sulfate, filtration, and evaporation of the ether, distillation (b.p. 60° at 1 mm.) led to 1.9 g. (12% of theory) of product, n^{25}_{D} 1.4626, shown by g.p.c. to be >95% pure. The infrared spectrum showed no absorption in the 6.38-μ region, characteristic of the strained double bond, and showed absorption at 3.25 (sh), 3.31 (sh), and 9.72 (s), characteristic of the cyclopropane ring, and at 5.70 (s) and 8.00 μ (s), due to the acetate group.

exo-exo-**Tricyclo[3.2.1.0^{2,4}]octan-6-yl *p*-Bromobenzenesulfonate (Ia).**—A mixture of 4.18 g. (0.0337 mole) of Ib and 8.62 g. (0.0337 mole) of *p*-bromobenzenesulfonyl chloride was dissolved in as little dry pyridine as possible and placed in the refrigerator for 50 hr. The solid material was then pulverized and the contents of the flask were transferred to a separatory funnel containing 100 ml. of 1 *M* hydrochloric acid at 0° and extracted into methylene chloride. The extracts were washed with cold aqueous bicarbonate and ice–water and dried over anhydrous potassium carbonate. Filtration, followed by evaporation of solvent under vacuum, gave a liquid brosylate which solidified on long standing in the refrigerator. The infrared spectrum showed characteristic cyclopropane absorption at 9.83 (m) and at 7.38 (s), 8.46 (s), and 8.53 μ (sh), due to the sulfonate group.

exo-endo-**Tricyclo[3.2.1.0^{2,4}]octan-6-yl Acetate (IIc).**—The Simmons–Smith reaction of 60.9 g. (0.40 mole) of a 4:1 mixture of *endo*- and *exo*-dehydronorbornyl acetates[20] was carried out as described for *exo*-dehydronorbornyl acetate with a reflux time of 120 hr. Fractional distillation under reduced pressure led to 10.6 g. (16% of theory) of liquid tricyclic acetate, b.p. 60° at 1 mm., n^{20}_{D} 1.4813, shown by g.p.c. to be >95% pure. The infrared spectrum showed absorption at 3.24 (s) and 9.65 (s), characteristic of the cyclopropane ring, and at 5.75 (s) and 8.02 μ (s), due to the acetate group. In addition, the near-infrared spectrum showed a band at 1.67 μ, characteristic of the cyclopropane ring.[21]

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.18; H, 9.07.

exo-endo-**Tricyclo[3.2.1.0^{2,4}]octan-6-ol (IIb).**—A 4.5-g. (0.027-mole) quantity of IIc was added to a slurry of 1.01 g. (0.027 mole) of lithium aluminum hydride in 50 ml. of anhydrous ether. After refluxing for 1 hr., 2 ml. of water, followed by 1.56 ml. of 10% sodium hydroxide, was added, with stirring. After standing for 12 hr., the resulting white precipitate was filtered off and the filtrate was dried over anhydrous magnesium sulfate. Filtration and evaporation led to 2.9 g. (86% of theory) of product. G.p.c. showed a single peak (>95%) having a retention time (Ucon Polar on Chromosorb) slightly longer than that of Ib. Sublimation and crystallization from petroleum ether gave material of m.p. 60–63°. The infrared spectrum showed absorption at 2.94 (s) (O–H stretching), and at 3.23 (sh), 3.29 (sh) and 9.71 μ (m), characteristic of the cyclopropane ring. The high-resolution spectrum (Perkin-Elmer Model 112 spectrophotometer, calcium fluoride optics, on supercooled liquid film) showed bands at 3067 (w), 3016 (m), 2943 (s), and 2886 cm.$^{-1}$ (w).

exo-endo-**Tricyclo[3.2.1.0^{2,4}]octan-6-yl *p*-Bromobenzenesulfonate (IIa).**—This compound was prepared as described for Ia. Two recrystallizations gave material of m.p. 81.5–82.5°. The infrared spectrum showed characteristic cyclopropane absorption at 3.21 (sh), 3.27 (sh), 9.66 (m), and 9.86 (s), and characteristic sulfonate group absorption at 7.21 (s), 8.40 (s) and 8.51 μ (m).

