Relative Reactivities in Amination of Benzene and Alkylbenzenes with Trichloramine–Aluminum Bromide. Evidence for σ Substitution[1,2]

Peter Kovacic and Joseph A. Levisky

Contribution from the Department of Chemistry, Case Institute of Technology, Cleveland, Ohio. *Received September 16, 1965*

Abstract: The relative rates of amination by trichloramine–aluminum bromide were ascertained for benzene, monoalkylbenzenes, and the xylenes. The reactivity order determined in ethylene dichloride or *o*-dichlorobenzene with toluene as reference was: benzene (0.02 or 0.005), toluene (1), ethylbenzene (0.8), isopropylbenzene (0.6), *o*-xylene (6), *p*-xylene (6–8), and *m*-xylene (48). Linear relationships are observed from logarithmic plots of the relative rates of amination *vs.* basicity, bromination, and chlorination. The data suggest that σ-complex formation is the rate-controlling step in amination. We propose that the reaction sequence involves generation of a chlorarenonium ion, nucleophilic attack by a nitrogen-containing entity, and then loss of hydrogen chloride. This study provides further support for the σ-substitution mechanism (addition–elimination).

Recent reports from this laboratory revealed that direct amination of aromatic compounds with halamines in the presence of a Lewis acid catalyst results in an unusual orientation.[3] For example, toluene–trichloramine–aluminum chloride yielded *m*-toluidine.[3,4] On the basis of rather limited evidence, an addition–elimination mechanism (σ substitution) was tentatively advanced.[4,5] The present communication, which is concerned with the nature of this novel aromatic amination reaction, provides additional information of a quantitative type derived from competitive amination studies with trichloramine–aluminum bromide.

Results and Discussion

In order to accomplish as high a degree of accuracy as possible, the relative reactivities were determined with toluene, rather than benzene, as the standard reference compound. The indicated aromatic reactants were studied *vs.* toluene in either ethylene dichloride (Table I) or *o*-dichlorobenzene (Table II): benzene, ethylbenzene, isopropylbenzene, *t*-butylbenzene, and *o*-, *m*-, and *p*-xylene. Our earlier work[5] established the nature of the derived products: *m*-alkylanilines from monoalkylbenzenes, 2,3- and 3,4-xylidine from *o*-xylene, 2,5-xylidine from *p*-xylene, and 3,5-xylidine from *m*-xylene.

Table I. Relative Rates of Aromatic Amination in Ethylene Dichloride[a]

ArH	ArH/ $C_6H_5CH_3$, *M*	$k_{ArH}/k_{C_6H_5CH_3}$ Obsd	Calcd
Benzene	2:1	0.04	0.02
Benzene	5:1	0.10	0.02
o-Xylene	1:2	3.4	6.8[b]
o-Xylene	1:1	5.2	5.2
p-Xylene	1:2	3.2	6.4
p-Xylene	1:1	5.3	5.3
m-Xylene	1:4	12	48
m-Xylene	1:2	24	48[b]
m-Xylene	1:1	49	49

[a] $NCl_3/AlBr_3/ArH/C_2H_4Cl_2$ = 1:3:*ca.* 50:*ca.* 50, 0°, 15 min. [b] Precipitate present at the end of reaction.

Table II. Relative Rates of Aromatic Amination in *o*-Dichlorobenzene[a]

ArH	ArH/ $C_6H_5CH_3$, *M*	$k_{ArH}/k_{C_6H_5CH_3}$ Obsd	Calcd
Benzene	1:1	0.0055	0.0055[b–d]
Benzene	2:1	0.0100	0.0050
Ethylbenzene	1:1	0.9	0.9
Ethylbenzene	1:1	0.8	0.8[b,e,f]
Ethylbenzene	1:1	0.7	0.7[b]
Isopropylbenzene	1:1	0.6	0.6[d]
Isopropylbenzene	1:1	0.6	0.6
Isopropylbenzene	1:1	0.6	0.6[d]
o-Xylene	1:1	6	6[d]
o-Xylene	1:2	3	6
p-Xylene	1:1	8	8[d]
p-Xylene	1:2	4.1	8.2[b,c,g]
p-Xylene	1:1	8.2	8.2
m-Xylene	1:1	57	57
m-Xylene	1:2	24.5	49
m-Xylene	1:2	24.5	49
m-Xylene	1:3	16	48[d]

[a] $NCl_3/AlBr_3/ArH/o\text{-}C_6H_4Cl_2$ = 1:3:*ca.* 50:*ca.* 50, 0°, 15 min. [b] Precipitate present at the end of reaction. [c] Catalyst/trichloramine = 2. [d] Small amount of solid present throughout (presumably residual material from the aluminum bromide catalyst). [e] Carried out exposed to the atmosphere. [f] 25 min. [g] 90 min.

