Electrophilic Aromatic Triphenylmethylation. Self-Consistent Field–Molecular Orbital Calculations on Aniline, *N*-Methylaniline, *N*,*N*-Dimethylaniline, and Ortho-Substituted Anilines

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SCF–MO calculations were carried out on aniline, *N*-methylaniline, *N*,*N*-dimethylaniline, 2-methyl-*N*,*N*-dimethylaniline, 2,6-dimethyl-*N*,*N*-dimethylaniline, and 2,6-dimethylaniline, using the CNDO/2 approximation. The results on triphenylmethylation have established the sequence $(CH_3)_2N > CH_3NH > NH_2$ in activating power. The calculations show a decrease in the HOMO energy levels in this sequence. This result indicates a considerable amount of charge transfer in the transition state in agreement with the idea of a late transition state. The results show further that the tritylation does not proceed *via* direct attack at the para position. Nitrogen inversion barriers were calculated, but were found to be too high (aniline, 6.4 kcal, experimentally estimated, 2 kcal). The frontier electron theory correctly predicts the reactivity of ortho-substituted aniline and *N*,*N*-dimethylaniline in electrophilic aromatic substitution. Experiments on the tritylation of 2,6-dimethylaniline and 2,6-dimethyl-*N*,*N*-dimethylaniline are reported.

Electrophilic aromatic substitution has been studied extensively both from an experimental and theoretical point of view.[2] One of the most selective electrophiles is the triphenylmethyl carbonium ion, which is known to react at the para position of anilines, alkoxybenzenes, and phenols, but does not react with alkylbenzenes, halobenzenes, and nitrobenzene.[3] Results of Kese and Chuchani[4] on the tritylation of anilines involving competition of the anilines for a trityl ion have shown the sequence $(CH_3)_2N > CH_3NH > NH_2$ in activating power. The purpose of this work was to see whether CNDO/2 calculations would predict correctly the above sequence of reactivity. In addition these calculations may allow us to draw certain conclusions concerning the detailed mechanism of the reaction and the nature of the transition state. The first problem in carrying out these calculations is to find out the favored structure of the anilines. We have therefore calculated the nitrogen inversion barriers for aniline, *N*-methylaniline, and *N*,*N*-dimethylaniline. Few semiempirical SCF–MO calculations of inversion barriers have been reported, mostly using the MINDO method.[5,6] The MINDO treatment gave good agreement with experimental values. It was therefore of interest to establish the usefulness of the CNDO/2 method for this type of calculation.

Results

The results of CNDO/2 calculations[7] on aniline, *N*-methylaniline, and *N*,*N*-dimethylaniline assuming different pyramidal structures are shown in Tables I–III. Symmetric structures were assumed. The following bond distances[8] were used: $C_{ar}–C_{ar}$, 1.392 Å; $C_{ar}–H$, 1.085 Å; $C_{ar}–N$, 1.431 Å; N–H, 1.04 Å; $N–CH_3$, 1.45 Å; $C_{ali}–H$, 1.09 Å. Different angles were used for the –N< groups as shown in Tables I–III. For the calculations of the ortho-substituted anilines the following bond distances were used: $C_{ar}–N$, 1.426 Å; $C_{ar}–CH_3$, 1.52 Å. All other distances were as stated above. The orientation of the methyl groups at the nitrogen were chosen so that all C–H bonds were staggered. The methyl groups at the aromatic ring were assumed to be symmetrical with respect to the plane perpendicular to the ring (as shown in Figure 1).

