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Hydrogenation of Alkyl-Substituted Naphthalenes Over Palladium

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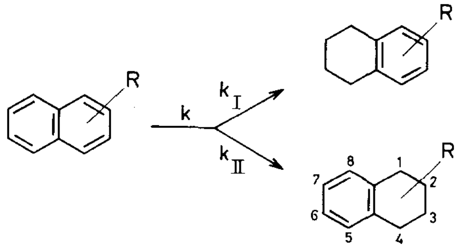
The kinetics of the hydrogenation of a series of alkyl- and dialkylnaphthalenes over palladium on carbon in acetic acid have been studied at 80°C and atmospheric pressure. Selective formation of tetrahydro derivatives was always observed. Equilibration experiments of pairs of alkyltetralins showed that the hydrogenations are kinetically controlled. The mechanism of hydrogen addition is discussed, especially on the basis of deuteration experiments. Competitive hydrogenations showed that bulky alkyl substituents weaken the strength of adsorption.

The rate of hydrogenation of 2-alkyl- and 2,6-dialkylnaphthalenes, except 2,6-di-*t*-butylnaphthalene, is somewhat lower than that of naphthalene. In 2-alkylnaphthalenes the unsubstituted ring is hydrogenated preferentially. For the 1-alkylnaphthalenes and the 1,4-, 1,5-, and 1,8-dialkylnaphthalenes the rate of hydrogenation was found to increase sharply with growing size of the alkyl groups. In the case of 1-*t*-butyl- and 1,4-di-*t*-butylnaphthalene a highly selective hydrogenation of the substituted ring was observed. These phenomena are discussed in terms of *peri* strain, the steric interaction of the 1-alkyl group with the 8-hydrogen atom or 8-alkyl group. Partial release of this strain during hydrogenation is supposed to give rise to increased rates and to govern the selectivity of ring attack.

INTRODUCTION

Recently, Weitkamp studied the deuteration and exchange of naphthalene (*1*) and the high pressure hydrogenation of methylnaphthalenes (*2*, *3*) on transition metal catalysts. From Weitkamp's and earlier literature data it is evident that the hydrogenation of the naphthalene nucleus proceeds in two steps: (i) selective formation of the tetrahydro derivatives, (ii) subsequent hydrogenation to decahydro products.

Qualitative data for the hydrogenation of monoalkylnaphthalenes to their tetrahydro derivatives (tetralins) on various catalysts and at elevated temperature and pressure demonstrate that in most cases the unsubstituted ring is hydrogenated preferentially (*2–8*). Kinetic data for the hydrogenation of alkylnaphthalenes are rather limited (*4*, *9–11*).



This paper presents our results for the liquid phase hydrogenation of alkyl- and dialkylnaphthalenes to tetralins on palladium (*12*). Using various alkyl substituents the overall hydrogenation rate constants k, the values of k_I and k_{II}, and the selectivity $S = k_I/k_{II}$ were measured. Alkyl substituents were chosen from the

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series methyl, ethyl, isopropyl, cyclohexyl, and *t*-butyl. In particular we were interested in the effects of 1-substituents in view of the *peri* strain (van der Waals interaction of the 1-R group with the 8-hydrogen atom) present in such systems.

For comparison with the results of hydrogenation the equilibria between the tetralins I and II have been measured at several temperatures.

Information concerning the relative strength of adsorption of alkylnaphthalenes was obtained from competitive hydrogenations. Furthermore some deuteration experiments have been included.

EXPERIMENTAL METHODS

Palladium, 10% on carbon, was purchased from Drijfhout N. V. (total surface 750 m^2/g, palladium area 11 m^2/g). Acetic acid p.a. was obtained from Merck A. G.

The preparation of most of the reactants has been described elsewhere (*13*). Liquid compounds were purified through their picrates, solid compounds by recrystallization.

