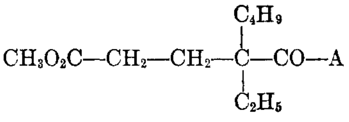
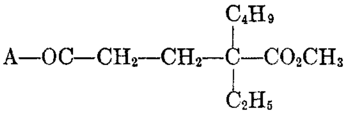


$$CH_3O_2C—CH_2—CH_2—\overset{C_4H_9}{\underset{C_2H_5}{C}}—CO—A$$

I. A = OH
II. A = C_4H_9



$$A—OC—CH_2—CH_2—\overset{C_4H_9}{\underset{C_2H_5}{C}}—CO_2CH_3$$

III. A = OH
IV. A = C_4H_9

the corresponding esters give sharper bands and larger signals with a thermal detector. Strangely enough, for equal weights of half esters I and III, a significantly larger signal is received from ester III. This is a definite exception to the report[6] that signal is a function of square root of molecular weight. Lower molecular weight acids, including formic and acetic acids may be separated on the silicone grease; however, broad unsymmetrical bands of somewhat variable retention times are obtained. The separation of branched-chain and normal fatty acid esters has been reported.[7]

EXPERIMENTAL

Preparation of column packing. There were used 4 parts of silicone grease[1] to 10 parts by weight of 30-60-mesh Celite (Johns-Manville "Chromosorb" or Celite firebrick which had been pulverized and sieved). The grease was dispersed by warming and stirring in 7-8 parts by weight of chloroform. A few minutes of vigorous mixing and stirring by hand are required for complete dispersion. The Celite, moistened with chloroform, was added to the stirred dispersion of grease, and the resultant mixture was shaken vigorously for a few minutes. The chloroform was removed at reduced pressure and the packing material was dried at 100° in a vacuum. Such packing material is just short of becoming sticky and has an appearance similar to the Celite before impregnation.

The packing material is cured by heating in a slow stream of nitrogen at 325-335°; higher temperatures tend to impair resolution and give too rapid a curing for satisfactory control. In large batches, an exothermic reaction may be noticeable as the temperature approaches 300° and this may necessitate turning off the heater for a few minutes. Heating may be accomplished[8] in a Pyrex tube, on which an electric heating wire has been wound. The heated tube should be placed in a vertical position with a short (20 mm.) outlet tube at the bottom of not less than 10 mm. o.d. During the first 30-50 hr. of heating, both a volatile, low-melting solid and a mobile liquid are swept from the tube; care must be exercised that the outlet is not plugged by the solid.

After 50-70 hr. of heating, when evolution of solid material has nearly ceased, heating should be discontinued, and the packing material should be tested for retention times of suitable compounds.[8] For some lots of silicone grease, this initial heating period has been sufficient. A retention time of 2-4 min. for methyl decanoate at 180° in a 1.5-m. column, helium pressure of 15-20 cm. of mercury, is in the range that is satisfactory. A representative rate of decrease of retention time with heating may be noted in Table I. The grease described as Lot II in this table gave, at 305° in the 2.5-m. column, a retention time for ethyl 10-methyltetracosanoate of 34 min. before curing, 22 min. after curing. A curing period of 5-8 days is normal, and the longest period that has been used was 12 days. If very high molecular weight materials are to be chromatographed, retention times may be shortened by extending the heating period, but deterioration of resolution eventually occurs. It is usually better to reduce retention times by decreasing the content of grease on the packing.

CHEMICAL LABORATORIES
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIF.

---

(6) R. H. Eastman, *J. Am. Chem. Soc.*, **79**, 4243 (1957).

(7) J. Cason and P. Tavs, *J. Biol. Chem.*, **234**, 1401 (1959).

(8) Commercial models of gas chromatography apparatus usually are not designed to permit heating above 300°; however, if one has apparatus which will withstand temperatures up to 340°, heating is conveniently done in the chromatography tube, where retention time may be checked by simply lowering the temperature to a suitable value. Heating may then be resumed as indicated.

Thermal Decomposition of Di-*n*-butyl Maleate

WILLIAM R. MILLER AND H. M. TEETER

Received June 15, 1959

During work on the addition of maleic acid derivatives to unsaturated fatty acids,[1] it was found that di-*n*-butyl maleate undergoes a decomposition reaction which has not been previously reported. The decomposition appears to be related to the well known pyrolysis of esters to form alkenes.[2] It may also be related to the decarboxylation of diaryl fumarates to form, first, aryl cinnamates and, then, stilbenes.[3] It differs from these reactions and is unusual in that decomposition is initiated at the relatively low temperature of 265°, the boiling point of dibutyl maleate. Another unusual feature of the decomposition is formation of 1-butanol.