Discussion

Several theoretical approaches to the problem of electrophilic aromatic substitution have been proposed.[2] There are basically three different methods: the "static approach," the "localization approach," and the "delocalization approach." The static approach considers the π-electron distribution in the isolated molecule, whereas the localization approach considers the energy of the localized σ complex or Wheland intermediate.[9] The interesting idea of early and late transition states, which combines these two approaches was proposed by Brown.[10] In an early transition state the aromatic is disturbed little by the electrophile and the π-electron densities in the aromatic will predict the reactivity, while a late transition state will resemble the products and the stability of the Wheland intermediates will be a measure of reactivity. The third approach is the delocalization approach. Among this category the most successful theory has been the "frontier electron theory" developed by Fukui and coworkers.[11] This theory is closely related to Mulliken's theory of charge

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[1] Puerto Rico Nuclear Center is operated by the University of Puerto Rico for the U. S. Atomic Energy Commission under Contract AT-(40-1)-1833.

[2] (a) For a recent review, see G. A. Olah, *Accounts Chem. Res.*, **4**, 240 (1971); (b) for a review of theory, see A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1957, p 307 ff. (c) K. Fujui, *Topics Current Chem.*, **15**, 1 (1970).

[3] C. A. McKenzie and G. Chuchani, *J. Org. Chem.*, **20**, 336 (1955); G. Chuchani, *Acta Cient. Venezolana, Supl. 3*, 328 (1967).

[4] V. Kese and G. Chuchani, *J. Org. Chem.*, **27**, 2032 (1967).

[5] M. J. S. Dewar and M. Shanshal, *J. Amer. Chem. Soc.*, **91**, 3654 (1969).

[6] For a review, see J. M. Lehn, *Topics Current Chem.*, **15** (3), 311 (1970).

[7] J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S 129 (1965). J. A. Pople and G. A. Segal, *ibid.*, **43**, S136 (1965); **44**, 3289 (1966). The program was obtained from the Quantum Chemistry Program Exchange, Bloomington, Indiana. The program was written by Dr. A. Dobosh.

[8] D. G. Lister and J. K. Tyler, *Chem. Commun.*, 152 (1966).

[9] G. W. Wheland, *J. Amer. Chem. Soc.*, **64**, 900 (1942).

[10] R. D. Brown, *Quart. Rev.*, **6**, 63 (1952).

[11] F. Fukui, T. Yonezawa, and H. Shingu, *J. Chem. Phys.*, **20**, 722 (1952); K. Fukui, T. Yonezawa, C. Nagata, and H. Shingu, *ibid.*, **22**, 1433 (1954); K. Fukui, T. Yonezawa, and C. Nagata, *Bull. Chem. Soc. Jap.*, **27**, 423 (1954); *J. Chem. Phys.*, **27**, 1247 (1957).

TABLE I

CNDO/2 CALCULATIONS ON ANILINE

Pyramidal angle, deg	109.5	110.0	110.5	111.0	113.0	120.0
Total energy, au	−59.557601	−59.55762	−59.55759	−59.55752	−59.55669	−59.54685
HOMO energy, au	−0.4433	−0.4426	−0.4419	−0.4411	−0.4378	−0.4231
Max HOMO coefficient (p_z) at						
N	−0.4728	−0.4780	−0.4832	−0.4884	0.5106	−0.6037
2	0.3304	0.3306	0.3308	0.3310	−0.3320	0.3395
3	−0.1854	−0.1844	−0.1834	−0.1825	0.1784	−0.1629
4	−0.4811	−0.4801	−0.4791	−0.4781	0.4743	−0.4632
p_z–π density at						
N	1.5883	1.6005	1.6125	1.6247	1.6772	1.9160
2	1.0596	1.0601	1.0606	1.0612	1.0638	1.0789
3	0.9759	0.9757	0.9755	0.9753	0.9744	0.9694
4	1.0390	1.0394	1.0398	1.0402	1.0422	1.0533

