tated in 45% yield. The product, recrystallized from methanol-water with charcoal treatment, was white: mp 145–146°; uv (water), 287 mμ (ϵ 22,600), in dilute HCl a reversible shift in uv max to 337 mμ was found; ir (mull), 2740, 1629, 1575, 1615, 1299, 1220, 1050, and 1016 cm^{-1}; nmr (DMSO), δ 3.78 (s, 3, CH_3O), 5.43 (d, 1, J = 3 Hz, CH of C4), 7.12 (d, 1, J = 3 Hz, CH of C-3), 7.2 (s, 1, CH=N), and 11.5 (s, NOH).

Anal. Calcd for $C_6H_7NO_3$: C, 51.06; H, 5.00; N, 9.93. Found: C, 50.96; H, 4.90; N, 9.78.

Kinetics of the Reaction of Nitrofurans with Sodium Methoxide.—For the determination of the rate of reaction the nitrofurans were mixed quickly with 0.25 M sodium methoxide in methanol already equilibrated at 38°. The final concentration of nitrofuran was 0.0355 M. At appropriate time intervals, two 0.5-ml aliquots were diluted (1) with methanol to determine total absorbance at 310 mμ and (2) with 4 M HCl to determine acid-stable absorbance at 310 mμ. The absorbance of the latter sample was measured after heating for 10 min in a 70° water bath. Spectra were recorded on the Beckman DB recording spectrophotometer.

Rate of Acid Hydrolysis of 5-Methoxy-2-furaldehyde.—5-Nitro-2-furaldehyde (3.55 mmol) was heated at reflux for 10 min in 100 ml of 0.25 M sodium methoxide in methanol. Without isolation of the 5-methoxy-2-furaldehyde the solution was diluted 1:10 with HCl to give a final acid concentration of 0.25 M. After appropriate intervals in a 67° water bath, aliquots were diluted with NaOH-phosphate buffer (final pH, 7.0) and the absorbance read at 310 mμ.

Registry No.—**2**, 16487-09-5; 4-oxoglutaraldehydic acid bissemicarbazone, 16487-29-9; **3**, 16487-30-2.

Acknowledgment.—Reference compounds were synthesized by Mr. Frank F. Ebetino of the Organic Chemistry Section, Eaton Laboratories. Dr. Julian Michels of the Analytical Chemistry Section, Eaton Laboratories, supplied the infrared spectra, and Dr. Jerrold Meinwald, Department of Chemistry, Cornell University, supplied the nmr spectra.

The Synthesis of Triarylalkyl Ammonium Salts[1]

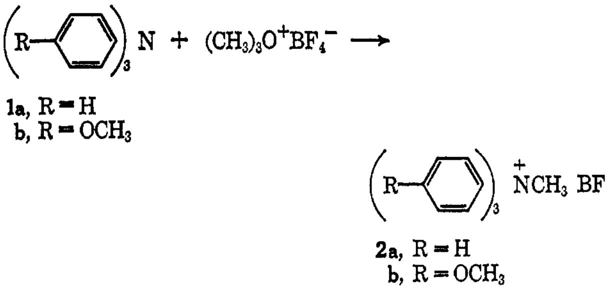
Stanley H. Pine

Department of Chemistry, California State College, Los Angeles, California 90032

Received January 19, 1968

In contrast to the extensive studies of alkyl quaternary ammonium salts,[2] aryl quaternary ammonium salts have only been slightly investigated. In part, this is probably due to the marked decrease in the basic and nucleophilic properties of aryl amines making quaternization somewhat difficult. Diaryldialkylammonium salts are mentioned only rarely in the chemical literature,[3] and triarylalkylammonium salts have not yet been reported.[4] In the following, we report the synthesis of the hitherto unknown triarylalkylammonium salts.

The synthesis of triarylmethylammonium salts **2** was accomplished through alkylation of the required triarylamine with trimethyloxonium tetrafluoroborate[5] in methylene chloride at 75°. As expected, the nucleophilicity of the nitrogen atom is significantly increased by the substitution of a *para* methoxyl group **1b** and the rate of formation of **2b** is considerably greater than for **2a**.



