Purification of *d*-Pimaric Acid.—A solution of 11 g. of *d*-pimaric acid[8] (melting point 218–220°) and 5 g. of freshly distilled maleic anhydride in 100 cc. of xylene was refluxed for five hours. The solution was allowed to stand at room temperature overnight and the crystals that separated were filtered off and discarded. The filtrate was shaken with water until the aqueous extract reacted neutral to congo red. The xylene was distilled with steam and the crystalline residue was dissolved in 200 cc. of acetone and 3 g. of diethylamine. The resulting diethylamine salt was recrystallized six times from acetone, then the acid was freed by addition of dilute hydrochloric acid and extracted with ether. The washed ether solution was evaporated to dryness and the residue recrystallized from alcohol. When dried in vacuum at room temperature, the *d*-pimaric acid melted at 218–219°; $[\alpha]^{20}\mathrm{D}$ +75° (2% absolute alcohol), yield, 3.5 g.

Summary

A hydroxy-lactone, $C_{20}H_{32}O_3$, has been prepared from *d*-pimaric acid by sulfonation at low temperatures.

Modifications of the structural formula of *d*-pimaric acid have been proposed.

A new method for the estimation of the maximum amount of *d*-pimaric acid present in the acid portion of oleoresin and rosin has been advanced.

The presence of dihydro-*l*-pimaric or dihydroabietic acid and *l*-pimaric acid in *d*-pimaric acid preparation has been demonstrated.

WASHINGTON, D. C. RECEIVED MAY 24, 1940

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

The Peroxide Effect in the Addition of Reagents to Unsaturated Compounds. XXV. The Effect of Metals on the Addition of Hydrogen Bromide to Allyl Bromide

BY M. S. KHARASCH, W. R. HAEFELE[1] AND FRANK R. MAYO

It has been shown by Kharasch and Mayo[2] that in the absence of air and peroxides, or in the presence of antioxidants, the interaction of allyl bromide and hydrogen bromide results in the formation of the normal addition product, 1,2-dibromopropane, whereas the oxygen- or peroxide-promoted reaction gives rise to the abnormal addition product, 1,3-dibromopropane.[3] It was subsequently reported by Urushibara and Takebayashi that when the reaction takes place in the presence of finely divided and freshly reduced iron, nickel, or cobalt, the major product is also the abnormal 1,3-dibromide[4a,c] even in the absence of oxygen and peroxides.

According to the hypothesis proposed by Kharasch, Engelmann and Mayo,[5] the abnormal addition is a chain reaction in which bromine atoms are chain carriers. At one time, Urushibara and co-workers maintained that the abnormal addition was the result of a physical effect due to the paramagnetism common to oxygen and the effective metals.[4d,6] They have now accepted the chain mechanism for the oxygen-promoted abnormal addition.[4j] Other work from their laboratory has shown that the metals are attacked to varying degrees by hydrogen bromide,[4a,b,c,i] and that catechol and hydroquinone,[4f] but not diphenylamine,[4b,f] inhibit the metal-promoted abnormal addition of hydrogen bromide to allyl bromide, as well as to undecenoic acid[4e,g,h] in toluene solution.

The present work was undertaken to verify the effects of metals on the addition of hydrogen bromide to allyl bromide and to correlate these effects with the bromine atom chain hypothesis for the abnormal addition reaction. This correlation has been accomplished in a study of the action of several metals and their bromides on hydrogen bromide–allyl bromide mixtures and of their effects on the normal and abnormal addition reactions.

Addition in the Presence of Iron.[7]—In a series of experiments in which 1.5–1.6 mole of hydrogen

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[1] This paper is a condensation of a thesis submitted by W. R. Haefele in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The University of Chicago, 1939. The dissertation should be consulted for exact details of the experiments cited in this paper.

[2] Kharasch and Mayo, THIS JOURNAL, **55**, 2468 (1933).

[3] It is possible to obtain either 1,2- or 1,3-dibromopropane exclusively. This correction to previous work, which indicated that only about 90% of either product could be formed, is explained in the experimental part of this paper.

