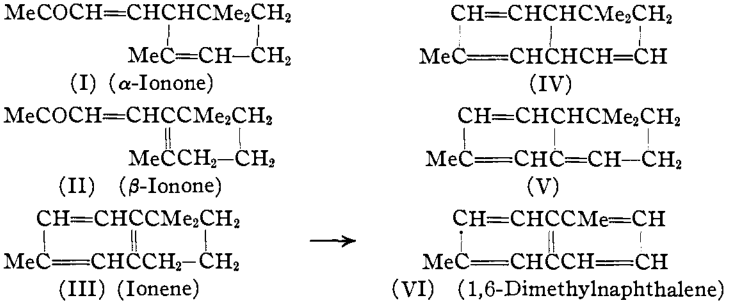
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY AND THE RESEARCH DEPARTMENT OF THE ASSOCIATED MANUFACTURERS OF TOILET ARTICLES]

The Catalytic Dehydration of Ionone and the Constitution of Ionene[1]

BY MARSTON TAYLOR BOGERT AND VICTOR GEORGE FOURMAN[2]

Tiemann and Krüger,[3] in their classical researches on ionones, $C_{13}H_{20}O$, discovered that when either α-ionone (I), or a mixture of α- and β-ionones, was heated for some time with hydriodic acid, in the presence of small amounts of phosphorus, a molecule of water was split out and a hydrocarbon, $C_{13}H_{18}$, which they christened "ionene," was formed, whose properties they described. Later, Tiemann[4] showed that β-ionone (II), similarly treated, likewise yielded ionene.


(I) (α-Ionone)
(II) (β-Ionone)
(III) (Ionene)
(IV)
(V)
(VI) (1,6-Dimethylnaphthalene)

Based upon the structure of its oxidation products, Tiemann and Krüger were disposed first to assign to ionene constitution (IV), but finally decided in favor of (V).

Three years later, Barbier and Bouveault[5] proposed formula (III) as the more likely, but cited no new experimental evidence in support of this opinion. Tiemann,[6] in his reply, insisted upon the correctness of his own formula (V). Baeyer and Villiger[7] likewise investigated the constitution of ionene, using their exhaustive bromination method, confirmed the presence of the carbon skeleton common to all three of the suggested formulas, but threw no new light upon the location of the double bonds.

Auwers and Eisenlohr,[8] as the result of their study of the molecular refractivity of ionene, decided in favor of (IV) rather than (V), but apparently failed to consider (III) at all.

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(1) Presented at the Washington Meeting of the American Chemical Society, March 28, 1933, before the Division of Organic Chemistry.

(2) Recently Research Assistant, Research Department, Associated Manufacturers of Toilet Articles; now Chemist for Compagnie Parento, Inc., Croton-on-the-Hudson, New York.

(3) Tiemann and Krüger, (a) *Ber.*, **26**, 2675 (1893); (b) **26**, 2693 (1893); (c) **31**, 808 (1898); Tiemann, (a) British Patent 8763 (May 1, 1893), and (b) 17,539 (Sept. 18, 1893).

(4) Tiemann, *Ber.*, **31**, 873 (1898).

(5) Barbier and Bouveault, *Bull. soc. chim.*, [3] **15**, 1008 (1896).

(6) Tiemann, *Ber.*, **31**, 854 (1898).

(7) Baeyer and Villiger, *ibid.*, **32**, 2429 (1899).

(8) Auwers and Eisenlohr, *J. prakt. Chem.*, [2] **84** 61 (1911).

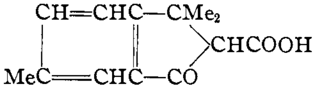
In the course of their researches in the naphthalene field, Ruzicka and Rudolph[9] distilled ionene with sulfur and obtained 1,6-dimethylnaphthalene (VI), using the Barbier and Bouveault formula (III) to explain the reaction. A year later, in his monograph on the sesquiterpenes,[10] Ruzicka accepted the carbon skeleton of ionene as satisfactorily established, but pointed out that the location of the double bonds was still unsettled.

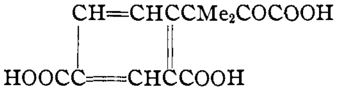
We believe that we have now cleared up this uncertainty, by the experimental work recorded in the present paper,. and by the complete synthesis of ionene, preliminary announcement of which appeared a few months ago.[11]

Our interest in the problem was heightened by the recent report of Heilbron, Morton and Webster[12] that when they distilled a vitamin A concentrate with selenium, they obtained 1,6-dimethylnaphthalene (VI) as one of the products, which led them to postulate ionene as an intermediate in this breakdown of the vitamin molecule.

In place of the method used by Tiemann and Krüger,[3] we have found that ionene can be prepared in much larger yield and higher purity by distilling ionone (either α or β) with a small quantity of iodine, a process based upon the observations of Hibbert[13] on the catalytic dehydrating effect of minute amounts of iodine although, so far as we are aware, it has not hitherto been employed for cyclo dehydrations of this type.

