The Chemistry of Nitrogen Radicals. VII. The Abstraction of Hydrogen from Substituted Toluenes by the Piperidinium Radical

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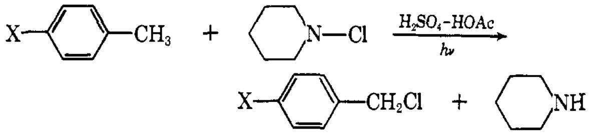
Abstract: The relativity reactivities of seven substituted toluenes toward benzylic hydrogen abstraction by the piperidinium radical $H\dot{N}^+(CH_2)_5$ have been determined in 2 *M* sulfuric acid–acetic acid and plotted against the σ^+ substituent constants. The ρ value thereby obtained was -1.36. The implications of this result are discussed.

Our previous studies have shown that aminium radicals $R_2\dot{N}^+H$ generated from dialkyl-N-chloramines in 4 *M* sulfuric acid in acetic acid add to carbon–carbon double bonds in decided preference to abstracting allylic hydrogen atoms; the major competing reaction to radical addition (amination) is electrophilic chlorination of the olefin, especially in the case of olefins which do not contain an electron-withdrawing group.[1] In the absence of a reactive olefinic compound, however, one would expect intermolecular hydrogen abstraction to occur, especially from benzylic centers, if the Hofmann–Loeffler rearrangement is precluded by inadequate chain length in the dialkylchloramine.

We now describe a study from which a ρ value for hydrogen abstraction from ring-substituted toluenes by the piperidinium radical was determined (eq 1), in order to establish better two aspects of such intermolecular hydrogen abstraction reactions. It was of particular interest to compare the result with the magnitude[2] of polar effects operating in similar reactions of other radicals, since this would be an indication of whether the unique presence of the positive charge at the radical site in the aminium radical had led to an unusually large polar influence of the ring substituents in the transition state. This possibility appeared especially attractive, since the partial charge separation involved in charge polarized transition states among neutral radicals would not be a factor in aminium radical reactions, *e.g.*



(1)

$$[ArCH_2{-}H + \cdot X \rightleftharpoons Ar\overset{+}{C}H_2\ \dot{H}\ \bar{X}] \quad \text{neutral radical}$$

$$[ArCH_2{-}H + H\overset{+}{\underset{\cdot}{N}}R_2 \rightleftharpoons Ar\overset{+}{C}H_2\ \dot{H}\ H\ddot{N}R_2] \quad \text{aminium radical}$$

It was also highly desirable to determine whether or not the chlorination reaction (1) could involve a free chlorine pathway instead of aminium radicals. A molecular chlorine reaction analogous to the Goldfinger mechanism of N-bromosuccinimide brominations[3] could be ruled out as a principal process if a significantly more negative ρ value than that known for chlorine atom ($\rho = -0.66$[2]) were observed.

Results

Since the nature of the solvent and the presence of amine salts precluded direct glpc analysis of the reaction mixtures, a procedure was established which involved glpc analysis of the products recovered from the work-up of reactions carried to partial completion. It was necessary to show at the outset that (1) the reaction in question was indeed free radical and was the major process, (2) the reaction products were stable up to the point of analysis, and (3) the use of differing concentrations of reactants as necessitated by the nature of the solvent and product analysis did not affect the relative reactivities of the two competing species. The satisfactory demonstration of these points and of certain checks on the validity of product analysis proceeded as follows, whereupon the competition data (Table I) were obtained as described in the Experimental Section; the results are graphically displayed in Figure 1, in which σ^+ constants[4] have been employed for reasons noted below.