[4] Urushibara and Takebayashi, *Bull. Chem. Soc. Japan*, **11**, (a) 692, (b) 754 (1936); **12**, (c) 51, (d) 173 (1937); **13**, (e) 331, (f) 400, (g) 404, (h) 574 (1938); Urushibara and Sinamura, *ibid.*, (i) **13**, 570 (1938); (j) **14**, 323 (1939).

[5] Kharasch, Engelmann and Mayo, *J. Org. Chem.*, **2**, 288 (1937).

[6] That the paramagnetic properties of oxygen might be responsible for the peroxide effect was considered by Kharasch and Mayo,[2] but the lack of effect of the strongly paramagnetic nitric oxide and nitrogen dioxide led to rejection of the hypothesis.

[7] Except as otherwise noted, all of the experiments described in this paper were carried out with peroxide-free allyl bromide at 20–30°, in the absence of air, solvents, and light. Proportions of reagents are expressed in mole % on the basis of the allyl bromide used. About 50% excess hydrogen bromide was used.

bromide reacted with one mole of allyl bromide in the presence of 0.32 mole of finely divided, freshly reduced iron, it was found that at the end of the allotted reaction times (three to seven days) the iron had reacted with the hydrogen bromide to extents varying from 11 to 82%. In all of these experiments substantially complete (93–99%) addition was attained; the proportion of abnormal addition product (1,3-dibromopropane) varied from 26 to 77%.

In a similar series of experiments (1.3 moles of hydrogen bromide; 0.02–0.41 mole of iron) in which the reaction mixtures were agitated on a shaking machine, reaction was substantially complete in one hour, and the product was 94 to 97% 1,3-dibromopropane. In these experiments the amount of iron reacting was less (4 to 23%) than in those in which the system was not agitated. A comparable effect of shaking on the rate of abnormal addition was noted when air was substituted for iron (97% yield of 1,3-dibromopropane was formed in one day).

The effect of antioxidants (0.03 mole) on the iron-promoted abnormal addition was investigated in a supplementary series of experiments. Catechol and thiophenol were found to suppress the abnormal reaction completely; phenol and resorcinol were less effective (17 and 13% of abnormal product, respectively); diphenylamine was even less effective (43–61% of abnormal product), partly, no doubt, because of the insolubility of hydrobromide in the reaction mixture.

Mechanism of the Iron-Promoted Abnormal Addition.—Experiments show that metals which do not react with hydrogen bromide do not promote abnormal addition. Therefore, the reaction of iron with hydrogen bromide in our experiments is taken to be significant and essential. If it be conceded that the demonstrated interaction of iron with hydrogen bromide may result in the availability of at least a few hydrogen atoms, the iron-promoted abnormal addition differs from the oxygen-promoted abnormal addition only in the manner in which chains are initiated. Some reactions which might lead to the formation of bromine atoms are suggested:

(1) $\mathrm{HBr + Fe \longrightarrow BrFe\cdot + H\cdot}$

(2) $\mathrm{HBr + H\cdot \longrightarrow H_2 + Br\cdot}$

(3a) $\mathrm{H_2C{=}CH{-}CH_2Br + H\cdot \longrightarrow H_3C{-}CH{-}CH_2Br}$

(3b) $\mathrm{H_3C{-}CH{-}CH_2Br + HBr \longrightarrow H_3C{-}CH_2{-}CH_2Br + Br\cdot}$

(4a) $\mathrm{H_2C{=}CH{-}CH_2Br + H\cdot \longrightarrow H_2C{=}CH{-}CH_2\cdot + HBr}$

(4b) $\mathrm{H_2C{=}CH{-}CH_2\cdot + HBr \longrightarrow H_2C{=}CH{-}CH_3 + Br\cdot}$

(5) $\mathrm{H_2C{=}CH{-}CH_2Br + Fe \longrightarrow H_2C{=}CH{-}CH_2\cdot + BrFe\cdot}$ (followed by 4b)

According to the hypothesis of Kharasch, Engelmann, and Mayo,[5] the bromine atom would acquire a sharing interest in one of the electrons of the doubly-bound carbon atom with the relatively negative charge, and reaction chains would be carried on as indicated in equations 6a and 6b