In order to procure homogeneity it was necessary to maintain a careful control of reaction conditions. Investigations with aluminum chloride catalyst demonstrated that reaction was rapid (Table III). Solution was favored by use of aluminum bromide in place of the more insoluble aluminum chloride. Short reaction times were preferred since precipitate formed during prolonged periods. Furthermore, addition of *o*-dichlorobenzene or ethylene dichloride proved advantageous since in the absence of solvent a small, lower, oily layer was present. The use of large amounts of catalyst, $AlBr_3/NCl_3$ = 3, was essential for the elimination of solid which separated at lower ratios, *e.g.*, 2. If

---

(1) Paper III: Chemistry of N-Halamines, presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

(2) From the M.S. Thesis, 1965, of J. A. L.

(3) P. Kovacic, R. M. Lange, J. L. Foote, C. T. Goralski, J. J. Hiller, Jr., and J. A. Levisky, *J. Am. Chem. Soc.*, **86**, 1650 (1964).

(4) P. Kovacic, C. T. Goralski, J. J. Hiller, Jr., J. A. Levisky, and R. M Lange, *ibid.*, **87**, 1262 (1965).

(5) P. Kovacic, J. A. Levisky, and C. T. Goralski, *ibid.*, **88**, 100 (1966).

Table III. Time Variation in Toluene Amination[a]

Time, hr	*m*-Toluidine yield, %
0.25	33
0.5	29
1	29
1.5	28
3	30

[a] $NCl_3/AlCl_3/o\text{-}C_6H_4Cl_2/C_6H_5CH_3 = 1:2:3:25$, −5 to +5°.

moisture was not carefully excluded, precipitation was observed to occur.

In competitive experiments, the problem of obtaining a uniform distribution of reactants must be considered. Since amination is relatively rapid, reaction may take place quickly at the point of entrance of the reagent without the necessary diffusion.[6] Thus, if there is a large difference in reactivity between the aromatics in competition for a very reactive electrophile, the more reactive species would become impoverished in the layer adjacent to the added electrophile. The error thus introduced would tend to make the competitors nearly equal in reaction rate. However, if the reactivity difference between the competitors is not large, the error probably would be small.[7] In order to minimize this possible difficulty, a dilute solution of trichloramine was introduced into the reaction mixture. Furthermore, the diffusion question has been the subject of most uncertainty and controversy in those cases where intermolecular selectivity is low and intramolecular selectivity high.[8] In our systems the relative rates observed with ordinary stirring point to electrophilic attack by a species possessing moderate activity.

With the aim of ascertaining the accuracy of the method, experiments were carried out to establish whether or not competition actually occurred under the experimental conditions. Altering the relative concentrations of the aromatic competitors showed that the relative rate remains the same within experimental error on the assumption of a first-order dependence in aromatic. As a further check on the validity, aromatic reactants other than toluene were employed as the reference compounds (Table IV). Except for one case, the systems cross-checked satisfactorily with respect to the various substrates in the two solvents. Consequently, with the single exception, the observed relative rates are real and represent direct competition of the substrates.

Table IV. Relative Rates of Amination[a]

ArH	ArH′	ArH/ArH′, *M*	$k_{ArH}/k_{ArH'}$ Obsd	$k_{ArH}/k_{ArH'}$ Calcd
p-Xylene	*o*-Xylene	1:1	1.3	1.3
p-Xylene	*m*-Xylene	1:1	0.14	0.14

[a] $NCl_3/AlBr_3/ArH,ArH'/o\text{-}C_6H_4Cl_2$ = 1:3:*ca.* 50:*ca.* 50, 0°, 15 min.

The lone discrepancy was encountered in the determination of $k_{C_6H_6}/k_{C_6H_5CH_3}$. Since an appreciably larger amount of by-product amine was found with this pair in *o*-dichlorobenzene, the data from ethylene dichloride would appear to be more reliable. However, the ratios from *o*-dichlorobenzene are in better accord with those observed by Stock and co-workers[8c] in chlorination catalyzed by stannic chloride ($k_{C_6H_6}/k_{C_6H_5CH_3} = 0.006$, $k_{p\text{-xylene}}/k_{\text{toluene}} = 9$). Hence, there is uncertainty concerning the correct value for benzene *vs.* toluene. No appreciable change in the relative rates was effected by the indicated variations: (1) time in the range 15 to 180 min, (2) temperature in the range, −25 to +10°, and (3) heterogeneous or homogeneous. Obviously the aspects making for heterogeneity exert a negligible influence on the competition reaction.

The value of the relative rate for *t*-butylbenzene *vs.* toluene could not be obtained by the standard method. In addition to the expected products, *m*-toluidine and *m*-*t*-butylaniline, the reaction yielded as the principal basic component, 3-*t*-butyl-5-methylaniline. Various means were used in identification of the dialkylaniline, including comparison with authentic material formed from σ amination of *m*-*t*-butyltoluene. The observed result from the competition study can be accounted for very nicely on the basis of disproportionation of *t*-butylbenzene in the presence of toluene yielding benzene and *t*-butyltoluene. Both direct substitution in toluene and rearrangement would yield *m*-*t*-butyltoluene. This hydrocarbon is apparently the component most prone to amination.

