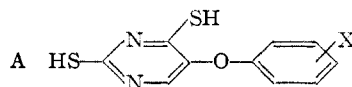
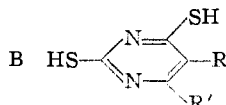


TABLE II  
 2,4-DIMERCAPTOPYRIMIDINES


X	Formula	M.p., <sup>b</sup> °C.	Analyses, %						Solvent
			Calcd.			Found			
			C	H	N	C	H	N	
4-Cl	C <sub>10</sub> H <sub>7</sub> ClN <sub>2</sub> OS <sub>2</sub>	292-294	44.4	2.6	10.4	44.3	2.3	10.6	Pptd. from dil. NaOH with AcOH
2,4-diCl	C <sub>10</sub> H <sub>6</sub> N <sub>2</sub> Cl <sub>2</sub> OS <sub>2</sub>	271-275	39.3	2.0	9.2	39.8	2.4	8.8	EtOH
3-CH <sub>3</sub> ,4-Cl	C <sub>11</sub> H <sub>9</sub> ClN <sub>2</sub> OS <sub>2</sub>	285-287	46.4	3.2	9.8	46.8	3.2	10.3	EtOH
2-Cl,4-C(CH <sub>3</sub> ) <sub>2</sub>	C <sub>14</sub> H <sub>15</sub> ClN <sub>2</sub> OS <sub>2</sub>				8.6			8.2	MeOH



R	R	Formula	M.p.	C	H	N	C	H	N	Solvent
-CH <sub>3</sub> ,C <sub>6</sub> H <sub>4</sub> Cl(4)	H	C <sub>11</sub> H <sub>9</sub> ClN <sub>2</sub> S <sub>2</sub>	255	49.2	3.4	10.4	49.6	3.5	10.8	EtOH
-C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub> (3,4) <sup>a</sup>	H	C <sub>10</sub> H <sub>6</sub> Cl <sub>2</sub> N <sub>2</sub> S <sub>2</sub>	300-303	41.5	2.1	9.7	41.9	2.2	9.7	EtOH
-H	-C <sub>6</sub> H <sub>4</sub> Cl(4)	C <sub>10</sub> H <sub>7</sub> ClN <sub>2</sub> S <sub>2</sub>	277-278			11.0			11.4	EtOH
-CH <sub>3</sub>	-C <sub>6</sub> H <sub>4</sub> Cl(4)	C <sub>11</sub> H <sub>9</sub> ClN <sub>2</sub> S <sub>2</sub>	265-266	49.2	3.4		49.2	3.4		EtOH

<sup>a</sup> Prepared from 5-(3',4'-dichlorophenyl)-2-thiouracil (P. B. Russell and G. H. Hitchings, *THIS JOURNAL*, 73, 3763 (1951). With decomposition.

**2,4-Dimercaptopyrimidines.**—These compounds were prepared by the treatment of the corresponding thiouracil with phosphorus pentasulfide.<sup>4,5</sup>

**6-Chloro-4-hydroxy-2-mercaptoquinazoline.**—6-Chlorobenzoyleneurea<sup>8,9</sup> was converted to the 4-hydroxy-2-mercaptoquinazoline by the method described earlier.<sup>5</sup> The benzoyleneurea on treatment with phosphorus pentasulfide, gave 6-chloro-2,4-dimercaptopyrimidin-5-yl phenyl ether which sublimes at 300-350° (not molten below 350°).

*Anal.* Calcd. for C<sub>8</sub>H<sub>5</sub>ClN<sub>2</sub>S<sub>2</sub>: C, 42.0; H, 2.2. Found: C, 41.8; H, 2.2.

Treatment of this compound with concentrated ammonium hydroxide solution on the steam-bath gave 4-amino-6-chloro-2-mercaptoquinazoline, which crystallizes from water as needles melting at 300-305° (dec.).

*Anal.* Calcd. for C<sub>8</sub>H<sub>6</sub>ClN<sub>3</sub>S: C, 45.4; H, 2.8. Found: C, 45.1; H, 3.0.

On refluxing this compound with 3 *N* hydrochloric acid, 6-chloro-4-hydroxy-2-mercaptoquinazoline was obtained as colorless needles from water, m.p. 353-354° (dec.).

