[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC COMPANY]

The Preparation of 1,4-Divinyl-2,3,5,6-tetrachlorobenzene and its Copolymerization with Styrene[1]

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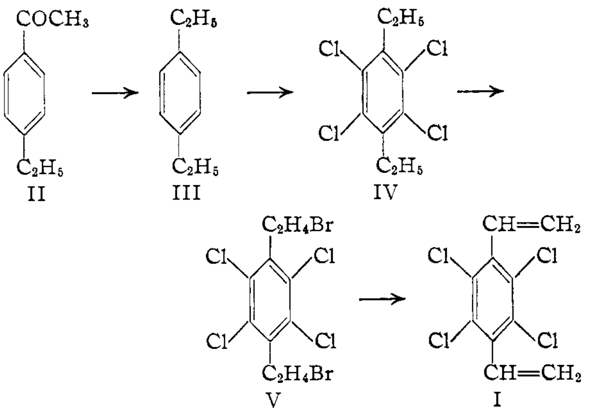
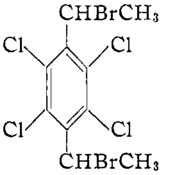
The effectiveness of 1,4-divinylbenzene as a cross-linking agent has been known since the pioneering research of Staudinger and his associates,[2] and it has been clearly demonstrated that the copolymerization of styrene with small percentages of 1,4-divinylbenzene results in a polymer having improved chemical resistance and higher heat distortion temperature, tensile strength, impact strength and hardness. In spite of these obvious advantages, 1,4-divinylbenzene has not found wide application in industry because of its extreme reactivity, which, with styrene, usually causes gelation to set in before an appreciable quantity of the styrene has polymerized. In an effort to obviate this difficulty, we have prepared 1,4-divinyl-2,3,5,6-tetrachlorobenzene, I. It is the purpose of the present paper to describe the reactions involved in the synthesis of I and the copolymerization of I with styrene.

1,4-Divinyl-2,3,5,6-tetrachlorobenzene, I, was prepared by the sequence of reactions shown below. *p*-Ethylacetophenone, II, prepared by the procedure of Mowry, Renoll and Huber,[3] was hydrogenated directly to 1,4-diethylbenzene, III. Chlorination of III gave 1,4-diethyl-2,3,5,6-tetrachlorobenzene, IV, which on bromination in carbon tetrachloride solution gave a dibromide, V. Dehydrobromination of V gave the desired divinyl compound, I.

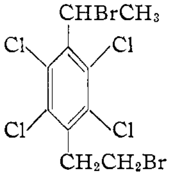


II III IV V I

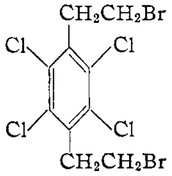
With exception of V all of these products have unequivocal structures. The dibromide, V, could not be crystallized to a constant melting point, but samples melting ten degrees apart analyzed correctly for $C_{10}H_8Cl_4Br_2$. Previous work from this Laboratory on ethylpentachlorobenzene,[4] which brominates cleanly in the α-position, suggests that V is a mixture of the *meso*- and *dl*-forms of VI. However, VII and VIII must be considered possible components of the mixture.[5]



VI



VII



VIII

The structure of V was established by converting it, *via* a diacetate and glycol, to a dicarbonyl compound, IX, $C_{10}H_6O_2Cl_4$, in which both asymmetric centers were destroyed. The over-all yield of IX was 47.6%. If it is assumed that the yields are about the same for each of the three steps, then, more than 75% of the original dibromide can be accounted for.

The dicarbonyl compound, IX, can be shown to be 1,4-diacetyl-2,3,5,6-tetrachlorobenzene and not either the ketoaldehyde or the dialdehyde, which would result from VII or VIII, respectively, by comparing its properties with the properties of the known hindered ketone, pentachloroacetophenone,[6] and pentachlorobenzaldehyde,[7] which is, if anything, more hindered than either of the expected aldehydes.