Hydrogenations were carried out in a 50 ml glass reactor equipped with thermometer, magnetic stirrer, injection rubber and gas-inlet and -outlet tubes. The catalyst (20–150 mg), the hydrocarbon reactant (ca. 1.5 mmole) and the solvent (20 ml) were placed in the reaction vessel. Then the air in the vessel was replaced by hydrogen, and water at 80.0 ± 0.1°C was circulated through the thermostat jacket. The reaction was followed by measuring the hydrogen uptake with a gas buret. Samples were taken at suitable intervals and analyzed by glc. The conversion calculated from the glc analysis was in good agreement with the uptake of hydrogen. Hydrogenations were found to be zero order in alkylnaphthalene and first order in catalyst. Selective formation of tetralins was observed. Reaction rate constants were calculated from the slope of the plots of the reactant and product concentrations versus time. Assuming the reactions to be first order in hydrogen pressure (*14*) these figures were corrected for deviations of pressure from 760 mm and for the vapor pressure of the solvent. Rate constants proved reproducible within 5%.

The tetralins obtained were purified by preparative glc and identified by NMR spectroscopy. Some other alkyltetralins were prepared by lithium–ammonia reduction of the alkylnaphthalenes (*28*).

Equilibration of pairs of alkyltetralins was performed by sealing one of the isomers (20 mg) and the palladium catalyst (5 mg) under nitrogen and hydrogen (4:1) in glass ampoules. The ampoules were heated by immersion in the vapor of a boiling liquid (mesitylene bp 165.4°C, xylene bp 140.0°C, methyl isobutyl ketone bp 115.2°C, and *n*-heptane bp 98.6°C). With intervals of 1 day ampoules were opened and the contents were analyzed by glc.

RESULTS

Hydrogenation

Kinetic data for the hydrogenation of alkyl- and dialkylnaphthalenes over palladium are presented in Tables 1 and 2. All experiments have been performed in duplicate.

The values of *S* show that in 2-alkylnaphthalenes the unsubstituted ring is

TABLE 1

HYDROGENATION OF MONOALKYLNAPHTHALENES OVER PALLADIUM[a]

Alkyl substituents	k	k_{I}	k_{II}	S
None	8.6	4.3	4.3	1.00
1-Methyl	4.9	3.3	1.7	1.95
1-Ethyl	6.8	3.8	3.1	1.24
1-Isopropyl	6.2	2.0	4.1	0.48
1-*t*-Butyl	22	0.54	21	0.024
1-Cyclohexyl	2.9	1.2	1.7	0.68
2-Methyl	5.5	3.4	2.1	1.65
2-Ethyl	5.3	3.5	1.8	1.89
2-Isopropyl	5.0	3.1	1.8	1.71
2-*t*-Butyl	2.5	1.5	1.0	1.53
2-Cyclohexyl	2.7	5[b]		

[a] Temp, 80°C; atmospheric H_2 pressure; solvent AcOH; Pd, 10% on carbon; rate constants in mole sec^{-1} g $catalyst^{-1}$ 10^6.

[b] No glc separation of the tetrahydro products achieved.

TABLE 2
Hydrogenation of Dialkylnaphthalenes Over Palladium[a]

Substituents	k^a	$k_{\rm I}$	$k_{\rm II}$	S
None	8.6	4.3	4.3	1.00
2,6-Dimethyl	4.7			
2,6-Diisopropyl	6.0			
2,6-Di-*t*-butyl	10.2			
2,6-Dicyclohexyl	2.0			
2,7-Di-*t*-butyl	5.4			
1,4-Dimethyl	7.6	4.1	3.4	1.21
1,4-Diethyl	7.1	2.1	5.0[b]	0.42
1,4-Diisopropyl	17.0	1.4	15.6[c]	0.093
1,4-Di-*t*-butyl	56	<0.2	56[d]	<0.006
1,5-Dimethyl	8.2			
1,5-Diisopropyl	17.5			
1,5-Di-*t*-butyl	48			
1,8-Dimethyl	59			
1,8-Diethyl	126			
1,8-Diisopropyl	353			

[a] See legend Table 1.
[b] 47:53 mixture of *cis*- and *trans*-isomer.
[c] 64:36 mixture of *cis*- and *trans*-isomer.
[d] >99% *cis*-isomer formed.

hydrogenated preferentially. All β-substituted alkylnaphthalenes except 2,6-di-*t*-butylnapthalene hydrogenate at a lower rate than naphthalene.