Small amounts of higher boiling basic by-products usually were generated in the competitive experiments involving monoalkylbenzenes. With the exception of the benzene–toluene system in *o*-dichlorobenzene, less than 10% of the total area (glpc analysis) is attributed to this fraction, thus introducing only a slight error in the value of the relative rate constant. No detectable higher boiling fraction was observed from the dialkylbenzenes. In one of the experiments, benzene *vs.* toluene, product distillation was carried out yielding <8% of residue.

Comparison with previous investigations (Table V) involving protonation[9,10] and halogenation[11–14] proves highly illuminating. The relative basicities of methylbenzenes with respect to formation of the σ complexes, $ArH_2^+BF_4^-$, have been determined.[9] Results from aluminum bromide–hydrogen bromide confirmed the order of basicity.[10] By plotting the logarithm of the relative rate of amination of the methylbenzenes against the logarithm of the relative basicities, a simple linear relationship is observed (Figure 1). Analogously, a graph of the logarithm of the relative rates of amination *vs.* the logarithm of the relative rates of bromination with molecular bromine[11,12] reveals a linear relationship (Figure 2). A similar correlation (very akin to Figure

---

[6] A. W. Francis, *J. Am. Chem. Soc.*, **48**, 655 (1926).

[7] G. A. Olah, S. J. Kuhn, S. H. Flood, and B. A. Hardie, *ibid.*, **86**, 1039 (1964).

[8] (a) C. D. Ritchie and H. Win, *J. Org. Chem.*, **29**, 3093 (1964); (b) W. S. Tolgyesi, *Can. J. Chem.*, **43**, 343 (1965); (c) A. Himoe, B. M Hoffman, J. K. Housinger, and L. M. Stock, unpublished work; (d) G. A. Olah and N. A. Overchuck, *J. Am. Chem. Soc.*, **87**, 5786 (1965).

[9] D. A. McCaulay and A. P. Lien, *ibid.*, **73**, 2013 (1951); D. A. McCaulay, B. H. Shoemaker, and A. P. Lien, *Ind. Eng. Chem.*, **42**, 2103 (1950).

[10] H. C. Brown and W. J. Wallace, *J. Am. Chem. Soc.*, **75**, 6268 (1953).

[11] P. W. Robertson, P. B. D. de la Mare, and B. E. Swedlund, *J. Chem. Soc.*, 782 (1953).

[12] H. C. Brown and L. M. Stock, *J. Am. Chem. Soc.*, **79**, 1421 (1957).

[13] H. C. Brown and L. M. Stock, *ibid.*, **79**, 5175 (1957).

[14] G. A. Olah, S. J. Kuhn, and B. A. Hardie, *ibid.*, **86**, 1055 (1964).

Table V. Relative Rates of Electrophilic Substitution with Benzene and Alkylbenzenes

	$k_{ArH}/k_{C_6H_5CH_3}$					
	Protonation,	Bromination		Chlorination, Cl_2		
	$HF-BF_3$[a]	Br_2-HOAc[b]	Br_2-HOAc[c]	HOAc[d]	$FeCl_3-CH_3NO_2$[e]	$AlCl_3-CH_3NO_2$[e]
Benzene	...	0.003	0.002	0.003	0.074	0.054
Toluene	1	1	1	1	1	1
Ethylbenzene	...	0.85	...	...	0.89	0.95
Isopropylbenzene	...	0.53	...	...	...	...
o-Xylene	200	...	8.6	6.1	2.8	3.8
p-Xylene	100	...	4.1	6	3.2	4
m-Xylene	2000	...	849	538	8.1	11

[a] Reference 9. [b] Reference 11. [c] Reference 12. [d] Reference 13. [e] Reference 14.

2) *vs.* amination is provided by the data of Brown and Stock[13] concerning halogenation of benzene and alkylbenzenes with molecular chlorine.

Previously Brown and Brady[15] obtained a linear logarithmic plot by graphing the relative rates of chlorination *vs.* relative basicities of the methylbenzenes. This was interpreted as indicating the crucial involvement of a σ-complex intermediate in the chlorination reaction. Also log *k* for protodedeuteration of methylbenzenes *vs.* the logarithms of relative equilibrium constants in hydrofluoric acid gives a linear relationship.[16a] In polynuclear systems, the logarithms of the relative reactivities in deuteriodeprotonation, nitration, and chlorination *vs.* the logarithms of relative equilibrium constants for protonation in hydrofluoric acid show a linear correlation.[16b] This parallelism is a good indication of similar energetics in the various cases.[16]

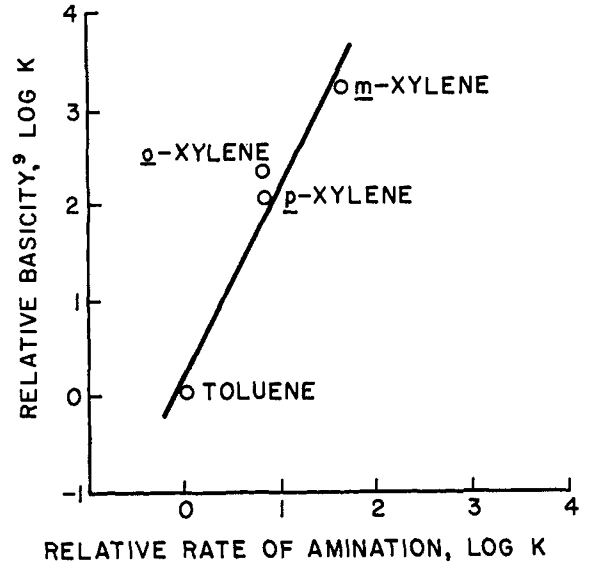


Figure 1. Relative rates of amination *vs.* relative basicity; amination in ethylene dichloride or *o*-dichlorobenzene; slope = 2.0.

