(0.0435 mole) of γ,γ-dimethylallyl bromide for 36 hr. at room temperature. An ether solution of the crude product was shaken with pyridine followed by water to remove the excess allylic bromide. Distillation gave 926 mg. of material, b.p. 112–118° (10 mm.). This was filtered through a column of alumina with pentane and redistilled through a 20-cm. Holzmann column to give two fractions: (a) 272 mg., b.p. 110–115° (10 mm.), n^{25}D 1.4926, $[\alpha]^{25}$D +1.5° (alcohol); and (b) 613 mg., b.p. 115–120° (10 mm.), n^{25}D 1.4858, $[\alpha]^{25}$D +8° (alcohol). That both (a) and (b) were mixtures of two similar and probably C_{15} components in different ratios was shown by vapor phase chromatography. The elution times of these components were 15.8 minutes and 20.4 minutes on a 2-meter column type "C" (Perkin-Elmer) at 178°. For comparison π-bromotricyclene was eluted in ten minutes.

Dihydro-α-santalene and π-*t*-Amyltricyclene.—Catalytic reduction of 186 mg. of fraction (a) above over platinum gave 134 mg. (71%) of distilled dihydro-(a), n^{25}D 1.4793. Vapor phase chromatography of this product at 180° and otherwise identical conditions as above gave two components having elution maxima at 15 and 16 minutes. The ratio of the components in fraction (a) and dihydro-(a) was about 1:1 in both cases. The infrared spectrum of dihydro-(a) manifested tricyclene absorption at 3055 and 855 cm.$^{-1}$ and no absorption characteristic of olefins.

Bi-π-tricyclyl.—From the Grignard reactions of π-bromotricyclene with magnesium there was obtained invariably *ca.* 20% of a neutral crystalline compound, m.p. *ca.* 98–106° crude, which on two recrystallizations from ethanol and sublimation had m.p. 113.5–114.5°. The analytical values indicated a bitricyclyl formula.

Anal. Calcd. for $C_{20}H_{30}$: C, 88.82; H, 11.18; mol. wt., 270.4. Found: C, 89.08; H, 11.17; mol. wt., 286 (Rast).

The infrared spectrum of bi-π-tricyclyl determined in carbon tetrachloride differs from the spectrum of tricyclene in the C–CH_3 region (single peak 1380 cm.$^{-1}$) and in having a single medium peak at 855 cm.$^{-1}$. Otherwise the curves are very similar. There is no absorption in the 1650 cm.$^{-1}$ region and the dimer gives a negative tetranitromethane test. The bi-π-tricyclyl structure seems probable for this compound.

Urbana, Illinois

[Contribution from the Department of Chemistry of the University of Michigan]

Reactions of Hindered α-Substituted Acids. V. The Effect of a β-Methyl Group on the Acid-Catalyzed Rearrangement[1,2]

By Wyman R. Vaughan and A. Charles Schoenthaler[3]

Received May 17, 1957

The role of the methyl group in promoting the acid-catalyzed rearrangement of 2-hydroxy-3-methyldibenzo[2.2.2]bicycloöctadiene-*trans*-2,3-dicarboxylic acid (Ia) to 2-*exo*-hydroxy-6-methyl-3,4,7,8-dibenzo[3.2.1]bicycloöctadiene-1-*cis*-6-dicarboxylic acid-2,6-lactone (IIa) is considered in the light of the failure of the desmethyl analog to undergo the rearrangement. The possibility of participation by the methyl group in the rearrangement is ruled out by the rearrangement of an optically pure sample of Ia to a correspondingly pure sample of IIa. Other examples in similar compounds wherein the methyl group facilitates rearrangement are also considered.