Anal. Calcd. for $C_{14}H_{15}BrO_3S$: C, 48.98; H, 4.40. Found: C, 49.01; H, 4.38.

Conversion of IIa to *exo*-Tricyclo[3.2.1.0^{2,4}]oct-6-ene.—A solution of 1.37 g. (0.004 mole) of IIa and 0.9 g. (0.008 mole) of potassium *t*-butoxide (incompletely dissolved) in 80 ml. of dioxane was heated at 60° for 12 hr. and then at 80° for 12 hr., with stirring. The solution was added to a large volume of saturated sodium chloride and extracted twice with pentane. The combined pentane extracts were washed with water and dried over anhydrous sodium sulfate. Evaporation of the pentane left a liquid residue from which some unreacted IIa crystallized on standing in the refrigerator. The infrared spectrum was superimposable upon that published[10] (9–11 μ) for the Simmons–Smith adduct of bicycloheptadiene and had sharp bands at 6.25 and 6.70 μ, characteristic[11] of the *exo* adduct, while bands at 9.54 and 11.3 μ, characteristic of the *endo* adduct,[11] were absent.

Kinetic Measurements.—Kinetic solutions were 0.03 *M* in ester (Ia or IIa), 0.04 *M* in sodium acetate in glacial acetic acid containing 0.02 *M* excess acetic anhydride. Rates at 25° were followed by periodic withdrawal of 5-ml. aliquots of kinetic solution directly from a volumetric flask immersed in a constant-temperature bath, quenching by addition to a 20-ml. volume of dioxane. For rates at the higher temperatures sealed ampoules were used and points quenched thermally. The extent of the reaction was followed by potentiometric titration of the excess sodium acetate using standard 0.03 *M* perchloric acid in glacial acetic acid. Rate constants were calculated by the expression $k = 2.303/t \log V_0 - V_\infty/V_t - V_\infty$, where t is the time and V_0, V_t, and V_∞ are the volumes of standard acid consumed initially (after thermal equilibrium), after time t, and after ten half-lives. Infinity titers for IIa were close to 100% of theory. The sample of Ia used in the kinetic measurements contained some unreacted alcohol and gave an infinity titer of 72% of theory.

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[20] K. Alder and H. F. Rickert, *Ann.*, **543**, 1 (1940).

[21] P. G. Gassman, *Chem. Ind.* (London), 740 (1962).

A Novel Preparation of Amidinium Arsenesulfonates

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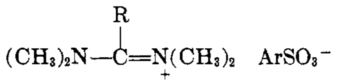
We would like to report a novel reaction between arenesulfonyl chlorides and dimethylformamide (DMF). When benzenesulfonyl chloride was refluxed for several hours in an excess of DMF, large colorless crystals could be isolated on cooling. Although exceedingly hygroscopic in this form, recrystallization from DMF or MeOH gave a nearly quantitative yield of material, the elemental analysis of which required the empirical formula $C_{11}H_{18}N_2O_3S$. This material was quite soluble in water, alcohol, and formamide, slightly soluble in hot acetone, and insoluble in ether, benzene, chloroform, and carbon tetrachloride. This suggested an ionic composition. The infrared spectrum revealed the presence of the benzenesulfonate anion, and in addition, possessed a strong absorption at 1710 cm.$^{-1}$ (DMF has a band at 1640 cm.$^{-1}$). The only reasonable structure consistent with these data is that of tetramethylformamidinium benzenesulfonate (I, R = H; Ar = C_6H_5). The infrared data agree well with that reported[1] for the corresponding chloride. This structure was firmly established on the basis of the n.m.r. spectrum in D_2O (TMS as internal reference), which displayed a single methyl resonance (3.16 p.p.m., 12 protons), a vinyl-like singlet (7.52 p.p.m., one proton), and a multiplet characteristic of a monosubstituted benzene ring (centered at about 7.8 p.p.m., five protons). The splitting of the methyl signal observed in some amidinium systems[2] and in the related octamethyloxamidinium cation[1] is absent, possibly owing to a strong "inside–outside" interaction.



$$(CH_3)_2N\text{—}\overset{R}{\overset{|}{C}}\text{=}\underset{+}{N}(CH_3)_2 \quad ArSO_3^-$$

I

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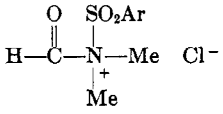
[1] N. Wiberg and J. W. Buchler, *Ber.*, **96**, 3223 (1963).

