALYTIC REDUCTION OF AROMATIC HYDROCARBONS.
XVII¹**

BY ROGER ADAMS AND J. R. MARSHALL²

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One of the few classes of reducible compounds which does not lend itself readily to reduction under ordinary laboratory conditions is the aromatic hydrocarbons. These compounds have frequently been reduced at high temperatures, using nickel or other metals as a catalyst, but no satisfactory method is available for their reduction under such conditions as are most conveniently used in a scientific laboratory, namely, room temperature or slightly above, atmospheric pressure or pressures not over two or three atmospheres and readily prepared catalyst. The reactions should be comparatively rapid and it should be possible to reduce large enough quantities to be sufficient for ordinary research purposes. The success of platinum-oxide platinum black as a catalyst for the addition of hydrogen to many unsaturated compounds, as compared with other forms of catalytic platinum, led to a study of its use in the reduction of aromatic hydrocarbons.

Willstätter³ and his associates report the hydrogenation of benzene and toluene at ordinary pressures and temperatures by means of hydrogen and platinum black prepared by the reduction of chloroplatinic acid and formaldehyde. However, the large amount of catalyst needed compared with the amount of material to be reduced renders the method impractical for ordinary work. For the reduction of 3.0 g. of benzene in 13 cc. of glacial acetic acid with 0.1 g. of platinum black, six hours was required; for 1.8 g. of toluene in 3 g. of acetic acid with 0.5 g. of platinum black, three and one-half hours; for 6 g. of xylene in 4 g. of acetic acid with 0.9 g. of platinum

¹ The previous article in this field is by Bray and Adams, *THIS JOURNAL*, **49**, 2101 (1927). Reference to the other work will be found in this article.

² This communication is an abstract of a thesis submitted by J. R. Marshall in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at the University of Illinois.

³ (a) Willstätter and Waldschmidt-Leitz, *Ber.*, **54**, 113 (1912); (b) Willstätter and Hatt, *ibid.*, **45**, 1471 (1921).

black, twenty-four hours. Other hydrocarbons were reduced under conditions comparable with those cited.

The benzene hydrocarbons have also been reduced by means of colloidal platinum. Skita^{4,5} and his associates reduced several, of which may be mentioned as examples, 1 g. of toluene in 120 cc. of acetic acid with 0.41 g. of colloidal platinum in three and one-half hours; 10 g. of xylene in 80 cc. of acetic acid with 1.5 g. of platinum in three to four hours, using in this instance, however, 3 atmospheres' pressure and 80° temperature.

The use of platinum-oxide platinum black has proved to be of value and to be a catalyst far more effective than those mentioned. Although the investigation is not entirely complete, publication of the results at hand is offered since, in an article recently published, Kuhn⁶ has noted in the course of an investigation on the addition reactions of conjugated systems that certain compounds such as diphenylbutadiene were reduced by platinum-oxide platinum black not merely to diphenyl substituted saturated hydrocarbons, but even further until the benzene nuclei were saturated. Thus the completely hydrogenated derivatives of diphenylbutane, diphenylhexane and diphenyloctane were prepared. Though alcohol has usually proved to be the most satisfactory solvent for reductions with platinum-oxide black, with ethyl acetate as the second most desirable, in the case of the aromatic hydrocarbons neither is as suitable as glacial acetic acid. The temperature was in practically all cases that of the room and the pressure was varied from two to three atmospheres. The following table indicates how readily various hydrocarbons may be reduced in practically quantitative yields with a small amount of catalyst.

The first seven compounds and the last two in the table could be reduced to completion with 0.2 g. of catalyst. The heavier molecules, however (in general those with more than one phenyl group), required several additions of 0.2 g. of catalyst to obtain complete reduction within a required time.

A few experiments were made with benzene, toluene and xylene, increasing the amount of catalyst and, as might be expected, the time of reduction was very materially decreased. In addition it might be stated that fluorene and α,α -diphenylpropane resisted all attempts at reduction by a similar procedure. It is the opinion of the authors that this difficulty was probably due to slight impurities, even though special precautions were taken to remove them. In general, the rate of reaction of these aromatic compounds seemed to be very dependent on the purity of the compounds and reagents. Presence of traces of impurities frequently diminished the rate of reduction markedly.

