Table I. Rate of Alkylation of Toluene and Benzene

Alkylating agent	Benzene Catalyst	k_2, l./mole sec.	Alkylating agent	Toluene 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

Alkylation	Present work, % G.l.p.c. ortho	meta	para	Infrared ortho	meta	para	Data from competitive alkylation,[4a-6] % G.l.p.c. 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.

N-nitroso-N-alkylacetamide gives identical results (reaction system completely homogeneous). Counterion product isomer composition,[1] i.e., the amount of rearrangement, is similar to that for the alkylarenes. It is significant that very little skeletal rearrangement occurs. However, if the reaction is effected under more protic conditions more rearrangement occurs (8–10%[4]; Table I).

Table I. Alkylation of Benzene[a]

| | Alkylarenes | | |
| | % yield[b,c] | | % product |
Amine	[AcOH][d]	[HCl][d]	composition[b]
n-Propyl	0.55	1.6	97 n-propyl, 3 isopropyl
n-Propyl[e]	0.40		97 n-propyl, 3 isopropyl
Isopropyl	0.50	1.1	100 isopropyl
n-Butyl[f]	1.5	2.5	98 n-butyl, 2 sec-butyl
Isobutyl	0.20	0.40	93 isobutyl, 7 sec-butyl[g]
sec-Butyl	0.30	0.50	100 sec-butyl

[a] Amine (50 mmoles), acid (50 mmoles), and alkyl nitrite (55 mmoles) in 100 ml. of benzene at reflux. [b] Quantitative g.l.p.c. analysis using Hy-Fi, 5% triisodecyl trimellitate and 5% Bentone 34, on Chromosorb P, H.M.D.S., 130–150°. [c] Average of several runs. [d] Total yields of alkylarenes when AcOH and HCl are proton sources, respectively. [e] Cf. ref. 2. [f] Decomposition of N-nitroso-N-n-butylacetamide in benzene gave identical results. [g] N.m.r. analysis of poorly resolved g.l.p.c. (15% DEGS on Chromosorb P, 120°) collected products indicated 6–10% sec-butylbenzene.

In order to determine the relative selectivity of the species toward benzene and toluene, isopropylation was studied since the analytical problems are minimized in that only cumene and the cymenes are formed (Table II). Aprotic diazotization of isopropylamine in excess

Table II. Isopropylation of Toluene–Benzene Mixtures. Relative Solvent Reactivity[a]

| | Cymene isomer distrbtn,[b] % | | | $k_{toluene}/$ |
Reactants	ortho	meta	para	$k_{benzene}$
Isopropylamine–HOAc–RONO	41	25	34	1.81 ± 0.13[c]
Isopropylamine–HOAc–RONO	42	24	34	2.86[c,d]
Isopropylamine–HCl–RONO	40	27	33	1.72 ± 0.17[c]
N-Nitroso-N-isopropyl-acetamide	40	25	35	1.76 ± 0.04[e]

[a] Reactants (50 mmoles) in 100 ml. of toluene–benzene mixtures. Toluene–benzene volume ratios were 3, 1, and 0.33. [b] Cymene yield and isomer distribution and cumene yield determined by g.l.p.c. analysis, using Hy-Fi, 15% Apiezon L on Chromosorb P, 130°. [c] Heterogeneous. [d] Reaction conditions according to ref. 2 except that decyl nitrite was used; single run. [e] Homogeneous.

toluene gave the isomeric cymenes, 40–42% ortho, 22–24% meta, and 33–35% para. This is in fair agreement with previously obtained data for the isopropylation of toluene under various reaction conditions.[5] Competitive experiments in benzene–toluene mixtures gave cumene and the same distribution of cymenes. The relative selectivity toward toluene and benzene varied from 1.7 to 2.9. These values are essentially independent of the counterion but markedly dependent upon the composition of the solvent mixture.

(4) Reaction conducted according to Pearson, et al.,[2] except that crude reaction mixture was analyzed directly without alkaline or acid treatment.

(5) P. Kovacic and J. J. Hiller, Jr., J. Org. Chem., 30, 1581 (1965), and references contained therein.

Isopropylation of anisole via aprotic diazotization gave a mixture of the isopropylanisoles, 58% ortho, 5% meta, and 37% para; ortho:para 1.6. The ortho:para ratio is in good agreement with Friedel–Crafts alkylation in nitromethane.[5] The meta value, however, is unusually high; this was also observed with toluene. Since the products are stable toward the reaction conditions the high amount of meta is a consequence of the activity of the cationic species. meta product could be obtained by direct attack on the arene or by rearrangement of the σ complex prior to loss of the proton.

