2-Methoxymethylpyridine N-Oxide.—Twenty milliliters (27.9 g, 0.227 mole) of 2-methoxymethylpyridine in 130 ml of acetic acid and 20 ml of 30% hydrogen peroxide (0.175 mole) was heated at 80° for 18 hr. Another 15 ml (0.14 mole) of 30% hydrogen peroxide was added and heating was continued for 8 more hr. The solvent was removed at reduced pressure and the residual oil was distilled under vacuum. The fraction distilling between 116 and 121° (3.2 mm) was collected and redistilled giving 6.84 g (31%) of pale yellow 2-methoxymethylpyridine N-oxide: bp 127–129° (3 mm), n^{22}D 1.5690. Nmr in deuterium oxide showed aromatic hydrogens at τ 1.84–3.02 (complex); methylene, 5.52 (singlet); and methoxyl, 6.66 (singlet). Ultraviolet showed λ_{max}^{EtOH} 261 mμ (ε 10,600). Physical constants and nmr spectrum were unchanged following redistillation.[15] *Anal.* Calcd for $C_7H_9NO_2$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.59; H, 6.63; N, 10.51.

Pyridine-4-carboxaldehyde Oxime.[17]—A solution of 121 mg (1.75 mmoles) of hydroxylamine hydrochloride and 283 mg (2.26 mmoles) of 4-hydroxymethylpyridine N-oxide in 10 ml of 1 *N* sodium hydroxide was heated on a steam bath. A few needles formed after a few hours. When no increase in precipitate was observed after 16 hr, an additional 100 mg (1.45 mmoles) of hydroxylamine hydrochloride was added. No increase in precipitate resulted. After 24 hr the solution was cooled; no further precipitate separated. However on neutralizing with acetic acid a copious precipitate of fine needles separated immediately. Crude pyridine-4-carboxaldehyde oxime, (123 mg, 45% yield) was collected and recrystallized from water, mp 131°.

Pyrazine-2-carboxaldehyde 4-Oxide Phenylhydrazone.—A solution of 154 mg (0.83 mmole) of 2-acetoxymethylpyrazine di-N-oxide[14] and 0.083 ml (0.83 mmole) of phenylhydrazine in 20 ml of water plus 0.32 ml (0.32 mmole) of 1 *N* sodium hydroxide was heated under a nitrogen atmosphere on a steam bath. A total of 1.02 ml of 1 *N* sodium hydroxide was added in portions over a 76-hr period. The yellow, crystalline phenylhydrazone (47 mg, 26% yield) which had precipitated during the first 46 hr was collected. No more precipitate formed on further heating. An analytical sample of pyrazine-2-carboxaldehyde-4 oxide phenylhydrazone (mp 239–341° dec) was prepared by two recrystallizations from ethanol: λ_{max}^{EtOH} 234 mμ (ε 16,200), 254 (17,200), 387 (24,500). *Anal.* Calcd for $C_{11}H_{10}N_4O$: C, 61.67; H, 4.71; N, 26.15; Found: C, 61.45; H, 4.69; N, 26.03.

2-Hydroxymethylpyridine.—Twenty-five milliliters of acetoxymethylpyridine prepared by the method of Boekelheide and Linn[3] was added to 50 ml of concentrated hydrochloric acid, and the mixture was heated at reflux for 3 hr. Solvent was then removed by evaporation. The residue was extracted with 90 ml of chloroform. The chloroform solution was shaken vigorously with potassium carbonate paste and filtered. Solvent was removed, and the residue was distilled. A 5-ml fraction of hydroxymethylpyridine was collected between 105 and 111° (25 mm) [lit.[18] bp 112–113° (16 mm)].

Detection of Aldehyde.[5]—The nmr spectrum of neat 2-hydroxymethylpyridine showed in addition to the expected signals (aromatic hydrogen, τ 1.45–2.76; methylene, 5.14) a signal at τ 0.7 attributed to the aldehydic hydrogen of pyridine-2-carboxaldehyde, estimated to be present in concentration of 1–2%. The infrared spectrum had a very weak carbonyl absorption at 1713 cm^{-1}. Heating 109 mg (1.0 mmole) of this preparation of hydroxymethylpyridine with 0.10 ml (0.98 mmole) of phenylhydrazine briefly in 5 ml of water gave 3.2 mg, 1.6% yield, of pyridine-2-carboxaldehyde phenylhydrazone identified by mixture melting point. No further phenylhydrazone was detected when reaction times were extended up to 5 days.

Registry No.—2-Methoxymethylpyridine N-oxide, 7727-04-0; pyridine-4-carboxaldehyde oxime, 696-54-8; pyrazine-2-carboxaldehyde 4-oxide phenylhydrazone, 7727-06-2; **2**, 7727-07-3; **11**, 7757-39-3; **6**, 7727-08-4; **10**, 7734-05-6; **14**, 7727-09-5; **12**, 7727-06-2.

