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Polynes. II. The Purification of β -Ionone^{1,2}

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The purification of commercial β -ionone by decomposition of its highly purified semicarbazone³ according to the frequently reported method of steam distilling the semicarbazone in the presence of phthalic anhydride was carried out in the usual manner.⁴ A spectrophotometric comparison of the β -ionone prepared by this procedure with the original starting material indicated that both products had identical maximum extinction coefficients. The failure of this well-known method of purification led to an investigation of the effects of various acidic media on the decomposition of β -ionone semicarbazone. The results of this study are presented in this paper along with a brief report of an attempted purification of β -ionone based on an expected difference in reaction rates of α - and β -ionone with perbenzoic acid.

The Purity of β -Ionone Prepared from its Semicarbazone.—Commercial β -ionone having absorption maxima at 296 $m\mu$ (ϵ 8600) and 222 $m\mu$ (ϵ 7350) was converted to the semicarbazone. This derivative was recrystallized repeatedly to constant melting point (148–149°) and extinction coefficient.⁵ The purified semicarbazone was decomposed in various acidic media, and the extinction coefficients (296 $m\mu$) of the product were measured in 95% ethanol to determine the degree to which isomerization into α -ionone occurred (see Table I).

(1) This paper was presented before the Organic Division of the American Chemical Society, Pittsburgh, Pa., September, 1943.

(2) This work was made possible by a research grant from Sharp and Donme, Inc. Original manuscript received September 7, 1943.

(3) Tiemann, *Ber.*, **31**, 867 (1898).

(4) (a) Kuhn and Morris, *ibid.*, **70B**, 853 (1937); (b) Burawoy, *J. Chem. Soc.*, 20 (1941); (c) Ruzicka, Seidel and Firmenich, *Helv. Chim. Acta*, **24**, 1434 (1941).

(5) The commercial ionones (Ionone Beta Extra and Ionone Alpha Extra White) were obtained from Maywood Chemical Works, Maywood, N. J. Purified β -ionone semicarbazone had λ_{\max} 282 $m\mu$, ϵ 22300 in 95% ethanol.

TABLE I
THE PURITY OF β -IONONE

Method of semicarbazone decomposition	Semicarbazone, g.	Amount of acid	n_D^{20}	ϵ_{\max} (296 $m\mu$) ^a	% Purity
Phthalic anhydride ^b	72	72 g.	1.5175	8600 ^c	80
Phthalic anhydride ^b	5	5 g.	1.5157	9600	90
Succinic acid ^b	5	0.17 eq.	1.5198	10100	95
Phosphoric acid ^b	5	0.12 eq.	1.5200	10100	95
Sulfuric acid ^c	68	1.0 eq.	1.5205	10100	95
Sulfuric acid ^b	5	0.12 eq.	1.5211	10500	98
Cold sulfuric acid ^d	5	0.10 eq.	1.5211	10700	100

^a The solvent was 95% ethanol. ^b The liberated β -ionone was steam distilled from the acid mixture. ^c Refluxed three hours with 300 ml. of 3 N sulfuric acid. ^d Method of Heilbron and co-workers⁶; it should be noted that the properties of purified β -ionone obtained by Heilbron (ϵ 12900, n_D^{20} 1.5178) are considerably different from those reported here. ^e Burawoy^{4b} reports ϵ_{\max} 8700 (abs. ethanol) and Ruzicka^{4c} reports ϵ_{\max} 8900 in absolute ethanol using the phthalic anhydride method.

Of the several methods tried for decomposing the semicarbazone, the one using sulfuric acid was the most reliable. In fact the modification of this procedure reported by Heilbron and co-workers⁶ while these studies were in progress has been tried and found to give β -ionone of the highest maximum extinction coefficient (λ_{\max} 296 $m\mu$, ϵ_{\max} 10700). This is considerably higher than that of the product obtained by the usual method with phthalic anhydride. In view of the fact that neither β -ionone nor its semicarbazone are isomerized by the conditions used in the hydrolysis it is likely that this method of Heilbron gives pure β -ionone. The extinction coefficients of β -ionone samples were not altered by exposing the samples to cold or hot dilute sulfuric acid.