The quantitative correspondence between the results for amination and the earlier investigations entailing protonation, bromination, and chlorination provides strong evidence for participation of a σ-complex intermediate in the rate-determining step in our studies. A comparison reveals the following order of activity for the electrophiles in these reactions: amination > chlorination > bromination > protonation. Activity is determined by a variety of factors including inherent energy, degree of charge or dipole, and kind and amount of solvation.

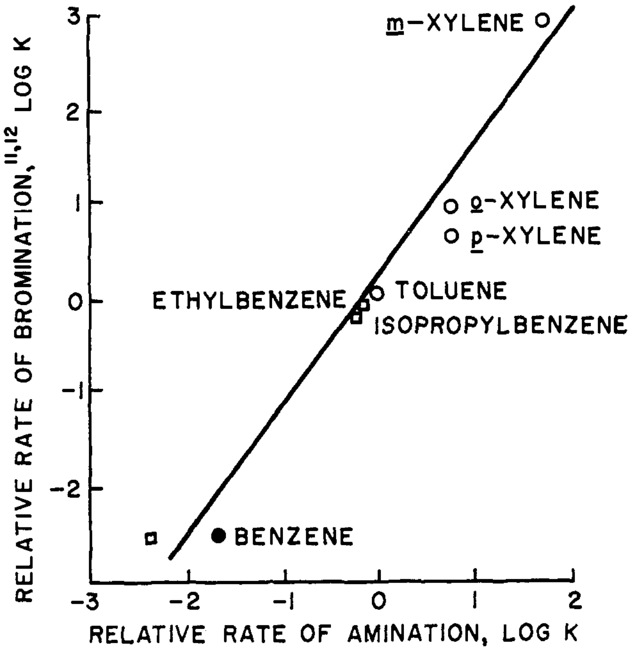


Figure 2. Relative rates of amination *vs.* bromination; amination in ethylene dichloride or *o*-dichlorobenzene (○), in ethylene dichloride (●), in *o*-dichlorobenzene (□); slope = 1.4.

In addition to the benzene/toluene/xylene data, the relative rate order for amination of monoalkylbenzenes, toluene > ethylbenzene > isopropylbenzene (Table II), and also the quantitative differences are in excellent agreement with findings from electrophilic substitutions including bromination (Table V, Figure 2) and chlorination.[17] This provides further confirmation of a σ-complex mechanism for amination.

In the case of *p*-xylene *vs.* *o*-xylene the rate was observed to be approximately equal in ethylene dichloride and slightly greater for the *para* isomer in *o*-dichlorobenzene. With reference to previous investigations various situations have been observed (Table V): *ortho* > *para*, *ortho* < *para*, and *ortho* ~ *para*. It should be noted that a π-complex mechanism was ad-

---

(15) H. C. Brown and J. D. Brady, *J. Am. Chem. Soc.*, **74**, 3570 (1952).

(16) A. Streitwieser, Jr., "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1961: (a) p 318; (b) pp 323–328.

(17) P. B. D. de la Mare and P. W. Robertson, *J. Chem. Soc.*, 279 (1943).

vanced to interpret the data from catalyzed chlorination.[14]

With this background, let us now consider the theoretical aspects of the amination reaction. σ Substitution apparently occurs when, (1) the appropriate arenonium ion forms, (2) nucleophilic attack of the σ complex competes favorably with proton elimination, and (3) subsequent rearomatization takes place with facility. The usual route following σ-complex formation is proton elimination. Why should the alternative pathway become attractive in the present case? Presumably, amination competes favorably because of the high degree of nucleophilicity associated with the nitrogen-containing base.

Investigations were carried out with the aim of obtaining insight into the nature of the intermediate σ complex. Two reasonable possibilities entail formation by attack of either a proton or chloronium ion (or $Cl^{\delta+}$). In order to test the protonation hypothesis, reactions were performed with added water which presumably should favor this route. Earlier work with the toluene–trichloramine–aluminum chloride–water system showed no increase in *m*-toluidine yield on introduction of water.[4] A similar result was observed in the present study with *sec*-butylbenzene (Table VI).