Skita^{4,5} fractionated very carefully 9 g. of reduced *m*-xylene. From this

⁴ Skita and Meyer, *Ber.*, **45**, 3589 (1912).

⁵ Skita and Schneek, *Ber.*, **55**, 144 (1922).

⁶ Kuhn and Winterstern, *Helv. Chim. Acta*, **11**, 123 (1928).

TABLE I
REDUCTION OF AROMATIC COMPOUNDS IN 50 CC. OF GLACIAL ACETIC ACID AT 25-30°
TEMPERATURE AND 2-3 ATMOSPHERES' PRESSURE

Compound used	B. p. or m. p., °C.	Amount of substance, g.	Amount of catalyst, g.	Time, hrs.
Benzene	79.5-80	15.6 (0.2 mole)	0.2	2.0
Toluene	110-111	18.4 (0.2 mole)	.2	2.75
Ethylbenzene	136-136.8	21.2 (0.2 mole)	.2	7.5
<i>m</i> -Xylene	139-140	21.2 (0.2 mole)	.2	21.5
Mixed xylenes	138-145	21.2 (0.2 mole)	.2	26.0
Mesitylene	164.5-166	12 (0.1 mole)	.2	8.5
Cymene	175-176.2	13.4 (0.1 mole)	.2	7.5
Diphenylmethane	27 (m. p.)	16.8 (0.1 mole)	.2	7.0
Triphenylmethane ^a	92.2-92.5 (m. p.)	8.74 (0.033 mole)	4 × 0.2	48.0
α,α -Diphenylethane	147 (15 mm.)	18.2 (0.1 mole)	3 × 0.2	26.5
Dibenzyl	52.5-53 (m. p.)	18.2 (0.1 mole)	3 × 0.2	37.0
Phenylacetic acid	76 (m. p.)	13.6 (0.1 mole)	.2	5.5
β -Phenylpropionic acid	48 (m. p.)	15.0 (0.1 mole)	.2	6.0
Compound obtained	B. p., °C.	n_D	d	Ref.
Cyclohexane	79-79.5 (752 mm.)	1.4242/20°	0.7769/20°	7, 3, 4
Methylcyclohexane	100-100.2 (742 mm.)	1.4198/20°	.7687/20°	7, 4
Ethylcyclohexane	129.8-130 (743 mm.)	1.4278/25°	.7899/25°	8
<i>m</i> -Dimethylcyclohexane	118.5-119 (747 mm.)	1.4230/25°	.773/25°	3b, 9, 10
Mixed dimethylcyclohexanes	118-123 (743 mm.)
Trimethylcyclohexane	135.5-136 (743 mm.)	1.4257/25°	.8250/25°	9
1-Methyl-4-isopropylcyclohexane	63 (22 mm.)	1.4370/25°	.8061/25°	9
Dicyclohexylmethane	110-110.5 (18 mm.)	1.4875/20°	.8884/20°	11
Tricyclohexylmethane	163.2 (4 mm.)	1.5264/20°	.9644/20°	12, 13
α,α -Dicyclohexylethane	112 (7 mm.)	1.4887/25°	.9070/25°	7, 14
α,β -Dicyclohexylethane	147-148.5 (12 mm.)	1.4760/18°	.8774/18°	4
Cyclohexylacetic acid	110-112 (3 mm.)	1.4558/30°	1.007/30°	16
β -Cyclohexylpropionic acid	112-114 (4 mm.)	1.4596/25°	1.0178/25°	15, 17

^a Temp., 60° C.; 100 cc. of acetic acid.