When di-*n*-butyl maleate is heated to 260-265°, the liquid turns deep red, the refractive index rises, and there is loss in weight. Heating for 2.5 hr. transforms about 40% of the ester into higher boiling material. 1-Butanol is found in the cold trap when this material is distilled under vacuum. If the ester is swept with nitrogen while being heated, 1-butene can be trapped from the off-gas. Attempts to distill dibutyl maleate at atmospheric pressure result in a slow distillation of butanol and evolution of butene. Low weight recoveries in these experiments indicated the presence of another volatile product, shown to be carbon dioxide.

Beside volatile products, there is a considerable residue of dark, viscous tar. This residue could be

---

(1) W. R. Miller, E. W. Bell, H. M. Teeter, and J. C. Cowan. Presented before the 32nd Fall Meeting of American Oil Chemists' Society, October 1958, Chicago, Ill.

(2) W. J. Bailey and W. N. Turek, *J. Am. Oil Chemists' Soc.*, **33**, 317 (1956).

(3) L. B. Flett and W. H. Gardner, *Maleic Anhydride Derivatives*, John Wiley and Sons, New York, 1952, p. 248.

separated into an ethanol-soluble viscous oil and an insoluble charcoal-like solid. Nothing was characterized in the residue except minute quantities of succinic and fumaric acids. A quantitative study of the volatile products (Table I) was undertaken to learn more about the nature of this decomposition.

TABLE I

THERMAL DECOMPOSITION OF DI-*n*-BUTYL MALEATE AND FUMARATE

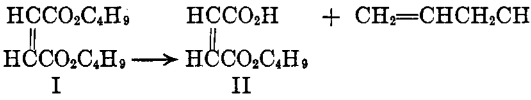
		Product, mmols.			Molar ratio		
Ester	Charge mmols.	Butanol	Butene	CO_2	Butanol	Butene	CO_2
Maleate[a]	438	287	145	234	1.87	1	1.61
	110	91	50	68	1.82	1	1.36
	175	173	86	...	2.02	1	..
Maleate[b]	175	124	71	116	1.75	1	1.63
	175	162	82	107	1.97	1	1.31
Fumarate	175	165	93	127	1.78	1	1.37

[a] Prepared with H_2SO_4 catalyst. [b] Prepared without catalyst.

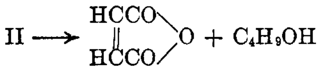
Butanol and butene were in a molar ratio of 2 to 1. The amount of carbon dioxide evolved was less on a molar basis than that of butanol but more than that of butene. For each mole of ester a maximum of about 1 mole of butanol was formed, with corresponding quantities of the other components.

An explanation for the ease of this decomposition was sought. The ester had been prepared from maleic anhydride and butanol, using concentrated sulfuric acid as catalyst. It was postulated that some acidic sulfur group, carried through the preparation and distillation of the dibutyl maleate, might have catalyzed the decomposition. Accordingly, dibutyl maleate was prepared without acid catalyst. This ester decomposed in exactly the same manner as did the ester prepared with acid catalyst. Di-*n*-butyl fumarate also was subjected to the same conditions. Results were identical, except that the butanol contained some water and high-boiling material while butanol from the maleic ester was pure.

It is not difficult to suggest reactions that would account qualitatively for the products. The evolution of butene suggests pyrolysis of the butyl ester (Eq. 1). The acid moiety so produced could react with another ester group on the same (Eq. 2) or on a different molecule (Eq. 3) to form an anhydride and butanol.[4] Again, the acid might decarboxylate to form butyl acrylate (Eq. 4). The diester might eliminate carbon dioxide in the manner of the diaryl fumarates,[3] to give in turn butyl β-butylacrylate and 5-decene (Eq. 5). In the latter case, the amount of carbon dioxide formed would be independent of the mechanism of ester pyrolysis and anhydride formation.



