

bright yellow-orange color. Triiodoacetic acid as golden yellow crystals settled out and was filtered after another hour. Air drying the product served also to remove a small amount of free iodine which was present. Weight 14.3 g. (57.6%), m.p. 135–140° (dec.); reported m.p. 150° (dec.).<sup>1</sup> Other samples of triiodoacetic acid prepared in this manner gave m.p.'s as high as 150–154° (dec.).

*Anal.* Calcd. for  $C_2HO_2I_3$ : I, 86.97%; eq. wt. 438. Found: I, 87.5%; eq. wt.<sup>7</sup> 449.

After removal of the triiodoacetic acid, the mother liquor became a dark color and deposited 1.2 g. of iodine; this was removed. By concentration of the solution, a total of 5.4 g. (20.3%) of diiodoacetic acid was isolated as pale yellow needles, m.p. 110–111°; reported<sup>1</sup> m.p. 110°. It was recrystallized from chloroform. Data obtained by varying the reactant ratio were as follows:

Weight Ratio $HIO_3$ /Malonic Acid	Yield, Wt. %	% Based on Iodine in $HIO_3$	
		$Cl_3COOH$	$CHI_2COOH$
0.60	0		58.6
1.00	19.2		51.8
1.00 <sup>a</sup>	39.6		—
1.00 <sup>a</sup>	26.4		—
1.26	37.2		30.4
1.50	46.8		28.2
1.50	57.6		20.3
1.50 <sup>a</sup>	51.6		28.2
1.75	22.8		21.4
2.00 <sup>a,b</sup>	0		14.7

<sup>a</sup> Reaction mixture was kept cold after the initial reaction.

<sup>b</sup> A trace of a white solid, m.p. 300°, was isolated.

*Diiodomalonic acid.* Diiodomalonic acid was prepared by the method of Willstätter.<sup>4</sup> A mixture of 10 g. (0.167 mole) of malonic acid, 6.8 g. (0.10 mole) of iodic acid, and 19.6 g. (0.20 mole) of finely divided iodine in 50 cc. of 90% formic acid was stirred at room temperature 3 hr. The reaction mixture was allowed to stand overnight in a refrigerator and then filtered while cold. The product was dried on a clay plate to allow excess iodine to evaporate, giving 20 g. (58%) of diiodomalonic acid as pale yellow crystals, m.p. 110° (dec.); reported m.p. 119–120° (dec.).<sup>4</sup>

*Conversion of diiodomalonic acid to triiodoacetic acid.* Ten g. of diiodomalonic acid was added to 20 cc. of water containing 1.0 g. of iodic acid and 2.85 g. of pulverized iodine. The mixture was allowed to stand at room temperature with frequent shaking for 3 hr. A pale yellow solid appeared almost immediately. After standing overnight, the mixture was filtered and the product air-dried 6 days to remove free iodine, giving 3.7 g. (30%) of triiodoacetic acid, m.p. 140–142° (dec.).

*Anal.* Calcd. for  $C_2HO_2I_3$ : eq. wt. 438. Found: eq. wt. 450, 439.

*Reaction of malonic acid with iodine and iodic acid.* A mixture of 10.0 g. (0.096 mole) of malonic acid, 29.3 g. (0.115 mole) of pulverized iodine, and 10.2 g. (0.058 mole) of iodic acid in 250 cc. of water was stirred vigorously. After about 20 min., a yellow solid appeared; in another 15–20 min., evolution of carbon dioxide started with considerable foaming. The reaction was slightly exothermic; the temperature was not allowed to exceed 45° by using a water bath when necessary. A heavy yellow solid appeared after 3.5 hr. After standing overnight in a refrigerator, stirring was resumed for 3 hr. at room temperature. The mixture was filtered and the yellow solid dried on a clay plate in the air to remove excess iodine, giving 17.5 g. (42%, based on malonic acid) of

the triiodoacetic acid, m.p. 131–132° (dec.). Other samples of the acid prepared in this manner had m.p. as high as 154–155° (dec.).

*Anal.* Calcd. for  $C_2HO_2I_3$ : I, 86.9%. Found: I, 86.4%.

After removal of the triiodoacetic acid, concentration of the mother liquors gave about 7 g. (16%) of diiodoacetic acid, m.p. 108–109° after recrystallization from chloroform.

*Preparation of salts of triiodoacetic acid. Calcium salt.* A solution of 0.25 g. of calcium acetate in 2–3 cc. of water was added to a freshly prepared solution of 1.00 g. of triiodoacetic acid in 5 cc. of dimethylformamide. Immediately a golden orange solid appeared, accompanied by evolution of a gas. After cooling in an ice bath, the solid was filtered. It decomposed on the filter paper. Similar results were obtained with acetic acid and with a carefully neutralized bicarbonate solution.

*Lead salt:* A solution of 2.0 g. of lead acetate in 10 cc. of water was added to a freshly prepared solution of 5.0 g. of triiodoacetic acid in 20 cc. of dioxane. After an induction period of a few seconds, a heavy bright yellow solid appeared. This was filtered and washed well with cold water. Drying on the filter in the air for 2 hr. did not change the color of the product. The salt was dried *in vacuo* over phosphorus pentoxide for 4 hr.; 5.1 g. of a light yellow tan product was obtained. On heating in a capillary tube, the product liberated iodine above 90° particularly at 130–140° to 180°, yielding a yellow solid which was stable at 260°.