TABLE II

CNDO/2 CALCULATIONS ON *N*-METHYLANILINE

Pyramidal angle, deg	109.5	110.0	110.5	111.0	112.0	113.0	120.0
Total energy, au	−68.25315	−68.25331	−68.25345	−68.25350	−68.25345	−68.25314	−68.24437
HOMO energy, au	−0.4382	−0.4372	−0.4352	−0.4341	−0.4320	−0.4297	−0.4107
Max. HOMO coefficient (p_z) at							
N	0.5095	0.5156	0.5249	−0.5311	0.5432	−0.5560	0.6532
2	−0.3036	−0.3032	−0.3034	0.3031	−0.3027	0.3026	−0.3086
3	0.1797	0.1786	0.1744	−0.1731	0.1707	−0.1680	0.1483
4	0.4463	0.4444	0.4389	−0.4371	0.4336	−0.4302	0.4123
5	0.1573	0.1555	0.1501	−0.1484	0.1453	−0.1421	0.1225
6	−0.3213	−0.3212	−0.3221	0.3221	−0.3219	0.3219	−0.3258
p_z–π density at							
N	1.5622	1.5741	1.5849	1.5973	1.6218	1.6486	1.8809
2	1.0577	1.0581	1.0578	1.0583	1.0593	1.0606	1.0741
3	0.9761	0.9759	0.9769	0.9767	0.9764	0.9760	0.9715
4	1.0370	1.0374	1.0396	1.0399	1.0407	1.0416	1.0519
5	0.9764	0.9762	0.9770	0.9769	0.9766	0.9762	0.9719
6	1.0582	1.0586	1.0578	1.0582	1.0592	1.3603	1.0735

TABLE III

CNDO/2 CALCULATIONS ON *N,N*-DIMETHYLANILINE

Pyramidal angle, deg	109.5	111.0	112.0	113.0	114.0	120.0
Total energy, au	−76.94918	−76.94977	−76.94987	−76.94968	−76.94930	−76.94118
HOMO energy, au	−0.4304	−0.4261	−0.4232	−0.4201	−0.4170	−3.4003
Max. HOMO coefficient (p_z) at						
N	0.5511	0.5706	0.5830	0.5958	0.6080	0.6790
2	−0.2976	−0.2945	−0.2930	−0.2918	−0.2910	−0.2928
3	0.1481	0.1417	0.1377	0.1337	0.1301	0.1166
4	0.4099	0.3998	0.3939	0.3884	0.3836	0.3706
p_z–π density at						
N	1.5512	1.5848	1.6078	1.6328	1.6576	1.8468
2	1.0561	1.0571	1.0579	1.0588	1.0599	1.0708
3	0.9779	0.9775	0.9773	0.9770	0.9767	0.9718
4	1.0387	1.0396	1.0402	1.0410	1.0419	1.0471

transfer.[12] To calculate reaction rates exactly one should calculate the whole energy surface for the reacting system and in this way determine the energy of the transition state. Since at the present time this type of calculation is impossible for large systems we have to limit ourselves to interpreting reaction rates in terms of the electronic structure of the reacting molecules. The transition state is treated as a perturbation of the ground state. The theoretical quantity which is used as a measure of the relative rate at different positions in a molecule or in different molecules is the reactivity index.

One reactivity index which was derived by Fukui, *et al.*,[2,11] through application of perturbation theory to the Schroedinger equation is the superdelocalizability defined for reaction with an electrophilic reagent as shown in eq 1 where $c_r^{(i)}$ is the coefficient of the i^{th} MO

$$S_r^{(E)} = 2 \sum_{i}^{\text{occ}} \frac{c_r^{(i)2}}{\alpha - \epsilon_i}(-\beta) \qquad (1)$$

at position r, α is the LUMO (lowest unoccupied molecular orbital) energy level of the electrophile, and ϵ_i is the energy level of the ith MO. α and ϵ_i are expressed in eq 1 in units of β, the resonance integral.

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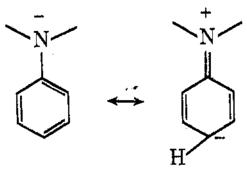
[12] R. S. Mulliken, *J. Amer. Chem. Soc.*, **74**, 811 (1952); *Recl. Trav. Chim. Pays-Bas*, **75**, 845 (1956).

