over 15 minutes; the temperature rose from 5 to 10° during the addition. The brown complex was stirred for 18 hours at room temperature, decomposed in the usual manner and distilled to give 5.0 g. of unreacted 9,10-dihydrophenanthrene, b.p. 145–146° (5 mm.), and 14.0 g. (42%) of the ester as a colorless oil, b.p. 160–163° (0.2 mm.), $n^{22}D$ 1.5803, λ_{max}. 266 mμ (log ϵ 4.10).

Anal. Calcd. for $C_{20}H_{22}O_2$: C, 81.60; H, 7.45. Found: C, 81.48; H, 7.53.

Ethyl β-(2-Phenanthryl)-butyrate (VII).—Ten grams (0.034 mole) of ester VI and 1.21 g. (0.038 mole) of recrystallized sulfur were heated in a test-tube at 250–270° for three hours. The crude reaction mixture was chromatographed on alumina in benzene–hexane (50:50) solution to give 8.9 g. (90%) of ester VII as a pale yellow oil, $n^{20}D$ 1.6315; λ_{max}. (log ϵ) 254 (4.67); 278 (4.03); 298 (3.97); 322 (2.49); 334 (2.51); 350 (2.40). All attempts to crystallize the material failed.

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.18; H, 6.90. Found: C, 81.95; H, 6.94.

1'-Keto-3'-methyl-1,2-cyclopentenophenanthrene (VIII). —Saponification of ester VII was carried out in the normal manner to give a 90% yield of crude acid, m.p. 100–112°, which was suitable for cyclization. This was accomplished by stirring 7.7 g. (0.029 mole) of the acid with 200 g. of polyphosphoric acid at 70° for 6 hours. The red solution was poured into water and the crude ketone extracted with ether. On standing, the ether solution deposited 0.3 g. of a pale yellow product, m.p. 201–202°, which formed bright yellow needles, m.p. 204–205°, on crystallization from ethyl acetate.

The main fraction was chromatographed on alumina using benzene–ether (95:5) as eluant. A small amount (0.6 g.) of a highly fluorescent oil preceded the main ketonic

fraction which consisted of 5.4 g. (76%) of a pale yellow solid, m.p. 100–110°, suitable in purity for the next step. A small sample crystallized from propanol as warts, m.p. 132–134°; lit.[11] m.p. 135–136°.

Anal. Calcd. for $C_{18}H_{14}O$: C, 87.78; H, 5.73. Found: C, 87.48; H, 5.80.

The 2,4-dinitrophenylhydrazone crystallized as red, powdery needles from ethyl acetate, m.p. 252–254° dec.

Anal. Calcd. for $C_{24}H_{18}N_4O_4$: C, 67.61; H, 4.25; N, 13.14. Found: C, 67.79; H, 4.28; N, 12.94.

3'-Methyl-1,2-cyclopentenophenanthrene (Diels Hydrocarbon) (IX).—The crude ketone from the cyclization (3.2 g., 0.013 mole) was dissolved in 25 ml. of diethylene glycol containing 2.0 g. of 85% hydrazine hydrate and the mixture was heated under reflux for three hours. Three grams of potassium hydroxide was added and the resultant orange solution heated to 185–190° for three hours. The dark brown mixture was poured into water and the crude hydrocarbon extracted with ether. The excess solvent was removed and the oil chromatographed on alumina using benzene–petroleum ether (50:50) as eluant. This gave 1.8 g. (60%) of the Diels hydrocarbon (IX), as colorless plates, m.p. 123–125°, identical in all respects with an authentic sample,[12] m.p. 124–126°.

The picrate crystallized from ethanol as orange-brown needles, m.p. 116–118°, lit.[13] m.p. 117–118°.

Anal. Calcd. for $C_{18}H_{16} \cdot C_6H_3N_3O_7$: C, 62.47; H, 4.15. Found: C, 62.66; H, 4.27.

(11) E. Bergmann and H. Hilleman, *Ber.*, **66**, 1302 (1933).