The reactant concentrations were usually 0.5 *M* in each of toe two competing hydrocarbons; this value was dictated by the limited solubility of the substrates in 2 *M* H_2SO_4 in acetic acid. The indicated acidic medium was chosen on the basis of our previous work[5] dealing with the Hofmann–Loeffler rearrangement of dibutylchloramine under several conditions of solvent acidity, and the present medium was judged most likely to promote clean, free-radical reactions while permitting the maximum solubility of the substituted toluenes. Since the ratio of strong acid to chloramine had to lie near 8:1,[5] the concentration of N-chloropiperidine could not exceed 0.25 *M*. In order to avoid the consumption of a major portion of the aromatic reactants, we elected to utilize this maximum chloramine concentration and carry our reactions to about 30% completion, rather than use about 0.05 *M* chloramine and run the reactions to near 100% completion. This choice was again based on the results of our earlier work,[5] in which we observed that the disappearance of positive chlorine *vs.* time in the chloramine rearrangement was linear over the first 80% of reaction but invariably slowed considerably thereafter. Since we did not investigate what was the specific cause of this behavior, we chose to avoid dealing with reactions involving the last remaining amounts of chloramine.

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(1) (a) R. S. Neale, *J. Org. Chem.*, **32**, 3263 (1967); (b) R. S. Neale and N. L. Marcus, *ibid.*, **32**, 3273 (1967).

(2) A compilation of ρ values for a variety of radicals has been given by G. A. Russell and R. C. Williamson, Jr., *J. Am. Chem. Soc.*, **86**, 2357 (1964).

(3) J. C. Martin and R. E. Pearson, *ibid.*, **85**, 354 (1963); G. A. Russell, C. DeBoer, and K. M. Desmond, *ibid.*, **85**, 365 (1963); C. Walling, A. L. Rieger, and D. D. Tanner, *ibid.*, **85**, 3129 (1963).

(4) H. C. Brown and Y. Okamoto, *ibid.*, **80**, 4979 (1958).

(5) R. S. Neale and M. R. Walsh, *ibid.*, **87**, 1255 (1965).

Table I. Competitive α Chlorination of Toluenes with 0.25 *M* N-Chloropiperidine in 2 *M* Sulfuric Acid–Acetic Acid at 20° under Ultraviolet Light Catalysis

Substrate A	Concn, *M*	Substrate B	Concn, *M*	Reaction time, min	Chloramine consumed, %	Substrate A-chloride[a] / substrate B-chloride	Point on Figure 1
p-*t*-$C_4H_9C_6H_4CH_3$	0.25[b]	*p*-$ClC_6H_4CH_3$	0.25	18	33	4.40	1[c]
p-*t*-$C_4H_9C_6H_4CH_3$	0.25	$C_6H_5CH_3$	0.25	25	41	1.44	2
p-$CH_3C_6H_4CH_3$	0.50	$C_6H_5CH_3$	0.50	11	35	1.75	3
p-$FC_6H_4CH_3$	0.50	$C_6H_5CH_3$	0.50	25	25	1.04	4
p-$ClC_6H_4CH_3$	0.25[b]	$C_6H_5CH_3$	0.25	19	29	0.608	5
p-$ClC_6H_4CH_3$	0.50	$C_6H_5CH_3$	0.50	13	27	0.524	6
m-$ClC_6H_4CH_3$	0.50	$C_6H_5CH_3$	0.50	67	31	0.264	7
m-$ClC_6H_4CH_3$	0.50	*p*-$ClC_6H_4CH_3$	0.50	110	25	0.471[d]	8[c]
p-$CNC_6H_4CH_3$	0.50	$C_6H_5CH_3$	0.50	39	50	0.122	9
p-$CNC_6H_4CH_3$	0.50	*p*-$ClC_6H_4CH_3$	0.50	23	30	0.187	10[c]
p-$NO_2C_6H_4CH_3$	0.25[b]	*p*-$ClC_6H_4CH_3$	0.25	215	23	0.0555	11[c]
p-$NO_2C_6H_4CH_3$	0.50	*p*-$ClC_6H_4CH_3$	0.50	150	24	0.0512	12[c]

[a] Relative amounts of the benzylic chlorides by glpc analysis. [b] Concentration of N-chloropiperidine, 0.12 *M*. [c] Ratio converted into basis of toluene as substrate B; see Experimental Section. [d] Analysis of products by infrared spectroscopy; see Experimental Section.