Tiemann and Krüger,[3] in their study of the oxidation products of ionene, using chromic acid and potassium permanganate as the oxidizing agents, isolated the 1,1,5-trimethyl-3-indanone-2-carboxylic acid (ionegenogonic acid) (VII), α-keto-β-(2,4-dicarboxyphenyl)-isovaleric acid (ionegenonetricarboxylic acid) (VIII), α-(2-carboxy-4-methylphenyl)-isobutyric acid (ionegenedicarboxylic acid) (IX), and α-(2,4-dicarboxyphenyl)-isobutyric acid (ioniregenetricarboxylic acid) (X). Under the conditions employed by us in oxidizing ionene with potassium permanganate, there were obtained (VIII), (X), and also the β-(2,4-dicarboxyphenyl)-isovaleric acid (XI).


(VII)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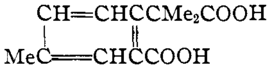
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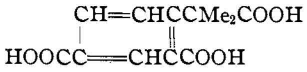
(X)


(XI)

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(9) Ruzicka and Rudolph, *Helv. Chim. Acta*, **10**, 918 (1927).

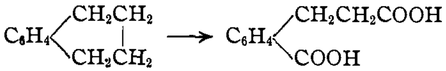
(10) "Ueber Konstitution und Zusammenhänge in der Sesquiterpenreihe," *Fortschr. d. Chem., Phys. u. physik Chem.*, **19**, No. 5, 9 (1928).

(11) Bogert, *Science*, [N. S.] **76**, 475 (1932).

(12) Heilbron, Morton and Webster, *Biochem. J.*, **26**, 1194 (1932).

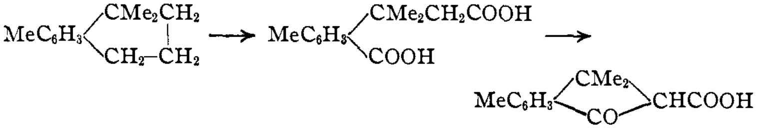
(13) Hibbert, THIS JOURNAL, **37**, 1748 (1915).

All of these compounds are normal oxidation products of an ionene of structure (III). Further, Bamberger and Kitschelt[14] have shown that when tetrahydronaphthalene (tetralin) was oxidized cold by dilute potassium permanganate in acid solution, there was produced the *o*-carboxyhydrocinnamic acid (XII). In other words, the hydroaromatic nucleus opens at the same point in the two cases:



$$C_6H_4\left<\begin{matrix}CH_2CH_2\\ |\\ CH_2CH_2\end{matrix}\right. \longrightarrow C_6H_4\left<\begin{matrix}CH_2CH_2COOH\\ \\ COOH\end{matrix}\right.$$

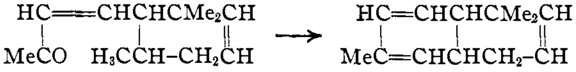
(XII)



$$MeC_6H_3\left<\begin{matrix}CMe_2CH_2\\ |\\ CH_2\text{–}CH_2\end{matrix}\right. \longrightarrow MeC_6H_3\left<\begin{matrix}CMe_2CH_2COOH\\ \\ COOH\end{matrix}\right. \longrightarrow MeC_6H_3\left<\begin{matrix}CMe_2\\ CO\end{matrix}\right>CHCOOH$$

(VII)

The formation of such a structure as (III) from *β*-ionone (II) involves a simple dehydration, exactly similar to that assumed by Tiemann and Krüger[3] in the conversion of the isomeric irone (XIII) into irene (XIV)



$$\begin{matrix}HC{=}{=}CHCHCMe_2CH\\ |\qquad\quad |\qquad\quad\ \|\\ MeCO\quad H_3CCH\text{–}CH_2CH\end{matrix} \longrightarrow \begin{matrix}HC{=}CHCHCMe_2CH\\ |\qquad\quad |\qquad\quad \|\\ MeC{=}CHCHCH_2\text{–}CH\end{matrix}$$

(XIII) (XIV)

whereas when *α*-ionone is the initial material, a shift in the position of one of the olefin bonds must occur during the reaction.

We found it so much more difficult to obtain *β*-ionone pure and at a price which we could afford, that the ionene used in our experiments was all prepared from *α*-ionone.

If it be urged that this distillation with iodine has itself shifted the position of the double bond in the ionene first formed, we might point out that such a change would be fully as likely to occur with the concentrated hydriodic acid used by Tiemann and Krüger as the dehydrating agent in their preparation of ionene; and that they obtained the same ionene from *α*- as from *β*-ionone.

It is pertinent to call attention to the fact that the b. p. of pure ionene is 240–242°, of 1-methylnaphthalene 240–242°, of 2-methylnaphthalene 242° and of tetrahydronaphthalene 206°.

