Institute of Science kindly supplied us with several of his manuscripts prior to publication.

## Appendix

**Photostationary State Composition with Irradiation at Several Wavelengths.** Consider the photoisomerization A ⇌ B brought about by light of several discrete frequencies $\nu_i$, with both isomers showing absorption at all these frequencies. In this derivation, the quantum yields are assumed to be independent of the concentration. Let $C_A$ and $C_B$ be the molar concentrations of A and B, respectively, at any time, and $C_A{}^0$ and $C_B{}^0$ the corresponding initial concentrations. Assuming that no side reactions occur, the total concentration is $C^0 = C_A + C_B = C_A{}^0 + C_B{}^0$. Other symbols are defined as follows, with the subscript $i$ referring to the parameter at $\nu_i$.

$X_A$ = $C_A/C^0$, mole fraction of A
$X_A{}^\infty$ = mole fraction of A in the photostationary state
$\phi_{A_i}$ = quantum yield for the change A → B
$\phi_{B_i}$ = quantum yield for the change B → A
$I_{T_i}$ = total light absorbed (einsteins/second)
$I_{0_i}$ = incident intensity (einstein/second)
$D_{T_i}$ = the total optical density, which is equal to $D_{A_i} + D_{B_i}$
$V$ = volume, in liters of solution receiving radiation
$\epsilon_{A_i}$ and $\epsilon_{B_i}$ are the molar extinction coefficients

Now $I_{T_i} = I_{A_i} + I_{B_i}$, the sum of the light absorbed by A and B, respectively. The latter quantities are clearly $I_{A_i} = D_{A_i}/D_{T_i}$ and $I_{B_i} = D_{B_i}/D_{T_i}$. From Beer's law, $I_{T_i} = I_{0_i}[1 - \exp(-2.3D_{T_i})]$, which is equal to $I_{0_i}$ when $D_{T_i}$ is large at high substrate concentrations.

The rate of formation of A is given by eq 13. Equating this rate to zero at the stationary state, and defining the optical densities in the usual manner (*e.g.*, $D_{A_i} = \epsilon_{A_i}C_Al$, where $l$ is the path length), relative intensities by $a_i = I_{0_i}/I_{0_i}$, and the difference in extinction coefficients as $\Delta\epsilon_i = \epsilon_{A_i} - \epsilon_{B_i}$, we finally obtain

$$\frac{dC_A}{dt} = C^0\frac{dX_A}{dt} = \frac{1}{V}\left[\sum_i \phi_{B_i}I_{0_i}D_{B_i}/D_{T_i} - \sum_i \phi_{A_i}I_{0_i}D_{A_i}/D_{T_i}\right] \quad (13)$$

$$X_A{}^\infty = \frac{\sum_i a_i\epsilon_{B_i}\phi_{B_i}/(\epsilon_{B_i} + X_A{}^\infty\Delta\epsilon_i)}{\sum_i a_i(\epsilon_{A_i}\phi_{A_i} + \epsilon_{B_i}\phi_{B_i})/(\epsilon_{B_i} + X_A{}^\infty\Delta\epsilon_i)} \quad (14)$$

This equation can, in principle, be solved for $X_A{}^\infty$ with the boundary condition $0 < X_A{}^\infty < 1$. It shows that, if light absorption is complete at every frequency, $X_A{}^\infty$ remains independent of the total concentration, $C^0$. Concentration dependence appears when there is only fractional light absorption at some frequencies. If, however, there is partial light absorption at every frequency such that the approximation $1 - \exp(-2.3D_{T_i}) = 2.3D_{T_i}$ holds, eq 14 becomes

$$X_A{}^\infty = \frac{\sum_i a_i\epsilon_{B_i}\phi_{B_i}}{\sum_i a_i(\epsilon_{A_i}\phi_{A_i} + \epsilon_{B_i}\phi_{B_i})} \quad (15)$$

With monochromatic irradiation, eq 14 and 15 reduce to $X_A{}^\infty = \epsilon_B\phi_B/(\epsilon_A\phi_A + \epsilon_B\phi_B)$, which is identical with eq 6 given in the appendix of Malkin and Fischer's paper.[32]

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[32] S. Malkin and E. Fischer, *J. Phys. Chem.*, **66**, 2482 (1962).

