ing the course of single experiments with the more dilute catalyst solutions.

The three results with heterogeneous systems are probably of little more than qualitative interest. Despite the complexity of the systems, solution of the copolymerization equation yielded reasonable values for r_1 and r_2, which were of the same order of magnitude as those found for other catalysts of the Friedel–Crafts type in homogeneous systems. The temperature (30° for zinc chloride, 0–40° for sulfuric acid) and solvent (ether for boron fluoride and zinc chloride, nitrobenzene for sulfuric acid) do not allow direct comparison with the other experiments.

Theories have been proposed in which the catalyst is intimately associated with all stages of polymerization.[6] It is suggested here that the varying r_1 and r_2 found are characteristic, not of a free carbonium ion, but of such an ion modified by the proximity of the catalyst.

With all the catalysts, 3,4-dichlorostyrene appears to be relatively more reactive than the 2,5-isomer, for which $r_1 = 14.8$, $r_2 = 0.34$.[3]

(6) (a) C. M. Fontana and G. A. Kidder, THIS JOURNAL, **70**, 3745 (1948); (b) F. R. Mayo and C. Walling, *ibid.*, **71**, 3845 (1949).

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Methylation of 5-Phenyltetrazole

BY RONALD A. HENRY

From the reaction of equivalent quantities of methyl iodide and 5-phenyltetrazole in alkaline solution Elpern and Nachod[1] isolated in 56% yield a product which they considered to be 2-methyl-5-phenyltetrazole since its melting point (41.9–46.9°) differed from that of the previously known 1-methyl-5-phenyltetrazole[2] (m.p. 103–104°). Although the melting point range for their product was very broad, they did not report any attempts either to improve its purity, or to detect the 1-methyl isomer which might have been formed simultaneously in the methylation.

A somewhat similar situation exists in some work by Mihina and Herbst,[3] who studied the reaction of potassium 5-phenyltetrazole with *p*-nitrobenzyl bromide and benzyl bromide. Although these latter authors stated that the structures of their products were not unequivocally established, their results seemed to indicate preferential alkylation at the 2-position on the ring.

We have found, however, that the methylation of 5-phenyltetrazole in alkaline solution consistently yields two isomeric compounds which can be separated by careful fractional crystallization. One of these, obtained in about 20% yield, is identical with 1-methyl-5-phenyltetrazole; the other isomer is formed in about 80% yield and, when free of the 1-methyl derivative, melts sharply at 50.5–51°. These results indicate that methylation does occur predominantly, but not exclusively, on the 2-position.

(1) B. Elpern and F. C. Nachod, THIS JOURNAL, **72**, 3379 (1950).

(2) J. von Braun and W. Rndolph, *Ber.*, **74**, 267 (1941); also E. K. Harvill, R. M. Herbst, E. C. Schreiner and C. W. Roberts, *J. Org. Chem.*, **15**, 662 (1950).

(3) J. S. Mihina and R. M. Herbst, *ibid.*, **15**, 1082 (1950).

Experimental[4]

2-Methyl-5-phenyltetrazole and 1-Methyl-5-phenyltetrazole.—A solution of 8.25 g. of methyl iodide (0.058 mole) in 95 ml. of acetone was added to a cold solution of 8.3 g. of 5-phenyltetrazole (0.057 mole) and 4.65 g. of sodium hydroxide (0.116 mole) in 23 ml. of water. The mixture was refluxed for two hours; at the end of one hour an additional 8.25 g. of methyl iodide was added to make up for losses due to evaporation. The solution was cooled, mixed with 100 ml. of benzene, and washed with water until the washings were no longer alkaline. After the benzene layer had been dried over calcium chloride, the solvent was evaporated to yield 9.1 g. (quantitative) of soft, yellow crystalline material; m.p. 41–46°.

The mixture of isomers was dissolved in 75 ml. of diethyl ether and 10 ml. of benzene, filtered, and the filtrate treated with 25 ml. of petroleum ether (Skellysolve B). Overnight cooling at 0° yielded 1.34 g. of colorless needles, m.p. 103–104°. A mixed melting point with an authentic sample of 1-methyl-5-phenyltetrazole[2] was 103–104°. Addition of more petroleum ether to a permanent turbidity and chilling gave 0.45 g. more of this same isomer, m.p. 101–103°. The total yield amounted to 19.7% of theory.

The 2-methyl-5-phenyltetrazole was recovered by evaporating the mother liquors to about 40 ml., decolorizing with Norite A, filtering, and chilling the filtrate. Long, coarse needles and prisms crystallized slowly; the first crop weighed 2.55 g. and melted at 50°. Additional, less pure, material could be obtained by evaporating the filtrate to dryness; the total recovery was about 80% of theory. One recrystallization from Skellysolve B raised the melting point to 50.5–51°.

Anal. Calcd. for $C_8H_8N_4$: C, 59.93; H, 5.04; N, 34.98. Found: C, 60.10; H, 5.13; N, 35.27.

(4) All melting points are corrected.

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Some New Pentavalent Salts of Triarylbismuth Compounds[1]

BY HENRY GILMAN AND HARRY L. YALE[2]

Pentavalent bismuth salts of the general formula $R_3Bi(O_2CR')_2$ have been prepared by two procedures[3]

$$R_3BiCO_3 + 2R'CO_2H \longrightarrow R_3Bi(O_2CR')_2 + CO_2 + H_2O \quad (1)$$

$$R_3BiCl_2 + 2R'CO_2M \longrightarrow R_3Bi(O_2CR')_2 + 2MCl\ (M = Ag \text{ or } Na) \quad (2)$$

The first method was of more general application.

While some of these pentavalent derivatives possessed potential water solubilizing groups, all attempts to prepare appropriate salts resulted in complete dissociation.

These pentavalent compounds crystallized from benzene or acetone with one or two molecules of solvent of crystallization. With some compounds, these transparent crystals, on heating, gave the powdery solvent-free product; with others, more profound decomposition to tarry products occurred.

The new pentavalent derivatives are listed in Table I.

(1) For the preceding paper in the series on organobismuth compounds, see H. Gilman and H. L. Yale, THIS JOURNAL, **72**, 8 (1950).

(2) E. R. Squibb and Sons, New Brunswick, N. J.

(3) Both procedures have been utilized by the earlier workers in the field; see H. Gilman and H. L. Yale, *Chem. Revs.*, **30**, 281 (1942), for a survey of the literature.