obtained from spent cloves,[5,10] $[\alpha]^{22}_{D}$ +70°, $\lambda_{max}^{CHCl_3}$ 5.80, 5.90 and 7.98 μ. The infrared spectra of the two specimens were identical.

Oleanolic acid methyl ester, prepared by diazomethane treatment in ether–methanol solution, crystallized from methanol–chloroform as colorless crystals with m.p. 198–199°, $[\alpha]^{22}_{D}$ +69°.[11]

Oleanolic acid acetate methyl ester, obtained by diazomethane treatment of the acetate, exhibited m.p. 217–219°, $[\alpha]^{22}_{D}$ +65°,[12] after crystallization from chloroform–methanol.

Acknowledgment.—The presently used plant specimens were obtained during a collection trip for related cacti under a grant from the American Heart Association.

[10] We are indebted to Dr. T. G. Halsall of the University of Manchester, England, for this sample.

[11] W. A. Jacobs and E. E. Fleck, *J. Biol. Chem.*, **96**, 341 (1932), report m.p. 197–198°, $[\alpha]_{D}$ +75° (chloroform).

[12] A. Winterstein and G. Stein, *Z. physiol. Chem.*, **199**, 64 (1931), give m.p. 218–220°, $[\alpha]_{D}$ +66.7°, +70.4°.

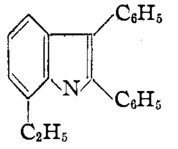
DEPARTMENT OF CHEMISTRY
WAYNE UNIVERSITY
DETROIT 1, MICHIGAN

Heterocyclic Compounds from Ethylanilines

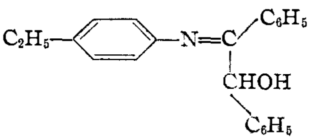
BY WILLIAM S. EMERSON, ROBERT A. HEIMSCH AND TRACY M. PATRICK, JR.

RECEIVED JANUARY 5, 1953

With the ready availability of *o*- and *p*-ethylnitrobenzene, it seemed desirable to hydrogenate them to the corresponding anilines and utilize these in organic syntheses. *o*-Ethylaniline reacted with benzoin in the presence of fused zinc chloride at 130° to give 49% of 2,3-diphenyl-7-ethylindole (I), a method used previously for the preparation of 2,3-diphenylindole itself.[1] Under the same conditions *p*-ethylaniline yielded only the Schiff base N-(1,2-diphenyl-2-hydroxyethylidene)-*p*-ethylaniline (II) in 20% yield.



I



II

o-Ethylaniline and *p*-ethylaniline gave 8- and 6-ethylquinolines, respectively, in 74 and 45% yields under the conditions of the Skraup reaction. Both quinolines were characterized as their methiodides. 6-Ethylquinoline was oxidized to the corresponding amine oxide by a standard procedure.[2] While the acetate resisted all attempts at purification, the picrate crystallized readily.

Experimental

***o*-Ethylaniline** was prepared by the hydrogenation of *o*-ethylnitrobenzene in the presence of Raney nickel. The yield was 78%, b.p. 99–105° (18 mm.) (210–211°),[3] n^{25}_{D} 1.5562.

2,3-Diphenyl-7-ethylindole.—A mixture of 60.5 g. of *o*-ethylaniline, 106 g. of benzoin, 75 g. of freshly dehydrated zinc chloride and 150 cc. of benzene was heated at 130° in a rocking autoclave for 3 hours. The resulting clear resin was dissolved in ethanol and diluted with water. The product which precipitated at this point was separated by filtration, washed with water and crystallized first from hexane and then from ethanol to yield 73 g. (49%) of 2,3-diphenyl-7-ethylindole, m.p. 112–114°. An analytical sample was recrystallized from ethanol, m.p. 113–114°.

Anal.[4] Calcd. for $C_{22}H_{19}N$: C, 88.9; H, 6.43; N, 4.72. Found: C, 89.1; H, 6.57; N, 4.94.

