2. A new series of phenyl ether derivatives has been prepared by the condensation of 2-chloro-5-nitrophenylarsonic acid with various substituted phenols. Condensations were carried out with phenol, *o*- and *p*-chlorophenol, and *o*- and *p*-cresol. *o*-Chlorophenol condensed with 2-chloro-5-nitrophenylarsonic acid to form 1-arsono-3-nitrodibenzofuran. The carboxyl derivatives of the cresol condensation products were also prepared. The amino derivatives have been prepared for all of the above phenyl ether arsenicals.

3. Halogen in 2-chloro-5-nitrophenylarsonic acid was found less active toward primary amines and phenols than halogen in 3-nitro-4-chlorophenylarsonic acid.

LINCOLN, NEBRASKA RECEIVED MAY 16, 1934

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

The Peroxide Effect in the Addition of Reagents to Unsaturated Compounds. VIII. The Addition of Hydrogen Iodide to Ethylene Compounds

BY M. S. KHARASCH AND CHESTER HANNUM

Introduction

Previous studies in this Laboratory on the addition of hydrogen bromide to ethylene compounds under carefully controlled conditions have indicated that the controlling factor guiding the addition to the double bond was the peroxide content of the reaction mixture.[1] However, simple experiments with peroxide containing unsaturated compounds demonstrated that hydrogen iodide is an excellent reagent for decomposing organic peroxides. It appeared very likely, therefore, that the addition of hydrogen iodide to ethylene compounds should not be affected by peroxides, and that under all conditions the "normal" addition product should be formed.

Previous Work.—Very little work has been recorded on the addition of anhydrous hydrogen iodide to ethylene compounds studied by us. The earlier investigators[2] are in agreement that isopropyl iodide is the only product of reaction between propylene and hydrogen iodide. Butene-1 has been treated with aqueous hydrogen iodide[3] and found to form secondary butyl iodide. Whitmore and Homeyer[4] report that neopentylethylene did not add hydrogen iodide to the double bond at 0°, when the olefin was saturated with hydrogen iodide, although hydrogen bromide under those conditions gave practically quantitative yields of 1-bromo-4,4-dimethylpentane.[5]

The addition of hydrogen iodide to allyl bromide has never been described. Simpson[6] reports having prepared the 1-bromo-2-iodopropane by the addition of an aqueous solution of bromoiodine to propylene. His product boiled at 160–168° with decomposition. It is quite evident that the structure of Simpson's compound has not been definitely established.

General Procedure of this Work

In this work anhydrous hydrogen iodide was added in equal molar quantities to the olefin in order to minimize any reduction of the iodide thus formed. The general technique of addition was the same as described in previous papers.[2] When bombs were run with peroxides such as terpene peroxide, ascaridole, etc., these substances were added to the olefin at least thirty minutes before the addition of the hydrogen iodide.

The reaction of olefins with hydrogen iodide is quite vigorous at room and even at low temperatures. The hydrogen iodide used by us was purified very carefully and, when cooled in liquid air, was always obtained in an absolutely white form entirely free of iodine. Table I summarizes briefly the results of our addition of hydrogen iodide to a number of unsaturated compounds. As stated, the only product of the reaction under peroxide and antioxidant conditions was the "normal product," the product analogous to that obtained under antioxidant conditions with hydrogen bromide. Under our method of addition there was not the slightest difficulty in adding the hydrogen iodide to neopentylethylene. The addition of hydrogen iodide to that molecule is ex-

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[1] Kharasch and Mayo, THIS JOURNAL, **55**, 2469 (1933); Kharasch, McNab and Mayo, *ibid.*, **55**, 2521 (1933); Kharasch, Hannum and Gladstone, *ibid.*, **56**, 244 (1934); Kharasch and Hannum, *ibid.*, **56**, 712 (1934); Kharasch and Hinckley, *ibid.*, **56**, 1212, 1243 (1934).

[2] Berthelot, *Ann.*, **104**, 184 (1857); Erlenmeyer, *ibid.*, **139**, 228 (1866); Butlerow, *ibid.*, **145**, 275 (1867); *cf.* Michael, *Ber.*, **39**, 2138 (1906).

[3] Wurtz, *Ann.*, **152**, 23 (1869).

[4] Whitmore and Homeyer, THIS JOURNAL, **55**, 4555 (1933).

[5] *Cf.* Kharasch, Hannum and Gladstone, Ref. 1.

[6] Simpson, *J. Chem. Soc.*, **27**, 564 (1874).