The rearrangement of 2-hydroxy-3-methyldibenzo[2.2.2]bicycloöctadiene-*trans*-2,3-dicarboxylic acid (Ia) to 2-*exo*-hydroxy-6-methyl-3,4,7,8-dibenzo[3.2.1]bicycloöctadiene-1-*cis*-6-dicarboxylic acid-2-6-lactone (IIa) and of the desmethyl bromoanalog (Ic) to the analogous lactone (IIb) or diacid (IIc) have been described in previous papers in this series.[4-6]

A review of the data presented in these papers indicates one salient feature of the rearrangement: it can compete best with concurrent reactions when the method of inducing reaction is one which favors S_{N1}–E_1 type behavior. Thus the action of 48% aqueous hydrogen bromide on Ia affords but one product, IIa, the rearranged lactone-acid.[4] Consequently it appeared that the most information about the rearrangement could be gained from a careful examination of the latter reaction. The comparatively more readily accessible desmethyl analog Ib seemed an attractive starting point for such an investigation in spite of an observation that it did not appear to react with 48% hydrobromic acid under the usual conditions[7]; but unfortunately numerous attempts to effect rearrangement afforded only the starting material or the starting material plus completely intractable tars, abundant confirmation for the earlier observation.

Since the expected lactone-acid IIb and the corresponding diacid IIc were both known to exist,[5] it appeared that the methyl group in Ia was in some manner influencing the course of the reaction. It already had been pointed out[2] that a methyl group is capable of promoting the rearrangement in the *cis*-chloroanhydride system, but in the latter the absence of the methyl group did not lead to complete inhibition of rearrangement or suppression of other recognizable reactions.

At this juncture another instance of similar behavior due to the methyl group was encountered: in the course of investigating methods for the synthesis of a series of monobasic haloacids structurally related to the dibasic acids already studied, hydrogen bromide in toluene was added to dibenzo[2.2.2]-bicycloöctatriene-2-carboxylic acid (IIIb) to produce *cis*-3-bromodibenzo[2.2.2]bicycloöctadiene-2-carboxylic acid (IVa),[8,9] but when the same reaction was attempted with the 3-methyl analog of IIIb (IIIa), none of the expected product was isolated. Instead there was obtained a very poor yield of a bromoacid V isomeric with the desired

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(1) Abstracted from a portion of the Ph.D. dissertation of A. C. Schoenthaler, University of Michigan, 1955.

(2) Preceding paper in this series, W. R. Vaughan and R. Q. Little, Jr., This Journal, **76**, 4130 (1954).

(3) Allied Chemical and Dye Corporation Fellow, 1954-1955.

(4) W. R. Vaughan and K. M. Milton, This Journal, **74**, 5623 (1952).

(5) W. R. Vaughan, M. V. Andersen, Jr., and R. Q. Little, Jr., *ibid.*, **76**, 1748 (1954).

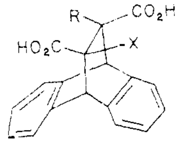
(6) W. R. Vaughan and R. Q. Little, Jr., *ibid.*, **76**, 2952 (1954).

(7) R. Q. Little, Jr., Ph.D. dissertation, University of Michigan, 1953, p. 63.

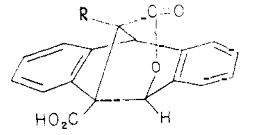
(8) For the stereospecific character of this addition *cf.* W. R. Vaughan, R. L. Craven, R. Q. Little, Jr., and A. C. Schoenthaler, This Journal, **77**, 1594 (1955).

(9) When hydrogen bromide-acetic acid was used the epimer IVb was obtained. Presumably the usual steric course of addition was followed to give IVa which is demonstrably epimerizable in hydrogen bromide–acetic acid to IVb.

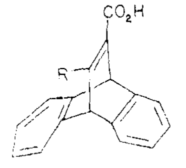
product. The nature of hydrobromination[8] and the failure of V to yield anthraquinone on oxidation with permanganate, with which its warm alkaline solution reacts readily, suggests that any hydrobromination in which the original skeleton remains intact is unlikely and permits the inference that rearrangement to the dibenzo[3.2.1]bicyclooctadiene system has supervened. The unsatisfactory yield in this reaction led us to defer further investigation in this direction, and no explicit proof of structure was undertaken. But again, the presence of a methyl group near the reacting center appears to promote rearrangement at the expense of any other reaction; and the interesting question is posed: "Is the effect of the methyl group always the same in the mechanistic sense?"