Inhibition by air and significant acceleration by light of the rate of loss of positive chlorine were first demonstrated in order to establish that the chlorinations were free-radical chain reactions. When a solution 1 *M* in toluene and 0.25 *M* in the chloramine was irradiated in the presence of air, no positive chlorine was lost, although a reaction began at a rapid rate soon after the air purge was replaced with nitrogen. The reaction ceased suddenly when the air purge was restored and then resumed when nitrogen was again swept through the solution. In a second reaction, only ~2% of the chloramine was decomposed in the presence of 1 *M* toluene when the mixture was stirred under nitrogen in the dark for 4 hr; irradiation produced an immediate reaction, which was 91% complete within 78 min and afforded 76% of benzyl chloride on work-up.

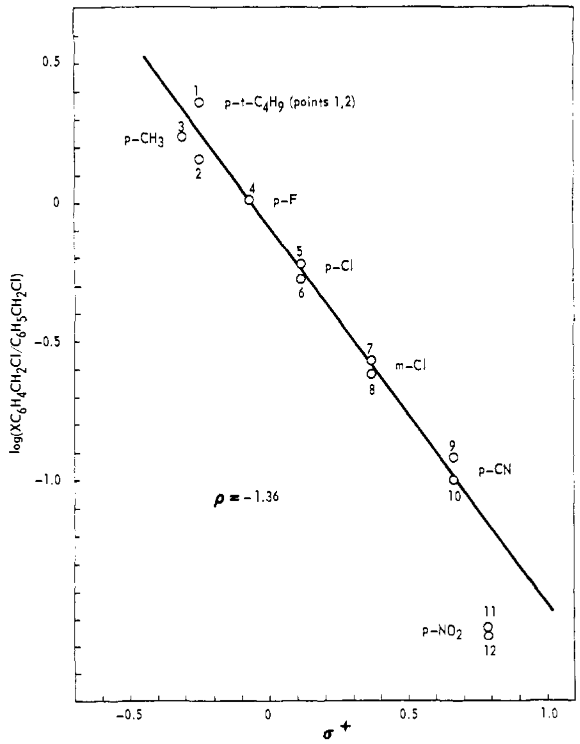

Figure 1. Relationship to substituent constants of the relative reactivities of substituted toluenes toward hydrogen abstraction by the piperidinium radical.

Any question of the stability of the benzyl chlorides formed in the principal reaction was forestalled when benzyl chloride, chosen as a representative benzylic reaction product, was found by glpc analysis to have given no benzyl acetate or benzyl alcohol after standing in the acid medium for 16 hr at 24° followed by work-up in the manner employed for the competition experiments. This involved pouring the acid mixture into ice and water, extracting the neutral reaction products into ether–pentane, decomposing unreacted chloramine with thiosulfate washes, and washing the organic extracts free of acetic acid with aqueous sodium bicarbonate. It was also found that no ester carbonyl band could be detected in the infrared spectra of any of the crude, neutral product mixtures from competition experiments before dilution to standard volumes for glpc analysis, nor did any peaks appear in the glpc spectra in the region known or anticipated for the various benzyl alcohols.

Finally, it was shown that no gross differences in product ratios should be expected as the result of the concentration of reactants when a competitive reaction between toluene and *p*-chlorotoluene under the usual conditions (Figure 1, point 6) gave about the same ratio of *p*-chlorobenzyl chloride:benzyl chloride, 0.524, as a second competition, 0.608 (Figure 1, point 5), which was carried out at one-half the concentration of both aromatics and chloramine. The latter experiment was felt to justify, including on an equal basis with the other competitive reactions, the results involving *p*-*t*-butyltoluene (Figure 1, points 1 and 2), which could only be studied at concentrations of 0.25 *M* because of lower than usual solubility of this hydrocarbon. Although the points involving *p*-nitrotoluene (Figure 1, points 11 and 12) failed to fall on the line of correlation, the similar results obtained at either the 0.5 or 0.25 *M* concentration level tend to confirm the absence of serious concentration effects on the product ratios.