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# Concerning Back-Bonding and Polar Effects in Aminoalkylbenzene Derivatives

J. H. SMITH[1] AND F. M. MENGER

*Department of Chemistry, Emory University, Atlanta, Georgia 30322*

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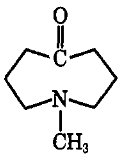
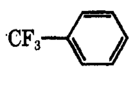
The infrared and ultraviolet spectral properties of $(CH_3)_2N(CH_2)_nC_6H_4COOCH_3$ ($n$ = 1–4) were studied to determine the presence of intramolecular interactions between the nonbonded nitrogen electrons and the $\pi$ system of the aromatic rings (*i.e.*, back-bonding). The results show that such interactions do not contribute to either the ground or excited states. Kinetic data on the basic hydrolysis of the four esters likewise demonstrate the absence of nonconjugative orbital overlap. In the second portion of the paper we determine how the rate of alkaline hydrolysis of $(CH_3)_3N^+(CH_2)_nC_6H_4COOCH_3$ varies with the value of $n$. The compounds possess a quaternary nitrogen, a powerful electron-withdrawing group, and an ester functionality whose hydrolysis rate is sensitive to polar effects. The data are compared with Kirkwood–Westheimer calculations using spherical and ellipsoidal cavities. Hammett $\sigma_p$ constants are reported for the $(CH_3)_2N(CH_2)_n$ and $(CH_3)_3N^+(CH_2)_n$ groups where $n$ = 1–4.

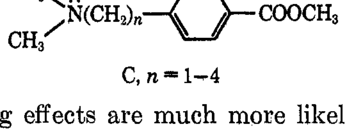
Intramolecular interaction between a carbonyl carbon and nonbonded amino nitrogen electrons (as occurs in compound A) is well known.[2] Sheppard[3] has proposed a similar type of interaction in benzotrifluoride (B) between a nonbonded pair of electrons on fluorine and the $\pi$ system. Subsequent work,[4,5] however, has shown that such back-bonding is of no importance in the case of benzotrifluoride. One of several arguments used against the back-bonding concept is that there is no analogy suggesting that this effect can be significant.[4] In the present paper we examine a series of methyl $p$-(N,N-dimethylaminoalkyl)benzoates (C, $n$ = 1–4) for the presence of p–$\pi$ overlap.



A



B



C, $n$ = 1–4

Back-bonding effects are much more likely in this set of compounds than in benzotrifluoride. The p

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[1] National Defense Education Act Predoctoral Fellow.

[2] N. J. Leonard, *Rec. Chem. Progr.*, **17**, 243 (1956).

[3] W. A. Sheppard, *J. Amer. Chem. Soc.*, **87**, 2410 (1965).

[4] M. J. S. Dewar and A. P. Marchand, *ibid.*, **88**, 354 (1966).

[5] F. W. Baker, R. C. Parish, and L. M. Stock, *ibid.*, **89**, 5677 (1967).

donor is a nitrogen rather than a fluorine atom; the aromatic rings are substituted with an electron-withdrawing ester group. Moreover, one would expect no steric problems preventing maximum orbital overlap when $n = 3$ or 4 (joining a nitrogen with the ring carbon *para* to the ester group closes a five- and six-membered ring, respectively). The amino esters seem well suited to display p–$\pi$ back-bonding if indeed this effect is of significance in organic chemistry.

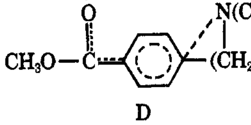
We have determined the extent of intramolecular interaction in C by infrared and ultraviolet spectroscopy. The carbonyl group of C provides a handle with which to detect p–$\pi$ overlap *via* infrared analysis. In a related series of compounds, the *para*-substituted acetophenones, the wavelength shifts of the carbonyl stretching band are a direct function of the calculated carbonyl bond orders.[6] Back-bonding in C would decrease the carbonyl bond order and move the carbonyl band to longer wavelengths in the same manner that a *p*-amino group perturbs the spectrum of acetophenone. In the ultraviolet spectrum, we would expect abnormally large $\lambda_m$ and $\epsilon_m$ values for C if back-bonding is significant. Diarylmethanes, for example, often absorb at longer wavelengths and with much greater intensity than the corresponding toluene because of nonconjugative interaction (homoconjugation).[7]

Oki and Iwamura[8] have obtained evidence for intramolecular hydrogen bonding between a hydroxyl group and the $\pi$ system of the aromatic ring of $Ar(CH_2)_nOH$. We synthesized fully alkylated amines (C) in order to preclude interference from this type of interaction.

