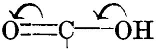
CCXXVI.—*The Reaction of Bromine with Aliphatic Acids. Part IV. Succinic Acid.*

By EDWARD DAVID HUGHES and HERBERT BEN WATSON.

INVESTIGATIONS of the bromination of succinic acid have led to discordant results. Thus, while Orlowski (*Centr.*, 1877, 4) obtained the mono- and the di-brominated acid by heating together dry succinic acid and bromine, several investigators (Perkin and Duppa, J., 1861, **13**, 102; Kekulé, *Annalen*, 1861, **117**, 120; Urech, *Ber.*, 1880, **13**, 1695) state that no reaction occurs under these conditions, but that the acid may be brominated in aqueous solution at temperatures of 100° and above. Kekulé (*loc. cit.*), who carried out the reactions in sealed tubes, makes the surprising statement that, although in presence of a little water the dibrominated acid is formed (compare also Bourgoin, *Ber.*, 1873, **6**, 624; Franchimont, *ibid.*, p. 199), yet the main product is monobromosuccinic acid when a comparatively large quantity of water is present, the proportion of bromine to succinic acid having no effect.

The authors find that no bromination occurs when open vessels are employed; in sealed tubes, however, both in presence and in absence of water, the bromine reacts completely after 2—4 days' heating at 100°. In no case is any monobromosuccinic acid obtained; in absence of water, 2 mols. of bromine give an almost theoretical yield of the dibrominated acid, whilst 1 mol. gives the dibrominated and the unsubstituted acid; the results are similar when succinic acid is brominated in presence of an equal weight of water. Introduction of a larger quantity of water leads to a considerable decrease in the yield of dibrominated acid and to the production of brominated hydrocarbons (compare Bourgoin, *Bull. Soc. chim.*, 1873, **19**, 148; Orlowski, *loc. cit.*).

The dibromosuccinic acid obtained in all these experiments sublimes above 250° and is sparingly soluble in water; it is thus the *meso*-form (McKenzie, J., 1912, **101**, 1196; Holmberg, *Svensk. Kemi Tidskr.*, No. 5, 1911). The racemic isomeride, *iso*dibromosuccinic acid (m. p. 167°, easily soluble), is never observed, perhaps because it is converted into the *meso*-isomeride by heating at 100° with hydrogen bromide (Michael, *J. pr. Chem.*, 1895, **52**, 289).

In acetic acid and its homologues, the failure of the carboxyl group to enolise may be ascribed (Orton, Watson, and Hughes, J., 1927, 2458) to the competition  $\overset{\curvearrowleft}{O{=}}\overset{\curvearrowleft}{C{-}}OH$. Malonic acid, on the other hand, is known to react with bromine in its enolic form (Meyer, *Ber.*, 1912, **45**, 2864; West, J., 1924, **125**, 1277), and this difference is probably due to the powerful electron affinity of the second carboxyl group. It may be suggested that the reaction of bromine with succinic acid is also preceded by enolisation, an idea which is confirmed by the authors' observation that mineral acids act catalytically. If this suggestion be correct, enolisation occurs less readily than in the case of malonic acid (which is rapidly brominated at 0°), owing to the screening effect of the second carbon atom (compare Ingold, *Ann. Report*, 1926, **23**, 130).

The absence of the monosubstituted acid from the products of bromination of succinic acid (see above) indicates that the former reacts with bromine more rapidly than the latter, and this is confirmed by the results of velocity measurements. The enolisation of monobromosuccinic acid should be facilitated by the presence of the bromine atom (this appears to be the case in monobromomalonic acid, West, *loc. cit.*), and this acid may also react with halogens in its enolic form. It is not possible, however, to form any definite conclusions, since monobromosuccinic acid decomposes readily to form fumaric acid (Volhard, *Annalen*, 1887, **242**, 158; Müller, *Z. physikal. Chem.*, 1902, **41**, 483; Müller and Suckert, *Ber.*, 1904, **37**, 2598; Lossen and Mendthal, *Annalen*, 1906, **348**, 261), and the dibrominated acid may result from the addition of bromine to this compound, a reaction which is known to yield the *meso*-acid.

