

where the metal ion appears to increase the rate of reaction and drives the reaction to completion by preventing decarboxylation of the product.^{37,38} Metal ions inhibit nonenzymatic decarboxylation of Schiff bases formed between amino acids and pyridoxal.³⁹ The reaction of a nucleophile with structure I may result in the formation of a carbonate-like chelate (structure III) with the oxygen atoms of a tetrahedral intermediate, and the metal ion could conceivably lower the energy barrier for this reaction by chelation with a transition state resembling the tetrahedral intermediate. Breakdown of a chelated tetrahedral intermediate requires reorganization of the chelate so that the electrons of the oxygen atom are

(38) (a) M. Stiles and H. L. Finkbeiner, *J. Am. Chem. Soc.*, **81**, 505 (1959); (b) K. J. Petersen, *Acta Chem. Scand.*, **3**, 676 (1949).

(39) G. D. Kalyankar and E. E. Snell, *Biochemistry*, **1**, 594 (1962).

made available to expel the imidazolidone group, and this is shown in eq. 12 in the conversion of structure III to II. Breakdown of the tetrahedral intermediate with C-N bond cleavage is facilitated by the metal ion since the leaving group is an analog of a neutral enol rather than an amine anion. As discussed above, saponification of N-methoxycarbonyl-2-imidazolidone proceeds without C-N bond cleavage, indicating that it is more difficult to displace the amine anion than methoxide ion. Structure III may not be an obligatory intermediate in these reactions, in which case structure II is formed directly from I.

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Communications to the Editor

Aromatic Substitution. XXIV.¹ The Alkylation of Toluene and Benzene *via* Diazotization of Amines with Nitrosonium Salts

Sir:

Pearson, *et al.*,² recently reported the isopropylation of benzene, toluene, and *p*-xylene *via* diazotization of isopropylamine with butyl nitrite in the presence of equimolar amounts of a carboxylic acid. Using competitive reaction conditions they found $k_{\text{toluene}}/k_{\text{benzene}} = 0.8$ and $k_{p\text{-xylene}}/k_{\text{benzene}} = 0.6$. It was suggested that the unusual reactivity ratios (toluene and *p*-xylene reacting *slower* than benzene) are a consequence of a solvent cage effect (the aromatic hydrocarbons being an essential part of the solvent system). The relative electronic and chemical properties of the aromatic hydrocarbons could not explain the observed data, nor was it possible to suggest that the observed relative rates reflect comparative reactivities of the aromatic substrates in kinetically controlled competitive reactions. Consequently doubt was expressed in the validity of any activity sequences obtained from competition reactions in nonpolar organic solvents.

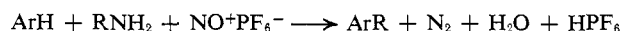
The above findings represented a serious challenge to all previous investigations dealing with relative reactivities of aromatics in alkylation and related electrophilic aromatic substitution systems based on competition experiments. In view of our previous interest in competitive rate determinations of benzene and alkylbenzenes in Friedel-Crafts type alkylations³ we felt obliged to extend our investigations to the alkylation of benzene and toluene *via* diazotization of amines.

(1) Part XXIII: G. A. Olah, J. A. Olah, and N. A. Overchuk, *J. Org. Chem.*, **30**, 3373 (1965).

(2) D. E. Pearson, Ch. V. Breder, and J. C. Craig, *J. Am. Chem. Soc.*, **86**, 5054 (1964).

(3) G. A. Olah, S. J. Kuhn, and S. H. Flood, *ibid.*, **84**, 1688 (1962); G. A. Olah, S. H. Flood, S. J. Kuhn, M. E. Moffatt, and N. A. Overchuk, *ibid.*, **86**, 1046 (1964); G. A. Olah, S. H. Flood, and M. E. Moffatt, *ibid.*, **86**, 1060 (1964).