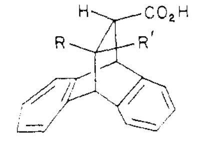
Ia, R = CH_3, X = OH
Ib, R = H, X = OH
Ic, R = H, X = Br



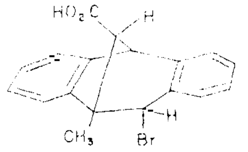
IIa, R = CH_3
IIb, R = H
IIc, R = H (hydroxyacid)



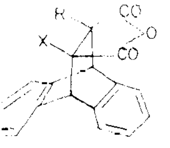
IIIa, R = CH_3
IIIb, R = H



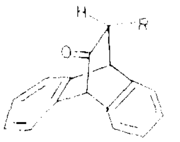
IVa, R = H, R' = Br
IVb, R = Br, R' = H



V



VIa, R = CH_3, X = Cl
VIb, R = H, X = Cl
VIc, R = H, X = OH
VId, R = CH_3, X = OH



VIII, R = H
VIII, R = CH_3

The answer, *a priori*, would appear to be no, since the methyl group is attached directly to the reacting center in IIIa, while in the anhydride VIa as well as in the *trans*-diacid Ia it is attached to the carbon *adjacent* to the reacting center. Furthermore, the suggestion that it may be involved by actual participation carries no weight in the reactions of either VIa or IIIa. However, as has been suggested,[5] methyl migration as Ia reacts may well be a precursor or competitor to the rearrangement; or it may account for its absolute dominance by assisting in the formation of the ionic intermediate. The stereospecificity of the reaction (only IIa is formed) as compared to the reaction of VIa, in which *both* of the possible *structurally* isomeric rearrangement products are formed, argues in favor of methyl participation. Unfortunately all attempts to produce the 2-bromo analog of Ia have failed,[10] and hence the extent to which this may be due to a difference in the modes of ionization of the conjugate acid of an alcohol and the corresponding bromide, under electrophilic attack, cannot be determined directly.

However, it would appear eminently reasonable to expect that any methyl participation in the rearrangement of Ia sufficient to account for the singleness of character displayed would reveal itself in racemization, partial or total, as the reaction proceeds from optically pure Ia to IIa, since the methyl bridged intermediate would possess a plane of symmetry, as does a camphene molecule racemizing by the methyl shift mechanism.[11,12] To this end both Ia and IIa were resolved until essentially optically pure materials were obtained, with attention being focused on the magnitude rather than the sign of rotation.

In initial attempts to resolve Ia using brucine the salt was recrystallized repeatedly from propanol, but the observed rotations were of the order of half a degree and approached no obvious maximum. The free acid obtained in this manner showed $[\alpha]^{33}\mathrm{D}$ −25.1° (absolute ethanol). Surprisingly an appreciably purer product was obtained by mixing brucine and Ia in absolute ethanol, refluxing for an hour and filtering off the undissolved salt from which 61% of the theoretically available (as a hemihydrate) (−)-Ia was liberated, $[\alpha]^{28}\mathrm{D}$ −28.7° (absolute ethanol).

The resolution of IIa was achieved smoothly with quinine, in absolute ethanol. Successive recrystallizations afforded a quinine salt with a constant melting point and rotation. The lactone-acid (+)-IIa was obtained as a monohydrate, $[\alpha]^{28}\mathrm{D}$ −253° (absolute ethanol).

When (−)-Ia was allowed to react with hot 48% hydrobromic acid, there was obtained a 69% yield of (+)-IIa monohydrate, $[\alpha]^{23}\mathrm{D}$ +256° (absolute ethanol). The near identity of magnitude of this rotation with that of the independently resolved IIa[13] effectively denies the possibility of a symmetrical intermediate in the rearrangement and unequivocally rules out methyl participation.

When one considers the camphene racemization, in which it is clearly obvious that one can control the competing rearrangement and to a certain extent control the mechanism of racemization by appropriate choice of conditions,[11] it may seem surprising that no methyl migration is encountered.

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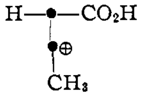
(10) W. R. Vaughan and K. M. Milton, *J. Org. Chem.*, **16**, 1748 (1951).