1a, R = H
b, R = OCH_3

2a, R = H
b, R = OCH_3

Both of the triarylalkylammonium tetrafluoroborates **2** are quite stable solids. They do not appear to be appreciably hygroscopic and have shown no signs of decomposition on storage. Both salts can be held above their melting points and recovered essentially unchanged. (Some color does develop on heating, but the spectra of the recovered materials are superimposable on those of the original salts.)

In contrast to the thermal stability of these materials, they are quite labile to treatment with base. Thus, when **2a** is allowed to react with a series of basic reagents (n-butyl lithium–hexane or dichloromethane, t-butyl lithium–pentane or tetrahydrofuran, phenyl lithium–benzene–ether, potassium methoxide–methanol, potassium t-butoxide–dimethyl sulfoxide), demethylation occurs to yield the parent triarylamine. A similar result is observed with **2b** using n-butyl lithium–hexane, dichloromethane, or potassium methoxide–methanol.

Crude kinetics of demethylation by potassium methoxide in methanol-OD have been followed using nmr spectroscopy. The second order rate constants at 0° are approximately 3 × 10^{-5} l. mol^{-1} sec^{-1} and 7 × 10^{-6} l. mol^{-1} sec^{-1} for **2a** and **2b**, respectively. No hydrogen–deuterium exchange of the N-methyl hydrogen atoms was observed in these reactions.

Experimental Section

Analytical Data.—Nmr spectra were obtained using a Varian A-60 spectrometer and chemical shifts are reported as downfield from internal TMS. Infrared spectra were obtained on a Perkin-Elmer Infracord as solutions in carbon tetrachloride or chloroform. Ultraviolet spectra were obtained on a Cary spectrophotometer as a solution in absolute ethanol. Melting points were obtained on a Hoover apparatus and are corrected.

Triphenylmethylammonium Tetrafluoroborate (2a).—To 2.7 g of triphenylamine in 27 ml of dichloromethane was added 2.7 g of trimethyloxonium tetrafluoroborate.[5] The reaction vessel was degassed and sealed under vacuum. It was stirred at 75° for 22 days. The resulting blue solution was evaporated to dryness and the resulting solid successively washed with diethyl ether to yield an ether-insoluble material. Recrystallization from absolute ethanol gave 0.6 g of material with mp 182.0–183.5°. An analytical sample had mp 185.5–186.0°; nmr ($CDCl_3$), δ 4.67 (s, 3, $^+NCH_3$), 7.1–7.8 (m, 15, C_6H_5); ir ($CHCl_3$), 3.3 (m), 6.3 (s), 6.7 (s), 7.9 (s), 9.4 (v.s.), 11.0 μ (s); uv max (absolute

---

[1] We gratefully acknowledge the Los Angeles State College Foundation for partial support of this work.

[2] See, for example, (a) A. C. Cope and E. R. Trumbell, *Org. Reactions*, **11**, 317 (1960); (b) H. E. Zimmerman in "Molecular Rearrangements," P. deMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 345.

[3] (a) D. A. Archer and H. Booth, *J. Chem. Soc.*, 322 (1963); (b) E. D. Hughes and D. J. Whittingham, *ibid.*, 806 (1960); (c) E. Muller, H. Huber-Emden, and W. Rundel, *Ann.*, **623**, 34 (1959).

[4] (a) P. A. S. Smith, "Chemistry of Open Chain Nitrogen Compounds," Vol. 1, W. A. Benjamin, Inc., N. Y., 1965, p 92; (b) I. T. Millar and H. D. Springall, "Sidgwick's Organic Chemistry of Nitrogen," Oxford University Press, London, 1966, p 162.

[5] H. Meerwein, G. Hinz, P. Hofmann, E. Kroning, and E. Pfeil, *J. Prakt. Chem.*, **147**, 257 (1937).