In order to carry out the alkylation of aromatics *via* diazotization of amines our work was not primarily directed to reproduce the conditions reported by Pearson, *et al.*,² where alkylation was only a minor reaction, the major product being propylene and isopropyl acetate (or related esters). We tried to find a more suitable way to carry out alkylations *via* diazotization of amines. We found that when aromatic hydrocarbons were allowed to react with amines and stable nitrosonium salts, like NO^+BF_4^- , NO^+PF_6^- , $\text{NO}^+\text{SbF}_6^-$, $\text{NO}^+\text{AsF}_6^-$, and $\text{NO}^+\text{HSO}_4^-$, alkylation *via* diazotization takes place and the corresponding alkylated aromatics are obtained. The reactions can be carried out in organic solvents like nitromethane and acetonitrile. As the size of the anion generally affects the solubility, it was found that the hexafluorophosphate salt, for example, is much more soluble than the tetrafluoroborate and it was used preferentially in present investigations.



Competitive alkylations of benzene and toluene were carried out by adding to a solution of 0.125 mole each of benzene and toluene and 0.05 mole of nitrosonium hexafluorophosphate (Ozark Mahoning Corp., Tulsa, Okla., purified from $\text{NO}_2^+\text{PF}_6^-$ impurity by washing with benzene) in 50 g. of nitromethane (acetonitrile) a solution of 0.025 mole of the amine in 20 g. of nitromethane. The addition was carried out over a period of 20 min., while the reaction mixture was vigorously stirred and kept in a constant temperature bath at 25°. The reaction mixture was then quenched with excess ice-water and neutralized, and the organic layer was washed, separated, and dried over anhydrous magnesium sulfate and analyzed by gas-liquid partition chromatography (using a high sensitivity Perkin-Elmer Model 226 gas chromatograph equipped with a 150-ft. open tubular (capillary) column coated with *m*-bis(*m*-phe-

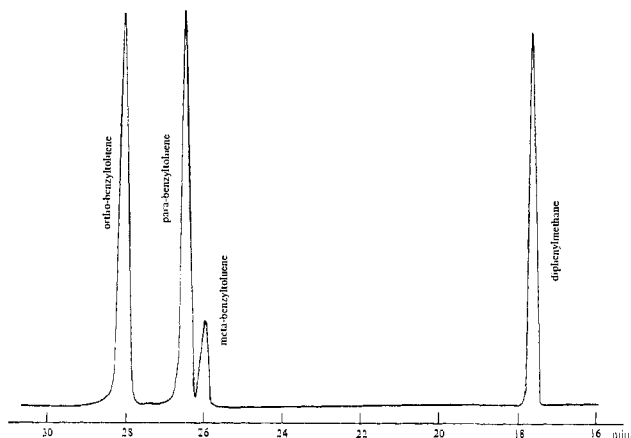


Figure 1.

noxyphenoxy)benzene modified with 20% Apiezon L grease and generally operated at 90° with a carrier He gas pressure of 20 p.s.i.). Figures 1 and 2 illustrate the gas-chromatographic separations achieved under these conditions.

Data of the competitive alkylations together with the isomer distributions are summarized in Table I. Data clearly show that the alkylation of toluene and benzene *via* diazotization of amines under the experimental conditions used gives relative reactivities in good agreement with data reported previously for the more conventional Friedel-Crafts type alkylations with alkyl halides and olefins.

Table I. Competitive Alkylation of Benzene and Toluene with Amines and Nitrosonium Hexafluorophosphate in Nitromethane Solution at 25°

Alkylating agent	Solvent	k_T/k_B	% isomer distribution		
			<i>ortho</i>	<i>meta</i>	<i>para</i>
Methylamine	Nitromethane		42.0	21.1	36.9
	Acetonitrile		41.2	20.6	38.2
Ethylamine	Nitromethane	1.52	35.8	48.5	15.7
	Acetonitrile	1.45	37.8	48.1	14.1
Isopropylamine	Nitromethane	2.52	51.7	20.3	28.0
	Acetonitrile	2.47	47.7	21.9	30.4
Benzylamine	Nitromethane	3.52	47.6	7.7	44.7
	Acetonitrile	3.56	47.5	8.6	43.9

