The Addition of Hydrogen Bromide to Allyl Bromide in the Presence of Various Substances. VII. The Effect of Nickel in the Form of Filings, and the Influence of Antioxidants on the Actions of Oxygen and Reduced Nickel.

By Yoshiyuki URUSHIBARA and Matsuji TAKEBAYASHI.

(Received March 31, 1938.)

In the presence of oxygen and peroxides hydrogen bromide adds slowly to allyl bromide and the product consists of nearly pure 1,2-dibromo-propane, while in the presence of oxygen or a peroxide the addition is rapid and 1,3-dibromo-propane is formed as the main product.⁽¹⁾ The addition of an antioxidant such as diphenylamine to the reaction mixture eliminates the effect of oxygen and peroxides.⁽¹⁾ Reduced nickel and reduced iron show an effect quite similar to that of oxygen so far as

---

(1) M. S. Kharasch and F. R. Mayo, *J. Am. Chem. Soc.*, **55** (1933), 2468.

the results of the reaction are concerned.(2) However, the action of these metals is not influenced by diphenylamine.(3) Further, it seems that no parallelism exists between the hydrogenating activity of reduced nickel and the effect on the addition: reduced nickel prepared at a temperature too high for a hydrogenating catalyst showed a very strong effect on the addition.(4) The present paper deals with an experiment on the effect of nickel filings and a comparative investigation of the influence of antioxidants on the actions of oxygen and reduced nickel. The results of experiments are summarized in the accompanying table.

Table.

Allyl bromide 24 g. (0.2 mol). Hydrogen bromide 20 g. (0.25 mol).
Addition in the dark at room temperature (12-15°). Reaction time 3 days.

Exp.	In presence of	Products		
		Total yield (%)	B. p. (°C./mm.)	1,3-Dibromo-propane (%)
1	None (vacuum)	25	28-32/10	4
2(5)	Oxygen 2.5 c.c.	53	42-51.5/9	96
3	Reduced nickel 3.5 g.	55	38-46.5/8	91
4	Nickel filings 7.0 g.	50	38-49.5/10	68
5	Diphenylamine 0.5 g. (1.5 mol %) Oxygen 2.0 c.c.	28	28-32/9	9
6	Diphenylamine 0.5 g. Reduced nickel 3.5 g.	55	43-55/12	81
7	Catechol 0.3 g. (1.5 mol %) Oxygen 2.0 c.c.	27	28-32/9	9
8	Catechol 0.3 g. Reduced nickel 3.5 g.	26	28-32/10	12
9	Hydroquinone 0.3 g. (1.5 mol %) Oxygen 2.0 c.c.	25	32-35/13	7
10	Hydroquinone 0.3 g. Reduced nickel 3.5 g.	29	35-40/14	20

Pure allyl bromide (24 g. or 0.2 mol) and hydrogen bromide (20 g. or 0.25 mol) were sealed in reaction tubes of Pyrex glass in addition of none (vacuum) (Exp. 1), oxygen (2.5 c.c.) (Exp. 2),(5) reduced nickel (3.5 g.) (Exp. 3), nickel filings (7.0 g.) (Exp. 4), oxygen (2.0 c.c.) and

---

(2) Y. Urushibara and M. Takebayashi, this Bulletin, **11** (1936), 692, 754; **12** (1937), 51.

(3) Y. Urushibara and M. Takebayashi, *ibid.*, **11** (1936), 754.

(4) Y. Urushibara and M. Takebayashi, *ibid.*, **12** (1937), 51.

(5) Exp. 12 of the fifth paper of this series, *ibid.*, **12** (1937), 140.

an antioxidant (1.5 mol%) (Exp. 5, 7, and 9), and reduced nickel (3.5 g.) and an antioxidant (1.5 mol%) (Exp. 6, 8, and 10). The substances used as antioxidants were diphenylamine (Exp. 5 and 6), catechol (Exp. 7 and 8), and hydroquinone (Exp. 9 and 10). The reaction tubes were shaken during daytime and left to stand still at night for three days in the dark at room temperature (12–15°C.). Then the yield and the composition of the products were determined.

Although it can be supposed that nickel filings might possess a comparatively small surface area in spite of the amount doubled and the nature of the surface might be quite different from that of the surface of reduced nickel, the filings exhibited an unexpectedly great effect (Exp. 4).