1-Methylnaphthalene behaves similarly to 2-methylnaphthalene. However, going from 1-ethyl via 1-isopropyl- to 1-*t*-butylnaphthalene the picture changes. An increase in rate and a decrease in the value of S is observed. For the 1,4-dialkylnaphthalenes even more pronounced effects are observed. An increase in hydrogenation rate with increasing bulkiness of the substituents is also observed for the 1,5- and 1,8-dialkylnaphthalenes, culminating in an observed maximum of $k_{\rm rel} = 41$ for 1,8-diisopropylnaphthalene.

For a number of alkylnaphthalenes hydrogenations were performed in the temperature range 30–80°C. Arrhenius plots are shown in Fig. 1. The enthalpies of activation were found to range from 7 kcal mole^{-1} for 1,8-diisopropylnaphthalene to 10 kcal mole^{-1} for 2-methylnaphthalene. These values rule out mass transfer control (*26*) as for these processes activation enthalpies of 1–3 kcal mole^{-1} are expected (*27*).

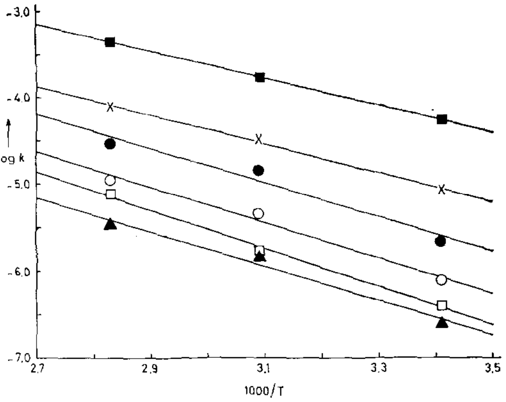


Fig. 1. Arrhenius plots for the hydrogenation of naphthalene (○), 2-methylnaphthalene (□), 1-*t*-butylnaphthalene (●), 2-*t*-butylnaphthalene (▲), 1,8-dimethylnaphthalene (×), and 1,8-diisopropylnaphthalene (■) over palladium.

The results of some deuteration experiments are given in Table 3. The tetrahydro products obtained upon deuteration of naphthalene and di-*t*-butylnaphthalenes were found to contain on the average four deuterium atoms in the saturated ring. Scrambling was more pronounced with the unsubstituted naphthalene. NMR analysis showed that neither in the (remaining) aromatic ring nor in the *t*-butyl groups had exchange occurred. 1,2-Dihydronaphthalene adopted rather cleanly two deuterium atoms whereas 1,4-dihydronaphthalene apparently underwent double bond migration prior to saturation.

Equilibration of Some Pairs of Alkyltetralins

The equilibrium constants for four selected pairs of alkyltetralins at four temperatures are presented in Table 4 together with ΔH- and ΔS-values. At the highest temperature the equilibrium was reached from both sides. Because of the low equilibrium rate at 80°C the equilibrium constants at 80°C were calculated by extrapolation. These values are listed in Table 5, along with the values of S found upon hydrogenation at 80°C for the corresponding alkylnaphthalenes.

TABLE 3
ANALYSIS OF ALKYLTETRALINS OBTAINED BY DEUTERATION OF NAPHTHALENES[a]

Reactant hydrocarbon		Naphthalene	1,4-Di-*t*-butyl	1,5-Di-*t*-butyl	2,6-Di-*t*-butyl	1,2-Dihydro[b]	1,4-Dihydro[b]
Mass analysis (%)	d_0	1	—	—	—	—	7
	d_1	2	1	1	—	9	11
	d_2	8	4	7	2	90	42
	d_3	22	23	31	19	1	40
	d_4	32	67	58	63	—	—
	d_5	26	3	2	13	—	—
	d_6	9	2	1	3	—	—
	$\bar{d}$	4.0	3.7	3.7	4.0	1.9	2.2
NMR analysis No. of D in position	1 and 4	2.3	2.0	2.0	2.0	1.0	0.6
	2 and 3	1.7	2.0	2.0	2.0	1.0	1.4
	arom.	0.1	0.1	0.1	0.1	0.1	0.1

[a] Deuterations carried out using 10% Pd/C in *n*-heptane at 80°C and atmospheric pressure; complete conversion.