8-Ethylquinoline was prepared by a modification of the previously described Skraup reaction[5] in 36% conversion and 74% yield, b.p. 132–135° (20 mm.) (256°),[5] n^{25}_{D} 1.5993 (n^{25}_{D} 1.6020).[5]

8-Ethylquinoline methiodide was prepared by heating 9 g. of the quinoline with 28 g. of methyl iodide in a bomb at 100° for 18 hours. The 8 g. (47%) of crude product was crystallized twice from ethyl acetate–methanol, m.p. 138–139°.

Anal. Calcd. for $C_{12}H_{14}NI$: C, 48.2; H, 4.69. Found: C, 47.5; H, 4.67.

***p*-Ethylaniline** was prepared in the same way as the ortho isomer in 93% yield, b.p. 98° (14 mm.)–108° (19 mm.) (95–96° (10 mm.))[6], n^{25}_{D} 1.5520 (n^{22}_{D} 1.5529)[7].

N-(1,2-Diphenyl-2-hydroxyethylidene)-*p*-ethylaniline was prepared by heating 60.5 g. of *p*-ethylaniline, 106 g. of benzoin, 75 g. of freshly dehydrated zinc chloride and 150 cc. of benzene in a bomb for 3 hours at 130°. After the reaction mixture had been diluted with ethanol, the crude product was separated by filtration, washed with water and dried. On boiling with hexane 2.0 g. of the zinc chloride salt of *p*-ethylaniline remained insoluble. It was separated by filtration and crystallized twice from ethanol, dec. pt. 244–247°. It was soluble in hot water and gave a flocculent precipitate with aqueous silver nitrate.

Anal. Calcd. for $C_8H_{11}N\cdot{}^1/_2ZnCl_2$: C, 50.8; H, 5.82; N, 7.41. Found: C, 51.4; H, 5.89; N, 7.75.

Cooling of the hexane solution yielded 30 g. (20%) of crude N-(1,2-diphenyl-2-hydroxyethylidene)-*p*-ethylaniline, m.p. 102–103°. This product was recrystallized twice for analysis, m.p. 103–104°.

Anal. Calcd. for $C_{22}H_{21}NO$: C, 83.8; H, 6.67; N, 4.40. Found: C, 83.3; H, 6.71; N, 4.43.

6-Ethylquinoline was prepared in the same way as the 8-isomer in 23% conversion and 45% yield, b.p. 132–140° (17 mm.), n^{25}_{D} 1.6017. Redistillation yielded pure 6-ethylquinoline, b.p. 135–136° (14 mm.), n^{25}_{D} 1.6009, d^{25}_{25} 1.043, M^{25}_{D} calcd. 51.73, M^{25}_{D} found 51.55.

Anal. Calcd. for $C_{11}H_{11}N$: C, 84.1; H, 7.01; N, 8.92. Found: C, 83.9; H, 6.92; N, 9.08.

6-Ethylquinoline picrate melted at 205.0–205.5°.

Anal. Calcd. for $C_{17}H_{14}O_7N_4$: C, 52.9; H, 3.63; N, 14.5. Found: C, 53.0; H, 3.59; N, 14.1.

6-Ethylquinoline methiodide was prepared by warming 8 g. of 6-ethylquinoline with 25 g. of methyl iodide. The crude product (15 g., 99%) was separated by filtration and crystallized twice from methanol, m.p. 194.0–194.5°.

Anal. Calcd. for $C_{12}H_{14}NI$: C, 48.2; H, 4.69. Found: C, 48.5; H, 4.83

6-Ethylquinoline-N-oxide Acetate.—A mixture of 73 g. of 6-ethylquinoline, 175 cc. of glacial acetic acid and 175 cc. of 30% hydrogen peroxide was held at 50° for 24 hours. Distillation at 25 mm. to a pot temperature of 110° left as a residue 87 g. (78%) of crude oxide. This material was crystallized three times from benzene with previous treatment of the solution with Norite, but the product always separated as an oil before crystallizing, m.p. 66–67°.

Anal. Calcd. for $C_{13}H_{15}O_3N$: C, 66.9; H, 6.44. Found: C, 64.3; H, 6.54.

6-Ethylquinoline-N-oxide picrate melted at 156–157°.