Pentachlorobenzaldehyde gives carbonyl derivatives and shows typical aldehyde reactivity. Pentachloroacetophenone does not form an oxime, phenylhydrazone or dinitrophenylhydrazone; it does not add methylmagnesium bromide; it does not reduce Tollens reagent or Fehling solution. It reacts with one mole of bromine in acetic acid to give 1-(ω-bromoacetyl)-2,3,4,5,6-pentachlorobenzene, but even with three or more moles of bromine only 1-(ω,ω-dibromoacetyl)-2,3,4,5,6-pentachlorobenzene is formed. Similarly, IX does not form an oxime, phenylhydrazone or dinitrophenylhydrazone and does not reduce Tollens reagent or Fehling solution. Even with excess bromine in acetic acid, 1,4-bis-(ω,ω-dibromoacetyl)-2,3,5,6-tetrachlorobenzene is the only product formed. This makes it highly certain that IX is 1,4-diacetyl-2,3,5,6-tetrachlorobenzene.

In an effort to obtain an authentic sample of dibromide, VI, we attempted to add hydrogen

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[1] This work was carried out under contract no. W36-039-sc-38110 with the Signal Corps of the United States Army.

[2] Staudinger, Heuer and Husemann, *Trans. Faraday Soc.*, **32**, 323 (1936). This paper contains references to Staudinger's earlier work in this field.

[3] Mowry, Renoll and Huber, THIS JOURNAL, **68**, 1105 (1946).

[4] Ross, Markarian and Nazzewski, *ibid.*, **69**, 2468 (1947).

[5] Structures having both bromine atoms on a single ethyl group are eliminated since they would not give I on dehydrobromination.

[6] Ross, THIS JOURNAL, **70**, 4039 (1949).

[7] Lock, *Ber.*, **72B**, 300 (1939).

TABLE I

Run no.	% by Weight			T, °C.	Reaction time, hr.	% Styrene reacted	% polymn.	Av. rate %/hr.	Analyses, %		
	Styrene	I	Bz_2O_2						Chlorine	Carbon	Hydrogen
1	99	0	1	49.2	38		40.9[a]	1.08			
2	98	0	2	49.2	39	62.9	62.9	1.61			
3	99	0	1	100	1.0	76.1	76.1	76.1			
4	98.8	0.2	1	49.2	38		41.1[a]	1.07			
5	97.8	.2	2	49.2	39	63.3					
6	98.6	.4	1	49.2	41	44.9					
7	97.6	.4	2	49.2	39	63.0					
8	98.6	.4	1	100	0.92	71.8					
9	98.2	.8	1	49.2	37		42.5[a]	1.15	0.98 1.14	91.24 91.39	7.75 7.67
10	98	1	1	49.2	36	39.7					
11	97	1	2	49.2	33	50.7					
12	98	1	1	100	0.90	72.4					
13	97	2	1	49.2	30	34.0					
14	96	2	2	49.2	29	44.2	45.7	1.57	1.85 1.69	89.75 89.89	8.09 7.87
15	96	2	2	49.2	12[b]	19.8	20.1	1.67	0.54 0.68	91.08 90.92	8.80 8.64
16	97	2	1	100	0.83	72.6					
17	95	4	1	49.2	16[c]	16.2					
18	94	4	2	49.2	14	21.4	22.2	1.58	1.99 2.12	90.04 89.82	7.72 7.88
19	94	4	2	49.2	6[b]	10.5	10.9	1.82	1.68 1.89	90.00 90.09	7.90 7.79
20	90	8	2	49.2	9[c]	13.1	14.3	1.59	4.67 4.81	88.03 88.07	7.40 7.59
21	90	8	2	49.2	6[b]	10.0	10.8	1.80	4.12 4.00	87.72 87.93	7.70 7.54

[a] % Polymerization determined by isolating and weighing the polymer. [b] Run interrupted before gelation point or appearance of popcorn polymer. [c] Run interrupted at first appearance of popcorn polymer.

bromide to I. Since we had previously found[8] that pentachlorostyrene gives 1-pentachlorophenyl-1-phenylethane in the Friedel–Crafts reaction with benzene, we expected that the ionic addition of hydrogen bromide to I would give VI. However, the product was a single pure compound, analyzing correctly for $C_{10}H_8Cl_4Br_2$ and different from VI. The possibility of addition by a radical mechanism[9] immediately suggested itself, and to investigate this possibility, we chose to study a model compound, pentachlorostyrene.