Aprotic diazotization of amines in glyme gave, in addition to the expected hydrocarbon and counterion products, compounds derived from ether cleavage[6]: $ROCH_2CH_2OCH_3$ and CH_3X (Table III). Greater

Table III. Alkylation of Glyme[a]

| | | $ROCH_2CH_2OCH_3$ | |
Reactants	% yield[b]	% product composition[b]	
n-Propylamine–HCl	5	88 n-propyl,	12 isopropyl
Isopropylamine–HCl	6	100 isopropyl	
n-Butylamine–HCl	6	93 n-butyl,	7 sec-butyl
n-Butylamine–AcOH	4	96 n-butyl,	4 sec-butyl
N-Nitroso-N-n-butylacetamide	5	97 n-butyl,	3 sec-butyl
Isobutylamine–HCl	3	70 isobutyl,	30 sec-butyl
Isobutylamine–HOAc	3	67 isobutyl,	33 sec-butyl
N-Nitroso-N-isobutyl-acetamide	2	75 isobutyl,	25 sec-butyl
sec-Butylamine–HCl	3	100 sec-butyl	

[a] Reactants (20 mmoles) and alkyl nitrite (20 mmoles) in 40 ml. of glyme. [b] G.l.p.c. analysis: 15% DEGS, Chromosorb P, 120°; 5% triisodecyl trimellitate and 5% Bentone 34 on Chromosorb P, H.M.D.S., 100°. Per cent yield of MeX equals per cent of ethers.

rearrangement is observed here compared to the alkylarenes. In the isobutyl system, for example, rearranged ether (sec-butyl) is formed to the extent of 25–33%.

Ether products are presumably formed via an oxonium ion intermediate.[7] The increase in rearranged products can be attributed to (a) solvent-stabilized species[8] which can give the free carbonium ion and/or (b) rearrangement of the intermediate oxonium ion. The nonrearranged ether could be formed (a) by S_N2 attack by glyme on the diazonium ion, (b) by collapse of a diazonium ion–glyme complex with loss of nitrogen, and/or (c) from the free carbonium ion prior to rearrangement.
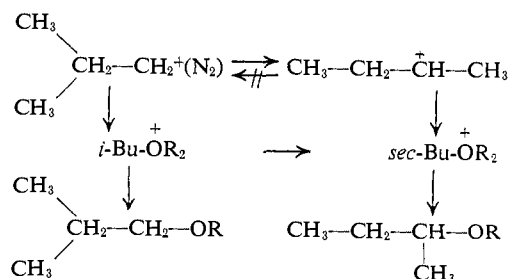
(6) Similar results are obtained in n-butyl ether.

(7) (a) Ether participation in solvolysis reactions has been previously observed, sometimes with concomitant cleavage: A. Streitwieser, Jr., and S. Andreades, J. Am. Chem. Soc., 80, 6553 (1958); H. Weiner and R. A. Sneen, ibid., 87, 287 (1965).

(8) Possibly a protonated methylcyclopropane.

The enhanced reactivity of cations generated in aprotic solvents is a reflection of the decreased solvating character of the media. Less polar solvents such as benzene, chloroform, etc., are unable effectively to stabilize the cation in the absence of a stabilizing anion such as hexafluoroantimonate, and thus kinetic control of products is observed. In more polar (and/or protic) media such as glyme,[9] glacial acetic acid, and ultimately water, cation stabilization is increased and more rearrangement is observed, a consequence of greater thermodynamic control and/or decreased counterion activity.

(9) Reactions in more polar aprotic solvents such as acetonitrile give extensive rearrangement as well as significant amounts of solvent-derived products ($\sim$20%): A. T. Jurewicz, unpublished data.

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Aprotic Diazotization of Aliphatic Amines. Intra- and Intermolecular Reactions of Poorly Solvated Cations[1]

Sir:

The fate of carbonium ions is assumed to be dependent upon their mode of formation and environment. For example, cationoid species formed by diazotization of amines in protic solvents are more "reactive" than those formed by solvolysis.[2] This has been ascribed mainly to differences in degree of solvation.[2] It is reported herein that diazotization in aprotic media[3] yields species that are markedly different from those formed in protic media in that hydrocarbon yields are greatly enhanced, skeletal rearrangements and double-bond migration are minimized, and cyclopropane formation is significantly increased.

The formation of cyclopropanes from cationoid precursors has been sporadically observed in terpene chemistry since the turn of the century.[4] More recently small amounts of cyclopropane products were reported in the protic diazotization of aliphatic amines[5] and the deoxidation of alcohols.[6] This is in contrast to the extensive amount of insertion observed in many of the corresponding carbenic systems.[7]

(1) (a) The results reported here for the isomeric C_4 amines are representative for a wide variety of aliphatic and alicyclic amines. (b) A premature account of part of this work was presented by L. Friedman and F. D. Mendicino, Abstracts of Papers, 145th National Meeting, American Chemical Society, New York, N. Y., Sept. 1963, p. 86Q.

(2) A. Streitwieser, Jr., J. Org. Chem., 22, 861 (1957); J. H. Ridd, Quart. Rev. (London), 15, 418 (1961).

