ucts was scrubbed with sufficient 10% caustic solution to remove the bulk of the dissolved solids. The caustic extract (vanillin content as determined by precipitation with *m*-nitrobenzoylhydrazine, 320 g.) was acidified with an excess of SO_2 and allowed to stand for several hours. A brown flocculent precipitate containing vanillil and some unidentified ligneous residues gradually precipitated out. After standing several hours the precipitate was filtered from the sodium bisulfite mother liquor, washed and dried; yield 16.6 g. This residue was then extracted with sodium bicarbonate solution and the crude vanillil precipitated from the extract as a pale pink floc by acidification with H_2SO_4. After several crystallizations from absolute alcohol, minute pale yellow prismatic crystals were obtained, m.p. 227–228°,[7] yield 10.2 g. (3.2% of the vanillin formed during the reaction). The pure material was fairly soluble in acetone, alcohol and butyl acetate, slightly soluble in ether and almost insoluble in water, benzene and toluene.

Anal. Calcd. for $C_{16}H_{14}O_6$: C, 63.57; H, 4.63; OCH_3, 20.53; mol. wt., 302. Found: C, 63.53; H, 4.61; OCH_3, 20.4; mol. wt.,[8] 288 and 312.

Vanillil (Mono) 2,4-Dinitrophenylhydrazone.—Attempts to form a semicarbazone were unsuccessful. The 2,4-dinitrophenylhydrazone, crystallized from alcohol, m.p. 247.5–248.5°, gave the correct analysis for the mono derivative.

Anal. Calcd. for $C_{22}H_{18}O_9N_4$: N, 11.62. Found: N, 11.5.

Vanillil Acetate.—1.0 g. of vanillil was refluxed for 1 hour with 5 ml. of acetic anhydride and then allowed to stand overnight. The resulting pale yellow needle-shaped crystals were filtered, washed free of acetic acid and dried; yield 1.15 g. (90%). After 3 crystallizations from absolute alcohol the m.p. was constant at 139.5–140.5°.

Anal. Calcd. for $C_{20}H_{18}O_8$: $OCOCH_3$, 30.57; OCH_3, 16.06. Found: $OCOCH_3$, 30.6; OCH_3, 16.0.

Quinoxaline Derivative of Vanillil (2,3-Di-(3-methoxy-4-hydroxyphenyl)-quinoxaline).—1.0 g. of vanillil was refluxed for 6 hours with 0.35 g. of *o*-phenylenediamine in 25 ml. of glacial acetic acid according to the method of Vanzetti.[9] The reaction product was placed in the refrigerator overnight and the resulting pale yellow crystals, yield 1.14 g. (92%), after being recrystallized twice from absolute alcohol, melted at 228.2–229.5°.

Anal. Calcd. for $C_{22}H_{18}O_4N_2$: OCH_3, 16.57. Found: OCH_3, 16.6.

Fully Methylated Vanillil.—One and one-half g. of vanillil was methylated repeatedly with NaOH and dimethyl sulfate. After each methylation the product was recovered by extraction with chloroform and its methoxyl content determined. The latter was constant after 4 methylations, yield 1.36 g. (83%). The fully methylated derivative crystallized from absolute alcohol as light yellow felted crystals with a m.p. of 219–221°. The m.p. was unchanged on further crystallization from glacial acetic acid. When mixed with an authentic sample of veratril, the m.p. was not depressed (mixed m.p. 218.5–220°)

Anal. Calcd. for $C_{18}H_{18}O_6$: OCH_3, 37.6. Found: OCH_3, 36.9.

Quinoxaline Derivative of Methylated Vanillil.—The procedure used was identical to that described above for the preparation of the quinoxaline derivative of vanillil. A yield of 0.82 g. (61.7%) was obtained (m.p. after two recrystallizations from absolute alcohol, 194–196°). A mixed m.p. with the quinoxaline derivative of an authentic sample of veratril was not depressed (mixed m.p. 194–195°.)

Anal. Calcd. for $C_{24}H_{22}O_4N_2$: OCH_3, 30.9. Found: OCH_3, 30.3.