(12) This sample of authentic Diels hydrocarbon was kindly supplied by Dr. Karl Miescher, Ciba A.-G., Basel, Switzerland.

(13) O. Diels, W. Gädke and P. Körding, *Ann.*, **459**, 1 (1927).

ITHACA, NEW YORK

The Catalytic Hydrogenation of the Benzene Nucleus. VIII. The Hydrogenation of Methyl-substituted Benzilic Acids

BY HILTON A. SMITH AND COMER D. SHACKLETT

Seventeen substituted benzilic acids have been hydrogenated in acetic acid solution over platinum catalyst, and the completely hydrogenated products isolated. The rate constants for the hydrogenations have been determined, and the influence of the number and position of substituents compared with earlier results dealing with the influence of substituents on the rate of hydrogenation of the benzene nucleus.

In an earlier publication the hydrogenation of compounds containing two benzene rings was discussed.[1] It was shown that many of these compounds underwent hydrogenation to form phenylcyclohexyl compounds and subsequently the dicyclohexyl derivatives, so that at the half hydrogenation point a pure compound could be obtained. In the case of benzilic acid, this is not found. Under the experimental conditions employed, the reaction mixture at the half-hydrogenation point contains about 65% of the phenylcyclohexylglycolic acid, with about 15% benzilic acid and 15% dicyclohexylglycolic acid.[2] Recently a number of methylsubstituted benzilic acids have been prepared,[3] and it seemed of interest to study the influence of the methyl substituents on the rate of catalytic hydrogenation of these compounds. The influence of the number and position of methyl substituents on the

hydrogenation of benzene[4] and of benzoic acid[5] has already been reported.

Experimental

The syntheses of the 16 benzilic acids together with their physical constants, neutral equivalents and elemental analyses have been described.[3] The general experimental details for making hydrogenation runs and for calculating rate constants have been given in previous papers in this series. All hydrogenations were carried out in the presence of pure acetic acid and Adams platinum catalyst. All rate constants were corrected to the usual standard, and were comparable with previous data.

After complete hydrogenation, the products were precipitated from the reaction mixtures, after removal of the catalyst by filtration, by diluting the solutions with water. The products were then washed several times with water and dried in a vacuum desiccator over sodium hydroxide. A summary of the products, together with the neutral equivalents and melting points of the products is given in Table I. It should be recognized that the products may exist in several isomeric forms. The sharpness of the melting points indicates that in most cases a single isomer was present. In a few cases, the range in melting point indi-

(1) H. A. Smith, D. M. Alderman, C. D. Shacklett and C. M. Welch, THIS JOURNAL, **71**, 3772 (1949).

(2) H. A. Smith, C. D. Shacklett and C. M. Welch, *ibid.*, **74**, 4534 (1952).

(3) C. D. Shacklett and H. A. Smith, *ibid.*, **75**, 2654 (1953).

(4) H. A. Smith and E. F. H. Pennekamp, *ibid.*, **67**, 279 (1945).

(5) H. A. Smith and J. A. Stanfield, *ibid.*, **71**, 81 (1949).

TABLE I

CHARACTERISTICS OF THE DICYCLOHEXYLGLYCOLIC ACIDS RESULTING FROM THE HYDROGENATION OF SUBSTITUTED BENZILIC ACIDS[a]