[2] G. S. Hammond and R. C. Neuman, Jr., *J. Phys. Chem.*, **67**, 1655 (1963).

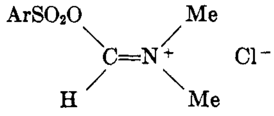
When p-toluenesulfonyl chloride was refluxed with DMF, the tetramethylformamidinium p-toluenesulfonate (I, R = H; Ar = p-$CH_3C_6H_5$) was isolated along with appreciable quantities of dimethylamine hydrochloride; rigorous exclusion of water did not retard formation of the latter.

Hall[3] proposed the formation of either II or III to



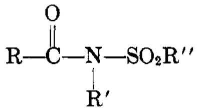
$\mathrm{H{-}\overset{\overset{O}{\|}}{C}{-}\underset{\underset{Me}{|+}}{\overset{\overset{SO_2Ar}{|}}{N}}{-}Me\quad Cl^-}$

II



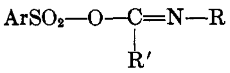
III

account for the fact that benzenesulfonyl chloride gave rise to conducting solutions in DMF at room temperature. Mixed imides of the type IV are known,[4] but the



$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}\underset{\underset{R'}{|}}{N}{-}SO_2R''}$

IV



$\mathrm{ArSO_2{-}O{-}\underset{\underset{R'}{|}}{C}{=}N{-}R}$

V

quaternary ammonium salts such as II are not.[5] Isolation of I would appear to implicate III as a reasonable intermediate. The latter is analogous to the complex presumed to form on addition of thionyl chloride to a dialkylamide[6]; treatment of the complex with an amine leads to the corresponding amidine.[7] Although amides are now known to undergo oxygen protonation in acid solution,[8] there is no assurance that the relative basicities of oxygen and nitrogen would be preserved with respect to other electrophiles. On the other hand, support for III as a likely sulfonylation intermediate can be found from several sources. The mild dehydration of amides to nitriles with benzenesulfonyl chloride[9] must proceed *via* the unstable imidosulfonate (V, R = H); treatment of N-monoalkylamides with this same reagent, in fact, does give an isolable imidosulfonate in some cases.[10] Furthermore, the reaction of α-chlorimines with salts of carboxylic acids to give diacyl amines[11] must certainly involve rearrangement of an intermediate imido ester. At the same time, the reaction of α-chlorimines with the silver salt of benzenesulfonic acid has been shown to produce material identical with that obtained from the Neber rearrangement of the corresponding oxime benzenesulfonate[12]; this product has been identified as the imido ester V.

When dimethylacetamide was substituted for DMF, the principal crystalline product obtained was dimethylamine hydrochloride, although traces of the expected tetramethylacetamidinium arenesulfonate (I, R = CH_3) could be detected in the infrared and n.m.r. spectra. When tetramethylurea (TMU) was employed instead of DMF, only the N,N-dimethylsulfonamides were obtained in quantity together with small amounts of dimethylamine hydroarenesulfonates and dimethylamine hydrochloride. The second NH_2 group in TMU might be expected to enhance the basicity of nitrogen relative to that of oxygen on the grounds of both electronic and statistical considerations. In this case an intermediate analogous to II would appear more likely and is indeed implicated by the nearly exclusive formation of the sulfonamides.

Although amidines and their hydrochloride salts have been prepared in great numbers,[13] only three preparations of quaternary amidinium salts have been reported.[1,14-16] One of these[15] describes the action of phosgene on DMF, a reaction analogous to the one reported here.

Experimental

Tetramethylformamidinium Benzenesulfonate.—A mixture of 128 ml. (1 mole) of benzenesulfonyl chloride and 500 ml. of DMF was allowed to stand for 2 hr. at room temperature, followed by 4 hr. of gentle refluxing. On slow cooling, large prismatic colorless crystals formed. Though these were exceedingly hygroscopic in this form, recrystallization from DMF or MeOH gave a nearly quantitative yield (240 g.) of tetramethylformamidinium benzenesulfonate, m.p. 132.5–133.0°.