(6) Heilbron, Johnson, Jones and Spinks, *J. Chem. Soc.*, 727 (1942).

Neither did exposing a sample of β -ionone semicarbazone to cold dilute sulfuric acid until about one-third of it had been hydrolyzed change the spectrum of the unhydrolyzed semicarbazone.

It does not seem likely that the presence of α -ionone in the product from the hydrolysis of β -ionone semicarbazone with phthalic anhydride should be attributed to the effect of the acidic medium on the liberated β -ionone since the ionone was steam distilled from the mixture as soon as it was formed. Attempts to study the effects of the phthalic anhydride medium on the semicarbazone itself have so far failed owing to difficulties involved in purifying the partially decomposed semicarbazone recovered from the medium.

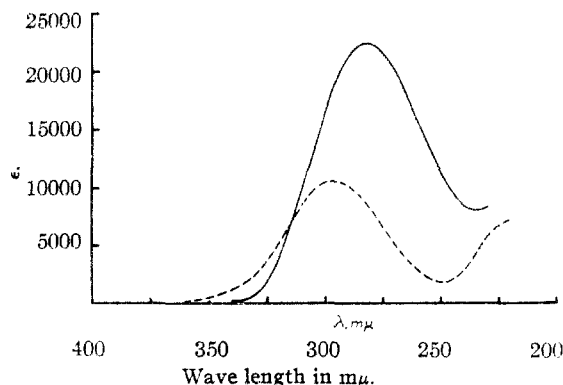


Fig. 1.—Spectra of pure β -ionone and β -ionone semicarbazone: β -ionone, ---; β -ionone, — semicarbazone.

In Fig. 1 are presented the absorption spectra of pure β -ionone semicarbazone and of β -ionone liberated from the semicarbazone by the use of sulfuric acid at room temperature measured in a solution of 95% ethanol. In Fig. 2 are given the spectra of commercial α - and β -ionone. The commercial α -ionone has absorption maxima at 227 $m\mu$, ϵ 12850 and 296 $m\mu$, ϵ 1950. Assuming that β -ionone obtained from its semicarbazone by decomposition with sulfuric acid at room temperature is 100% pure and that pure α -ionone

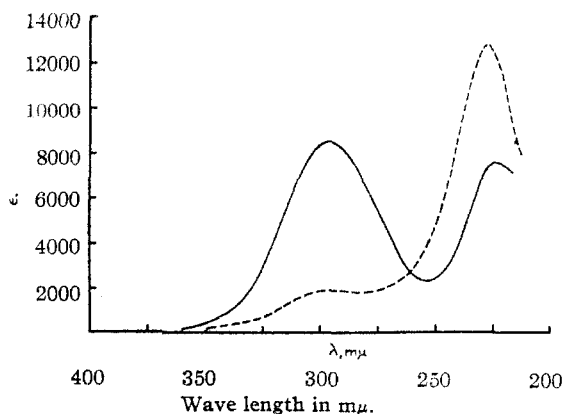


Fig. 2.—Spectra of commercial α - and β -ionone: α , —; β , ---.

displays no light absorption at 296 $m\mu$ it was calculated by use of the extinction coefficients at 296 $m\mu$ that the commercial α -ionone sample was 82% pure and that the commercial β -ionone (λ_{\max} 296 $m\mu$, ϵ 8600) was 80% pure.⁷

The Rates of Reaction of Some Unsaturated Carbonyl Compounds with Perbenzoic Acid.—It has been reported that α,β -unsaturated carbonyl compounds react only very slowly with perbenzoic acid.⁸ It was hoped that this hindered reactivity toward perbenzoic acid would be transmitted through two double bonds conjugated with a carbonyl group and that the isolated double bond in the α -ionone ring would react with perbenzoic acid much faster than would the double bond in the β -ionone ring, affording a means of purifying β -ionone. A comparative study of the rates of reaction of perbenzoic acid with commercial β -ionone (ϵ_{\max} 8600) and with relatively pure β -ionone (ϵ_{\max} 10100) showed that the samples consumed perbenzoic acid at an equal rate which was much faster than the rate for ordinary α,β -unsaturated carbonyl compounds (ethylideneacetone, crotonaldehyde, and benzalacetone).