[b] At 25°C.

TABLE 4
EQUILIBRATION OF SOME PAIRS OF ALKYLTETRALINS

Alkyltetralins		Values of K = I/II at °K					ΔH (kcal mole^{-1})	ΔS (cal mole^{-1} degree^{-1})
I	II	371.8[a]	388.4[a]	411.9[a]	438.6[a]	438.6[b]		
1-Methyl-	5-Methyl-	7.99	7.60	6.40	5.70	5.71	−1.7	−0.3
1-*t*-Butyl-	5-*t*-Butyl	0.107	0.115	0.130	0.152	0.153	+1.7	+0.2
2-Methyl-	6-Methyl-	4.30	3.76	3.31	3.18	3.19	−1.5	−1.1
2-*t*-Butyl-	6-*t*-Butyl-	8.34	7.39	7.00	6.33	6.05	−1.3	+0.8

[a] Starting from tetralins I, II, I, and I, respectively.

[b] Starting from tetralins II, I, II, and II, respectively.

TABLE 5
SELECTIVITY IN HYDROGENATION AND EQUILIBRIUM FOR SOME PAIRS OF ALKYLTETRALINS AT 80°C

Alkyltetralins		Equilibrium	Product ratio S upon hydrogenation
II	I	K	on Pd
1-Methyl-	5-Methyl-	9.1	1.95
1-*t*-Butyl-	5-*t*-Butyl-	0.094	0.024
2-Methyl-	6-Methyl-	4.61	1.65
2-*t*-Butyl-	6-*t*-Butyl-	8.93	1.53

Competition Experiments

Several mixtures of reactants were hydrogenated and the reactions followed by sampling and glc analysis. The equilibrium constants K_{AB} for the equilibrium:

$$A_{sol} + B_{ads} \leftrightarrows A_{ads} + B_{sol}$$

were calculated according to Rader and Smith (*15*). The results are summarized in Table 6.

For comparison some alkylnaphthalenes were hydrogenated over platinum and rhodium catalysts. The kinetic data obtained are shown in Table 7 together with the figures for the palladium catalyst.

DISCUSSION

General Considerations

In hydrogenation of alkylnaphthalenes over palladium selective formation of tetralins is observed. This selectivity is

TABLE 6
THE ADSORPTION EQUILIBRIUM CONSTANTS DETERMINED FROM COMPETITIVE HYDROGENATIONS

Competition between A	Competition between B	K_{AB}
Naphthalene	2-Methylnaphthalene	2.3
	2-Ethylnaphthalene	2.2
	2-Isopropylnaphthalene	3.3
	2-*t*-Butylnaphthalene	4.1
	1-Methylnaphthalene	1.6
	1-Ethylnaphthalene	2.6
	1-Isopropylnaphthalene	2.8
	1-*t*-Butylnaphthalene	14
	1,4-Di-*t*-butylnaphthalene	140
	1,8-Diisopropylnaphthalene	1.1
1-*t*-Butylnaphthalene	2-*t*-Butylnaphthalene	0.4
2,6-Di-*t*-butylnaphthalene	2,7-Di-*t*-butylnaphthalene	1.1

governed by (i) the stronger adsorption of the naphthalenes and (ii) the lower hydrogenation rate of the tetralins.

The adsorption of naphthalenes on the catalyst surface may be of the π-complex type (*16–22*). In Fig. 2 the geometry of a naphthalene molecule on the (111) plane of palladium is shown. Two palladium atoms might be involved in the surface complex.

Under our conditions the catalyst has the β-palladium hydride constitution (*23*), and most of the octahedral holes of the palladium structure will be filled with absorbed hydrogen. The addition of hydrogen to the hydrocarbon is assumed to occur exclusively from the surface. The process is supposed to start at an α-position and this step may be rate determining because the loss of resonance energy is substantial. Subsequent addition can take place in the order C_2, C_3, C_4, retaining after each successive addition the maximum conjugated system, or in the order C_4, C_3, C_2.