(7) Ipat'ev, *Ber.*, **40**, 1281 (1907); (8) Sabatier and Senderens, *Compt. rend.*, **132**, 566 (1901); (9) Skita and Schneck, *Ber.*, **55**, 144 (1922); (10) Skita, *Z. angew. Chem.*, **34**, 230 (1901); (11) Sabatier and Senderens, *Compt. rend.*, **132**, 210 (1901); (12) Ipat'ev and Dolgov, *Compt. rend.*, **183**, 304 (1926); (13) Godchot, Marcel, *Compt. rend.*, **147**, 1057 (1918); (14) Sabatier and M. Murat, *Compt. rend.*, **154**, 1771 (1923); (15) Zelinsky, *Ber.*, **41**, 2676 (1908); (16) Treudler and Damond, *Compt. rend.*, **141**, 594 (1915); (17) Ipat'ev, *Ber.*, **41**, 1003 (1908).

he reports that he was able to obtain two constant boiling fractions, one at 119° and the other at 121.5°, which he assumed to be the *trans* and *cis* forms, respectively. In the reduction with platinum-oxide platinum black the product, even though available in much larger quantities than reported by Skita, could not be fractionated into two constant boiling compounds. It appears that the largest proportion of the product was probably the *trans* form. In the same way, at least the greater proportion of the reduction product of cymene was a single compound.

Experimental

Platinum Black.—The platinum oxide was prepared from c. p. chloroplatinic acid in the manner described previously.¹⁸ The apparatus was the same as has been used in the previous investigations.

¹⁸ Adams and Shriner, *THIS JOURNAL*, **45**, 2171 (1923); *Org. Syn.*, **8**, 92 (1928).

Purification of Substances to be Reduced.—Commercial c. p. products were obtained and further purified. Thiophene-free benzene, toluene, ethylbenzene, xylene, mesitylene, cymene and diphenylmethane were refluxed for three hours over sodium and then distilled. Only the constant boiling fraction was used for the reduction. Triphenylmethane, α, α -diphenylethane, dibenzyl, phenylacetic acid and β -phenylpropionic acid were crystallized alternately from alcohol and glacial acetic acid. After several recrystallizations the compounds were used for reduction.

Method of Isolation of Products.—After filtration and evaporation of the solvent, the reduced compounds, with the exception of the two acids, were treated several times with a mixture of 10 cc. of concd. nitric acid and 25 cc. of sulfuric acid at 0–5° for five to ten minutes. After each treatment the compound was washed with water. When the acid mixture no longer turned yellow, the compound was considered to be pure and was washed, dried and distilled.

The cyclohexylacetic acid and the β -cyclohexylpropionic acid were merely distilled from the acetic acid in order to purify them.

Summary

It has been found that platinum-oxide platinum black is an excellent catalyst in the reduction with hydrogen of various types of aromatic hydrocarbons in glacial acetic acid as a solvent.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

THE EFFECT OF THE CYANIDE GROUP ON THE BASICITY OF ALIPHATIC AMINES AS DETERMINED IN WATER AND ALCOHOL SOLUTIONS

By T. D. STEWART AND VIVIEN COOK

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Stewart and Aston¹ studied the influence of alkoxy substitution upon the basicity of tertiary aliphatic amines, using derivatives of the type $\text{ROCH}_2\text{N}(\text{C}_2\text{H}_5)_2$. They found that methoxy, ethoxy and *isobutoxy* substitution lowered the base strength and gave to the basic dissociation constants of the amino ethers the values 3.6×10^{-9} , 1.8×10^{-8} and 4×10^{-7} , respectively. The comparisons were made colorimetrically in alcohol, using methylaniline and benzylamine as standards. By assuming that the relative base strengths in water and alcohol solution would be the same, the above figures were assigned as for an aqueous solution. The work of Goldschmidt and Mathiesen² indicates that in general amines are stronger bases in alcohol than in water, but with notable exceptions, so that comparisons of basicity in alcohol cannot be considered to offer a similar comparison in water. The above values, then, must be considered not as absolute but as relative to themselves and to methylaniline in alcohol solution only. It is, nevertheless, apparent that alkoxy sub-

¹ Stewart and Aston, *THIS JOURNAL*, **48**, 1642 (1926).

² Goldschmidt and Mathiesen, *Z. physik. Chem.*, **119**, 439 (1926).