It was the behavior of ionene with nitric and with sulfuric acids which first led us to doubt the correctness of the Tiemann formula (V), and resulted in our reëxamination of the problem, for we found that this hydrocarbon could be easily sulfonated or nitrated. This seemed to us indicative of the presence of a true aromatic nucleus and at variance with the terpene type of structure assumed by Tiemann. He and Krüger noted that ionene dissolved in concentrated sulfuric acid, but did not investigate the reaction or isolate the products. They observed that when irene was treated with fuming nitric acid, there resulted a product with the musky odor of the

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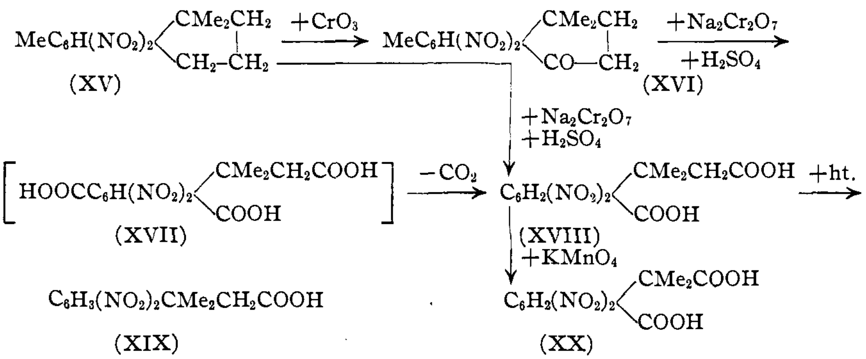
(14) Bamberger and Kitschelt, *Ber.*, **23**, 1561 (1890).

polynitrocymenes, but they failed to isolate or identify the products of the reaction, nor did they subject ionene to treatment with nitric acid.

In our own experiments, sulfonation yielded a monosulfo and nitration a dinitro derivative (XV). The position of these groups on the nucleus has not been determined. Reduction of the dinitro formed the nitroamino derivative and not the diamine. Chromic acid oxidized the dinitroionene to a ketone (XVI), which was rearranged to an isomeric form when dissolved in acetic anhydride and treated with a drop of concentrated sulfuric acid. Stronger oxidation of the dinitroionene (XV), or of the ketone (XVI), with dichromate mixture, gave a β-(2-carboxy-dinitrophenyl)-isovaleric acid (XVIII), proving that the two nitro groups were in one and the same ring, *i. e.*, the aromatic cycle. Heating this dicarboxylic acid above its m. p. split out one carbon dioxide with formation of the monocarboxylic acid (XIX). Using acid permanganate solution upon this same dibasic acid (XVIII), oxidized it to the next lower homolog (XX).



$$\mathrm{MeC_6H(NO_2)_2}\left<\begin{matrix}\mathrm{CMe_2CH_2}\\ |\\ \mathrm{CH_2{-}CH_2}\end{matrix}\right. \xrightarrow{+\mathrm{CrO_3}} \mathrm{MeC_6H(NO_2)_2}\left<\begin{matrix}\mathrm{CMe_2CH_2}\\ |\\ \mathrm{CO{-}CH_2}\end{matrix}\right. \xrightarrow[+\mathrm{H_2SO_4}]{+\mathrm{Na_2Cr_2O_7}}$$

(XV) (XVI)

$$\xrightarrow[+\mathrm{H_2SO_4}]{+\mathrm{Na_2Cr_2O_7}}$$

$$\left[\mathrm{HOOCC_6H(NO_2)_2}\left<\begin{matrix}\mathrm{CMe_2CH_2COOH}\\ \mathrm{COOH}\end{matrix}\right.\right] \xrightarrow{-\mathrm{CO_2}} \mathrm{C_6H_2(NO_2)_2}\left<\begin{matrix}\mathrm{CMe_2CH_2COOH}\\ \mathrm{COOH}\end{matrix}\right. \xrightarrow{+\mathrm{ht.}}$$

(XVII) (XVIII)

$$\xrightarrow{+\mathrm{KMnO_4}}$$

$$\mathrm{C_6H_3(NO_2)_2CMe_2CH_2COOH} \qquad \mathrm{C_6H_2(NO_2)_2}\left<\begin{matrix}\mathrm{CMe_2COOH}\\ \mathrm{COOH}\end{matrix}\right.$$

(XIX) (XX)

The presumptive intermediate tribasic acid (XVII) was not isolated.

Preliminary experiments with commercial "methylionone" show that it is likewise easily dehydrated when distilled with iodine, and that the methylionene so produced is readily nitrated to a dinitro derivative, but this line of research has been suspended pending the development of methods of preparing the different isomeric methylionones in satisfactory yield and purity.

Further, we suspect that the so-called "irene," obtained by Tiemann and Krüger[3] by dehydration of irone, is identical with ionene, the slight difference in their molecular refractivities being due to the presence of small amounts of impurities, but this investigation also has had to be postponed because of the present high price ($900 per pound) of irone and the lack of convenient methods for its preparation synthetically.

Acknowledgments.—This investigation was made possible by the generous financial support of the Associated Manufacturers of Toilet Articles, notably of Mr. G. A. Pfeiffer, President of Richard Hudnut, Inc.;

and also of the Warren Fund Committee, American Academy of Arts and Sciences. To the courtesy of Mr. A. Doolittle, President of Compagnie Parento, Inc., Croton-on-the-Hudson, N. Y., we are indebted for generous supplies of various ionones; and to Mr. F. Firmenich, President of M. Naef & Co., Geneva, Switzerland, for some very fine specially distilled β-ionone.

