and the contents of the beaker were vigorously stirred. The coupling was completed as much as possible before adding a fresh quantity of the diazo solution, the presence of unaltered diazo compound being tested by means of an alkaline solution of β-naphthol. After all the diazo solution had been added, the stirring was continued for about an hour. The beaker was taken out of the cold bath, and the solution acidified with dil. acetic acid when unaltered fluorescein separated as a yellow precipitate. The solution was cooled and then filtered. To a test portion of the filtrate, dil. acetic acid was added drop by drop but no further precipitate was formed. Dil. sulfuric acid was next added to the filtrate and the red precipitate formed was filtered off and washed with cold water, dissolved in a dil. solution of sodium hydroxide, and the dye precipitated by means of dil. sulfuric acid. The precipitate was filtered off, washed and dried. This compound is a red powder soluble in hot water; it dyes wool orange. The alkaline solution shows red-green fluorescence.

Analysis. Subs., 0.1340: 6.4 cc. of N_2 (29°, 759.6 mm.). Calc. for $C_{26}H_{16}O_8N_2S$: N, 5.43. Found: 5.19.

Summary

1. Three types of azo-triphenylmethane dyes have been studied containing, respectively, one, two and three azo groups in the *para* position to the central carbon atom. It has been found that the introduction of one azo group deepens the color, of two azo groups lightens the color, and of three makes it still lighter.

2. The effect of the multiplication of chromophores has also been studied by introducing simultaneously an azo-methine group and an azo group into chrysoidine, rosaniline, safranine and congo red, and in each case the color becomes lighter. The direct dyeing property of congo red also disappears.

3. The introduction of one azo group has been found to deepen the color in the case of an indamine dye as well as in the case of fluorescein.

CALCUTTA, INDIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

CONDENSATION OF CITRAL WITH KETONES AND SYNTHESIS OF SOME NEW IONONES[1]

BY HAROLD HIBBERT AND LAURA T. CANNON

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Theoretical Discussion

In connection with a series of studies on the condensation and polymerization of aldehydes and ketones, it seemed desirable to reinvestigate the behavior of citral towards acetone in the presence of alkaline condensing media. This offered the possibility of obtaining further evidence on

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[1] This paper is constructed from a dissertation presented by Laura T. Cannon in June, 1921, to the Faculty of the Graduate School, Yale University, in candidacy for the degree of Doctor of Philosophy. The thesis contains a review of the scientific and patent literature on citral, ionones and related compounds as well as of the work on "the relation between odor and constitution."

the correlation of odor and constitution, especially with respect to the influence of alkyl substitution, and also of securing information regarding the nature of specific aldehyde-ketone condensations, in particular, that pertaining to unsaturated aldehydes as bearing on the constitution of lignin.

The data relating to the manufacture of pure citral, pseudo-ionone and the ionones, are scattered widely through the literature, so that considerable effort was necessary in order to ascertain the best methods to employ for the preparation of the pure raw materials. Tiemann and Krueger[2] showed that citral condenses readily with acetone in alkaline media with formation of pseudo-ionone and that this on treatment with acids is converted into the cyclic derivative, ionone, the transformation being effected by the primary addition of water, followed by its removal and formation of the cyclic compound.

There are two isomeric ionones (α and β), the difference in their constitution being attributable to the variation in the position of the double bond in the ring. Both substances, in dilute solution, possess the fragrant odor of violets.

In view of the more agreeable odor possessed by ketones of higher molecular weight, experimental work was carried out on the condensation of citral with methylpropyl, methylphenyl, diethyl and dipropyl ketones. It was found that the first two react readily with citral under the influence of either metallic sodium or sodium ethylate to give pseudo-ionones from which, on treatment with condensing agents such as phosphoric and sulfuric acids, the corresponding ionones can be prepared.

