[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

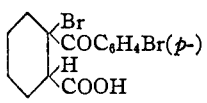
Walden Inversion in the Formation of β-Lactones. The Configurations of the Bromoacids of Kohler and Jansen

BY PAUL D. BARTLETT AND PAUL N. RYLANDER

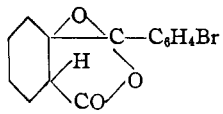
Kohler and Jansen in 1938 made a careful study of the reactions of compounds related to the lactone of 1-bromo-1-*p*-bromobenzoylcyclohexane-2-carboxylic acid (I), concluding that the closure of this lactone ring and its opening by hydrogen bromide or sodium hydroxide proceeded with retention of configuration. A number of these compounds have been prepared and their infrared spectra examined. Evidence has been found for a reassignment of configurations leading to the conclusion that the ring closure and opening in question are normal displacement reactions with Walden inversions.

The Problem.—Careful studies of the stereochemical course of the closure and opening of simple β-lactone rings, and supplementary kinetic and isotopic studies, have made it probable[1,2,3] that all closures and openings occurring at the β-position are normal displacement reactions involving Walden inversions. Against this growing body of evidence stands the conclusion reached by Kohler and Jansen[4,5] in the case of 1-bromo-1-*p*-bromobenzoylcyclohexane-2-carboxylic acid (I). In a thorough and ingenious study they assigned configurations to the geometrical isomers of this acid and found that a β-lactone could be formed only from the isomer in which the carboxyl group and the bromine atom were assigned the *cis*-relationship.

This case can be accounted for today only by one of three possibilities: (1) A double inversion occurs in the ring closure, by the participation of some neighboring group. (2) The product is not a β-lactone, but has an alternative structure such as that of the epoxy-γ-lactone II. (3) The configurations of the bromo-acids have been incorrectly assigned.



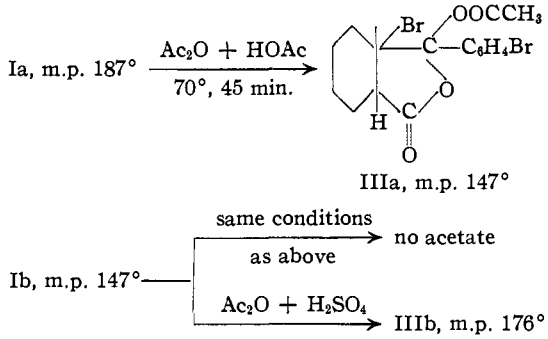
I



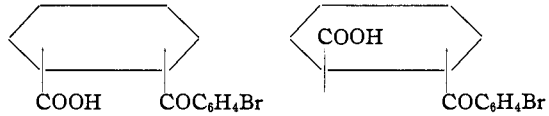
II

The first possibility is not an attractive one, since even singly bonded oxygen is so weakly nucleophilic as to participate as a neighboring group in displacement reactions with only a small driving force.[6] The phenyl group has been known to participate in such reactions,[7] but in order to do so in this case it would be necessary for it to form a rather strained structure in competition with a direct displacement of a substituted phenacyl bromide, which is one of the most rapid displacements known.[8] Therefore for the experimental approach to this problem we have chosen to examine the second and third possibilities, utilizing the tool of infrared spectroscopy which was not available at the time of the original work.

The Configurations of Kohler and Jansen.—The configurations were assigned by Kohler and Jansen on the basis of the relative rates at which the two isomers of I were converted into cyclic acetates

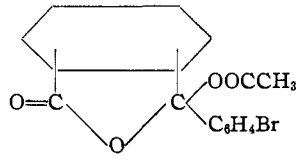


Not only was it reasonable that the relatively strain-free *cis* ring closure should occur with the greater ease, but such was actually shown to be the case in the unbrominated analogs IVa and IVb, whose configurations were known with certainty by their method of synthesis, and in which the cyclization of the *cis*-isomer to Va was markedly

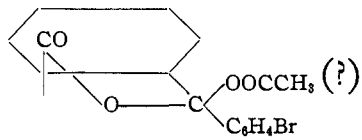


IVa, m.p. 171° IVb, m.p. 164°

more rapid than that of the *trans*-isomer to Vb.



Va, m.p. 149°



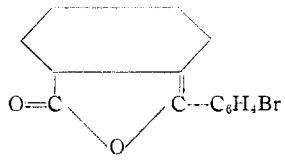
Vb, m.p. 96° (unstable)

On this basis Kohler and Jansen assigned to Ib the configuration in which the carboxyl group was *trans* to the *p*-bromobenzoyl group and *cis* to the bromine atom. It was this acid which yielded a β-lactone.