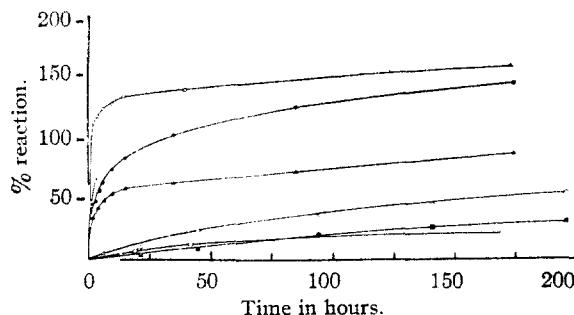


Fig. 3.—Reaction rates of unsaturated carbonyl compounds with perbenzoic acid at 8°.

Compound	Init. concn.	Init. concn. $C_6H_5CO_3H$
○, β -ionone (ϵ_{\max} 10100)	0.0297 <i>M</i>	0.0605 <i>M</i>
×, β -ionone (ϵ_{\max} 8600)	.0309	.0313
×, β -ionone (ϵ_{\max} 10100)	.0332	.0313
●, cinnamalacetone	.0275	.0605
▲, dibenzalacetone	.0309	.0605
Δ, ethylideneacetone	.0288	.0299
■, crotonaldehyde	.0333	.0299
□, benzalacetophenone	.0394	.0312

In Fig. 3 are plotted the rates of reaction of several unsaturated carbonyl compounds with perbenzoic acid at 8° in toluene or benzene solution. Values of the per cent. reaction vary from 0 to 200, since in some of the rate studies on dienes sufficient perbenzoic acid was used to react with two moles of carbon-carbon double bond.

In order to determine whether or not the rapid reaction of β -ionone with perbenzoic acid was

(7) These are the commercial ionones used in synthetic work reported by Young, Andrews and Cristol, *THIS JOURNAL*, **66**, 520 (1944).

(8) Böeseken, *Rec. trav. chim.*, **45**, 838 (1926).

characteristic of α,β , γ,δ -unsaturated carbonyl compounds the rates of reaction of β -ionone and cinnamalacetone with two moles of perbenzoic acid were measured and compared. In both cases when one mole of perbenzoic acid was consumed, the reaction rate dropped off rapidly and became comparable to that of an α,β -unsaturated carbonyl compound. Presumably, then, the double bond in the β -ionone ring is the one which consumes the first mole of perbenzoic acid. Dibenzalacetone in the presence of two moles of perbenzoic acid reacted very rapidly until about half a mole of perbenzoic acid had been consumed. Then the rate of reaction decreased to that of a compound having one ethylenic linkage to a carbonyl group.

Experimental Part

β -Ionone Semicarbazone.—To a solution of 50 g. of semicarbazide hydrochloride and 44 g. of potassium acetate in 150 ml. of water was added a solution of 85 g. of commercial β -ionone in 150 ml. of ethanol. Sufficient ethanol to dissolve the β -ionone was added. The solution was cooled in an ice-bath to induce crystal formation. The crude product was purified by four to six recrystallizations from absolute ethanol or 75% methanol to constant melting point (148–149°) and extinction coefficient in 95% ethanol (λ_{\max} 282 m μ , ϵ_{\max} 22300). Fifty grams of purified product was obtained (45%).

Acid Decomposition of β -Ionone Semicarbazone.— β -Ionone semicarbazone (68 g.) was refluxed with 300 ml. of 3 *N* sulfuric acid for three hours. The liberated oil was extracted with 100 ml. of ether, and the ether solution was dried over sodium sulfate. After removal of the ether, the β -ionone was distilled, b. p. 142–144° (18 mm.) (wt. 35 g., 76%).

