

TABLE I  
REACTION OF HALIDES WITH SODIUM TRITHIOCARBONATE

Halide	Reaction conditions	Product	Yield, <sup>a</sup> %
CICH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Cl	5 hr at 60°	HSCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> SH	61
CICH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> Cl	2 hr at 60°	HSCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> SH	66
CICH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> Cl	5 hr at 60°	HSCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> SH	77
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	1 hr at 60°	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SH	25

<sup>a</sup> No attempt was made to optimize yields.

mercaptan: bp 86° (0.4 mm) (lit.<sup>7</sup> bp 125–131° (5 mm)); infrared spectrum, 2557 cm<sup>-1</sup>; pmr spectrum (neat),  $\tau$  8.08 (S–H, 3), 7.33 (CH<sub>2</sub>–S, 2 × 3), 6.43 (CH<sub>2</sub>–O, 3). The infrared spectrum was identical with an authentic sample.

**Benzyl Mercaptan.**—To 135 ml (0.3 mol) of aqueous sodium trithiocarbonate at 25° was added 25.2 g (0.2 mol) of benzyl chloride in 21 min. The reaction mixture was warmed to 60° and allowed to stir at 60° for 1 hr. Isolation of the product as described in the general procedure afforded 6.2 g (25%) of benzyl mercaptan: bp 88–89° (11 mm) (lit.<sup>8</sup> bp 100° (22 mm)); infrared spectrum, 2560 cm<sup>-1</sup>; pmr spectrum (CS<sub>2</sub> solution),  $\tau$  8.43 (S–H, 3), 6.48 (CH<sub>2</sub>–S, 2), 2.88 (C<sub>6</sub>H<sub>5</sub>, 1). This material was identical in all respects with an authentic sample.

**Registry No.**—1,4-Butanedithiol, 1191-08-8;  $\beta$ , $\beta'$ -dimercaptodiethyl ether, 2150-02-9; triglycol dimercaptan, 14970-87-7; benzyl mercaptan, 100-53-8.

**Acknowledgments.**—The authors are grateful to Mr. J. Lake for his able technical assistance and to Mr. R. Pearce for obtaining the nmr spectra.

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### The Reaction of Lead Tetraacetate with Malonic Acid

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Received October 25, 1967

Since the effect of malonic acid on lead tetraacetate (LTA) decomposition was first reported,<sup>3</sup> it has generally been assumed that the source of this effect is due to the methylene hydrogens of malonic acid. This assumption, which was not tested, received support from the success of methylmalonic acid and ethyl acetoacetate and the failure of dimethylmalonic acid in effecting methylation of aromatic compounds.<sup>3</sup>

We have found, however, that malonic acid is not attacked by LTA except by carboxylate exchange to yield an insoluble mixed salt which decomposes much more readily than does LTA itself.

Our interest in this interaction arose because of the possibility that malonic acid might give rise to a methylenelike species through oxidative bisdecarboxylation similar to that observed with 1,2-dicarboxylic acids.<sup>4</sup> Since the fate of the malonic acid in Fieser's

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(3) L. F. Fieser and F. C. Chang, *J. Amer. Chem. Soc.*, **64**, 2043 (1942).

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work was not determined, such a process could have occurred to an appreciable extent without being detected.

Whereas LTA and malonic acid separately do not evolve gas in pyridine at room temperature, a mixture of the two yields 0.6 ± 0.2 mol of CO<sub>2</sub> per mole of LTA in less than 2 hr. The amount of CO<sub>2</sub> remains essentially constant over a range of LTA–malonic acid mole ratios of 0.2 to 1.0. Before gas evolution begins, a precipitate forms. A similar result is obtained in benzene except that decomposition occurs at an appreciable rate only at reflux. The precipitate can be collected; heating it produces the same results, with insoluble material remaining after gas evolution is complete. Both precipitates have been analyzed (Table I);

TABLE I  
PRECIPITATES FORMED FROM LTA AND VARIOUS ACIDS

Acid	% Pb	Acetate/ acid	Moles of CO <sub>2</sub> / mole of Pb	Half-life, hr <sup>a</sup>
Malonic <sup>b</sup>	45.4	3.5	0.5	1.4
Malonic <sup>c</sup>	57.2	1.2		
Succinic <sup>b</sup>	37.5	1.6	1.25	1.6
Dimethylmalonic <sup>b</sup>	37.4	2.2	0.6	1.0

<sup>a</sup> Time required for half of the total CO<sub>2</sub> to be evolved in refluxing benzene. <sup>b</sup> Precipitate before heating. <sup>c</sup> Precipitate obtained after CO<sub>2</sub> evolution was complete.

clearly, the percentage of malonate increases during decomposition. The data in Table I are not intended to correspond to molecular formulas; the precipitates are probably polymeric.<sup>5</sup> Heating the filtrate produces no gas evolution, thus ruling out formation of acetyl peroxide in the exchange process.<sup>6</sup> From 80 to 90% of the original malonic acid routinely has been accounted for in the final precipitate, and the acid has been recovered and positively identified.

Attempts were made to detect methylene formation by inclusion of cyclohexene under a variety of reaction conditions. Both cyclohexene and norcarane react with LTA, but at a rate slower than does malonic acid.<sup>7</sup> No materials could be detected which implied formation and further reaction of norcarane.