In view of the recent interest in the mechanism of the transmission of polar effects,[4,5,9,10] we prepared the methiodide salts of C ($n$ = 0–4) and determined how the rates of basic hydrolysis vary with chain length. The five salts possess a quaternary nitrogen, a powerful electron-withdrawing group, and an ester functionality whose hydrolysis rate is sensitive to polar effects.[11] In the Discussion we compare our data with Kirkwood–Westheimer calculations, and we report the previously unknown Hammett $\sigma_p$ parameters for the $(CH_3)_2N(CH_2)_n$ and $(CH_3)_3N^+(CH_2)_n$ groups.

## Results and Discussion

The infrared and ultraviolet spectral data for C ($n$ = 1–4) and for the reference compounds, methyl *p*-methylbenzoate and methyl *p*-(N,N-dimethylamino)-benzoate, are summarized in Table I. A decrease in the carbonyl stretching frequency of C relative to the methyl-substituted compound would be expected if back-bonding (structure D) makes an important contribution to the ground state of the molecules. The carbonyl stretching frequency for the *p*-dimethylamino-substituted ester (1716 cm$^{-1}$, $CCl_4$) and for the *p*-methyl reference compound (1729 cm$^{-1}$, $CCl_4$) may be regarded as extreme possible values for C (corresponding to maximal and minimal interaction). The difference in $\nu_{C=O}$ between the reference compounds is more than tenfold larger than the experimental error in the frequency measurements. Clearly, there is no significant decrease in frequency in any of the C compounds relative to methyl *p*-methylbenzoate. We conclude that there is no appreciable p–$\pi$ overlap in the ground states of the compounds studied.



D

Table I

Spectral Data for $XC_6H_4COOCH_3$

| $X^a$ | Carbonyl stretching frequency $\bar{\nu}$, cm$^{-1}$ CCl$_4$ | CHCl$_3$ | Ultraviolet, $\lambda_{max}$ ($\epsilon \times 10^{-4}$) Heptane | Methanol |
|---|---|---|---|---|
| $-CH_3$ | 1729 | 1718 | 235 (1.57) | 238 (1.51) |
| $-N(CH_3)_2$ | 1716 | 1704 | 298 (2.81) | 310 (2.88) |
| $-CH_2N(CH_3)_2$ | 1729 | 1721 | 233 (1.61) | 234 (1.56) |
| $-(CH_2)_2N(CH_3)_2$ | 1728 | 1720 | 236 (1.46) | 237 (1.56) |
| $-(CH_2)_3N(CH_3)_2$ | 1727 | 1719 | 237 (1.54) | 238 (1.64) |
| $-(CH_2)_4N(CH_3)_2$ | 1728 | 1719 | 237 (1.61) | 238 (1.65) |

[a] Registry no.: X = $CH_3$, 99-75-2; X = $N(CH_3)_2$, 1202-25-1.

Electronic interactions between "nonclassically conjugated" groups occur primarily in the excited states of the systems.[7] In order to determine whether or not back-bonding is present in the excited states of C, we examined their ultraviolet spectra in a polar and nonpolar solvent (methanol and heptane). It is difficult to predict which solvent would be more favorable for p–$\pi$ overlap. On the one hand a polar solvent like methanol favors the creation of charge (see D); on the other hand, methanol can compete with the aromatic ring for the unshared pair of nitrogen electrons *via* hydrogen bonding. From the data in Table I one may quite definitely conclude that back-bonding occurs in neither solvent. The spectra of C resemble closely that of methyl *p*-methylbenzoate and not that of methyl *p*-(N,N-dimethylamino)benzoate.

Our results bear on the question of whether or not back-bonding occurs in benzotrifluoride as has been proposed.[3] Since the ability of fluorine to donate electrons to a $\pi$ system is undoubtedly much less than that of an amino group, and since there is no back-bonding in our amino esters, back-bonding in benzotrifluoride is highly unlikely. This conclusion is in agreement with that of other workers.[4,5] The only known example of back-bonding, as we have defined it, seems to be spiro-Meisenheimer complex formation in compounds such as 1-(2′-hydroxyethoxy)-2,4,6-trinitrobenzene.[12] Since a $\sigma$ bond is formed here between the donor oxygen atom and a carbon of the nitrated aromatic ring, this complex might be regarded as an extreme case of back-bonding.

