

SELECTIVE POISONING OF PALLADIUM-CATALYSED HYDROGEN-EXCHANGE REACTIONS

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CARBON monoxide has been shown (1) to selectively poison the exchange of *p*-xylene with deuterium gas over evaporated nickel films, the rate of exchange of the ring hydrogens being reduced more than that of the methyl hydrogens. We report selective pyridine poisoning of the palladium-catalysed hydrogen exchange of some benzene derivatives with deuterium oxide, and selective exchange of the same compounds with deuterium oxide over unpoisoned nickel on kieselguhr. When the degree of selectivity is sufficiently high the convenience of these reactions makes them well suited for the preparation of compounds labelled with deuterium or tritium in specific positions.

In typical experiments 10% palladium on charcoal (0.1 g) pre-activated with hydrogen, the substrate (0.3 ml), and deuterium oxide (2 ml) were agitated at 99° for several hours in evacuated sealed tubes. Under these conditions all the hydrogens of benzene, toluene, the xylenes, and ethylbenzene exchanged extensively, a result consistent with that of Hirota and Ueda (2) for the exchange of *p*-xylene under similar conditions. In experiments in which pyridine (0.02 ml) was added to the system, ring hydrogens ortho to alkyl groups exchanged much more slowly than the rest. When the deuterium oxide was replaced by pyridine- $d_5$ , exchange of all the ring hydrogens was much slower than that of the alkyl hydrogens. Much slower exchange of the ring than of the alkyl hydrogens also occurred when deuterium oxide was used with a 20% nickel-on-kieselguhr catalyst, which is consistent with the work of

TABLE 1

## Isotopic Composition of Exchanged Materials

Substrate	Catalyst	D Source	Re-action time (hr.)	Average no.* of D atoms/molecule in					H atoms †
				CH <sub>3</sub>	CH <sub>2</sub>	ortho	meta+para	all ring	
Ethylbenzene	Pd	D <sub>2</sub> O	4	2.58	1.75	-	-	3.38	0
Ethylbenzene	Pd + C <sub>5</sub> H <sub>5</sub> N	D <sub>2</sub> O	3.5	2.63	1.78	-	-	2.15	2
Benzoic acid from oxidation of exchanged ethylbenzene (above)				-	-	0.22	2.06	2.28	-
Ethylbenzene	Pd	C <sub>5</sub> D <sub>5</sub> N	3.5	1.42	1.65	-	-	0.02	5
Ethylbenzene	Ni	D <sub>2</sub> O	3.5	1.57	1.17	-	-	0.05	5
Ethyl benzoate	Pd	D <sub>2</sub> O	5	0.01	0.04	0.16	2.70	2.86	5-7
Ethyl benzoate	Pd + C <sub>5</sub> H <sub>5</sub> N	D <sub>2</sub> O	3.5	-0.02	0.03	-0.02	2.07	2.05	7
				benzylic CH <sub>3</sub>	ortho to CH <sub>3</sub>	ortho to CO <sub>2</sub> Et	ethyl CH <sub>2</sub>	ethyl CH <sub>3</sub>	
Ethyl <i>p</i> -toluate	Pd	D <sub>2</sub> O	3.5	2.80	0.56	0.15	0.06	0.13	5-7
Ethyl <i>p</i> -toluate	Pd + C <sub>5</sub> H <sub>5</sub> N	D <sub>2</sub> O	3.5	2.81	0.01	0.01	0.06	0.01	9
Ethyl <i>p</i> -toluate	Ni	D <sub>2</sub> O	19	2.52	-0.03	-0.03	0.09	-0.02	9

\* Calculated from the distribution of residual protium determined by p.m.r. and the average deuterium content determined mass spectrometrically.

† Number of H atoms with retarded exchange rates, deduced from the pattern of the mass-spectrometrically determined relative abundances of deuterated species.

Hirota and Ueda (2) on the nickel-catalysed exchange of *p*-xylene with deuterium oxide.

In experiments (Table 1) using the palladium catalyst with ethyl benzoate and ethyl *o*-, *m* and *p*-toluates as substrates the hydrogens ortho to a carbethoxy group exchanged more slowly than the other ring hydrogens even in the absence of pyridine. Addition of pyridine reduced the rate of exchange of hydrogens ortho to a carbethoxy group as well as that of hydrogens ortho to a methyl group. The carbethoxy hydrogens exchanged very slowly if at all. The only hydrogens to exchange extensively with deuterium oxide over nickel on kieselguhr were those in the benzylic methyl groups of the ethyl toluates.

Slower exchange of the ortho than of the other ring hydrogens has been reported in the platinum-catalysed exchange of sodium benzoate (3), and the halobenzenes (4) with deuterium oxide, though in these cases the selectivity was not as great as in the present work, and in the exchange of alkylbenzenes with deuterium gas over evaporated nickel films (5).

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