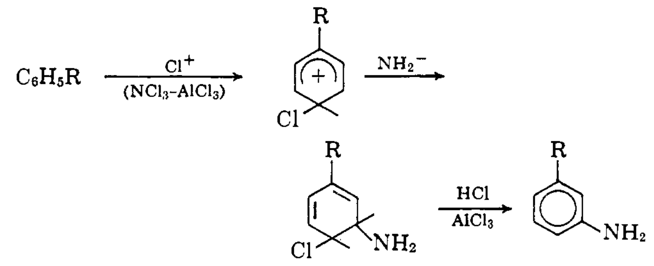
Table VI. Effect of Variation in Water Content in Amination of *sec*-Butylbenzene

Conditions[a]	*sec*-Butylbenzene, mole	NCl_3, mole	$AlCl_3$, mole	*o*-$C_6H_4Cl_2$, moles	*m*-*sec*-Butylaniline yield, %
Standard	1	0.107	0.214	1.75	23–27
Dry	0.8	0.085	0.170	1.4	28–31
Wet	1	0.107	0.214	1.75	24–28

[a] See the Experimental Section.

Although not conclusive, these findings suggest principal participation of the chloroarenonium ion, rather than the σ complex from protonation. Perhaps the same type of positively charged entity is involved in both amination and chlorination by trichloramine. N-Chloramines are known to effect aromatic halogenation.[4,18,19] Evidence for nucleophilic attack upon a chloroarenonium ion is provided by formation of *p*-chloroaniline as a product from fluorobenzene or anisole with this aminating agent.[20]

Although recent data[5] indicate that trichloramine is not involved as such, the question of the actual nucleophile which participates still remains unanswered. For the sake of simplicity, amide ion is used in the mechanistic scheme which portrays the over-all transformation. It is indeed remarkable that nucleophilic behavior of this type is exhibited by a system containing strong Lewis acids. The elimination step is analogous to the reported conversion of 1-methylcyclohexadiene-1,4 monofluoride to toluene by treatment with silver tetrafluoroborate.[21]



Olah has proposed formation of an oriented π complex in the rate-determining step in certain electrophilic aromatic substitutions.[22] The examples are characterized by high intramolecular selectivity, but low intermolecular selectivity, *e.g.*, $k_{\text{toluene}}/k_{\text{benzene}} = 1.67$ and $k_{m\text{-xylene}}/k_{\text{benzene}} = 1.65$. Since the corresponding values in amination are much higher, $k_{\text{toluene}}/k_{\text{benzene}} = 51$ (or 200) and $k_{m\text{-xylene}}/k_{\text{benzene}}(\text{calcd}) = 2448$, the σ-complex intermediate appears more likely in this case. There are indications of a gradual blending together of the σ- and π-complex mechanisms.[22d] Hence, it may well be that, since the electrophile in our case exhibits moderate activity the positively charged entity derived from the aromatic substrate possesses the character of an oriented π complex to some degree. It should be recognized that the π-complex mechanism is the subject of current controversy.[8]

Several reports have appeared recently of aromatic substitution reactions which apparently proceed by addition–elimination. Such a pathway was proposed by Myhre and Owen[23] for formation of 2,4,6-tri-*t*-butylphenyl acetate, one of the products arising from exposure of 1,3,5-tri-*t*-butylbenzene to bromine and sodium acetate. This well might constitute a special case because of the crowded nature of the aromatic reactant. Working in the polynuclear series, de la Mare and Koenigsberger demonstrated that 9-acetoxyphenanthrene is generated in the phenanthrene–chlorine–acetic acid system *via* the intermediate acetoxychloride adduct.[24a] Similarly, 9-methoxyphenanthrene can be formed from interaction with bromine in methanol.[24b] Certainly, these constitute a special category in the general mechanistic picture because of the pronounced olefinic character of the 9,10-position in phenanthrene. In the case of olefins, an analogous reaction has been observed, *e.g.*, conversion to the acetoxychloride adduct in chlorine–acetic acid, followed by formation of the corresponding vinyl acetate through elimination of hydrogen chloride.[24a] Furthermore, there have been suggestions that acetoxylation, which accompanies aromatic nitration in certain systems, may occur by addition–elimination.[23,24a]

Although we favor the σ-substitution mechanism, it would be prudent to ponder alternative interpretations of the available data for amination. Let us first consider the possibility of classical electrophilic substitu-

---

(18) N. Stoll, *Bull. Soc. Chim. Belges*, **38**, 71 (1929); *Chem. Abstr.*, **23**, 4456 (1929); G. N. Dorofeenko, *Nauchn. Zap Lugansk. Sel'skokhoz. Inst.*, **7**, 203 (1961); *Chem. Abstr.*, **58**, 2393 (1963).

(19) M. D. Carr and B. D. England, *Proc. Chem. Soc.*, 350 (1958); L. O. Brown and F. G. Soper, *J. Chem. Soc.*, 3576 (1953).

(20) P. Kovacic, J. J. Hiller, Jr., J. F. Gormish, and J. A. Levisky, *Chem. Commun.*, No. **22**, 580 (1965).

(21) G. A. Olah, A. E. Pavlath, and J. A. Olah, *J. Am. Chem. Soc.*, **80**, 6540 (1958).

