boiled at 134–137° (25 mm.). Its acetyl derivative melted at 88–89° (89–90°).[7]

N-Nitroso-N-methylmesidine.—N,N-Dimethylmesidine was prepared from nitromesitylene by the method of Emerson, Neumann and Moundres.[1b] It was converted to N-nitroso-N-methylmesidine by the above procedure, 6 g. (100%) of the latter being obtained from 5.5 g. of the tertiary amine. A sample distilled at 113–117° (3 mm.): $n^{20}{}_D$ 1.5344, $d^{20}{}_{20}$ 1.047, $M^{20}{}_D$ calcd. 53.7, $M^{20}{}_D$ found 52.8.

N-Methylmesidine.—Six grams of the nitroso derivative was reduced with stannous chloride and hydrochloric acid yielding 2.5 g. (50%) of N-methylmesidine: b. p. 107–118 (30 mm.), $n^{20}{}_D$ 1.5248, $d^{20}{}_{20}$ 0.951, $M^{20}{}_D$ calcd. 49.4, $M^{20}{}_D$ found 48.0. The *p*-toluenesulfonamide melted at 147.0–147.5° (145–146°)[8] after one crystallization from aqueous alcohol.

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[7] German Patent 176,474, *Chem. Zentr.*, **78**, I, 142 (1907).

[8] Hey, *J. Chem. Soc.*, 1581 (1931).

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Antimony Electrode. A Correction

BY FRANK HOVORKA AND G. H. CHAPMAN

Dr. Duncan A. MacInnes has kindly called our attention to the fact that there is a simple explanation for the difference of the *p*H values for 0.05 *M* potassium acid phthalate that he recommends[1] and the other values quoted in our paper on the "Antimony Electrode."[2] His value is based on the *p*H scale proposed by MacInnes, Belcher and Shedlovsky,[3] and our value is obtained by using Sörensen's value for E_0, and the two values are not comparable. The difference between the two values is about 0.02 *p*H unit. When our value is recalculated on this proposed scale, the agreement is excellent and is within the experimental error.

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[1] MacInnes, "Principles of Electrochemistry," Reinhold Publishing Corporation, New York, N. Y., 1939.

[2] Hovorka and Chapman, THIS JOURNAL, **63**, 955 (1941).

[3] MacInnes, Belcher and Shedlovsky, *ibid.*, **60**, 1094 (1938).

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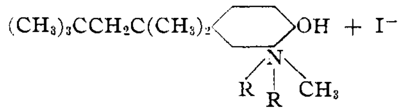
Phenolic Invert Soaps

BY JOSEPH B. NIEDERL AND FRANK A. ABBRUSCATO[1]

Since none of the previously reported capillary active and water soluble "invert soaps"[2,3] contain a free phenolic hydroxyl group, it was thought desirable to prepare and study such types of compounds. For this purpose *p*-$\alpha,\alpha,\gamma,\gamma$-tetrametho-butylphenol (diisobutylphenol)[4] was condensed with formaldehyde and a series of secondary amines. The resulting tertiary amines were then converted into the respective phenolic invert soaps upon treatment with methyl iodide. These quaternary ammonium salts possess the structure



Experimental Procedure

To a solution of 20 g. of diisobutylphenol and 0.1 mole of the secondary amine in 35 cc. of methanol was added with stirring 10 g. of 30% aqueous formaldehyde solution.[5] The reaction mixture was then allowed to stand at room temperature until two layers had formed. The tertiary amine, the bottom layer, was separated and either crystallized (morpholine, piperidine) or subjected to further purification by precipitation with ammonia of the amine from its filtered solution in dilute acetic acid. The crystalline methiodides were prepared by dissolving the purified amine in an equal amount of methyl iodide and allowing the reaction mixture to stand at room temperature until the quaternary salt crystallized out.

TABLE I

Compounds	Formulas	M. p., °C. (uncor.)	Nitrogen anal., Calcd.	Nitrogen anal., Found
N-(2-Hydroxy-5-$\alpha,\alpha,\gamma,\gamma$-tetrametho-butyl)-benzyl-				
Morpholine	$C_{19}H_{31}NO_2$	44–45	4.59	4.45
Methiodide	$C_{20}H_{34}NIO_2$	176–177.5	3.13	3.03
Piperidine	$C_{20}H_{33}NO$	92–93	4.62	4.73
Methiodide	$C_{21}H_{36}NIO$	162–163.5	3.15	3.00
Ammonium iodides				
Methyl-diethyl	$C_{20}H_{36}NIO$	124–125	3.23	3.41
Methyl-di-*n*-propyl	$C_{22}H_{40}NIO$	135–136.6	3.06	3.04
Methyl-di-*n*-butyl	$C_{24}H_{24}NIO$	132–133	2.86	2.88

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[1] Abstracted from the thesis presented by Frank A. Abbruscato to the Graduate School of New York University in partial fulfillment of the requirement for the degree of Master of Science, June, 1941.

[2] R. Kuhn and D. Jerchel, *Ber.*, **73**, 1100 (1940).

[3] J. B. Niederl and co-workers, THIS JOURNAL, **63**, 945, 1475 (1941).

[4] J. B. Niederl, *Ind. Eng. Chem.*, **30**, 1269 (1938).