(11) J. D. Roberts and J. A. Yancey, THIS JOURNAL, **75**, 3165 (1953).

(12) W. R. Vaughan and R. Perry, Jr., *ibid.*, **75**, 3168 (1953).

(13) The correspondence in magnitude of rotation for the form obtained by rearrangement with that obtained by resolution affords independent evidence for the optical purity of the Ia obtained by resolution, which is the more interesting in view of the unusual simplicity of the resolution. The melting behavior, hydrate formation and non-identity of the infrared spectra of Nujol mulls of the active forms and racemic form make it clear that the inactive form is a racemic compound rather than a simple mixture, and it is formed readily on melting equal parts of the active forms together. The existence of (−)-Ia as a hemihydrate indicates that (±)-Ia is also a racemic compound.

Thus it is difficult to see just how the methyl group in any way promotes this reaction unless it is by its effectively preventing the only other reaction open to the system, inversion at C^3.

There remains to be explained the rearrangement facilitating effect of methyl in IIIa and VIa. In the former it would appear that a major contribution is to the stabilization of the initially formed protonated intermediate through the recognized resonance and inductive effects of the methyl group, *e.g.*,  $H{-}\overset{\bullet}{C}(CH_3)^{\oplus}{-}CO_2H$ or its "non-classical" equivalent, for a long enough time to permit rearrangement. A second form of stabilization would be purely steric, *e.g.*, sufficient inhibition of approach of bromide so that rearrangement takes precedence. In the absence of methyl (IIIb), the carbonium ion is secondary and therefore enough electronically less stable and sterically more accessible to attack by bromide to permit normal hydrobromination to occur in spite of the higher order of the latter reaction.[8]

In the rearrangement of VIa as compared to VIb the methyl group also acts, though less effectively, electronically to stabilize a carbonium ion transition state whose formation is assisted sterically by extrusion of the halide from a region wherein the methyl group contributes significantly to the crowding.

Thus in the three rearranging species in which the same skeletal changes are effected and wherein the presence of a methyl group appears to affect the course of the reaction, the function of the methyl group appears to vary from compound to compound. In two instances, IIIa and VIa, its effect is clearly steric and to a greater (IIIa) or lesser (VIa) extent electronic; in the third instance (Ia) its effect may be described as structural, since it replaces the one substituent which is sufficiently labile (hydrogen) to afford a more conventional reaction route (epimerization).

Experimental[14]

3-Bromodibenzo[2.2.2]bicycloöctadiene-*cis*-2-carboxylic Acid (IVa).—Dibenzo[2.2.2]bicycloöctatriene-2-carboxylic acid[4] (IIIb, 2.98 g., 0.0120 mole) was dissolved in 300 ml. of sodium-dried toluene and cooled to 0° in an ice-bath. Then a stream of hydrogen bromide (dried by passage through anhydrous calcium sulfate) was bubbled through the solution for two hours. Precipitation commenced on the walls of the flask after about an hour. Most of the excess hydrogen bromide was swept from the solution by a stream of nitrogen prior to filtration of the white solid. The product was washed with toluene and then dried over potassium hydroxide. The yield of IVa was 1.74 g. (44%), m.p. 203.5–204.5° dec. One recrystallization from acetic acid–water gave a white microcrystalline solid, m.p. 205.5–206.5° dec. A mixed melting point taken with the *trans* isomer was 202–205° dec.

Anal. Calcd. for $C_{17}H_{13}BrO_2$: C, 62.02; H, 3.98; Br, 24.28. Found (S): C, 62.09; H, 4.01; Br, 23.99.

The methyl ester was prepared (diazomethane) and recrystallized from methanol–water as fine white needles, m.p. 192.5–193.5°.

Anal. Calcd. for $C_{18}H_{15}BrO_2$: C, 62.99; H, 4.41; Br, 23.29. Found (S): C, 63.03; H, 4.56; Br, 23.31.