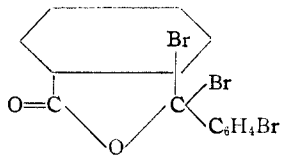
In this configuration assignment, apart from the lack of inversion on ring closure, there was but one puzzling point. The preparation of the bromoacids was effected by way of the unsaturated lactone VI, which on bromination yielded a dibromo-

(1) F. A. Long and A. R. Olson, *J. Phys. Chem.*, **41**, 267 (1937).
(2) A. R. Olson and R. J. Miller, THIS JOURNAL, **60**, 2687 (1938).
(3) A. R. Olson and J. L. Hyde, *ibid.*, **63**, 2459 (1941).
(4) E. P. Kohler and J. E. Jansen, *ibid.*, **60**, 2142 (1938).
(5) J. E. Jansen, Thesis, Harvard University, 1937.
(6) S. Winstein, E. Grunwald and L. L. Ingraham, THIS JOURNAL, **70**, 820 (1948).
(7) D. J. Cram, *ibid.*, **71**, 3863, 3875 (1949).
(8) J. B. Conant, W. R. Kirner and R. E. Hussey, *ibid.*, **47**, 488 (1925).

lactone VII. This compound might have been expected to be formed with the less strained *cis* ring junction since either configuration would be possible from the unsaturated lactone. Actually, hydrolysis of the dibromolactone led to the bromo-acid Ib preponderantly in acetic acid–acetic anhydride mixture, and exclusively when acetic anhydride was the solvent. Acetolysis of the lactone led to the cyclic acetate IIIb. The configurations assigned to these products were *trans*.

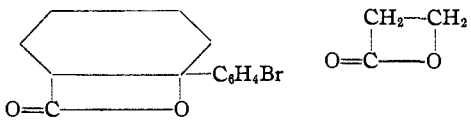


VI, m.p. 95°



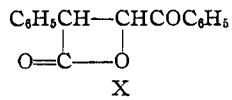
VII, m.p. 122°

Confirmation of the β-Lactone Structure.—The lactone VIII, m.p. 81–82° (Kohler and Jansen, 82–83°) was prepared by the directions of the previous workers. Its infrared spectrum, determined in chloroform, with a Baird spectrometer, shows a double peak extending from 5.40 to 5.48 μ (curve 1) which is not present in any of the other compounds of the series. Both β-propiolactone IX (curve 2), and α-phenyl-β-benzoyl-β-propiolactone X[9] (curve 3) in carbon tetrachloride show a sharp peak at 5.44 μ, which in the former case is the dominant feature of a rather simple spectrum, and must hence be regarded as characteristic of the β-lactone structure.



VIII

IX

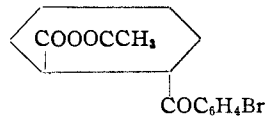


X

Because of the strain involved in the *trans*-fusion of a four- to a six-membered ring, the assumption seems justified that the one obtainable lactone of the structure VIII must be *cis*. We are thus led to reopen the question of the configurations of the bromo-acids Ia and Ib.

The Reference Acids, IVa and IVb.—Curves 4 and 5 show that the infrared spectra of the reference acids, IVa and IVb, are almost identical. They show intense absorption with a double maximum at 5.9–6.0, attributable to the carboxyl and carbonyl groups. It is clear that configuration alone has no characteristic influence upon the infrared spectra of these compounds.

The Acetates, Va and Vb.—The *cis* cyclic acetate, Va, m.p. 149°, has an infrared spectrum (Curve 6) in keeping with the assigned structure. The spectrum in the near region is dominated by an intense absorption with two maxima at 5.62 and 5.73 μ, apparently due to the lactone and ester groupings, respectively, and closely reproduced in the spectra of IIIa and IIIb (see below). The *trans*-acetate, previously regarded as having the structure Vb, has a quite different spectrum (Curve 7), and lacks this double peak entirely. Instead, it has peaks at 5.58, 5.78, and 5.99 μ, the last suggesting the reappearance of a ketonic group. Suspecting that Vb might actually be a mixed anhydride, we determined the spectrum of the anhydride of cyclohexanecarboxylic acid. Curve 8 shows intense peaks at 5.57 and 5.77 μ, with the same relative intensities as those of Vb, the order of their intensities being the reverse of that usually observed in anhydrides of unbranched carboxylic acids. The acetate Vb accordingly has the structure Vb′



Vb′

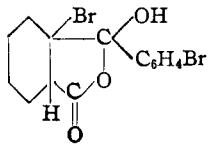
This result has an indirect bearing on the configurational conclusions that follow, in that it is consistent with the idea that the equilibrium between a cyclohexane derivative and a hydrindanic isomer is more favorable to the monocyclic isomer in the *trans* case than in the *cis*.[10] Incidentally, it also means that the reaction rates of acetate formation which formed the basis of reference for the configurational assignment of Kohler and Jansen were, in one case at least, not rates of cyclization at all. This method is accordingly not directly informative as to the strain involved in ring closure.