(6a) $\mathrm{H_2C{=}CH{-}CH_2Br + Br\cdot \longrightarrow BrH_2C{-}\underset{\cdot}{C}H{-}CH_2Br}$

(6b) $\mathrm{BrH_2C{-}\underset{\cdot}{C}H{-}CH_2Br + HBr \longrightarrow BrH_2C{-}CH_2{-}CH_2Br + Br\cdot}$

Presumably, agitation of the reaction mixtures facilitates the utilization of atomic hydrogen as a chain-initiator. The inhibitory effects of antioxidants are probably related to their relative efficiencies as chain-breakers.

Mechanism of the Normal Addition.—Urushibara and Sinamura[4] have suggested that the normal addition of hydrogen bromide to allyl bromide is also a chain reaction in which the hydrogen atom is the chain carrier

(7a) $\mathrm{H_2C{=}CH{-}CH_2Br + H\cdot \longrightarrow H_3C{-}\underset{\cdot}{C}H{-}CH_2Br}$

(7b) $\mathrm{H_3C{-}\underset{\cdot}{C}H{-}CH_2Br + HBr \longrightarrow H_3C{-}CHBr{-}CH_2Br + H\cdot}$

They do not suggest the source of hydrogen atoms in ordinary normal additions nor do they explain why in reaction 6b (with 6a now accepted by them as satisfactorily representing the course of the peroxide-promoted abnormal addition), the 1,3-dibromoisopropyl radical combines with the hydrogen of hydrogen bromide, whereas in reaction 7b the 1-bromoisopropyl radical combines with the bromine of hydrogen bromide. On the basis of estimated bond energies (C–H, 88 kcal.; C–Br, 50 kcal.; H–Br, 87 kcal.), reaction 7b would appear to be endothermic by 37 kcal. The activation energy may exceed this value. These considerations throw considerable doubt on the mechanism proposed by Urushibara and Sinamura for the normal reaction. It is more likely that this reaction involves ions and/or molecular complexes.[8]

Effects of Other Metals and Metal Halides.—Attempts to initiate abnormal addition with metals other than iron, nickel, and cobalt failed. Neither tungsten nor silicon reacts appreciably

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[8] Kinetic studies that promise to throw more light on the mechanism of the normal addition are now in progress in this Laboratory by one of us (F. R. M.).

with hydrogen bromide under the experimental conditions employed; hence, on the basis of the mechanism proposed, it is not surprising that neither promoted the abnormal addition.

Rapid normal addition reaction in the presence of zinc, zinc bromide, and thallium (98–100% in one day), as compared with the uncatalyzed reaction (67–71% in eight days), shows that bromides of these metals are powerful catalysts for the normal addition reaction. This effect obscures any other that the metals might have in promoting a competing abnormal addition. These additions were probably complete in a fraction of the full day permitted to elapse.

Cadmium, copper, lead, and tin react with hydrogen bromide to yield halides which are only weak accelerators of the normal addition reaction but which were found to be inhibitors for the abnormal addition reaction.[2] Hence any tendency of these metals to yield hydrogen atoms on reaction with hydrogen bromide is overshadowed by the inhibiting properties of their bromides. The effect is best illustrated by experiments with copper. Copper reacts readily with hydrogen bromide,[2] but cuprous bromide (even 0.5%), added at the beginning of the reaction or formed from the metal, prevents completely the abnormal addition which ordinarily would take place in the presence of air, or even of reduced iron. Similar effects are indicated by experiments with tin and stannous bromide,[2] but apparently the amount of stannous bromide present and its susceptibility to oxidation by air are critical factors in determining the products of the reaction. The bromides formed from cadmium and lead also inhibit the air-promoted abnormal addition.[2]

These experiments indicate that the bromides of iron, nickel, and cobalt, the metals which cause abnormal addition of hydrogen bromide to allyl bromide, must be neither strong catalysts for the normal addition nor strong inhibitors of the abnormal addition. Supplementary experiments confirm this conclusion. Ferrous, nickelous, and cobaltous bromides are weak to moderate accelerators of the normal reaction. That they are weak inhibitors of the abnormal reaction is shown by the fact that they inhibited the abnormal addition induced by air, but not by reduced iron. Experiments with organic antioxidants similarly show that it is more difficult to inhibit the iron-promoted than the air-promoted abnormal reaction.