Succinyl Bromide.—There is no reference in the literature to the isolation of *succinyl bromide*; the authors have now prepared this compound as a liquid, b. p. 105—106°/13 mm., by treatment of succinic acid with *two* mols. of phosphorus pentabromide (compare the similar preparation of succinyl chloride, Gerhardt and Chiozza, *Annalen*, 1853, **87**, 293). The acid bromide reacts with bromine relatively quickly; 1 mol. of the halogen disappears after 4 hours at 90°, giving principally monobromosuccinyl bromide; a second mol. reacts less rapidly, yielding a mixture of the isomeric dibrominated bromides.* These results are analogous to those obtained by the bromination of the chlorides of dicarboxylic acids (Lassar-Cohn, *Annalen*, 1889, **251**, 335; Willstätter and Lessing, *Ber.*, 1902, **35**, 2066; Le Sueur, J., 1909, **95**, 273; Ingold, J., 1921, **119**, 305, 951; Bernton, Ing, and Perkin, J., 1924, **125**, 1492; Ing and Perkin, *ibid.*, p. 1814; J., 1925, **127**, 2387).

Succinic Anhydride.—It was observed by Volhard (*Annalen*, 1887, **242**, 141) that succinic anhydride and bromine, when heated on the water-bath, do not react unless a little phosphorus is added; the authors have confirmed this result, which appears to indicate that the anhydride is brominated at an appreciable rate only through the intermediate formation of an acid bromide. Further, in sealed tubes at 100°, bromination occurs at a rate which increases to a maximum and then decreases (compare acetic anhydride; Orton, Watson, and Hughes, *loc. cit.*). With 1 mol. of bromine, the product is a liquid which, on release of the pressure, evolves hydrogen bromide, and the monobrominated anhydride is easily isolated by fractional distillation under reduced pressure (b. p. 130—133°/11

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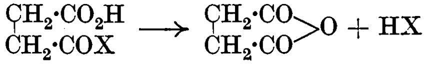
* The close proximity of the boiling points of the substituted bromides makes their separation almost impossible, and they were identified by examination of their products of hydrolysis.

mm.; compare Anschütz and Bennert, *Ber.*, 1882, **15**, 640). Two mols. of bromine give dibromomaleic anhydride.

Succinic anhydride does not react with hydrogen bromide under ordinary conditions, as acetic anhydride does; on the contrary, the production of succinic anhydride by the interaction of molar quantities of phosphorus pentahalide and succinic acid (Gerhardt and Chiozza, *loc. cit.*) must involve the *release* of hydrogen halide in one of the following ways: *

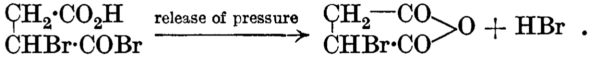


$$\begin{array}{l}CH_2\cdot CO_2H\\ CH_2\cdot COX\end{array} \longrightarrow \begin{array}{l}CH_2\cdot CO\\ CH_2\cdot CO\end{array}\!\!>O + HX \quad . \quad . \quad . \quad (1)$$

or

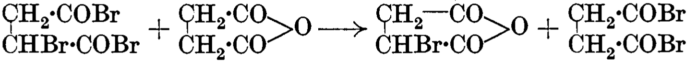
$$\begin{array}{l}CH_2\cdot COX\\ CH_2\cdot COX\end{array} + \begin{array}{l}CH_2\cdot CO_2H\\ CH_2\cdot CO_2H\end{array} \longrightarrow 2\begin{array}{l}CH_2\cdot CO\\ CH_2\cdot CO\end{array}\!\!>O + 2HX \quad . \quad (2)$$