(15) The 2-methoxymethylpyridine was characterized by the following physical constants: bp 76–78° (18 mm),[16] n^{22}D 1.4978. Nmr in deuterium oxide showed aromatic hydrogens at τ 1.68–3.20 (complex), methylene 5.62 (singlet), and methoxyl 6.75 (singlet).

(16) T. Naito and K. Veno, *Yakugaku Zasshi*, **79**, 1277 (1959).

(17) S. Veibel and I. G. K. Andersen, *Anal. Chim. Acta*, **14**, 320 (1956).

(18) C. Harries and G. H. Lenart, *Ann.*, **410**, 107 (1915).

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Obedience to the Brown Selectivity Relationship in a Heterogeneous System. Competitive Ethylations over a Zeolite Catalyst

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While zeolites (molecular sieves) have long been utilized as adsorbents and ion exchangers,[1] it is only recently that their catalytic application has come into prominence.[2,3] Notably, the faujasite family of zeolites, with their highly accessible, intracrystalline volume, has presented unusual opportunities for catalysis, when appropriate base exchange to substantially eliminate their alkali metal content was practiced. Thus, we have found that rare earth exchanged X- and Y-type faujasites are versatile catalysts for organic reactions such as alkylation and related reactions,[4,5] the condensation of carbonyl compounds with aromatics to form bisarylalkanes,[6] and the aldol condensation.[6]

Generally, the patterns of substrate reactivity and product distribution in the zeolite-catalyzed alkylations were similar to the corresponding features reported for alkylations with strong protonic acids such as sulfuric and hydrofluoric acids, and promoted Lewis acids.[4] For alkylation of simple aromatics with olefins, transfer of a catalyst proton to olefin was proposed, with the generation of an *adsorbed* carbonium ion-like species, which was then attacked in a Rideal-like mechanism by aromatic to form alkylaromatic product.[5] Recently, we have studied the competitive alkylation of toluene and benzene with ethylene using a rare earth exchanged X-type zeolite and found that not only were *ortho–para* orientation and substrate selectivity observed, but also quantitative correlation of these data with Brown's selectivity relationship.[7]

Experimental Section

Gas chromatographic analyses of alkylbenzenes were carried out with a Perkin-Elmer 154-DG chromatograph with flame-ionization detector, using a 300-ft stainless steel capillary column containing a 3:2 mixture of 1,2,3-tris(2′cyanoethoxy)-propane and oxybis(2-ethylbenzoate). The column temperature was 80° and the hydrogen flow rate was 3 cc/min. Retention times (in minutes) relative to injection were benzene (5.52), toluene (7.53), ethylbenzene (10.62), *p*-ethyltoluene (16.9),

(1) R. M. Barrer, *Endeavour*, **23**, 122 (1964).

(2) P. B. Weisz, V. J. Frilette, R. W. Maatman, and E. B. Mower, *J. Catalysis*, **1**, 307 (1962).

(3) V. J. Frilette, P. B. Weisz, and R. L. Golden, *ibid.*, **1**, 301 (1962).

(4) P. B. Venuto, L. A. Hamilton, P. S. Landis, and J. J. Wise, *ibid.*, **5**, 81 (1966).

(5) P. B. Venuto, L. A. Hamilton, and P. S. Landis, *ibid.*, **5**, 484 (1966).

(6) P. B. Venuto and P. S. Landis, *ibid.*, **6**, 237 (1966).

(7) L. M. Stock and H. C. Brown, *J. Am. Chem. Soc.*, **81**, 3323 (1959), and references therein.

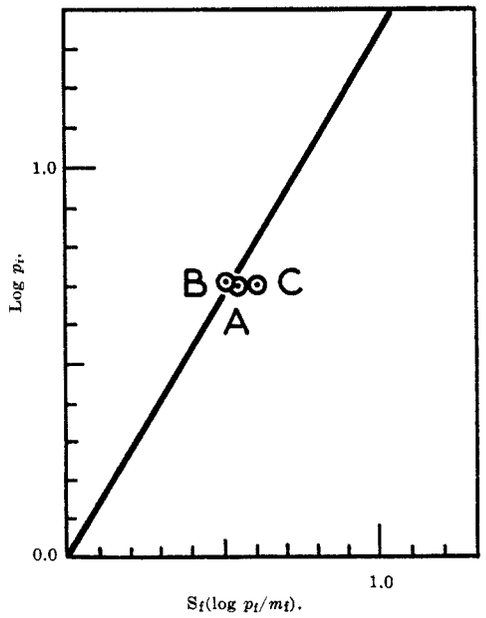

Figure 1.—Plot of log p_t and selectivity factor (S_t) for data from Table I.

m-ethyltoluene (17.1), and *o*-ethyltoluene (20.9). Neither the toluene nor benzene showed any impurities detectable by mass spectroscopic analysis and they were dried over Linde 5A Molecular Sieves to a water level of 10–12 ppm (Karl Fischer titration).