Addition of Hydrogen Bromide to Other Olefins.—In two experiments similar to the allyl bromide experiments already described, allyl chloride was allowed to react with hydrogen bromide in the presence of iron. Addition products containing 36 and 38% of the abnormal 1-bromo-3-chloropropane were obtained.

It has previously been reported[9] that an inhibitor is required to suppress the abnormal addition of hydrogen bromide to vinyl chloride, even in the absence of air. Ferrous bromide served the purpose fairly well, for when a mixture was shaken with ferrous bromide in the absence of air for three days an 84% yield of addition product containing 95% of the normal 1-bromo-1-chloroethane was obtained. In a similar experiment in which 0.26 mole of iron (but no initial ferrous bromide) was present, a 92% yield of addition product containing 87% of the abnormal 1-bromo-2-chloroethane was obtained. This may be construed as at least presumptive evidence that iron promotes the abnormal addition of hydrogen bromide to vinyl chloride.

Attempts to induce abnormal addition of hydrogen bromide to propylene, isobutylene, and styrene by means of iron failed completely, doubtless because of the fact that the normal additions are so rapid in these cases that reaction is complete before a significant amount of iron has had opportunity to react with hydrogen bromide.

General Conclusions

On the basis of the interpretation of metal-promoted abnormal addition already outlined, it is concluded from the data presented that the conditions for efficacy are that the metal react fairly readily with anhydrous hydrogen bromide, and that the metallic bromide formed be neither a strong accelerator of the normal addition nor a powerful inhibitor (chain-breaker) for the abnormal addition.

From the fact that some substances (*e. g.*, diphenylamine, and ferrous, nickelous, and cobaltous bromides) suppress abnormal addition initiated by atmospheric oxygen, but not by reduced iron, whereas other substances (*e. g.*, thiophenol, and cuprous and stannous bromides) suppress abnormal addition initiated by either air or iron, it is concluded that iron and hydrogen bromide are more effective chain-initiators than air and hydrogen bromide. The efficacy of some inhibitors in

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[9] Kharasch and Hannum, THIS JOURNAL, **56**, 712 (1934).

low concentrations suggests that the average chain length in an abnormal addition reaction must be great. The intermediate inhibitory power of resorcinol and phenol (as compared with diphenylamine, on the one hand, and with catechol, on the other) indicates that not all potentially chain-terminating collisions are effective. However, the inefficacy of diphenylamine and of some of the metallic bromides may be due, in part at least, to insolubility rather than to intrinsic inefficiency.

Experimental

Reagents.—Allyl bromide was prepared by the method of Kharasch and Mayo[2] and fractionally distilled; $n^{20}D$ 1.4695. Peroxides were removed by washing with aqueous ferrous sulfate and sulfuric acid, and drying was effected by distillation from phosphorus pentoxide.

Reduced iron was obtained from Merck and Co., and immediately before use was further treated for one hour with dry oxygen-free hydrogen at a temperature just below red heat. The iron was cooled in a current of hydrogen and weighed into the reaction tube. The tube was then alternately evacuated to 10^{-5} mm. and filled with hydrogen several times at 350°. The evacuated tubes were then closed off by a stopcock until used. Check experiments showed no difference between individual samples so treated and used and material not exposed to air at all after the first reduction.

Tungsten was finely powdered commercial metal; silicon was the gray powder obtained by thermal decomposition of silane; zinc was "Baker's Analyzed" (30-mesh); thallium was in the form of 40-mesh particles of fused metal; cadmium turnings from a bar of c. p. metal; lead, 70-mesh granulated; copper, reduced copper oxide, and Eimer and Amend electrolytic powder; tin, Mallinckrodt c. p. granulated (*ca.* 20-mesh); cuprous bromide, Baker purified, powdered; stannous bromide (anhydrous), from metal and aqueous hydrogen bromide; ferrous bromide (anhydrous), from metal and aqueous hydrogen bromide, dried by heating in a stream of hydrogen bromide; nickelous bromide (anhydrous), from carbonate and anhydrous hydrogen bromide.