In addition to meeting the three criteria cited above, a final control was required when we could obtain a reasonably accurate product ratio for *p*-nitrotoluene only in a competitive reaction with *p*-chlorotoluene, rather than with toluene itself. Since the resulting value was well away from the line of correlation (Figure 1, point 12), competitive experiments of *p*-chlorotoluene with *p*-cyanotoluene (point 10) and with *m*-chlorotoluene (point 8) were carried out and the results converted into the basis of toluene as the common coreactant. Values close to those obtained from the direct competitions were obtained in these latter two reactions and the result obtained with *p*-nitrotoluene is therefore considered to be as accurate as the results obtained with the other substrates.

One other aspect of the systems studied was also probed briefly. We have assumed that any errors arising from changing relative concentrations of the aromatic reactants as the reactions proceeded under the chosen conditions were small in comparison with the larger probable errors naturally associated with a procedure that did not permit the direct glpc analysis of the reaction mixtures. To ascertain whether it was really necessary to limit the extent of chloramine consumption (Table I), two competitions with 0.5 *M* aromatic reactants were carried to 80% reaction of the chloramine. Although the ratio *p*-chlorobenzyl chloride–benzyl chloride, 0.530, was the same as that observed at lower conversion, 0.524 (Table I), the ratio of the benzyl chlorides formed from *p*-xylene and toluene rose from 1.75 at 35% chloramine consumption (Table I) to 2.83 at 81% consumption, *i.e.*, in the wrong direction from the viewpoint of changing concentrations of reactants. This unexplained increase appeared again in a reaction involving 0.25 *M p*-xylene and 0.5 *M* toluene carried to 78% chloramine consumption, in which the ratio was 2.71; the same statistical correction was made for the presence of two methyl groups in *p*-xylene in this experiment as in the two preceding. Although we cannot be certain that the apparent reactivity of *p*-xylene at 30% conversion is more "correct" than that at higher conversion, we have included the lower conversion result in Figure 1 in order that all the points represent similar reaction conditions.

Discussion

The influence of ring substituents on the rates of abstraction of a methyl hydrogen atom from various toluenes is suggested to be significant by the ρ value of -1.36 determined from the competition results displayed in Figure 1. The substituent constants σ^+ rather than σ were employed in the plot in order that the present results be obtained on the same basis as the ρ values already known for several other radicals; a plot analogous to Figure 1 using σ values resulted in the little changed ρ value of -1.5, although the scatter of the points was slightly greater. Toluenes bearing substituents such as methoxy or phenoxy, which would serve to distinguish between a σ and σ^+ correlation, were not studied in the present system because electrophilic chlorination of the resulting activated rings was anticipated to be severe.

It is evident that the presently observed ρ value on comparison with values[2] obtained for other radical reactions with substituted toluenes locates the aminium radical within the previously established range; thus, a series of common radicals placed in order of increasing ρ values is as follows: $\cdot C_6H_5$ (0), $\cdot Cl$ (-0.66), $\cdot OC(CH_3)_3$ (-0.83), $\cdot N^+H(CH_2)_5$ (-1.36), $\cdot Br$ (-1.46), $\cdot CCl_3$ (-1.46). It appears, therefore, that the presence of the positive charge on the aminium radical did not lead under the chosen conditions to an unusually enhanced dependence of the radical on the polar properties of the aromatic substituents in attaining the transition state for abstraction of a benzylic hydrogen atom.