[5] H. A. Bruson, U. S. Patents 2,031,557, 2,033,092 (1936).

THE CHEMICAL LABORATORIES
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Indole Preparation

BY FLOYD T. TYSON

The author has found that the intramolecular condensation of *o*-formotoluide is a convenient method for the preparation of indole. Verley[1] used sodium amide as the condensing agent. No yields or details with respect to indole preparation were given by Verley although this author describes a procedure for the preparation of 2-

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[1] Verley, *Bull. soc. chim.*, **35**, 1039 (1924).

methylindole from *o*-acetotoluide in a yield of 85% of the theoretical, and mentions that indole can be prepared from *o*-formotoluide and recommends the use of a diluent.

Madelung[2] used sodium alkoxides as condensing agents on various toluides to prepare 2-substituted indoles, including 2-methylindole but reports failure to isolate any indole from attempts to condense *o*-formotoluide.

The author was unsuccessful in preparing indole in satisfactory yields by the use of sodium amide, monoxide, or alkoxides on *o*-formotoluide. However, by the use of potassium or potassium amide in liquid ammonia, or potassium ethoxide, or methoxide, or *t*-butoxide, essentially pure indole can be prepared readily in yields as indicated in the following table.

YIELDS OF INDOLE PER MOLE OF *o*-FORMOTOLUIDE

Potassium cpd. used	Molar ratio of potassium cpd.	Indole, g.	*o*-Toluidine recovered, g.	Yield, %[a]
Potassium in liquid ammonia	1.0	30	..	51
Amide in liquid ammonia	1.0	28	..	48
Methoxide	1.0	37	53	63
Ethoxide	1.0	37	52	63
Ethoxide	1.5	40	..	68
t-Butoxide	1.0	41	50	70
t-Butoxide	1.5	46	..	79

[a] These yields are calculated on the assumption that 2 moles of formotoluide are required theoretically for the production of 1 mole of indole. The extra mole of formotoluide can be accounted for almost quantitatively as isolated toluidine.

Sufficient of the absolute alcohol for the solution of potassium was placed in a three-necked Pyrex flask connected for reflux, and the apparatus was filled with nitrogen gas. The potassium was added in convenient portions with external cooling. The required *o*-formotoluide was added and the condenser was set for distillation. The excess alcohol was removed by distillation with the aid of a metal bath, and the residue heated to 350–360° for twenty minutes. During this twenty minute interval, combustible gas was evolved, chiefly carbon monoxide and hydrogen, and liquid was condensed from which *o*-toluidine was recovered upon redistillation.

Water was added, after cooling, to the residue in the flask, and the mixture was steam distilled until indole ceased to come over. The distillate was ether extracted, the ether extract was treated with cold dilute (5%) hydrochloric acid, water, and dilute sodium carbonate (5%) solution and dried over sodium sulfate. Upon removal of ether, and distillation under reduced pressure, essentially pure indole was obtained; b. p. 128° (10 mm.), m. p. 53°.

The potassium amide was prepared in liquid ammonia, and the *o*-formotoluide was added to the liquid ammonia solution, with subsequent treatment essentially as described above.

Numerous experiments with higher molecular properties of the above-mentioned potassium compounds and at various temperature ranges resulted in no improvement in yields.

Attempts to prepare indole by the use of sodium amide with or without solution in liquid ammonia, or by the use of a diluent such as diethylaniline or kieselguhr resulted in practically negligible yields of indole; the same result was obtained when sodium monoxide was used as the condensing agent. Attempts to substitute sodium ethoxide, or methoxide, or *t*-butoxide for the corresponding potassium compounds were likewise unsuccessful.

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(2) Madelung, *Ber.*, **45**, 1130 (1912).

The Resonance Energies of Unsaturated and Aromatic Molecules

BY G. W. WHELAND

Mulliken and Rieke[1] have shown that, in the approximate quantum mechanical treatment of molecules by the molecular orbital LCAO method, the usual assumption[2,3,4] of orthogonality between adjacent atomic orbitals is not necessary. In the special case in which the integrals[5] α, β, γ and S are considered to be constant, the procedure of these authors can be put into a somewhat simpler, but equivalent form, in the following manner. When the non-orthogonality integral S is included, the energy of the ith molecular orbital is given by

$$E_i = \frac{\alpha + n_i\gamma}{1 + n_iS}$$

where n_i is a numerical constant obtained by solution of the same secular equation that is used when $S = 0$. This expression for E_i is too complicated as it stands to be easily used, but it is changed by the substitution

$$n_i = \frac{m_i}{1 - m_iS}$$

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(1) R. S. Mulliken and C. A. Rieke, THIS JOURNAL, **63**, 1770 (1941).

(2) E. Hückel, *Z. Elektrochem.*, **43**, 752, 827 (1937).

(3) G. W. Wheland, *J. Chem. Phys.*, **2**, 474 (1934).

(4) J. E. Lennard-Jones, *Proc. Roy. Soc.* (London) **A158**, 280 (1937).

(5) The notation used here is that of Mulliken and Rieke.[1] The quantities α, γ, and E have been previously called α, β and w, respectively, by Hückel,[2] and q, β and w, respectively, by Wheland.[3] In addition, Lennard-Jones[4] has used the symbol δ for the present S, and he has had somewhat different expressons for α and γ.