Acid	M.p., °C.	Neut. equiv. Calcd.	Neut. equiv. Found	Formula	Composition, %[b] Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
2-Methyl-	153.6–154.8	254.4	255.0	$C_{15}H_{26}O_3$	70.82	70.89	10.30	10.48
3-Methyl-	130.2–131.8	254.4	257.1	$C_{15}H_{26}O_3$	70.82	70.91	10.30	10.48
4-Methyl-	164.0–165.0	254.4	256.8	$C_{15}H_{26}O_3$	70.82	70.52	10.30	10.46
2,2'-Dimethyl-	160.8–174.2	268.4	269.1	$C_{16}H_{28}O_3$	71.60	71.49	10.51	10.60
3,3'-Dimethyl-	110.4–112.4	268.4	270.3	$C_{16}H_{28}O_3$	71.60	71.62	10.51	10.59
4,4'-Dimethyl-	165.4–166.6	268.4	267.6	$C_{16}H_{28}O_3$	71.60	71.45	10.51	10.71
2,3-Dimethyl-	159.2–160.0	268.4	269.6	$C_{16}H_{28}O_3$	71.60	71.63	10.51	10.38
2,4-Dimethyl-	117.2–123.0	268.4	265.9	$C_{16}H_{28}O_3$	71.60	71.59	10.51	10.68
2,6-Dimethyl-	165.2–167.0	268.4	265.1	$C_{16}H_{28}O_3$	71.60	71.53	10.51	10.60
3,4-Dimethyl-	123.5–126.0	268.4	269.9	$C_{16}H_{28}O_3$	71.60	71.51	10.51	10.37
3,5-Dimethyl-	158.8–159.6	268.4	270.5	$C_{16}H_{28}O_3$	71.60	71.59	10.51	10.64
2,3,5-Trimethyl-	164.6–171.4	282.4	284.5	$C_{17}H_{30}O_3$	72.36	72.46	10.72	11.02
3,4,5-Trimethyl-	138.4–142.4	282.4	284.7	$C_{17}H_{30}O_3$	72.36	72.10	10.72	10.75
2,3,4,5-Tetramethyl-	72.2– 80.0[c]	296.4	316.7	$C_{18}H_{32}O_3$	72.93	72.99	10.88	10.89
2,3,5,6-Tetramethyl-	199.6–201.4	296.4	300.7	$C_{18}H_{32}O_3$	72.93	73.13	10.88	10.83
3,5,3',5'-Tetramethyl-	181.0–186.8	296.4	301.6	$C_{18}H_{32}O_3$	72.93	72.91	10.88	10.92
4,4'-Diisopropyl-	143.0–145.8	324.5	334.0	$C_{20}H_{36}O_3$	74.02	74.05	11.18	11.17

[a] For preparation of the corresponding benzilic acids, see Shacklett and Smith, ref. 3. [b] Analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn. [c] The 2,3,4,5-tetramethyldicyclohexylglycolic acid became completely transparent and glassy between 72–80°, but not really fluid in nature. This behavior combined with the high neutral equivalent probably indicates solvent of crystallization. Elementary analysis was performed on a sample which had been dried in a vacuum oven at 100° for 24 hours.

cates a mixture of isomers. No attempt was made to isolate partially hydrogenated intermediates.

Experimental Calculations and Results

As in previous hydrogenation experiments dealing with the benzene nucleus, these reactions were zero order with respect to the hydrogen acceptor, first order with respect to hydrogen pressure, and directly proportional to the weight of catalyst used. Therefore rate constants were calculated from the equation

$$\log p°_{H_2}/p_{H_2} = kt/2.303 V$$

where $p°_{H_2}$ represents the initial hydrogen pressure, p_{H_2} represents the hydrogen pressure at time t, and V is the volume of the hydrogen gas in the system, generally 390 ml. Values for each rate constant, k, were obtained from plots of log $p°_{H_2}/p_{H_2}$ against time by multiplication of the slope of the line thus obtained by 2.303 V.[6] For those compounds in which the two rings are substituted differently, one would not expect a single rate constant from the beginning to the end of the reaction, but a different rate constant for the hydrogenation of each ring. Whether it is possible to isolate two slopes would depend on whether one ring was essentially completely hydrogenated before the hydrogenation of the other commenced,[2] as well as the relative magnitude of the two rates. Figure 1 is an example of a plot showing two regions of linearity. It should be possible to calculate the rate constant for hydrogenation of the second ring from the slope of the second straight-line portion of the curve. This was not done since many of the plots did not show definite breaks. In addition, catalyst poisoning would tend to give unreliable rate constants from the slopes of the latter portion of the hydrogenation curves.

