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—		
			ortho	meta	para
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
Isopropyl-	Nitromethane	2.52	51.7	20.3	28.0
amine	Acetonitrile	2.47	47.7	21.9	30.4
Benzylamine	Nitromethane	3.52	47.6	7.7	47.7
	Acetonitrile	3.56	47.5	8.6	43.9

Next we turned our attention to reinvestigate alkylations under conditions[2] 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 $k_{\text{toluene}}/k_{\text{benzene}} = 1.8–2.0$.[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 $k_T/k_B = 1.7–1.8$, 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.
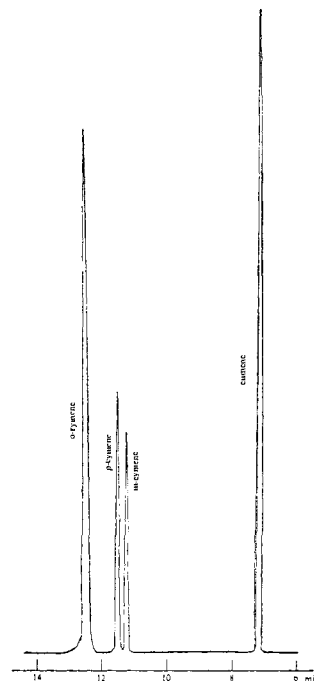

Figure 2.

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 Benzylation, 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 benzylation,[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).
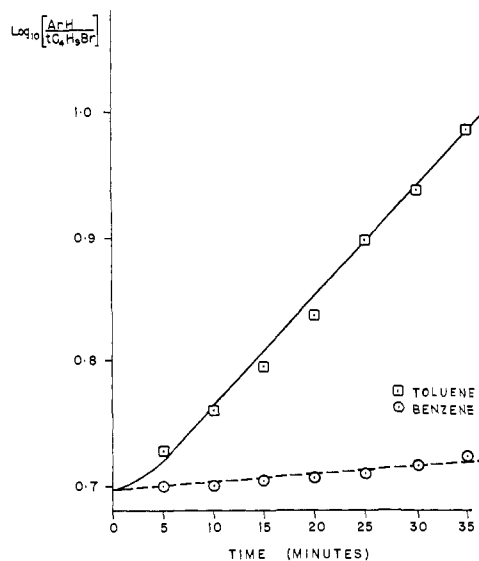
Figure 1. t-Butylation of toluene and benzene.

Figure 2. Isopropylation of toluene and benzene.

propylation,[4b] and t-butylation.[4c] The observed low substrate (intermolecular) but generally higher positional (intramolecular) selectivities were explained by suggesting the importance of both π- and σ-complex type transition states. The first was suggested to be responsible for the substrate selectivity, the latter for the positional selectivity. Critics of the suggested mechanism pointed out that, in a fast, indiscriminant interaction of an incipient highly reactive carbonium ion (or its precursor) with reactive aromatic hydrocarbons, statistical rather than competitive kinetic reaction conditions could prevail. We discussed previously our views relating this problem in connection with experiments (like variation of the concentration of the competing aromatic hydrocarbons over a wide range) designed to check the effect of possible nonkinetic conditions in competition experiments. We wish to report now on the selectivity of the Friedel-Crafts benzylation, isopropylation, and t-butylation of toluene and benzene under noncompetitive reaction conditions.

The rates of alkylation of toluene and benzene with alkyl chloride (bromide) in nitromethane solution were measured at 25° using aluminum chloride and stannic chloride as catalyst. Stock solutions of the resublimed (redistilled) catalysts in highly purified solvents were used, thus eliminating any difference due to the purity of catalyst in various runs. Analytical grade hydrocarbons (toluene, benzene) were used after distillation from CaH$_2$. The solutions during all runs were strictly homogeneous. The rates of alkylation of toluene and benzene were measured in separate runs following time–product composition data using a known amount of internal standard (cyclohexane). Samples were withdrawn periodically, quenched with water, extracted with ether, dried, and analyzed with a gas-chromatographic analytical method. Conditions were kept strictly identical in all runs ([aromatic] 1.75 M; [alkyl halide] 0.15 M; [AlCl$_3$] or [SnCl$_4$] 0.10 M) including the addition of [water] 0.02 M to provide a uniform amount of the possible major impurity.