Pentachlorostyrene reacted readily with hydrogen bromide in benzene solution to give the known 1-pentachlorophenyl-2-bromoethane,[4] X. The same product was obtained when a little benzoyl peroxide was added. All of our efforts to reverse the direction of this addition have been unsuccessful. Even after a benzene solution of pentachlorostyrene was purified by three cycles of evacuating and flushing with nitrogen prior to saturation with hydrogen bromide, the product, after one hundred and fifty hours in the dark, was X. In glacial acetic acid no addition took place, but in anhydrous ether X was again obtained. Pentachlorostyrene failed to react in twenty-four hours with hydrogen bromide in nitrobenzene containing a catalytic quantity of aluminum chloride. The same reaction in carbon disulfide gave X after 150 hours. Finally, we added 5 g. of pentachlorostyrene to 150 cc. of benzene containing 0.2 g. of quinone and flushed for thirty minutes with nitrogen and one hour with hydrogen bromide. The flask was then sealed and stored in the dark for one hundred and fifty hours, at the end of which time the pentachlorostyrene was recovered unchanged. 1,4-Divinyl-2,3,5,6-tetrachlorobenzene, I, was also recovered unchanged after identical treatment.

Thus, even when the radical mechanism is completely inhibited, the ionic mechanism does not occur to any detectable extent. It is not, at this time, possible to offer an explanation which encompasses both the facile radical addition of hydrogen bromide to these compounds and the complete failure of the ionic mechanism. It is, however, reasonably certain that the product resulting from the addition of hydrogen bromide to I has structure VIII.

To show the utility of 1,4-divinyl-2,3,5,6-tetrachlorobenzene we have determined the extent of conversion at gelation at 49.2 and 100° with one and two weight per cent. benzoyl peroxide for styrene containing 0.2–8% I. The results of representative runs are summarized in Table I. The values given are for the gelation point unless otherwise noted. With pure styrene, the per cent. styrene reacted is equivalent to the per cent. polymerization at any given time, but in runs with I, the per cent. polymerization is greater than the per cent. styrene reacted by the amount of I which enters the copolymer. The average rate is an estimate obtained from the values of per cent. polymerization and reaction time.

Figures 1 and 2 show plots of flow time *versus* reaction time for runs at 49.2° with 1 and 2% benzoyl peroxide. It is to be noted that, whereas

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(8) Ross, Markarian and Nazzewski, THIS JOURNAL, 71, 396 (1949).

(9) Kharasch and co-workers, *ibid.*, 55, 2468, 2521, 2531 (1933).

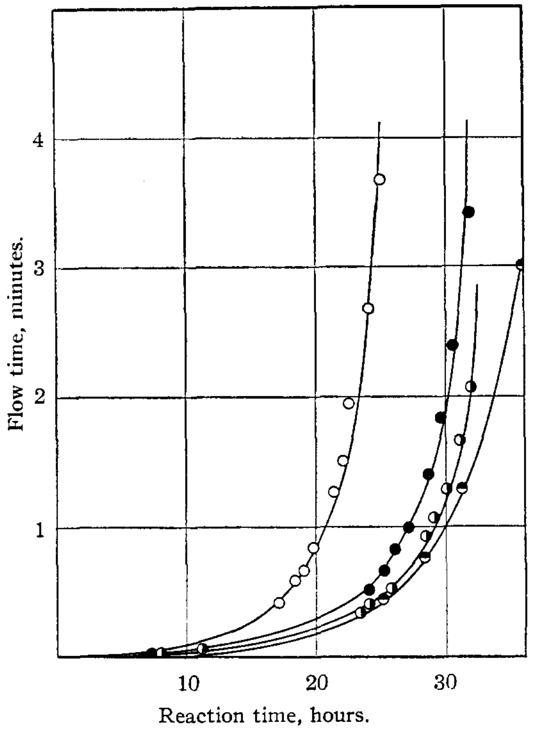

Fig. 1.—Flow time *vs.* reaction time at 49.2°, 1% benzoyl peroxide: ○, 2% I; ●, 1% I; ◑, 0.8% I; ⊖, 0% I.