General Procedure.—The general procedure was like that described by Kharasch and Mayo,[2] one-twelfth mole of allyl bromide being used. Reaction tubes, containing iron and/or other non-volatile materials employed, were sealed to a vacuum line and evacuated to 10^{-5} mm. Hydrogen bromide and allyl bromide (or other unsaturated compound) were then distilled over phosphorus pentoxide into the reaction tube, which was sealed off without admission of air. Experiments carried out in the presence of air did not undergo the drying and distillation procedures.

Analyses of Reaction Products.—In several of the initial experiments, the iron consumed was determined by both of the following methods, which were found to be in satisfactory agreement. (1) The reaction tube, cooled with liquid nitrogen, was attached by means of a piece of rubber pressure tubing to an evacuated vessel of known volume. The tip of the reaction tube was broken within the rubber tubing, and the amount of hydrogen released was estimated manometrically. (2) Non-volatile residues remaining after distillation of reaction mixtures were washed with water, and bromide ion present was determined volumetrically. Only the latter procedure was employed in most experiments.

In all experiments, allyl bromide and the dibromopropanes were distilled at 10–20 mm. from the reaction tube into a receiver cooled to −78°. The composition of the distillate and the yield of dibromopropanes was then determined by index of refraction as described by Kharasch and Mayo. For separation of the allyl bromide from the dibromopropanes, the Podbielniak column was found to be more convenient than the dimethylaniline procedure of Kharasch and Mayo and to give the same results within the experimental error (±3%). The addition products were distilled through this column at 30 mm., at which pressure allyl bromide does not condense. The first few drops of distillate were discarded. "Hold-up" was avoided by reducing the pressure at the end of the distillation so that bulb and column became dry. The ratio of 1,3- to 1,2-dibromide, as determined by refractive index, was checked by the distillation curve.

Redetermination of Refractive Indices of Dibromopropanes.—1,2-Dibromopropane was prepared by addition of bromine to propylene at −78°. The product was washed with water, dried over potassium carbonate, and distilled through a Podbielniak column. Ten fractions distilling within the range 50.0–50.8° at 30 mm. had the same refractive index: $n^{20}D$ 1.5200. Propylene bromide obtained by fractionation of allyl bromide–hydrogen bromide addition products had the same boiling range and refractive index.

A sample of commercial 1,3-dibromopropane containing trimethylene bromohydrin, after being washed with concentrated sulfuric acid, was distilled through a Podbielniak column at 30 mm. Ten fractions boiling within the range 70.2–71.6° all had the same refractive index: $n^{20}D$ 1.5230. Trimethylene bromide obtained by fractionation of addition products gave ten fractions of which the first seven had the refractive index $n^{20}D$ 1.5230, while the last three had the refractive index $n^{20}D$ 1.5231. Inasmuch as the most probable impurities (chloro and hydroxy derivatives and 1,2-dibromopropane) all have lower indices, the higher value is accepted as that of the pure compound.

Kharasch and Mayo, who had no efficient columns available, used different indices for the dibromopropanes. In the present work, indices of refraction of representative addition products were found to be as reported by Kharasch and Mayo, but the composition reported by them (%KM) in the range 16–9% 1,3-dibromopropane should be adjusted to the basis used in this paper (%H) by means of the equation $\%H = 3.22\ [(\%KM/2.63) - 6]$.

Summary

1. The iron-promoted abnormal addition of hydrogen bromide to allyl bromide is associated with the reaction of iron with hydrogen bromide and is shown to be consistent with the bromine-atom chain mechanism already proposed for the oxygen-promoted abnormal addition.

2. Certain metals are incapable of exerting

such an effect because they do not react sufficiently rapidly with anhydrous hydrogen bromide, because their halides catalyze the competing normal addition reaction, or because their halides inhibit the abnormal chain reaction.