Anal. Calcd. for $C_{17}H_{14}O_8N_4$: C, 50.7; H, 3.48; N, 13.9. Found: C, 51.1; H, 3.55; N, 13.8.

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[1] F. R. Japp and T. S. Murray, *J. Chem. Soc.*, **65**, 889 (1894).

[2] H. J. Den Hertog and W. P. Combe, *Rec. trav. chim.*, **70**, 581 (1951).

[3] F. Beilstein and A. Kuhlberg, *Ann.*, **156**, 206 (1870).

[4] All of the analyses are microanalyses performed by Mr. Donald Stoltz, Miss Winifred Harden and Mrs. Helen LeMay of these laboratories.

[5] R. A. Glenn and J. R. Bailey, THIS JOURNAL, **63**, 639 (1941).

[6] G. Vavon and V. M. Mitchovitch, *Bull. soc. chim.*, [4] **45**, 961 (1929).

[7] E. Schreiner, *J. prakt. Chem.*, [2] **81**, 599 (1910).

A mixture of this picrate with that of 6-ethylquinoline melted at 147–150°.

CENTRAL RESEARCH DEPT.
MONSANTO CHEMICAL CO.
DAYTON 7, OHIO

Metathetical Reactions of Silver Salts in Solution. II. The Synthesis of Alkyl Sulfonates[1]

BY WILLIAM D. EMMONS AND ARTHUR F. FERRIS

RECEIVED JANUARY 2, 1953

Alkyl sulfonates have normally been prepared by the base-catalyzed action of a sulfonyl chloride upon an alcohol.[2] This method is dependent on the availability of the appropriate alcohol and is limited to the preparation of those esters which are not sensitive to base. A less useful method has been the heating of a silver sulfonate with an alkyl iodide.[2] This procedure is severely limited by the

$$RSO_3Ag + R'I \longrightarrow RSO_3R' + AgI$$

heterogeneous reaction conditions employed and the relatively high temperatures frequently necessary to effect complete reaction.

We have been able to make a significant improvement in the preparation of alkyl sulfonates by the silver salt method using acetonitrile as a solvent for the reaction. The silver salts of methanesulfonic acid, *p*-toluenesulfonic acid and benzenesulfonic acid are all extremely soluble in acetonitrile at room temperature. Accordingly, the metathetical reaction between these silver salts and primary alkyl halides may be carried out smoothly under mild conditions and with nearly quantitative yields of esters. The following mesylates were all prepared from silver methanesulfonate and the corresponding alkyl iodides except where noted: methyl mesylate (97% yield), ethyl mesylate (94% yield), butyl mesylate (97% yield), allyl mesylate (96% yield from allyl bromide), methallyl mesylate (81% yield from methallyl chloride), methylene bis-mesylate (72% yield from methylene iodide) and benzyl mesylate (92% yield from benzyl bromide). Tosylates were prepared by essentially the same procedure: methyl tosylate (77% yield), ethyl tosylate (76% yield), ethylene bis-tosylate (65% yield from ethylene bromide), methylene bistosylate (88% yield from methylene iodide) and benzyl tosylate (52% yield from benzyl chloride). Methyl benzenesulfonate was also prepared in 69% yield from methyl iodide and silver benzenesulfonate.

The reaction of silver sulfonates in solution with secondary and tertiary halides was, as might be expected, of no synthetic value for the preparation of sulfonates. Under these conditions dehydrohalogenation takes place; indeed, from *t*-butyl bromide and silver tosylate the only product isolated was *p*-toluenesulfonic acid.

Experimental[3]

The procedures described herein for allyl mesylate and methylene bis-mesylate are typical of those used for preparation of all the other esters. Physical constants and analytical data are given for those esters which have not been described previously in the literature. The yields reported in the discussion refer in most cases to the distilled product. The silver salts were conveniently prepared by addition of a slight excess of silver oxide to an acetonitrile solution of the sulfonic acid. Evaporation of the solvent gave the silver salts in excellent yield and purity. All melting points and boiling points are uncorrected.

