certain conditions, a second band appears parallel to the first one in its original position; both bands now travel parallel and sometimes even a third one develops. These phenomena are presumably due to diffusion and convection and may be in the nature of Liesegang rings, caused by the opposite gradients of light intensity and oxygen concentration, under the assumption that dissolved oxygen is used up in the course of the "secondary" reaction. Since these phenomena were observed in a quiescent solution only, and since they may influence intensity measurements in a rather complicated manner, the effects of flushing with inert gases might have been caused by the resulting turbulence rather than by diminution of oxygen concentration; however, in control experiments with mechanical stirring instead of nitrogen bubbling, the fluorescence intensity took a course identical with that in the quiescent experiment.

The rise-and-fall type of curve was not only encountered in pure alcoholic solutions, but also in mixtures of ethanol or methanol with benzene up to definite proportions of admixture; above a percentage of 65–70 of benzene the fluorescence/time curve abruptly assumed the level type observed in pure benzene (curve "5").

All these observations were made with vitamin A concentrates (OLEUM PERCOMORPHUM Mead Johnson) which contain vitamin A in the form of its natural esters with higher fatty acids. They were reproduced in all essentials with a fresh sample of crystalline vitamin A acetate (Distillation Products Co.). Crystalline vitamin A alcohol, of which a fresh and an eight months old sample were tested, does not increase in fluorescence upon ultraviolet irradiation in alcoholic solution. The intensity of its initial fluorescence conforms with that of an equivalent concentration of its acetate, but it begins to drop immediately as illustrated by curve "6."

A vitamin A_2 concentrate, prepared from fresh-water fish liver,[3] displayed the same features as the vitamin A concentrates used. This indicates that the difference between vitamins A_2 and A is vested in a part of the molecule that has no direct influence on fluorescence.

We are now studying the effect of these phenomena upon the Carr–Price reaction and upon the ultraviolet absorption with a view to elucidate the underlying mechanism. We are indebted to Mrs. W. Winternitz for valuable assistance.

Summary

The fluorescence of vitamin A esters in alcoholic solution first increases, then decreases under continued ultraviolet irradiation. Both processes are of photochemical nature, but the second one is impeded by flushing with inert gases. The phenomenon is shown by vitamin A_2 ester, but not by the free vitamin A alcohol.

[3] G. Wald, *J. Gen. Physiol.*, **22**, 391 (1939).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, LABORATORIES OF THE MOUNT SINAI HOSPITAL]

Studies on Ionone. I. Cleavage of Ethyl Ionylidene Acetate[1]

BY HARRY SOBOTKA, EDITH BLOCH AND DAVID GLICK

β-Ionylidene acetaldehyde is an important intermediate for syntheses in the carotenoid group. The preparation of this substance by reduction of the corresponding ethyl ionylidene acetate has been claimed by Kuhn and Morris.[2] Neither Karrer[3] nor Krauze[4] found this method practicable or satisfactory; the latter claimed better yields by the reaction of β-ionone with the Grignard compound of bromoacetal, but they failed to characterize their product by physical constants or derivatives. Our own experiences with Kuhn's method, also with modifications using stannous chloride instead of chromous chloride and aniline instead of *o*-toluidine, and with chloro-acetal were likewise unsatisfactory.

In 1935 Davies, Heilbron, Jones and Lowe[5] had described the preparation of β-ionylidene acetaldehyde by the dry distillation of a mixture

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[1] The work described in this paper was done under a contract, recommended by the Committee on Medical Research, between the Office of Scientific Research and Development, and The Mount Sinai Hospital.

[2] R. Kuhn and C. J. R. Morris, *Ber.*, **70**, 853 (1937); U. S. Patent 2,223,375 (April 22, 1941).

[3] P. Karrer and A. Ruegger, *Helv. chim. acta*, **23**, 284 (1940).

[4] M. V. Krauze and J. M. Slobodin, *J. Gen. Chem.* (Russian), **10**, 907 (1940).

[5] (a) W. H. Davies, I. M. Heilbron, W. E. Jones and A. Lowe, *J. Chem. Soc.*, 584 (1935); (b) I. M. Heilbron, W. E. Jones, A. Lowe and H. R. Wright, *ibid.*, 561 (1936).

of barium ionylidene acetate and barium formate. The identity of the reaction product with ionylidene acetaldehyde was questioned[2,4]; Burawoy,[6] in Heilbron's laboratory, suggested on the basis of ultraviolet absorption spectra that the product does not contain three ethenoid linkages in conjugation with each other, but is an α,β-unsaturated carbonyl compound.