Stability of Vanillil toward Alkali.—0.6444 g. of vanillil was dissolved in 18 ml. of water containing 2 g. of NaOH and the solution refluxed for 1 hour. It was then diluted to 100 ml. with water and extracted with three 100-ml. portions of butanol to remove any cleavage products present. An ultraviolet absorption curve on 0.5 ml. of the butanol extract indicated the presence of only vanillil. The remainder of the butanol extract was evaporated to dryness, the residue taken up in a minimum of water and acidified with sulfuric acid. A white flocculent precipitate was obtained (0.04 g.) which had a m.p. of 220° and hence was considered to be vanillil.

Acknowledgments.—The work described herein was carried out under a Fellowship of The Ontario Paper Company Limited and as part of its investigation, under the direction of Dr. Charles A. Sankey, of means to utilize sulfite waste liquor. The authors acknowledge with thanks permission of the Ontario Paper Company Limited to publish this paper. Grateful acknowledgment is also made to Miss Mary Krizsan for assistance in carrying out these experiments.

DEPARTMENT OF CHEMISTRY
ONTARIO RESEARCH FOUNDATION
TORONTO, CANADA

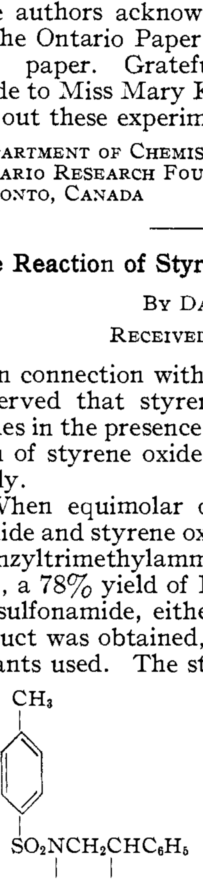
The Reaction of Styrene Oxide with Sulfonamides

BY DAVID A. JOHNSON

RECEIVED DECEMBER 2, 1954

In connection with another problem, it has been observed that styrene oxide reacts with sulfonamides in the presence of a basic catalyst. This reaction of styrene oxide has not been reported previously.

When equimolar quantities of *p*-toluenesulfonanilide and styrene oxide were heated with Triton B (benzyltrimethylammonium hydroxide) as catalyst, a 78% yield of I was obtained. With *p*-toluenesulfonamide, either the mono II or the bis III adduct was obtained, depending on the ratio of reactants used. The structures were assigned on the assumption that nucleophilic attack occurred preferentially at the primary carbon atom of styrene oxide. No further work was conducted to examine the scope of the reaction, but it appears to be general for primary and secondary sulfonamides.



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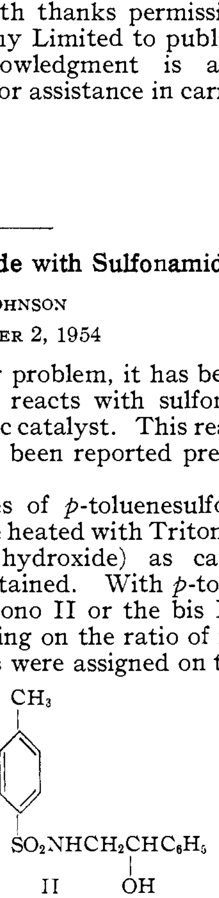

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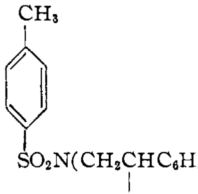

III

Experimental[1,2]

N-(β-Hydroxy-β-phenethyl)-N-phenyl-*p*-toluenesulfonamide (I).—A mixture of styrene oxide (6.0 g., 0.050 mole), *p*-toluenesulfonanilide (12.4 g., 0.050 mole) and Triton B (0.5 ml.) was heated on a steam-cone for 2 hours. The resulting glass was dissolved in 25 ml. of hot toluene and stored at 5° whereupon 12.3 g. of hard prisms separated, m.p. 116.5–121°. Dilution of the filtrate with Skellysolve A (b.p. 28–38°) yielded a second crop of 2.0 g., m.p. 98–115°, bringing the total yield of crude I to 78%. Recrystalliza-

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[7] All melting points reported in this investigation are uncorrected.

