

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 $k(\text{toluene})/k(\text{benzene})$ 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

TABLE I
VARIATION OF CONVERSION, ISOMER DISTRIBUTION, AND
RELATIVE RATES WITH TEMPERATURE^a

Temp, °C	Conv ^b	Isomer distribution in ethyltoluenes			Reactivity ratio, $k(\text{toluene})/k(\text{benzene})$
		<i>ortho</i>	<i>meta</i>	<i>para</i>	
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 ($\pm 6.05\%$), reactivity ratios ($\pm 3.26\%$), isomer proportions ($\pm 1.92\%$). ^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.

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 Å, and more “classical” acid catalyst systems, has been demonstrated.

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 Reagents¹

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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.

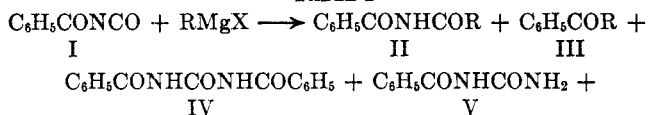
(2) National Defense Education Act Fellow, 1963–1964.

(3) C. L. Arcus and B. S. Prydal, *J. Chem. Soc.*, 1091 (1957).

(4) O. C. Billeter, *Ber.*, **36**, 3218 (1903).

Somewhat strangely, VII was also recovered in substantial amounts from the reactions of I with both *t*-butylmagnesium bromide and cyclohexylmagnesium bromide. It is most probable that VII was derived from 2 moles of isocyanate, but the Grignard reagent is apparently necessary to bring this about. Table I summarizes the results of the reactions of I with various Grignard reagents.

TABLE I



R	Yield of products, %					
	II	III	IV	V	VI	VII
CH ₃ (f) ^a		23.6	32.0			
CH ₃ (r) ^a		5.0	32.7			
C ₂ H ₅ (f)		26.1	38.5		6.0	
C ₂ H ₅ (r)		6.8	24.6			
(CH ₃) ₂ CH (f)			50.9			
(CH ₃) ₂ CH (r)	52.3			20.0		
(CH ₃) ₃ C (f)			8.0	20.0		30.0
(CH ₃) ₃ C (r)			45.2			31.3
C ₆ H ₁₁ (f)		19.3	49.0			Trace
C ₆ H ₁₁ (r)		2.0	14.9			48.9
C ₆ H ₅ (f)		15.0	79.0		4.0	
C ₆ H ₅ (r)	79.0 ^b	3.5			9.2	79.0 ^b
<i>o</i> -CH ₃ OC ₆ H ₄ (f)	3.5		25.7			
<i>o</i> -CH ₃ OC ₆ H ₄ (r)	14.4		27.4			
<i>p</i> -CH ₃ C ₆ H ₄ (f)			69.3			
<i>p</i> -CH ₃ C ₆ H ₄ (r)	22.1		6.0			

^a Forward addition is indicated by f and r denotes reverse addition. ^b In this case II and VII are the same.

Experimental Section

Benzoylisocyanate (I) was prepared according to the procedure of Arcus and Prydal.⁵ Ether was dried over sodium before use. The halides used were all commercial products. The experiments below typify the techniques used with all Grignard reagents.

Reaction of I with Phenylmagnesium Bromide. A. Forward Addition.—Phenylmagnesium bromide was prepared with 7.63 g (0.0486 mole) of bromobenzene and 1.06 g (0.0436 g-atom) of magnesium in 50 ml of ether. To the Grignard reagent was added with stirring under N₂ 5.96 g (0.0406 mole) of I in 30 ml of ether at room temperature during 20 min. After stirring for 2 hr, the mixture was hydrolyzed with 100 ml of 1 N HCl and during hydrolysis 4.30 g (79.0%) of N,N'-dibenzoylurea (IV) precipitated, mp 180–190°. Recrystallization from toluene and from CHCl₃ gave IV with constant mp 213–214°; with authentic IV, mmp 214–215°.

Anal. Calcd for C₁₅H₁₂N₂O₃: C, 67.16; H, 4.48; N, 10.45. Found: C, 67.16; H, 4.78; N, 10.34.