The replacement of one of the methyl groups in ionone by propyl gives a product possessing a fragrant violet odor, while the substitution of phenyl for methyl gives an ionone with little or no violet odor. On the other hand attempts to condense citral with ketones not containing a methyl radical directly attached to the carbonyl group (for example, diethyl and dipropyl ketones) were unsuccessful. Some evidence of condensation was obtained in the case of the diethyl derivative but none in that of butyrone. This behavior is in harmony with the poor yield obtained on condensing the latter with benzaldehyde[3] and the general inertness of both ketones (as compared with the lower homologs) towards chemical reagents.[4]

As most of the information concerning citral condensations is found only in the patent literature, this was subjected to a careful review and in the experimental part methods are given for the isolation of pure citral, pseudo-

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[2] (a) Tiemann and Krueger, *Ber.*, **26**, 2692 (1893); see also Tiemann, *Ber.*, **31**, (b) 808, (c) 867, 1736, 2313 (1898); **32**, 827 (1899); **33**, 3708 (1900). Haarmann and Reimer, *Ber.*, **27**, Ref., 319, 768 (1894).

[3] *Ber.*, **30**, 2264 (1897).

[4] (a) Grimm, *ibid.*, **157**, 263 (1871). (b) Kurtz, *Ann.*, **161**, 205 (1872).

ionone and ionones of high purity, thus making more readily available a series of important products of considerable value in the study of problems such as those of "unsaturated aldehydes" and "the relation of odor to constitution."

Thus, the manufacture of sulfite pulp is based on the removal of lignin from the wood as a soluble calcium sulfonate, produced by the addition of calcium bisulfite to the unsaturated complex present in the lignin molecule. In spite of the fundamental importance of such reactions our scientific knowledge of them is decidedly vague and limited to a relatively few derivatives such as acrylic aldehyde, crotonaldehyde, cinnamic aldehyde, citral, citronellal, styrol.[5]

Experimental Part

To obtain chemically pure ionones, it is necessary (1) to remove products such as citronellal, methyl heptenone, terpenes, etc., from the commercial citral, and (2) to isolate pure pseudo-ionone, by chemical means.

Regarding the first, it was found, after a thorough study of the literature that the following procedure, based on Tiemann's method[6] gave the most satisfactory product.

Isolation of Pure Citral

A mixture of 1750 g. of crystalline sodium sulfite ($Na_2SO_3.7H_2O$), 625 g. of sodium bicarbonate and 5 liters of water was agitated at room temperature for about two hours, or until the solid carbonate had disappeared. The solution was then cooled by means of an ice-bath to 5–10° and 500 g. of commercial citral added, with vigorous agitation, which was continued for 3 to 4 hours' intimate contact being effected between oil and solution and air excluded as much as possible. Under these conditions only the citral went into solution, namely, as the labile dihydro-disulfonic acid derivative. The solution was agitated thoroughly with about 500 cc. of ether, the ether removed and the process repeated in order to remove all undissolved impurities.

Recovery of Citral from the Solution

Citral is very unstable towards alkalies, readily undergoing polymerization so that it is inadvisable to treat the whole of the solution in one operation unless suitable equipment is on hand for immediate extraction of the liberated citral. It was found better to proceed as follows.

To 400 cc. of the solution of citral dihydro-disulfonic acid was added about 150 cc. of ether, followed by a solution of 10% sodium hydroxide (with thorough stirring during the addition) until the precipitation of oil was *almost* complete.[7] The mixture was shaken vigorously for half a minute, the ether separated, any traces of alkali *at once* neutralized

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[5] A review is being made of the scientific literature and it is the intention of one of the authors (H. H.) to carry out some fundamental scientific work in this field as soon as time and opportunity permit.

[6] Tiemann, *Ber.*, **31**, 3319, 3339 (1898).

[7] This is best accomplished by running in small quantities of the alkali and shaking the mixture after each addition, until the further addition produces only a relatively faint, white, oily emulsion. The operation should be carried out as rapidly as possible.

by washing the liquid with a few cubic centimeters of dil. tartaric acid solution and the latter removed by shaking the liquid with a little water. The precipitation of the citral in the same sample of mother liquor was effected by first adding ether, and then alkali, until precipitation was completed. The mixture was shaken, neutralized, washed as before, and the two ether extracts were combined.

The process was repeated with an additional 400 cc. of the citral dihydro-disulfonic acid solution until the entire quantity had been thus treated. The ether solution was dried with sodium sulfate, the ether removed and the residue distilled under diminished pressure. With a good grade of commercial citral the yield is about 80%; b. p., 110–111° (11 mm.).