On the basis of the principle of narrowing of the interfrontier level separation and the growing of the frontier electron density along the reaction path Fukui[2,11] has pointed out that the frontier term is the dominant term in eq 1. Thus $S_r^{(E)}$ can be approximated by the frontier term only, where c_r^{HO} and ϵ_{HO} are the coefficient

$$S_r^{(E)} = 2\,\frac{c_r^{(HO)2}}{\alpha - \epsilon_{HO}}\,(-\beta) \qquad (2)$$

in the HOMO (highest occupied molecular orbital) and the energy level of the HOMO respectively. If we are interested only in intramolecular reactivity a comparison of reactivity can be made by the numerator of eq 2 only. $2C_r^{(HO)^2}$ is known as the frontier electron density. Comparing the reactivity of different molecules with the same electrophile we see from eq 2 that $S_r^{(E)}$ increases with increasing HOMO coefficient and with increasing (*i.e.*, less negative) HOMO energy. The results (Table I–III) show that the maximum HOMO ecoefficients are at the nitrogen and para positions. The absolute magnitude of the HOMO coefficient at the nitrogen increases from aniline to *N*,*N*-dimethylaniline, and the HOMO energy level becomes less negative in this series. The reactivity index $S_r^{(E)}$ therefore is increasing in agreement with the experimentally observed reactivities. Tables I–III show the results on aniline, *N*-methylaniline and *N*,*N*-dimethylaniline assuming a number of different pyramidal structures. With increasing substitution at the nitrogen the pyramid gets flattened and the inversion barrier is decreasing. This is due to nonbonded repulsions which are stronger in the pyradmidal than in the planar state. From microwave spectroscopy data Lister and Tyler[8] estimated the inversion barrier of aniline to be about 2 kcal/mole. The CNDO/2 calculations give 6.4 kcal/mol, a considerably higher value. However the CNDO/2 method correctly predicts the decrease in inversion barrier with increasing N substitution. Since conjugation of the amino group with the ring is more favorable in the planar state the π-electron density in the ring is expected to increase from aniline to *N*,*N*-dimethylaniline, which is indeed borne out by the calculations. The p_z–π density is greater in the ortho than in the para position. π-Electron density obviously does not correlate well with the experimental results on tritylation which gives exclusively para substitution. This is not surprising since only in reactions with very reactive electrophiles where we have an early transition state can we expect a correlation with π-electron density. With decreasing reactivity of the electrophile a greater degree of charge transfer has to take place in the transition state for reaction to take place. Triphenylmethyl carbonium ion is certainly a weak electrophile and will form a late transition state. The large amount of charge transfer in the transition state for tritylation is quite evident from the high solute selectivity. Trityl does react with anilines, but does not react with toluene, chlorobenzene, or nitrobenzene (HOMO energy levels of −0.4730, −0.4677, and 0.4741 au, respectively).[13] These latter compounds have considerably lower lying HOMO energy levels than the anilines.



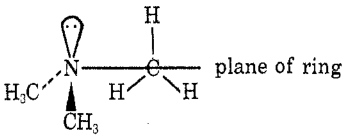
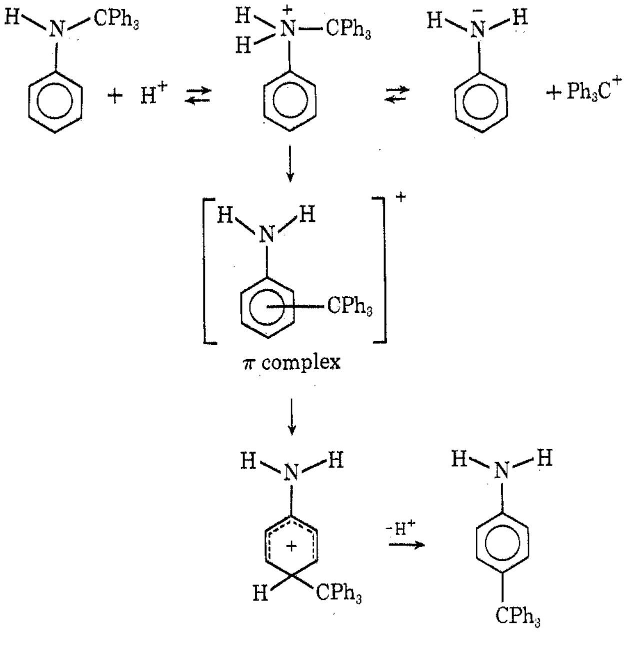