Allyl Mesylate.—To a solution of 10.2 g. (0.05 mole) of silver methanesulfonate in 50 ml. of dry acetonitrile was added 7.3 g. (0.06 mole) of allyl bromide. The mixture was allowed to stand one hour and was then filtered. The solvent was removed at reduced pressure and the liquid residue distilled. There was obtained 6.5 g. (96%) of colorless allyl mesylate, b.p. 45–47° (0.05 mm.), n^{20}_{D} 1.4435.

Anal. Calcd. for $C_4H_8O_3S$: C, 35.28; H, 5.92; sapn. equiv., 136.2. Found: C, 35.04; H, 5.66; sapn. equiv., 133.0.

Methylene Bis-mesylate.—To a hot solution of 22.3 g. (0.11 mole) of silver methanesulfonate in 100 ml. of acetonitrile was added 26.8 (0.1 mole) of methylene iodide. The solution was stirred at reflux for 20 hours. It was then filtered and the volatile solvent removed at reduced pressure. The solid product was dissolved in 150 ml. of warm ethylene dichloride and then filtered to remove the excess silver methanesulfonate. The solvent was removed by distillation yielding the crystalline product which was recrystallized from ethanol; yield 7.4 g. (72%), m.p. 75–76°.

Anal. Calcd. for $C_3H_8S_2O_6$: C, 17.64; H, 3.95; sapn. equiv., 102.1. Found: C, 17.83; H, 3.87; sapn. equiv., 103.6.

Methallyl Mesylate.—This compound was prepared by heating 10.2 g. (0.05 mole) of silver methanesulfonate and 6.4 g. (0.07 mole) of methallyl chloride in 50 ml. of acetonitrile for one hour; yield 6.1 g. (81%), n^{20}_{D} 1.4468, b.p. 54–56° (0.02 mm.).

Anal. Calcd. for $C_5H_{10}O_3S$: C, 39.98; H, 6.71; S, 21.35; sapn. equiv., 150.2. Found: C, 40.39; H, 6.60; S, 20.95; sapn. equiv., 151.5.

Benzyl Mesylate.—This ester was prepared from 11.2 g. (0.055 mole) of silver methanesulfonate and 8.5 g. (0.05 mole) of benzyl bromide. The product decomposed on attempted distillation, and the data reported here were obtained from the crude sample; yield 8.6 g. (92%), n^{20}_{D} 1.5199.

Anal. Calcd. for $C_8H_{10}O_3S$: C, 51.59; H, 5.41; S, 17.22; sapn. equiv., 186.2. Found: C, 52.42; H, 5.51; S, 17.32; sapn. equiv., 183.9.

Methylene Bis-tosylate.—A solution of 14.0 g. (0.05 mole) of silver *p*-toluenesulfonate and 6.0 g. (0.023 mole) of methylene iodide in 50 ml. of acetonitrile was heated under reflux for 24 hours. The product was worked up in the same manner as methylene bis-mesylate. The crystalline solid was recrystallized from absolute ethanol, yield 7.0 g. (87%), m.p. 116–117°.

Anal. Calcd. for $C_{15}H_{16}O_6S_2$: C, 50.55; H, 4.53; S, 17.99; sapn. equiv., 178.2. Found: C, 50.27; H, 4.44; S, 17.61; sapn. equiv., 182.1.

ROHM AND HAAS COMPANY
JOSIAH GORGAS LABORATORY
REDSTONE ARSENAL RESEARCH DIVISION
HUNTSVILLE, ALABAMA

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[1] This work was carried out under Army Ordnance Contract W-01-021-ORD-334.

[2] C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 514.

[3] We are indebted to Mr. Al Kennedy and Miss Annie Smelley for analytical data.

Estimation of Entropy

BY GEORGE HOOD

RECEIVED SEPTEMBER 30, 1952

Various methods furnish estimates of the standard entropy of a compound with an uncertainty of a few entropy units. A better estimate can be obtained for the members of a substitution series such as CH_4, CH_3Cl, . . . , CCl_4 if the standard entropies of two members are known.

Figure 1 shows that the translational and vibra-