The Addition of Hydrogen Bromide to Undecenoic Acid in Toluene Solution. I. The Effect of Reduced Nickel.

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The effect of air on the addition of hydrogen bromide to undecenoic acid in toluene solution was first observed by one of the authors (Y. U.)⁽¹⁾ when he was at a synthetical experiment relating to carpaine with G. Barger and R. Robinson.⁽²⁾ Later R. Ashton and J. C. Smith⁽³⁾ investigated the problem in the light of the observations of M. S. Kharasch and co-workers,⁽⁴⁾ who had found meanwhile the so-called peroxide effect in the addition of hydrogen bromide to unsaturated compounds. Smith and Kharasch with their co-workers have since published respectively several papers on the effect of peroxides and oxygen on the addition reactions of unsaturated compounds.

The present authors, studying the effects of various substances other than oxygen and peroxides on the addition of hydrogen bromide to allyl bromide, observed that reduced nickel and reduced iron influenced this reaction quite in the same way as oxygen.⁽⁵⁾ Since, the effects of ferromagnetic metals as well as of oxygen and peroxides on the addition of hydrogen bromide or bromine to ethylenic compounds have been investigated in this laboratory.⁽⁶⁾ Further, one of the authors⁽⁷⁾ observed

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(1) R. Robinson, *Chemistry & Industry*, **52** (1933), 219.

(2) *J. Chem. Soc.*, **1937**, 714.

(3) *J. Chem. Soc.*, **1934**, 435.

(4) *J. Am. Chem. Soc.*, **55** (1933), 2468, 2521, 2531; **56** (1934), 244.

(5) This Bulletin, **11** (1936), 692, 754; **12** (1937), 51.

(6) J. C. Smith gives an excellent summarizing article on "the 'Peroxide' or 'Oxygen' Effect," *Chemistry & Industry*, **56** (1937), 833. He quotes fully the present authors' works, and on page 836 of that article he writes, "They found a close parallel between the percentages of 1:3-dibromopropane from allyl bromide containing peroxide equivalent to x c.c. of oxygen and from pure allyl bromide to which x c.c. of oxygen had been added before sealing; the total yields of dibromo-compounds were also equal. ....." But, what the present authors intended to show by the results collected in Table 1 of the fifth paper on the addition of hydrogen bromide to allyl bromide, this Bulletin, **12** (1937), 140, is somewhat different from Smith's interpretation, and was really that "both the total yield of the product and the proportion of 1,3-dibromopropane in the product are greater in additions with peroxide-free allyl bromide in the presence of oxygen than in the additions with peroxide-containing allyl bromide in vacuum," and that "while the action of oxygen is very regular ..... the action of the peroxide is rather irregular .... " Discussions on these observations and conclusions drawn from them are given in the mentioned paper (p. 142).

(7) Y. Urushibara and O. Simamura, this Bulletin, **12** (1937), 507.

a close parallelism between the effects of oxygen and reduced nickel on the catalytic action of hydrogen bromide in the isomerization of isostilbene into stilbene. However, ferromagnetic metals have not yet been examined in other addition reactions except in an unsuccessful attempt with cinnamic acid and bromine.(8) Now the authors have returned to undecenoic acid, and the present paper records the results of experiments on the effect of reduced nickel on the addition of hydrogen bromide to undecenoic acid in toluene solution.

Undecenoic acid used was a commercial product (Kahlbaum, "extra pure") melting at 23.8° (corr.) and can be regarded fairly pure. It gave no colouration with ammonium thiocyanate and ferrous ammonium sulphate, being free from peroxide. Hydrogen bromide was prepared by the action of purified bromine on hot tetralin, washed by passing through cold tetralin and over moist red phosphorus, then dried with anhydrous calcium bromide and with phosphorus pentoxide. Toluene, free from thiophene, was redistilled over metallic sodium.

The apparatus is shown schematically in Fig. 1. The whole is made of Pyrex glass. A is a side tube of 22 mm. diameter and 120 c.c. capacity, B the reaction tube of 22 mm. diameter and 130 c.c. capacity, C the inlet tube of 7 mm. diameter for hydrogen bromide and hydrogen, and D the outlet for excessive hydrogen bromide and for evacuation. C was connected with the source of purified hydrogen bromide. Between them two three-way cocks were inserted, one way of the cock nearer to C being connected with the source of hydrogen through another three-way cock. These cocks were provided for manipulation of excluding air. During the passing of hydrogen bromide a calcium chloride tube was attached to D.

In experiments in presence of air undecenoic acid and toluene were directly mixed in B and hydrogen bromide was passed with cooling in ice water. In additions in vacuum (in absence of air) undecenoic acid was dissolved in a required amount of toluene in A, the volume of the solution was marked on A, and further 5–6 c.c. of the solvent was added. The excess of toluene was distilled off at room temperature by evacuation through D, while tube B was warmed in a hot water bath to avoid the condensation of toluene in it. In this way air was driven out. When the volume of the solution reached the mark, the stopcock of D was closed, B cooled in ice water, the contents of A decanted into B, and hydrogen bromide passed into the solution with caution. In experiments with reduced nickel, the catalyst was placed in B beforehand and heated in

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(8) This Bulletin, **12** (1937), 506.

a hot water bath during the distillation of toluene as above. When the solution in A was reduced to the required volume, it was frozen by cooling in liquid air while the nickel in B was heated to 350–360°, evacuation being continued. The stopcock of D was closed, hydrogen introduced from C, and after a while the vessel evacuated again. This process was repeated three times, cooling of A and heating of B being continued. Then B was cooled to room temperature under evacuation. D was closed, A taken out of liquid air, and B immersed in ice water. The nickel was sometimes washed with hydrogen bromide gas. Then the solution in A was decanted on reduced nickel in B, and hydrogen bromide introduced.