Figure 1.—In calculations on toluene we have found that the orientation of the methyl group affects the HOMO energy level, the π- and total electron densities to an insignificant extent.

As we have pointed out above intramolecular reactivity should be proportional to the frontier electron density or simply the absolute value of the HOMO coefficient. With the exception of aniline where the HOMO coefficients at the nitrogen and para position are about equal, the maximum HOMO coefficients are at the nitrogen. It is well known that *N*-tritylaniline will rearrange in acid media to *p*-tritylaniline. In experiments of cross-migration from *N*-tritylaniline to phenol or *N*,*N*-dimethylaniline in acid media, Chuchani and Rodríguez-Uzcanga[14] found evidence for inter and intramolecular rearrangement (Scheme I).

SCHEME I



Cross-migration between *N*-tritylaniline and *N*,*N*-dimethylaniline gave *p*-tritylaniline and *p*-trityl-*N*,*N*-dimethylaniline in a ratio of about 1:2, whereas direct tritylation of a mixture of aniline and *N*,*N*-dimethylaniline by trityl perchlorate gave exclusively *p*-trityl-*N*,*N*-dimethylaniline. The rearrangement most likely will involve π complexes. The intermolecular migration requires that the *N*-tritylaniline in acid media splits into trityl ion and aniline. On the basis of the experimental evidence and the results of the CNDO/2 calculations we propose the mechanism shown in Scheme II for tritylation. The long range interaction between the trityl ion and the aromatic amine is

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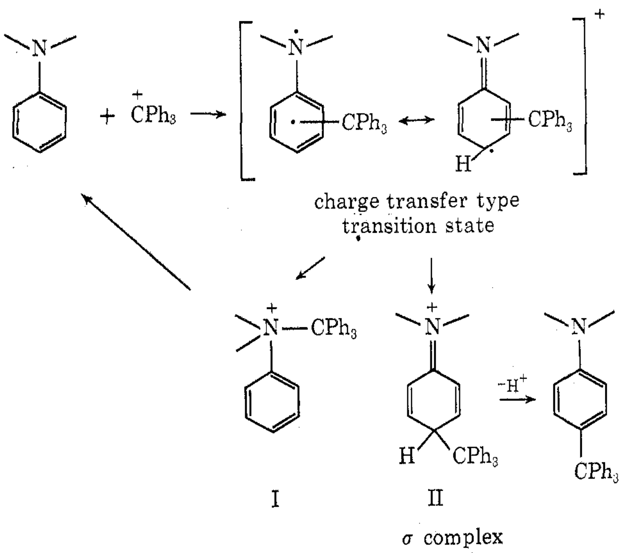
[13] M. K. Eberhardt and M. Yoshida, unpublished results.

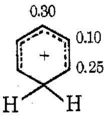
[14] G. Chuchani and V. Rodríguez-Uzcanga, *Tetrahedron*, **22**, 2665 (1966).