[8] Rast camphor method.

[9] B. L. Vanzetti, *Gazz. chim. ital.*, **57**, 162 (1927).

[1] The microanalyses were performed by Mr. Richard M. Downing.

[2] All melting points are corrected.

tion of the first crop from acetone–water afforded colorless needles, m.p. 118.5–120.5°.

Anal. Calcd. for $C_{21}H_{21}NO_3S$: C, 68.65; H, 5.76; N, 3.81. Found: C, 68.5; H, 6.18; N, 3.88.

N-(β-Hydroxy-β-phenethyl)-*p*-toluenesulfonamide (II).—A solution of *p*-toluenesulfonamide (17.1 g., 0.10 mole) and Triton B (1.0 ml.) in styrene oxide (12.0 g., 0.10 mole) was heated on a steam-cone for 2 hours. Crystallization of the resulting oil from 50 ml. of toluene afforded 17.0 g. (58.5%) of colorless needles, m.p. 95–110°. To remove traces of III present, the crude product was dissolved in 5% aqueous sodium hydroxide, the solution was filtered and acidified with concentrated hydrochloric acid. The crystalline precipitate was collected and recrystallized from methanol–water to yield colorless needles of m.p. 112.5–113° (reported m.p. 113°).[3]

N,N-Bis-(β-hydroxy-β-phenethyl)-*p*-toluenesulfonamide (III).—Styrene oxide (24.0 g., 0.20 mole) and *p*-toluenesulfonamide (17.1 g., 0.10 mole) were heated with Triton B (1.0 ml.) on a steam-cone for 2 hours. The crystalline mass which separated during this time was dissolved in 50 ml. of hot toluene. On cooling, there was deposited 14.9 g. (36.3%) of colorless needles, m.p. 166–174°. Several recrystallizations from toluene yielded an analytical sample, m.p. 178.5–179.5°.

Anal. Calcd. for $C_{23}H_{25}NO_4S$: C, 67.14; H, 6.12; N, 7.78. Found: C, 67.1; H, 6.14; N, 7.71.

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(3) M. S. Kharasch and H. M. Priestley, THIS JOURNAL, **61**, 3425 (1939).

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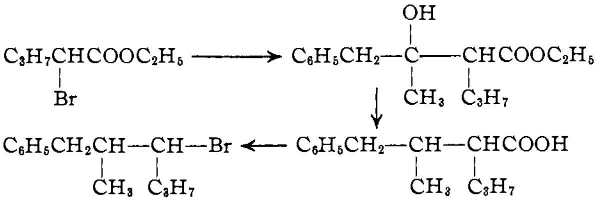
Attempted Preparation of 1-Phenyl-2-methyl-3-Bromohexane by Brominative Decarboxylation[1]

BY ALBERT V. LOGAN, E. N. MARVELL AND NORMAN R. ODELL[2]

RECEIVED OCTOBER 11, 1954

In the course of some work on another problem it was necessary to prepare 1-phenyl-2-methyl-3-bromohexane. It is a well-known fact that this type alkyl halide cannot be prepared from the alcohol,[3] nor will addition of hydrogen bromide to an olefin produce the desired compound. Since brominative decarboxylation has not been investigated previously for the preparation of such bromides, we proposed to carry through the sequence of reactions given in Fig. 1.

In order to prove the structure of the bromide which was obtained in low yield, the following reactions were studied. Qualitative tests with sodium iodide in acetone and silver nitrate in alcohol indicated that the bromide was secondary and not tertiary. The carbon–hydrogen analysis confirmed the empirical formula given. Although a Grignard reagent was obtained in low yield, carbonation gave no acidic material. An unsaturated compound was recovered from this process but no structure proof was attempted. Due to this lack of success in carbonating the Grignard and the low yield of bromide obtained, this procedure was of no value to the investigation at hand and further work was discontinued. Thus no definite structure assignment can be made for the bromide.



$$C_3H_7CH(Br)COOC_2H_5 \longrightarrow C_6H_5CH_2C(OH)(CH_3)CH(C_3H_7)COOC_2H_5 \longrightarrow C_6H_5CH_2CH(CH_3)CH(C_3H_7)COOH \longrightarrow C_6H_5CH_2CH(CH_3)CH(C_3H_7)Br$$

Fig. 1.