However, there are three considerations which suggest that the value of ρ observed in this study should be considered a minimum one. Although a chlorine atom mechanism has now been ruled out as the predominant route to the α-chlorination of toluenes in our system by the magnitude of the ρ value, there could still occur a fraction of the total chlorination reactions by this relatively nondiscriminating route. The admixture of this process ($\rho = -0.66$) with that due to hydrogen abstraction by the aminium radical would have lowered somewhat the over-all ρ actually observed. It appears, however, that the extent of any such process involving chlorine atom as the chain-carrying species must have been minor in this study because of the behavior of the *p*-*t*-butyltoluene–toluene system. Here we found no evidence in the monochlorinated reaction product of the isomer containing a chlorinated *t*-butyl group, although the relative reactivity of toluene *vs.* *t*-butylbenzene toward chlorination of the alkyl group by chlorine in the liquid phase is known[6] to be only 2.2:1. Also relevant are some recent results on the chlorination of aliphatic esters by the dimethylaminium radical under related, although distinctly different, conditions; the observed preference in each ester for chlorination of the methylene group farthest removed from the ester carbonyl stood in contrast to the far less selective results known for chlorine atom and was taken as evidence against chlorine atom participation.[7]

Another reason that our results may reflect a minimal ρ value is suggested by the results of Dewar and Marchand,[8] who showed that the electron-withdrawing field effects of aromatic substituents were significantly less in a very polar solvent (D_2O) than in a less polar one (nitromethane). If a polar medium such as ours can satisfy part of the electron demand of the attacking radical, which is charged and undoubtedly highly solvated, there would be anticipated a lesser effect of substituents in the polar medium than in a nonpolar one.

Since it is physically impossible to obtain results analogous to Figure 1 in a nonpolar medium, it is pertinent to consider whether the ρ values of neutral radicals, which have been determined in carbon tetrachloride or an aromatic hydrocarbon, would be much changed in a polar medium. Solvation of transition states could lower the substituent response of a neutral radical by satisfying some of the electron demand of the radical, or the ρ value could be increased if solvation had no effect but to facilitate the separation of charge. Unfortunately, such solvent effects have not been studied, although other influences of polar solvents relevant to our results in acetic acid have been considered. Thus, Walling and Wagner[9] observed a marked increase in β scission of *t*-butoxy radicals in reactions with cyclohexane and a decrease in the selectivity for hydrogen abstraction from 2,3-dimethylbutane when acetic acid

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(6) G. A. Russell, A. Ito, and D. G. Hendry, *J. Am. Chem. Soc.*, **85**, 2976 (1963). One would not anticipate the chlorine atom to exhibit a selectivity significantly different from this in the present solvent due to any complexing effects: E. S. Huyser in "Advances in Free-Radical Chemistry," Vol. I, G. H. Williams, Ed., Logos Press, London, 1965, p 97.

(7) F. Minisci, R. Galli, A. Galli, and R. Bernardi, *Tetrahedron Letters*, 2207 (1967).

(8) M. J. S. Dewar and A. P. Marchand, *J. Am. Chem. Soc.*, **88**, 354 (1966).

(9) C. Walling and P. Wagner, *ibid.*, **85**, 2333 (1963).

instead of the usual halocarbon was employed as solvent. When acetonitrile as a polar but nonhydrogen bonding solvent was used, there appeared little effect on the β-scission reaction. Thus, it is evident that the solvation of transition states by acetic acid significantly and possibly uniquely influences the reactivity of *t*-butoxy radicals. It would therefore be anticipated that solvation of transition states by acetic acid instead of a halocarbon solvent might lead to interesting effects in other radical systems and especially in those involving charged radicals.

Finally, we should note that in comparing ρ values one is dealing with polar effects apparent in transition states which probably occur with different degrees of C–H bond breaking;[2] the ρ values are not, therefore, strictly comparable since a given ρ value will decrease as the extent of bond breaking in the transition state decreases.[10] The moderate magnitude of the ρ value for the piperidinium radical presently observed could therefore indicate that the electron demand of the radical can be satisfied in part by the solvent and is of a low order of magnitude in the first place, or that bond breaking is not particularly well advanced in the transition state. In regard to the latter possibility, it is pertinent to recall that bond breaking does appear to be well advanced in the *intra*molecular abstraction of hydrogen by an aminium radical in hot, aqueous sulfuric acid.[11]