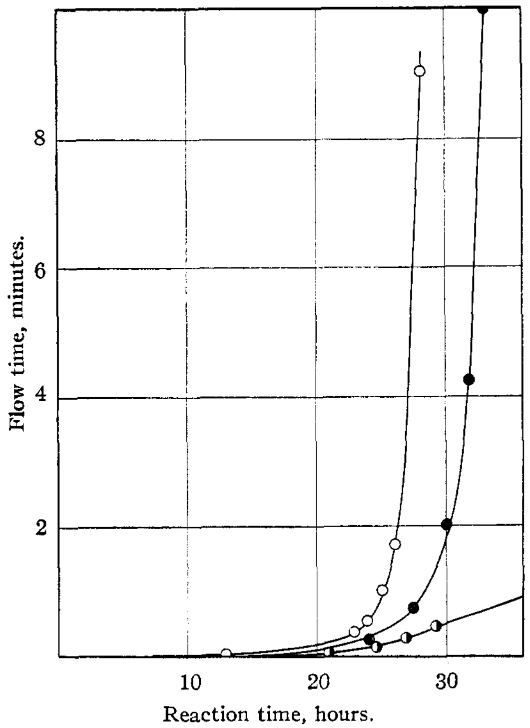

Fig. 2.—Flow time *vs.* reaction time at 49.2°, 2% benzoyl peroxide: ○, 2% I; ●, 1% I; ◑, 0% I.

runs with the cross-linking agent, I, approach a line perpendicular to the abscissa as a limit, runs with pure styrene, in which no gelation takes place, do not. Thus, with I present, the viscosity increases more rapidly with conversion than in the case where the cross-linking agent is absent.[10]

For a given copolymerization system, capable of giving a cross-linked product, the extent of conversion prior to gelation is largely inherent in the monomer reactivity ratios. The problem has been thoroughly discussed by Cohen, *et al.*[11] Modifications may be effected by varying the polymerization conditions[11a] or by using regulators.[11b] The limits of the first approach are determined by the monomer reactivity ratios. The second approach introduces materials which deteriorate the electric properties of the resulting polymer.

For electrical applications, the problem resolves itself into one of finding a cross-linking agent having appropriate reactivity. 1,4-Divinyl-2,3,5,6-tetrachlorobenzene is, as we shall see, such a material. In its copolymerization with styrene the following propagation reactions are involved

$$\mathrm{S\cdot} + \mathrm{S} \xrightarrow{k_{11}} \mathrm{S\cdot}$$
$$\mathrm{S\cdot} + \mathrm{D} \xrightarrow{k_{12}} \mathrm{D\cdot}$$
$$\mathrm{D\cdot} + \mathrm{D} \xrightarrow{k_{22}} \mathrm{D\cdot}$$
$$\mathrm{D\cdot} + \mathrm{S} \xrightarrow{k_{21}} \mathrm{S\cdot}$$

where S· and S are styrene radical and monomer, respectively, and D· and D are radical and monomer of I. The monomer reactivity ratios are $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$. To obtain extensive conversion prior to gelation r_1 must be relatively large and r_2 relatively small. Our choice of I was based on copolymerization studies with styrene–pentachlorostyrene carried out by Alfrey and Ebelke.[12] For these two monomers at 70° r_1 was found to be 1.33 and r_2, 0.10. It seemed reasonable to us that r_1 and r_2 for styrene–I would have the same order of magnitude. It is not possible to determine r_2 for this latter system, because the polymer, obtained when the mole fraction of I is high, is too insoluble, but, using the method of Alfrey and co-workers,[13] we have calculated r_1 at 49.2° from the data of runs 19 and 21 in Table I. Taking the initial mole fraction of I as twice its actual mole fraction because of its bifunctionality, we obtained a value of 2.62 for r_1 at 49.2°. This is almost twice the value obtained by Alfrey for styrene–pentachloro-

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[10] Polymers, obtained by polymerizing styrene alone and styrene with 0.4% I at 100° and interrupting the reaction at approximately 75% polymerization, were dissolved in toluene (0.29 g./100 cc.) for viscosity measurements. The values of N_{sp}/C obtained were 0.30 for the pure polystyrene and 0.47 for the copolymer.