Experimental Part

Unless otherwise stated, the melting points recorded in the following pages are all corrected, and were taken by raising the temperature of the bath at the rate of approximately 3° per minute.

α-Ionone (I).—The best grade commercial product was rectified twice, at a pressure of 17 mm., and the fraction boiling at 134–136°, n_D^{20} 1.5041, was used in our experiments. Its *p*-bromophenylhydrazone softened at 134° and melted at 142–143°. Tiemann and Krüger[3] gave the constants for their α-ionone as follows: b. p. at 17 mm., 134–136°, n_D^{20} 1.4980; *p*-bromophenylhydrazone[4,15] softens at 134°, m. p. 142–143°.

Ionene (1,1,6-Trimethyltetralin) (III).—When a mixture of one mole (192 g.) of α-ionone with 1 g. of iodine was heated, the iodine gradually dissolved, and when the temperature of the solution reached about 130°, the evolution of steam began. At 140° the reaction was vigorous at first, but gradually subsided and the distillation was continued until the temperature of the liquid in the flask rose to 250°. The initial distillate consisted almost wholly of the water split out. The crude ionene distilled at 240–245°. It amounted to 140 g., or a yield of 80%, and 12 g. of water was collected. After removal of the water, the crude hydrocarbon was again distilled with 1 g. of iodine and 3 g. more of water was obtained. The ionene which came over was washed with a dilute sodium thiosulfate solution, to free it from traces of iodine, and then with water until colorless. On standing overnight, however, it turned a brownish-red and this color was not removed by washing with thiosulfate solution. Dried over calcium chloride and distilled twice over sodium, a colorless limpid liquid was obtained, b. p. 240–242° at atmospheric pressure; yield 105 g., or 60%. The total water collected was 15 g., or 83%.

Anal. Calcd. for $C_{13}H_{18}$: C, 89.58; H, 10.42. Found: C, 89.40; H, 10.54.

Ionene is a colorless, highly refractive liquid which can be distilled over sodium at atmospheric pressure without apparent decomposition. Tiemann and Krüger[3] reported that their ionene resinified when exposed to the air for a long time, but our product after standing for over a year in contact with the air exhibited no sign of resinification and had only become slightly yellowish.

The constants for the two products are as follows

	Bogert and Fourman	Tiemann and Krüger
B. p. at 10 mm., °C.	107	106–107
B. p. at 14 mm., °C.	114	
B. p. at 752 mm., °C.	240–242	
n_D^{20}	1.5225	1.5244
d^{20}	0.9331	0.9338
d_4^{20}	0.9303	
M_D (Lorentz–Lorenz)	57.13 (56.43)	57.18 (56.43)
EM_D	+0.70	+0.75

Tiemann and Krüger failed to report the yield of ionene obtained by their method, but Ruzicka and Rudolph,[9] on repeating it, obtained a yield of 45% of a product having

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[15] Tiemann, *Ber.*, **28**, 1755 (1895).

a boiling point range of 6°. Tiemann and Krüger also found that a glacial acetic acid solution of bromine was decolorized by the addition of their ionene. When this test was applied to our own sample of ionene, hydrobromic acid was evolved and the solution was decolorized.

We had already carried out the distillation of ionene with sulfur, by the method of Vesterberg,[16] and obtained 1,6-dimethylnaphthalene, before we discovered that Ruzicka and Rudolph[9] had done this in 1927. Our results, therefore, present nothing new, except that our yield of the hydrocarbon was slightly better (12% instead of 10%) and the m. p. (113°) of our 1,6-dimethylnaphthalene picrate somewhat higher than theirs (109°). Weissgerber and Kruber[17] recorded the m. p. of this picrate as 114°, and Heilbron, Morton and Webster[12] as 113–114°.

Oxidation of Ionene

Our process of oxidation differed somewhat from that of Tiemann and Krüger,[3] and of Tiemann,[4] and is therefore recorded here.

β-(2,4-Dicarboxyphenyl)-isovaleric Acid (XI).—To a boiling solution of 2 g. of ionene in 100 cc. of water containing a few drops of dilute sodium hydroxide, there was added gradually a solution of 14 g. of potassium permanganate in 300 cc. of hot water and the whole was refluxed for seven hours. The mixture was filtered hot, the filtrate concentrated to about 50 cc. and acidified with dilute hydrochloric acid. The colorless needles which separated carried a mole of water of crystallization and melted, after repeated crystallization from water or dilute alcohol, at 220°; yield, 1.3 g., or 43%.

Anal. Calcd. for $C_{13}H_{16}O_7$: C, 57.72; H, 5.67. Found: C, 57.87; H, 5.58.

Dried to constant weight at 180°, one mole of water was driven off.

Anal. Calcd. for $C_{13}H_{14}O_6$: C, 58.63; H, 5.29 Found: C, 58.33; H, 5.04. Acid equivalent: calculated, 88.7; found, 87.2. *Mol. wt.* Calcd., 266; found, 262.