The evaluation of Hammett $\sigma$ parameters for the aminoalkyl group confirms the above conclusions based on spectral data. We obtained these constants by measuring the rates of base-catalyzed hydrolysis of the ester groups of C. This reaction is ideal for our purposes because the rates of basic ester hydrolysis

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(6) J. Tanaka, S. Nagakura, and M. Kobayashi, *J. Chem. Phys.*, **24**, 311 (1956).

(7) L. N. Ferguson and J. C. Nnadi, *J. Chem. Educ.*, **42**, 529 (1965), and references cited therein.

(8) M. Oki and H. Iwamura, *J. Chem. Soc. Jap.*, **32**, 955, 1135 (1959).

(9) P. E. Peterson, R. J. Bopp, D. M. Chevli, E. L. Curran, D. E. Dillard, and R. J. Kamat, *J. Amer. Chem. Soc.*, **89**, 5902 (1967).

(10) C. F. Wilcox and C. Leung, *ibid.*, **90**, 336 (1968).

(11) E. Tommila and C. N. Hinshelwood, *J. Chem. Soc.*, 1801 (1938).

(12) R. Foster, C. A. Fyfe, and J. W. Morris, *Rec. Trav. Chim. Pays-Bas*, **84**, 516 (1965).

are sensitive to the electronic properties of the acyl portion of the substrates,[13] and because the reaction is run at a high pH value where the amine is unprotonated. In addition to p–π effects, the hydrolysis could conceivably be affected by inductive withdrawal toward the nitrogen through the σ bonds of the side chains. Since the number of bonds between the nitrogen and the reactive site is large, especially where $n = 3$ or 4, this effect would be expected to be small indeed for a neutral nitrogen. In any event, inductive withdrawal is an accelerative effect. The presence of p–π overlap, however, would be manifested by an unusual rate reduction because the electron density of the aromatic π system (and of the carbonyl which is in conjugation with it) is increased. Thus σ values which are larger negative numbers than those for the unsubstituted alkyl chains would constitute evidence for p–π overlap.

The kinetic data for the basic hydrolysis of esters C are presented in Table II. A Hammett plot for the five reference compounds is a straight line obeying eq 1.

$$\log k = 1.66\sigma - 1.92 \qquad (1)$$

The heretofore unreported substituent constants for the $(CH_3)_2N(CH_2)_n$ groups are also tabulated in Table II, and clearly these groups show no unusual electron-donating ability that could be attributed to p–π interaction.

TABLE II

KINETIC DATA FOR BASIC HYDROLYSIS OF $XC_6H_4COOCH_3$ IN 0.2 *N* NaOH AT 25°

| X | −Log *k* | $\sigma^a$ |
|---|---|---|
| $OCH_3$ | 2.397 | −0.268 |
| $CH_3$ | 2.171 | −0.170 |
| H | 1.886 | 0.000 |
| Cl | 1.590 | 0.227 |
| $NO_2$ | 0.620 | 0.778 |
| $N^+(CH_3)_3$ | 0.717 | 0.723 |
| $CH_2N^+(CH_3)_3$ | 1.182 | 0.444 |
| $(CH_2)_2N^+(CH_3)_3$ | 1.706 | 0.129 |
| $(CH_2)_3N^+(CH_3)_3$ | 1.883 | 0.023 |
| $(CH_2)_4N^+(CH_3)_3$ | 1.987 | −0.040 |
| $CH_2N(CH_3)_2$ | 1.903 | 0.011 |
| $(CH_2)_2N(CH_3)_2$ | 2.065 | −0.087 |
| $(CH_2)_3N(CH_3)_2$ | 2.136 | −0.129 |
| $(CH_2)_4N(CH_3)_2$ | 2.182 | −0.157 |

[a] The first five σ constants are taken from J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1963. The remaining σ constants were evaluated from the equation $\sigma = 1.15 + 0.601 \log k$.

