

terium oxide alone would indicate that the exchange is catalyzed by oxonium ions. Within the limits of experimental error, the rate of exchange is proportional to the acid concentration over a fivefold change in the concentration of hydrochloric acid. The values in the above experiments with a deuterium content of about 98% will be somewhat lower than the rates that would be obtained if it were possible to keep the solution 100% with respect to deuterium. However, the difference is probably within the experimental error. From the rates at the two temperatures, the activation energy for the exchange reaction would appear to be about 23.9 kcal.

The rate constant for the acid catalyzed exchange reaction of biacetyl can be compared with the rate of exchange for acetone measured by Reitz⁶ in 90% deuterium oxide. At 25° the rate of the exchange reaction for acetone was found to be about 5×10^{-4} min.⁻¹ for 1 *M* hydrochloric acid. It is apparent that with two carbonyl groups in the molecule the acid catalyzed exchange reaction is considerably slower than the reaction for a molecule with one carbonyl group. It may be assumed that the rate of the acid catalyzed deuterium exchange for biacetyl is determined by the rate of enolization, as was demonstrated in the case of acetone.⁶ In the acid catalyzed enolization the first step involves the transfer of a proton from the oxonium ion to the ketone and the second step is the removal of a proton from the intermediate ion to form the enol. For a number of ketones it has been shown that the second process is the rate determining step for enolization and that the first step is an equilibrium reaction.⁷ Therefore, a change in structure of the ketone can affect the rate of enolization by shifting the equilibrium point of the first step, with the resultant change in concentration of the intermediate ion, and by altering the rate of removal of the proton from the intermediate ion. However, the present results alone do not permit an exact evaluation of the effect of change in structure upon the separate processes. Of interest in this connection, particularly with regard to the first step, are the recent spectroscopic results of Gordy and Stanford⁸ which show no significant difference in the proton-attracting powers

of acetone and biacetyl, within the limits of experimental error of the method.

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The Isolation of Some Compounds from North Dakota Lignite

BY L. ZECHMEISTER AND W. T. STEWART

Two years ago extracts of a lignite, originating in Hungary, were submitted to chromatographic analysis and small quantities of two crystalline compounds were isolated: a triterpene (m. p. 244–247°) and the potassium salt of a strongly reducing organic acid.¹ Recently North Dakota lignite (from the Velva district, Truax–Traer camp area) was investigated by similar methods. While we were unsuccessful in finding the compounds mentioned, some other crystalline, fluorescing substances were isolated in the following way.

Thirty kilos of lignite were shaken with 30 liters of 90% acetone. After twofold dilution, the filtrate was extracted with 3×600 ml. of petroleum ether (b. p. 60–70°). The extracts were concentrated *in vacuo* to 75–100 ml. and chromatographed on five slaked-lime columns (25 × 5 cm.). The chromatograms were developed with petroleum ether until several sharply bordered and strongly fluorescing zones were visible under a quartz lamp. About 11 cm. below the top a greenish, fluorescent line appeared. The next lower 5-cm. section was heterogeneous and ended with a fluorescing blue line, about 1.5 cm. thick. This whole section, including the latter zone, was cut from each column. The combined fractions were eluted with a 1:1 alcohol–petroleum ether mixture, the alcohol was washed out, the upper layer dried and evaporated. White crystals appeared, contaminated with some yellowish oil. The substance was recrystallized repeatedly from hot petroleum ether in which it is slightly soluble; yield, 12 mg., m. p. 328–330° (cor., slight decomp.). The compound shows chromatographic homogeneity; it is free from nitrogen and ash.

Anal. Calcd. for $(C_{10}H_{18}O)_n$: C, 78.88; H, 10.60. Found: C, 79.13 and 79.18; H, 10.33 and 10.35.

Due to difficulties in the micro-molecular weight determination the value of *n* could not be definitely established. Probably *n* = 3.

(1) L. Zechmeister and O. Frehden, *Nature*, **144**, 331 (1939).

(6) Reitz, *Z. physik. Chem.*, **A179**, 119 (1937).

(7) Zucker and Hammett, *THIS JOURNAL*, **61**, 2785 (1939); Cohn and Urey, *ibid.*, **60**, 679 (1938); Bonhoeffer and Reitz, *Z. physik. Chem.*, **A179**, 135 (1937).

(8) Gordy and Stanford, *J. Chem. Phys.*, **9**, 204, 215 (1941).

The compound forms long, flexible, colorless needles which may be grouped in sheaves. It is easily soluble in cold chloroform, insoluble in aqueous acids or bases. It does not reduce permanganate and the usual sterol reactions are negative.

From other fluorescing zones five more colorless, crystallized substances were obtained in small quantities (1-3 mg. per 30 kilos of lignite). The melting points were: 261-264°, 273-274°, 238-240°, 297-298° and 249-251°.

We wish to express our sincere thanks to Professor L. C. Harrington of the University of North Dakota for the raw material he kindly placed at our disposal.