Preparation of Methylpropyl, Diethyl and Dipropyl Ketones

These were prepared by the method of Senderens[8] by passing the vapors of the corresponding acid or acids over thorium dioxide heated to 400–430°. The reaction is a general one: $RCOOH + R'COOH = R{-}CO{-}R' + H_2O + CO_2$.

The apparatus consisted of an electrically-heated furnace fitted with a quartz tube (95 cm. long) wound with resistance wire and covered with an insulating asbestos jacket in order to maintain a temperature between 400° and 430°. For the preparation of the contact mass, small pieces of silica fire-brick were saturated with a concentrated solution of pure thorium nitrate (free from sulfate),[9] the solution evaporated to dryness over a Meker burner, and the residue (in presence of the silica support) heated until red fumes ceased to appear. It was transferred to the quartz tube, the temperature raised to 420° and the acid, or mixture of acids, introduced into one end in the form of fine drops, the vapors emerging from the other being condensed and collected. The entire quantity was then subjected, where necessary, to a second and third treatment. The crude distillate, containing both unchanged acids and crude ketones, was first shaken with a slight excess of sodium carbonate solution, and the crude ketones were then extracted with ether, washed, dried and subjected to fractional distillation.

Methylpropyl Ketone.—A mixture of two parts of glacial acetic to one part of butyric acid was employed.

Diethyl Ketone.—Prepared in a similar manner, using propionic acid.

Dipropyl Ketone.—Butyric acid (b.p., 160–165°) was circulated thrice over the contact mass; yield of ketone (b.p. 137–147°), 62%. Addition of 10% of water to the acid decreased the yield.

Preparation of Ionone

Condensation of Citral[10] with Acetone. Synthesis of Pseudo-ionone.—It was not found possible from the information given in the patent literature[11] to obtain a satisfactory yield of *pure* pseudo-ionone. Some of the results obtained are summarized below (Expts. 1–4.—Table I).

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[8] Senderens, *Bull. soc. chim.*, [4] **5**, 483 (1909); *Ann. chim. phys.*, [8] **28**, 270, 288 (1913); *Compt. rend.*, **146**, 1212 (1908); **148**, 929 (1909); **149**, 213 (1909).

[9] If sulfate is present this gives rise to the formation of organic sulfur derivatives and at the same time results in the poisoning of the catalyst.

[10] The citral employed was a high grade commercial product; C. P. citral, whenever used, refers to material purified by Tiemann's method.

[11] A list of patents and information concerning them is to be found in the thesis. The authors are indebted to Dr. Emmet Reid for help in compiling the following list. Ger. pat. 73,089, 106,512, 108,335, 116,637, 122,466, 123,747, 124,227, 124,228, 130,457,

Substitution of alcoholic sodium hydroxide as the condensing agent, and operating at a lower temperature, increased the yield considerably (Expt. 5), but the product was not pure as shown by the wide range in its boiling point.

Use of Metallic Sodium as Condensing Agent.—In view of the fact that metallic sodium may be successfully employed for the synthesis of acetaldol,[12] various experiments were performed using this material as a condensing agent, good yields of ionone being obtained, as indicated in Expt. 6. A variation from 0.2 to 6.0 g. in the quantity of metallic sodium employed in a series of experiments did not increase the yield, whereas lengthening the time of condensation diminished it. Attempts to lower the alkalinity by bubbling carbon dioxide through the liquid during the progress of the reaction decreased the amount of condensation considerably.

The use of metallic sodium as condensing agent was found to offer no advantage over that of sodium ethylate as employed by Stiehl.[13] His process, used in conjunction with Tiemann's purification treatment, is described below.

Method.—A mixture of 50 g. of pure citral and 200 g. of acetone was cooled to —5° or —8° and to this a cooled solution of 2.3 g. of sodium in 50 cc. absolute alcohol was slowly added, while the mixture was vigorously agitated, during a period of ten minutes, the agitation being then continued for a further 3–4 minutes at the same temperature (—5°). After removal of the alkali by shaking the solution with the calculated quantity of tartaric acid dissolved in 50 cc. of water, the product was washed with water to ensure complete neutrality and the excess of acetone removed by distillation with steam.