*Sodium salt:* Two grams of triiodoacetic acid was dissolved in a solution of 0.4 g. of sodium bicarbonate in 10 cc. of water. Immediately 4 g. of sodium acetate was added to salt out the product and beautiful golden yellow, glistening leaves settled out. These were filtered and air dried, wt. 2.1 g. Upon heating in a melting point tube, the solid started losing iodine at 90°, darkened gradually from 170–180°, and became quite dark colored at 230°. The salt appeared to be relatively stable to air at room temperature.

*Preparation of calcium diiodoacetate.* Treatment of diiodoacetic acid solution in the same manner as afforded the calcium salts of triiodoacetic acid gave none of the desired salt. It was observed that the salts were more water soluble than the parent acid. Calcium diiodoacetate was obtained as a pale yellow solid in the following manner. Six g. of the acid in 10 cc. of warm water gave a two-phase liquid system. This was neutralized with 1 g. of calcium carbonate. The two layers disappeared and a clear solution resulted until the neutralization point was almost reached, then the calcium salt started crystallizing. Water was added and excess carbonate was filtered off. The solution was concentrated under reduced pressure to 5–10 cc. and cooled to give 4.9 g. of the calcium diiodoacetate, dec. above 200° with liberation of iodine.

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## Infrared Analysis of a Cyclopropane Polymer

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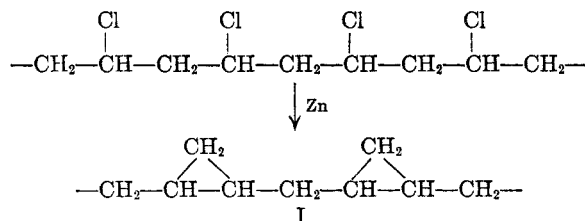
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In 1939, C. S. Marvel and co-workers reported<sup>2</sup> the preparation of a polymer containing cyclopropane rings by dehalogenation of polyvinyl chloride with zinc.

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(2) C. S. Marvel, J. H. Sample, and M. F. Roy, *J. Am. Chem. Soc.*, **61**, 3241 (1939).

(7) After allowing a sample of the acid to stand several weeks at room temperature, the eq. wt. was redetermined and found to be 451.



The dehalogenated polymer (I) was shown to be resistant to ozone and permanganate but added chlorine on chlorination. On vigorous nitric acid oxidation, no products could be isolated that would have been characteristic of a dehydrohalogenated polymer.

The preparation of I was repeated in order to obtain additional evidence for the original structure designation and to investigate the position of characteristic cyclopropane bands in a polymer environment. Only 60% of the total chlorine was removed in our experiments, compared to 85% obtained in the previous work; but this seems sufficient for infrared analysis. Films of I were cast directly on salt plates from dioxane solution, dried *in vacuo*, and compared to films of polyvinyl chloride prepared in a like manner. The spectrophotometer was a Perkin-Elmer Model 21 with sodium chloride optics.

Two new bands appeared in I in positions expected from prior band assignments in nonpolymeric cyclopropane structures. A band at  $9.83\mu$ , characteristic of the nonsymmetrical ring deformations of cyclopropanes<sup>3,4</sup> and a band at  $3.2\mu$ , characteristic of the methylene hydrogens of a cyclopropane ring<sup>4,5</sup> confirm the original assignment. Bands associated with carbon-carbon double bonds were either not present or obscured by carbon-chlorine overtone bands between 6.0 and  $6.5\mu$  and past  $10\mu$  by various skeletal vibrations.

It was not possible to obtain interpretable nuclear magnetic resonance spectra of I because of its low solubility in organic solvents.

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### Metalation of Cyclopropane by Amylsodium<sup>1</sup>

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Metalation of hydrocarbons has been observed only when some unsaturation was present, a pre-

vious success with decalin<sup>2</sup> having been found due to some impurity.<sup>3</sup> The first experiments with cyclopropane were carried out about ten years ago in the presence of isopropoxide with the expectation that the ring would open to give allylsodium. Thereby an alternative method for the preparation of an Alfin catalyst<sup>4,5</sup> would be provided. The product of this reaction, however, did not cause Alfin polymerization of butadiene. Carbonation yielded an acid which did not resemble vinylacetic but was similar to cyclopropanecarboxylic acid.

Recently cyclopropane was again metalated, but in the absence of an alkoxide, in order to study the absorption spectrum for the cyclopropyl anion. The infrared spectrum showed bands not far from those of cyclopropane itself and entirely distinct from those for allylsodium or amylsodium. Carbonation produced cyclopropanecarboxylic acid which was converted to the known amide for identification.

Although cyclopropane has a formula in which all four valencies for each carbon appear saturated, it still possesses a fair degree of olefinic character according to Coulson and Moffit<sup>6</sup> and Vogel.<sup>7</sup> Accordingly the statements previously made to the effect that some unsaturated system was necessary<sup>8</sup> for metalation of a hydrocarbon and that no indiscriminate removal of hydrogen by a supposedly all-powerful anion<sup>9</sup> took place are still valid.

### EXPERIMENTAL

*Metalation in the presence of isopropoxide.* Amylsodium was prepared<sup>10</sup> from 1 g.-atom of sodium and 0.5 mole of amyl chloride in the usual manner. Isopropyl alcohol (15 ml.) was added and 15 min. later the mixture was saturated with cyclopropane. All operations were under an atmosphere of dry nitrogen and the mixture was continuously stirred at 5000 r.p.m. After a total time of 6.5 hr. the reaction mixture was transferred to a bottle and stored under nitrogen. A portion (20 ml. of suspension) was tested as a polymerizing agent for 30 ml. of butadiene in 180 ml. of pentane, but did not produce the thick gel characteristic for Alfin polybuta-

(1) This work was performed as a part of research projects sponsored by the Reconstruction Finance Corp., Office of Synthetic Rubber, and by the National Science Foundation.

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