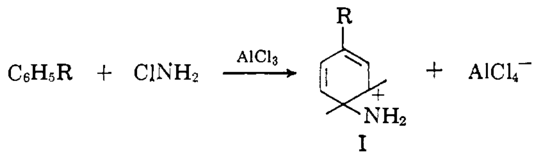
(22) (a) G. A. Olah, S. J. Kuhn, S. H. Flood, and B. A. Hardie, *ibid.*, **86**, 1039 (1964); (b) G. A. Olah, S. J. Kuhn, and S. H. Flood, *ibid.*, **84**, 1688 (1962); (c) G. A. Olah, S. J. Kuhn, and S. H. Flood, *ibid.*, **83**, 4571 (1961); (d) G. A. Olah, S. H. Flood, S. J. Kuhn, M. E. Moffatt, and N. A. Overchuck, *ibid.*, **86**, 1046 (1964).

(23) P. C. Myhre and G. S. Owen, Abstracts of Papers, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965.

(24) (a) P. B. D. de la Mare and R. Koenigsberger, *J. Chem. Soc.*, 5327 (1964); (b) L. F. Fieser, R. P. Jacobsen, and C. C. Price, *J. Am. Chem. Soc.*, **58**, 2163 (1936).

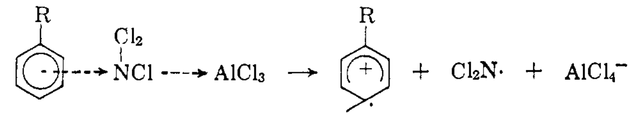
tion. The observed *meta* orientation argues strongly against this viewpoint. Earlier work[4] indicated that, for toluene amination, the toluidine isomers were stable to rearrangement under simulated reaction conditions. Thus, initial electrophilic attack followed by isomerization of the end product can be ruled out. However, there is the possibility that an intermediate, such as I, may be highly susceptible to rearrangement. A favorable driving force would be the presence of an unshared pair on nitrogen. Nevertheless, we deem this to be a weak argument. Analogous atoms or groups introduced by the indicated processes do not demonstrate a high propensity to isomerization: amination by hydroxylamines[25,26] and azides,[26-28] halogenation,[12] and oxygenation by peroxides.[29]

$$NCl_3 + 2C_6H_5R \xrightarrow{AlCl_3} ClNH_2 + 2ClC_6H_4R$$



I

In view of the versatility of N-halamines, an additional route should be considered. The illustrated radical cation II might well be energetically similar to the conventional σ complex. Appropriate subsequent transformations can be envisioned leading to the end products. This type of intermediate was recently proposed in the formation of *p*-piperidinoanisole from anisole–N-chloropiperidine–ferrous salt.[30] Also, in this general category should be mentioned the possible participation of $Cl_2(H)N\cdot^+$. A nitrogen radical–cation has been invoked in a mechanistic interpretation of the Hofmann–Löffler reaction.[31]



II

Evidence has already been presented[4] against direct nucleophilic, radical, or nitrene substitution mechanisms for the amination reaction.

In general the neutral fractions were not examined in this study. Previously the neutral product from toluene was shown to be mainly chlorotoluene, *ortho/meta/para* = 68:1:31.[4]

Experimental Section[32]

Warning: Exercise the necessary precautions in working with N-halamines (toxicity and explosion hazards).

Materials. Ethylene dichloride was fractionally distilled from calcium hydride. The other reagents are described in the preceding paper.[5]

Analytical Procedures. Infrared analyses were made as previously noted.[5] Gas chromatography was carried out with a homemade unit. All three vpc columns used in the companion study[5] were employed in the investigations involving toluene *vs. m-* or *p*-xylene. Analysis of the competitive aminations with *o*-xylene, and *m- vs. p*-cylene was carried out with column 3.[5] Except for the *t*-butylbenzene case, use was made of calibration curves obtained with authentic mixtures. Estimated precision of the data is ±3%.

Preparation of Trichloramine Solutions. These solutions in the various solvents were prepared by the procedure (method B) previously described.[5]

Competitive Aminations.[33] In a glove bag were placed sealed aluminum bromide, a mortar and pestle, and a dry, 250-ml, glass-stoppered flask of known weight. The bag was purged for 10 min with dry nitrogen and then kept inflated by means of a positive pressure of nitrogen. The aluminum bromide was pulverized and placed in the flask which was stoppered, removed from the bag, and weighed in order to determine the amount of aluminum bromide.

In a second glove bag under nitrogen, the aluminum bromide was added at −5° to a mixture of the aromatic reactants and solvent in a 500-ml, glass-stoppered flask. After being shaken vigorously the mixture was filtered by suction from a minute amount of insoluble material into a dry 1-l. three-neck flask with a magnetic stirring bar. Next, the vessel was equipped with a thermometer, dropping funnel, drying tube, and a $\overline{T}$ 45-50 ground-glass stopper, and removed from the nitrogen atmosphere. The calculated amount (based on a 3:1 $AlBr_3/NCl_3$ ratio) of trichloramine solution was measured, diluted with 100 ml of solvent, and added to the mixture during 15 min. Examination of the reaction mixture before, during, and after addition of the trichloramine solution revealed a homogeneous system. Filtration afforded no solid material. The solution was then immediately added with stirring to a mixture of ice–hydrochloric acid. The usual work-up procedure was followed.[5]

In some of the competitive experiments in which the filtration step was omitted minute amounts of solid were present. In certain cases precipitate formed during reaction.

