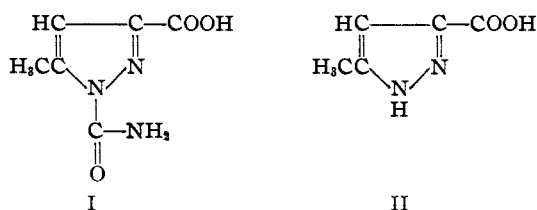


By altering the conditions employed by von Auwers and Cauer, it was found that the expected carbamyl compound could be obtained easily and in large yields. Furthermore, the reason for their failure to obtain the compound became apparent on studying its properties.

This substance was found to hydrolyze readily to 5-methylpyrazole-3-carboxylic acid in water or in water-alcohol solutions on standing for several days at room temperature or on heating for short periods, with or without added acid. The long reaction periods employed by von Auwers and Cauer probably provided for the conversion of the primary product I into II.



The product of hydrolysis of the carbamyl compound was isolated and identified as 5-methylpyrazole-3-carboxylic acid.<sup>3</sup>

### Experimental

**1-Carbamyl-5-methylpyrazole-3-carboxylic Acid.**—To a solution of 1.30 g. of acetopyruvic acid (prepared as previously described<sup>1</sup>) in 10 ml. of water was added 1.11 g. of semicarbazide hydrochloride dissolved in 10 ml. of water. The mixture was stirred and gently warmed. A white voluminous mass of microscopic needles immediately precipitated. The mixture was stirred for two minutes, filtered, washed copiously with cold water and dried over phosphorus pentoxide. The compound was thus obtained pure without recrystallization; yield, 80–85%; m. p. (dec. started at 155°, clear melt at 232–234° (cor.).

*Anal.* Calcd. for C<sub>6</sub>H<sub>7</sub>O<sub>3</sub>N<sub>3</sub>: C, 42.60; H, 4.17; N, 24.85. Found: C, 42.74; H, 4.13; N, 24.67. Amide N: Calcd. 8.28. Found (hydrolysis with H<sub>2</sub>SO<sub>4</sub>, followed by alkaline distillation of ammonia and titration), 8.12.

**Hydrolysis to 5-Methylpyrazole-3-carboxylic Acid.**—A suspension of 1.0 g. of the compound obtained above in 20 ml. of water was brought to the boiling point for one minute (evolution of carbon dioxide was apparent) and cooled. Crystals of 5-methylpyrazole-3-carboxylic acid separated. These were recrystallized from water; m. p. 236–236.5° (cor.); melting point of authentic sample (prepared according to Knorr and MacDonald<sup>3</sup>) 236–237°; a mixed melting point test showed no depression.

*Anal.* Calcd. for C<sub>6</sub>H<sub>6</sub>O<sub>3</sub>N<sub>2</sub>: C, 47.61; H, 4.80. Found: C, 47.42; H, 4.60. There was no detectable amide nitrogen.

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## The Polymerization of Styrene Catalyzed by *p*-Bromobenzenediazonium Hydroxide

BY CHARLES C. PRICE AND DOROTHY ANN DURHAM

The presence of fragments from the catalyst in polystyrene and polymethyl methacrylate prepared in the presence of substituted peroxides<sup>1</sup> has been interpreted as evidence strongly supporting the suggestion that such catalysts first dissociate into free radicals<sup>2</sup> which then initiate the polymerization process.<sup>3</sup>

Since the reaction of alkaline diazotized *p*-bromoaniline with benzene and its derivatives to form *p*-bromobiphenyl and the corresponding derivatives<sup>4</sup> has been ascribed to the decomposition of the diazonium hydroxide to a *p*-bromophenyl free radical,<sup>2</sup> the action of the diazonium hydroxide as a catalyst for the polymerization of styrene has been tested.

*p*-Bromobenzenediazonium hydroxide has indeed been found to catalyze the polymerization of styrene. The directions followed for carrying out the polymerization were those described for the preparation of *p*-bromobiphenyl<sup>4</sup> with the single exception that styrene replaced benzene. Alkali was added slowly to a vigorously-stirred suspension of 30 cc. of styrene in an aqueous solution of 11 g. of diazotized *p*-bromoaniline at 0°. After the addition of alkali was complete, the reaction mixture was allowed to warm up to room temperature. The aqueous layer was decanted and alcohol was added to the viscous organic layer. The polystyrene which precipitated was purified further by several reprecipitations from ether solution by pouring into ice-cold alcohol. The viscosity of a sample of this polymer in tetralin was measured at 20°;  $\eta_{sp.}/C_{gm.} = 1.16$ . Using the revised<sup>5</sup> value for the constant of the Staudinger equation relating this expression to molecular weight, the polymer contained an average of about twenty-two styrene units.

*Anal.* Calcd. for BrC<sub>6</sub>H<sub>4</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>20</sub>C<sub>6</sub>H<sub>4</sub>Br: C, 88.07; H, 7.27; Br, 4.65. Calcd. for BrC<sub>6</sub>H<sub>4</sub>-

(1) Price, Kell and Krebs, *THIS JOURNAL*, **64**, 1103 (1942).

(2) Hey and Waters, *Chem. Rev.*, **21**, 169 (1937).