[11] (a) Cohen, Ostberg, Sparrow and Blout, *J. Polymer Sci.*, **3**, 264 (1948); (b) Cohen and Sparrow, *ibid.*, **3**, 693 (1948).

[12] Alfrey and Ebelke, THIS JOURNAL, **71**, 3235 (1949).

[13] Alfrey, Goldberg and Hohenstein, *ibid.*, **68**, 2464 (1946); Alfrey, *Transactions of the N. Y. Academy of Sciences*, **10**, 298 (1948).

styrene, but it is clearly of the correct order of magnitude for our purpose.[14]

The effectiveness of I in increasing the per cent. conversion at the gelation point is apparent from Table I. With higher percentages of I there is a tendency to form popcorn polymers. An increase either in temperature or catalyst concentration results in a higher rate of initiation and higher conversions at the gelation point, probably because of shorter chain lengths. The use of 0.4–2% I and 1% catalyst at 100° represents a practical set of polymerization conditions, since the average rate of polymerization is greater than 72%/hour, the per cent. conversion at the gelation point is higher than 70%, and the resulting polymers have adequate molecular weights.[10]

Experimental[15]

1,4-Diethylbenzene, III.—*p*-Ethylacetophenone (1297 g., 8.75 moles), distilled from Raney nickel, was hydrogenated over copper chromite catalyst (66 g.) at 200° and an initial pressure of 1100 lb./sq. in. The initial uptake was rapid, but after the bomb had been refilled with hydrogen for the second time, the uptake became slow. The reaction was interrupted, and the crude hydrogenation product was worked up in the usual manner and separated by distillation into a 1,4-diethylbenzene fraction and a methyl *p*-ethylphenylcarbinol fraction. The carbinol fraction was resubjected to hydrogenation as above. This process was repeated once again to give, finally, 900 g. of crude 1,4-diethylbenzene. The crude hydrocarbon was treated overnight with sodium at room temperature and finally distilled from sodium at atmospheric pressure; yield 857 g. (73%); b. p. 178–180°.

1,4-Diethyl-2,3,5,6-tetrachlorobenzene, IV.—1,4-Diethylbenzene (857 g., 6.4 moles) was chlorinated in the presence of iron powder (6.4 g.) to a gain in weight of 880 g. The crude product was dissolved in benzene and washed with water, dilute hydrochloric acid, water again and, finally, dilute sodium hydroxide. The benzene was dried and removed, and the crude product distilled at 0.3 mm. yielding 1365 g. of b. p. 108–110°. Crystallization from methanol gave 870 g. (50%) of m. p. 71–72°. *Anal.* Calcd. for $C_{10}H_{10}Cl_4$: C, 44.16; H, 3.71. Found: C, 43.72, 43.89; H, 3.59, 3.75.

1,4-Bis-(α-bromoethyl)-2,3,5,6-tetrachlorobenzene VI.—Bromine (998 g., 6.24 moles) was added slowly to 1,4-diethyl-2,3,5,6-tetrachlorobenzene (850 g., 3.12 moles) in carbon tetrachloride (4 liters). The solution was illuminated and maintained at the boiling point by a projection bulb inserted directly into the solution. Removal of the solvent gave 1340 g. (100%) of the dibromide of m. p. 100–114°. The dibromide could not be crystallized to a constant melting point. A sample had m. p. 133–135° after six crystallizations from ligroin (b. p. 90–120°) and m. p. 142–143° after eleven crystallizations. *Anal.* Calcd. for $C_{10}H_8Cl_4Br_2$: C, 27.97; H, 1.86. Found for compd. of m. p. 133–135°: C, 27.76, 27.60; H, 1.71, 1.80. Found for compd. of m. p. 142–143°: C, 27.78, 27.95; H, 1.90, 1.74.