The Bromo-acids Ia and Ib.—The bromo-acid Ia is obtainable only as a minor product by conducting the bromination of the unsaturated lactone VI in acetic acid of or the acid IVa in acetic acid–acetic anhydride solution. By both methods we obtained a product melting at 172–174° after many recrystallizations from benzene, rather than the acid of m.p. 184–187° obtained by Kohler and Jansen. Nevertheless, this substance has an infrared spectrum entirely consistent with the assigned structure. Again there is the double peak at 5.88 and 6.00 μ (curve 9) which was seen in the reference keto-acids. This bromo-acid also yields a cyclic acetate identical in properties with that of Kohler and Jansen.

The isomeric bromo-acid, Ib, which is the principal product of bromination and which yields the β-lactone upon appropriate treatment, was obtained with the reported melting point of 147°. Its spectrum is very interesting. The twin peaks present in Ia are greatly reduced in intensity, and a new peak, twice as intense as these, has appeared at 5.65 μ, close to the location of the intense lactone absorption seen in the cyclic acetates Va, IIIa and IIIb. The spectrum, curve 10, also shows a hydroxylic peak at 2.94 μ which is absent in the other carboxylic acids. This spectrum provides clear evidence of the equilibrium Ib ⇄ XI.

(9) E. P. Kohler and R. H. Kimball, THIS JOURNAL, 56, 729 (1934).

(10) W. Hückel and H. Friedrich, *Ann.*, 451, 152 (1926).

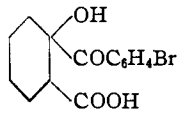


XI

Since the melting point of Ib is sharp, but the spectrum indicates a mixture with substantial amounts of both components, we must suppose that the equilibrium between the acid and the lactol XI is rapidly established. If this is true, it follows from the spectrum of Ia that the amount of lactol in equilibrium with Ia is vanishingly small compared to that in equilibrium with Ib. This is the most direct single piece of evidence for the configurations of Ia and Ib, and indicates a *cis* relationship of the carboxyl and benzoyl groups in Ib, contrary to the assignment of Kohler and Jansen.

The Cyclic Acetates, IIIa and IIIb.—The cyclic acetate IIIa was obtained with melting point 146–147°, and had the infrared absorption spectrum shown in curve 11. Its isomer, from the readily available lactone-forming acid, melted at 162–164° after repeated recrystallizations, rather than at the 176° of Kohler and Jansen. Its spectrum (curve 12) is, like that of IIIa, normal for a compound with a carbonyl group and a lactone ring. Attention was called by the previous authors to the added possibilities of isomerism due to the new asymmetric carbon atom generated in the formation of the cyclic acetates. This provides a possible explanation for the present discrepancy in melting points.

The Hydroxy-acids.—Boiling with 1% aqueous sulfuric acid converted the β-lactone of Kohler and Jansen into the hydroxy-acid XIIa, m.p. 187°, while sodium bicarbonate or potassium hydroxide led to the hydroxy-acid XIIb, m.p. 134°.

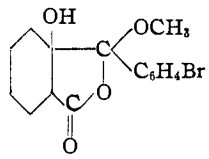


XII
a, m.p. 187°
b, m.p. 134°

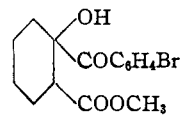
The infrared spectra of XIIa and XIIb differ in the same way as those of the bromo-acids. The lower-melting isomer shows strong absorption at 5.60 μ which is totally absent in its isomer (curves 13 and 14) and which indicates the formation of a lactol in equilibrium with the hydroxy-acid. The carboxyl and ketone groups are accordingly *trans* in XIIa and *cis* in XIIb. The alkaline hydrolysis of the lactone is, like the ring closure, a displacement reaction at the beta position with Walden inversion. The occurrence of this reaction under conditions where simple β-lactones give normal ester hydrolysis is to be explained by the powerful effect of the benzoyl group in facilitating displacement reactions at a center adjacent to it. The occurrence of normal ester hydrolysis in $N/5$ sulfuric acid is to be expected in any case. These two reactions were more difficult to explain on the previous basis of lactone formation without inversion, since then all methods of ring opening would have been expected to yield products with the same configuration.