EtOH), 250 mμ (ε 0.9 × 10^3), 257 (1 × 10^3), 261 (1 × 10^3), and 268 (0.9 × 10^3).

Anal. Calcd for $C_{19}H_{18}NBF_4$: C, 65.73; H, 5.23; N, 4.03. Found: C, 65.71; H, 5.45; N, 3.68.

Tri-*p*-anisylmethylammonium Tetrafluoroborate (2b).—To 0.7 g of tri-*p*-anisylamine[6] in 7 ml of dichloromethane was added 0.7 g of trimethyloxonium tetrafluoroborate.[5] The reaction vessel was degassed and sealed under vacuum. It was stirred at 75° for 7 days. The resulting blue solution was evaporated to dryness and the recovered material was successively washed with diethyl ether to give an ether-insoluble solid. Recrystallization from absolute ethanol gave 0.5 g of solid with mp 173.0–175.0°. An analytical sample had mp 175.5–176.0°; nmr ($CDCl_3$), δ 3.85 (s, 9, OCH_3), 4.54 (s, 3, $^+NCH_3$), 6.8–7.4 (m, AA'BB', 12, C_6H_4); ir, 3.3 (m), 6.3 (s), 6.7 (s), 6.9 (s), 7.0 (s), 7.7 (s), 7.9 (s), 8.5 (s), 9.5 μ (vs); uv max (absolute EtOH), 234 mμ (ε 2.9 × 10^4), 273 (5.1 × 10^3), 281 (4.3 × 10^3).

Anal. Calcd for $C_{22}H_{24}NO_3BF_4$: C, 60.43; H, 5.53; N, 3.20. Found: C, 60.47; H, 5.62; N, 3.28.

Base Reactions.—The lithium bases were obtained commercially (Foote or Alfa chemicals) as was the potassium *t*-butoxide (M. S. A. Research Corp., Callery, Pa.). The potassium methoxide was prepared by carefully adding potassium metal to ice-cold methanol. Solvents were dried and distilled.

A typical run is as follows. To the required amount of quaternary ammonium salt in a dry, nitrogen-purged vessel was placed the calculated amount of base and solvent was added. The materials were then allowed to react for the desired time. Water was added and the organic material was recovered by further extraction with ether or pentane.

The kinetic runs were carried out by adding the required amount of basic reagent to a solution of the salt in methanol-OD in an nmr tube at 0°. The tube was purged with nitrogen, then the progress of the reaction followed at 0° by observing the decrease in the aromatic resonance of the salt and the appearance of the aromatic resonance of the tertiary amine.

Registry No.—2a, 16457-64-0; 2b, 16457-65-1.

[6] H. Wieland and E. Wecker, *Chem. Ber.*, **43**, 699 (1910).

Benzene-Induced Nuclear Magnetic Resonance and Dipole Moment Shifts of Five-Membered Rings Containing Heteroatoms

E. Thomas Strom, B. S. Snowden, Jr., H. C. Custard,
D. E. Woessner, and J. R. Norton

Mobil Research and Development Corporation,
Field Research Laboratory, Dallas, Texas 75221

Received January 25, 1968

The five-membered ring heterocycles provide an interesting series of compounds to investigate the factors which affect the benzene solvent shift in the nmr spectra because their geometry is fixed, there are only two basic types of protons (if the plane of the ring is a symmetry plane), and the chemical shifts of the α and β protons are generally well separated. Benzene solvent shifts of the high resolution nuclear magnetic resonance (nmr) spectra have been reported[1-5] as useful in elucidating the proton geometry in carbonyl compounds. Protons behind the carbonyl carbon are shielded while those in front are deshielded with respect to the corresponding values in CCl_4. Shielding effects have also been observed for other functional groups.[6-14] Some generalizations have been made[11] concerning the mechanism of the shielding effects on the solute molecules in benzene. The solvent shifts are thought to result from the formation of a nonplanar association between the solute molecule and benzene at a local electron-deficient site in the solute. The orientation of the benzene is believed[11] to be such that the benzene ring avoids the negative end of the dipole in a nonplanar preferred configuration. A benzene molecule appears to be associated with each electron deficient site in the solute molecule. It is convenient to depict the nonplanar average association between benzene and the heteroatom-containing solute as a "complex;" however, the use of the term "complex" in this context only implies the effects resulting from a slight minimum in the potential energy surface of the benzene–solute molecular interactions.