SCHEME II



governed by the total electron density, which is always highest at the nitrogen. As the trityl ion approaches its empty orbital begins to overlap with the HOMO of the aromatic. This overlap is proportional to the absolute magnitude of the HOMO coefficient. The highest HOMO coefficients are usually p_z orbitals, unless otherwise indicated in the tables. This means that the most favorable approach of the trityl ion is from the top of the plane of the aromatic ring. For σ-bond formation to occur charge transfer has to take place in the transition state. The ease of formation of the charge transfer type transition state is governed by the HOMO–LUMO overlap and the energy level of the HOMO, *i.e.*, the reactivity index $S_r^{(E)}$. $S_r^{(E)}$ increases in the series: $NH_2 < NHCH_3 < N(CH_3)_2$. The charge transfer type transition state can lead to σ-bond formation either at the nitrogen (I) or at the para position (II). These two positions have the highest spin density in the radical cation of the anilines. Only intermediate II will give a stable final product, whereas I will dissociate to starting components. With increasing alkyl substitution at the nitrogen the formation of II might be favored over I due to steric hindrance.

Since we are dealing with a late transition state the stability of the Wheland intermediates should also correlate with the inter- and intramolecular reactivity. Based on the charge distribution of benzenium ion Olah[2] has pointed out that a substituent will exert a more powerful effect on the stability of the benzenium ion when it is para to the attacking electrophile than when it is ortho. This will lead to high para/ortho ratios as in indeed observed in high selectivity reactions (trityl ion presenting the extreme case of exclusively para substitution). Since in the series NH_2, $NHCH_3$, and $N(CH_3)_2$ we have increasing electron-donating power (Tables I–III) we expect the stability of the σ complexes to increase. The superdelocalizability predicts the relative rates of a series of compounds, whereas the Wheland intermediate reflects the stability of the final products. The experimental reactivity sequence $NH_2 < NHCH_3 < N(CH_3)_2$ has been established using the nonkinetic competition method. Our calculations indicate the same reactivity sequence whether we have a kinetically or a thermodynamically controlled process. In the tritylation of some alkoxybenzenes rate constants have been determined[15] and were found to correlate with the superdelocalizability as well as the stability of the σ complexes.[16]



To lend further support to our interpretation of the relative reactivities based on the frontier electron theory, we have carried out some calculations on 2,6-dimethylaniline (I) and 2,6-dimethyl-*N*,*N*-dimethylaniline (II) (Charts I and II). We find that the amino group in I has a low barrier of rotation, whereas the *N*,*N*-dimethylamino group in II cannot rotate freely, but it twisted 90° out of the plane of the ring. On the

CHART I

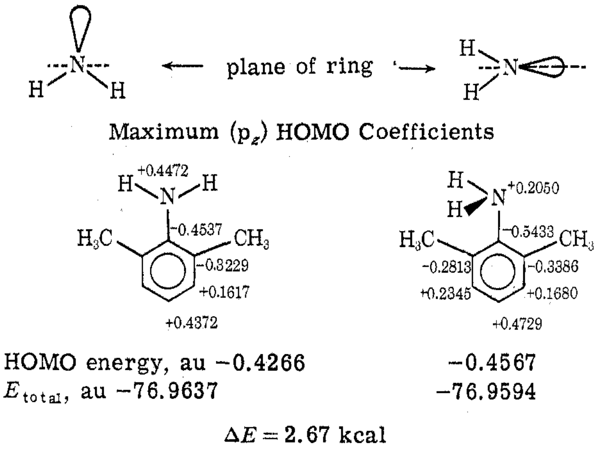
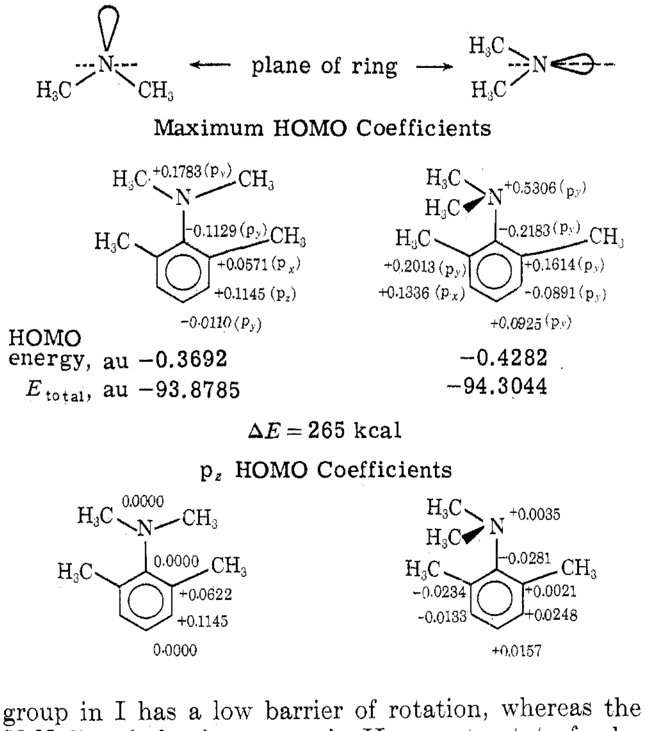