We have also succeeded in converting the non-lactone-forming bromo-acid Ia by means of sodium carbonate, into the hydroxy-acid XIIb, m.p. 134°. This conversion, under conditions almost certain to lead to inversion, is consistent with the new assignment of configurations.

The Methyl Esters.—Infrared analysis shows that the ester of m.p. 139–141° (Kohler and Jansen, 142°), obtained from XIIb by methanol and sulfuric acid, or from the β-lactone with methanol and sodium methoxide, possesses a cyclic structure. There is strong lactonic absorption at 5.63 μ and no ketonic peak at 6.0 μ (curve 15). That this ester (XIII) should be formed with methanol and sulfuric acid while the isomeric open ester XIV is produced by diazomethane is in accord with the experience with the normal and pseudo-esters of *o*-benzoylbenzoic acid.[11,12] It is worth noting, however, that whereas acids isomerize methyl-pseudo-*o*-benzoylbenzoate into the open isomer, either acids or bases isomerize the open XIV into the cyclic XIII. This observation points to stereochemical conditions especially



XIII
m.p. 139–141°



XIV

favorable for the closure of the five-membered ring. It would be difficult to account for this except with the carboxyl-*cis*-benzoyl configuration which we have assigned.

The Mechanism of Formation of the Cyclic Acetates.—We have shown that the relative rates of reaction with acetic anhydride of the two bromo-acids Ia and Ib do not constitute a well-grounded method for the establishment of configuration since the reference compounds IVa and IVb of known configuration do not both yield cyclic acetates during this treatment. However convinced we are that this kinetic method is an unreliable one, it is nevertheless remarkable that the cyclic acetate IIIa, which we now believe to be *trans* and hence under strain, should actually be formed more rapidly than its isomer IIIb which is relatively unstrained. This fact is the more puzzling since the starting material for the formation of the *cis*-acetate is already in the lactol form and seemingly has only to undergo direct acetylation of its hydroxyl group in order to yield the product. We have not found any evidence which would establish the exact mechanism of the ring closure with acetic anhydride and at present we can only point out that there are a number of reasonable possibilities for this mechanism other than a direct acetylation of the lactol. Indeed Kohler and Jansen showed that there must be at least two readily available mechanisms for the formation of these acetates since the reaction of acetic anhydride alone on the keto-acid leads to a different cyclic acetate from the one obtained in the presence of either acetic acid or sulfuric acid. The difference between the isomers

(11) H. Meyer, *Monatsh.*, **28**, 1231 (1907).
(12) G. Egerer and H. Meyer, *ibid.*, **34**, 69 (1913).