All the antioxidants so far used eliminated nearly completely the effect of oxygen (Exp. 5, 7, and 9), a confirmation of the results of Kharasch and Mayo,(1) while the effect of reduced nickel was diminished only slightly by diphenylamine (Exp. 6) in accord with previous observations(3) but rather heavily by catechol (Exp. 8) and by hydroquinone (Exp. 10). Parallel results have been obtained in the addition of hydrogen bromide to undecenoic acid as reported in the following paper.

An assurance that the effect of ferromagnetic metals is due to the action of the metals themselves and not of oxygen which might be present by chance was afforded by the fact that diphenylamine eliminates the effect of oxygen but not that of ferromagnetic metals.(3) This remains still true, but such an assurance could not have been obtained by the experiments with catechol and hydroquinone. However, that the ferromagnetic metals themselves are responsible for the effect observed in the addition in their presence was further established by the experiments with the metals which had never been in contact with oxygen (air) after repeated reduction in the reaction tube.(4)

Kharasch and co-workers(6) propose a hypothesis that bromine atoms are responsible for the effect of oxygen and peroxides in the addition of hydrogen bromide to unsaturated compounds. It is supposed that bromine atoms are produced by the action of oxygen or a peroxide on hydrogen bromide. However, it can not reasonably be assumed that reduced nickel would exhibit an oxidation-like effect on hydrogen bromide to produce bromine atoms, and, therefore, the influence of catechol and hydroquinone on the action of reduced nickel can hardly be attributed to the antioxidant effect of these substances. It is very probable that

---

(6) M. S. Kharasch, H. Engelmann, and F. R. Mayo, *J. Org. Chem.*, **2** (1937), 298.

the modes of influence of the antioxidants on the actions of nickel and oxygen are so much different as the modes of action of these catalysts on the addition. The authors will come back to this problem some other time.

Experimental.

Allyl bromide was purified by drying over calcium chloride and then redistilling in addition of hydroquinone. The absence of peroxides was ascertained by the test with ferrous ammonium sulphate and ammonium thiocyanate. 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. Diphenylamine and hydroquinone were purified by recrystallization from ligroin and from alcohol respectively, while commercial catechol (E. Merck) was used directly. Reduced nickel was prepared by reducing nickel oxide (Kahlbaum) with hydrogen at about 400°. Nickel filings were prepared from an ordinary thick nickel wire with a new file.

The experimental procedure was as follows. Exp. 5, 7 and 9: Allyl bromide (24 g. or 0.2 mol) and the antioxidant (1.5 mol per cent) were taken in the reaction tube, and cooled in a mixture of solid carbon dioxide and chloroform. Hydrogen bromide was passed into the tube until the required increase in the volume of the liquid (corresponding to 20 g. or 0.25 mol of hydrogen bromide) was reached (total volume 27 c.c.). Then the tube was cooled in liquid air, evacuated, and sealed off after admission of oxygen (2.0 c.c.). Exp. 1: Allyl bromide was taken in a mixing tube and hydrogen bromide condensed. Then the mixture was frozen in liquid air, the mixing tube was joined by fusion with the reaction tube, and the whole system was evacuated. The mixing tube was taken out of liquid air and the reaction tube was put into liquid air, whereby the mixture distilled into the reaction tube in vacuum. The tube was then sealed off without entrance of air. Exp. 3 and 4: Reduced nickel (3.5 g.) or nickel filings (7.0 g.) were taken in the reaction tube already joined with the mixing tube containing the frozen mixture of allyl bromide and hydrogen bromide, and, while the mixture was cooled in liquid air, the nickel was heated to 350–360° or above in the atmosphere of hydrogen, hydrogen being renewed three times by evacuation and introduction. Then the tubes were evacuated, the nickel cooled down, the mixing tube taken out of liquid air, and the reaction tube put into liquid air and sealed off in vacuum when the distillation of the mixture was over. Exp. 6, 8 and 10: The mixture of allyl bromide and the antioxidant was decanted in vacuum into the reaction tube cooled in solid carbon dioxide and chloroform after the reduced nickel was treated as mentioned above, and hydrogen bromide was passed into the reaction tube. The mixture was frozen in liquid air and sealed in vacuum.

The reaction tubes were slipped into iron pipes, and shaken during daytime at room temperature. After three days the reaction mixtures were treated according to the directions of Kharasch and Mayo,(1) and the compositions of the products were determined from the refractive indices, while the total yields from the weights.

Diphenylamine and hydroquinone gave yellow and brown colours respectively to the reaction mixtures in presence of oxygen, while catechol a reddish violet colour in presence of either reduced nickel or oxygen.

The authors thank the Imperial Academy of Japan for a grant.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.