Epimerization of IVa with 30% Hydrogen Bromide in Acetic Acid.—A mixture of 0.218 g. (0.000662 mole) of IVa and 20 ml. of 30% hydrogen bromide in acetic acid was allowed to stand, with occasional shaking, at room temperature for three weeks. The mixture remained heterogeneous throughout this period. Evaporation of the supernatant liquid left a red-brown mass which, after three recrystallizations from acetic acid–water, gave 0.148 g. (68%) of pure IVb, m.p. 216.0–216.5° dec. (showing no depression with an authentic sample of IVb prepared as described below).

3-Bromodibenzo[2.2.2]bicycloöctadiene-*trans*-2-carboxylic Acid (IVb). (A) By Diels–Alder Reaction.—A mixture of 2.06 g. (0.0137 mole) of β-bromoacrylic acid,[15] 2.45 g. (0.0137 mole) of anthracene and a few milligrams of hydroquinone was refluxed in 15 ml. of sodium dried toluene for 12 days. Cooling the solution gave 2.44 g. of dirty gray solid, m.p. 193–208°. Trituration of the gray solid with 50 ml. of boiling absolute ethanol left, after cooling, 0.37 g. (15%) of impure anthracene. The ethanol was evaporated in an air stream, the residue dried in a vacuum desiccator over calcium chloride, finely powdered, and subjected to a 20-hour vacuum sublimation at 100° (0.1 mm.) to remove a further small amount of anthracene. The residue weighed 1.82 g. (40%), m.p. 212.0–214.5° dec. Two recrystallizations from acetic acid–water gave 1.44 g. (32%) of IVb as fine prisms, m.p. 216.0–216.5° dec.

Anal. Calcd. for $C_{17}H_{13}BrO_2$: C, 62.02; H, 3.98; Br, 24.28. Found (G): C, 62.05; H, 3.97; Br, 24.30 (S).

The methyl ester was prepared (diazomethane) and was recrystallized from methanol–water as fine plates, m.p. 125–126°.

Anal. Calcd. for $C_{18}H_{15}BrO_2$: C, 62.99; H, 4.41; Br, 23.29. Found (G): C, 63.11; H, 4.24; Br, 23.22 (S).

(B) By Addition of Hydrogen Bromide.—In 75 ml. of 30% hydrogen bromide in acetic acid, 6.68 g. (0.0269 mole) of IIIb was dissolved and allowed to stand, with occasional shaking, for 18 hours. The solid which had separated was filtered, washed with acetic acid and dried in an evacuated desiccator over potassium hydroxide. The crude yield was 6.39 g. (72%), m.p. 215.5–217.5° dec. One recrystallization from acetic acid–water gave 5.03 g. (57%) of fine prisms, m.p. 216.0–216.5° dec., showing no depression with the material prepared *via* method A.

The methyl ester was prepared (diazomethane) and failed to depress the m.p. of the previous sample on admixture.

The infrared spectra of the two samples of ester, as well as those of the acids from which they were made, were completely superimposable.

Reaction of 3-Methyldibenzo[2.2.2]bicycloöctatriene-2-carboxylic Acid with Hydrogen Bromide.—The unsaturated acid (IIIa, 0.797 g., 0.00305 mole) was treated with 25 ml. of 30% hydrogen bromide in acetic acid. The mixture was shaken occasionally until all of the acid had dissolved and then was allowed to stand for four days. The white solid which by then had separated was filtered off: 0.346 g., m.p. 192–194° dec., with solidification and remelting at 239.5–243.5°. The crude product was recrystallized twice from xylene resulting in 0.076 g. (7%) of a white microcrystalline solid, m.p. 178.0–179.5° dec., on slow heating.

Anal. Calcd. for $C_{18}H_{15}BrO_2$: C, 62.99; H, 4.41; Br, 23.29. Found (S): C, 62.91; H, 4.59; Br, 23.60.

The material was seemingly unaffected by cold dilute sodium bicarbonate; treatment with cold dilute sodium hydroxide caused formation of a gum which dissolved on warming. The hot alkaline solution readily decolorized permanganate; a vat test[16] run on the crude reaction mixture indicated no anthraquinone had been formed. When oxidation was conducted in acetic acid on a fresh sample of the material, the vat test was again negative.