TABLE I[a]

Olefin	Moles of olefin	Agent added	Moles of agent	Moles of HI	Technique	Reaction time, hours	Addition product Yield, %	B. p., °C.	Refractive index 20(D)
Propylene	0.069	Ascaridole	0.0012	0.073	Air	6	76	89–89.2	1.4985[b]
Propylene	.079	Diphenylamine	.0029	.084	Vacuo	4.5	79	89–89.2	1.4985[b]
Butene-1	.049	Ascaridole	.0012	.048	Air	3	52	119.5–119.8	1.4998[c]
Butene-1	.079	Diphenylamine	.0029	.079	Vacuo	3	73	119.5–119.8	1.4991[c]
Neopentylethylene	.049	Ascaridole	.0012	.054	Air	2	92	57.6(15 mm.)	1.4892[d]
Neopentylethylene	.048	Diphenylamine	.0029	.048	Vacuo	20	60	57.6(15 mm.)	1.4891[d]
Neopentylethylene	.049	......	...	.048	Vacuo	2	83	57.6(15 mm.)	1.4892[d]
2-Iodo-4,4-dimethylpentane	.022	......	...	.044	Air	18 (0)	68	57.6(15mm.)	1.4895[d]
Allyl bromide	.081	Ascaridole	.0012	.088	Air	2	81	66.2(20 mm.)	1.5908[e]
Allyl bromide	.082	Ascaridole	.0012	.082	Air	6 (−38)	59	66.2(20 mm.)	1.5914[e]
Allyl bromide	.070	Diphenylamine	.0029	.075	Vacuo	2	12		1.5900[f]
Allylbromide	.100	Diphenylamine	.0029	.100	Vacuo	2 (0)	16 (40%)		1.5867[f]
							(60%)		1.5896[f]
Allyl bromide	.100	Diphenylamine	.0029	.100	Vacuo	5 (−38)	0		1.4671[g]

[a] All the additions described in this table were carried out in the dark. The purity of the starting materials was checked, whenever possible, by boiling point and index of refraction. In the case of propylene and butene-1, the materials were purified by careful fractionation. [b] Index of refraction corresponds to isopropyl iodide. ("I. C. T.," n_D^{20} 1.4997) *n*-propyl iodide n_D^{20} 1.5051. [c] Index of refraction corresponds to *s*-butyl iodide as prepared by us. This index is not recorded in the literature. [d] Index of refraction corresponds to 2-iodo-4,4-dimethylpentane. This experiment proves that hydrogen iodide has no effect on the product formed by the interaction of neopentylethylene and hydrogen iodide. [e] The material was 1-bromo-2-iodopropane. [f] Some 1-bromo-2-iodopropane and a large quantity of low boiling material (65–85° at 760 mm.). [g] Unchanged allyl bromide.

tremely rapid both in the presence of antioxidants *in vacuo* and in the presence of peroxides. The final product in both cases was the 2-iodo-4,4′-dimethylpentane.[7]

As far as the addition of hydrogen iodide to propylene, butene- and 4,4′-dimethylpentene is concerned, the peroxides *apparently* have no effect on the speed or direction of addition. However, our work with allyl bromide indicates that while hydrogen iodide decomposes peroxides, yet these substances have definite effects on the velocity of addition although they may not influence the direction of addition. Thus, at room temperature (two hours) or at −38° (six hours) excellent yields of the addition product of hydrogen iodide to allyl bromide were obtained in the presence of peroxides. The low temperature of addition has the advantage in that no reduction products of the 1-bromo-2-iodopropane are formed, and the final mixture contains the dihalopropane and unchanged allyl bromide only. However, in the absence of peroxides and in the presence of antioxidants the formation of the dihalopropane is seriously hindered. Thus, at −38°, in a vacuum and in the presence of diphenylamine, no addition of hydrogen iodide occurred, and the allyl bromide was recovered unchanged. At 0° and in the absence of peroxides a low yield of the dihalopropane was obtained together with much unchanged allyl bromide, a low boiling material and a great deal of tar. The only constituent of the low-boiling material which was definitely identified was isopropyl iodide.[8] Furthermore, the yield of the dihalopropane decreased very rapidly as the temperature of addition was varied between 0 and 20°, and the quantities of tar and isopropyl iodide were increased.

The formation of the isopropyl iodide in the addition of hydrogen iodide to allyl bromide is in agreement with the observation of Malbot[9] and that of Sorokin[10] that isopropyl iodide is readily obtained when 1,2-dihalopropane is treated with hydrogen iodide.

The proof of structure of the 1-bromo-2-iodopropane, obtained by us, was made by the Gladstone and Tribe method.[11]

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(7) The structure of the iodo compound thus obtained was proved by converting the iodide into the corresponding mercury compound by the usual methods. The iodine in the mercury compound was then displaced by bromine by shaking the mixture with silver bromide. The melting point of the mercury compound thus obtained was 116°, and it did not depress the melting point of the mercury compound prepared from the addition product of hydrogen bromide to neopentylethylene under antioxidant conditions.

(8) The identification was made by refluxing the low boiling material dissolved in benzene, with a suspension of the silver salt of 3,5-dinitrobenzoic acid, and crystallizing the benzene soluble material from 80% alcohol. The ester thus obtained melted at 115–116°, and the melting point was not depressed when mixed with a known sample of that material.

