The Effect of Reduced Nickel on the Addition of Hydrogen Bromide to Undecenoic Acid in Various Solvents.

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(Received February 24, 1940).

In the previous work with Y. Urushibara⁽¹⁾ it was established that, while hydrogen bromide adds to pure undecenoic acid in toluene solution in the absence of oxygen to yield nearly pure 10-bromoundecanoic acid, the presence of reduced nickel reverses the direction of addition to some extent and, for instance, about one-third of the product formed in moderately dilute toluene solution is 11-bromoundecanoic acid (oxygen is far more potent in producing the same effect). In the previous experiments toluene was used exclusively as the solvent. The present paper records the results of the additions in the presence of reduced nickel in various solvents, which are summarized in the accompanying table.

Hydrogen bromide was passed into a solution of 1.0 g. undecenoic acid in 15 c.c. of the solvent in the presence of 2.3 g. of reduced nickel at 0°C. in the dark for one hour. The mixture was left to stand overnight and the product was examined. The reaction was always complete. The proportion of 10- and 11-bromoundecanoic acids in the reaction product was determined by observing the melting (clearing) point.

In benzene, toluene, ligroin, and carbon tetrachloride, reduced nickel suffered no change during the reaction, and the effect was as marked as previously observed in toluene (somewhat smaller in ligroin) (Exp. 1, 2, 3 and 7). On the other hand, in acetic acid and ether reduced nickel was attacked seriously by hydrogen bromide, the solution being coloured greenish, and the effect of the metal was found very weak (Exp. 4 and 5). In chloroform, the metal was attacked slightly but the solution was not

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(1) Y. Urushibara and M. Takebayashi, this Bulletin, **13** (1938), 331, 404, 574.

Exp. No.	Solvent	Product	
		Melting point (°C.)	11-Bromo-acid (%)
1	Benzene	26.0	33
2	Toluene	25.8	33
3	Ligroin	27.3	28
4	Acetic acid	32.0	12
5	Ether	(liquid)	
6	Chloroform	29.8	20
7	Carbon tetrachloride	26.0	33

coloured, and the proportion of 11-bromo-acid in the product was intermediate (Exp. 6). These results appear to be in harmony with the previous experiences in the addition of hydrogen bromide to allyl bromide that the abnormal (reversely directed) addition was caused only by the metallic surface of the ferromagnetic metals, viz., nickel and iron, whereas their salts, viz., ferric chloride added,(2) nickel bromide formed in case of the contamination of the metal by its oxide,(3) and cobalt bromide produced owing to the little resistance of metallic cobalt to the attack by hydrogen bromide,(3) promoted the normal addition. However, in view of the fact that the action of oxygen on the addition of hydrogen bromide to undecenoic acid was impeded in acetic acid and ether,(4) the effect of reduced nickel might not be allowed to appear even if the metal were not attacked by hydrogen bromide in these solvents.

Experimental.

Materials. 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 generated by the action of bromine on hot tetralin, passed through cooled tetralin, over anhydrous calcium bromide and anthracene, and through a tube cooled with ice and salt, condensed in a vessel cooled with solid carbon dioxide and ether, and vaporized, the middle fraction only being used. Reduced nickel was prepared by reducing nickel oxide (Kahlbaum) with hydrogen at 350–400°C. and reduced again in the atmosphere of hydrogen at 350°C. in the reaction tube.

Benzene and toluene, free from thiophene, were redistilled over metallic sodium. Ligroin was washed with sulphuric acid, aqueous sodium carbonate, and water, dried over calcium chloride, and distilled over sodium (boiling point 80–95°C.). Acetic acid was refluxed with 2% of its weight of potassium permanganate, distilled, dried over phosphorus pentoxide, and purified by fractional distillation. Ether was washed repeatedly with concentrated sulphuric acid until the latter remained colourless, shaken with an alkaline aqueous solution of potassium permanganate, washed with water, dried over calcium chloride, and distilled. The ether purified in this way was free from peroxide. Chloroform was shaken several times with about half its volume of water and then dried over calcium chloride, and distilled over phosphorus pentoxide. Carbon tetrachloride was refluxed with an alkaline solution of potassium permanganate, washed with water, dried over calcium chloride, distilled, and redistilled with the addition of phosphorus pentoxide.

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(2) M. S. Kharasch and F. R. Mayo, *J. Am. Chem. Soc.*, **55** (1933), 2468.
(3) Y. Urushibara and M. Takebayashi, this Bulletin, **11** (1936), 755; **12** (1937), 51.
(4) R. Ashton and J. C. Smith, *J. Chem. Soc.*, **1934**, 435.

Apparatus and Experimental Procedures. The main part of the apparatus consists of a reaction tube (R) of 22 mm. diameter and 100 c.c. capacity, a side tube (S) of 22 mm. diameter and 90 c.c. capacity an inlet tube (I) for hydrogen bromide and hydrogen, and an outlet (O) for excessive hydrogen bromide and for evacuation. The whole is made of Pyrex glass.

Undecenoic acid (1.0 g.) was dissolved in a required amount (15 c.c.) of the solvent in S, the volume of the solution was marked on S, and further 5 c.c. of the solvent was added. Reduced nickel was placed in R. The whole system was evacuated at room temperature. Thus the excess of the solvent was distilled off through O. In this way air was driven out. When the volume of the solution reached the mark, the solution was frozen by cooling in liquid air while the nickel in R was heated to 350°C., evacuation being continued. The stopcock of O was closed, hydrogen introduced from I, and after a while the vessel evacuated again. This process was repeated several times, cooling of S and heating of R being continued. Then R was cooled to room temperature under evacuation. O was closed, and S taken out of liquid air. Then the solution in S was decanted on reduced nickel in R, and hydrogen bromide introduced.

Hydrogen bromide was passed at 0°C. in the dark for one hour. The mixture was left to stand at room temperature in the dark overnight. The solvent and the excess of hydrogen bromide were removed in vacuum at 50°C., and the remaining substance was collected with the solvent. The nickel was filtered off and washed with the solvent. The solution was again evaporated in vacuum at 60°C. The product was always obtained in quantitative yield, and did not decolourize bromine. The product was cooled to crystallization and pressed on cooled porous plates.

The proportion of 10- and 11-bromoundecanoic acids in the reaction product was determined by observing the melting (clearing) point. For this purpose the data of Ashton and Smith(4) for the binary mixtures of the two bromo-acids were employed.

The author expresses his hearty thanks to Prof. Y. Urushibara of the Imperial University of Tokyo for his kind guidance and to Prof. K. Ishikura, the director of the Osaka Higher School, for his encouragement. Thanks are also due to the Imperial Academy of Japan and to Hattori Hoko Kwai for grants.

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