The methiodide salts of C were studied to determine the dependence of log $(k_X/k_H)$ values for ester hydrolysis on chain length. Recent publications concerned with the transmission of polar effects favor the direct field model over the inductive model.[5,10,14] Critical discussion of the topic is abundant and will not be attempted here. We were primarily interested in the effect of cavity shape on the log $(k_X/k_H)$ values for the alkaline hydrolysis of the esters. The only mathematically feasible cavity models are the sphere and ellipsoid of revolution. Within these limitations one would predict that as *n* in the above series of compounds in increased from 0 to 4, the shape of the cavity would change from spherical to ellipsoidal. This is verified by Kirkwood–Westheimer calculations presented in Table III (see Appendix for details of these calculations). When $n = 0$ and 1 the spherical model is in good agreement with experiment, while the ellipsoidal model is better for $n = 3$ and 4. In the intermediate case where $n = 2$, the experimental value of log $(k_X/k_H)$ is between that calculated for the two models. It is also seen from Table III that the observed attenuation (*i.e.*, the rate decrease per carbon) is greater than that calculated for either of the models. Perhaps this could be corrected if it were possible to use the lobed cavity suggested by Tanford.[15] The most important reason for the discrepancy between experimental and theoretical values when *n* is large (3 and 4) is the considerable error in estimating the distance between the substituent and the reactive site as the alkyl chain is lengthened. Nevertheless, the Kirkwood–Westheimer method provides a reasonable estimate of the relative rates of hydrolysis of the substituted benzoate esters when a spherical cavity is used for short-chain substituents and an ellipsoidal cavity for the long-chain groups. Hammett σ parameters for the $(CH_3)_3N^+(CH_2)_n$ groups are reported for the first time in Table II.

TABLE III

CALCULATED AND EXPERIMENTAL VALUES OF LOG $(k_X/k_H)$ FOR BASIC HYDROLYSIS OF $(CH_3)_3N^+(CH_2)_nC_6H_4COOCH_3$

| *n* | Sphere | Ellipsoid | Exptl$^a$ |
|---|---|---|---|
| 0 | 1.25 | 0.66 | 1.20 |
| 1 | 1.09 | 0.58 | 1.02 |
| 2 | 0.77 | 0.41 | 0.46 |
| 3 | 0.70 | 0.38 | 0.27 |
| 4 | 0.57 | 0.31 | 0.17 |

[a] Log $k_H$ values were calculated from eq 1 using 0.00, −0.17, −0.15, −0.14, and −0.14 as $\sigma_p$ constants for hydrogen, methyl, ethyl, *n*-propyl, and *n*-butyl, respectively.

## Experimental Section

The five compounds used for reference purposes (methyl benzoate and the methyl esters of *p*-chloro-, *p*-methyl-, *p*-methoxy-, and *p*-nitrobenzoic acid) were obtained commercially and purified by distillation or recrystallization prior to use. New compounds, with their physical properties and elemental analyses, are all listed in Table IV. Melting and boiling points are uncorrected.

**Methyl *p*-(N,N-dimethylamino)benzoate** was prepared from the corresponding acid using Fischer esterification conditions. Crystallization from aqueous EtOH gave colorless crystals, mp 99–100° (lit.[16] mp 102°).

**Methyl *p*-(N,N-dimethylaminomethyl)benzoate** was prepared as shown in Scheme I. Details are given below.

**α-Chloro-*p*-toluic Acid.**—*p*-Toluic acid (35 g, 0.26 mol) was chlorinated by passing chlorine gas through a melt at 190–195° while irradiating with a 100-W Hg vapor lamp. After 1.25 hr the reaction had to be stopped because of clogging of the chlorine inlet by precipitated product. The reaction mixture was cooled and washed five times with cold MeOH and once with heptane to give 7 g (16%) of product, mp 199–202° (lit.[17] mp 203°).

***p*-(N,N-Dimethylaminomethyl)benzoic Acid.**—α-Chloro-*p*-toluic acid (8 g, 0.047 mol) was heated in 25% aqueous dimethylamine containing 2 g of NaI for 2 days at 70–80°. The solvent was removed and the residue dissolved in a minimum amount of water. This solution was made basic (pH >12) and filtered. The filtrate was acidified (pH <2) and again filtered. Removal of the water from the filtrate left a residue which was extracted

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(13) M. L. Bender, *Chem. Rev.*, **60**, 53 (1960).

(14) R. Golden and L. M. Stock, *J. Amer. Chem. Soc.*, **88**, 5928 (1966).

(15) C. Tanford, *ibid.*, **79**, 5348 (1957).

(16) R. Willstatter and W. Kahn, *Chem. Ber.*, **37**, 401 (1904).