*Anal.* Calcd. for C<sub>8</sub>H<sub>5</sub>ClN<sub>2</sub>OS: C, 45.2; H, 2.4. Found: C, 45.4; H, 2.3.

**Acknowledgment.**—We wish to thank S. W. Blackman and N. Martinez, Jr., for the microanalyses reported here.

(8) R. L. McKee, M. K. McKee and R. W. Bost, *ibid.*, 69, 940 (1947).

(9) F. H. S. Curd, J. K. Landquist and F. L. Rose, *J. Chem. Soc.*, 1759 (1948).

THE WELLCOME RESEARCH LABORATORIES  
TUCKAHOE, NEW YORK RECEIVED APRIL 13, 1951

## Catalyst Specificity in Friedel-Crafts Copolymerization

BY R. E. FLORIN

It has been established recently that copolymerization of two vinyl monomers can proceed by three different mechanisms—free-radical, carbonium-ion and carbanion—which depend upon the catalyst used and lead to products of different composition.<sup>1</sup> The relative rates at which two monomers M<sub>1</sub> and

M<sub>2</sub> enter the polymer are given in all cases by the copolymerization equation

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1] r_1 [M_1] + [M_2]}{[M_2] r_2 [M_2] + [M_1]}$$

where [M<sub>1</sub>] and [M<sub>2</sub>] are concentrations of monomers and r<sub>1</sub> and r<sub>2</sub> are certain ratios of rate constants, but the numerical values of r<sub>1</sub> and r<sub>2</sub> differ sharply for the three mechanisms.

When a given pair of monomers is copolymerized by any free-radical catalyst, *e.g.*, persulfate ion or any organic peroxide, the reactivity parameters r<sub>1</sub> and r<sub>2</sub> are found to be strictly constant for the monomer pair and temperature, regardless of the solvent or specific catalyst employed. It was desired to test whether a similar constancy would hold for all catalysts of the Friedel-Crafts type, which are thought to effect polymerization by a carbonium-ion mechanism. In the present study, mixtures of styrene (M<sub>1</sub>) and 3,4-dichlorostyrene (M<sub>2</sub>) were copolymerized at 0° with the catalysts aluminum chloride, aluminum bromide, stannic chloride, titanium tetrachloride, boron fluoride, zinc chloride (at 30°) and sulfuric acid, and the values of r<sub>1</sub> and r<sub>2</sub> were calculated from analytical data by the method of Mayo and Lewis.<sup>2</sup>

### Experimental

General methods of polymerization, purification and analysis have been reported in an earlier note.<sup>3</sup> In most experiments of the present series, the solvent was carbon tetrachloride. Monomer mixtures, of composition identified by the numerals and described in Table I, were diluted with an equal volume of carbon tetrachloride (unless otherwise specified) and polymerized by adding small portions of catalyst solutions identified by letter symbols and described below. In the more rapid experiments, temperature control was probably not very satisfactory; during the addition of typical portions of aluminum chloride and bromide solutions to styrene, the temperature rose from 0 to 5°. After sufficient reaction, the whole product was diluted, precipitated with methanol, purified by double reprecipita-

(1) For a comprehensive review, see F. R. Mayo and C. Walling, *Chem. Revs.*, 46, 191 (1950).

(2) F. R. Mayo and F. M. Lewis, *THIS JOURNAL*, 66, 1594 (1944).

(3) R. E. Florin, *ibid.*, 71, 1867 (1949).

tion, dried, weighed and analyzed for chlorine. Per cent. conversion and weight per cent. dichlorostyrene in polymer are shown in Table II for the catalyst-monomer combinations indicated.

**Materials.**—Commercial C.P. products were used ordinarily. Aluminum chloride and the boron fluoride ether solution were Eastman Kodak Co. practical grade. Solvents were dried over calcium chloride or magnesium sulfate and redistilled, and monomers were freshly distilled at reduced pressure. 3,4-Dichlorostyrene was prepared by the method of Brooks.<sup>4</sup> The preparation boiled at 86–88° under 5 mm., froze at –27° and had specific gravity  $d_{20}^4$  1.248 and refractive index  $n_D^{20}$  1.5818. Although the properties differ somewhat from those reported by Brooks, the fractions obtained by slow freezing did not differ perceptibly in repeated determinations of freezing-point, nor vary more than  $\pm 0.0007$  in refractive index.