In the mother liquors from this acid, there was evidence of the presence of a small amount of an acid of lower m. p., probably the **α-(2,4-dicarboxyphenyl)-isobutyric acid (ioniregenetricarboxylic Acid) (X).**—A mixture of 0.1 mole of ionene (17.4 g.), 0.2 g. of sodium hydroxide, 140 g. of potassium permanganate and one liter of water, was refluxed until the solution was colorless (twelve hours), then filtered, the precipitate washed thoroughly with hot water and the combined filtrate and washings evaporated to about 100 cc. and acidified with dilute hydrochloric acid. The crude acid (9.5 g.) which separated was crystallized from water; yield, 7 g., or 28%; m. p. 216.5–218.5°. A sample of the acid recrystallized thrice from water, and which consisted of long colorless needles, m. p. 217°, was analyzed.

Anal. Calcd. for $C_{12}H_{12}O_6$: C, 57.12; H, 4.80. Found: C, 57.45; H, 4.80.

This is evidently the "ioniregenetricarboxylic acid" of Tiemann and Krüger, who found that it lost water at 150°, with formation of an anhydride, m. p. 214°.

Increasing the proportion of the permanganate or the duration of the oxidation gave the same acid (m. p. 217°) in lower yield.

Trimethyl Ester.—Prepared by the action of dry hydrogen chloride upon a solution of the above acid in absolute methyl alcohol, and purified by crystallization first from dilute methyl alcohol and then from hot ethyl alcohol diluted to cloudiness, it formed long colorless needles, m. p. 91°. Tiemann and Krüger recrystallized their methyl ester from ligroin and reported its m. p. as 93°.

Anal. Calcd. for $C_{15}H_{18}O_6$: C, 61.20; H, 6.17. Found: C, 61.29; H, 5.97.

When Tiemann and Krüger heated the silver salt of this acid, they obtained a hydrocarbon which they believed to be isopropylbenzene, but which they failed to identify.

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(16) Vesterberg, *Ber.*, **36**, 4200 (1903).

(17) Weissgerber and Kruber, *ibid.*, **52**, 346 (1919).

As the identification of this hydrocarbon seemed to us to be of importance in establishing the constitution of the parent tricarboxylic acid (X) and thus, indirectly, the structure of ionene itself, we distilled an intimate mixture of the finely ground dry potassium salt (from 18 g. of the acid) with twice its weight of pulverized soda-lime. About 5 g. of hydrocarbon distillate was collected which, after drying over calcium chloride, was redistilled and yielded about 4 g. of a fraction b. p. 140–155° and less than 1 g. of a fraction b. p. 155–160°. The first fraction on rectification gave 3.6 g. boiling at 145–155° (equivalent to a yield of about 40%), most of which came over at 152–153°. The boiling point of isopropylbenzene recorded in the literature is 153°.

This rectified hydrocarbon was heated for thirty minutes at 100° with twice its volume of concentrated sulfuric acid, and the sulfo acid so obtained was then converted into its sulfo chloride and sulfonamide, which latter was crystallized twice from hot alcohol diluted to cloudiness, and then melted at 106°. Mixed with a sample of authentic isopropylbenzene *p*-sulfonamide, prepared from Eastman isopropylbenzene, there was no change in the melting point. The melting point recorded in the literature for this sulfonamide is 107°.

α-Keto-β-(2,4-dicarboxyphenyl)-isovaleric Acid (Ionegenonetricarboxylic Acid) (VIII).—The mother liquors from the preparation of the immediately preceding acid (X) were combined, concentrated to 50 cc. and to the solution more hydrochloric acid was added. Less than 1 g. of crude organic acid was thus obtained from the initial 17.4 g. of ionene. After several crystallizations from water, it appeared in minute colorless needles, which melted at 140–145°, re-solidified at 150°, and then melted at about 206°. These properties coincide with those reported by Tiemann and Krüger[3] for their "ionegenonetricarboxylic acid."

Anal. Calcd. for $C_{13}H_{12}O_7$: % COOH, 48.2; found, 47.7 and 48.0.

Experiments in oxidizing ionene with acid permanganate solutions proved abortive. Part of the ionene was burned to carbon dioxide and the rest was recovered unaltered.

Sulfo Derivatives of Ionene

Ionenesulfonic Acid, $C_{13}H_{17}SO_3H$.—In general, the method was based upon the experience of Hixson and McKee[18] in the sulfonation of cymene, and of Schroeter[19] with tetrahydronaphthalene.

The ionene (17 g.) was first shaken, at room temperature, with an equal volume of concentrated sulfuric acid, to free it from possible traces of unsaturated contaminants. The ionene layer was then separated, mixed with an equal volume of fresh concentrated sulfuric acid, and the mixture stirred vigorously at 90° for two hours. After standing overnight at room temperature, it was poured into 200 cc. of water and ice, the solution made faintly alkaline with dilute sodium hydroxide, heated to boiling and about 50 g. of salt (sodium chloride) added. The sodium sulfonate which separated was crystallized from 150 cc. of water half saturated with sodium chloride; yield, 18 g., or 50%. The sample analyzed was recrystallized thrice more from small volumes of water, and then formed colorless needles which carried five moles of water of crystallization, which was driven off at 180°.