Experimental

Ethyl β-Hydroxy-β-methyl-γ-phenyl-α-propylbutyrate.—A mixture of 43.0 g. (0.321 mole) of phenylacetone and 63.0 g. (0.30 mole) of ethyl α-bromo-*n*-valerate dissolved in 120 ml. of benzene and 105 ml. of toluene was added dropwise to 21.0 g. (0.321 mole) of 40-mesh zinc. The reaction was initiated by heating with a steam-bath, and then the solution was added at a rate which kept the reaction mixture gently boiling. After the addition had been completed the reaction mixture was heated for two hours. After cooling, the reaction mixture was decomposed with dilute sulfuric acid, the organic layer separated and dried over sodium sulfate. The product was isolated by distillation, b.p. 110–113° (0.1 mm.), as a colorless liquid in a yield of 60%, $n^{22}D$ 1.4970.

Anal. Calcd. for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.62; H, 9.13.

Ethyl β-Methyl-γ-phenyl-α-propylcrotonate.—Dehydration of the above hydroxyester was attempted by the Hibbert[4] method and by the use of 90% formic acid,[5] but both methods proved unsuccessful.

A solution containing 57.4 g. (0.217 mole) of the above hydroxyester dissolved in 200 ml. of anhydrous benzene was heated under reflux for four hours with 40.0 g. (0.282 mole) of phosphorus pentoxide. The inorganic materials were taken up in ice water, the organic layer separated and dried. An 84% yield of colorless ester, b.p. 93–94° (0.1 mm.), $n^{27}D$ 1.5043, was obtained.

Anal. Calcd. for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.36; H, 9.04.

β-Methyl-γ-phenyl-α-propylcrotonic Acid.—A solution containing 27.0 g. (0.11 mole) of the above ester and 18.4 g. (0.328 mole) of potassium hydroxide in 100 ml. of 30% ethanol was heated under reflux for 12 hours. The solvent was removed by evaporation and the solid residue dissolved in a minimum of cold water. This solution was made distinctly acid and the organic product extracted with ether. Distillation gave 16.6 g. (69%) of a colorless oil, b.p. 130–131° (0.1 mm.), $n^{28}D$ 1.5286.

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.0; H, 8.32; neut. equiv., 218.1. Found: C, 77.29; H, 8.41; neut. equiv., 217.0.

β-Methyl-γ-phenyl-α-propylbutyric Acid.—A sample, 16.5 g. (0.076 mole), of the unsaturated acid was dissolved in 50 ml. of glacial acetic acid and hydrogenated over 100 mg. of platinum oxide at room temperature using three atmospheres hydrogen pressure. Separation of the catalyst and distillation gave 15.0 g. (90%) of the saturated acid, b.p. 125–130° (0.1–0.15 mm.), $n^{20}D$ 1.5088.

Anal. Calcd. for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15; neut. equiv., 220.3. Found: C, 76.28; H, 8.96; neut. equiv., 222.4.

Silver β-Methyl-γ-phenyl-α-propylbutyrate.—A solution of 7.72 g. (0.0454 mole) of $AgNO_3$ in 60 ml. of distilled water was added to 120 ml. of a solution containing 10 g. (0.0454 mole) of the acid and 2.55 g. (0.0454 mole) of potassium hydroxide. The voluminous white precipitate that formed was removed by filtration, washed with cold water, methanol and dried in a vacuum oven at 60° for six hours. Storage even in the dark caused this salt to darken slightly.

Anal. Calcd. for $C_{14}H_{19}O_2Ag$: C, 51.39; H, 5.85. Found: C, 51.29; H, 5.97.

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(2) This article is based on a thesis submitted by Norman R. Odell in partial fulfillment of the requirements for the Doctor of Philosophy degree at Oregon State College.

(3) Frank C. Whitmore and Franklin Johnston, THIS JOURNAL, **60**, 2265 (1938).

(4) H. Hibbert, *ibid.*, **37**, 1748 (1915).

(5) H. Rupe, H. Steiger and F. Fielder, *Ber.*, **47**, 63 (1914).