(3) Norrish and Brookman, *Proc. Roy. Soc. (London)*, **A171**, 147 (1939); Norrish, *Trans. Faraday Soc.*, **35**, 1087 (1939); Kamenskaya and Medvedev, *Acta Physicochem., U. S. S. R.*, **13**, 565 (1940); Price and Kell, *THIS JOURNAL*, **63**, 2798 (1941).

(4) Gomberg and Bachmann, *ibid.*, **46**, 2339 (1924). See also Gilman and Blatt, "Organic Syntheses," Collected Volume I, 2nd Edition, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 113.

(5) Kemp and Peters, Division of Paint, Varnish and Plastics, 103rd meeting of the American Chemical Society, Memphis, Tenn., April, 1942.

$(C_8H_8)_{17}OH$ : C, 87.75; H, 7.31; Br, 4.11.  
Found: C, 87.77; H, 7.24; Br, 4.2.<sup>6</sup>

Since no polystyrene was formed in a parallel experiment in which the diazonium salt was omitted, it appears that the *p*-bromophenyl radicals from the decomposition of *p*-bromobenzene-diazonium hydroxide are capable of initiating the polymerization of styrene and are thereby incorporated in the polymer.

(6) This analysis was carried out by wet oxidation with silver and potassium dichromate in sulfuric acid. The halogen was absorbed in alkaline hydrogen peroxide according to Zacherl and Krainick (*Mikrochemie*, 11, 61 (1932)) but analysis by titration of excess alkali was entirely unsatisfactory, evidently due to volatilization of organic acids. Volhard titration for bromide ion in the alkaline peroxide, however, proved very convenient and accurate.

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### The Composition of Alkylmagnesium Chloride Solutions in Ethyl Ether

BY C. R. NOLLER AND A. J. CASTRO

In previous work on the composition of *n*-butylmagnesium chloride solutions in ethyl ether,<sup>1</sup> it was thought that the values obtained were true equilibrium values expressing the relation between the amounts of *n*-butylmagnesium chloride, di-*n*-butylmagnesium and magnesium chloride as etherates in ether solution. On attempting to repeat, refine and extend this work, we have found that other factors seem to be involved. For example, in the original experiments it appeared that equilibrium was reached after fifty to one hundred and fifty hours. In the new series of experiments, at least in the higher concentrations, much less magnesium chloride had precipitated after seventy days than had been precipitated after 150 hours in the first series and did not reach the latter value until after 300 days. The only difference in procedure of which we are aware is that in the second series the solutions were kept in sealed glass tubes whereas in the first series the tubes were closed by stopcocks. It is possible, too, that in the second series somewhat more care may have been given to avoiding contact with air.

That exposure to air may be the cause of the discrepancy was indicated by a third series in which extreme care was taken to avoid contact with air by preparing the reagent and carrying out all transfers in an atmosphere of purified nitrogen. After 160 days practically no magnesium chloride had precipitated. In fact the chloride concentra-

tion of the solution was still greater than the alkylmagnesium concentration, a condition which had never been observed previously even in freshly prepared solutions of Grignard reagent. If no magnesium chloride precipitates, one should, of course, have an excess of chloride over alkylmagnesium because of side reactions which do not result in the formation of Grignard reagent. Similar but even more marked results were obtained with Grignard solutions from tertiary butyl chloride which after 150 days contained over 2.5 equivalents of chloride for each two equivalents of alkylmagnesium.

When increasing amounts of oxygen reacted with a 0.5 *N* solution of *n*-butylmagnesium chloride, the ratio of halogen to basic magnesium in the precipitate was about three to one for one-fourth oxidation, about one to one for the next fourth while complete oxidation caused removal of all of the halogen from the solution and all but a trace of basic magnesium. This indicates that if  $ROMgCl$  is the product of oxidation, it is capable of bringing down with it additional magnesium chloride, presumably by using the unshared electrons of the oxygen atom to form a complex with magnesium chloride much in the same way as dioxane forms an insoluble complex or as ether forms a soluble complex. If this is the case one might expect the precipitate to have ultimately the composition  $ROMgCl \cdot 2MgCl_2$  in which the ratio of chloride to basic magnesium would be 5:1. To explain the behavior of the Grignard solutions on standing one might assume that, in the absence of oxygen, magnesium chloride is soluble in the Grignard solution either because the reagent is entirely in the form  $RMgCl$  or because the Grignard solution is a much better solvent for magnesium chloride than pure ether.<sup>2</sup> If oxygen is present,  $ROMgX$ , which itself is relatively insoluble, would be precipitated fairly rapidly, carrying down some magnesium chloride with it. This precipitate would then slowly go over to the still less soluble  $ROMgCl \cdot 2MgCl_2$ , causing slow precipitation of more magnesium chloride.

This picture, however, is incomplete because in the case of Grignard solutions from benzyl chloride, magnesium chloride precipitates fairly rapidly in spite of all precautions we have taken

(2) At present the latter seems to be the better explanation since we have obtained Grignard solutions from tertiary butyl chloride which contained as much as 0.3 mole of magnesium chloride per 1000 g. of solution above the 1:1 ratio while the solubility of magnesium chloride etherate in pure ether is of the order of 0.001 mole.

(1) Noller and Raney, *THIS JOURNAL*, 62, 1749 (1940).