3. Indices of refraction of 1,2- and 1,3-dibromopropanes have been redetermined.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Fluorinated Derivatives of Ethane and Ethylene. VI. Corrective Data

BY ALBERT L. HENNE AND EMIL G. WIEST

The determination of the fluorine position in some organic polyfluorides rests sometimes partly on reasons of analogy in physical properties. One of the lines of analogy most frequently used claims that when two polyfluorides are fully halogenated, they differ by only one or two degrees in boiling points, but by a substantially larger amount in freezing points. The asymmetrical compound boils lower and freezes higher than its symmetrical isomer. It proved therefore desirable to verify some of our very early data[1] which had been obtained on minute amounts, and did not seem as well in line as one might have wished, and also to clear up a marked discrepancy reported recently by Bigelow and co-workers.[2]

It is well established that $CClF{=}CClF$ boils about 21°.[1,3] Its isomer $CCl_2{=}CF_2$ was first reported to boil about 15°[1]; an unpublished repetition of the work[4] indicated 19°, which was regarded as well in line with expectations. However, the boiling point found by Bigelow is reported as 0°, a discrepancy which would very seriously undermine several phases of our previous work. The compound was, therefore, prepared once more, purified, measured and transformed into crystallizable derivatives. The experiments confirmed and slightly improved our preceding values. They also allowed an opportunity to correct a gross clerical error made on another compound.

1. **$CCl_2{=}CF_2$.**—The compound is obtained from well-crystallized CCl_3CClF_2 by reaction with zinc in alcohol. The reaction is swift, complete, and yields a single olefin, boiling at 18.9 to 19.0° (cor.). One half of the material was sent to Dr. Bigelow who rectified it, found a boiling point of 19–20°, a freezing point of −116 to −115°, and a molecular weight of 133 (theory 133).[5] These properties are (as would be expected) about two degrees lower than the boiling point of *cis*-$CClF{=}CClF$, and about 15° higher than its melting point.[1]

2. **CCl_3CClF_2.**—This compound was obtained by chlorination of the preceding one. The boiling point, 91.5°, and the melting point, 40.6°, confirmed our previously reported values.[1] The same operation, carried out by Dr. Bigelow, gave him a compound boiling close to 92°, and melting from 39 to 41°.

3. **CCl_2BrCF_2Br.**—This compound was obtained by bromination of $CCl_2{=}CF_2$. Its freezing point is 45.5° and its corrected boiling point 138.8–139.0°. This corrects the obviously wrong boiling point of 117.1° given in our first paper[1] and confirms the contention that symmetrical and asymmetrical fully halogenated compounds boil only one or two degrees apart (see following paragraph).

4. **$CClFBrCClFBr$.**—This compound was prepared as in our first paper, and the new experimental data are confirmations with only slight improvements. The freezing point is 32.9–32.6° and the corrected boiling point 139.8–140.0°. A comparison with the properties of the asymmetrical compound in the preceding paragraph shows the expected one degree difference in boiling point, and twelve degrees difference in freezing point.

5. **CCl_3CF_3.**—This derivative was obtained by chlorination of CH_3CF_3 in sunlight. According to our contentions, the melting point is the only physical property which should distinguish it markedly from its isomer, CCl_2FCClF_2. The corrected boiling point is 45.9° (nearly two degrees lower than that of CCl_2FCClF_2); freezing point 14.2°; d^{20}_4 1.5790 (improving the previously reported value); $n^{20}\text{D}$ 1.3610; the molecular refraction calculated from the new datac omes to 26.18, from which the refractive increment for fluorine is computed as 1.15. These values are

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(1) Locke, Brode and Henne, THIS JOURNAL, **56**, 1726 (1934).

(2) Bigelow, *et al.*, *ibid.*, **62**, 267 (1940).

(3) Booth, Burchfield, Bixby and McKelvey, *ibid.*, **55**, 2231 (1933).

(4) By Mary Renoll, in this Laboratory, in 1937.

(5) Private communication.