Anal. Calcd. for $C_{11}H_{18}N_2O_3S$: C, 51.1; H, 7.02; N, 10.8; S, 12.4. Found: C, 50.6, 50.9; H, 7.1, 7.1; N, 10.7, 10.8; S, 12.0, 11.8.

Tetramethylformamidinium p-Toluenesulfonate.—A mixture of 100 g. (0.524 mole) of p-toluenesulfonyl chloride and 200 ml. of DMF was handled as above. On cooling in ice–water some dimethylamine hydrochloride crystallized and was removed by filtering. The mother liquor was then diluted with twice the volume of acetone and chilled in an ice bath. The tetramethylformamidinium p-toluenesulfonate crystallized in long needles; recrystallization from DMF gave 108 g. (79%) of material with m.p. 140° which contained traces of dimethylamine hydrochloride.

Anal. Calcd. for $C_{12}H_{20}N_2O_3S$: C, 53.2; H, 7.42; N, 10.3. Found: C, 52.8, 52.8; H, 7.5, 7.6; N, 10.5, 10.7.

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[3] H. K. Hall, Jr., *J. Am. Chem. Soc.*, **78**, 2717 (1956).

[4] P. Oxley and F. W. Short, *J. Chem. Soc.*, 382 (1947).

[5] Salts of the type $R'CON^+R_3$ have been prepared by F. Klages and E. Zange [*Ann.*, **607**, 35 (1957)] and were shown to be unstable.

[6] H. H. Bosshard, R. Mory, M. Schmidt, and H. Zollinger, *Helv. Chim. Acta*, **42**, 1653 (1959).

[7] H. Eilingfeld, M. Seefelder, and H. Weidinger, *Angew. Chem., Intern. Ed. Engl.*, 45 (1961).

[8] A. R. Katritzky and R. A. Y. Jones, *Chem. Ind.* (London), 722 (1961); A. R. Katritzky and R. E. Reavill, *ibid.*, 753 (1963), and other papers in this series.

[9] For example, see P. Oxley, *et al.*, *J. Chem. Soc.*, 763 (1946); C. R. Stephens, E. J. Bianco, and F. J. Pilgrim, *J. Am. Chem. Soc.*, **77**, 1701 (1955).

[10] P. Oxley, D. A. Peak, and W. F. Short, *J. Chem. Soc.*, 1618 (1948); R. J. W. Crewlyn, *ibid.*, 1641 (1961).

[11] O. Mumm, H. Hesse, and H. Volquartz, *Ber.*, **48**, 379 (1915).

[12] M. Kuhara, K. Matsumiya, and N. Matsunami, *Mem. Coll. Sci. Univ. Kyoto*, **1**, 25, 105 (1914); *Chem. Abstr.*, **9**, 1613 (1915). For a discussion of the mechanism of the Neber rearrangement, see C. O'Brien, *Chem. Rev.*, **64**, 81 (1964).

[13] R. L. Shriner and F. W. Neumann, *ibid.*, **35**, 351 (1954).

[14] A. Vilsmeir and A. Haack, *Ber.*, **60**, 119 (1927).

[15] Z. Arnold, *Chem. Listy*, **52**, 478 (1958); *Chem. Abstr.*, **53**, 4120i (1959). Z. Arnold, *Collection Czech. Chem. Commun.*, **24**, 760 (1959); *Chem. Abstr.*, **53**, 12168b (1959). *Cf.* W. König and R. Regners, *Ber.*, **63**, 2823 (1930).

[16] Note Added in Proof.—Since this writing another method for the preparation of the tetramethylformamidinium system has been reported: H. Bredereck, F. Effenberger, and G. Simchen, *ibid.*, **98**, 1078 (1965).

The Reaction of Arylamines with Diethylthiocarbamoyl Chloride. A New Synthesis of Aryl Isothiocyanates

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The general synthesis of isothiocyanates from primary amines and thiophosgene is rendered undesirable by the toxicity and unavailability of the thiophosgene. The alternate synthetic approach, based on the reaction of primary amines with carbon disulfide with further