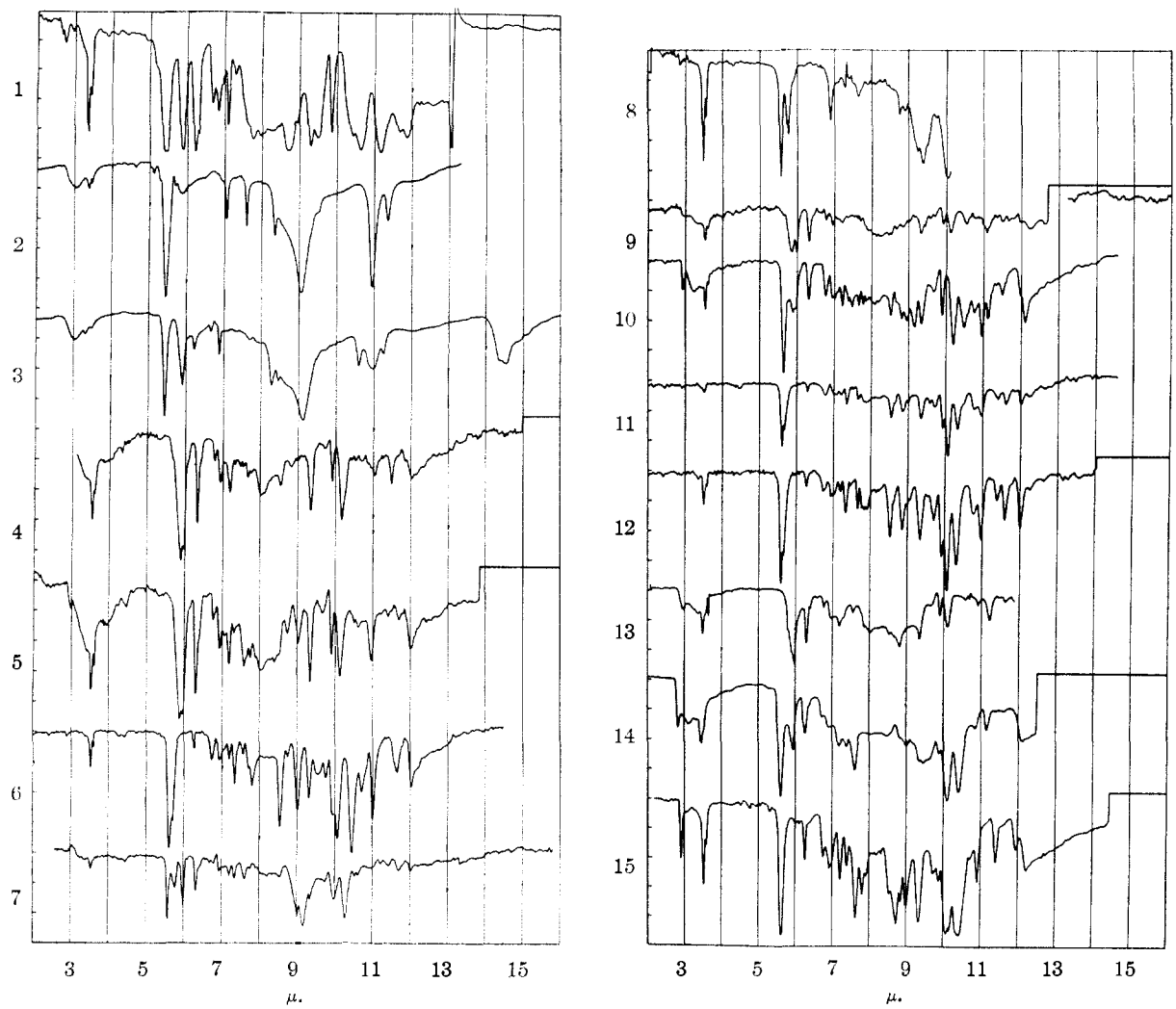
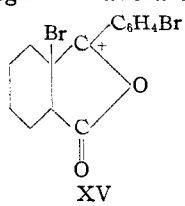


Fig. 1.—Infrared absorption spectra; all in chloroform except as noted: 1, VIII; 2, IX in carbon tetrachloride; 3, X in carbon tetrachloride; 4, IVa; 5, IVb; 6, Va; 7, Vb; 8, cyclohexanecarboxylic acid anhydride; 9, Ia; 10, Ib; 11, IIIa; 12, IIIb; 13, XIIa; 14, XIIb; 15, XIII.

was attributed to the asymmetric carbon atom which appears during the reaction.

The conversion of the lactol into the cyclic acetate would not be expected to occur readily as an attack of the OH upon the anhydride. This hydroxyl group is tertiary and must have a diminished reactivity toward acylating agents in common with tertiary alcoholic groups generally. The presence of strong acid might be favorable to the ion XV



XV

which, however, would probably not occur in the absence of acid. The behavior of the acid chlorides of *o*-benzoylbenzoic acid and of anthraquinone-1-carboxylic acid[13,14,15] seems to indicate a rapid interconversion between the open-chained "normal" acid chloride and the cyclic "pseudo" structure related to the lactol; or, as some investigators prefer, an ability of one of these forms to react as if entirely equivalent to the other. It is therefore a possible mechanism of cyclic acetate formation that a linear mixed anhydride with acetic acid is the first product and that this is able to cyclize in a follow-up reaction analogous to the attack of acetic anhydride upon acetaldehyde.[16] If this is the mechanism, then in the *cis*-keto-acid Ib it is necessary for the lactol to isomerize into the open acid as a step in the formation of the cyclic acetate, and this would account for the fact that in the case of the acids I where the *cis* form exists as a lactol the *cis* form is cyclized more slowly than the *trans*.

Conclusions.—The following facts are more consistent with the assignments of configurations in this paper than with those previously adopted. (1) The bromo-acid Ib, which yields a β-lactone, exists to a substantial extent at equilibrium in solution as a lactol whereas the isomer Ia does not. (2) The hydroxy acid XIIb, which is produced from

(13) H. C. Martin, THIS JOURNAL, **38**, 1142 (1916).

