with diazotized sulfanilic acid, an orange color with dimethylaminobenzaldehyde in hydrochloric acid, a brown color with ferric chloride solution and decolorized a dilute chameleon solution. Its R_f value was 0.24 on a paper chromatogram developed with butanol–acetic acid–water; 4:1:5. The ultraviolet absorption spectra had a maximum at 405 mμ at *p*H 11.4, and a maximum at 378 mμ at *p*H 4.8.

Our synthetic 5-hydroxykynurenine is said[6] to have no influence upon the eye color of the *vbw* strain, one of the Drosophila mutants, but to show some effect on the *cnbw* strain.

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(6) Kikkawa, private communication.

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Elimination of *p*-Ethylbenzenesulfonamide from N-*t*-Octyl-*p*-ethylbenzenesulfonamide. Some N-Substituted *p*-Ethylbenzenesulfonamides

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During a study of the relative ease of acid hydrolysis of a variety of N-substituted *p*-ethylbenzenesulfonamides, we have observed an apparently previously unreported type of elimination reaction in which N-(*t*-octyl)-*p*-ethylbenzenesulfonamide was converted to *p*-ethylbenzenesulfonamide and isoöctene (2,4,4-trimethyl-2-pentene). In this note we wish to record the data substantiating this unusual reaction and the data characterizing nine previously undescribed N-substituted *p*-ethylbenzenesulfonamides.

On refluxing N-(*t*-octyl)-*p*-ethylbenzenesulfonamide with 9% hydrochloric acid, a reaction takes place with the separation of an oily liquid. This liquid boils at 95–98° and gives typical unsaturation tests. Refractionation gave four fractions with refractive indices ($n^{20}\text{D}$ 1.4086–1.4131) and boiling ranges (98–101°) indicating that the material was a mixture of 2,4,4-trimethyl-2-pentene and 2,4,4-trimethyl-1-pentene. The yield of crude liquid was 54% of the theoretical amount assuming it to be the mixture of isomeric pentenes. The other product of this reaction is *p*-ethylbenzenesulfonamide obtained in 96.7% yield. Elimination reactions are common with the tertiary alcohols and have been encountered in attempts to acylate *t*-octylamine. Apparently this is the first time a reaction of the type described has been encountered.

The N-substituted *p*-ethylbenzenesulfonamides were prepared from the sulfonyl chloride, prepared as previously described,[1] and the amine by three different techniques. With morpholine, dimethylamine, diethylamine and piperidine, excess amine was heated with the sulfonyl chloride. The diluted reaction mixture was acidified to precipitate the amide in 44.9–81.2% yields of recrystallized product. With diphenylamine, diisopropylamine and *t*-octylamine (2,4,4-trimethyl-2-aminopentane), equimolar quantities of amine and sulfonyl chloride were refluxed in pyridine. Dilute (10%) sulfuric acid was added to the reaction mixture to complete the precipitation of the amide in 21.2–49.8% yields of recrystallized product. With piperazine the reactants were refluxed together in benzene using excess amine. The reaction mixture was filtered to collect the precipitated bis-sulfonamide and then extracted with 10% sulfuric acid. The benzene layer was evaporated to obtain additional bis-sulfonamide. The total yield of recrystallized bis-amide was 39.7%. The monoamide, which precipitated on making the acid layer basic, was obtained in 5.2% yield of recrystallized product. The yields and analytical data are summarized in the Table and typical experimental details are given in the Experimental section.

TABLE I

N-SUBSTITUTED *p*-ETHYLBENZENESULFONAMIDES

Amide	M.p., °C.	Yield,[a] %	Nitrogen, % Calcd.	Nitrogen, % Found
N,N-Dimethyl	48–48.5	45 E	6.57	6.40
N,N-Diethyl	52.5–53	66 P	5.78	5.66
N,N-Diisopropyl	64–64.5	21 P	5.20	5.44
N-*t*-Octyl[b]	98–98.5	50 A	4.71	5.15
Piperidide	69.5–70	52 E	5.53	5.30
Morpholide	120–121	81 E	5.49	5.41
Piperazide				
Bis	231–232	40 E[c]	6.63	6.67
Mono	93	5 E[c]	10.99	10.90
N,N-Diphenyl[d]	133–134	29 E	4.15	4.28

[a] Yield after recrystallization to constant m.p. from E, ethanol; P, petroleum ether; A, aqueous ethanol. [b] Calcd. for $C_{16}H_{27}NO_2S$: C, 64.60; H, 9.15. Found: C, 64.84; H, 9.18. [c] Isolated in same runs. [d] Calcd. for $C_{20}H_{19}NO_2S$: C, 71.19; H, 5.68. Found: C, 71.28; H, 5.78.