CHART II



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[15] G. Chuchani, H. Díaz, and J. Zabicky, *J. Org. Chem.*, **31**, 1573 (1966).

[16] M. K. Eberhardt and G. Chuchani, *ibid.*, **37**, 3654 (1972).

basis of the very small HOMO coefficients of II we expect a very low reactivity for this compound. Experimentally it was indeed found to be completely unreactive toward the trityl ion. The HOMO coefficients of I and aniline are not very different, but the HOMO energy level of I is considerably higher than in aniline (−0.4266 *vs.* −0.4420 au) which should make the former more reactive. This was again confirmed by experiment.

A decrease in reactivity upon ortho substitution was also observed by Brown, Widiger, and Letang.[17] These authors measured the rate of deuterium exchange of a variety of ortho-substituted *N,N*-dimethylanilines, and they found a considerable decrease in rate upon ortho substitution in agreement with the decrease of the HOMO coefficients. Friedlander[18] found that 2,6,*N,N*-tetramethylaniline does not couple with diazotized amines.

Experimental Section

Triphenylmethanol (Matheson Coleman and Bell) was purified by recrystallizations from glacial acetic acid. Aniline (Matheson Coleman and Bell), *N,N'*-dimethylaniline (Matheson Coleman and Bell), and 2,6-dimethylaniline (Aldrich) were purified by distillations under vacuum. Triphenylmethyl perchlorate was prepared as previously described.[15] Synthesis of other compounds are described below. Ir spectra were determined with a Perkin-Elmer Model 337 spectrometer. Nmr spectra were determined with a Varian A-60 instrument. For mass spectra a Hitachi Perkin-Elmer RMU-6H was used. Melting points were taken with a Fisher-Johns apparatus.

4-Amino-3,5-dimethyltetraphenylmethane. Method A.—Triphenylmethanol (0.10 mol), 2,6-dimethylaniline (0.015 mol), glacial acetic acid (50 ml), and concentrated hydrochloric acid (4.0 ml) were refluxed for 1 week. The reaction mixture was diluted with water, then treated with 20% solution of sodium hydroxide, and the filtered solid was warmed in a solution of potassium hydroxide in ethanol. The product was recrystallized from ethanol (yield 66%) and had mp 185° (lit.[19] mp 177°).

Method B.—2,6-Dimethylaniline (0.015 mol) was added to triphenylmethyl perchlorate (0.010 mol) and heated to 75–80° for 6 hr under nitrogen. The solid mass was dissolved in acetone, diluted with water, and treated with 10% solution of sodium hydroxide. The product, warmed with a solution of potassium hydroxide in ethanol, filtered off, and recrystallized from ethanol (yield 73%), had mp 183–184°, not depressed on a mixture with the product obtained by method A. The ir, nmr, and mass spectra of the products obtained by both methods were identical: ν_{max} (KBr) 3425 and 3380 cm^{-1} (HNH); δ ($CDCl_3$) 2.1 (s, CH_3), 3.4 (s, NH_2), and 7.2 ppm (m, aromatic); M^+ *m/e* 363. *Anal.* Calcd for $C_{27}H_{25}N$: C, 89.2; H, 6.9; N, 3.9. Found: C, 88.7; H, 7.1; N, 3.6.