(14) R. Scholl, *Ann. Acad. Sci. Fennicae*, **29**, No. 13 (1927); *C. A.*, **22**, 1155 (1928).

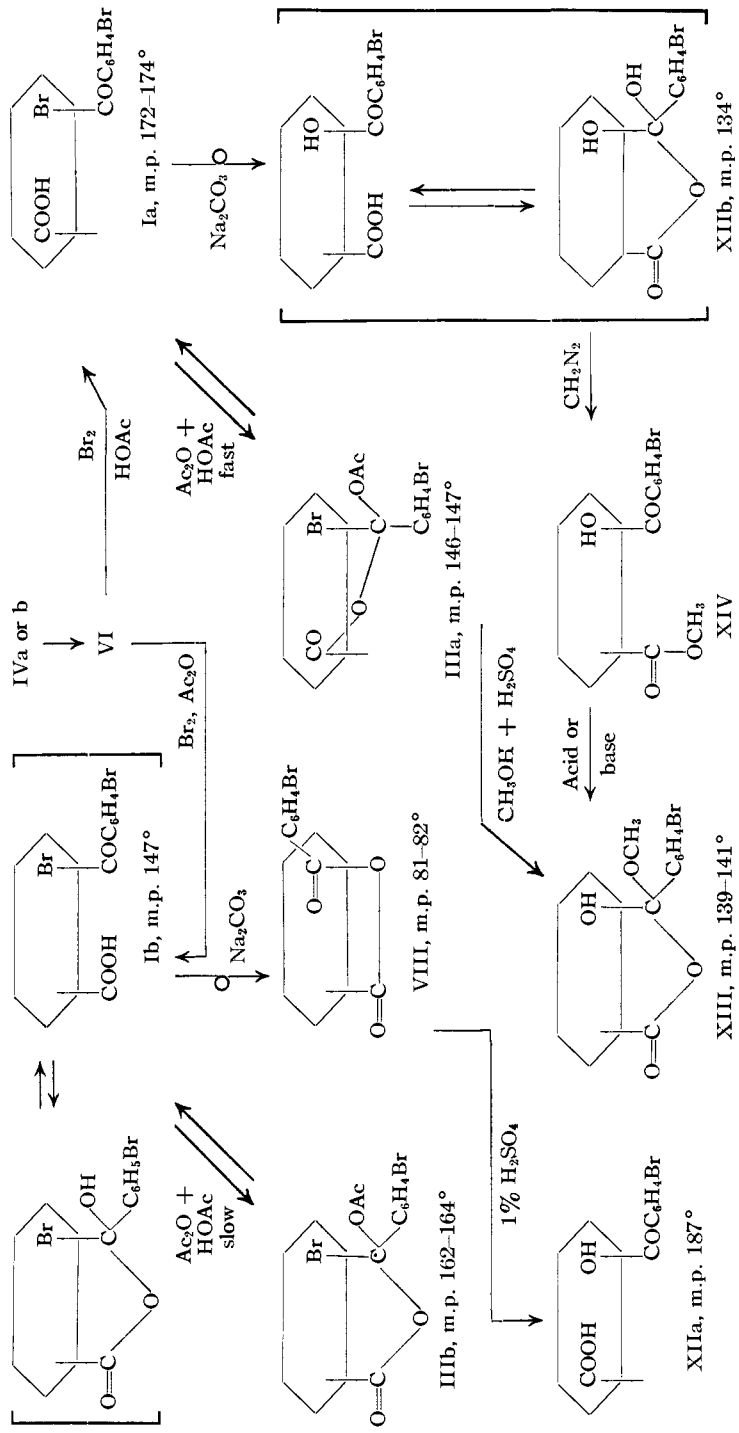
(15) R. Scholl and J. Donat, *Ber.*, **62B**, 1295 (1929).

(16) A. Geuther, *Ann.*, **106**, 249 (1958).

the lactone by attack of hydroxyl ion, exists as a lactol at equilibrium while the isomer XIIa does not. (3) That a preference for cyclization is associated with the *cis* configuration is supported by the fact that the *cis* unbrominated acetate Va is cyclic while its *trans* isomer has the structure of a mixed anhydride, the configurations in this case being known by the method of synthesis. (4) In the attack of a brominating agent upon the unsaturated lactone VI the *b* configuration strongly predominates in the product. By any reasonable mechanism of bromination, the entrance of a bromine atom into bonding with the ring carbon should occur preferentially in such a manner as to produce the unstrained *cis* configuration. (5) The acyclic methyl ester XIV produced from the hydroxy acid XIIb is isomerized by acids or bases into the "pseudo" ester XIII. This, being contrary to the direction of change in model compounds, must indicate a configuration favorable to ring closure. (6) It is the upshot of all recent work on the closure and β-opening of β-lactones that these reactions involve normal displacement with Walden inversion.