1,4-Divinyl-2,3,5,6-tetrachlorobenzene, I.—The above dibromide VI (21.5 g., 0.05 mole) was refluxed two hours with potassium hydroxide (11.2 g., 0.20 mole) in absolute ethanol (150 cc.). The product was precipitated by the addition of water (600 cc.) and crystallized from methanol; yield 7.2 g. (53.6%); m. p. 86–87°. *Anal.* Calcd. for $C_{10}H_6Cl_4$: C, 44.85; H, 2.26. Found: C, 45.06, 45.20; H, 2.47, 2.41. I was also obtained by dehydrobromination of VIII as above and by the vapor phase dehydrobromination of VI over aluminum oxide at 400° in the presence of nitrogen saturated with water vapor at room temperature.

1,4-Diacetyl-2,3,5,6-tetrachlorobenzene, X.—The dibromide VI (30.6 g., 0.071 mole) was refluxed twenty hours with potassium acetate (39.2 g., 0.4 mole) in acetic acid (300 cc.) poured into water and extracted with benzene. The benzene was removed, and the resulting crude diacetate was refluxed overnight with a solution of concentrated hydrochloric acid (10 cc.) in dioxane (400 cc.) and water (100 cc.). The mixture was poured into water and extracted with benzene, and the benzene was removed as before. To the product were then added acetic acid (500 cc.) and, in portions, chromic acid (14.2 g., 0.142 mole). The mixture was refluxed one-half hour, permitted to cool to room temperature and finally poured into water to yield the crude product, which was crystallized two times from benzene–ethanol; yield 10.2 g. (47.8%); m. p. 229–230°. *Anal.* Calcd. for $C_{10}H_6O_2Cl_4$: C, 40.06; H, 2.02. Found: C, 40.42, 40.24; H, 2.04, 1.96.

Our attempts to isolate the intermediate diacetates and glycols met with only partial success. Fractional crystallization of the crude diacetate from methanol resulted in very low yields of two products, one melting at 182–184° and another, of questionable purity, melting from 122–125°. *Anal.* Calcd. for $C_{14}H_{14}O_4Cl_4$: C, 43.32; H, 3.64. Found for 182–184° compd.: C, 43.28, 43.44; H, 3.80, 3.68. Found for 122–125° compd.: C, 42.77, 42.69; H, 3.80, 3.68. Acid hydrolysis of the high-melting diacetate gave a quantitative yield of a glycol; m. p. 203–205° from methanol–water. *Anal.* Calcd. for $C_{10}H_{10}O_2Cl_4$: C, 39.52; H, 3.32. Found: C, 39.22, 39.31; H, 3.56, 3.61. Oxidation of the above glycol gave IX. We were not able to isolate a crystalline product from the hydrolysis of the low-melting diacetate.

1-(ω-Bromoacetyl)-2,3,4,5,6-pentachlorobenzene.—Bromine (8.0 g., 0.05 mole) was added as rapidly as taken up to a stirred solution of pentachloroacetophenone (14.6 g., 0.05 mole) in acetic acid (100 cc.). The reaction mixture was poured into water; the product was filtered and crystallized from ligroin (b. p. 90–100°); yield 12 g. (64%); m. p. 140–141°. *Anal.* Calcd. for $C_8H_2OCl_5Br$: C, 25.87; H, 0.54. Found: C, 25.77, 25.53; H, 0.60, 0.51.

1-(ω,ω-Dibromoacetyl)-2,3,4,5,6-pentachlorobenzene.—Bromine (24.0 g., 0.15 mole) was added to pentachloroacetophenone (14.6 g., 0.05 mole) as above. Not all of the bromine reacted even after a twenty-four-hour period. The product which separated was filtered and crystallized from ligroin; yield 16 g. (71%); m. p. 125°. *Anal.* Calcd. for $C_8H_1OCl_5Br_2$: C, 21.32; H, 0.22. Found: C, 21.34, 21.15; H, 0.28, 0.25.

