Anal. Calcd. for $C_{10}H_{11}Br$: Br, 37.8. Found: Br, 31.1.

A second treatment with base reduced the bromine content to 27.4%. One more step did not change this.

The removal of more than the one atom of bromine in the first step, as indicated by the analysis, might arise from the mixture of products starting with the presence of some 2-phenyl-1-butene along with 2-phenyl-2-butene in the original olefin[3] which in turn would lead to mixtures of dibromides and monobromides in which the ease of hydrogen bromide removal would vary with structure.

When the monobromide of 31.1% bromine content was treated with molten potassium hydroxide under the conditions used for the preparation of phenylacetylene from β-bromostyrene,[7] the product failed to give the expected adduct with maleic anhydride. With excess sodium amide in liquid ammonia or ether solution for reaction times as long as 6.5 hours the removal of bromine from the monobromide was incomplete. The greatest dehydrobromination obtained in several experiments was about 20% of the calculated. The product contained no phenylbutadiene according to a reaction with maleic anhydride.

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(7) J. C. Hessler, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 438.

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RECEIVED NOVEMBER 12, 1951

Addition of Hydrogen Chloride to 1-Phenyl-2-methyl-1-propene

BY ROSS H. HALL, R. G. PYKE AND GEORGE F WRIGHT

It is well-known that the addition of hydrogen chloride to styrene forms exclusively 1-phenyl-1-chloroethane. In the same manner 1-phenylpropene-1 is converted to 1-phenyl-1-chloropropane[1] in high purity. Since the homologous 1-phenyl-2-methyl-1-propene had not been examined in this manner we treated it with hydrogen chloride and were able to isolate only one product, 1-phenyl-2-methyl-2-chloropropane. The mode of addition is thus opposite to those characteristic of the lower homologs and is similar to the hydrohalogenation of 2-methyl-2-butene. No presently-known theory of bond polarization or polarizability seems adequate to explain these several modes of orientation, especially since mixtures of structural isomers have not been observed during addition to the phenylalkenes.

The characterization of 2-methyl-1-phenyl-2-chloropropane was accomplished in two ways. Firstly, it was hydrolyzed to 2-methyl-1-phenylpropanol-2 which was identified as its phenylurethane by comparison with an authentic sample. Secondly, the halide was converted to its Grignard reagent which, upon treatment with phenylisocyanate, was converted to the known anilide of 2,2-dimethyl-3-phenylpropanoic acid.[2]

Experimental[3]

2-Methyl-1-phenyl-2-chloropropane.—Ten grams (0.076 mole) of freshly-distilled 2-methyl-1-phenyl-1-propene (prepared by dehydration of 2-methyl-1-phenylpropanol-2,[4] n^{20}_D 1.5376, d^{20}_4 0.903, washed with dilute ferrous sulfate) was cooled in an ice-water-bath while dry hydrogen chloride was bubbled through it slowly during six hours. Water and ether were then added. The non-aqueous layer was washed with dilute aqueous sodium carbonate, then dried and distilled, yielding 12.0 g. (94%), b.p. 95–97° (10 mm.), n^{20}_D 1.5155.

2-Methyl-1-phenylpropanol-2.—A mixture of 5.0 g. (0.029 mole) of the halide just described with 16 g. (0.137 mole) of potassium carbonate in 100 ml. of water was stirred on the steam-bath for 11 hours. The cooled mixture was twice extracted with ether. This etherous solution was dried with magnesium sulfate and distilled, yield 3.5 g. (78%), b.p. 97–102° (10 mm.), n^{20}_D 1.5170. A 0.6-g. portion (0.004 mole) was treated with 0.35 ml. (0.003 mole) of phenyl isocyanate and 0.2 ml. of dry pyridine. This mixture yielded 0.5 g. (64%) of the phenylurethan melting at 86–88°, and contaminated with carbanilide. Six crystallizations from 95% ethanol (1 ml. per g.) raised this melting point to 93.0–93.7°. A mixed melting point with an authentic sample prepared from dimethylbenzylcarbinol (Eastman Kodak Co.) was not lowered.

Anal. Calcd. for $C_{17}H_{19}NO_2$: C, 75.8; H, 7.12; N, 5.20. Found: C, 75.6; H, 7.23; N, 5.28.

2,2-Dimethyl-3-phenylpropanoyl Anilide.—The preparation was identical with that reported by Whitmore.[2] The product melted at 106.5–107.5° whereas Whitmore reported 107–108°.

Anal. Calcd. for $C_{17}H_{19}ON$: C, 80.6; H, 7.55. Found: C, 79.8; H, 7.45.

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RECEIVED OCTOBER 8, 1951

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(1) A. A. Shamshurin, *Trudy Uzbekskogo Gosudarst Univ. Sbornik Rabot Khim,* **15**, 75 (1939); *C. A.*, **35**, 3984 (1941).

(2) F. C. Whitmore, *et al.*, THIS JOURNAL, **65**, 1469 (1943).

(3) All melting points have been corrected against reliable standards.

(4) M. Tiffeneau and A. Orekoff, *Bull. soc. chim.*, **29**, 816 (1921).

Absence of Exchange of Sulfur between Sulfide and Thiocyanate Ions in Aqueous Solution

BY G. B. HEISIG AND R. HOLT

We have found that little or no exchange of sulfur occurs between 0.1 *M* sulfide and 0.1 *M* thiocyanate ions in slightly alkaline aqueous solutions after 23 hours at 25 or 50° or in 47 hours at 100°.

The experiments were made by using S^{35} as a tracer. In some runs $S^{*=}$ prepared by bubbling H_2S^* into the calculated volume of sodium hydroxide was used, while in others S^*CN^- from KSCN[1] contained the tracer. The KCNS was prepared by digesting a mixture of K_2S^*, KCN and S. The H_2S^* was obtained from BaS^* prepared by reducing $BaSO_4$ with carbon.[2] The S* was obtained from the A.E.C. as the $S^{*=}$ but was actually present as $S^*O_4^=$.

The reaction mixtures were heated for the desired time in glass-stoppered bottles or sealed tubes from which the air had been displaced by nitrogen. Following the reaction period the $S^=$ ions were removed from the reaction mixtures by treating with freshly precipitated cadmium carbonate. The precipitated cadmium salts were separated from the solution by centrifugation and the sulfide was oxidized to $SO_4^=$ by bromine. The activity of the $BaSO_4$ was determined.[3]

The centrifugate was freed of any traces of $SO_4^=$ by adding more of these ions as a carrier and precipitating with Ba^{++}. The SCN^- were then oxidized with bromine, the $SO_4^=$ precipitated with Ba^{++} and the activity of the precipitate determined.[3]

In two runs made at 100°, one at 50° and four at 25°, the greatest transfer of activity from the active to the inactive form was 5% and this was accounted for by the small amount of thiosulfate ions or possibly the polythionate ions present in the active thiocyanate reagent. The per cent. of exchange at 100° was essentially the same for 23 hours as for 47 hours.

We wish to acknowledge the aid of Dr. Armstrong in determining the activity of the samples.

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RECEIVED MAY 7, 1951

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(1) I. M. Kolthoff and J. J. Lingane, THIS JOURNAL, **57**, 2126 (1935).

(2) A. E. Wells, *J. Ind. Eng. Chem.*, **8**, 770 (1916).

(3) W. D. Armstrong and J. Schubert, *Anal. Chem.*, **20**, 270 (1948).