Next we turned our attention to reinvestigate alkylations under conditions² where the unusual toluene-benzene reactivities were reported. Quenching the reaction mixture with an aqueous alkaline solution (instead of sulfuric acid washing) and analyzing by the same open tubular column gas-chromatographic method we consistently obtained $k_{\text{toluene}}/k_{\text{benzene}} = 1.8\text{--}2.0$.⁴ Thus we must conclude that there is no specific "cage effect" involved in alkylation *via* diazotization of amines or any other irregularity involving the relative reactivities of toluene and benzene. The competitive method of rate determination is applicable to these systems. The isomer distributions generally show a higher percentage of the *meta* isomer than obtainable in alkylations with alkyl halides and olefins, but it is no inten-

(4) After our work was completed Prof. D. E. Pearson kindly informed us that his reinvestigation of the toluene-benzene isopropylation system gave $k_T/k_B = 1.7\text{--}1.8$, a normal ratio for alkylation. We are also grateful to Prof. L. Friedman for informing us of his results relating alkylation *via* diazotization prior to publication.

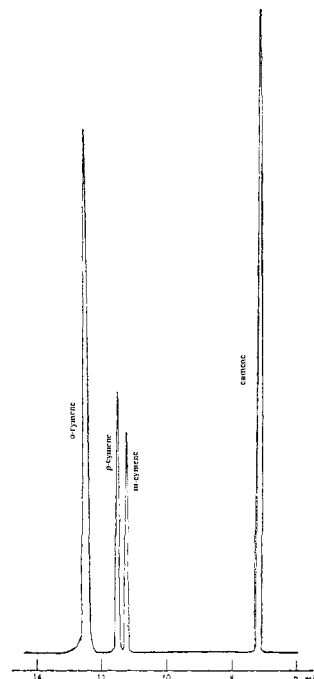


Figure 2.

tion of the present communication, before further extensive data are obtained, to evaluate this fact.

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Aromatic Substitution. XXV.¹ Selectivity in the Friedel-Crafts Benzoylation, Isopropylation, and *t*-Butylation of Benzene and Toluene

Sir:

Friedel-Crafts alkylations are notorious for their unreliable kinetic behavior.² It is this reason why very few kinetic investigations of the reactions were ever undertaken. Fortunately, most interest is directed toward the knowledge of relative rates of alkylation, like that of toluene compared with benzene, and not so much toward the accurate knowledge of absolute rates of the alkylations.

The relative reactivities of toluene and benzene (as well as of related other alkylbenzenes) in a number of Friedel-Crafts alkylations were measured by Brown and his collaborators.³ We have previously reported the relative reactivities (obtained in competitive experiments) of the same substrates in benzoylation,^{4a} iso-

(1) Part XXIV: G. A. Olah, N. A. Overchuk, and J. C. Lapierre, *J. Am. Chem. Soc.*, **87**, 5785 (1965).

(2) For relevant references see "Friedel-Crafts and Related Reactions," Vol. I-IV, G. A. Olah, Ed., Wiley-Interscience Publishers, New York, N. Y., 1963-1965.

(3) H. C. Brown and C. R. Smoot, *J. Am. Chem. Soc.*, **78**, 6245, 6255 (1956); S. U. Choi and H. C. Brown, *ibid.*, **81**, 3315 (1959); H. C. Brown and B. A. Bolto, *ibid.*, **81**, 3320 (1959).

(4) (a) G. A. Olah, S. J. Kuhn, and S. H. Flood, *ibid.*, **84**, 1688 (1962); (b) G. A. Olah, S. H. Flood, S. J. Kuhn, M. E. Moffatt, and N. A. Overchuk, *ibid.*, **86**, 1046 (1964); (c) G. A. Olah, S. H. Flood, and M. E. Moffatt, *ibid.*, **86**, 1060 (1964).