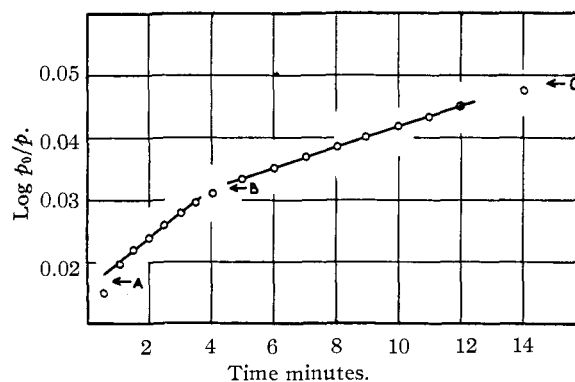(6) J. F. Fuzek and H. A. Smith, THIS JOURNAL, **70**, 3743 (1948).

Fig. 1.—Hydrogenation of 3-methylbenzilic acid. A represents theoretical hydrogen consumption for reduction of PtO_2; B, for reduction of one benzene ring; C, for reduction of two benzene rings.

The initial rate constants for the hydrogenations studied are given in Table II. These values represent the average of several determinations. Individual values were generally within 5%, but variations as great as 10–15% were obtained occasionally. The value for benzilic acid is a little higher

TABLE II

RATE CONSTANTS FOR THE HYDROGENATION REACTIONS

Benzilic acid hydrogenated	$k°_{30}$, 1. min.$^{-1}$ g.$^{-1}$	Benzilic acid hydrogenated	$k°_{30}$, 1. min.$^{-1}$ g.$^{-1}$
Unsubstituted	0.0168	2,6-Dimethyl-	0.0089
2-Methyl-	.0089	3,4-Dimethyl-	.0151
3-Methyl-	.0168	3,5-Dimethyl-	.0217
4-Methyl-	.0244	2,3,5-Trimethyl-	.0093
2,2'-Dimethyl-	.0049	3,4,5-Trimethyl-	.0253
3,3'-Dimethyl-	.0128	2,3,4,5-Tetramethyl-	.0111
4,4'-Dimethyl-	.0244	2,3,5,6-Tetramethyl-	.0049
2,3-Dimethyl-	.0115	3,5,3',5'-Tetramethyl-	.0239
2,4-Dimethyl-	.0115	4,4'-Diisopropyl-	.0097

than previously given,[1] but more in line with that for phenylcyclohexylglycolic acid.

Discussion

It has previously been shown that the rate constants for hydrogenation of toluene and the xylenes are[4]

Toluene	0.180	m-Xylene	0.143
o-Xylene	.093	p-Xylene	.188

Thus, symmetrical substitution increases the rate of hydrogenation. On this basis, one might expect that the unsubstituted ring would be hydrogenated first for 2-methyl- and 3-methylbenzilic acids, and that the rate constants for the first portion of the hydrogenation would be the same as for benzilic acid, while for the 4-methyl compound, the substituted ring would hydrogenate first, and at a rate faster than for benzilic acid itself. The results,

Benzilic acid	0.0168	3-Methylbenzilic acid	0.0168
2-Methylbenzilic acid	.0089	4-Methylbenzilic acid	.0244

are in line with expectations except that the 2-methyl compound hydrogenates slower than benzilic acid itself. This seems to be the case for all the 2-substituted acids. Here the initial rate constants are all very close to 0.01.

2-Methyl-	0.0089	2,6-Dimethyl-	0.0089
2,3-Dimethyl-	.0115	2,3,5-Trimethyl-	.0093
2,4-Dimethyl-	.0115	2,3,4,5-Tetramethyl-	.0111

Apparently an *ortho* group on the ring not adsorbed on the catalyst interferes with the penetration of the hydrogen.

The results with single methyl groups substituted on both rings are in line with expectations.