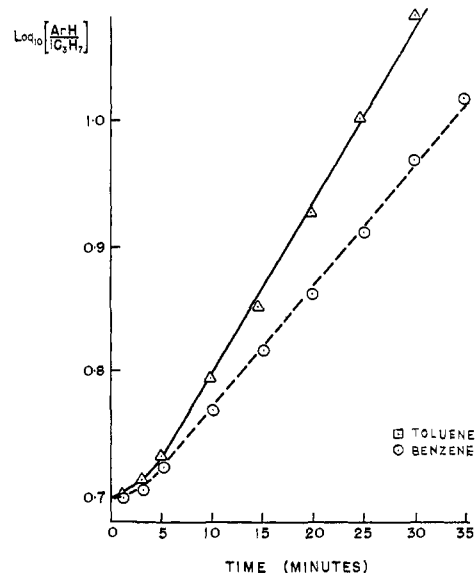Pseudo-second-order rate plots were obtained (see Figures 1–3) assuming
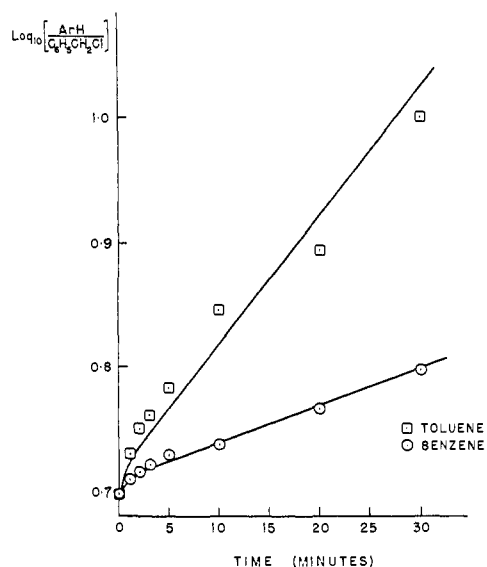

Figure 3. Benzylation of toluene and benzene.

$$\frac{d[product]}{dt} = k[AlCl_3][aromatic][alkyl\ halide]$$

and that [AlCl$_3$] stays constant; thus

$$\frac{d[product]}{dt} = k'[aromatic][alkyl\ halide]$$

where $k' = k[AlCl_3]$.

The rates of Friedel–Crafts alkylations depend not only on the reagents, catalyst, and solvent but also on impurities (and the concentrations affecting these). Difficulties to control all variables and provide a uniformly "clean" system are substantial. We wish to stress that in the present investigation the emphasis was on the alkylation of toluene and benzene under strictly identical conditions, but not necessarily under well enough defined conditions to claim absolute rate

Table I. Rate of Alkylation of Toluene and Benzene

| | Benzene | | | Toluene | |
Alkylating agent	Catalyst	k_2, l./mole sec.	Alkylating agent	Catalyst	k_2, l./mole sec.
$C_6H_5CH_2Cl$	$AlCl_3$–CH_3NO_2	2.2×10^{-4}	$C_6H_5CH_2Cl$	$AlCl_3$–CH_3NO_2	7.7×10^{-4}
i-C_3H_7Br	$AlCl_3$–CH_3NO_2	1.7×10^{-4}	i-C_3H_7Br	$AlCl_3$–CH_3NO_2	2.8×10^{-4}
t-C_4H_9Br	$SnCl_4$	1.3×10^{-5}	t-C_4H_9Br	$SnCl_4$	1.7×10^{-4}