TABLE I  
MONOMER MIXTURES

Mixture number	1	2	3	4	5
Dichlorostyrene, %	30.46	74.85	73.27	29.40	50.65

**Catalyst Solutions:** Cl, Br.—Dilute solutions of aluminum chloride and bromide were prepared by boiling the crushed anhydrous solid with carbon tetrachloride and cooling rapidly.

**Sn, Ti.**—Relatively concentrated solutions, about 5–10% of anhydrous liquid stannic chloride and titanium tetrachloride in carbon tetrachloride, were required. Polymerization was slow, from 15 min. to overnight being required for appreciable conversion.

**B.**—The ether solution of boron fluoride was added to carbon tetrachloride and shaken. The mixture did not become homogeneous and was used as an emulsion.

**Zn.**—No solution was prepared. Anhydrous zinc chloride was fused and allowed to solidify as a thick coat on the wall of the reaction tube. Monomers were added, followed by about 10% by volume of anhydrous ether. Two days at room temperature were required for sufficient polymerization. In a control sample of monomer, ether alone produced little polymer. Precipitation showed only a turbidity estimated at much less than 1% conversion.

**HN.**—Concentrated sulfuric acid was mixed with about twice its volume of nitrobenzene. The clear solution was diluted with about twenty times its volume of nitrobenzene; the resultant emulsion was used as catalyst. In experiments with this catalyst and the following, the monomer diluent was nitrobenzene. Polymerization was violent, and the temperature uncontrollable.

TABLE II  
ANALYTICAL RESULTS OF POLYMERIZATIONS

Identification	Conversion, %	Dichlorostyrene content of polymer, %	
1 Cl	26.5	13.85	14.22
2 Cl	17.7	55.4	
1 B	73.6	20.8	19.9
2 Br	30.4	56.2	59.4
4 Br	14.9	13.46	13.67
5 Br	17.0	29.3	30.5
1 Sn	47.5	7.81	8.04
3 Sn	15.0	23.2	
5 Sn	16.6	13.59	14.00
1 Ti	59.4	9.64	10.03
3 Ti	48.0	51.0	53.0
1 B	26.3	8.30	8.39
2 B	13.1	39.9	40.6
4 Zn	34.6	10.51	10.53
5 Zn	22.4	20.7	21.5
3 HN	51.7	58.6	59.8
4 HN	20.5	13.85	
5 HN	37.8	26.4	27.7
4 CIN	48.5	11.78	12.26
5 CIN	33.6	20.8	

(4) Brooks, THIS JOURNAL, 66, 1295 (1944).

**CIN.**—Crushed anhydrous aluminum chloride, 0.05 g., was warmed with 3 ml. of nitrobenzene and the clear solution cooled.

**Results.**—The values for the reactivity parameters appear in Table III. They were calculated by the method of Mayo and Lewis<sup>2</sup> based on the integrated equation.

TABLE III  
REACTIVITY PARAMETERS FOR COPOLYMERIZATION

Catalyst	$r_1$	$r_2$
	$3.1 \pm 0.1$	$0.48 \pm 0.08$
AlCl <sub>3</sub>	$2.8 \pm .2$	$.45 \pm .10$
AlBr <sub>3</sub>	$6.8 \pm .8$	$.0 \pm .2$
TiCl <sub>4</sub>	$7.2 \pm .5$	$.38 \pm .20$
BF <sub>3</sub> (etherate)	$5.9 \pm .2$	$.27 \pm .07$
ZnCl <sub>2</sub> (solid + ether)	$4.2 \pm .2$	$.10 \pm .05$
H <sub>2</sub> SO <sub>4</sub> (nitrobenzene)	$3.0 \pm .5$	$.20 \pm .15$
AlCl <sub>3</sub> (nitrobenzene)	$3.5 \pm .5$	$.0 \pm .2$

Limits of error were calculated for experiments 1Cl, 1Ti, 2Cl and 3HN only, representing low and high conversion combined with low and high dichlorostyrene content, and were assigned to other experiments from their similarity to these cases. The method was to repeat the calculation, altering low dichlorostyrene contents by 0.2%, high dichlorostyrene contents by 1% and conversions by 2%. Precision is quite poor in experiments having simultaneous high conversion and high dichlorostyrene content, fair or good in all other cases. The errors reported for aluminum bromide, stannic chloride and sulfuric acid also take into account the failure of the three or more lines on the Mayo and Lewis plot to form a perfect intersection; this error was fairly consistent with the assumed analytical error.

