liberated amino acid does not yield quantitative amounts of carbon dioxide, and therefore the nitrous acid method was employed. The rate of hydrolysis of the susceptible L-isomer of N-chloroacetyl-DL-isovaline by acylase I is 38 micromoles per hour per mg. protein N. The digest was treated with a few drops of toluene, and allowed to incubate at 38° for 24 hours. Analyses on an aliquot of the digest revealed that the hydrolysis of the compound had proceeded to 50%. Another gram of the enzyme was added, and the digest allowed to stand for 12 hours longer. Analysis again revealed 50% hydrolysis. Acetic acid was added to *p*H 5, and the protein filtered off with the aid of Norit. The filtrate was evaporated at 40° *in vacuo*, and the small amount of protein which flocculated was again removed by filtration. The filtrate contained L-isovaline, chloroacetic acid and chloroacetyl-D-isovaline. Treatment with excess ethanol in the usual manner[2-5] failed to bring about the separation of the highly soluble L-isovaline. Treatment with concd. HCl to *p*H 1.7 led to the separation in 50% yield of chloroacetyl-D-isovaline. After recrystallization from acetone-ether, the m.p. was 158° (cor.), and $[\alpha]^{25}D$ −9.0° for a 2% solution in absolute ethanol. In 2% aqueous solution, the rotation of the compound was imperceptible.

Anal. Calcd. for $C_7H_{12}O_3NCl$: N, 7.2. Found: N, 7.1.

Chromatographic Separation of the Enzymatic Products.—A general chromatographic procedure for the separation of the amino acid products obtained by the enzymatic resolution method has been developed in this Laboratory and will be described more fully in a subsequent publication.[11] A brief description of the procedure as it applied to the present problem is as follows. A 100-ml. aliquot of a deproteinized and concentrated isovaline resolution mixture (corresponding to 25.8 g. of chloroacetyl-DL-isovaline in the original digest) was poured onto the top of a column 87 cm. high and 6.5 cm. in diameter composed of 20 to 50 mesh Dowex 50 resin in the acid phase.[12]

Elution with water was carried out at a flow rate of 40 to 60 ml. per hour. Chloroacetyl-D-isovaline appeared in the effluent after approximately 250 ml. of water had passed through the column, as indicated by a fall in *p*H from about 7 to about 3. Aliquots taken from the hour-long fractions were hydrolyzed in 2 *N* HCl for 2 hours and tested for color development with ninhydrin. By this means it was demonstrated that the N-acyl derivative was eluted in approximately 3 liters of effluent. No free isovaline was present in the fractions collected during this interval since ninhydrin tests on unhydrolyzed aliquots were all negative. After further washing of the column with an additional 1.5 liters of water, elution was begun with 2.5 *N* HCl. L-Isovaline began to appear after about 4 liters of solution had passed through the column, as shown by positive ninhydrin tests. The entire L-isovaline was eluted after an additional 3800 ml. of solution had passed through the column.

All the fractions containing chloroacetyl-D-isovaline were combined and evaporated to dryness *in vacuo*, and the residue was taken up in absolute ethanol to remove sodium chloride[13] and any residual protein. The ethanol was evaporated and the residue taken up in acetone and filtered to ensure further the absence of any L-isovaline or sodium chloride. The chloroacetyl-D-isovaline was then isolated by evaporation of the acetone and crystallization from acetone–ether; m.p. 158° (cor.); yield 55% of theory, based on the original amount of chloroacetyl-DL-isovaline; $[\alpha]^{25}D$ −9.0° for a 2% solution in absolute ethanol.

Anal. Calcd. for $C_7H_{12}O_3NCl$: N, 7.2. Found: N, 7.2.

Thus the chloroacetyl-D-isovaline isolated from the column was identical in properties with that obtained by acidification of the resolution mixture. Five grams of chloroacetyl-D-isovaline was refluxed for 2 hours with 100 cc. of 2 *N* HCl. The solution was decolorized with Norit, and the filtrate evaporated *in vacuo* to dryness. The residue was dissolved in 100 cc. water and the solution treated with a slight excess of silver carbonate. The silver chloride was filtered off, and the filtrate saturated with hydrogen sulfide gas. The final filtrate was evaporated to dryness *in vacuo* and the residual D-isovaline taken up in a little water, the solution filtered, and acetone added in excess to the clear filtrate. The D-isovaline crystallized as long needles in nearly quantitative yield, $[\alpha]^{25}D$ −11.28° for a 5% solution in water.

Anal. Calcd. for $C_5H_{11}O_2N$: C, 51.2; H, 9.4; N, 12.0. Found: C, 51.0; H, 9.5; N, 12.0.

The combined fractions containing the L-isovaline were evaporated to dryness *in vacuo*, and the residue taken up in absolute ethanol and filtered to remove sodium chloride.[13] The ethanol was evaporated, and the residue treated successively with silver carbonate and hydrogen sulfide as described for the D-enantiomorph. The yield after crystallization from water with excess acetone was 77% of the theoretical, based on the original amount of chloroacetyl-DL-isovaline; $[\alpha]^{25}D$ +11.13° for a 5% solution in water.