Together with the previously studied reactions of aminium radicals with olefins[1] and *intra*molecular hydrogen abstraction by aminium radicals (Hofmann–Loeffler rearrangement[5,12]), the present information on *inter*molecular hydrogen abstraction completes a basic descriptive characterization of the reactivity of aminium radicals generated from chloramines under the conditions we have consistently[1,5] employed. It is now evident that the presence of a positive charge on an amino radical induces it to add efficiently to olefins in preference to abstracting allylic hydrogen. Furthermore, aminium radicals undergo both facile internal rearrangement[5,12] and β cleavage,[13] as do alkoxy radicals,[14] and abstract activated hydrogen in a rather selective manner in common with the more electrophilic radicals. The principal effect of the positively charged radical center therefore turns out to be a mechanical one; *i.e.*, a strongly acidic solvent has thus far been required and nonpolar, inert media cannot be used. It would now be pertinent to the general synthetic use of amino radicals to obtain an analogous reactivity profile for neutral amino radicals and to show how similar, besides a tendency to add to olefins,[15] amino radicals generated by redox reactions of chloramines (or related precursors) with ferrous or cuprous ion[16] are to aminium radicals.

Two details of the results shown in Figure 1 require a further brief comment. It is evident that the points for *p*-nitrotoluene fall well away from the line of correlation, which was drawn by eye without giving weight to the nitro points. One explanation of the particularly low reactivity of the nitro compound may lie in the known[17] tendency of aromatic nitro compounds to act as radical traps. Thus, the *p*-nitrobenzyl radical might be subject to reactions that would divert this species from the formation of the desired benzyl chloride, thus lowering the apparent reactivity of nitrotoluene. However, of the previous studies of polar effects in radical reactions, those[2] involving chlorine atoms or peroxy radicals successfully included *p*-nitrotoluene among the substrates investigated. Although the σ_p^+ value $+0.790$[4] was employed in these studies as in ours, the "correct" value for the nitro compound, *i.e.*, a best average of values obtained from several types of electrophilic reactions,[4] has not been determined for a lack of data. If we had used the value $\sigma_p^+ = +0.933$ calculated[4] for triarylcarbinol solvolyses,[18] the nitro points would have fallen closer to but still not on the line drawn in Figure 1. Since the other three σ^+ values available from the triarylcarbinol reactions which could be applied to the present work (*p*-CH_3, *p*-Cl, and *m*-Cl) are in good agreement with the σ^+ values obtained[4] for *t*-cumyl chloride solvolyses, the value for $\sigma_{p\text{-}NO_2}^+$ that should have been used in Figure 1 is somewhat uncertain.

Finally, it is remarkable that we were able to observe relatively clean α-chlorination reactions to the virtual exclusion of ring chlorination or amination, since two groups of investigators have independently reported significant yields (50% or better) of either ring chlorinated or aminated aromatics in sulfuric acid media from reactions between N-chloramines and aromatic substrates. Although the German workers[19] reported that no benzylic chlorination products were formed on irradiation of dimethylchloramine and toluene in concentrated sulfuric acid, the Italian group[20] did report the formation of benzyl chloride from Fe(II)-catalyzed reactions of dialkylchloramines in 3:1 sulfuric acid–acetic acid. The yields of benzyl chloride (12–61%) and of toluidines (0–52%) varied with the nature of the chloramine alkyl groups, however, and the specific reaction between N-chloropiperidine (used to obtain Figure 1) and toluene gave 41% of a mixture of piperidinotoluenes and only 20% of benzyl chloride. We cannot presently offer a convincing argument to explain why our reactions proceeded in moderate yield to benzyl chloride (65–75% in the case of toluene) accompanied by only a few per cent of amination products.

Experimental Section

All the compounds involved in this work were purchased with the exception of three benzyl chlorides; each of these was prepared by the photolysis of an 8:1 mixture of the appropriate toluene and N-chloropiperidine in 2 *M* sulfuric acid–acetic acid and isolated in pure form by preparative glpc. Thus the following were prepared: *p*-*t*-butylbenzyl chloride, $n^{24}D$ 1.5164 (lit.[21] $n^{24}D$ 1.5194); *p*-fluoro-

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[10] R. L. Huang and K. H. Lee, *J. Chem. Soc., Sect. C*, 935 (1966).