Reaction Conditions.—The catalyst was a rare earth exchanged, X-type near-faujasite; its preparation, activation, and analysis have been described.[4] Alkylations were run in a continuous-flow vapor phase glass reactor system[4] After *in situ* activation followed by a nitrogen purge, the catalyst bed temperature was lowered to 125°, and ethylene, together with an equimolar mixture of benzene and toluene (LHSV = 2.72),[8] was admitted. The total aromatic/ethylene molar ratio was 6.9. The liquid effluent for the first 20 min was discarded, and the product for the next 30 min was collected and analyzed by gas chromatography. Similar runs were made at 150 and 180°. Table I summarizes the experimental results.

Results and Discussion

While k(toluene)/k(benzene) decreased moderately with temperature (Table I), distinct selectivity for attack of the electrophile on toluene was observed at 125–180°. Further, *ortho–para* substitution was evident at all temperatures. The low *ortho/para* ratios suggest the operation of moderate steric effects.

In Figure 1 is shown a plot of the data from Table I (circles) on the line obtained from 47 electrophilic substitution reactions by Brown and co-workers.[7] Points A, B, and C, representing the runs at 125, 150, and 180°, respectively, fall close to the line, which represents a linear-free-energy relationship in both positional and substrate selectivity. These data, then constitute the first report of a correlation with the Brown selectivity relationship in a *heterogeneous system.* Thus, an unusual link between an extremely polar, porous zeolite catalyst with entry pore size of 8–9 A, and more "classical" acid catalyst systems, has been demonstrated.

TABLE I

VARIATION OF CONVERSION, ISOMER DISTRIBUTION, AND RELATIVE RATES WITH TEMPERATURE[a]

Temp, °C	Convn[b]	Isomer distribution in ethyltoluenes, *ortho*	*meta*	*para*	Reactivity ratio, k(toluene)/k(benzene)
125	2.83	30.8	25.6	43.6	1.92
150	5.87	22.6	30.6	46.8	1.84
180	9.20	17.7	26.6	55.7	1.50

[a] Average deviations from the mean for triplicate runs at the temperatures indicated: conversions (±6.05%), reactivity ratios (±3.26%), isomer proportions (±1.92%). [b] Conversion of aromatic to monoalkyl aromatic; only trace amounts of dialkylate formed at 150 and 180°.

(8) LHSV = liquid hourly space velocity, *i.e.*, the volume (at 25°) of liquid reactant(s) pumped per hour divided by the volume of the catalyst bed.

Registry No.—Benzene, 71-43-2; toluene, 108-88-3; ethylbenzene, 100-41-4; *p*-ethyltoluene, 622-96-8; *m*-ethyltoluene, 620-14-4; *o*-ethyltoluene, 611-14-3.

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Reaction of Benzoylisocyanate with Grignard Reagents[1]

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Benzoylisocyanate (I) has been shown to react with ammonia, aniline, benzamide, benzenesulfonamide, urea, and an alcohol to yield, respectively, N-benzoylurea, N-benzoyl-N′-phenylurea, N,N′-dibenzoylurea, N-benzoyl-N′-benzenesulfonylurea, N-benzoylbiuret, and a urethan.[3,4] The reactions of I were similar to those of ordinary isocyanates except considerably faster.

The reactions of I with Grignard reagents, reported herein, produced $C_6H_5CONHCOR$ (II), C_6H_5COR (III), N,N′-dibenzoylurea (IV), N-benzoylurea (V), benzamide (VI), and N-benzoylbenzamide (VII). The amount of each product depended upon the type of Grignard reagent used, the sequence of reagent addition, and the ratio of isocyanate to Grignard reagent. The lower molecular weight Grignard reagents gave predominantly III and IV in both forward and reverse additions. The forward addition of I to Grignard reagent also favored III and IV. Large excesses of Grignard reagent gave mostly III, indicating that C_6H_5COR is formed by the reaction of more than 1 mole of Grignard reagent per mole of isocyanate.

The reverse addition of Grignard reagent usually favored $C_6H_5CONHCOR$ (II) at the expense of IV in those reactions where II and IV were products. The difference in forward and reverse additions was most dramatic with phenylmagnesium bromide. Employing a 1:1 ratio of reagents in both cases, 79% IV was obtained from the forward addition and 79% N-benzoylbenzamide (VII) from the reverse addition.

(1) Abstracted in part from the M.S. Thesis of R. L. H., DePauw University, 1965.
(2) National Defense Education Act Fellow, 1963–1964.
(3) C. L. Arcus and B. S. Prydal, *J. Chem. Soc.*, 1091 (1957).
(4) O. C. Billeter, *Ber.*, **36**, 3218 (1903).