

in Table II, were synthesized by heating the sulfonates with dry pyridine at 130–140°.<sup>3</sup>

TABLE II

N-*n*-ALKYLPYRIDINIUM BENZENESULFONATES, C<sub>6</sub>H<sub>5</sub>NRC<sub>4</sub>H<sub>5</sub>-SO<sub>3</sub>

R	M.p., °C.	Yield, %	Sulfur, %		Nitrogen, %	
			Calcd.	Found	Calcd.	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 <sup>a</sup>	63–64	70	10.43	10.59	4.56	4.53
Butyl <sup>b</sup>	81–82	35	10.43	10.77	4.56	4.42

<sup>a</sup>  $\gamma$ -Picolinium benzenesulfonate. <sup>b</sup>  $\alpha$ -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°,  $n_D^{20}$  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.<sup>4</sup> The first fraction had a molecular weight of 116 (cryoscopic method in benzene); calcd. for C<sub>8</sub>H<sub>12</sub>, 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 $\alpha$ -Diazo-*o*-methoxyacetophenone to Coumaranone

BY AJAY KUMAR BOSE AND PETER YATES

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Marshall, Kuck and Elderfield<sup>1</sup> have reported that coumaranone is formed when  $\alpha$ -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

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

and have found that the reaction proceeds in the presence of a catalytic amount of hydrochloric acid. It seems hardly likely that  $\alpha$ -chloro-*o*-methoxyacetophenone is an intermediate in the reaction under these conditions in view of the stability of  $\alpha$ -chloro-*o*-methoxyacetophenone in acetic acid.<sup>2</sup>

$\alpha$ -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.<sup>3</sup> A measured volume of standard hydrochloric acid was added to an aqueous suspension of the diazoketone and the nitrogen evolved was measured.

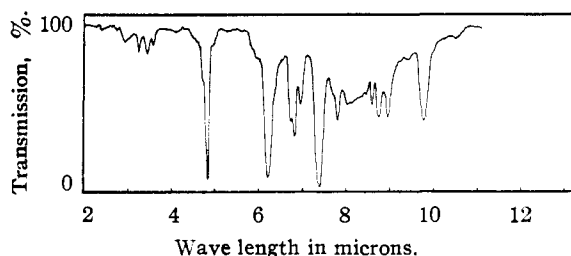


Fig. 1.—Infrared spectrum of  $\alpha$ -diazo-*o*-methoxyacetophenone in chloroform solution.

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<sup>4</sup> (Fig. 2) with that of an authentic sample prepared by the action of sodium acetate on  $\alpha$ -chloro-*o*-hydroxyacetophenone.<sup>5</sup>

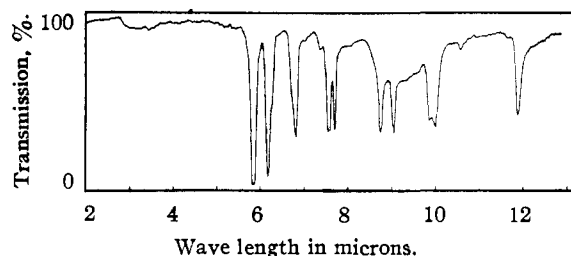


Fig. 2.—Infrared spectrum of coumaranone in chloroform solution

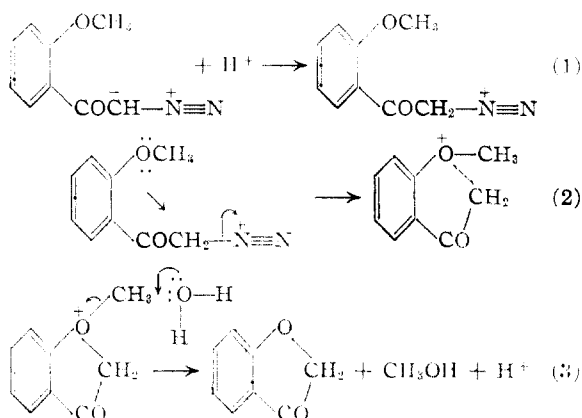
In view of the fact that only a fraction of an equivalent of acid is required to liberate one molar equivalent of nitrogen, a reaction scheme compatible with the catalytic nature of the acid is formulated as

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

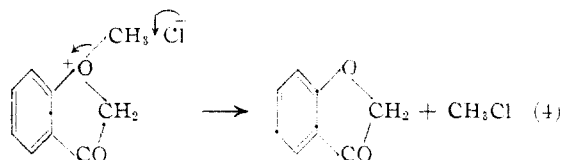
(3) The absence of appreciable amounts of chloroketone is demonstrated by the weakness of the 5.95 $\mu$  band in the infrared spectrum (Fig. 1): the band at 4.83 $\mu$  and the displacement of the carbonyl band to ca. 6.2 $\mu$  are characteristic of aliphatic diazoketones (P. Yates, to be published).

(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.



In reaction (2) the nucleophilic methine carbon of the diazoketone is attacked by a proton to give an aliphatic diazonium ion<sup>6</sup> which then loses nitrogen by a displacement reaction on carbon involving an unshared electron pair on oxygen (equation (2)).<sup>7</sup> The oxonium ion thus formed is then attacked by the solvent water to give coumaranone and methanol and at the same time the proton is regenerated. Reactions (2) and (3) might well be concerted. Although this scheme conforms with the catalytic nature of the action of the hydrochloric acid, the acid will be partially consumed by an alternative final step—the attack of a chloride ion on the oxonium intermediate



However, this will only occur as a side reaction since the presence of water in large excess ensures much more frequent attack by solvent than by chloride ion.