[11] E. J. Corey and W. R. Hertler, *J. Am. Chem. Soc.*, **82**, 1657 (1960).

[12] M. E. Wolff, *Chem. Rev.*, **63**, 55 (1963); R. S. Neale, M. R. Walsh, and N. L. Marcus, *J. Org. Chem.*, 30, 3683 (1965).

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[14] C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **85**, 1593, 1597 (1963); F. D. Greene, M. L. Savitz, F. D. Osterholtz, H. H. Lau, W. N. Smith, and P. M. Zanet, *J. Org. Chem.*, **28**, 55 (1963).

[15] F. Minisci, R. Galli, and G. Pollina, *Chim. Ind.* (Milan), 47, 736 (1965).

[16] F. Minisci, R. Galli, and M. Cecere, *ibid.*, **48**, 132 (1966).

[17] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 168.

[18] N. C. Deno and A. Schriesheim, *J. Am. Chem. Soc.*, 77, 3051 (1955); N. C. Deno and W. L. Evans, *ibid.*, **79**, 5804 (1957).

[19] M. Bock and K. Kompa, *Chem. Ber.*, **99**, 1357 (1966).

[20] F. Minisci, R. Galli, and R. Bernardi, *Tetrahedron Letters*, 699 (1966).

[21] E. E. Royals and R. N. Prasad, *J. Am. Chem. Soc.*, 77, 1696 (1955).

benzyl chloride, n^{24}D 1.5108 (lit.[22] n^{20}D 1.5130); and *m*-chlorobenzyl chloride, n^{24}D 1.5540 (lit.[23] n^{25}D 1.5556).

Glpc spectra were obtained under isothermal conditions on a Perkin-Elmer column "O" when nitro or cyano compounds were present and on diisodecyl phthalate supported on Chromosorb W in all the other examples. The ultraviolet source was a Hanovia 100-w medium-pressure mercury lamp filtered through Vicor and maintained at 6 in. from the near wall of the 300-ml Pyrex reaction vessel, which was the same as previously described.[5]

Competition Reactions. The procedure was as follows in each example: when only one-half the reactants were used, due to limited solubilities or for other reasons (see above), all other aspects of the procedure remained the same.

An acetic acid solution 2.0 *M* in sulfuric acid and 0.5 *M* in each of two substituted toluenes was cooled to 16° as nitrogen was bubbled through the vigorously stirred solution for 10 min. N-Chloropiperidine, bp 44° (16 mm), n^{25}D 1.4706, (0.05 mole), was then added *via* syringe, irradiation was immediately begun, and the consumption of electropositive chlorine was followed as usual.[5] The reaction was terminated by removal of the ultraviolet lamp as near to 25–30% decomposition of the chloramine as possible and the reaction mixture (usually colorless) was poured into 500 ml of water containing 200 g of ice. The resulting mixture was extracted with 125-, 50-, and 25-ml portions of 3:1 pentane–ether; the combined extracts were washed with 2.5 *N* sodium thiosulfate solution until the remaining chloramine (insoluble in dilute acid) was decomposed. The organic solution was then washed with 100 ml of water, two 25-ml portions of 2 *N* sulfuric acid, and finally with saturated sodium bicarbonate solution. The dried solution was evaporated to a small volume and then made up to 100 ml with ether for glpc analysis of the chlorination products.

The acidic, aqueous solution was partially neutralized by the addition of 125 ml of 12 *N* sodium hydroxide solution at or below 25° and extracted with two 100-ml portions of 2:1 ether–pentane. The resulting extract, which was usually completely free of positive chlorine, was neutralized with sodium bicarbonate solution, dried, and evaporated. The residue was then made up to 5 ml with ether for glpc analysis of the minor amination products. No significant amounts of products were obtained from any of the remaining aqueous solutions after complete basification.