In pyridine, a 15% yield of picolines, based on CO<sub>2</sub> evolution, is obtained. The ratio of 2- to 3- and 4-picolines is approximately 2:1, which corresponds to the ratio reported for free-radical attack.<sup>8</sup> Electrophilic substitution proceeds almost entirely in the 3

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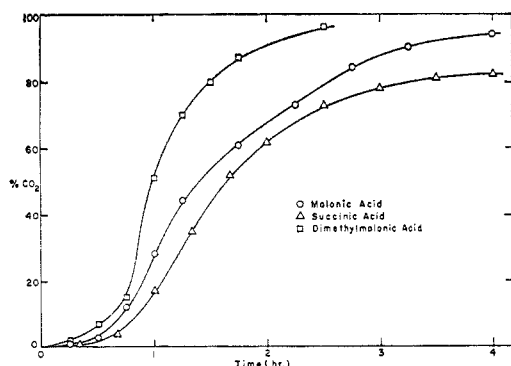


Figure 1.—CO<sub>2</sub> evolution at 80° in benzene from mixed salts of LTA and dicarboxylic acids.

position,<sup>8</sup> whereas methylene insertion produces only 2-picoline.<sup>9</sup> This in fact offers a convenient test for the nature of an attacking reagent, when suitable, since analysis can easily be made by vpc. Methylene diacetate is also produced, in less than 1% yield. This could have resulted from the malonic acid,<sup>10</sup> but has been found in decompositions of LTA alone.<sup>6</sup> One other unidentified product was detected in trace amounts; it is probably an  $\alpha$ -acetoxypicoline.<sup>11</sup> Polymeric materials similar to those obtained by Bartlett and Gortler from peroxy derivatives of malonic acid<sup>12</sup> could not be detected.

Contrary to Kochi's results with pentanoic acids,<sup>13</sup> the rate of total gas evolution is unaffected by oxygen or copper salts.

Dimethylmalonic and succinic acids were briefly examined for comparison. They both behave similarly, as shown in Table I. The relative rates of decomposition in refluxing benzene (Figure 1) parallel increased bulk at the  $\alpha$  carbon of the acid, indicating a steric basis for promotion of the decomposition. However, this conclusion must be tempered by the fact that these acids are involved in the decomposition itself, in contrast to malonic acid.<sup>3,4,10</sup> This difference is evident in the increased yield of gas from the succinic acid precipitate. Also, work-up of the final mixture from decomposition of the dimethylmalonic acid precipitate afforded a small amount of sweet-smelling oil, probably 2,2-diacetoxyp propane.<sup>10</sup> Neither of these decompositions produced well-defined precipitates which could be analyzed meaningfully.

The absence of oxygen inhibition, combined with the isomer distribution of the picolines produced in pyridine, thus point to a nonchain, free-radical decomposition of the mixed salt. Its insolubility precludes any significant attack by radicals in a potential chain-propagating step. In pyridine, exchange is apparently possible to yield pyridine-containing complexes which are even more labile than are the simple mixed salts. Therefore, whereas ethyl acetoacetate and other nonacidic materials may promote methylation by LTA because of the reactivity of an activated methylene group, the behavior of malonic acid must be attributed only to its ability to form a less stable, mixed salt. Other

dicarboxylic acids act similarly; the mode of decomposition, however, depends on the acid employed.

#### Experimental Section

Lead tetraacetate moist with acetic acid was placed in a tared flask which was then evacuated to a constant weight. Solvent was drawn into the flask instead of air until the LTA was covered, thus greatly reducing the sensitivity of dry LTA to atmospheric moisture. Pyridine reacts with LTA with evolution of heat to form a Pb(IV) complex. When it was used, the contents were allowed to return to room temperature. The flask was then opened to dry air or nitrogen and attached by means of Gooch tubing to a flask containing a known amount of solid acid. The other attachment was through a condenser either to a gas buret (total gas) or to a series of cold traps and weighed Ascarite tubes (CO<sub>2</sub>). The whole apparatus was flushed with nitrogen before the acid was added; when measuring CO<sub>2</sub>, the flow was continued throughout the run. The effect of oxygen was determined by measuring the rate of gas evolution after addition of a known amount of oxygen through a rubber septum. In some experiments, cuprous chloride was added during the run. No change in the rate of gas evolution was noted in either case.

In some experiments, the precipitate was collected in a drybox and dried to constant weight in a vacuum desiccator. It was used by adding it as quickly as possible to benzene at reflux temperature, care being taken to avoid excessive foaming.

Products were analyzed by vpc as individual fractions after fractional distillation of the filtered reaction mixture. Diphenyl ether was added to ensure complete distillation of picolines.

Precipitates were analyzed for lead by EDTA titration at pH 10, using Eriochrome T indicator,<sup>14</sup> after digestion in hot nitric acid. The acetate to acid ratios were determined by nmr analyses of centrifuged water solutions obtained by treating the precipitates with excess sulfide ion.

**Registry No.**—Lead tetracetate, 546-67-8; malonic acid, 141-82-2; succinic acid, 110-15-6; dimethylmalonic acid, 595-46-0.

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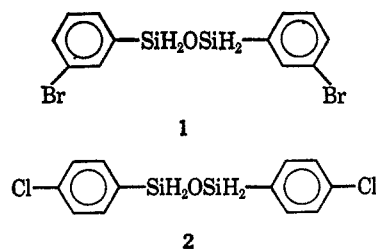
### 1,3-Bis(*m*-bromophenyl)- and 1,3-Bis(*p*-chlorophenyl)disiloxane

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Received December 16, 1966

We wish to report the synthesis of 1,3-bis(*m*-bromophenyl)disiloxane (1) and 1,3-bis(*p*-chlorophenyl)disiloxane (2) and an unusual redistribution reaction



which accompanies their hydrolysis. Only five 1,3-dialkyldisiloxanes<sup>1,2</sup> and one diaryldisiloxane, 1,3-

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