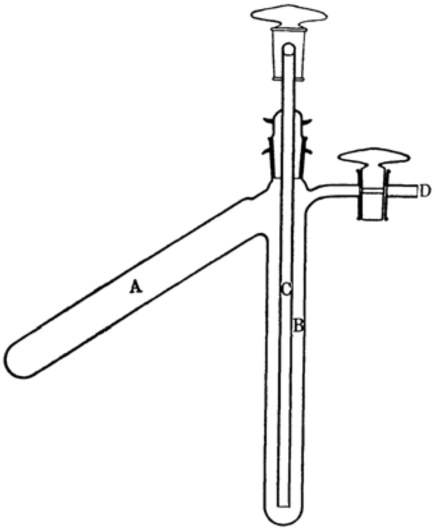

Fig. 1.

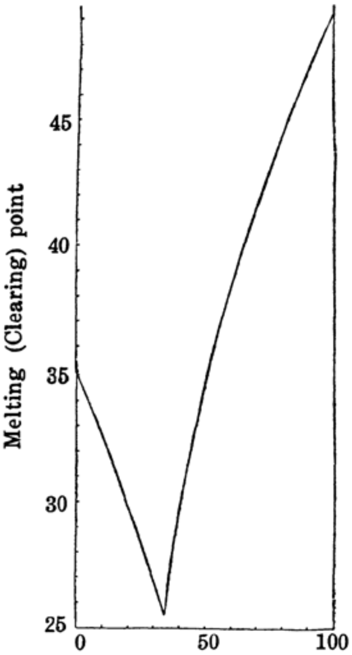

Fig. 2.

Hydrogen bromide was passed at 0°C. in the dark for one hour. The mixture was left to stand overnight at 0°C. in the dark. Toluene and the excess of hydrogen bromide were removed in vacuum at 50°, and the remaining substance was collected with toluene. When reduced nickel was used, the catalyst was filtered off and washed with toluene. The toluene solution was again evaporated in vacuum at 50°. The product was obtained always in quantitative yield, and did not decolourize bromine.

It was brought to crystallization by cooling to −5° if necessary, and pressed on cooled porous plates.

The proportion of 10- and 11-bromo-undecoic acids in the reaction product was determined by observing the melting (clearing) point. For this the data of Ashton and Smith(9) for the binary mixtures of the two bromo-acids were used. A melting points–composition curve (Fig. 2) was drawn and the compositions of the samples were obtained on the curve. To decide on which side of the eutectic point a sample fell, the melting points of mixtures with suitable amounts of 11-bromo-undecoic acid were observed.

No. of exp.	Undecenoic acid (g.)	Toluene (c.c.)	In presence of	Product	
				Melting point (°C.)	11-Bromo-acid (%)
1	5.0	5	None (vacuum)	34.5	2
2	3.68 (0.02 mol)	20	None (vacuum)	34.7	1
3	5.0	5	Hydrogen	34.7	1
4	5.0	5	Air	29.8	20
5	3.68	20	Air	48.7	97
6	5.0	5	Reduced nickel 3.0 g.	33.0	8
7	2.5	20	Reduced nickel 3.0 g.	25.5	34
8	2.5	20	Reduced nickel 3.0 g. HBr passed for 1.5 hrs.	31.1	42
9	3.68	20	Reduced nickel 1.2 g.	29.5	21
10	3.68	20	Reduced nickel 3.5 g. +Hydrogen	30.0	19
11	3.68	20	Reduced nickel 6.0 g.	25.6	34

The results of experiments are given in the accompanying table. As regards the effect of air the observations of Ashton and Smith were con-

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(9) *J. Chem. Soc.*, **1934**, 440.

firmed: In vacuum the product was nearly pure 10-bromo-undecoic acid no matter whether the solution was concentrated (Exp. 1) or dilute (Exp. 2). The effect of air, giving rise to the formation of 11-bromo-undecoic acid, was comparatively small in the concentrated solution (Exp. 4), while it was marked in the dilute solution (Exp. 5).

An effect similar to that of oxygen was observed with reduced nickel. Moreover, an analogous relation was found between the concentration of undecenoic acid and the effect of reduced nickel: the smaller the former the greater the latter (Exp. 6 and 7). Experiments on the relation between the amount of reduced nickel and the proportion of the 11-bromo-acid resulted as expected: as the former increased, so did the latter (Exp. 9 and 11). However, the effect of reduced nickel on the addition of hydrogen bromide to undecenoic acid in toluene solution has been found rather small compared with that of oxygen in view of the strong effect of the former in the case of allyl bromide. Hydrogen showed no significant effect (Exp. 3 and 10). The greater proportion of the 11-bromo-acid obtained on passing hydrogen bromide for a longer time (Exp. 8) was probably caused by correspondingly longer agitation of the reaction mixture.

While reduced nickel suffered no change during the reaction, reduced iron was attacked by hydrogen bromide or undecenoic acid in an addition in its presence.

Now experiments on the influence of antioxidants on the effect of oxygen and reduced nickel are under way, and the results will soon be ready for publishing.

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