Analysis of Primary Products. The relative amounts of benzylic chlorination products from each competition reaction were determined in a straightforward manner by glpc analysis once the detector response to each compound had been determined with known mixtures and the response had been shown to be linear over the range of product concentrations encountered. In the case of the experiments leading to points 1, 8, 10, 11, and 12 in Figure 1, the relative yields were converted into the basis of toluene as the reference substrate by simple comparisons of appropriate ratios, *e.g.*, a/ref = (a/b)(b/ref). The competition between *m*- and *p*-chlorotoluene could not be defined by glpc because of a coincidence in the retention time of the two benzylic chlorides; these were therefore collected together by preparative glpc and analyzed by infrared spectroscopy (point 8). The agreement with the glpc-determined ratio of the direct competition of *m*-chlorotoluene with toluene (point 7) was excellent.

Absolute yields, based on reacted chloramine, were determined for only one competitive reaction; 62% of the mixed benzyl chlorides from toluene and *p*-chlorotoluene (point 6) was obtained. In this and other analyses for yields by glpc (below), chlorobenzene was used as an internal standard. In the reactions with 1 *M* toluene alone, in which the extents of 0.25 *M* chloramine reaction were 91, 65, and 56%, the yields of benzyl chloride were 76, 59, and 64%. In each of these reactions, 99% of the benzyl chloride was found in the extracts of the diluted reaction mixture and only 1% in the extracts of the partially neutralized aqueous solutions.

Minor Products. No significant amounts of ring chlorinated products were produced in any of the reactions. The extent of such electrophilic chlorination was actually determined only in the high conversion reactions involving toluene alone; at 56–65% chloramine consumption, the yields of chlorotoluenes (mainly *para*) were 1.0–1.3% and the yield at 91% conversion was 2.3%. At low conversion in competition reactions (Table I), only 2–5% of *all* side products were obtained (from the partially neutralized solution only), of which ring chlorinated products constituted less than 10%.

In reactions involving toluene as a coreactant, ring amination products were observed as the major constituent (~70%) of the minor products noted immediately above. These were only tentatively identified, however, and similar products present in other reactions involving the more reactive aromatics were not isolated owing to the very small amounts produced. Three principal compounds, present in all the minor product mixtures from toluene reactions, were isolated by preparative glpc from the competitive reaction between toluene and tolunitrile, in which the largest amount of these products was produced. All three compounds were bases and their yields calculated for the probable compositions below were compound A, 0.7%; compound B, 2%; compound C, 2%.

Compound A appears to be N-*p*-tolylpiperidine on the basis of the infrared spectrum (no N-H, all bands present as expected[24] for 1,4-disubstituted aromatics) and nmr spectrum; the latter, obtained in CCl_4 in a spherical microcell, contained a symmetrical pattern centered at τ 3.2 (aromatic protons), a poorly resolved triplet (7.0) and broad singlet (8.1) characteristic in our experience of the piperidine protons, and a singlet at 7.8 (ring methyl group). The relative areas were close to the expected 4:4:3:6.

Compound B appears to be a mixture of the two chlorinated tolylpiperidines, *e.g.*, N-(2- and 3-chloro-4-methylphenyl)piperidine, on the basis of the nmr spectrum. The aromatic proton signals, τ 2.8–3.4, were not symmetrical, the piperidine protons were again present (7.1 and 8.38), and two methyl signals were now observed (7.65 and 7.75), the higher field of the two appearing as a close doublet. The relative areas were nearly 3:4:3 (combined methyl signals):6 as required.

Compound C was similarly assigned the probable composition of a mixture of dichlorotolylpiperidines; the nmr spectrum consisted of aromatic proton signals at τ 2.7–3.5 (2 H), diffuse triplet at 7.1 (4 H), two methyl singlets at 7.55 and 7.73 (3 H, nearly equally sized signals), and an unresolved absorption centered at 8.4 (6 H).

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