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peri EFFECT IN THE HYDROGENATION OF 1-t-BUTYL- AND 1,4-DI-t-BUTYLNAPHTHALENE ON PALLADIUM

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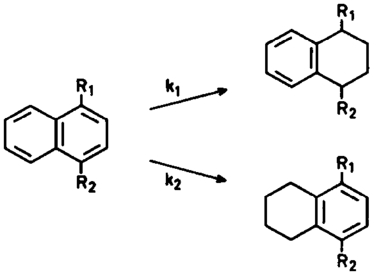
peri Effects on reactivity have been reported for several substitution and side chain reactions of α-substituted naphthalenes (1). So far, studies dealing with these phenomena did not include reactions involving addition to the ring system.

We have investigated the liquid phase hydrogenation of some 1-alkyl- and 1,4-dialkylnaphthalenes on palladium. Experiments were carried out in a stirred glass reactor with a thermostat jacket. Kinetics were studied by GLC analysis. Products were isolated by preparative GLC and identified by NMR.

Reactions were found to be zero order in substrate and followed the scheme



TABLE

Hydrogenation [a] of 1-alkyl- and 1,4-dialkylnaphthalenes

R_1	R_2	k [b]	k_1 [c]	k_2 [c]
H	H	8.6	1.00	1.00
Me	H	5.0	0.40	0.76
Me	Me	7.7	0.80	0.98
t-Bu	H	22.2	5.0	0.12
t-Bu	t-Bu	57	13.3	< 0.01

a. In acetic acid at 80° ; 1 atm H_2; palladium (10% on C) as the catalyst.

b. mole sec^{-1} g $catalyst^{-1}$ x 10^6.

c. relative to naphthalene.

1-Methyl- and 1,4-dimethylnaphthalene were found to be hydrogenated at a lower rate than naphthalene (see Table). The 2-alkylnaphthalenes behaved similarly, e.g. for 2-t-butylnaphthalene relative reaction rates of $k_1 = 0.24$ and $k_2 = 0.34$ were observed. This decrease of the rate of hydrogenation by alkyl substituents is in harmony with investigations in the benzene series (2,3). Secondly, some preference for hydrogenation of the unsubstituted ring was observed, in line with the idea (4) of preferred initial attack at unsubstituted positions of benzene nuclei.

The α-t-butyl substituted compounds were found to deviate strongly in showing (i) an increased rate of hydrogenation and (ii) a highly selective hydrogenation of the substituted ring.

Release of peri strain in the transition state of hydrogenation is assumed to be mainly responsible for the high value of k_1. More precisely, hydrogenation of the substituted ring - with transition into a neopentylbenzene system - releases steric strain more effectively than hydrogenation of the unsubstituted ring - with transition into a 2-t-butyltoluene system. Moreover, the loss of chemisorption energy should be less in the former transition state of hydrogenation than in the latter.

When hydrogenating a mixture of naphthalene and 1,4-di-t-butylnaphthalene we observed a selective hydrogenation of naphthalene in spite of the higher inherent rate of the competitor. Clearly, naphthalene is the more strongly adsorbed species and monopolizes the palladium surface in the first stage of the hydrogenation.

1,4-Di-t-butylnaphthalene, m.p. 62-62.5°, was synthesized by a six step synthesis starting from 1,4-dibromonaphthalene. We consider the literature (5), mentioning m.p. 132°, to be in error. The NMR spectrum of 1,4-di-t-butylnaphthalene in carbontetrachloride at about 40° shows the t-butyl protons (singlet) at $\delta = 1.63$ ppm and the 2,3-protons (singlet) at $\delta = 7.32$ ppm; the 5,8- and 6,7-protons form an AA'XX'-system, $\delta_A = 8.43$ ppm and $\delta_X = 7.35$ ppm (δ-values from TMS as an internal reference). The considerable downfield shift found for the peri protons is noteworthy (6).

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