1,4-Bis-(ω,ω-dibromoacetyl)-2,3,5,6-tetrachlorobenzene.—1,4-Diacetyl-2,3,5,6-tetrachlorobenzene, treated with bromine exactly as above, gave a 92% yield of product; m. p. 210.5–212.5°. *Anal.* Calcd. for $C_{10}H_2O_2Cl_4Br_4$: C, 19.52; H, 0.33. Found: C, 19.21, 19.56; H, 0.38, 0.35.

1-Pentachlorophenyl-2-bromoethane.—In a typical experiment a solution of pentachlorostyrene (10 g.) in benzene (100 cc.) was flushed with nitrogen, saturated with anhydrous hydrogen bromide, sealed and left standing at room temperature for one hundred and sixty hours. The benzene solution was washed with water and dried. The benzene was removed, and the crude product was crystallized from ethanol; yield 11 g. (85%); m. p. 98–99°. The product showed no depression on mix-melting with an authentic sample of the β-bromide.

1-4-Bis-(β-bromoethyl)-2,3,5,6-tetrachlorobenzene VIII.—1,4-Divinyl-2,3,5,6-tetrachlorobenzene (10 g.) in benzene (200 cc.) treated as above gave 10 g. (62.5%) of

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[14] The above simplified treatment of the coplymerization of I assumes that there are no significant differences between the rates of reaction of the fully unreacted material and the single reactive vinyl group attached to a chain by previous reaction of the other vinyl group. This assumption is reasonable in this case since I is a symmetrical molecule, the data used in calculating the monomer reactivity ratio are for runs in which the extent of conversion was low, and the change from a vinyl group to a polymer chain would not be expected to have a large effect on the reactivity of the remaining vinyl group.

[15] The microanalyses are by Dr. Carl Tiedcke.

VIII; m. p. 126–128° from ethanol. *Anal.* Calcd. for $C_{10}H_8Cl_4Br_2$: C, 27.97; H, 1.88. Found: C, 27.72, 27.88; H, 1.70, 1.51.

Measurements.—Eastman Kodak Co. white label styrene was extracted with 10% aqueous sodium hydroxide to remove the inhibitor, *t*-butylcatechol, washed with water, dried over magnesium sulfate and distilled at reduced pressure. Purified material was stored in Dry Ice before use, but never for longer than twenty-four hours. 1,4-Divinyl-2,3,5,6-tetrachlorobenzene was crystallized repeatedly from absolute ethanol until the m. p. was constant at 86–87°. Paragon benzoyl peroxide was crystallized from methanol.

Gelation times were determined as follows. The copolymerizations were carried out in sealed Pyrex tubes (15 mm. × 240 mm.) containing a steel sphere (11 mm. diameter) and 25 ml. of the solution under study. Solutions were prepared by dissolving the requisite quantities of benzoyl peroxide and I in styrene. Air was removed by two cycles of freezing in Dry Ice–trichloroethylene, evacuating on the water-pump, thawing and flushing with dry nitrogen, before sealing under 200–250 mm. nitrogen pressure. The sealed tubes were stored in Dry Ice if not placed immediately in the constant temperature oil-bath. Measurements were made at 49.2° with one and two weight % benzoyl peroxide and at 100° with 1% catalyst. The approach to the gelation point was followed by timing the fall of the steel sphere through the polymerizing mixture between two marks 4 inches apart. An electromagnet was used to position the sphere prior to its fall. The time was less than 0.01 minute for several hours in each case, rose gradually, then sharply. The time of fall was plotted against the time of reaction, and the gelation point was taken as that at which the curve approached the vertical. This corresponds to the point at which the viscosity of the system approaches infinity.

Tubes were removed from the thermostat as near the gelation point as possible and frozen in Dry Ice until they could be opened for analysis. Weighed samples were dissolved in carbon tetrachloride and analyzed for residual styrene by the standard bromide–bromate titration. Due to the ortho chlorine atoms, the vinyl groups in I do not add bromine under these conditions. The precision of the determination was in the order of 2–3%.