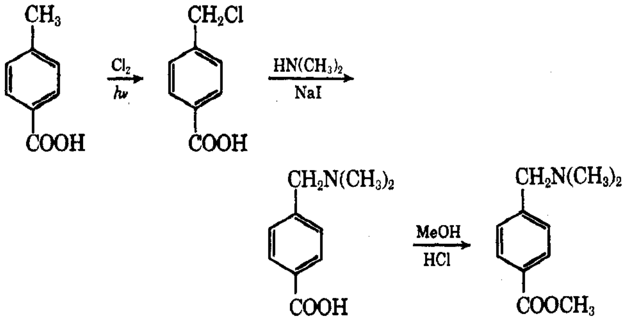
(17) S. C. J. Olivier, *Rec. Trav. Chim. Pays-Bas*, **42**, 516 (1923).

Table IV

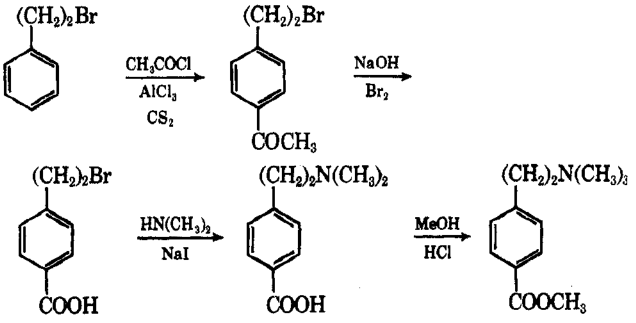
Substituted Methyl Benzoates. Properties and Analyses

| $CH_3OOCC_6H_4X$, X | Registry no. | Mp, °C | Bp (mm), °C | Calcd, % C | Calcd, % H | Calcd, % N | Found, % C | Found, % H | Found, % N |
|---|---|---|---|---|---|---|---|---|---|
| $CH_2N(CH_3)_2$ | 18153-53-2 | | 77–78 (0.3) | 68.37 | 7.82 | 7.25 | 68.35 | 8.12 | 6.99 |
| $(CH_2)_2N(CH_3)_2$ | 18153-54-3 | | 80–83 (0.001) | 69.53 | 8.27 | 6.76 | 69.42 | 8.18 | 6.89 |
| $(CH_2)_3N(CH_3)_2$ | 18153-55-4 | | 80–96 (0.001) | 70.56 | 8.65 | 6.33 | 70.55 | 8.69 | 6.27 |
| $(CH_2)_4N(CH_3)_2$ | 18153-56-5 | | 124 (0.3) | 71.45 | 9.00 | 5.95 | 71.72 | 9.02 | 6.03 |
| $CH_2N(CH_3)_3I$ | 18153-57-6 | 198 dec | | 43.00 | 5.41 | 4.18 | 42.90 | 5.55 | 4.11 |
| $(CH_2)_2N(CH_3)_3I$ | 18153-58-7 | 196–197 | | 44.71 | 5.77 | 4.01 | 44.78 | 5.88 | 3.89 |
| $(CH_2)_3N(CH_3)_3I$ | 18153-59-8 | 178.5–179.5 | | 46.29 | 6.11 | 3.86 | 46.29 | 6.22 | 3.82 |
| $(CH_2)_4N(CH_3)_3I$ | 18153-60-1 | 179–180 | | 47.75 | 6.41 | 3.71 | 47.99 | 6.44 | 4.03 |

Scheme I



Scheme II



with MeOH. The crude product was isolated from the MeOH and used without further purification.

**Methyl p-(N,N-Dimethylaminomethyl)benzoate.**—Fischer esterification of p-(N,N-dimethylaminomethyl)benzoic acid produced the ester which was purified by distillation (see Table IV).

**Methyl p-(2-N,N-Dimethylaminoethyl)benzoate.**—The synthesis of this material is shown in Scheme II. Conversion of (2-bromoethyl)benzene into p-(2-bromoethyl)benzoic acid was accomplished by the method of Foreman and McElvain.[18] The amino ester was secured using a procedure similar to that described for the preparation of methyl p-(N,N-dimethylaminomethyl)benzoate.

**Methyl p-(3-N,N-Dimethylaminopropyl)benzoate.**—The procedure for preparation of this compound from (3-bromopropyl)benzene is similar to that described above. Yield was 28%.