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PASADENA, CALIFORNIA RECEIVED JULY 5, 1941

NEW COMPOUNDS

N-Alkyl Anthraquinone- β -sulfonanilides

Anthraquinone- β -sulfonanilide.—This sulfonanilide was prepared essentially by the method of MacHoul.¹

An intimate mixture of 2 g. of Eastman Kodak Co. technical sodium anthraquinone- β -sulfonate and 5 g. of phosphorus pentachloride was heated under reflux in an oil-bath at 150° for thirty minutes. The sulfonyl chloride formed was extracted with boiling toluene and the hot extract, after being filtered and cooled, was washed with several portions of water. After adding 3 cc. of aniline to the toluene solution and cooling, a gelatinous precipitate formed. This was filtered off and the filtrate was evaporated to about one-third of the original volume to give, upon cooling, 1.2 g. of yellowish-brown crystals of anthraquinone- β -sulfonanilide. Washing with several portions of a 1:1 mixture of methanol and water produced crystals sufficiently pure, in practically all cases, for the purpose desired. Greater purity, m. p. 192.5-193.5° (MacHoul² gives 193°), may be obtained by crystallization from toluene.

N-Alkyl- β -sulfonanilides.—These derivatives were prepared from the potassium salt of anthraquinone- β -sulfonanilide, readily produced by adding a slight excess of 5% alcoholic potassium hydroxide to a boiling solution of the sulfonanilide in toluene. The insoluble brownish-red salt was filtered while hot and washed with several portions of boiling toluene before use. To 1 g. of the dry salt in a round-bottomed flask was added 0.5 to 1 cc. of the alkyl halide (the larger quantity for the more volatile halides) and 1 cc. of water. Upon refluxing gently for an hour and

cooling, the derivative separated out in plates or needles. The solid was washed with 10 cc. of aqueous 5% potassium hydroxide and then with water until the red color disappeared. Further purification was achieved by dissolving the dried compound in a minimum amount of boiling toluene and throwing it out of solution with about 10 cc. of ethanol. The solid derivative was finally washed with several portions of methanol and dried. Yields varied from about 0.05 to 0.1 g. for the iso and secondary to about 0.3 g. for the primary halides.

TABLE I

Derivative ^a	Formula	M. p., °C. cor.	Nitrogen, %	
			Calcd.	Found
Ethyl (I, Br)	C ₂₂ H ₁₇ O ₄ NS	192.0-193.0	3.58	3.57 3.52
Propyl (I, Br)	C ₂₃ H ₁₉ O ₄ NS	206.5	3.46	3.46 3.38
Isopropyl (I, Br)	C ₂₃ H ₁₉ O ₄ NS	256.0	3.46	3.43 3.47
Butyl (Br)	C ₂₄ H ₂₁ O ₄ NS	172.5-173.0	3.34	3.36 3.24
Isobutyl (Br)	C ₂₄ H ₂₁ O ₄ NS	210.5-211.0	3.34	3.38 3.44
<i>s</i> -Butyl (Br)	C ₂₄ H ₂₁ O ₄ NS	214.5-215.5	3.34	3.25 3.22
Amyl (Br)	C ₂₅ H ₂₃ O ₄ NS	153.0-154.0	3.23	3.20 3.17
Isoamyl (Br)	C ₂₅ H ₂₃ O ₄ NS	172.0-173.0	3.23	3.23 3.21
Hexyl (Br)	C ₂₆ H ₂₅ O ₄ NS	145.5-146.0	3.13	3.13 3.17
Heptyl (Br)	C ₂₇ H ₂₇ O ₄ NS	141.0-141.5	3.04	2.98 2.94
Benzyl (Cl)	C ₂₇ H ₁₉ O ₄ NS	194.0-195.0	3.09	3.08 3.01
Allyl (Br)	C ₂₈ H ₁₇ O ₄ NS	194.0-194.5	3.47	3.39 3.49

^a Halide used in parentheses.

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Mesitoic Anhydride

In an attempt to prepare mesitoyl cyanide, mesitoyl chloride was heated with potassium cyanide in the presence of pyridine. A compound was isolated in good yield (73%) but was found to contain no nitrogen. Investigation showed this compound to be mesitoic anhydride. The same compound was obtained by the interaction of sodium mesitoate and mesitoyl chloride in the presence of pyridine.

Ten grams of sodium mesitoate, 10 g. of mesitoyl chloride, and 75 cc. of pyridine were heated in an oil-bath at 150°. The reaction mixture was stirred and refluxed for two hours. It was cooled, diluted with benzene and poured into water. The benzene solution was washed repeatedly with a dilute solution of hydrochloric acid. It was then washed successively with water, dilute potassium bicarbonate solution and water. The benzene solution was dried over calcium chloride, treated with norite and distilled under slightly reduced pressure. The residue solidified and was crystallized from a mixture of benzene and low-boiling petroleum ether; m. p. 106-107°; yield 9 g.

*Anal.*¹ Calcd. for C₂₀H₂₂O₃: C, 77.42; H, 7.10. Found: C, 77.69; H, 7.20.

Hydrolysis.—About 200 mg. of the compound was heated with 30 cc. of 10% sodium hydroxide solution. When the material did not appear to react readily, 20 cc. of ethanol was added to increase its solubility. After two hours of refluxing, all of the oily droplets had disappeared. The mixture was cooled, filtered and made acid with concentrated hydrochloric acid. A white solid separated from the solution and was recrystallized several times from

(1) MacHoul, *Ber.*, **13**, 692 (1880).

(2) Although MacHoul does not state which anthraquinone sulfonanilide he prepared, his compound was apparently the β since the α form melts at 216° (cor.), Ullmann and Kertesz, *ibid.*, **52**, 551 (1919).

(1) Microanalysis by Mr. L. G. Faule and Miss Mary S. Kreger.