The % styrene which polymerized was obtained by subtracting these residual styrene values from the initial styrene, and the total % polymerization was obtained either by precipitating and weighing the polymer or by correcting the wt. % of styrene polymerized by an approximation based on the chlorine content of the copolymer.

Polymers for chlorine analysis were twice dissolved in benzene and reprecipitated with methanol. In some cases this resulted in a powdery product suitable for drying. With others it was necessary to redissolve in benzene and utilize the frozen benzene technique[16] to obtain material suitable for subsequent drying *in vacuo* at 64°.

Summary

A synthesis of 1,4-divinyl-2,3,5,6-tetrachlorobenzene has been described.

The dibromide obtained by bromination of 1,4-diethyl-2,3,5,6-tetrachlorobenzene has been shown to be 1,4-bis-(α-bromoethyl)-2,3,5,6-tetrachlorobenzene by its conversion to 1,4-diacetyl-2,3,5,6-tetrachlorobenzene.

Hydrogen bromide adds to pentachlorostyrene and 1,4-divinyl-2,3,5,6-tetrachlorobenzene to give β-bromo substituted products. It was not found possible to reverse the direction of this addition. In the presence of quinone no addition took place.

The copolymerization of 1,4-divinyl-2,3,5,6-tetrachlorobenzene and styrene has been studied. The reactivity of the divinyl compound is such that high degrees of conversion are obtained at the gelation point.

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[16] Lewis and Mayo, *Ind. Eng. Chem., Anal. Ed.*, **17**, 134 (1945).

NORTH ADAMS, MASSACHUSETTS

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CONTRIBUTION FROM THE SUGAR RESEARCH FOUNDATION, INC., AND THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Unsaturated Esters of Sucrose

BY MORRIS ZIEF

Although the synthesis and polymerization of many unsaturated compounds have been described in recent years, relatively few investigations have been concerned with the preparation of monomers from sucrose. The only derivative that has received particular attention is allylsucrose,[2] which has potential use as a resistant, protective and decorative coating and adhesive. In our work with ether derivatives, we found that the polymerization of a heptaallylsucrose is promoted by replacing the remaining hydroxyl group with an unsaturated acyl residue such as the methacrylyl group.[2e] This work suggested the study of unsaturated esters, and this report describes the preparation and properties of six unsaturated esters of sucrose, namely, methacrylyl, crotonyl, furoyl, cinnamoyl, undecylenoyl and allyloxycarbonyl.

While the preparation and polymerization of some monofunctional derivatives of these acids have been described in the literature[3] very little work on polyfunctional derivatives is on record.[4] In the carbohydrate field the methacrylates of glucose, maltose, dextrin and starch were described by Treadway and Yanovsky.[5] Outside of ill-characterized linoleic[6] and rosin[7] esters Oden's[8] preparation of cinnamoylsucrose is virtually the

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

[2] (a) Tomecko and Adams, THIS JOURNAL, **45**, 2698 (1923); (b) Frey, Dissertation, Eidgenoss. Techn. Hochschule, Zurich, 1926; (c) Nichols and Yanovsky, THIS JOURNAL, **67**, 46 (1945); (d) Nichols and Yanovsky, *Sugar*, **42**, No. 9, 28 (1947); (e) Zief and Yanovsky, *Ind. Eng. Chem.*, **41**, 1697 (1949).

[3] Neher, *Ind. Eng. Chem.*, **28**, 267 (1936); Liebermann and Zsuffa, *Ber.*, **44**, 841 (1911); Sapiro, Linstead and Newitt, *J. Chem. Soc.*, 1784 (1937); Ross, Gebhart and Gerecht, THIS JOURNAL, **67**, 1275 (1945).

[4] Muskat and Strain, U. S. Patents 2,384,115, 2,384,120 (1945).

[5] Treadway and Yanovsky, THIS JOURNAL, **67**, 1038 (1945).

[6] Rosenthal and Lenhard, U. S. Patent 1,739,863 (1929).

[7] Rheineck and Rabin, U. S. Patent 2,077,371 (1937).

[8] Oden, *Arkiv Kemi Mineral. Geol.*, **7**, no. 15, 23 (1918).