The crude pseudo-ionone was best purified by Tiemann's method,[2b] in that one part of it was boiled for 5 to 6 hours with 2 parts of a 35% solution of sodium bisulfite and 1 part of water. The insoluble impurities such as higher-boiling polymerization products were extracted with ether and the aqueous solution of the bisulfite addition compound decomposed as follows, by repeated addition of small quantities of 10% sodium hydroxide, in order to avoid resinification of the pseudo-ionone by any excess of alkali:

About 50–60 cc. of the aqueous bisulfite solution was mixed in a liter separatory funnel with just sufficient 10% sodium hydroxide solution so that the addition of a further small quantity produced no additional turbidity. It was then *at once* extracted with ether. (The best method of operating is to add a small quantity of the alkali solution, to shake the mixture with ether, and to continue the addition of alkali and rapid extraction until no further turbidity is shown on addition of a further quantity of the alkali.) The entire quantity of the aqueous bisulfite solution was subjected to the same treatment,

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129,027, 127,831, 127,661, 127,424, 126,959, 126,960, 134,672, 133,758, 133,563, 133,145, 132,222, 139,959, 138,939, 138,100, 143,724, 150,771, 147,839, 157,647, 160,834, 164,505, 164,366, 183,855, 172,653, 199,550, 200,654. U. S. pat.: Tiemann, 559,636, 556,944, 556,943, 583,719, 583,720, 650,028, 658,411; Schmidt, 762,765, 779,187, 775,251; Sembitzki, 688,131; Strebel, 715,896; Mehrling and Welde, 743,305, 782,679; Krauth, 652,969; Klimant, 637,209; Ziegler, 601,193; Wack, 896,942; Blackmore, 809,900, 830,044; Chuit, 765,459; deLaire, 600,429.

[12] Unpublished researches of the senior author.

[13] Stiehl, *J. prakt. Chem.*, **58, 79** (1898).

Table I

Yields of Pseudo-ionone

Exp.	Ger. patent	Proportions used Citral G.	Acetone G.	Condensing agent	Time hours	Temp. °C.	Removal of citral	Distillation of crude product	Yield %
1	73,089	50	50	20 cc. of 5% aqueous barium hydroxide	54	18–20	Steam distillation for $1^1/_2$ hours	15.8 g. b. p. 138–158° (16 mm.)	26
2	127,661	50	50	5 g. of sodium peroxide	Mixture took fire	.....	....	.....	..
3	127,661	25	50	0.5 g. of sodium peroxide	18	18–20	Steam distillation for 1 hr.	12.7 g. b. p. 147–170° (20 mm.)	44
4	127,661	25	75	2.5 g. of barium peroxide	48	18–20 for 24 hrs. 100 for 24 hrs.	80% citral recovered by steam distillation	.....	..
5	.....	50	150	7 cc. of 10% alcoholic sodium hydroxide	1 1 1	at −5 at 18–20 at 100	Steam distillation for 2 hrs. yielded 9 g. citral	29.5 g. b. p. 120–140° (3 mm.)	52
6	.....	50 (c. p.)	200	1.5 g. of sodium wire	1	0	Steam distillation 2 hrs.	35 g. b. p. 138–158° (12 mm.)	62

TABLE II

CONVERSION OF PSEUDO-IONONE INTO IONONE

20 g. of Pseudo-ionone was used in each experiment except No. 12, in which 35 g. was employed. **Pseudo-ionone** refers to material purified by fractional distillation, usually boiling within 10°. *Pure* pseudo-ionone refers to material purified by the bisulfite method.