(9) Malbot, *Ann. chim.*, [6] **19**, 355 (1890).

(10) Sorokin, *Z. Chem.*, **6**, 519 (1870).

(11) Gladstone and Tribe, *Ber.*, **7**, 364 (1874).

Summary

1. A study of the addition of hydrogen iodide to ethylenic compounds which are capable of forming "normal" and "abnormal" addition products with hydrogen bromide (depending on the "peroxide" content of the reactant mixture) has shown that only the "normal" product of addition is formed, even in the presence of peroxides.

2. The normal addition of hydrogen iodide is assumed to be due to the reducing action of this halogen acid on organic peroxides.

3. It is noteworthy that "peroxides" even though they do not affect the direction of addition of hydrogen iodide to unsaturated compounds, increase the velocity of addition, and in the case of allyl bromide allow the isolation of an addition product, which without added peroxides is formed to a slight extent only.

CHICAGO, ILL.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DEPAUW UNIVERSITY]

An Examination of the Fatty Oil from Pumpkin Seed. The Constitution of Linoleic Acid

BY J. L. RIEBSOMER AND G. A. NESTY

Since our knowledge regarding the fatty oil from the common pumpkin seed is derived almost solely from the early work of Power and Salway,[1] it appeared desirable to reinvestigate this material using the more modern methods available.

The pumpkin seed[2] was found to contain 9.6% moisture and 36.6% of an ether extractable oil whose physical and chemical characteristics, as determined by standard methods, were as given in Table I.

TABLE I

PHYSICAL AND CHEMICAL CHARACTERISTICS OF PUMPKIN SEED OIL

Specific gravity (20°/4°)	0.9159
Refractive index (Abbe 20°)	1.4737
Iodine number (Hanus)	116.8
Saponification value	174.2
Mean molecular weight saturated acids	269.0
Mean molecular weight unsaturated acids	289.2
Iodine number unsaturated acids	138.2
Iodine number saturated acids	9.6
Unsaturated acids (basis of oil) (corrected %)	76.3
Saturated acids (basis of oil) (corrected %)	11.4
Unsaponifiable matter, %	1.58
Reichert-Meissl number	1.5
Acetyl value[3]	2.76
Acid value	12.49

Unsaturated Acids

Preparation of Methyl Esters.—The unsaturated acids were separated by the lead salt–ether method. Their methyl esters were prepared and distilled at 4.5 mm. pressure. The boiling range of 175–180° indicated that the mixture contained acids with the same number of carbon atoms. The mean molecular weight further indicated 18 carbon atom acids.

Bromination.—The unsaturated acids were brominated using the method of Eibner and Muggenthaler,[4] 3.0042 g. of the unsaturated acids yielded 2.0316 g. of the tetrabromide (m. p. 114°). This corresponds to 0.9482 g. of linoleic acid or 31.5% of the acids brominated. Since the iodine number (138.2) of the unsaturated acids indicated the presence of 52.9% of linoleic acid, there must have been present the so-called beta-linoleic acid, the tetrabromide of which is soluble in petroleum ether. No hexabromide was produced, which indicated the absence of linolenic acid.

Ozonolysis.—Ninety grams of the methyl esters was treated with ozone using the method of Riebsomer and Johnson[5] and the resulting methyl esters from this process fractionally distilled in vacuum using a modified Claisen flask, with the following results. With the pressure at 24 mm.: fraction (1) b. p. 54–58°, weight 4.5 g.; fraction (2) b. p. 58–103°, weight 2.8 g.; fraction (3) b. p. 103–106°, weight 8.3 g. Remainder of distillation was at 5 mm.: fraction (4) b. p. 70–117°, weight 4.8 g.; fraction (5) b. p. 117–123°, weight 25.0 g.; fraction (6) b. p. 123–175°, weight 1.0 g. Undistillable, 9.0 g.

Fractions (2), (4) and (6) were obviously intermediates and were not investigated.

Fraction (1) as obtained above contained caproic acid together with a small amount of material not acidic in nature. The entire fraction was saponified and the potassium salt solution extracted with ether to remove the impurity. Treatment of the potassium salt with hydrochloric acid produced the acid, which was distilled. The neutral equivalent for the acid was 117.7. For pure caproic acid this figure is 116.1. The anilide was prepared and melted at 95–95.5°, and a mixed melting point with the anilide of known caproic acid was 95.5–96° (m. p. of known anilide 96°). From these data the presence of caproic acid was inferred.

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(1) Power and Salway, THIS JOURNAL, **32**, 346 (1910).

(2) Obtained from Carroon and Company, Fowler, Indiana.

(3) Lewkowitsch, *J. Soc. Chem. Ind.*, **16**, 503 (1897).

(4) Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," 6th ed., Vol. I, p. 585, 1921.

(5) Riebsomer and Johnson, THIS JOURNAL, **55**, 3352 (1933).