Anal. Calcd. for $C_{13}H_{17}SO_3Na \cdot 5H_2O$: H_2O, 24.60. Found: 24.90.

Anal. Calcd. for $C_{13}H_{17}SO_3Na$: C, 56.48; H, 6.21. Found: C, 56.58; H, 6.73.

The free sulfonic acid was very easily soluble in water.

Barium Salt.—This separated in colorless glistening plates, when a solution of barium chloride was added to one of the sodium sulfonate. It crystallized from water with three moles of water of crystallization.

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(18) Hixson and McKee, *Ind. Eng. Chem.*, **10**, 982 (1918).

(19) Schroeter, *Ann.*, **426**, 1–160 (1922).

Anal. Calcd. for $(C_{13}H_{17}SO_3)_2Ba\cdot 3H_2O$: H_2O, 7.7. Found: 7.3.

Anal. Calcd. for $(C_{13}H_{17}SO_3)_2Ba$: C, 48.46; H, 5.32; $BaSO_4$, 36.25. Found: C, 48.39; H, 5.11; $BaSO_4$, 36.82.

Sulfochloride.—Prepared from the anhydrous sodium sulfonate and phosphorus pentachloride, the crude product was purified by solution in benzene and addition of petroleum ether, which precipitated small amounts of tar. After a repetition of this purification, the benzene solution was evaporated and the residue crystallized from ligroin. Small colorless crystals resulted, m. p. 89°; yield, 1.7 g. from 2.5 g. of sodium sulfonate, or 70%.

Anal. Calcd. for $C_{13}H_{17}SO_2Cl$: C, 57.24; H, 6.27. Found: C, 57.28; H, 6.31.

Sulfonamide.—When the sulfochloride was digested with concentrated ammonium hydroxide solution and the crude product recrystallized thrice from 50% alcohol, this sulfonamide was obtained in colorless lustrous plates, m. p. 157–158°; yield from 1 g. of sulfochloride, 0.7 g. or 75%.

Anal. Calcd. for $C_{13}H_{19}O_2NS$: C, 61.61; H, 7.57. Found: C, 61.74; H, 7.71.

Variations in the temperature (30–110°) or duration of the heating of the ionene–sulfuric acid mixture, made no change in the product, as evidenced by the m. p. of the sulfochlorides and sulfonamides prepared thereform. The position of the sulfo group in the nucleus has not been determined.

Schroeter[19] obtained the 2-sulfo acid when he sulfonated tetrahydronaphthalene with concentrated sulfuric acid, and a mixture of the 1- and 2-sulfo acids when he used chlorosulfonic acid. He found that the barium salt of the 1-acid crystallized with three moles of water, whereas the barium salt of the 2-acid crystallized water-free.

Nitration of Ionene

Dinitroionene (XV).—In the course of ninety minutes, 40 g. of ionene was introduced, drop by drop and with vigorous stirring, into 150 cc. of nitric acid (sp. gr., 1.5) containing 30 g. of phosphorus pentoxide, keeping the flask in an ice-pack. After all the ionene had been added, and without removing the flask from the ice-pack, the stirring was continued for a further half hour and the flask left at the same temperature for several hours longer, after which its contents were poured into 1500 cc. of water and ice, the precipitated nitro derivative filtered out, washed with water and crystallized from alcohol; yield, 45 g., or 70%. Further purification was accomplished by recrystallization from hot alcohol diluted to cloudiness, glacial acetic acid, benzene or boiling concentrated nitric acid. The pure compound formed pale yellowish plates, m. p. 103°; yield, 38 g., or 58%.

Anal. Calcd. for $C_{13}H_{16}O_4N_2$: C, 59.06; H, 6.11; N, 10.61. Found: C, 58.97; H, 6.18; N, 10.72.

The above method is based upon that used by Behrend and Roth[20] in the nitration of β-pentacetylglucose. The same product was secured when the nitration was conducted in the presence of concentrated sulfuric acid, instead of phosphorus pentoxide, but the yields were not as good. No trace of an isomeric dinitro derivative was detected in these nitration experiments, but there was formed, as a by-product, a small amount of a red oil, which may have contained a mononitro derivative, but from which no pure compound could be isolated.

Schroeter,[19] in his study of the nitration of tetrahydronaphthalene with a mixture of nitric and sulfuric acids, obtained a eutectic mixture of the 1,2- and 1,3-dinitro derivatives, the former of which could be further nitrated (to the 1,2,4-trinitro derivative), but not the latter. All attempts to introduce a third nitro group into our dinitroionene

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(20) Behrend and Roth, *Ann.*, **331**, 381 (1904).

proved fruitless, and the fact that this dinitro derivative is unchanged by boiling concentrated nitric acid is scarcely in accord with the assumption of any terpene type formula for ionene.