(3) Solvents that are not proton donors. Other examples of such diazotizations are summarized by D. Y. Curtin, J. A. Kampmeier, and B. R. O'Connor, J. Am. Chem. Soc., 87, 863 (1965).

(4) For example: G. Wagner, S. Moycho, and F. Zienkowski, Chem. Ber., 37, 1035 (1904); G. M. Komppa and G. A. Nyman, Ann., 535, 252 (1938); W. Hückel and G. Meinhardt, Chem. Ber., 90, 2025 (1957); M. Bredt-Savelsberg, ibid., 56, 554 (1923). The intermediacy of cyclopropane intermediates was postulated, but not proven, by many investigators to explain extensively rearranged olefinic products.

(5) (a) M. Silver, J. Org. Chem., 28, 1686 (1963); (b) P. S. Skell and I. Starer, J. Am. Chem. Soc., 82, 2971 (1960); (c) O. E. Edwards and M. Lesage, Can. J. Chem., 41, 1592 (1963); (d) M. Hanach and H. Schneider, Tetrahedron, 20, 1863 (1964).

(6) P. S. Skell and R. J. Maxwell, J. Am. Chem. Soc., 84, 3963 (1962).

(7) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, pp. 52–64.

Diazotization of isobutylamine (Table I) in solvents such as chloroform, benzene, and cyclohexane with alkyl nitrites in the presence of 1 equiv. of acetic acid[8a] gives hydrocarbon products in approximately 30% yield. The hydrocarbons are mainly isobutylene (70–73%) and the insertion product methylcyclopropane (14–16%).[8b] Of the skeletal-rearranged products (the butenes), 1-butene predominates. The ratio of acetates to alcohols is 25; while the ester portion is mainly isobutyl acetate ($\sim$89%), much rearrangement ($\sim$66%) is observed in the alcohol products. As the medium becomes more protic, e.g., 50% aqueous acetic acid, the ratio of acetates to alcohols drops to 5, hydrocarbon yields are decreased, and extensive rearrangement occurs.[9]

In aqueous systems the cationic species are stabilized by solvation and thus rearrangement to thermodynamically more stable intermediates occurs. However, under aprotic conditions products are derived from kinetic rather than thermodynamic factors.[10]

The effect of the reaction medium on product composition from the diazotization of n-butylamine (Table I) is similar; methylcyclopropane ($\sim$4%) and 1-butene ($\sim$90%) are formed with a minimum of products (6%) from 1,2-hydride shift in the more aprotic environments. As the medium becomes more highly protic methylcyclopropane is formed in only trace amounts and the amount of cis- and trans-2-butenes increases extensively at the expense of 1-butene.

Diazotization of sec-butylamine over a wide range of conditions yields only sec-butyl derivatives, whose nature (i.e., ratio of alcohol to ester or halide) reflects the activity of the counterions[10] in the medium. However, the composition of the hydrocarbon products is more revealing. In aprotic media the sec-butyl cation or diazonium ion yields mainly 1-butene (X^- = Cl, 76%; AcO^-, 57%),[11] while in aqueous systems the 2-butenes predominate. The relatively large amounts of 1-butene formed are not far removed from an expected statistical result (60%) based on available protons if an E2-type mechanism or cyclic elimination sequence is considered wherein the transition state more closely re-reflects reactants (Hofmann rule). In more protic media E1-type eliminations predominate.[2] The formation of significant amounts of methylcyclopropane ($\sim$4%) is of interest since in this case none is formed in the corresponding carbenic system.[12] This is just one of several instances where intramolecular carbonium ion insertion occurs to a greater extent than carbene insertion.[13]

(8) (a) Nitrous oxide is quantitatively formed from free alkylamine and alkyl nitrite; (b) methylcyclopropane (0.5%) was also observed in the hydrocarbon products ($\sim$1% yield) from the solvolysis of isobutyl tosylate.

(9) This is even more striking in acetonitrile and acetonitrile–water mixtures. Concomitant changes occur in hydrocarbon product formation: A. T. Jurewicz, unpublished data.

(10) D. H. Froemsdorf and M. E. McCain, J. Am. Chem. Soc., 87, 3983 (1965).

(11) The large amount of terminal olefin formed from the aprotic diazotization of both sec- and isobutylamine may reflect the amount of E2 type elimination (ref. 10) and the relative stability of the three conformers of the sec-butyl cation (cf. D. J. Cram and M. R. V. Sahyun, ibid., 85, 1257 (1963)). The difference observed with different counterions might be related to the solvating (i.e., stabilizing) ability of the counterion in the ion pair.

(12) Cf. ref. 7, p. 55.

(13) For example, bicyclobutane formation: J. Bayless, L. Friedman, J. A. Smith, F. B. Cook, and H. Shechter, J. Am. Chem. Soc., 87, 661 (1965).