In sealed tubes, however, where a considerable pressure of hydrogen bromide is developed, it is quite likely that these reactions may be reversed; the resulting acyl halide would then be brominated, and the substituted anhydride produced by one of the changes†



$$\begin{array}{l}CH_2\cdot CO_2H\\ CHBr\cdot COBr\end{array} \xrightarrow{\text{release of pressure}} \begin{array}{l}CH_2—CO\\ CHBr\cdot CO\end{array}\!\!>O + HBr \quad . \quad (3)$$

or



$$\begin{array}{l}CH_2\cdot COBr\\ CHBr\cdot COBr\end{array} + \begin{array}{l}CH_2\cdot CO\\ CH_2\cdot CO\end{array}\!\!>O \longrightarrow \begin{array}{l}CH_2—CO\\ CHBr\cdot CO\end{array}\!\!>O + \begin{array}{l}CH_2\cdot COBr\\ CH_2\cdot COBr\end{array} \quad (4)$$

The presence of a second mol. of bromine will then lead to further substitution by a similar series of changes; the ultimate product (dibromomaleic anhydride) would be formed readily from the dibrominated succinic anhydride (compare Pictet, *Ber.*, 1880, **13**, 1669).

It appears, therefore, that the bromination of succinic anhydride, like that of acetic anhydride, proceeds through a somewhat complex series of reactions, which includes the bromination of an acyl bromide.

Bromination of Succinic Acid by the Hell–Volhard Method.—In an extensive investigation of the bromination of acids by the Hell–Volhard method, Auwers and Bernhardi (*Ber.*, 1891, **24**, 2209) found that dicarboxylic acids with a hydrogen atom situated in the α-position with respect to each carboxyl group were easily converted into dibrominated derivatives; the proportions of carboxylic acid,

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* Compounds $CO_2H\cdot CH_2\cdot CH_2\cdot COX$ have never been isolated, but the reaction (2) of succinyl chloride with succinic acid has been carried out by Anschütz (*Ber.*, 1877, **10**, 1881) and by Möller (*J. pr. Chem.*, 1880, **22**, 194).

† Reaction (4) has an analogy in the production of acetyl chloride and acetic chloroacetic anhydride from chloroacetyl chloride and acetic anhydride (Watson and Gregory, J., 1929, 1373).

phosphorus pentabromide, and bromine were 1 : $\frac{2}{3}$: 2, and the reactions were carried out in open vessels. Succinic acid was an exception, for the product consisted here almost entirely of the monobrominated derivative (compare also Auwers and Imhäuser, *ibid.*, p. 2233), although dibromosuccinic acid had been obtained easily by this method by Hell (*Ber.*, 1881, **14**, 891) and by Gorodetzky and Hell (*ibid.*, 1888, **21**, 1729), who used sealed tubes. The earlier results of Volhard (*loc. cit.*) were in agreement with those of Auwers and Bernhardi; he, however, also isolated succinic anhydride from the products, and the authors have observed a very large conversion into anhydride under these conditions.

These phenomena may now be explained in a simple manner. When succinic acid is treated with phosphorus and bromine in an open vessel, in the proportions used by the above investigators, one or both of the acid bromides will be formed. It is to be anticipated that the bromide $CO_2H\cdot CH_2\cdot CH_2\cdot COBr$ would readily yield a monobrominated but not a dibrominated derivative, and release of hydrogen bromide to form anhydride will occur simultaneously. The authors have shown that succinyl bromide, $COBr\cdot CH_2\cdot CH_2\cdot COBr$, is also converted rapidly into monobromosuccinyl bromide, while the entry of a second bromine atom is a slower process; reaction of the bromide with unchanged succinic acid (to form anhydride) will doubtless occur before any appreciable quantity of dibrominated product is formed, and hence in open vessels only the monobrominated derivative is obtained. In sealed tubes, on the other hand, anhydride formation is prevented by the presence of hydrogen bromide under pressure, and the acid bromide may be converted into both its mono- and its di-substitution product.

EXPERIMENTAL.

Bromination of Succinic Acid in Sealed Tubes at 100°.—1. Pure acid and bromine (2 mols.). 5 G. of succinic acid (Kahlbaum) and 13·5 g. of bromine (A.R.) were heated in a Carius furnace for 4 days; the product (10 g.; calc., 11·5 g.) sublimed at 250—280°, and after recrystallisation from hot water gave Br, 57·83% (Calc. for $CO_2H\cdot CHBr\cdot CHBr\cdot CO_2H$: Br, 57·94%).