Analysis by gas chromatography was made on the undistilled amine product. In one experiment distillation of the basic product from the benzene–toluene competitive amination revealed a negligible amount of residue.

3-Methyl-5-*t*-butylaniline. A. From Competitive Amination of Toluene and *t*-Butylbenzene. The basic product from this relative rate study contained the indicated components: 3-methyl-5-*t*-butylaniline (70%), *m*-toluidine (17%), *m-t*-butylaniline (8%), and unidentified higher molecular weight material (5%). Infrared analysis of the principal component showed characteristic absorption maxima for the NH_2 group at 3300–3500 (s) and 1600 (s) cm^{-1}. Bands at 845 (m), 830 (s), and 700 (s) cm^{-1} indicated 1,3,5-substitution.

The proton magnetic resonance spectrum (tetramethylsilane as external reference) provided evidence for the presence of *t*-butyl, methyl, and amino groups (in ppm): singlet at τ 1.24 ($ArCH_3$), singlet at 2.22 (ArC*H*), singlet at 3.42 ($ArNH_2$), and three singlets at 6.2–6.6 (Ar*H*); relative intensities, 9:3:2:3.

A sample for analysis was collected by gas chromatography.

Anal. Calcd for $C_{11}H_{17}N$: C, 80.98; H, 10.43; N, 8.59. Found: C, 80.73; H, 10.55; N, 8.67.

B. From Amination of *m-t*-Butyltoluene. *m-t*-Butyltoluene was prepared (reaction time of about 35 min) in a Dry Ice bath from the *para* isomer in hydrogen fluoride–boron trifluoride according to the procedure of Pearson and co-workers for *m*-cymene.[34] A gross mixture resulted from which *m-t*-butyltoluene was isolated in 18% yield by fractional distillation, bp (capillary) 186–188° (uncor), $n^{25}D$ 1.4914; lit.[35] bp 189°, $n^{20}D$ 1.4945. The infrared spectrum, which was essentially identical with that of authentic material, pointed to the presence of a small amount of *para*-isomer impurity.

Amination according to the standard procedure[5] yielded a mixture of amines, the major component of which possessed an in-

---

[25] P. Kovacic and J. L. Foote, *J. Am. Chem. Soc.*, **83**, 743 (1961); P. Kovacic, R. P. Bennett, and J. L. Foote, *ibid.*, **84**, 759 (1962); P. Kovacic and R. P. Bennett, *ibid.*, **83**, 221 (1961); P. Kovacic, R. P. Bennett, and J. L. Foote, *J. Org. Chem.*, **26**, 3013 (1961).

[26] R. N. Keller and P. A. S. Smith, *J. Am. Chem. Soc.*, **66**, 1122 (1944).

[27] P. Kovacic, R. L. Russell, and R. P. Bennett, *ibid.*, **86**, 1588 (1964).

[28] W. Borsche and H. Hahn, *Ber.*, **82**, 260 (1949).

[29] P. Kovacic and S. T. Morneweck, *J. Am. Chem. Soc.*, **87**, 1566 (1965); P. Kovacic and M. Kurz, *ibid.*, **87**, 4811 (1965); A. J. Davidson and R. O. C. Norman, *J. Chem. Soc.*, 5404 (1964); C. A. Buehler and H. Hart, *J. Am. Chem. Soc.*, **85**, 2177 (1963).

[30] F. Minisci and R. Galli, *Tetrahedron Letters*, No. **8**, 433 (1965).

[31] M. E. Wolff, *Chem. Rev.*, **63**, 55 (1963).

[32] Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

[33] We are grateful to Mr. C. T. Goralski for a preliminary study of the benzene–toluene system.

[34] We are grateful to Professor D. E. Pearson for making available this procedure: D. E. Pearson, R. D. Wysong, and J. M. Finkel, unpublished work.

[35] K. J. Serijan, H. F. Hipsher, and L. C. Gibbons, *J. Am. Chem. Soc.*, 71, 873 (1949).

frared spectrum identical with that of the principal product from competitive amination of *t*-butylbenzene and toluene.

Water Cocatalytic Studies with ***sec*****-Butylbenzene. A. Dry.** Aluminum chloride (Fisher sublimed), freshly opened in a dry nitrogen atmosphere, was weighed and placed in a 1-l. three-neck flask, equipped with stirrer, condenser, thermometer, and drying tube, containing freshly distilled *sec*-butylbenzene at 10° under nitrogen. To this was added a trichloramine solution dried for 3 hr over magnesium sulfate before use. The standard reaction procedure was followed.[5]

B. Wet. The dried trichloramine solution (200 ml) was shaken with 50 ml of water. After standing for 5 min, the layers were separated and the volumes were measured. The amount of water absorbed was 2.0 ml (0.11 mole). The wet trichloramine solution was added to the aluminum chloride-*sec*-butylbenzene mixture at 10°. The standard reaction procedure was followed.[5]

Acknowledgment. We are grateful to the National Science Foundation for support of this work.

