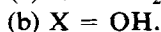# Substitutive Aromatization
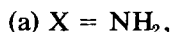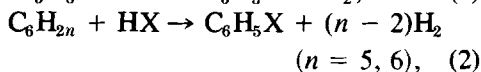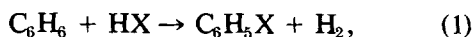
The most common methods for preparing aromatic compounds involve electrophilic substitution on a preformed aromatic ring (*1*). Because of the relative unavailability of the electrophiles NH_2^+ and OH^+, such large-volume industrial commodities as aniline and phenol are produced by multistep procedures (*2*). The direct interaction of benzene and water or ammonia to produce substituted aromatic compounds and hydrogen (Eqs. (1a) and (1b)) has a positive free energy change at all temperatures (*3*).

Aromatic hydrocarbons can be manufactured by catalytic dehydrogenation of alicyclic or aliphatic precursors with Group VIII metal catalysts (*4*). Phenol can be produced by dehydrogenating preformed oxygenated cyclohexanes (*5*), but the direct synthesis of substituted aromatic compounds from nonaromatic hydrocarbons and nucleophiles has been neglected (*6, 7*).

We have discovered catalytic reactions (Eq. (2)) by which substituted aromatics can be prepared directly from nucleophiles and nonaromatic precursors such as cyclohexanes and cyclohexenes. Ammonia gives anilines; water gives phenol. The reactions involve dehydrogenation and are carried out without added oxidizing agents (*8, 9*).

$$C_6H_6 + HX \rightarrow C_6H_5X + H_2, \qquad (1)$$
$$C_6H_{2n} + HX \rightarrow C_6H_5X + (n - 2)H_2$$
$$(n = 5, 6), \quad (2)$$
$$\text{(a) } X = NH_2,$$
$$\text{(b) } X = OH.$$

Reactions (2a) and (2b) are endothermic (ΔH) by 60–70 kcal/mole, but the equilibrium constants become more favorable with increasing temperature, crossing unity at about 750°K. Reactions (2a) and (2b) are always less favorable than the simple formation of benzene from cyclohexane.

Some catalysts for phenol synthesis are given in Table 1. Remarkable synergistic effects occur when certain pairs of oxides such as zinc–vanadium and zinc–titanium are used, suggesting dual-function catalysts. Hydrocarbon by-products include benzene, which can be recycled, and methylcyclopentane, which is the thermodynamically favored C_6H_{12} isomer at high temperature. In the ammonia reaction, benzonitrile is a major by-product with more acidic catalysts, but it can be essentially eliminated by including water in the feed (*10*). About 0.1% of the carbon feed is deposited as coke with our preferred catalysts, and this by-product limits the short-term catalyst life to less than 12 hr. The catalysts can be repeatedly regenerated by careful air oxidation.

Methylcyclohexane and ammonia give comparable amounts of aniline, toluidines, and benzonitrile with zinc–titania catalysts. The three toluidines are formed in the ratio

TABLE 1

Catalysts for Phenol Synthesis

Catalyst	Conditions[a]	Rate of phenol formation (mg/g cat/hr)	Temp. (°K)
V_2O_5	a	4	775
TiO_2	a	5	825
ZnO	a	0.2	800
Zn:V:O	b	11	800
Zn:2V:O	b	63	800
Zn:2.5V:O	b	100	800
Zn:4Ti:La:O	a	36	825
Zn:2V:O	c	200	800

[a] Conditions: (a) 6 ml/hr each cyclohexane and water, 20 ml/min N_2 carrier gas, 3 cm³ catalyst; (b) 5.6 ml/hr cyclohexane, 3.6 ml/hr water, 3 cm³ catalyst; (c) same as b, except cyclohexene is the hydrocarbon.
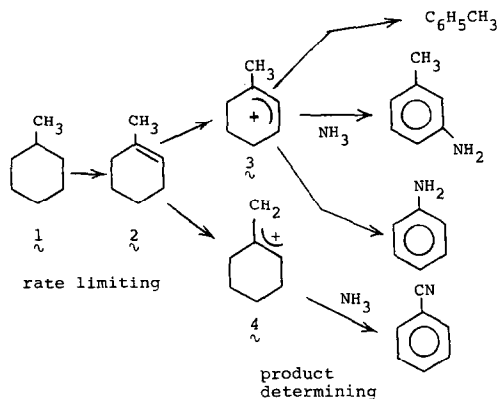
FIG. 1. Mechanism of substitutive aromatization.

$o:m:p = 22:55:22$. A possible mechanism is given in Fig. 1. Initial dehydrogenation of cyclohexane **1** gives first cyclohexene **2**. Cyclohexene reacts faster than cyclohexane suggesting that the initial dehydrogenation is rate limiting. The toluidine isomer distribution suggests the intermediacy of allylic carbenium ions such as **3** and **4** which are attacked by the nucleophile in the product-determining step. Simple aromatization competes with the nucleophilic substitution at low nucleophile concentrations.

A typical catalyst can be prepared by neutralizing a dilute, aqueous solution of titanium tetrachloride, zinc nitrate, and zirconium oxychloride in the mole ratio 50:2.5:1 to pH 7 with ammonia. The gel is digested, filtered, washed thoroughly with water, dried, and finally calcined at 825°K overnight. Passing cyclohexane, ammonia, and water in the mole ratio 53:36:11 over the above catalyst at 775°K and 1 atm with a space velocity of 3000 hr^{-1} gives an exit stream containing 3 mole% aniline. The initial catalyst productivity is 76 mg aniline per gram of catalyst per hour. The yield of aniline taking into account the recyclable by-products benzene and cyclohexene is 85%.

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FRANK J. WEIGERT[1]
THOMAS W. DEL PESCO

Central Research and Development Department
Chemicals and Pigments Department
Experimental Station
E. I. Du Pont de Nemours and Company
Wilmington, Delaware 19898

[1] To whom correspondence should be addressed.