Intermediate 1,2- or 1,4-dihydro products may desorb from the surface. In the case of the 1,4-dialkylnaphthalenes this may have stereochemical consequences as desorbed 1,2-dihydro-1,4-dialkylnaphthalenes can readsorb with the other side on the catalyst surface yielding *trans*-1,4-

TABLE 7
HYDROGENATION OF 1,8-DIALKYLNAPHTHALENES OVER Pd, Pt, AND Rh

Reactant hydrocarbon	10% Pd/C $k \times 10^6$ [a]	5% Pt/C[b] $k \times 10^6$	5% Rh/C[b] $k \times 10^6$
Naphthalene	3.9	2.1	1.4
1,8-Dimethylnaphthalene	26.6	10.1	8.7
1,8-Diethylnaphthalene	83.5	14.2	8.2
1,8-Diisopropylnaphthalene	142	18.4	7.1

[a] k in mole sec^{-1} g $catalyst^{-1}$, in acetic acid at 50°C and atmospheric pressure.

[b] Deviation of zero order kinetics; k calculated as zero order for the first part of the reaction.

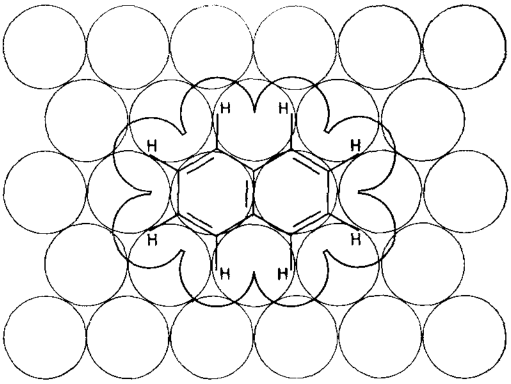


FIG. 2. Naphthalene on the (111) plane of palladium.

dialkyltetralins. These products are also formed if an adsorbed 1,2-dihydro-1,4-dialkylnaphthalene undergoes a roll-over (*24*) on the surface. The decrease in percentage *trans*-1,4-dialkyltetralin (Table 2) going from ethyl to *t*-butyl substitution may be due to a more pronounced 1,4-hydrogen addition caused by the increasing *peri* strain (see below) and/or to suppression of roll-over processes by the bulky alkyl substituents.

The tetralins obtained upon deuteration of naphthalene and 1,4-dihydronaphthalene show an excess of deuterium at the benzylic positions (Table 3) in contrast to the deuteration products of 1,2-dihydronaphthalene and of di-*t*-butylnaphthalenes. Moreover, in the di-*t*-butyltetralins the deuterium distribution is rather narrow, suggesting that here simple *cis*-addition of four hydrogen atoms predominates. The absence of deuterium in the aromatic part of the tetralins excludes reversible dissociative adsorption of naphthalenes and indicates that the first attack generally decides which ring is reduced. Kinetic control in the hydrogenation of alkylnaphthalenes also is evident from a comparison of selectivity values of hydrogenation and equilibrium constants of pairs of alkyltetralins (Table 5).

The Hydrogenation of β-Substituted Alkylnaphthalenes

As might be expected the relative strength of adsorption of alkylnaphthalenes decreases on going from methyl to *t*-butyl substitution (Table 6). If a reactant is less strongly adsorbed the energy of the initial state is increased. However, the substituent for steric reasons may also increase the energy of the transition state of hydrogenation. The balance between both factors will result in a higher or lower rate than naphthalene.

The unexpectedly high rates of hydrogenation of 2,6- and also 2,7-di-*t*-butylnaphthalene are attributed to the weak adsorption of these hydrocarbons. In fact, the adsorption of 2,6-di-*t*-butylnaphthalene is so weak that no K_{AB} value could be measured in a competition experiment with naphthalene: 2,6-di-*t*-butylnaphthalene was not measurably hydrogenated before all of the naphthalene was converted into tetralin.

For the 2-alkylnaphthalenes a gradual decrease in adsorption strength was found (Table 6). Apparently the decrease in k is mainly a result of an increase in steric strain in the transition state. Furthermore, the decrease in k will partly originate from the increased catalyst surface area occupied by an alkylnaphthalene molecule.