The most significant experiments are those with aluminum bromide and with stannic chloride, which yield rather definite values of  $r_1$  and  $r_2$ , widely separated for the two catalysts. The values of  $r_1$  and  $r_2$  obtained with aluminum chloride and titanium tetrachloride are probably fair approximations, assuming that the fundamental equation holds; as they are based upon two mixture-ratios only, they do not in themselves suffice to prove the existence of any unique values of  $r_1$  and  $r_2$ , nor to establish these values very accurately.

When nitrobenzene was substituted for carbon tetrachloride as the solvent, with aluminum chloride as catalyst,  $r_1$  was raised slightly and  $r_2$  lowered considerably. Not much weight can be attached to the result of this single pair of experiments, but it appears that dielectric constant of the medium (39 for nitrobenzene, 2.25 for chloroform) may also influence the reactivity parameters.<sup>5</sup>

In this study it has been assumed that  $r_1$  and  $r_2$  are insensitive to the relatively small changes of dielectric constant incident to the variation of mixture ratios and the progress of polymerization. It has also been assumed that these parameters are insensitive to catalyst concentration, which was only roughly known, and varied by many orders of magnitude, both in the comparison of catalysts and dur-

(5) For the system *p*-chlorostyrene-styrene at 0° catalyzed by stannic chloride, there is no large change in reactivity ratios with change in dielectric constant. Private communication from C. G. Overberger, Polytechnic Institute of Brooklyn.

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 ( $30^\circ$  for zinc chloride,  $0-40^\circ$  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.<sup>6</sup> 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  $r_1 = 14.8$ ,  $r_2 = 0.34$ .<sup>3</sup>

(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).

LINCOLN 8, NEBR.

RECEIVED SEPTEMBER 23, 1950

### 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<sup>1</sup> isolated in 56% yield a product which they considered to be 2-methyl-5-phenyltetrazole since its melting point ( $41.9-46.9^\circ$ ) differed from that of the previously known 1-methyl-5-phenyltetrazole<sup>2</sup> (m.p.  $103-104^\circ$ ). 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,<sup>3</sup> 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  $50.5-51^\circ$ . 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. Rudolph, *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<sup>4</sup>

**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.  $41-46^\circ$ .

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  $0^\circ$  yielded 1.34 g. of colorless needles, m.p.  $103-104^\circ$ . A mixed melting point with an authentic sample of 1-methyl-5-phenyltetrazole<sup>2</sup> was  $103-104^\circ$ . Addition of more petroleum ether to a permanent turbidity and chilling gave 0.45 g. more of this same isomer, m.p.  $101-103^\circ$ . 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  $50^\circ$ . 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  $50.5-51^\circ$ .

*Anal.* Calcd. for  $C_9H_8N_4$ : 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.

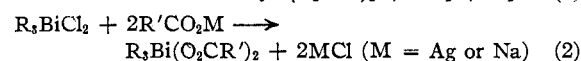
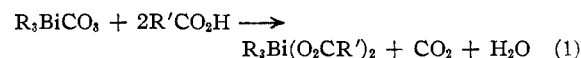
INORGANIC CHEMISTRY BRANCH  
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CHINA LAKE, CALIFORNIA

RECEIVED MARCH 5, 1951

### Some New Pentavalent Salts of Triarylbi-muth Compounds<sup>1</sup>

BY HENRY GILMAN AND HARRY L. YALE<sup>2</sup>

Pentavalent bismuth salts of the general formula  $R_3Bi(O_2CR')_2$  have been prepared by two procedures<sup>3</sup>



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.