The following expression, analogous to that of Bhacca and Williams,[15] was used to analyze the data

$$\Delta = \gamma_{CCl_4}{}^{H} - \gamma_{C_6D_6}{}^{H} \qquad (1)$$

where $\gamma_{CCl_4}{}^{H}$ = the center of resonance for a particular kind of proton at infinite dilution in CCl_4 with respect to TMS in CCl_4 and $\gamma_{C_6D_6}{}^{H}$ = the corresponding center of resonance in C_6D_6. The γ values in eq 1 will approach the corresponding chemical shift values (δ) as the system approaches first-order behavior. When planar five-membered ring molecules exist with benzene in solution, there is a certain amount of ordering due to the average planarity of the rings. In order to study only the ordering due to the heteroatom, a Δ value is determined for cyclopentane. The Δ values for the five-membered rings containing heteroatoms are only significant if they exceed this Δ value of cyclopentane. If we assume that the average configuration of the five-membered ring is planar, we note that for all solutes the plane of the five-membered ring is a plane of symmentry of the molecule. These compounds, together with their Δ and γ values, are listed in Table I. Also given in this table are the available literature values for the dipole moments in benzene. It can be seen from the values given that, for most compounds listed, the γ values are indeed chemical shifts.

Figure 1 shows a plot of the solvent shift (Δ^{β}) of the protons β to the functional group *vs.* the dipole moment in benzene ($\mu_{C_6H_6}$) for the molecules. Except for the selenium compound, there seeems to be a linear relationship between $\mu_{C_6H_6}$ and Δ^{β}. A similar relationship between the solvent shift of the α protons (Δ^{α}) is not as apparent. A correlation of the Δ's with dipole moment is expected in the absence of steric effects.[6,9] In general, the larger the dipole moment, the greater the electron deficiency of certain sites in the molecule.

---

[1] J. D. Connally and R. McCrindle, *Chem. Ind.* (London), 379 (1965).

[2] N. S. Bhacca and D. H. Williams, *Tetrahedron*, **21**, 2021 (1965).

[3] C. J. Timmons, *Chem. Commun.*, 576 (1965).

[4] Y. Fujise and S. Itô, *Chem. Pharm. Bull.* (Tokyo), **14**, 797 (1966).

[5] D. W. Boykin, A. B. Turner, and R. E. Lutz, *Tetrahedron Lett.*, 817 (1967).

[6] T. L. Brown and K. Stark, *J. Phys. Chem.*, **69**, 2679 (1965). For a summary of earlier work, see the first eleven references therein.

[7] D. H. Williams and N. S. Bhacca, *Tetrahedron*, **21**, 1641 (1965).

[8] J. E. Anderson, *Tetrahedron Lett.*, 4713 (1965).

[9] J. H. Bowie, J. Ronayne, and D. H. Williams, *J. Chem. Soc., Sect. B*, 785 (1966).

[10] H. M. Fales and K. S. Warren, *J. Org. Chem.*, **32**, 501 (1967).

[11] J. Ronayne and D. H. Williams, *Chem. Commun.*, 712 (1966); *J. Chem. Soc. Sect. B*, 540 (1967).

[12] M. Honda, Y. Kawasaki, and T. Tanaka, *Tetrahedron Lett.*, 3313 (1967).

[13] Y. Kawasaki, *Mol. Phys.*, **12**, 287 (1967).

[14] D. J. Barraclough, P. W. Hickmott, and O. Meth-Cohn, *Tetrahedron Lett.*, 4289 (1967).

[15] N. S. Bhacca and D. H. Williams, *ibid.*, 3127 (1964).