Resolution of 2-Hydroxy-3-methyldibenzo[2.2.2]bicyclooctadiene-*trans*-2,3-dicarboxylic Acid (Ia).—A 1.62-g. (0.0050 mole) sample of Ia[4] was dissolved by warming in 100 ml. of absolute ethanol on the steam-bath. Brucine (0.99 g., 0.0025 mole) in 100 ml. of absolute ethanol was

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[14] Melting points are uncorrected. Analyses by Mrs. Anna Griffen, University of Michigan (G) and Spang Microanalytical Laboratory, Ann Arbor, Michigan (S). Infrared spectra obtained on a Perkin-Elmer model 21 double beam recording spectrophotometer.

[15] E. Gryszkiewicz-Trochimowski, W. Schmidt and O. Gryzkiewicz-Trochimowski, *Bull. soc. chim.*, 593 (1948). For stereochemistry (*trans*) *cf.* ref. 8 and W. R. Vaughan and R. L. Craven, THIS JOURNAL, **77**, 4629 (1955).

[16] L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed., D. C. Heath and Co., Boston, Mass., 1955, p. 163.

then added slowly, and the resulting mixture was refluxed for one hour. After cooling to room temperature the fine precipitate was filtered off: 1.00 g. of white powder, m.p. 185–187° dec. A second crop was obtained by concentrating the filtrate to 40 ml.: 0.36 g., m.p. 185–187° dec. These were combined and stirred with 150 ml. of $^2/_3\%$ aqueous potassium hydroxide whereupon complete solution followed by precipitation of brucine occurred. The brucine was filtered off and the filtrate was acidified carefully with concd. hydrochloric acid (3 ml.). The resulting oily precipitate was digested at 0° until it crystallized and then it was recrystallized from chlorobenzene to give a product which appeared to decompose above 130°, resolidify and melt with decomposition at 211–212°, $[\alpha]^{28}\mathrm{D}$ −28.7° (absolute ethanol, *l* 1 dm., *c* 4.61 g./100 ml.).

Anal. Calcd. for $C_{19}H_{16}O_5 \cdot H_2O$: C, 66.66; H, 5.30. Found (S): C, 66.31, 66.27; H, 5.10, 5.14.

Resolution of 2-*exo*-Hydroxy-3,4,7,8-dibenzo[3.2.1]bicycloöctadiene-*cis*-6-dicarboxylic Acid-2,6-lactone (IIa).—The lactone-acid (IIa,[4] 3.51 g., 0.0115 mole) was dissolved in 20 ml. of hot absolute ethanol and added to 3.72 g. (0.0115 mole) of quinine in a like volume of the same solvent. Cooling the mixture in an ice–salt-bath caused the separation of 4.52 g. of salt, m.p. 207.5–210.5° dec. This was recrystallized four times from absolute ethanol until a constant melting point and rotation were obtained. The recrystallizations were conducted by dissolving the salt in excess solvent then evaporating the solution in a current of air to the point of incipient turbidity on the steam-bath. Enough alcohol then was added to dissolve the solid completely, and the solution was allowed to cool to room temperature, then further cooled in an ice–salt-bath.

The final product (m.p. 221.0–222.0° dec., $[\alpha]^{28}\mathrm{D}$ −209°, dimethylformamide, *l* 1 dm., *c* 5.55 g./100 ml.) was triturated with 15 ml. of 10% hydrochloric acid causing separation of a gum which became crystalline after several minutes scratching with a glass rod. The resulting solid was filtered off and recrystallized from acetic acid–water as the monohydrate of (−)-IIa (fine white prisms); the yield was 0.283 g. (15%). The rotation of the material was taken in absolute ethanol and showed $[\alpha]^{28}\mathrm{D}$ −253° (*l* 1 dm., *c* 6.25 g./100 ml.).

When heated in a capillary tube, the material sintered to form a translucent bead on the wall at 116–118°. As the temperature was raised slowly, gas began to evolve. The evolution was complete at 145° by which time the bead had gradually fallen into a transparent glass at the bottom of the tube. It remained in this state when removed from the bath and allowed to cool, so remelting behavior could not be observed.