Work-up of the ether layer gave a thick oil. The use of vpc (column of 5% SF-96 60–80 Chromosorb G) at 200° showed the oil to contain a 15.0% yield of benzophenone (III), and a 4.0% yield of benzamide (VI). Further confirmation of III was obtained by preparing the 2,4-dinitrophenylhydrazone, mp 238–240°; with the derivative from authentic III, mmp 239–240°.

The addition of I to 3 moles of Grignard reagent under the above conditions gave an oil. Analysis by vpc showed 60.6 and 13.4% yields, respectively, of III and VI, along with other unidentified materials.

B. Reverse Addition.—Grignard reagent prepared from 5.12 g (0.0326 mole) of bromobenzene and 0.769 g (0.0316 mole g-atom) of magnesium in 45 ml of ether was added during 15 min at room temperature to 4.59 g (0.0312 mole) of I in 20 ml of ether. The reaction mixture was stirred vigorously for 2 hr at room temperature and hydrolyzed as above. During hydrolysis

5.40 g (77.0%) of solid precipitated, mp 137–144°. Another 0.14 g (2.0%) of similar material was obtained from work-up of the ether layer. Recrystallization from benzene gave N-benzoylbenzamide (VII) with a constant melting point of 149–150° (lit.⁶ mp 148°).

Anal. Calcd for C₁₄H₁₁NO₂: C, 74.67; H, 4.89; N, 6.22. Found: C, 74.60; H, 4.99; N, 6.04.

An independent synthesis of VII was effected by the method of Titherley,⁶ mp 148–149°; with VII above, mmp 148–149°. The infrared spectrum of VII showed bands at 3350, 1700, and 1675 cm⁻¹. The nmr spectrum showed an NH band at τ 0.75 and aromatic hydrogens in the 2.18–2.50 range.

Analysis of the oil residue from the reaction by vpc and by the use of 2,4-dinitrophenylhydrazine gave a 3.5% yield of III and a 9.2% yield of VI.

Registry No.—I, 4461-33-0; VII, 614-28-8.

(6) A. W. Titherley, *ibid.*, **85**, 1684 (1904).

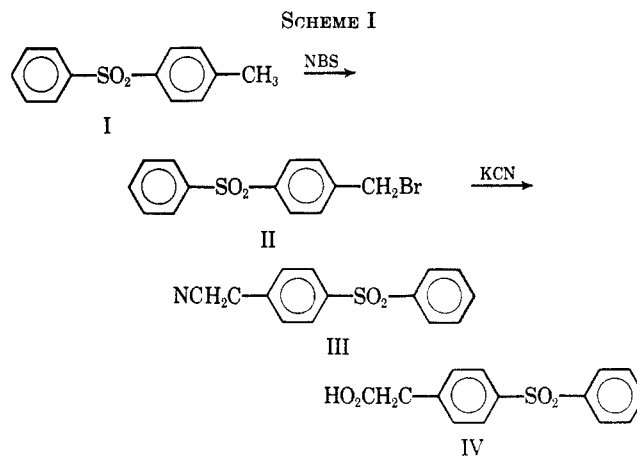
The Reaction of Potassium Cyanide with *p*-Phenylsulfonylbenzyl Bromide

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During the course of our studies on vitamin A esters, we were interested in preparing *p*-phenylsulfonylphenylacetic acid (IV) for use as a possible "handle" in the purifications of vitamin A. Initially the preparation of this acid was attempted according to Scheme I.



The bromination of *p*-phenylsulfonyltoluene (I) with N-bromosuccinimide proceeded smoothly resulting in a high yield of brominated product. However, this product could not be successfully purified by crystallization or column chromatography over aluminum oxide. The bromination product yielded a solid devoid of halogen when treated with methanolic alkali. The hydrolyzed material could not be crystallized to a sharp melting point and the infrared spectrum showed no evidence of a carbonyl or hydroxyl band. However, the infrared spectrum did exhibit an absorption band at 1101 cm⁻¹ indicating the presence of an ether linkage. Evidently the reactivity of the halogens was

(5) C. L. Arcus and B. S. Prydal, *J. Chem. Soc.*, 4018 (1954).