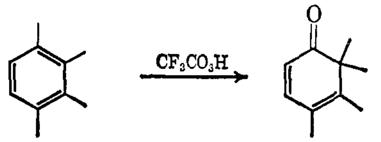
Preparation, Chemistry, and Photochemistry of Hexaalkyl-2,4-cyclohexadienones[1-3]

Harold Hart, Peter M. Collins, and Anthony J. Waring

Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan 48823. Received October 27, 1965

Abstract: Hexamethyl- and hexaethylbenzene are oxidized by peroxytrifluoroacetic acid-boron fluoride to hexaalkyl-2,4-cyclohexadienones **1** and **2**, respectively. The dienones do not dimerize, but **1** gives Diels-Alder adducts with maleic anhydride and other dienophiles. The enolate anion of **1** is much more easily formed at the C-3 methyl than at the C-5 methyl, which enables these methyls to be selectively deuterated. Reaction of **1** with methylmagnesium iodide leads to 1,2,3,3,4,5-hexamethyl-6-methylene-1,4-cyclohexadiene (**8**). Reduction of **1** or **2** with lithium aluminum hydride gives the secondary alcohols **11** and **13** which, on treatment with acid, are converted either to cross-conjugated trienes or to hexaalkylbenzenes, depending on controllable conditions. Factors which affect this partition of the intermediate carbonium ion are discussed. Catalytic reduction of **1** gave a conjugated and nonconjugated enone, the latter being formed by "1,4" addition of hydrogen. Irradiation of **1** or **2** leads to bicyclo[3.1.0]hexanes **18** or **22**. These are a novel type of photorearrangement product, not previously obtained from 2,4-cyclohexadienones. Labeling experiments show that a "bond-crossing" mechanism, not alkyl migration, is involved.

Earlier reports[3] from this laboratory have illustrated the use of peroxytrifluoroacetic acid-boron fluoride as a reagent for the oxidation of aromatic compounds. With a partially substituted aromatic ring, phenols were obtained, the yield being quite good if positions *ortho* or *para* to the entering hydroxyl group were blocked, to retard further oxidation. When the oxidation was applied to prehnitene (1,2,3,4-tetramethylbenzene), one of the products, isolated in very low yield, was 4,5,6,6-tetramethyl-2,4-cyclohexadienone.[4]



This could be accounted for by attack of the cationic oxidant at an already substituted position (C-1) of the hydrocarbon, followed by a Wagner-Meerwein methyl migration and proton loss. This result suggested to us that if the original hydrocarbon were entirely alkylated, conversion to dienone might become the dominant reaction path. This hope was fulfilled,[5] and the present paper reports the oxidation of hexamethyl- and hexaethylbenzene to dienones, as well as some of the interesting ground state and photochemistry of these products.

Results and Discussion

Synthesis of Dienones and Structure Proof. Oxidation of hexamethylbenzene with peroxytrifluoroacetic acid and boron fluoride in methylene chloride at 0° afforded hexamethyl-2,4-cyclohexadienone (**1**) in excellent yield. Similarly, hexaethylbenzene gave the ethyl analog (**2**).[6] The oxidation can also be accomplished with 90% hydrogen peroxide in a mixture of acetic and sulfuric acids, although the reaction is less clean and the yield somewhat lower. The latter reagent is of the type used by Waters and Derbyshire[7] to convert mesitylene to mesitol. Epoxidation of the dienones is probably suppressed because of the lower reactivity of conjugated systems[8] and because only a limited excess of oxidant was used.

---

(1) We gratefully acknowledge support by the National Science Foundation (GP-71). P. M. C. thanks the Board of Governors of Birkbeck College, London, for a leave of absence.

(2) Portions of this work have been reported in preliminary form in the following communications: (a) A. J. Waring and H. Hart, *J. Am. Chem. Soc.*, **86**, 1454 (1964); (b) H. Hart and A. J. Waring, *Tetrahedron Letters*, No. **5**, 325 (1965).

(3) Paper V in a series on Oxidations with Peroxytrifluoroacetic Acid-Boron Fluoride. For paper IV, see H. Hart, C. A. Buehler, A. J. Waring, and S. Meyerson, *J. Org. Chem.*, 30, 331 (1965).

(4) H. Hart and C. A. Buehler, *J. Org. Chem.*, **29**, 2397 (1964).

(5) It turns out, however, that it is not necessary that all positions be blocked; pentamethylbenzene and durene give predominantly dienones with peroxytrifluoroacetic acid. These results will be reported in detail later.

(6) Professor E. M. Arnett advises us that application of our reaction to hexaisopropylbenzene did not lead to dienones.

(7) W. A. Waters and D. H. Derbyshire, *Nature*, **165**, 401 (1950); no experimental details were given.

(8) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, p 115. A mass spectrum of **1** does show