Hydrogenation of the unsubstituted ring of the 2-alkylnaphthalenes is slightly preferred over hydrogenation of the substituted ring. This is in line with the stabilities of the tetralins but Table 5 shows that for 2-methyl- and 2-*t*-butylnaphthalene the product distributions are far from the equilibrium values.

The Hydrogenation of α-Substituted Alkylnaphthalenes

α-Alkylnaphthalenes differ rather strongly from the β-isomers (Tables 1 and 2) in hydrogenation behavior. This must be due to the strain between the 1-alkyl group and the 8-hydrogen atom or *peri* hydrogen, i.e., the *peri* strain. As an example, the substantial van der Waals overlap in 1-*t*-butylnaphthalene is illustrated in Fig. 3.

The observed hydrogenation phenomena can be understood when accepting that (i) in the transition state the *peri* strain is released, at least partially, resulting in an

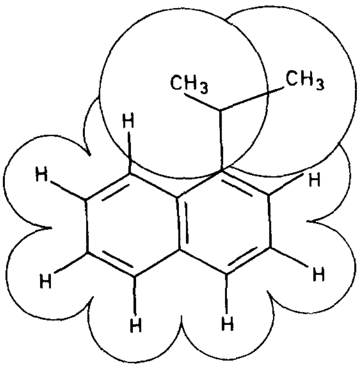
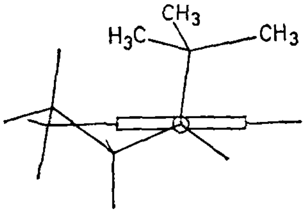


FIG. 3. 1-*t*-Butylnaphthalene with van der Waals spheres.

increased reaction rate for the strained molecules, and (ii) the *peri* strain is released to a greater extent in the transition state for hydrogenation of the substituted ring than in the transition state for hydrogenation of the unsubstituted ring, resulting in a low value of S.

The second assumption is supported by the equilibration of some pairs of alkyltetralins (Table 4). Contrary to the other pairs, for 1- and 5-*t*-butyltetralin the isomer with the *t*-butyl group in the saturated ring is the most stable. Models show that the preferred conformation of 1-*t*-butyltetralin probably has the *t*-butyl group in a *pseudo* axial position:



This is supported by literature data stating that in 6-*t*-butyl-1-phenylcyclohexene the *t*-butyl group occupies a *pseudo* axial position (*25*).

In the hydrogenation of 1-*t*-butylnaphthalene the first hydrogen atom is added from below in such a way that in the transition state the *peri* strain is released most effectively. This will be at the 1-position: steric hindrance will easily be overcome by release of strain as the *t*-butyl group swings to the *pseudo* axial position. The same holds for the other 1-alkylnaphthalenes though for methyl, ethyl, and isopropyl the *peri* strain is much smaller. The values of S below unity for 1-isopropyl- and 1-cyclohexylnaphthalene suggest that for these molecules upon adsorption a *peri* strain is introduced by rotation of the substituent.

The differences in rate of hydrogenation and in S found for the 1,4-dialkylnaphthalenes can be explained in the same way. As the *peri* strain acts twice in these compounds, the effects are more pronounced.

For symmetry reasons the 1,5-dialkylnaphthalenes give one product and only an effect on the rate of hydrogenation can be observed. The release of *peri* strain in a 1,5-dialkylnaphthalene upon hydrogenation will be the sum of the release in *peri* strain for the formation of a 1-alkyltetralin and a 5-alkyltetralin from a 1-alkylnaphthalene. This results in a relative rate which, at least for 1,5-diisopropyl- and 1,5-di-*t*-butylnaphthalene, is somewhat higher than $k_{\text{II rel}}$ for the corresponding 1-alkylnaphthalenes.

As in the 1,8-dialkylnaphthalenes the *peri* position is still more crowded, a further increase in rate is observed (Table 2). Upon hydrogenation of acenaphthene no strain is released, resulting in a low reaction rate. It may be noted that 1,8-diisopropylnaphthalene is rather strongly adsorbed (Table 6). It may be suggested that upon adsorption of this molecule the *peri* strain is partially released by bond lengthening in the aromatic nucleus.