Experimental[2]

The amines used in the following experiments were obtained from various laboratory supply firms and used as received except the *t*-octylamine which was generously supplied by Dr. C. E. Denoon, Rohm and Haas Company, Philadelphia, Penna.

4-(*p*-Ethylphenylsulfonyl)-morpholine.—Twenty and five-tenths grams (0.1 mole) of *p*-ethylbenzenesulfonyl chloride was added slowly to 50 ml. of morpholine. The mixture was heated on a steam-bath for one-half hour, diluted with 100 ml. of 10% sulfuric acid to precipitate the amide. The precipitate was collected and recrystallized several times from ethanol to obtain 20.7 g., 81.2%, of 4-(*p*-ethylphenylsulfonyl)-morpholine, m.p. 120–121°.

N,N-Diphenyl-*p*-ethylbenzenesulfonamide.—Twenty and five-tenths grams (0.1 mole) of *p*-ethylbenzenesulfonyl chloride was added slowly with stirring to a solution of 16.9 g. (0.1 mole) of diphenylamine in 70 ml. of pyridine. The mixture was refluxed for 12 hours and acidified with 10% sulfuric acid. The precipitated amide was collected and recrystallized from ethanol to obtain 9.7 g., 28.6%, of N,N-diphenyl-*p*-ethylbenzenesulfonamide, m.p. 133–134°.

1-(*p*-Ethylphenylsulfonyl)-piperazine and 1,4-Bis-(*p*-ethylphenylsulfonyl)-piperazine.—Ten and four-tenths grams (0.05 mole) of *p*-ethylbenzenesulfonyl chloride was added slowly to 28.5 g. (0.15 mole) of piperazine hexahydrate in 60 ml. of benzene. The mixture was refluxed for one-half hour and filtered to collect the precipitated bis-sulfonamide. The benzene layer was extracted with 10% sulfuric acid and evaporated to obtain additional bis-sulfonamide. The collected crude material was recrystallized to give 8.4 g., 39.7%, of 1,4-bis-(*p*-ethylbenzenesulfonyl)-piperazine, m.p. 231–232°. The aqueous layers were made basic to precipitate the monosulfonamide. Recrystallization gave 0.66 g., 5.2%, of 1-(*p*-ethylbenzenesulfonyl)-piperazine, m.p. 93°.

Hydrolysis of N-(*t*-Octyl)-*p*-ethylbenzenesulfonamide.—A mixture of 10.16 g. (0.0342 mole) of N-(*t*-octyl)-*p*-ethylbenzenesulfonamide and 30 ml. of 9% hydrochloric acid was refluxed for 12 hours. During this time the amide dissolved and an oily solid separated. The reaction mixture was made basic and 2.1 g., 54%, of crude 2,2,4-trimethylpentenes separated. Distillation gave 1.55 g. of liquid, b.p. 96–99°, which gave positive unsaturation tests with bromine and potassium permanganate. Fractionation of the liquid gave four fractions: (1) b.p. −99°, $n^{20}\text{D}$ 1.4086; (2) b.p. 99-

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(1) R. H. Wiley and R. P. Davis, THIS JOURNAL, **74**, 6142 (1952).

(2) Analyses by Micro Tech Laboratories.

102°, n^{20}_D 1.4112; (3) b.p. 102–103°, n^{20}_D 1.4131; (4) residue, n^{20}_D 1.4131. Reported[3] values for 2,4,4-trimethyl-2-pentene are b.p. 101°, n^{20}_D 1.4082; for 2,4,4-trimethyl-2-pentene, b.p. 104.5°, n^{20}_D 1.4158. The alkaline, aqueous phase was acidified. The precipitate was collected and recrystallized to give 6.13 g. (96.7%) of *p*-ethylbenzenesulfonamide, m.p. 108°, identified by the method of mixed melting points with an authentic sample prepared as previously described.[4]

Acknowledgment.—This research was supported in part under contract AT-(40-1)-229 between the Atomic Energy Commission and the University of Louisville.

[3] C. O. Tongberg, J. D. Picken, M. R. Fenske and F. C. Whitmore, THIS JOURNAL, **54**, 3706 (1932).

[4] R. Fricke and G. Spilker, *Ber.*, **58**, 1595 (1925).

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Infrared Spectra of Magnesium and Bismuth 8-Quinolinolates

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The insolubility of magnesium 8-quinolinolate dihydrate in chloroform has been noted[1,2] in the literature, but why this inner complex compound should be insoluble whereas others such as the bismuth and ferric compounds are soluble has not been explained. Miller and McLennan[3] have reported the decomposition of the dihydrate on drying at 160° as being

$$\mathrm{Mg(OQ)_2{\cdot}2H_2O} \longrightarrow \mathrm{MgO} + \mathrm{Q_2O} + \mathrm{2H_2O}$$

where OQ represents the 8-quinolinolate ion. This behavior is similar to the hydrolysis observed on heating hydrated magnesium chloride and suggests that the inner complex character of magnesium 8-quinolinolate dihydrate may be less than usually ascribed to the compound.