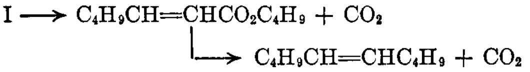
$$\underset{\text{I}}{\begin{array}{c}HCCO_2C_4H_9\\ \|\\ HCCO_2C_4H_9\end{array}} \longrightarrow \underset{\text{II}}{\begin{array}{c}HCCO_2H\\ \|\\ HCCO_2C_4H_9\end{array}} + CH_2{=}CHCH_2CH_3 \qquad (1)$$



$$\text{II} \longrightarrow \begin{array}{c}HCCO\\ \|\\ HCCO\end{array}\!\!\!\!\!\!>O + C_4H_9OH \qquad (2)$$

$$\text{II} + \text{I} \longrightarrow C_4H_9OCOCH{=}CHCO_2COCH{=}CHCO_2C_4H_9 + C_4H_9OH \qquad (3)$$

$$\text{II} \longrightarrow H_2C{=}CHCO_2C_4H_9 + CO_2 \qquad (4)$$



$$\text{I} \longrightarrow C_4H_9CH{=}CHCO_2C_4H_9 + CO_2 \longrightarrow C_4H_9CH{=}CHC_4H_9 + CO_2 \qquad (5)$$

On the basis of these reactions, the relatively nonvolatile products of the decomposition should include at least some of the following: Butyl hydrogen maleate, maleic anhydride and/or a more complex ester anhydride, butyl acrylate, butyl β-butylacrylate, 5-decene, further degradation products, and the geometric isomers of the maleic derivatives. Only a little fumaric acid was found. The acrylic derivatives would probably be polymerized very readily, possibly copolymerizing with the maleic derivatives.

Quantitatively these reactions require a butanol: butene ratio of 1:1, whereas the observed ratio was 2:1. If the carbon dioxide resulted from decarboxylation of the half ester (Eq. 4), there should be proportionately more butene than butanol formed. If the carbon dioxide came from the diester (Eq. 5), it should not affect the butanol:butene ratio significantly. Thus reactions in Equations 1–3 must not represent the true course of the decomposition.

Other reactions can be postulated, but all run into the same objection or require unprecedented vinyl hydrogen reactivity in the maleic ester. A molecule of butanol possibly could be split out of the ester with formation of a ketene, but this seems most unlikely. If it did happen, for each two ester groups that react in this manner, a third would have to react by a different route to split out butene. There seems to be no cogent reason for this sort of variation. Further, there is one piece of inconclusive evidence, based on an incomplete decomposition, that butene is evolved before, or faster than, butanol.

Work on the kinetics of this decomposition and investigation of the reactions of related esters might serve to elucidate the mechanism. Because further study of this decomposition is beyond the scope of our program, we shall be glad to have others explain the true course of this unusual decomposition.

EXPERIMENTAL

Di-*n*-butyl maleate was prepared from maleic anhydride and 1-butanol and redistilled before use. An analytically pure sample of the ester had n_D^{30} 1.4412. The maleate used in the experiments had n_D^{30} 1.4409–1.4411. Use of sulfuric acid catalyst in the synthesis had no effect on the properties of the ester. Di-*n*-butyl fumarate was prepared from fumaric acid and 1-butanol using dry HCl as catalyst, n_D^{30} 1.4420.

---

(4) W. Nagel and R. H. Abelsdorff, *Wiss. Veroffentl Siemens-Konzern.* **5**, 193 (1926).

Decompositions were carried out in a flask fitted with a nitrogen ebullator; a thermometer; and an absorption train consisting of a water-cooled condenser with receiver, a trap cooled by an ice salt freezing mixture, another trap containing concentrated sulfuric acid and finally, a U-tube containing Ascarite.[5] Typically the pot containing the ester was heated to about 265°, at which temperature the ester would start to boil. A slow stream of nitrogen was used to sweep out the decomposition products. A liquid, n_D^{30} 1.3950, was collected in the receiver of the water-cooled condenser. This was identified as 1-butanol by preparation of an α-naphthylurethan which melted at 69–70.5° and did not depress the melting point of an authentic sample. Butene was absorbed in the sulfuric acid and carbon dioxide in the Ascarite. In preliminary experiments butene was identified by condensation in a cold trap, the liquid was evaporated, and the gas passed into a solution of bromine in carbon tetrachloride to give a liquid boiling at 164°; n_D^{30} 1.507; d^{29} 1.76. These values are in reasonable agreement with literature values[6] for 1,2-dibromobutane: B.P. 166°, n_D^{25} 1.5125, d^{25} 1.787. These data indicate that the butene is primarily 1-butene, although there may have been some rearrangement. Decomposition was continued until evolution of volatile material had stopped.

Acknowledgment. The authors acknowledge their appreciation to J. L. O'Donnell for preparation of the esters.