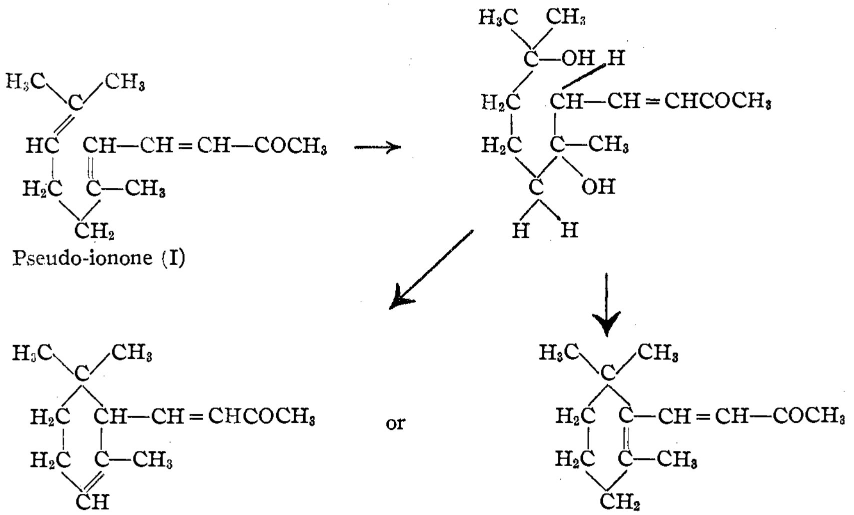
Exp.	Ger. patent	Condensing agent	Time hours	Temp. °C.	Boiling point of product obtained °C.	Yield %
1	73,089	Water, 100 g. Concd. (93%) sulfuric acid 2.5 g. Glycerol, 100 g.	5	100	112–122 (12 mm.)	54
2	133,563 129,027	Phosphoric acid (d., 1.54), 80 g.	1	40	95–120 (2.5 mm.) Considerable resinification	25
3	138,100	Sulfuric acid (70%), 80 g.	$^3/_4$	30	95–120 (2.5 mm.) Considerable resinification	40
4	.....	Phosphoric acid (d., 1.34=85%), 80 g.	3	30	100–110 (5 mm.)	52
5	.....	Sulfuric acid (50%), 150 g. Crystalline borax, 25 g.	$^1/_2$	18–20	Pseudo-ionone unchanged	..
6	.....	Sulfuric acid (70%), 100 g. Crystalline borax, 25 g.	$^3/_4$	30	12 g. 112–120 (4 mm.)	60
7	.....	Sulfuric acid (70%), 100 g.	$^3/_4$	30	8 g. 95–120 (2.5 mm.). Large amount of resinification	40
8	.....	Sulfuric acid (80%), 100 g.	$^3/_4$	30	6 g. Resinification very pronounced	30
		In the following experiments *pure* pseudo-ionone was employed				
9	.....	Sulfuric acid (70%), 150 g.	1	30	13.5 g. 126–134 (12 mm.)	65
10	.....	Concd. sulfuric acid, 2.5 cc. Water, 100 g. Glycerol, 100 g.	5	Boiling point	7 g. 128–138 (12 mm.). 9 g. 138–149 (12 mm.)	35 Unchanged pseudo-ionone
11	.....	Phosphoric acid (85%), 150 g.	$^1/_2$	30	16 g. 125–135 (12 mm.)	80
12	.....	Phosphoric acid (85%), 275 g.	$^1/_3$	30	27 g. 126–131 (12 mm.)	79

and in this way the contact between the liberated pseudo-ionone and free alkali was limited as much as possible.

The united ether extracts were washed with water, dried with anhydrous sodium sulfate, the ether evaporated, and the residue fractionated under reduced pressure; yield, 55% of pure pseudo-ionone; b. p., 145–150° (12 mm.).

Conversion of Pseudo-ionone to Ionone

Pseudo-ionone, as shown by Tiemann,[2] is converted under the influence of acids into a mixture of α- and β-ionones, the artificial "violet perfume."



Pseudo-ionone (I)

α-Ionone (II)

β-Ionone (III)

According to the patent literature[14] the action of dil. sulfuric acid gives a mixture of the α and β isomers, while the concentrated acid gives almost entirely β-ionone. On the other hand, 85% phosphoric acid is stated to give a product consisting essentially of the α isomer. The boiling points of both isomers lie very close together.[15]

A large number of experiments was carried out on the conversion of pseudo-ionone into ionone in which the following factors were varied: (a) nature and concentration of the acids; (b) nature of the addendum (borax, glycerol, etc.); (c) time; (d) temperature. The results are summarized in Table II.