2,6-Dimethyl-*N,N'*-dimethylaniline.—This compound was prepared according to the method described by Bamberger and Rudolf.[20] The product was distilled at 89.5–90.9° (20 mm) [lit.[20] 76.8–77.2° (11 mm): ν_{max} (pure) 1140 cm^{-1} [=CN(CH_3)$_2$]; δ ($CDCl_3$) 2.3 (s, CH_3), 2.8 (s, CH_3), and 7.0 ppm (m, aromatic). *Anal.* Calcd for $C_{10}H_{15}N$: C, 80.5; H, 10.1; N, 9.4. Found: C, 79.7; H, 9.6; N, 9.6.

The tritylation of 2,6 dimethyl-*N,N*-dimethylaniline does not give the corresponding tetraphenylmethane derivative. Method A yields triphenylmethane (69%), mp 92–93° (lit.[3] mp 93–94°), and 9-phenylfluorene (14%), mp 144–145° (lit.[21] mp 145.5°). These compounds were separated by neutral alumina column chromatography (Woelm, grade I) and identified by mixture melting point and ir spectral comparison with an authentic sample. In method B, the reagent triphenylmethyl perchlorate is recovered quantitatively as triphenylmethanol.

I. Competitive Tritylation of Aniline and 2,6-Dimethylaniline. Method A.—Aniline (0.05 mol), 2,6-dimethylaniline (0.05 mol), and triphenylmethyl perchlorate (0.005 mol) were heated at 75–80° for 18 hr under nitrogen and protected from light. The reaction mixture was dissolved in acetone and diluted with water and concentrated hydrochloric acid added until no further precipitate formed. The solid is warmed in potassium hydroxide–ethanol solution for 10 min, diluted with water, dried, and dissolved in small amount of chloroform, and the compounds were separated by column chromatography. The column was packed with acid alumina (40 g, Woelm, grade I) and eluted with petroleum ether and then with a mixture of benzene–chloroform (2:1 by volume). Products and yields follow: triphenylmethane, 8.1%; 4 amino-3,5-dimethyltetraphenylmethane, 57.2%; and 4-aminotetraphenylmethane, 13.6% [mp 254–256° (lit.[3] mp 256–257°)]. Each compound obtained was checked by mixture melting point and ir and nmr spectral comparison with the corresponding authentic sample.

Method B.—A mixture of aniline (0.10 mol), 2,6-dimethylaniline (0.10 mol), triphenylmethanol (0.01 mol), glacial acetic acid (100 ml), and concentrated hydrochloric acid (8 ml) was refluxed for 1 week. The reaction mixture was diluted with water and treated with 20% sodium hydroxide solution, and the filtered solid was warmed in potassium–ethanol solution for 15 min. The products are separated as indicated in method A. Products and yields follow: 4-amino-3,5-dimethyltetraphenylmethane, 66.4%, and 4-acetamido-3,5-dimethyltetraphenylmethane, 24.9% (mp 284–285°). The identification of these compounds were accomplished by mixture melting point and ir, nmr, and mass spectral comparison with authentic samples. The structural proof of the 4-acetamido-3,5-dimethyltetraphenylmethane was made by the common method of acetylation[22] of the 4-amino-3,5 dimethyltetraphenylmethane.

Registry No.—Aniline, 62-53-3; *N*-methylaniline, 100-61-8; *N,N*-dimethylaniline, 121-69-7; 4-amino-3,5-dimethyltetraphenylmethane, 35925-46-3; 2,6-dimethyl-*N,N'*-dimethylaniline, 769-06-2; 4-acetamido-3,5-dimethyltetraphenylmethane, 35895-52-4.

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