The flow sheet summarizes the reactions of Kohler and Jansen as they are viewed in the light of the revised configurations.

Acknowledgment.—We thank the B. F. Goodrich Co. for support of a project to which this work was incidental. Dr. J. E. Jansen has given us encouragement and helpful discussions.



Experimental

Except as noted the compounds were prepared by the methods of Kohler and Jansen as reported in the paper and thesis cited. In general our yields approached those of Kohler and Jansen on successive repetitions of the preparation. Only in occasional instances were the yields of these authors improved.

The Bromo-acid Ia.—This acid was prepared according to the directions in Jansen's thesis[17] by the bromination of the unsaturated lactone VI and also by the bromination of the *cis*-keto acid IVa in acetic acid–acetic anhydride solution. In both cases the melting point of our product, 172–174°, was not raised after six recrystallizations from benzene and one from ether. The melting point reported by Jansen was 184–187°. Despite this fact the infrared spectrum is quite similar to those of the acids IV (compare curves 4, 5 and 8) and the acid yielded the same cyclic acetate as reported by Kohler and Jansen.

Anal. Calcd. for $C_{14}H_{14}O_3Br_2$: C, 43.1; H, 3.6. Found: C, 43.65; H, 3.70. Calcd. for IVa, $C_{14}H_{15}O_3Br$: C, 54.0; H, 4.8.

The Cyclic Acetate (IIIb) of the 147° Bromo-acid.—The cyclic acetate of the 147° bromo-acid was prepared by the reaction of the bromo-acid with acetic anhydride and by bromination of *cis*-β-(*p*-bromobenzoyl)-hexahydrobenzoic acid in acetic anhydride solution and in acetic acid–acetic anhydride solution, all according to the directions of Jansen. In each case the product obtained melted at 162–164° instead of 174–176° as reported. Repeated recrystallizations from various solvents did not raise the melting point. It was hydrolyzed readily to the 147° bromo-acid.

Anal. Calcd. for $C_{16}H_{16}O_4Br_2$: C, 44.50; H, 3.74. Found: C, 44.85; H, 3.76.

The infrared spectrum (curve 11) is normal for the structure assigned.

Reaction of Bromo-acid Ia with Sodium Carbonate.—One gram of the bromo-acid Ia was dissolved in 50 cc. of 5% sodium carbonate solution and allowed to stand for about ten days. The insoluble sodium salt was filtered off, acidified with dilute hydrochloric acid, extracted with ether and dried over sodium sulfate. Evaporation of the ether left an oil which was allowed to stand in a covered beaker. Crystalli-

(17) Ref. 5, p. 75.

zation had begun in a month and by the end of three months the whole mass was solid. By recrystallization from ether–petroleum ether the melting point was raised from 124–129° to 133–134°. The mixed melting point with an authentic sample of the 134° hydroxy acid XIIb showed no depression and the infrared spectra of the two were identical.

Cyclohexane Carboxylic Acid Anhydride.—Fifteen grams of cyclohexane carboxylic acid (0.117 mole), 30 g. (0.294 mole) of acetic anhydride, and 0.5 ml. of concentrated hydrochloric acid were heated on a steam-bath for six hours. The solution became black. It was fractionally distilled and the portion boiling at 140–146° (5 mm.) was collected. This was twice more fractionally distilled and the center portion boiling at 142–143° (5 mm.) was collected; $n^{25.0}$D 1.4748.

Anal. Calcd. for $C_{14}H_{22}O_3$: C, 70.55; H, 9.31. Found: C, 71.05; H, 9.14.

This anhydride has been prepared previously by Lumsden[18] from sodium hexahydrobenzoate and hexahydrobenzoyl chloride; b.p. 280–283°, $M_{Na}^{15°}$ 1.48189.

(18) J. S. Lumsden, *J. Chem. Soc.*, **87**, 90 (1905).

CAMBRIDGE 38, MASSACHUSETTS
RECEIVED MARCH 29, 1951

[CONTRIBUTION FROM THE CHEMICAL DIVISION OF THE PROCTER & GAMBLE CO.]