It is evident that the addition of borax is of no particular advantage, but that each of the factors, namely quantity, concentration of acid, temperature and time of condensation, plays an important role.[16]

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[14] Ger. pat. 75,120, 73,089, 127,424, 133,563, 138,100, 138,939.

[15] Tiemann (Ref. 2c, p. 879) gives the following boiling points: α-ionone, 123–124° (11 mm.); β-ionone, 127–128.5° (10 mm.); natural ionone 126–128° (12 mm.).

[16] The addition of borax was investigated in view of its known value in preventing resinification during the synthesis of acetaldehyde from acetylene (Hibbert and Morton, U. S. pats., 1,213,486 and 1,213,487).

The product used in Expts. 1–8 (inclusive) undoubtedly contained some unchanged ionone and higher-boiling polymerization products. When the resulting ionone is subjected to steam distillation the greater part of the resinification products of citral is removed. Nevertheless, the small amount passing over with the ionone exerts an unfavorable influence on the odor and renders it sufficiently impure so that it is not possible to isolate *crystalline* derivatives (semicarbazone, oxime, etc.) from it.

No attempt was made to separate the α- and β-ionones, either in these or the later experiments. Phosphoric acid (which, as is evident from the tabulated results, gives the best yield) was employed as condensing agent in all of the later work. The products thus obtained (to judge from the patent literature[14]) represent essentially α-ionones.

The following procedure was found to give the best yield (77–80%) of α-ionone.

Preparation of α-Ionone

Method.—Twenty g. of pure pseudo-ionone was added, drop by drop, with constant agitation to 150 g. of 85% phosphoric acid, and the temperature kept either at 30° for 30 minutes, or at 30–35° for 25 minutes. The reaction product was poured into 500 cc. of cold water, extracted with ether, washed with water, dried over sodium sulfate and after removal of the ether, subjected to steam distillation for 4 to 5 hours, the ionone passing over and leaving behind the resinification and polymerization products. The aqueous distillate was extracted with ether, dried, the ether evaporated, and the remaining liquid distilled under reduced pressure. The ionone thus obtained boiled at 126–131° (12 mm.) and presumably consisted almost entirely of the α isomer;[17] yield, 77–80%.

Preparation of Homologs of Ionone. Synthesis of Ethyl Ionone[18]

Preparation of Pseudo-ethyl Ionone.—Fifty g. of citral was condensed with 180 g. of methylpropyl ketone (b. p., 97–107°) under the same conditions as employed in the case of acetone. The crude product was washed with a saturated solution of sodium chloride to prevent loss of the methylpropyl ketone; yield, 49 g. (70%); b. p., 155–170° (8 mm.).

The material was purified by the bisulfite process as used in the case of pseudo-ionone and yielded 25 g. (35%) of pure pseudo-ethyl ionone as an almost odorless, pale yellow oil; b. p., 155–158 (8 mm.).

Analyses. Calc. for $C_{15}H_{24}O$: C, 81.81; H, 10.91. Found: C, 80.90, 81.61; H, 10.98, 10.90.

Preparation of Ethyl Ionone.—Fifteen g. of the pure pseudo-ethyl ionone was treated with 150 g. of 85% phosphoric acid as in the case of pseudo-ionone. The yield of pure ethyl ionone was 12 g. (b. p., 137–141° (8 mm.)) of which 70% boiled between 138° and 140°.

Analyses. Calc. for $C_{15}H_{24}O$: C, 81.81; H, 10.91. Found: C, 81.50, 81.60; H, 10.52, 10.62.

Ethyl ionone is a pale yellow oil possessing a pleasant odor of violets.

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[17] Haarmann and Reimer, Ger. pat., 127,424; *Chem. Centr.*, **1902**, I, 235.

[18] The condensation of citral with methylpropyl ketone is mentioned in Ger. pat., 150,771 (1904) but no details and no information as to the boiling point and physical properties of pseudo-ethyl ionone or ethyl ionone are given.