It is of interest in connection with the present work to consider a recent report by Seth and Deshpande<sup>8</sup> that  $\alpha$ -diazo-*o*-methoxyacetophenone decomposes spontaneously with the evolution of nitrogen to give a crystalline solid, m.p. 104°. This substance was assigned the molecular formula C<sub>9</sub>H<sub>8</sub>O<sub>2</sub> and two derivatives were described but no structure assignment was made. The properties of this product (Table I) and its source suggested to us that it might be coumaranone. Our sample of  $\alpha$ -diazo-*o*-methoxyacetophenone, however, gave no visible evidence of decomposition on standing at 25–28° for six days; furthermore, the intensity and position of bands in the infrared spectrum of the diazoketone before and after storage were identical in every respect, confirming that pure  $\alpha$ -diazo-*o*-methoxyacetophenone does not decompose spontaneously.<sup>9</sup>

(6) Cf. J. F. Lane and R. L. Feller, *THIS JOURNAL*, **73**, 4230 (1951).

(7) The geometry of the system favors this reaction rather than direct attack on the diazonium ion by the solvent, as in the case of simple diazoketones (cf. ref. 6).

(8) U. S. Seth and S. S. Deshpande, *J. Ind. Chem. Soc.*, **27**, 429 (1950).

(9) It is noteworthy that neither Marshall, Kuck and Elderfield<sup>1</sup> nor P. Pfeiffer and E. Enders, *Ber.*, **84**, 247 (1951), report any spontaneous decomposition of their samples of this diazoketone.

TABLE I

Seth and Deshpande's product		Coumaranone
Melting point, °C.	104	101–102°
Analysis:	C <sub>9</sub> H <sub>8</sub> O <sub>2</sub> requires:	C <sub>9</sub> H <sub>8</sub> O <sub>2</sub> requires:
Found:	C, 72.5; H, 4.7	C, 71.6; H, 4.5
Molecular weight:	140	134
Semicarbazone:		
Melting point, °C.	220	231°
Analysis:	C <sub>16</sub> H <sub>13</sub> O <sub>2</sub> N <sub>3</sub> requires	C <sub>9</sub> H <sub>8</sub> O <sub>2</sub> N <sub>2</sub> requires
Found:	N, 20.5	N, 22.0
Product with bromine:		
Melting point, °C.	147	142°
Analysis:	C <sub>9</sub> H <sub>8</sub> O <sub>2</sub> Br <sub>2</sub> requires	C <sub>9</sub> H <sub>8</sub> O <sub>2</sub> Br <sub>2</sub> requires
Found:	Br, 53.1	Br, 54.8

<sup>1</sup> D. A. Clibbens and M. Nierenstein, *J. Chem. Soc.*, 1493 (1915). <sup>2</sup> R. Stoerner and F. Bartsch, *Ber.*, **33**, 3178 (1900). <sup>3</sup> K. Fries and W. L. Pfaffendorf, *ibid.*, **45**, 161 (1912).

### Experimental

**$\alpha$ -Diazo-*o*-methoxyacetophenone.**—An ethereal solution of 3 g. of *o*-methoxybenzoyl chloride<sup>10</sup> was added drop by drop with thorough shaking to an ethereal solution of a large excess (about 4 molar equivalents) of diazomethane at 0°. After a brief induction period nitrogen was evolved vigorously. The reaction mixture was allowed to stand overnight at room temperature and was then filtered to remove a small amount of solid that had separated. After removing the excess diazomethane and ether by distillation under reduced pressure at 30–40° a golden yellow oil (3.1 g., quantitative yield) was obtained. A sample on standing at room temperature (25–28°) for six days showed no visible sign of decomposition and its infrared spectrum was found to be identical with that of the freshly prepared material.

**Coumaranone.**—In a flask fitted with a calibrated dropping funnel and connected to a gas buret were placed 1 g. of  $\alpha$ -diazo-*o*-methoxyacetophenone and 5 ml. of distilled water. To this was added by means of the dropping funnel, 0.1 ml. of 1.13 *N* hydrochloric acid during vigorous stirring with a magnetic stirrer; a steady evolution of gas was observed. A second 0.1 ml. of acid was added after 1 hour, when the gas evolution had slackened. The reaction was complete in three hours with the evolution of one molar equivalent of nitrogen. Further addition of acid was without effect. The crystalline solid that had separated was collected by filtration and dried. A light yellow solid (0.65 g., 86.5%), m.p. 95–97°, was thus obtained. Purification by sublimation at 1 mm. gave an almost colorless crystalline powder of m.p. 100–101.5°, undepressed on admixture with an authentic sample of coumaranone.

(10) J. T. Marsh and H. Stephen, *J. Chem. Soc.*, 1635 (1925).

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## The High Field Conductance of Copper Sulfate Relative to Potassium Chloride at 25°<sup>1</sup>

BY DANIEL BERG AND ANDREW PATTERSON, JR.

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The high field conductance of magnesium sulfate has been determined by Bailey and Patterson.<sup>2</sup> It was found that the high field conductance was insensitive to change of temperature over the range 5–55° when plotted as the fractional high field conductance quotient,  $\Delta\lambda/\lambda_0(\%)$ , although the actual conductance varied markedly with temperature. It was also found that the experimental results were decidedly larger than the values pre-

(1) Contribution No. 1100 from the Department of Chemistry, Yale University.

(2) F. E. Bailey and A. Patterson, *THIS JOURNAL*, **74**, 4426 (1952).