Anal. Calcd. for $C_5H_{11}O_2N$: C, 51.2; H, 9.4; N, 12.0. Found: C, 51.0; H, 9.5; N, 12.2.

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(11) C. G. Baker and H. A. Sober, in preparation.

(12) Cationic exchange resin from the Dow Chemical Company. The resin was regenerated by two cycles of washing with 5 *N* HCl, water, 1 *N* NaOH and water, followed by a final 5 *N* HCl and water wash.

(13) Large volumes of water were used for the final wash of the resin during its regeneration. However, even after the effluent was neutral to phenolphthalein, additional sodium chloride was obtained. The coarse mesh resin employed probably requires a longer equilibration period than does the resin of a finer mesh.

Some Alkyl Benzenesulfonates[1,2]

BY BERTIN L. EMLING

RECEIVED MAY 12, 1952

Six alkyl benzenesulfonates and their pyridinium salts have been synthesized. Their physical properties and yields are given in Tables I and II. None of these compounds has been reported previously in the chemical literature, although a commercial grade of *n*-butyl benzenesulfonate is produced by the Wyandotte Chemicals Corporation.

Attempts to synthesize *t*-butyl arylsulfonates were unsuccessful. Besides the method used to make the normal alkyl sulfonates, the addition reaction of isobutylene with a sulfonic acid was tried, but the *t*-butyl esters could not be isolated. *t*-Butyl alcohol was produced when water was present, while dimers and trimers of isobutylene were obtained under anhydrous conditions.

Experimental

n-Alkyl Benzenesulfonates.—The sulfonates listed in Table I were prepared from benzenesulfonyl chloride, pyridine and the appropriate alcohol according to the procedure of Sekera and Marvel.[3] The pyridinium salts, listed

TABLE I

n-ALKYL BENZENESULFONATES, $C_6H_5SO_3$-R

R	B.p. °C.	Mm.	Yield, %	$n^{25}D$	d^{25}_4	S analyses, % Calcd.	Found
C_4H_9	147–149	4	65	1.4997	1.148	14.97	15.15
C_5H_{11}	136–138	1	75	1.4969	1.119	14.04	13.96
C_6H_{13}	135–136	0.5	58	1.4952	1.099	13.23	13.36
	M.p.						
$C_{14}H_{29}$	25–25.5		63			9.04	8.82
$C_{16}H_{33}$	35–36		79			8.38	8.45
$C_{18}H_{37}$	45–46		85			7.81	7.80

(1) Based on a paper presented, March 26, 1952, at the 121st Meeting of the American Chemical Society, Buffalo, N. Y.

(2) The author wishes to acknowledge the assistance of John Palkiewicz and Carl Miskowicz of King's College; of Jane Furikawa, Mary Wassel and Joan Boersig of Marian College; of Maragret Jevnik of Caldwell College; and of Paul Mosso and Arthur Marcozzi of St. Vincent College.

(3) V. C. Sekera and C. S. Marvel, THIS JOURNAL, **55**, 346 (1933).

in Table II, were synthesized by heating the sulfonates with dry pyridine at 130–140°.[3]

TABLE II

N-*n*-ALKYLPYRIDINIUM BENZENESULFONATES, $C_5H_5NRC_6H_5SO_3$

R	M.p., °C.	Yield, %	Sulfur, % Calcd.	Sulfur, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Butyl	86–87	42	10.9	10.7	..	..
Amyl	95–96	50	10.43	10.30	..	..
Hexyl	105–106	50	9.97	9.98	..	..
Tetradecyl	117–118	90	7.39	7.12	3.21	3.15
Hexadecyl	118–118.5	88	6.94	6.88	3.03	2.96
Octadecyl	120.5–121.5	80	6.55	6.58	2.86	2.87
Butyl[a]	63–64	70	10.43	10.59	4.56	4.53
Butyl[b]	81–82	35	10.43	10.77	4.56	4.42

[a] γ-Picolinium benzenesulfonate. [b] α-Picolinium benzenesulfonate.

Reaction of Isobutylene and *p*-Toluenesulfonic Acid.—Twenty grams of *p*-toluenesulfonic acid monohydrate (Eastman Kodak Co. Reagent Grade) dissolved in 9 g. of water was placed in the pressure bottle of a Parr low pressure gas apparatus, and isobutylene was passed in at room temperature at 19–28 lb. gage pressure with continuous agitation. The reaction mixture was made strongly basic with potassium hydroxide and extracted with ether. The ether extract was dried over anhydrous potassium carbonate and distilled through a 10 in. helix packed partial take-off column. Sixteen and one-half grams of *t*-butyl alcohol was obtained; b.p. 78–81°, $n^{25}D$ 1.3870. There was no sulfur present in the ether extract.