2. Pure acid and bromine (1 mol.). 7·5 G. of succinic acid and 10 g. of bromine were heated for 3 days, the product agitated with ether, and the insoluble portion (3·5 g.) recrystallised from water; it then melted at 185° (unchanged succinic acid). The ethereal solution gave 6 g. of a solid which, after recrystallisation from hot water, sublimed above 250° (Found : Br, 58·12%).

3. Equal weights of succinic acid and water (5 g. each) and 2 mols. of bromine (13·5 g.). On opening the tube, a smell resembling that

of chloroform was detected. The product (9 g.; Calc., 11·5 g.; Found : Br, 58·04%) sublimed above 250°.

4. Equal weights of succinic acid and water (5 g. each) and 1 mol. of bromine (7 g.). After agitation with ether, the insoluble portion obtained (3 g.) melted at 185°, and the ethereal extract yielded 2 g., subliming above 250° (Found : Br, 58·05%). No other product could be isolated.

5. Succinic acid (5 g.) and water (10 g.) with 2 mols. of bromine (13·5 g.). The product (6 g.; Calc., 11·5 g.) consisted of succinic and dibromosuccinic acids (subl. above 250°).

6. Succinic acid (7·5 g.) and large excess of water (50 g.) with 2 mols. of bromine (20 g.). The product consisted of a yellow oil (Found : Br, 94·54%) and an aqueous solution, which contained only unchanged succinic acid.

7. Hydrobromic acid as catalyst. 5 G. of succinic acid, 4 c.c. of water, 1 c.c. of constant-boiling hydrobromic acid, and 13·5 g. of bromine were used. All the bromine had reacted in 2 days, and the product (9 g.) sublimed above 250° (Found : Br, 57·67%).

8. Hydrochloric acid as catalyst. 5·5 G. of bromine reacted completely with 2 g. of succinic acid and 10 c.c. of constant-boiling hydrochloric acid in less than 24 hours, and 0·6 g. of dibromosuccinic acid was isolated.

Velocity of bromination in presence of catalysts. 2 C.c. portions of each of the following reaction mixtures (aqueous solution) were heated in sealed tubes at 100°, and titrated against *N*/50-sodium thiosulphate after stated periods. Titres are given in c.c.

Conc. of succinic acid.	Substance added.	Initial titre.	Fall in titre after (hours).			
			2.	4.	6.	8.
0·51*M*	Nil	9·65	1·20	1·85	2·40	2·90
0·51*M*	HBr, 0·85*M*	9·90	1·70	3·35	5·30	7·40
0·42*M*	H_2SO_4, 0·92*M*	10·00	2·10	4·30	7·00	8·90

No conclusions of a quantitative nature can be drawn from these figures, but they indicate the increased speed due to the presence of mineral acids.

Velocity of bromination of monobromosuccinic acid. The acid was obtained from monobromosuccinyl bromide (see below). Conc. of acid, 0·51*M*; initial titre (*N*/50), 11·7 c.c.

Time (mins.)	10	20	30	40	45
Fall in titre	5·10	7·70	9·90	10·90	11·50

Reaction of Phosphorus Pentabromide with Succinic Acid.—1. Succinic acid (3 mols.), phosphorus pentabromide (2 mols.). Bromine (45 g.) was run slowly into a mixture of 20 g. of succinic acid and 3·5 g. of red phosphorus, and refluxed at 95° till evolution of hydrogen bromide had ceased. The solid obtained (12·5 g.), when recrystallised from chloroform, had m. p. 119—120°, and reacted with water to give succinic acid.

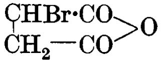
2. Succinic acid (1 mol.), pentabromide (2 mols.). Bromine (340 g.) was run into a mixture of 50 g. of succinic acid and 26·3 g. of red phosphorus, and refluxed at 100° for 2 hours; the product was distilled under reduced pressure, and the fraction distilling at 57—84°/11 mm. solidified (Found: Br, 82·74. Calc. for $POBr_3$: Br, 83·62%), whereas 53 g. distilling at 92—108° on redistillation gave a main fraction, b. p. 105—106°/13 mm., of *succinyl bromide* (Found: Br, 65·45; Br as COBr, 65·59. $COBr{\cdot}CH_2{\cdot}CH_2{\cdot}COBr$ requires Br, 65·57%).