In order to establish the nature of this product we prepared it according to the procedure of Davies,[5] and also obtained a number of nitrogenous derivatives from the resulting carbonyl compound. Their elementary analysis as well as that of the carbonyl compound itself clearly indicated the composition $C_{13}H_{20}O$, identical with that of ionone. The derivatives differed from the corresponding derivatives of β-ionone, but proved identical by melting point and mixed melting point with the corresponding derivatives of α-ionone. Subsequently, we prepared ethyl α-ionylidene acetate from highly purified α-ionone, converted it into the barium salt and subjected it to dry distillation with barium formate. The resulting product was again found to be identical with α-ionone.

These findings show that the barium salts of ionylidene acetic acids undergo cleavage of the α,β-double bond on dry distillation. In separate experiments we could demonstrate that the presence of barium formate was unnecessary for this reaction. Analogous scissions have been described in the literature for ethenoid linkages in α,β-position to carbonyl groups. Verley[7] observed the breakdown of citral into methylheptenone and acetaldehyde in boiling aqueous sodium carbonate solution. A number of similar reactions were surveyed by Meyer,[8] who reached the conclusion that in this type of cleavage the hydrogen atoms of water attach themselves to the carbon atom in α-position to the original carbonyl group, whereas the oxygen atom gives rise to a new carbonyl group in the other fragment of the molecule. This reaction is most frequently encountered with substances carrying no hydrogen on the β-carbon atom; thus the new carbonyl compound is usually a ketone (but *cf.* Cahnmann[9]).

The unexpected convergence during these reactions toward α-ionone, regardless of the steric configuration of the starting material, requires an explanation. The β-ionone, used in these experiments, was at least 90% pure according to its refractive index. The over-all yield of α-ionone in this cycle of reactions was much higher than whatever amounts of α-ionone may have been present in the starting material. Besides, the properties of the crude nitrogenous derivatives of the distillation product are such as to exclude the presence of significant amounts of the β-isomer. The question arises whether the shift in the cyclic double bond occurs during the degradation of the barium salt or during the Reformatsky synthesis and subsequent dehydration. It seems probable, from the physical constants of the ethyl "α"- and "β"-ionylidene acetates, given below, that the slight differences between them are not due to a difference in position of the cyclic double bond. Studies of the ultraviolet absorption spectra of the two esters, carried out in collaboration with H. H. Darby of the Department of Biochemistry, College of Physicians and Surgeons, Columbia University, will be reported at a future date; they likewise indicate that no system of four conjugated double bonds, as contained in ethyl β-ionylidene acetate, could be present in the ester obtained from β-ionone. It is suggested that some isomerization takes place during the Reformatsky reaction, which is compatible with Karrer's[10] statement that ethyl "β"-ionylidene acetate is a mixture of isomers.

Experimental

Ethyl Ionylidene Acetates.—These esters were prepared from α-ionone (n^{22}D 1.5008) and β-ionone (n^{22}D 1.5186) respectively according to Karrer.[10] Table I summarizes yields and properties.

TABLE I

	Ester from α-ionone	Ester from β-ionone
Yield in pct. of theor.	80	66
B. p. at 1 mm., ° C.	155–156	155
Acid equivalent (calcd. 262)	263	260
n^{23}D	1.4971	1.5020

Preparation of Barium Ionylidene Acetates.—The esters were saponified overnight with twice the theoretical amount of alcoholic potassium hydroxide at room temperature. The acids were extracted with ether and dried over sodium sulfate. The crystalline acid of m. p. 125°, described by Karrer[10] and Wittig[11] could not be obtained. The acids were converted into the potassium salts, and the

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(6) A. Burawoy, *J. Chem. Soc.*, 20 (1941).

(7) A. Verley, *Bull. soc. chim.*, [3] **17**, 175 (1897).

(8) R. E. Meyer, *Helv. chim. acta*, **18**, 461 (1935).

(9) H. Cahnmann, *Bull. soc. chim.*, [5] **4**, 226 (1937).

(10) P. Karrer, H. Salomon, R. Morf and O. Walker, *Helv. Chim. Acta*, **15**, 878 (1932); P. Karrer, R. Morf and K. Schoepp, *ibid.*, **16**, 557 (1933).

(11) G. Wittig and H. Hartmann, *Ber.*, **72**, 1387 (1939).

barium salts prepared by precipitation with barium chloride.

Dry Distillation of Barium Salts.—Six parts of barium ionylidene acetate, thoroughly mixed with 5 parts of barium formate and an equal volume of "140 mesh" silica, or powdered soft glass, was heated for two hours on a metal bath at 150° under 2 mm. pressure. The distillation was then completed on a sand-bath or over an open flame. The distillate was rectified, and the fraction collected below 100° under 1.3 mm. pressure equaled about one-fourth of the weight of the barium ionylidene acetate used. An identical product was obtained by similar distillation in the absence of barium formate. The fractionated oil showed the elementary composition of ionone.