The location of these two nitro groups on the aromatic nucleus was not determined. It seems most likely that they will be found to be ortho to the methyl group, *i. e.*, on either side of it, which would make them meta to each other.

Nitroaminoionene.—A solution of 2 g. of dinitroionene in 200 cc. of ethyl alcohol was reduced in an Adams hydrogenator, in the presence of 0.1 g. of platinum oxide catalyst.[21] The hydrogen was absorbed rapidly at the outset, but this rate fell quickly during the first ten minutes, and at the end of an hour and a half the reduction was complete. The catalyst was removed and the alcoholic solution concentrated. As the solution cooled, the nitroamine crystallized in canary-yellow needles, m. p. 166.5°. Purified through the hydrochloride, and then crystallized from alcohol, it melted at 171°; yield, 1.4 g., or 80%.

Anal. Calcd. for $C_{13}H_{18}O_2N_2$: C, 66.62; H, 7.75. Found: C, 66.78; H, 7.78.

Hydrochloride.—The amine was dissolved in dilute hydrochloric acid, the solution warmed gently and concentrated hydrochloric acid added until crystallization began. These colorless crystals were removed, washed with concentrated hydrochloric acid, redissolved in dilute hydrochloric acid, reprecipitated by the concentrated acid, filtered out and dried in a desiccator. They were partially hydrolyzed by cold water or even on standing exposed to air and moisture. Heated at the rate of 4° per minute, the salt decomposed at 237–239°. Addition of dilute ammonium hydroxide to a dilute aqueous solution of the salt, liberated the free base.

Acetyl Derivative.—Prepared from the nitroamine and acetic anhydride and purified by crystallization from 60% ethyl alcohol, it formed colorless needles, m. p. 158°; yield, 75–80%.

Anal. Calcd. for $C_{15}H_{20}O_3N_2$: C, 65.17; H, 7.30. Found: C, 65.07; H, 7.68.

Attempts were made to reduce the dinitro or nitroamino derivative of ionene to the diamine, either catalytically, or with the aid of stannous chloride, tin and hydrochloric acid, phenylhydrazine or other reducing agents. All failed. When the dinitro derivative was the initial material, the only reduction product was the nitroamine. When the latter was the initial material, there was usually no reaction short of total decomposition.

Oxidation of Dinitroionene

α-Dinitroionenone (XVI).—To a suspension of 15 g. of dinitroionene in a mixture of 400 cc. of glacial acetic and 60 g. of concentrated sulfuric acid, there was added gradually, in the course of two hours, 10 g. of chromium trioxide with vigorous stirring, keeping the mixture at first in an ice-pack and then allowing it to warm to room temperature. Upon the completion of the oxidation, the mixture was poured into water, the precipitate removed, washed with water until the washings were colorless and then crystallized from alcohol. There was thus obtained 9 g. of very pale yellow needles, m. p. 157°. From the mother liquor 2 g. additional was recovered, making a total yield of 11 g., or 70%.

Anal. Calcd. for $C_{13}H_{14}O_5N_2$: C, 56.09; H, 5.07; N, 10.07. Found: C, 56.23, 55.79; H, 5.02, 4.97; N, 10.38. *Mol. wt.* (borneol, Rast): calcd., 278; found, 266.

The product was insoluble in sodium hydroxide or in hydrochloric acid. It dissolved in cold concentrated sulfuric acid and reprecipitated unaltered when this solution was poured upon ice. An alcoholic solution was colored wine-red by the addition of dilute sodium hydroxide. Under similar treatment, an acetone solution turned brown,

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[21] Adams, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1932, Coll. Vol. I, p. 452.

but no indigo derivative was formed, an evidence that the compound was not an *o*-nitrobenzaldehyde. It did not reduce an ammoniacal silver nitrate solution in the cold, nor dilute permanganate when heated with its acetone solution.

Oxime.—When a solution of 1.4 g. of the above ketone in 10 cc. of alcohol was refluxed for fifteen minutes with a molar equivalent of hydroxylamine hydrochloride and three of sodium hydroxide, and the mixture then poured into ice and dilute hydrochloric acid, a pale brown precipitate separated, which was collected, washed with water and crystallized repeatedly from alcohol, when it formed colorless needles, m. p. 188.5°; yield 1.1 g., or 74%.

Anal. Calcd. for $C_{13}H_{15}O_5N_3$: C, 53.28; H, 5.16; N, 14.34. Found: C, 53.39; H, 4.87; N, 14.57.

The compound was insoluble in dilute hydrochloric acid. In dilute sodium hydroxide it dissolved and the sodium salt of the oxime crystallized in bright yellow needles which decomposed at about 125°.

No oxime was formed when sodium carbonate was used instead of sodium hydroxide upon the mixture of ketone and hydroxylamine, even after refluxing for three hours, the initial ketone being recovered unchanged.

β-Dinitroionenone.—After adding one drop of concentrated sulfuric acid to a solution of 4 g. of α-dinitroionenone in 15 cc. of acetic anhydride, the solution was refluxed for an hour and left overnight at room temperature. The acetic anhydride was then distilled off under diminished pressure and the residue, as it cooled, solidified. This solid was washed with petroleum ether and crystallized, first from hot acetic acid diluted to cloudiness, and then from alcohol, when it appeared in small pale yellow needles, m. p. 99°; yield, 3.5 g., or 87%.