Infrared spectra of 8-quinolinol, magnesium 8-quinolinolate dihydrate, anhydrous magnesium 8-quinolinolate, bismuth 8-quinolinolate monohydrate and anhydrous bismuth 8-quinolinolate were recorded in the rock salt and calcium fluoride regions using Nujol mulls. As may be seen in Figs. 1 and 2 there is a marked difference between the spectrum of 8-quinolinol and the spectra of the salts, but only slight differences between the spectra of the magnesium and bismuth salts. The removal of the hump at about 3 μ and the decrease in the peak at about 8.3 μ on drying indicate the removal of water.[4] If the hydrated magnesium salt contained magnesium hydroxide, a peak at 6.7–6.8 μ[5] should disappear on drying the salt. If this peak is present, it is covered by an 8-quinolinolate peak and cannot be observed.

From the evidence presented here it must be concluded that magnesium 8-quinolinolate and bismuth 8-quinolinolate have essentially the same

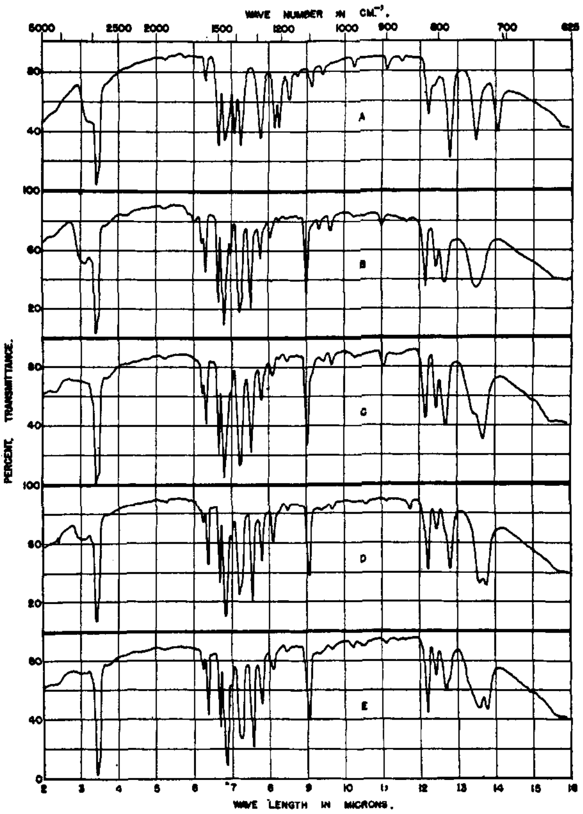

Fig. 1.—Infrared spectra with NaCl prism: A, 8-quinolinol; B, magnesium 8-quinolinolate dihydrate; C, magnesium 8-quinolinolate; D, bismuth 8-quinolinolate monohydrate; E, bismuth 8-quinolinolate.

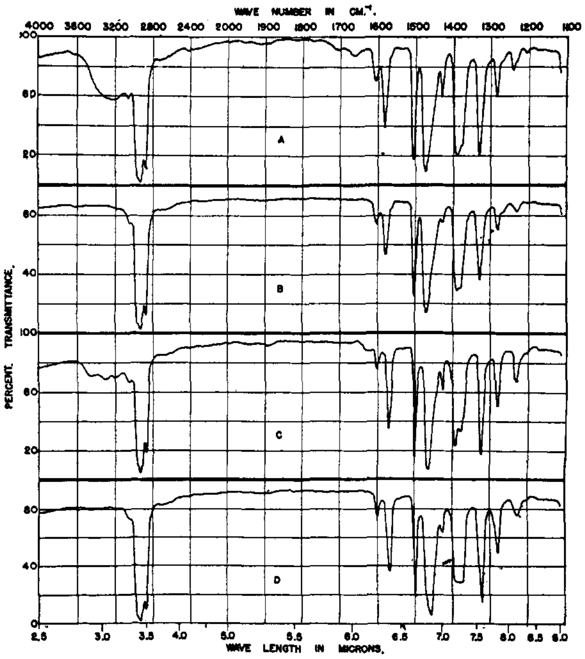

Fig. 2.—Infrared spectra with CaF_2 prism: A, magnesium 8-quinolinolate dihydrate; B, magnesium 8-quinolinolate; C, bismuth 8-quinolinolate monohydrate; D. bismuth 8-quinolinolate.

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[2] C. P. Sideris, *Ind. Eng. Chem.*, *Anal. Ed.*, **12**, 232 (1940).

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