Constitution of Ethyl Pseudo-ionone and Ethyl Ionone.—It is apparent that the condensation of citral with methylpropyl ketone may give rise to one or both of two products, namely, $(CH_3)_2C{=}CHCH_2CH_2C(CH_3){=}CHCH{=}CHCOC_3H_7$ (IV) and $(CH_3)_2C{=}CHCH_2CH_2C(CH_3){=}CH\text{-}CH{=}C(C_2H_5)COCH_3$ (V). It is known that Type IV is formed by the action of *alkaline* condensing agents while *acids* give rise to Type V.[19] Thus in alkaline solution benzaldehyde condenses with methylethyl ketone[19b] and methylpropyl ketone[19c] to give α-benzal-methylethyl ketone (C_2H_5—CO—CH=CH—C_6H_5) and α-benzal-methylpropyl ketone (C_3H_7—CO—CH=CH—C_6H_5), respectively. On the other hand, in acid solution, the same two ketones and benzaldehyde yield γ-benzal-methylethyl ketone [CH_3—CO—C(CH_3)=CH—C_6H_5] and γ-benzal-methylpropyl ketone [CH_3—CO—C(CH_2—CH_3)=CH—C_6H_5], respectively. It is thus very probable that the condensation product from citral and methylpropyl ketone is represented by Formula IV rather than V.

Since 85% phosphoric acid has been shown to favor the formation of the α-ionone from the pseudo-ionone,[19] it follows that the ethyl ionone product obtained above in all probability consists essentially of the α-ethyl ionone derivative.

Condensation of Citral with Acetophenone

Preparation of Phenyl Pseudo-ionone.—To a mixture of 50 g. of citral with 200 g. of acetophenone at room temperature was slowly added, with constant stirring, 2.5 g. of sodium dissolved in 50 cc. of absolute alcohol. After 15 minutes the condensation was terminated by the addition of 10 g. of tartaric acid dissolved in 50 cc. of water. After the mixture was washed and dried and the excess of acetophenone removed by distillation under reduced pressure, the crude product (75 g.) was purified by boiling it for 5–6 hours, with 150 cc. of a 35% solution of sodium bisulfite and 75 cc. of water. The insoluble material was extracted with ether, the bisulfite solution then decomposed by addition of 10% sodium hydroxide solution and the pure phenyl pseudo-ionone immediately extracted with ether, as outlined in the foregoing experiments with pseudo-ionone and pseudo-ethyl ionone. The ether extract was dried, the ether removed and the residual oil fractionated under reduced pressure. There was obtained 29 g. of phenyl pseudo-ionone (b. p., 182–185° (4.5 mm.)) as an odorless, viscous, pale yellow oil; yield, 35%.

Analyses. Calc. for $C_{18}H_{22}O$: C, 85.04; H, 8.66. Found: C, 84.91, 84.75; H, 8.53, 8.42.

Preparation of Phenyl Ionone.—To 150 g. of 85% phosphoric acid warmed to 30°, 20 g. of phenyl pseudo-ionone was added drop by drop at the same temperature and the mixture well stirred for 30 minutes. After dilution with water, extraction with ether, and removal of the latter, the product was distilled in a rapid current of steam. The oily distillate was extracted and fractionated under diminished pressure; yield **11** g. (55%); b. p., 172–175° (4.5 mm.).

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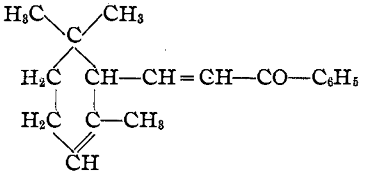
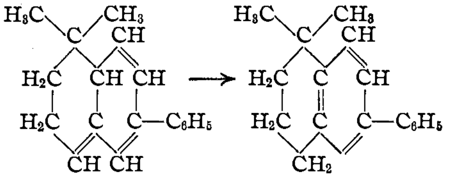
[19] (a) Goldschmiedt and co-workers, *Monatsh.* **18,** 437 (1897); **19,** 406 (1898); **22,** 659 (1901). (b) Harries and Mueller, *Ber.,* **35,** 966 (1902). (c) Harries and Bromberger, *Ber.,* **35,** 3088 (1902). (d) Harries and Busse, *Ber.,* **29,** 376 (1896).

Analyses. Calc. for $C_{18}H_{22}O$: C, 85.04; H, 8.66. Found: C, 86.9, 86.72, 87.00, 87.3; H, 8.54, 8.46, 8.46, 8.74.

