The Influences of Aldehydes and Hydroxyaldehydes on the Addition of Hydrogen Bromide to Undecenoic Acid in Presence and in Absence of Oxygen or Reduced Nickel.

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While hydrogen bromide adds to undecenoic acid in benzene or toluene solution under the normal conditions to yield nearly pure 10-bromoundecanoic acid, oxygen(1) and reduced nickel(2)(3)(4) reverse the direction of addition to give rise to the formation of more or less 11-bromoundecanoic acid. Impurities in the undecenoic acid originating in the preparation of the acid from ricinus oil increase the sensitiveness of the acid to oxygen,(1)(5) while the effect of reduced nickel appears not to be influenced by the impurities.(5) On the other hand, antioxidants such as catechol and hydroquinone inhibit the actions of both oxygen and reduced nickel.(3) Ashton and Smith(1) showed that α-heptenylheptaldehyde formed by the action of alcoholic potash on heptaldehyde was a powerful agent to make undecenoic acid sensitive to oxygen and suggested that the heptaldehyde formed during the distillation of ricinus oil must be the origin of the powerful agent in the impure undecenoic acid.

The author has examined the influences of some aldehydes and hydroxyaldehydes, with a view to seeing if there could be a substance capable of exhibiting opposite influences on the effects of oxygen and of reduced nickel, but without finding any. Benzene instead of toluene was used as the solvent throughout the experiments described below, because it has been shown that they give similar results.(1)(4)

The effects of some aldehydes alone on the addition were first examined. Hydrogen bromide was passed into a solution of pure undecenoic acid (1.0 g.) in benzene (15 c.c.) with the addition of the aldehyde (25 mols % to the acid) at 0°C. in the dark for one hour. The mixture was allowed to stand at room temperature in the dark overnight. The reaction was always complete. The composition of 10- and 11-bromoundecanoic acids in the product was determined from the melting (clearing) point as previously. The results are given in Table 1. Compare them with the data quoted in Table 2 from the previous work.

Propylaldehyde, benzaldehyde and salicylaldehyde, which were practically free from peroxides, exhibited but a small influence, if any, on the addition of hydrogen bromide to undecenoic acid (Exp. 1, 3, and 4). On the other hand, the crotonaldehyde used contained peroxide, and accordingly the direction of addition was reversed to some extent (Exp. 2).

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(1) R. Ashton and J. C. Smith, *J. Chem. Soc.*, **1934**, 435.
(2) Y. Urushibara and M. Takebayashi, this Bulletin, **13** (1938), 331.
(3) *Idem, ibid.*, **13** (1938), 404.
(4) M. Takebayashi, *ibid.*, **15** (1940), 113.
(5) Y. Urushibara and M. Takebayashi, *ibid.*, **13** (1938), 574.

Table 1.

Exp. No.	Aldehyde	Product	
		Melting point (°C.)	11-Bromo-acid (%)
1	Propylaldehyde, 0.1 g.	33 0	8
2	Crotonaldehyde containing peroxide, 0.1 g.	29.0	23
3	Benzaldehyde, 0.15 g.	33.2	8
4	Salicylaldehyde, 0.2 g.	33.3	7

Table 2. Undecenoic acid 3.68 g. in the first two exp., 2.5 g. in others. Toluene, 20 c.c.

In presence of	Product	
	Melting point (°C.)	11-Bromo-acid (%)
None (vacuum)	34.7	1
Air	48.7	97
Reduced nickel, 3.0 g.	25.5	34
Air+Catechol, 0.3 g. (22 mols %)	33.5	6
Reduced nickel, 3.0 g.+Catechol, 0.3 g.	33.0	8
Air+Hydroquinone, 0.3 g. (22 mols %)	34.2	3
Reduced nickel, 3.0 g.+Hydroquinone, 0.3 g.	32.6	10

The influences of aldehydes and hydroxyaldehydes on the effects of oxygen and reduced nickel were then examined. The results are summarized in Table 3. Hydrogen bromide was passed into a solution of

Table 3.