Table II. Relative Reactivities of Toluene and Benzene in Alkylations

	Present work	Competitive data [3a-c]
Benzylation	3.45	3.20
Isopropylation	1.65	2.03
t-Butylation	13.1	16.6

The small amount of *meta* isomer in the low substrate selectivity benzylation of toluene indicates that positional and substrate selectivity are not necessarily interconnected in the alkylation systems. Isopropylation and *t*-butylation gave so far no such clear indication. We believe that our present data substantiate previous findings and help to eliminate some of the

Table III. Isomer Distribution of the Alkylations of Toluene

| | Present work, % | | | | | | Data from competitive alkylation,[4a-6] % | | |
| | G.l.p.c. | | | Infrared | | | G.l.p.c. | | |
Alkylation	ortho	meta	para	ortho	meta	para	ortho	meta	para
Benzylation	44.0	4.5	51.5	44.0	4.0	52.0	43.5	4.5	52.0
Isopropylation	47.7	18.2	35.1	46.8	16.4	36.8	46.7	14.7	38.6
t-Butylation	0	5.9	94.1	0	6.1	93.9	0	6.4	93.6

data of general validity. Having, however, carried out the alkylations of toluene and benzene under identical conditions, we obtained well-reproducible second-order rate constants from the slopes of the kinetic curves 1–3 which are summarized in Table I (all data are the average of three parallel determinations).

The relative reactivities of the alkylations of toluene and benzene calculated from the ratios of the separate rate determinations of toluene and benzene are shown in Table II, compared with previously reported competitive relative reactivity data.

The comparison of data of Table II clearly indicates that the relative reactivities of toluene and benzene in the investigated alkylations are in the limit of the experimental error in both competitive and noncompetitive determinations. Thus, suggestions that statistically (diffusion) and therefore nonkinetically controlled conditions are responsible for the observed low substrate selectivities must be rejected.

The isomer distributions in the investigated alkylations of toluene were determined both 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*-phenoxyphenoxy)benzene modified with 20% Apiezon L grease operated at 165 and 100°, respectively, for the analysis of the benzylation and isopropylation systems, and a polypropylene glycol coated similar column operated at 100° for the *t*-butylation system) and by infrared spectroscopy (using the out-of-plane hydrogen deformation absorption bands at 13.24–13.28 μ for the *ortho*, at 12.82–12.85 μ for the *meta*, and at 12.30 μ for the *para* isomers). The isomer distributions obtained are summarized in Table III, together with the previously reported isomer distributions of the competitive experiments.

objections raised to the validity of competitive rate determinations showing low substrate, but at the same time high positional selectivity.

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Reaction of Poorly Solvated Alkyl Cations with Arenes and Ethers

Sir:

Poorly solvated alkyl cations are formed by aprotic diazotization of aliphatic amines.[1] When these species are generated in aromatic solvents (Table I) such as benzene, toluene, and anisole or in ethers such as glyme (1,2-dimethoxyethane) and *n*-butyl ether, alkylation of solvent occurs, albeit in low yield. The alkylarenes are formed with a *minimum* of rearrangement and are characteristic of *normal* electrophilic aromatic substitution and substrate–solvent reactivity. These results are not in agreement with recently reported data.[2]

The yield of alkylarene is dependent upon the amine and the proton donor; primary straight-chain amine hydrochlorides are most effective. Reactions under these conditions are partially hetereogeneous inasmuch as the amine hydrochlorides are only slightly soluble in the reaction mixture and a water layer is observed at the end of the reaction.[3] However, this is of no consequence since decomposition of the corresponding

(1) J. H. Bayless, F. D. Mendicino and L. Friedman, *J. Am. Chem. Soc.*, **87**, 5790 (1965).
(2) D. E. Pearson, C. V. Breder and J. C. Craig, *ibid.*, **86**, 5054 (1964).
(3) Reaction mixture initially homogeneous when amine acetates are employed.