In one experiment carried out according to the directions of Kuhn and Morris^{4a} a mixture of 58.6 g. of β -ionone semicarbazone and an equal weight of phthalic anhydride was steam distilled and the β -ionone in the distillate extracted with ether. The distilled product, b. p. 143–146° (18–20 mm.), weighed 35.7 g. (75%).

In separate experiments 5.0 g. of β -ionone semicarbazone was steam distilled from a constant volume of 40 ml. of water containing 5 g. of phthalic anhydride, 0.17 equiv. of succinic acid, 0.12 equiv. of phosphoric acid, or 0.12 equiv. of sulfuric acid. The recovered β -ionone weighed 3.0 g. (78%) in each case (properties in Table I).

Five grams of the semicarbazone was shaken at room temperature for three and one-half days with a mixture of 20 ml. of petroleum ether and 48 ml. of 2 *N* sulfuric acid.⁶ The organic layer was washed with water and dilute sodium bicarbonate solution and dried. The distilled β -ionone weighed 2.7 g. (70%).

The Stability of β -Ionone and its Semicarbazone toward Dilute Sulfuric Acid.—Five grams of β -ionone semicarbazone (m. p. 148–9°, ϵ_{\max} 21400), 20 ml. of petroleum ether, and 48 ml. of 2 *N* sulfuric acid were shaken at room temperature for twenty-four hours. The remaining white

solid was filtered, washed with petroleum ether and water and dried. The 3.1 g. of recovered semicarbazone melted 148–149.5° and had ϵ_{\max} 21300 in 95% ethanol.

Five grams of β -ionone (ϵ_{\max} 8600) was shaken for two days with petroleum ether and 2 *N* sulfuric acid as described for the decomposition of β -ionone semicarbazone. The β -ionone recovered (3.3 g.) as previously described had ϵ_{\max} 8900 in 95% ethanol.

Ten-gram samples of β -ionone were refluxed for four hours with 100 ml. of 3 *N* sulfuric acid. The ionone was extracted with ether and the solution washed with water and dilute sodium bicarbonate solution and dried. The distilled product weighed 8 g. A sample of β -ionone, ϵ_{\max} 8600, gave a product, ϵ_{\max} 8400, and a sample having ϵ_{\max} 5560 gave a product of ϵ_{\max} 5200 in 95% ethanol.

Absorption Spectrum Measurements.—The ultraviolet absorption spectra in 95% ethanol solution of the several ionone samples were measured on a Beckman spectrophotometer.

Reaction Rates of Unsaturated Carbonyl Compounds with Perbenzoic Acid.—A chloroform solution of 0.343 *M* perbenzoic acid was prepared according to the method of Braun.⁹ A sample (about 0.003 mole) of the unsaturated compound was weighed into a 100-ml. volumetric flask which was then partially filled with solvent (dry benzene or toluene), and a 10 or 20 ml. pipet sample of the perbenzoic acid solution was added. The flask was filled to the mark with solvent and placed in the refrigerator (8°). Ten-ml. pipet samples were removed from time to time and analyzed according to the method of Braun.⁹ A blank run was made to follow the rate of perbenzoic acid decomposition. These determinations were not strictly quantitative owing to the somewhat inaccurate temperature control and timing used. The percentage of the unsaturated compound which had reacted over any given length of time *t* was calculated from the amount of perbenzoic acid consumed in this length of time by the use of the equation

$$\frac{\% \text{ unsaturated compound}}{\text{reacted at time } t} = \frac{\text{moles of perbenzoic acid consumed at time } t}{\text{moles of unsaturated compound at } t = 0} \times 100$$

Summary

The method of purification of β -ionone by decomposition of its semicarbazone in acid media has been studied. Decomposition with sulfuric acid gives β -ionone of greater purity than decomposition with weaker acids.

A study of the reaction rates of perbenzoic acid with α,β , γ,δ -unsaturated carbonyl compounds including β -ionone, indicates that the hindrance to reactivity furnished to one double bond by a carbonyl group is not transmitted through two conjugated double bonds.

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(9) Braun, "Organic Syntheses," **13**, 86 (1933).