Exp. No.	In presence of	Product	
		Melting point (°C.)	11-Bromo-acid (%)
5	Air+Benzaldehyde, 0.15 g.	47.4	92
6	Reduced nickel, 2.3 g.+ Benzaldehyde, 0.15 g.	26.3	32
7	Air+Salicylaldehyde, 0.2 g.	47.2	91
8	Reduced nickel, 2.3 g.+ Salicylaldehyde, 0.2 g.	26.2	32
9	Air+Protocatechualdehyde, 0.2 g.	35.5	52
10	Reduced nickel, 2.3 g.+ Protocatechualdehyde, 0.2 g.	29.2	22
11	Air+Vanillin, 0.2 g.	42.2	72
12	Reduced nickel, 2.3 g.+ Vanillin, 0.2 g.	29.0	23

pure undecenoic acid (1.0 g.) in benzene (15 c.c.) at 0°C. in the dark in the presence of the aldehyde (25 mols % to the acid) and either air (Exp. 5, 7, 9, and 11) or reduced nickel (2.3 g.) (Exp. 6, 8, 10, and 12). Compare the results with Table 2.

Benzaldehyde and salicylaldehyde exhibited negligibly small influences on the actions of oxygen and of reduced nickel (Exp. 5, 6, 7, and 8). Protocatechualdehyde and vanillin exerted weak but noticeable inhibiting influences on the actions of both oxygen and reduced nickel (Exp. 9, 10, 11, and 12). Their inhibiting actions, however, were found far smaller than those of catechol and hydroquinone (compare Table 2).

Experimental.

Materials. Undecenoic acid, reduced nickel, hydrogen bromide, and benzene were the same as described in the previous paper.(4) Propylaldehyde (Kahlbaum, "extra pure") was distilled carefully on the day of use. It gave a very faint colouration with ammonium thiocyanate and ferrous ammonium sulphate, being almost free from peroxide. Crotonaldehyde used was a commercial product containing peroxide in a quantity. Benzaldehyde, a pure product, was distilled in vacuum and used immediately. Salicylaldehyde, a commercial pure material, was distilled in vacuum. It was free from peroxide. Protocatechualdehyde and vanillin were commercial specimens (Kahlbaum, "extra pure") melting at 152° and 80.5°, respectively.

Apparatus and Experimental Procedures. The apparatus was the same that was used in the previous work.(4) In experiments in the presence of aldehydes, undecenoic acid (1.0 g.) and the aldehyde (25 mols % to the acid) were dissolved in a required amount (15 c.c.) of benzene and further 5–6 c.c. of benzene was added. The excess of benzene was distilled off in vacuum at room temperature. In this way air was driven out. Hydrogen bromide was passed into the solution at 0°C. in the dark for an hour. The mixture was left to stand overnight at room temperature in the dark. The reaction mixtures were coloured. The solvent, the aldehyde, and the excess of hydrogen bromide, were removed in vacuum at 60°, and the remaining substance was collected with benzene. The solution was washed with water, dried over calcium bromide, decolourized with animal charcoal, and evaporated in vacuum at 60°.

In the additions in the presence of air and aldehydes, undecenoic acid and the aldehyde were dissolved in benzene. Protocatechualdehyde and vanillin were sparingly soluble in benzene and mostly remained undissolved. Hydrogen bromide was passed into the solution with cooling in ice water for one hour. The reaction mixture was treated as mentioned above. Salicyladehyde was driven out by evacuation. Protocatechualdehyde and vanillin remaining as coloured solids in the solutions were filtered off at 0°C. after hydrogen bromide had been removed in vacuum.

In experiments with reduced nickel and aldehydes, undecenoic acid and the aldehyde were dissolved in benzene beforehand, and the experiments were carried out in the same way as described in the previous paper.(4) The reaction mixture was treated as mentioned above.

The reaction was always complete and the product did not decolourize bromine. The composition of the product was determined from the melting point as previously.

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