Reaction of Isobutylene with Benzenesulfonic Acid.—Fifteen grams of reagent grade benzenesulfonic acid was dehydrated by heating at 135° for five hours and was then distilled at 147–149° at 2 mm. The acid was dissolved in 20 ml. of dry dioxane, placed in a Parr pressure bottle and exposed with shaking to C.P. isobutylene at 10–20 lb. gage pressure for 13 hours at room temperature. Two layers formed, a lower water-soluble layer and an insoluble layer. The upper layer was separated, washed with water and saturated potassium carbonate solution, dried over calcium sulfate and distilled through a two-foot helix-packed partial take-off column. Two principal fractions were obtained boiling at 99.5–100.2° (16 g.), and 175.3–175.6° (31 g.) at 725 mm. The first fraction was diisobutylene, and the second triisobutylene.[4] The first fraction had a molecular weight of 116 (cryoscopic method in benzene); calcd. for C_8H_{12}, mol. wt., 112.

Acknowledgment.—We wish to thank the Research Corporation for a Frederick Gardner Cottrell grant-in-aid in support of this work.

(4) C. O. Tongberg, J. D. Pickens, M. R. Fenske and F. C. Whitmore, THIS JOURNAL, **54**, 3706 (1932); F. C. Whitmore, *et al.*, *ibid.*, **63**, 2035 (1941).

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The Conversion of α-Diazo-*o*-methoxyacetophenone to Coumaranone

BY AJAY KUMAR BOSE AND PETER YATES

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Marshall, Kuck and Elderfield[1] have reported that coumaranone is formed when α-diazo-*o*-methoxyacetophenone is treated with cold acetic acid. In connection with a general study of the reactions of diazoketones we have investigated further the details of this interesting ring closure and have found that the reaction proceeds in the presence of a catalytic amount of hydrochloric acid. It seems hardly likely that α-chloro-*o*-methoxyacetophenone is an intermediate in the reaction under these conditions in view of the stability of α-chloro-*o*-methoxyacetophenone in acetic acid.[2]

α-Diazo-*o*-methoxyacetophenone was prepared by the slow addition of a cold ethereal solution of *o*-methoxybenzoyl chloride to a large excess (about 4 molar equivalents) of ethereal diazomethane, thus minimizing the formation of any chloroketone.[3] A measured volume of standard hydrochloric acid was added to an aqueous suspension of the diazoketone and the nitrogen evolved was measured.

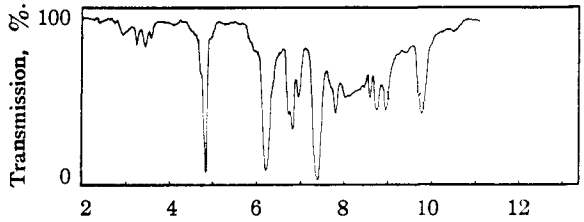

Fig. 1.—Infrared spectrum of α-diazo-*o*-methoxyacetophenone in chloroform solution.

The addition of only 0.05 molar equivalent of acid led to the evolution of one molar equivalent of nitrogen and to the separation of crystalline coumaranone, which was obtained by filtration in 86.5% yield. The identity of the coumaranone was established by a mixed melting point and comparison of the infrared spectrum[4] (Fig. 2) with that of an authentic sample prepared by the action of sodium acetate on α-chloro-*o*-hydroxyacetophenone.[5]

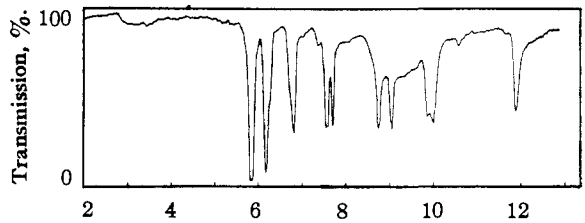

Fig. 2.—Infrared spectrum of coumaranone in chloroform solution

In view of the fact that only a fraction of an equivalent of acid is required to liberate one molar equivalent of nitrogen, a reaction scheme compatible with the catalytic nature of the acid is formulated as

(1) E. R. Marshall, J. A. Kuck and R. C. Elderfield, *J. Org. Chem.*, **7**, 444 (1942).

(2) K. v. Auwers, *Ber.*, **59**, 2899 (1926).

(3) The absence of appreciable amounts of chloroketone is demonstrated by the weakness of the 5.95μ band in the infrared spectrum (Fig. 1): the band at 4.83μ and the displacement of the carbonyl band to *ca.* 6.2μ are characteristic of aliphatic diazoketones (P. Yates, to be published).

(4) It is interesting to note that the spectrum of coumaranone exhibits two peaks of equal intensity in the carbonyl region.

(5) We are grateful to Mr. Edward Trachtenberg for making available to us a sample of coumaranone prepared by this method and its infrared spectrum.