The Polymorphism of 2-Acetyl-, 2-Butyryl- and 2-Caproyldistearin and -dipalmitin

BY F. L. JACKSON, R. L. WILLE AND E. S. LUTTON

A study of polymorphism by thermal and diffraction methods is reported for six symmetrical diacid triglycerides in which the 2-position is occupied by a very short chain. Solid forms observed were as follows: for 2-acetyldistearin and 2-acetyldipalmitin—sub-alpha-1 and beta-3; for 2-butyryldistearin and 2-butyryldipalmitin—sub-alpha-1, alpha-1, superalpha-1, and beta-3; for 2-caproyldistearin and 2-caproyldipalmitin—sub-B-beta-3, sub-A-beta-3 and beta-3 and also sub-alpha-1 for the former glyceride but sub-alpha-3 for the latter. The polymorphism of these compounds thus shows several hitherto unreported features—specifically the sub-alpha-1, alpha-1 and super-alpha-1 forms and the multiplicity of beta-type forms for the caproyl glycerides. Such abnormalities in behavior presumably result from the relatively large role played by the carbonyl portions of the short acyl groups.

In previous communications from this Laboratory, the thermal and X-ray diffraction characteristics of certain mixed saturated diacid triglycerides were discussed.[1–4] These compounds show considerable uniformity of polymorphic behavior by exhibiting, in most cases, the three forms—alpha, beta prime and beta—each with a characteristic melting point. Outstanding individuality is shown by 2-stearyldipalmitin[2] and 1-palmityldibehenin[4] which fail to show a beta form, and by 2-myristyldistearin which shows four forms (alpha-2, beta prime-2, beta prime-4 and beta-3 forms[1]). In addition, the unsymmetrical dibehenyl triglycerides show a new sub-alpha form[4] which transforms reversibly to alpha.

The shortest chain in glycerides previously prepared in this Laboratory was lauryl,[3] and Malkin in his extensive studies of mixed glyceride polymorphism did not deal with shorter chains than capryl.[5,6] In the present paper there are discussed the X-ray diffraction and thermal characteristics of six symmetrical diacid triglycerides involving very short acyl chains—2-acetyldistearin (SC_2S), 2-acetyldipalmitin (PC_2P), 2-butyryldistearin (SC_4S), 2-butyryldipalmitin (PC_4P), 2-caproyldistearin (SC_6S) and 2-caproyldipalmitin (PC_6P). Three of these compounds, PC_2P, SC_4S and PC_4P, have not been discussed previously in the literature, while complete melting points were reported for the others by Grün.[7]

The polymorphism of these six glycerides is unique in many respects. None of them shows a beta prime form. SC_2S and PC_2P show only sub-alpha-1 and beta-3 forms. SC_4S and PC_4P show three "alpha" forms—sub-alpha-1, alpha-1 and super-alpha-1, and also a beta-3 form. SC_6S and PC_6P show three "beta" forms each—sub-B-beta-3, sub-A-beta-3 and beta-3. SC_6S also shows a clear-cut alpha-1 form transforming from sub-alpha-1; PC_6P shows sub-alpha-3 at low temperatures, but no true alpha form transforming therefrom, perhaps due to the rapid development of beta.

Experimental

The six symmetrical mixed triglycerides were prepared by reacting 1,3-distearin and 1,3-dipalmitin with an excess of the appropriate acid chloride in the presence of pyridine according to established methods. The diglycerides were prepared by directed rearrangement according to the method of Eckey and Formo.[8] The acetyl and butyryl chlorides were purchased from Eastman Kodak Co. Caproyl chloride was prepared as follows: Starting with carefully purified sorbic acid, successive esterification, hydrogenation, saponification and acidification gave caproic acid which was converted into caproyl chloride by reacting with excess thionyl chloride. The caproyl chloride was distilled before use.

Final purification of the glycerides was accomplished by several (4–6) crystallizations from alcohol–ether followed by thorough drying *in vacuo* over phosphorus pentoxide. Analytical constants for the final products are given in Table I.

TABLE I

TRIGLYCERIDE ANALYTICAL CONSTANTS

	Saponification value		Acid value		M.p., °C.		
	Calcd.	Found	Calcd.	Found	Found	Lit.	Ref.
SC_2S	252.3	252.9	0	0.1	62.8	64	7
PC_2P	275.5	276.4	0	0.1	54.8		
SC_4S	242.0	241.4	0	0.3	54.8		
PC_4P	263.4	263.3	0	0.3	46.5		
SC_6S	232.5	233.9	0	<0.3	53.1	47.2	7
PC_6P	252.3	252.1	0	<0.3	44.5	66	7

The polymorphism of the glycerides was studied by X-ray and m.p. techniques described previously.[5] A General

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