Anal. Calcd. for $C_{13}H_{14}O_5N_2$: C, 56.09; H, 5.07; N, 10.07. Found: C, 56.39, 56.21; H, 4.86, 4.90; N, 10.06. *Mol. wt.* (borneol, Rast): calcd., 278; found, 268.

When this product (1 g.) was dissolved in concentrated sulfuric acid (5 cc.) and the solution poured upon ice, a solid separated which, when washed with water and crystallized from alcohol, proved to be the α-isomer (m. p. 157°), as shown by a mixed melting point and by its other properties. The addition of either dilute or concentrated hydrochloric acid to an alcoholic solution of the β isomer caused no change. Isomerization of the β to the α form was also accomplished by adding several drops of dilute sodium hydroxide to a solution of the β form (1 g.) in alcohol (5 cc.), when the solution turned red and the product which crystallized out proved to be the α isomer. One isomer could not be converted into the other by heating above its melting point, nor by seeding the molten material with crystals of its isomer. Without the addition of the drop of concentrated sulfuric acid, acetic anhydride was powerless to rearrange the α to the β isomer. It might be mentioned also that had this dinitroionenone been an aldehyde and not a ketone, the treatment with acetic anhydride and sulfuric acid should have yielded the aldehyde diacetate.

Oxidation of Dinitroionene and of Dinitroionenone

β-(2-Carboxy-dinitrophenyl)-isovaleric Acid (XVIII).—A solution of 5 g. of dinitroionene in 150 g. of glacial acetic acid and 75 cc. of concentrated sulfuric acid was refluxed for an hour, while a solution of 30 g. of $Na_2Cr_2O_7.2H_2O$ in 60 cc. of water was added dropwise. After standing overnight at room temperature the mixture was poured into ice water, the precipitate filtered out, washed with water until the washings were colorless, dissolved in dilute sodium hydroxide solution, filtered and the filtrate acidified with dilute hydrochloric acid. The precipitated acid was crystallized thrice from water, 100 parts of which at 100° dissolved 1.6 parts of the acid; yield, 3.4 g., or 54%. The purified acid formed yellow needles, carrying one mole of water of crystallization. At 150°, the acid melted with elimination of this water of crystallization, resolidified and melted then at 177°.

Anal. Calcd. for $C_{12}H_{14}O_9N_2$: C, 43.62; H, 4.27; N, 8.49. Found: C, 43.49; H, 4.40; N, 8.74. *Acid equivalent.* Calcd., 165; found, 168.

This same acid was obtained by similarly oxidizing dinitroionenone (α or β form) in glacial acetic acid solution with sodium dichromate and concentrated sulfuric acid.

β-Dinitrophenyl-isovaleric Acid (XIX).—The above dicarboxylic acid (XVIII) was kept at a temperature just above its melting point as long as carbon dioxide was evolved. The melt was allowed to resolidify and was then dissolved in alcohol, the solution filtered, and the filtrate diluted with water until crystallization began. Recrystallized from water, it formed pale yellowish needles, m. p. 166.5–168.5°; yield, 1.5 g. from 2.5 g. of initial dicarboxylic acid, or 74%. It was very easily soluble in alcohol, but much less soluble in water than its antecedent dicarboxylic acid.

Anal. Calcd. for $C_{11}H_{10}O_6N_2$: C, 49.24; H, 4.51. Found: C, 48.81; H, 4.74.

α-(2-Carboxydinitrophenyl)-isobutyric Acid (XX).—A solution of 2.5 g. of the corresponding isovaleric acid (XVIII) in 250 cc. of water, 5 cc. of concentrated sulfuric acid and 0.7 g. of potassium permanganate, was refluxed until the color of the solution was discharged (forty minutes). The manganese dioxide precipitated was filtered out, washed thoroughly with hot water, and the combined washings and filtrate concentrated. The colorless needles which separated were dissolved in dilute sodium hydroxide, the solution filtered and the filtrate precipitated by the addition of dilute hydrochloric acid. After crystallization twice from water, the product melted at 170.5°; yield, 1.9 g., or 84%. Its solubility was about 1.3 parts in 100 parts of water at 100°.

Anal. Calcd. for $C_{11}H_{10}O_8N_2$: C, 44.28; H, 3.38. Found: C, 44.47; H, 3.63.

Summary

1. Ionene is conveniently prepared, in excellent yield, by the distillation of α- or β-ionone with small amounts of iodine.

2. That ionene is a true 1,1,6-trimethyltetralin is evidenced by its smooth sulfonation and nitration, and by the oxidation products obtained from ionene itself and from its dinitro derivative.

3. Dinitroionenone can be obtained in two isomeric forms which are mutually interconvertible.

NEW YORK, N. Y.

RECEIVED JULY 24, 1933
PUBLISHED NOVEMBER 7, 1933