Hydrogenation Over Platinum and Rhodium

The effects discussed above are rather specific for palladium. Over platinum and rhodium catalysts the values of k are far less affected by steric crowding in the reactant molecules (Table 7). For hydrogenation of 1-*t*-butylnaphthalene over platinum, rhodium, and palladium catalysts the values of S are 0.42, 0.71, and 0.024, respectively.

REFERENCES

1. WEITKAMP, A. W., *J. Catal.* **6**, 431 (1966).

2. WEITKAMP, A. W., BANAS, E. M., AND JOHNSON, G. D., *Amer. Chem. Soc. Div. Petrol. Chem. Prepr.* **7**, C-139 (1962).

3. WEITKAMP, A. W., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 18, p. 1. Academic Press, New York, 1968.

4. PAVLOVA, K. A., AND KALECHITS, J. V., *Tr. Vost.-Sib. Filiala, Akad. Nauk SSSR, Ser. Khim.* **1961**, 61; *Chem. Abstr.* **57**, 7185d (1962).

5. BAILEY, A. S., SMITH, J. C., AND STAVELEY, C. M., *J. Chem. Soc., London* **1956**, 2731.

6. PAPA, D., AND SCHWENK, E., *U. S. Pat.* 2,475,718; *Chem. Abstr.* **43**, 7501i (1949).

7. Fieser, L. F., and Jones, R. N., *J. Amer. Chem. Soc.* **60,** 1940 (1938).
8. Levy, G., *C. R. Acad. Sci.* **192,** 1397 (1931).
9. Levy, G., *C. R. Acad. Sci.* **193,** 174 (1931).
10. Kalechits, J. V., Nakhmanovich, A. S., and Kazantseva, V. M., *Kinet. Katal.* **4,** 395 (1963).
11. Kalechits, J. V., and Nakhmanovich, A. S., *Reakts. Zhidk. Fare, Tr. Vses. Konf.* 166 (1962); *Chem. Abstr.* **60,** 10497f (1964).
12. van Bekkum, H., Nieuwstad, T. J., van Barneveld, J., and Wepster, B. M., *Tetrahedron Lett.* **1967,** 2269.
13. van Bekkum, H., Nieuwstad, T. J., van Barneveld, J., Klapwijk, P., and Wepster, B. M., *Recl. Trav. Chim. Pays-Bas* **88,** 1028 (1969).
14. Sokol'skii, D. V., "Hydrogenation in Solutions." Israel Program for Scientific Translations, Jerusalem, 1964.
15. Rader, C. P., and Smith, H. A., *J. Amer. Chem. Soc.* **84,** 1443 (1962).
16. Garnett, J. L., and Sollich-Baumgartner, W. A., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 16, p. 95. Academic Press, New York, 1966.
17. Rooney, J. J., and Webb, G., *J. Catal.* **3,** 488 (1964).
18. Gault, F. G., Rooney, J. J., and Kemball, C., *J. Catal.* **1,** 255 (1962).
19. Rooney, J. J., *J. Catal.* **2,** 53 (1963).
20. Völter, J., *J. Catal.* **3,** 297 (1964).
21. Garnett, J. L., and Sollich, W. A., *J. Catal.* **2,** 350 (1963).
22. Shopov, D., and Andreev, A., *J. Catal.* **6,** 316 (1966).
23. Scholten, J. J. F., and Konvalinka, J. A., *J. Catal.* **5,** 1 (1966).
24. Burwell, R. L., *Accounts Chem. Res.* **2,** 289 (1969).
25. Garbisch, E. W., Jr., *J. Org. Chem.* **27,** 4249 (1962).
26. Acres, G. J. K., and Cooper, B. J., *J. Appl. Chem. Biotechnol.* **22,** 769 (1972).
27. Satterfield, C. N., "Mass Transfer in Heterogeneous Catalysis," pp. 5–9. MIT Press, London, 1970.
28. Nieuwstad, T. J., and van Bekkum, H., *Recl. Tran. Chim. Pays-Bas* **91,** 1069 (1972).