Bromination of Succinyl Bromide.—1. *With* 1 *mol. of bromine.* 36·5 G. of succinyl bromide and 24 g. of bromine were refluxed at 90°. The bromine had all reacted after 4 hours, and the product was distilled under reduced pressure, b. p. 80—114°/13 mm. (38·5 g.). On decomposition with water, it gave a small quantity of solid (m. p. 185°) insoluble in ether. From the ethereal solution a small quantity of solid subliming above 250° was obtained, together with a good yield of a substance soluble in water, m. p. 159—160° (Found: Br, 40·73. Calc. for $CO_2H{\cdot}CHBr{\cdot}CH_2{\cdot}CO_2H$: Br, 40·60%).

2. *With* 2 *mols. of bromine.* 45 G. of succinyl bromide and 60 g. of bromine were refluxed at 100°. Reaction was rapid at first but became slower later, and was complete in about 18 hours. The product boiled at 110—135°/13 mm. The fraction of b. p. 125—130° (Found: Br, 79·36. Calc. for $COBr{\cdot}CHBr{\cdot}CHBr{\cdot}COBr$: Br, 79·60%), on treatment with water (without heating), yielded both dibromosuccinic acid (subl. above 250°) and *iso*dibromosuccinic acid, which after recrystallisation from ether–benzene, had m. p. 167° (Found: Br, 58·39%).

Action of Hydrogen Bromide on Succinic Anhydride.—A slow stream of dry hydrogen bromide was passed through the anhydride (recrystallised from chloroform) at its m. p. (120°), but practically the whole of it was recovered unchanged.

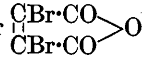
Bromination of Succinic Anhydride in Sealed Tubes at 100°.—1. *With* 1 *mol. of bromine.* 10 G. of anhydride and 16 g. of bromine were heated for 24 hours. The product, a brown liquid which released hydrogen bromide, left a small residue of unchanged anhydride on extraction with ether, and the extract yielded a small quantity of dibromomaleic anhydride, but principally a liquid, b. p. 130—133°/11 mm. (Found: Br, 43·10. Calc. for



$\begin{array}{l}\text{CHBr}{\cdot}\text{CO}\\ \text{CH}_2\text{—CO}\end{array}\!\!>\text{O}$:

Br, 44·69%). On hydrolysis, monobromosuccinic acid was obtained, m. p. 159° (Found: Br, 40·18%).

2. *With* 2 *mols. of bromine.* The same quantity of anhydride

but double the weight of bromine were similarly treated. A small quantity of monobromosuccinic anhydride was obtained, but the main product distilled at 112—116°/12 mm., and after recrystallisation from ether–ligroin melted at 118—119° (Found : Br, 62·96. Calc. for  $\left.\begin{array}{l}\mathrm{CBr{\cdot}CO}\\ \;\|\\ \mathrm{CBr{\cdot}CO}\end{array}\right>\mathrm{O}$: Br, 62·5%). It yielded with water a product, m. p. 120—122° (Found: Br, 57·45. Calc. for $\mathrm{CO_2H{\cdot}CBr{:}CBr{\cdot}CO_2H}$: Br, 58·4%).

Velocity of Bromination of Succinic Anhydride.—0·1 G. of the anhydride was weighed into each of several small tubes, 2 c.c. of a chloroform solution of bromine were added to each, and the tubes heated at 100°. The initial concentration of the anhydride was thus 0·50*M*, and the titre at zero time against *N*/50-thiosulphate was 12·80 c.c.

Time (hours)	12	24	37	47	53	65	72
Fall in titre	0·60	1·45	3·30	4·90	8·60	11·90	12·60

In conclusion, the authors wish to place on record their indebtedness to the late Professor Orton, F.R.S., for his kindly interest and helpful criticism during the progress of this research.

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