Derivatives of Carbonyl Compounds.—The 2,4-dinitrophenylhydrazones, the 4-phenylsemicarbazones, and the *p*-chlorobenzoylhydrazones were prepared from the reaction products of both the α- and β-ionone series, and also from α- and β-ionone themselves. The dinitrophenylhydrazones were prepared in glacial acetic acid, the others in ethanol containing a few drops of acetic acid. Their melting points and mixed melting points are summarized in Table II, their elementary analyses in Table III. The data confirm that the reaction products in both instances are of the composition $C_{13}H_{20}O$, and that they are identical with each other and with α-ionone.

TABLE II

Melting points of derivatives of	2,4-Dinitrophenylhydrazone	4-Phenylsemicarbazone	*p*-Chlorobenzoylhydrazone
(a) α-Ionone	143	183–184	214–215
(b) β-Ionone	125–127	160–162	218–219
(c) Carbonyl cpd. from "α-ionylidene acetate"	143	181–182	214–215
(d) Carbonyl cpd. from "β-ionylidene acetate"	143	180–182	213–214
Mixture (c) and (d)	143	180–182	212–214
Mixture (c) and (a)	143	181–182	214
Mixture (a) and (b)	112–115	148–150	207–208
Davies' "aldehyde"	Not prep.	181–185	202–203

TABLE III

	Carbonyl cpd. Fraction b. p. 90–92° 1 mm.)		2,4-Dinitrophenylhydrazone			4-Phenylsemicarbazone	*p*-Chlorobenzoylhydr.
	C	H	C	H	N	N	Cl
Calculated for $C_{15}H_{22}O$	83.6	10.1	63.3	6.5	14.1	11.9	9.6
Calculated for $C_{13}H_{20}O$	81.7	10.4	61.3	6.5	15.1	12.9	10.4
Found	81.4	10.4	62.0	6.6	15.2	13.0	10.4

Summary

The carbonyl compound which Davies, Heilbron, *et al.*,[5] obtained from the so-called barium β-ionylidene acetate by dry distillation with barium formate was found to be identical with α-ionone. The same cleavage occurs in the case of barium α-ionylidene acetate.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

cis- and *trans*-8-Methyl-1-hydrindanone[1]

BY W. E. BACHMANN AND S. KUSHNER[2]

8-Methyl-1-hydrindanone (VI), which is of interest because it contains the structural features of the C and D rings of most of the sex hormones, has been prepared by a number of investigators[3–8] by several different methods. Of the two possible forms, *cis* and *trans*, only one and the same form was obtained in all of the syntheses. At first this form was considered to be the *trans* form, but more recently the *cis* configuration has been assigned to it tentatively by Linstead, Millidge and Walpole.[9] We have now prepared this *cis* form by another procedure and have also succeeded in preparing the *trans* form.

The *cis* form was prepared by the same procedures which were employed in the synthesis of equilenin[10] and related compounds.[11] Chuang, Tien and Huang[12] had prepared 2-methyl-2-carboxycyclohexane-1-acetic acid (III) from 2-carbethoxycyclohexanone. We have made some improvements in the yields of some of the intermediates and have varied the procedures in certain steps. The product obtained through the Reformatsky reaction from 2-carboethoxycyclohexanone and ethyl bromoacetate was dehydrated and hydrolyzed to a mixture of two isomeric unsaturated acids, which probably possess the structures I and II, although there is a possibility that they are geometrical isomers of I. Both unsaturated acids gave III on reduction with Adams platinum catalyst. In addition to the

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[1] Presented before the Organic Division at the Ninth Organic Symposium, Ann Arbor, Michigan, December 29, 1941.

[2] From the Ph.D. dissertation of S. Kushner.

[3] Chuang, Tien and Ma, *Ber.*, **69**, 1494 (1936).

[4] Kon, Linstead and Simons, *J. Chem. Soc.*, 814 (1937).

[5] Robinson and Walker, *ibid.*, 1160 (1937).

[6] Elliott and Linstead, *ibid.*, 660 (1938).

[7] Burnop and Linstead, *ibid.*, 720 (1940).

[8] Nenitzescu and Przemetsky, *Ber.*, **74**, 676 (1941).

[9] Linstead, Millidge and Walpole, *J. Chem. Soc.*, 1140 (1937).

[10] Bachmann, Cole and Wilds, THIS JOURNAL, **62**, 824 (1940).

[11] See Bachmann, Kushner and Stevenson, *ibid.*, **64**, 974 (1942), for the most recent article in this series.

[12] Chuang, Tien and Huang, *Ber.*, **68**, 866 (1935).