**Methyl p-(4-N,N-dimethylaminobutyl)benzoate** was prepared by the same method given above (see Scheme II). The required (4-bromobutyl)benzene was obtained from 4-phenyl-1-butanol by treatment with $PBr_3$. Yield of amino ester based on 4-phenyl-1-butanol was 9%.

**Methiodide Salts of Methyl p-(N,N-Dimethylaminoalkyl)benzoates.**—The salts were made by mixing the amines with $CH_3I$ in ether. The resulting precipitates were crystallized from EtOH. All salts are new compounds (see Table IV) except that of methyl p-(N,N-dimethylamino)benzoate, mp 173° dec (lit.[16] mp 170° dec).

**Kinetics.**—Solutions of the 14 compounds in methanol were prepared with a concentration of about $10^{-3}$ *M* except for the p-nitro and p-methoxy esters which were about $10^{-4}$ *M*. The following procedure is typical of that used for each compound. A cuvette was filled with 3.00 ml of 0.2 *N* NaOH and placed in the thermostated chamber (25.0 ± 0.1°) of a Cary 14 recording spectrophotometer. After the base had come to thermal equilibrium with the chamber, 50 μl of a methanolic solution of a substrate was added by means of a small stirring rod flattened at one end. In each case the decrease in absorbance was followed as a function of time for at least eight half-lives. The rates of hydrolysis for the p-nitro and p-trimethylammonium esters were too fast to be measured in the 0.2 *N* NaOH solution. For these compounds a 0.04 *N* NaOH solution was used.

**Infrared Spectra.**—All infrared spectra were taken on a Perkin-Elmer Model 257 spectrophotometer using a 0.1-mm path length cell. Spectra were calibrated with a 0.05-mm polystyrene film. Solutions were used immediately after their preparation. Sunlight was excluded from the $CCl_4$ solutions of the amines by wrapping the containers in Al foil. Solvents were of Spectrograde quality. The carbonyl stretching frequencies were found to be independent of the concentration in the range 0.01–0.1 *M*.

**Ultraviolet Spectra.**—All ultraviolet spectra were taken with a Cary 14 recording spectrophotometer using 1.0-cm cuvettes. We used Spectrograde solvents.

## Appendix

**Kirkwood–Westheimer Calculations.**—Calculations of log $(k_X/k_H)$ for basic hydrolysis of $(CH_3)_3N^+(CH_2)_n$-$C_6H_4COOCH_3$ ($n$ = 0–4) in 0.2 *N* NaOH at 25.0° were based on the equation

$$\log (k_X/k_H) = (e/2.3kT)[(e/D_ER)_X - (\mu \cos \theta/R^2D_E)_H]$$

where $\mu = 0.4$, $\cos \theta = 1$, and X represents the trimethylammonium group. The effective dielectric constant $D_E$ was evaluated from the tables of Kirkwood and Westheimer[19,20] assuming an internal dielectric constant of 2.00 and using a solvent dielectric constant of 74.[21] For the spherical cavity model, the Tanford parameter[15] $d$ was assumed to be 1.0 Å for the negative charge developed in the transition state for ester hydrolysis, 1.5 Å for the CH dipole, and 2.1 Å for the positive charge of the $-N^+(CH_3)_3$ group. For the ellipsoidal cavity model, a value for $d$ of 1.5 Å was used for both the charge–dipole and charge–charge interactions. The values of $R$ and $D_E$ used in the calculations are shown in Table V.

Table V

Parameters for Kirkwood–Westheimer Calculations

| $n$ | $R_H$ | $R_X$ | Sphere $(D_E)_H$ | Sphere $(D_E)_X$ | Ellipsoid $(D_E)_H$ | Ellipsoid $(D_E)_X$ |
|---|---|---|---|---|---|---|
| 0 | 6.27 | 7.20 | 5.26 | 25.0 | 9.80 | 47.6 |
| 1 | 7.45 | 7.75 | 6.49 | 27.2 | 11.05 | 51.9 |
| 2 | 8.07 | 8.85 | 6.75 | 33.5 | 14.48 | 63.4 |
| 3 | 8.96 | 9.35 | 7.24 | 35.5 | 18.34 | 67.3 |
| 4 | 9.73 | 10.36 | 7.66 | 39.2 | 19.69 | 73.7 |

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