2,2'-Dimethyl-	0.0049	Benzilic	0.0168
3,3'-Dimethyl-	.0128	4,4'-Dimethyl-	.0244

The results with 3,5-dimethyl- and 3,5,3',5'-tetramethylbenzilic acids show rate constants somewhat greater than the anticipated values. Although

Benzilic	0.0168	3,5,3',5'-Tetramethyl-	0.0239
3,5-Dimethyl-	.0217	3,4,5-Trimethyl-	.0253

mesitylene (1,3,5-trimethylbenzene) reacts almost as rapidly as toluene, and the symmetrical substitution is probably responsible for these cases also. The high result with 3,4,5-trimethylbenzilic acid is unexpected and not readily explained.

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KNOXVILLE, TENNESSEE

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t-Alkyl Groups. II. Use of the *t*-Butyl Group as a Blocking Group in the Synthesis of 1,2,3-Trialkylbenzenes[1]

BY MAURICE J. SCHLATTER

The *t*-butyl group is an unusual removable blocking group because it blocks not only the position it occupies, but the two adjacent positions as well. As a substituent on aromatic nuclei it increases the ease of further substitution in the *meta* and particularly in the *para* positions. It can be removed readily from aromatic hydrocarbons without disturbing the remaining alkyl groups. Use of these properties in the synthesis of pure 1,2,3-trimethylbenzene, 1,3-dimethyl-2-ethylbenzene, 1,3-dimethyl-2-*n*-decylbenzene and 1,3-dimethyl-2-*n*-octadecylbenzene is demonstrated. Factors affecting its application in the synthesis of other alkylaromatic hydrocarbons are discussed.

The *t*-butyl group readily can be introduced and removed from aromatic nuclei without disturbing other alkyl substituents. Although it activates the nucleus toward further substitution, its bulk not only prevents it from entering adjacent to another group but, as a substituent, causes it to exert a considerable hindrance to substitution of the two adjacent positions. Therefore, the *t*-butyl group is especially suited for use as a removable blocking group in synthesis. The preparation of several 1,2,3-trialkylbenzenes is described here.[2] Factors affecting its application in the synthesis of other 1,2,3-trialkylbenzenes, 1,2-dialkylbenzenes and analogously substituted bi- and polycyclic hydrocarbons are discussed.

1,2,3-Trimethylbenzene (V) was synthesized

from *m*-xylene (I) by a process in which the *t*-butyl blocking group may be used repeatedly. The *t*-butylation of *m*-xylene (I) ordinarily gives only 1,3-dimethyl-5-*t*-butylbenzene (II) which in turn gives only the 2-chloromethyl derivative (III) when treated with formaldehyde and hydrochloric acid. Reduction of this yields 1,2,3-trimethyl-5-*t*-butylbenzene (IV) which, on equilibration with *m*-xylene (I) over a suitable catalyst, gives pure 1,2,3-trimethylbenzene (V) and 1,3-dimethyl-5-*t*-butylbenzene (II); the latter may be recycled in the process. With the exception of the *t*-butyl transfer step, these reactions have been carried out by Fuson, Denton and Kneisley.[3] They are straightforward and give excellent yields.

A similar sequence of reactions was carried out using *o*-xylene. The principal difference observed was the need for more vigorous conditions to convert the less reactive 1,2-dimethyl-4-*t*-butylbenzene to 1,2-dimethyl-3-chloromethyl-5-*t*-butylbenzene than was required to chloromethyl-

(1) Presented in part before the Petroleum Division of the American Chemical Society, Chicago, Ill., Sept. 9, 1953; "Symposium on Petrochemicals in the Postwar Years," Publication No. 28, Division of Petroleum Chemistry, p. 79.

(2) The *t*-butyl group apparently has not been used previously as a blocking group in the synthesis of vicinally substituted aromatic hydrocarbons. Its application in the synthesis of some phenols has been reported by D. R. Stevens, U. S. Patent 2,603,662 (July 15, 1952).

(3) R. C. Fuson, J. J. Denton and J. W. Kneisley, THIS JOURNAL, 63, 2652 (1941).