Phenyl ionone is a pale yellow, viscous oil, the odor of which is not particularly agreeable, the fragrance of violets being practically entirely suppressed, due to the presence of the phenyl group. In comparing the odors of phenyl pseudo-ionone and phenyl ionone, however, the former is dull and comparatively negative, while the latter is somewhat pungent and reminiscent of violets. Considering the condensing agent employed, namely, sirupy phosphoric acid, it seems probable, judging by analogy, that the product obtained was essentially the α isomer (VI).



VI



VII VIII

An examination of the analytical data for the phenyl ionone shows that the carbon content is approximately 2% high and, in spite of considerable effort and time spent in attempting to purify the material, it was not found possible to obtain a closer agreement. The phenyl pseudo-ionone used was a pure product and the only explanation which can be suggested is the possibility that the phenyl ionone undergoes a partial further condensation with formation of the bicyclic hydrocarbon ($C_{18}H_{20}$, VII or VIII), the presence of which is responsible for the high carbon values.[20]

Condensation of Diethyl Ketone with Citral

Attempts to condense citral with diethyl ketone were unsuccessful, this inactivity of the latter being in harmony with its behavior towards other reagents.[4a]

Attempted Condensation of Dipropyl Ketone (Butyrone) with Citral

In spite of numerous attempts it was not found possible to condense dipropyl ketone with citral, its inertness in this respect being analogous to that shown in its failure to form addition compounds with sodium bisulfite and ammonia.[4b]

The experiments of Vorländer[3] on the condensation of this ketone with benzaldehyde show that the reaction goes only with difficulty and is much more incomplete than a similar condensation with diethyl ketone.

Summary

1. The best method for purifying citral is the one developed by Tiemann. A detailed description of this method is given, thus rendering it more accessible.

2. Of the numerous condensing agents employed, in both the patent

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[20] This contains C = 91.53, H = 8.47 and as will be noted from the analyses, the figures obtained fall between these values and those for phenyl ionone. An attempt is to be made to isolate the hydrocarbon by operating under more drastic conditions, since there is the possibility that its constitution may be more accurately represented by VIII.

and the scientific literature, for the production of pseudo-ionones, sodium ethylate is the most satisfactory. It is found that metallic sodium is very efficient. The method and technique of this condensation have been improved and good yields of much purer products obtained. The bisulfite method of purification is capable of general application in the purification of pseudo-ionones.

3. One of the best catalytic agents for the conversion of pseudo-ionones into ionones is 85% phosphoric acid; the conditions necessary for high yields and purity are indicated.

4. The actions of alkaline condensing agents on mixtures of citral and dimethyl ketone, methylpropyl ketone, acetophenone, diethyl ketone and dipropyl ketone, have been investigated. From the second and third, new ionones have been synthesized, the one from methylpropyl ketone having an agreeable violet odor, while that from acetophenone merely suggests the presence of such a fragrance.

5. It is thus evident that the introduction of propyl in place of methyl in ordinary ionone does not materially affect the character of the odor, while that of phenyl causes it to disappear almost completely.

6. Furthermore, those ketones, in which both alkyl groups attached to the —CO—group are other than methyl, condense with citral only with great difficulty, or not at all, this behavior being in harmony with their incomplete condensation with benzaldehyde and other reagents. Thus diethyl ketone apparently reacts, but with considerable difficulty while dipropyl ketone cannot be induced to undergo condensation.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE CAUSATION OF ORGANIC REACTIONS BY ALUMINA, AND THEORIES OF CATALYSIS

BY HOMER ADKINS AND BRYNJULV H. NISSEN

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After a considerable experience in the use of the difficultly reducible oxides, alumina, titania, and thoria, as catalysts the conclusion was reached that the differences attributed to the oxides by Sabatier were due to modifiable physical characteristics rather than to distinctive chemical differences.[1] In experimental verification of this idea we were able to activate alumina selectively for the two reactions in the decomposition of ethyl acetate at the surface of alumina by modifying as we believe the spacial relationships of the molecules or "active points" of the catalyst.[2] Six dis-

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[1] Adkins, THIS JOURNAL, **44**, 385 (1922).

[2] Adkins, *ibid.*, **44**, 2175 (1922).