Northern Regional Research Laboratory
Northern Utilization Research and Development Division
Agricultural Research Service
U. S. Department of Agriculture
Peoria, Ill.

---

[5] Mention of firm names or trade products are furnished for convenience, and this information does not constitute an endorsement of them or their products by the Department of Agriculture.

[6] R. T. Dillon, W. G. Young, and H. J. Lucas, *J. Am. Chem. Soc.*, **52**, 1954 (1930); N. A. Lange, *Handbook of Chemistry*, Seventh Edition, Handbook Publishers, Inc., Sandusky, Ohio, 1946, p. 446.

Iodination of Benzoic Acid in Acetic Acid-Sulfuric Acid Mixture Containing Iodate

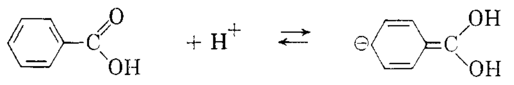
Robert S. Ajemian and A. J. Boyle

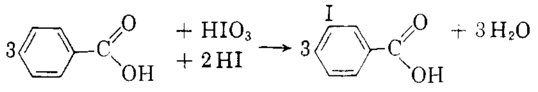
Received June 24, 1959

The direct halogenation of benzoic acid is inhibited by the deactivating influence of the carboxyl group. It is possible however, to obtain yields of *m*-chlorobenzoic acid as high as 50% by the use of potassium permanganate, hydrochloric acid, and benzoic acid in aqueous medium.[1] The iodination of benzoic acid was attempted in acidified aqueous medium in the presence of iodide and iodate. Perchloric, nitric, sulfuric, and acetic acids, respectively, failed to produce even the slightest yield of *m*-iodobenzoic acid.

The use of 1:1 glacial acetic and sulfuric acids containing benzoic acid and sodium iodate produces a 70% yield of *m*-iodobenzoic acid when sodium iodide, dissolved in glacial acetic acid, is added dropwise over a period of one hour to the heated (85°) mixture. Subsequently, it was determined that a mixture of 45% glacial acetic and 55% sulfuric acids by volume proved to be the most effective environment. Sodium iodide in acetic acid, or iodine plus sodium iodide, presented a convenient way in which to introduce iodine. The latter combination makes possible the solution of 20 g. of iodine in 50 ml. of acetic acid.

It would appear that in the presence of glacial acetic and sulfuric acids the benzoic acid is rather basic and may be considered a proton acceptor.[2] Acquiring a proton, the carboxyl group now permits more negativity at the *meta-* position (I), a situation which seems to facilitate iodination. The presence of water in this system provides a much stronger base than benzoic acid and thus hydronium ion is formed which effectively prevents a proton combination with the carboxyl group. The reaction (II) is most rapid in the presence of a slight excess of iodate and free iodine which is liberated on the addition of iodide as described above. The acetic acid solubilizes both iodine and benzoic acid which enhances the rate of reaction.

I


II


A temperature above 100° promptly stops the reaction. Lowering the temperature at this point does no good. Above 100° elemental sulfur (III) appears

$$\text{III}\ H_2SO_4 + 6HI \xrightarrow{>100^\circ} 3I_2 + S + 4H_2O$$

on the colder parts of the reaction flask. At the optimum temperature for the reaction to proceed, an excess of iodide over the equivalent of iodate will stop the iodination. Iodate must always be in slight excess over the iodide added. The addition of more iodate when iodide is in excess will restore the iodination process.

EXPERIMENTAL

Benzoic acid (12.0 g.) was placed in a 3-necked flask, with condenser, along with glacial acetic acid (90 ml.) and stirred to dissolve the benzoic acid. Concentrated sulfuric acid (110 ml.) was added slowly with stirring. To this mixture was added sodium iodate (6.0 g.). The mixture was maintained at 85° throughout the reaction. Acetic acid (50 ml.), containing sodium iodide (10 g.), was added dropwise while the mixture was vigorously stirred mechanically. The free iodine concentration was permitted to be in considerable excess. As the reaction progresses the iodine color disappears and more iodide must be added to keep the rate optimum. In these circumstances the time required is approximately 50 min.

The mixture was decolorized by the use of sodium sulfite. The addition of water equivalent to 3 times the volume of the

---

[1] H. Y. Yee and A. J. Boyle, *J. Chem. Soc.*, 4139 (1955).

[2] L. P. Hemmet, *Chem. Revs.*, 16, 67 (1935).