

"DEUTERATED" RANEY NICKEL: DEUTERATION (REDUCTION) OF ALKENES, CARBONYL COMPOUNDS AND AROMATIC RINGS. PROTON-DEUTERIUM EXCHANGE OF "ACTIVATED" ALIPHATIC AND AROMATIC RING HYDROGENS.

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In the absence of deuterium gas, the reaction of deuterated Raney nickel with benzene derivatives, carbonyl compounds, alkenes and activated methylene groups gave either fully deuterated (reduced) products or led to hydrogen-deuterium exchange.

In the absence of gaseous hydrogen, Raney nickel has been known for some time to reduce alkenes and alkynes and to deoxygenate aldehydes and ketones conjugated to aromatic rings.¹ A majority of these investigations employed an alcohol as a hydrogen donor although the need for such a donor was questionable.^{1a}

Partial aromatic hydrogen-deuterium (or tritium) exchange has also been observed when the substrate was heated with a catalyst such as platinum or Raney nickel in deuterium oxide (or tritiated water).² Recently, deuterated benzoic acids³ and phenols⁴ were synthesised by reductive dehalogenation using Raney Cu-Al alloy in alkaline deuterium oxide. Again, some aromatic hydrogen-deuterium exchange was observed as a side reaction.

This communication reports preparative scale (1) exchange of activated aliphatic hydrogens for deuterium (2) reduction (deuteration) of alkenes and carbonyl compounds (3) aromatic hydrogen-deuterium exchange (4) reduction of aromatic rings to fully deuterated cyclohexanes. These reactions were performed under mild conditions and in the absence of deuterium gas or a deuterium donor.

Reactions Conditions⁵

A stirred solution of the substrate (0.5 g) was refluxed for 18 hrs with deuterated Raney nickel⁶ (2 ml wet). For aromatic hydrogen-deuterium exchange, the temperature was kept around 70°. The solvent (5 ml) was tetrahydrofuran (rarely dioxan) or heavy water (carboxylic acids and phenols were deuterated as sodium salts). The product was isolated in the usual manner after filtration to remove the Raney nickel. Yields were 70% or above.

Deuterium Exchange of Benzylic Protons and Active Methylenes

Diphenylmethane gave 1,1-dideuterodiphenylmethane. However, some aromatic hydrogen-deuterium exchange took place. Reduction of trans-stilbene gave 1,2-diphenyl-1,1,2,2-tetradeuteroethane (and not the expected dideuterated material).

Ethyl benzoylacetate was reduced to ethyl 2,2,3,3-tetradeutero-3-phenylpropionate. In the latter two cases, aromatic hydrogen-deuterium exchange was minimal.

Reduction of Alkenes

As mentioned above, trans-stilbene gave 1,2-diphenyl-1,1,2,2-tetradeuteroethane. Sodium cinnamate (in heavy water at 70°) gave 2,2,3,3,2',3',4',5',6'-nonadeuterophenylpropanoic acid (I). (The aromatic hydrogens were exchanged under these conditions). Cinnamaldehyde gave a deuterated material (i.r., n.m.r.) the mass spectrum of which showed that it was polymeric. Maleic acid (at 101°) gave 2,2,3,3-tetradeuteriosuccinic acid.

Reduction of Carbonyl Compounds

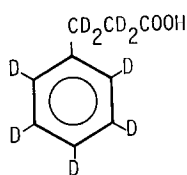
Benzophenone reacted smoothly to give 1,1-dideuterodiphenylmethane with some ring hydrogen-deuterium exchange. Ethyl benzoylacetate was reduced to ethyl 2,2,3,3-tetradeutero-3-phenylpropionate. The reaction of cyclohexanone with ("undeuterated") Raney nickel gave low yields of phenol while camphor was recovered unchanged even after 24 hours refluxing dioxan.

Aromatic Hydrogen/Deuterium Exchange

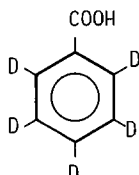
As mentioned above, the reaction of sodium cinnamate with deuterated Raney nickel at 70-80° gave nonadeuterophenylpropanoic acid (I). Similarly, sodium benzoate gave pentadeuterobenzoic acid (II) and nicotinic acid gave 2,4,5,6-tetradeuteronicotinic acid.

Reduction of Aromatic Nucleus

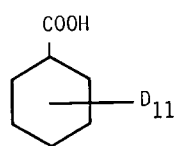
The refluxing of sodium benzoate with "deuterated" Raney nickel in heavy water gave the fully deuterated (D₁₁) cyclohexanecarboxylic acid (III). Under the same conditions, sodium phenoxide gave fully deuterated (D₁₁) cyclohexanol, contaminated with some (approx. 10%/o) cyclohexanone.



(I)



(II)



(III)

References

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