Anal. Calcd. for $C_{19}H_{14}O_4 \cdot H_2O$: C, 70.36; H, 4.98. Found (S): C, 70.33, 70.27; H, 5.08, 5.11.

Reaction of (−)-2-Hydroxy-3-methyldibenzo[2.2.2]bicycloöctadiene-*trans*-2,3-dicarboxylic Acid with 48% Hydrobromic Acid.[4]—In 75 ml. of 48% hydrobromic acid, 0.561 g. (0.00173 mole) of (−)-Ia ($[\alpha]^{28}\mathrm{D}$ −28.7°) was dissolved by warming on the steam-bath. Solution was complete after a few hours and the mixture was heated for a total of 24 hours. The solution was then evaporated on a hot-plate to *ca.* half its original volume by an air stream. One recrystallization from acetic acid–water with the aid of Norit left 0.387 g. (69%) of the monohydrate of rather indefinite melting point. Three successive recrystallizations from acetic acid–water resulted in fine white prisms which exhibited melting behavior similar to the (−)-form described above.

A mixed melting point determination with roughly an equivalent amount of the (−)-form showed softening beginning at 112°, but the melt resolidified by the time the temperature reached 130°. It then melted with decomposition at 224.0–227.5°. When a mixture containing roughly three parts of the (+)-form to one part of the (−)-form was heated in a capillary tube the melting behavior was very similar to the pure (+)-form except that at 170° formation of a few crystals on the side of the capillary began. These began to soften around 190° and continued to soften gradually until by 230° the whole had been transformed into a transparent glass.

The infrared spectrum of this material was identical with that of its enantiomer obtained by resolution, and both optically active forms showed an absorption at 3440 cm.^{-1} which was lacking in the anhydrous racemic compound.

The optical rotation was observed in absolute ethanol and found to be $[\alpha]^{23}\mathrm{D}$ +256° (*l* 1 dm., *c* 7.95 g./100 ml.).

Anal. Calcd. for $C_{19}H_{14}O_4 \cdot H_2O$: C, 70.36; H, 4.98. Found (S): C, 70.54, 70.54; H, 5.52, 5.52.

The methyl ester was prepared (diazomethane) and recrystallized from methanol–water. It became crystalline only after standing three days in the refrigerator. The melting point was indefinite, the material never became liquid; only a transparent glass was formed slowly, beginning at about 75°. Recrystallization from methanol–water and drying over phosphorus pentoxide 48 hours at 56° (0.05 mm.) failed to alter the melting behavior. The infrared spectrum of this material was identical with the spectrum of the methyl ester of racemic IIa.[4]

Anal. Calcd. for $C_{20}H_{16}O_4$: C, 74.99; H, 5.03. Found (S): C, 74.90; H, 4.98.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF UTAH]

Crystalline 4-*O*-Benzoyl-1,2:5,6-di-*O*-isopropylidene-D-arabo-3-hexulose. A New Route to Talitol Derivatives

BY JAMES M. SUGIHARA AND GEORGE U. YUEN

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Monobenzoylation of 1,2:5,6-di-*O*-isopropylidene-D-mannitol followed by oxidation with chromic acid–pyridine gave crystalline 4-*O*-benzoyl-1,2:5,6-di-*O*-isopropylidene-D-*arabo*-3-hexulose. Lithium aluminum hydride reduction of the latter yielded 1,2:5,6-di-*O*-isopropylidene-D-talitol and -D-mannitol. The application of a cation-exchange resin to catalyze the hydrolysis of isopropylidene groups is described.

Although aldohexoses and 2-hexuloses have been studied extensively, the 3-hexuloses have received but limited attention. Recently, the preparation of sirupy 2-*O*-methyl-L-*xylo*-3-hexulose, characterized as its crystalline 2,5-dichlorophenylhydrazone, was described.[1] The direct conversion of the methyl ether to the parent sugar does not appear to be feasible. In this investigation an approach was planned which to us appeared to offer more possibilities in realizing the synthesis of an unsubstituted 3-hexulose.

1,2:5,6-Di-*O*-isopropylidene-D-mannitol was used as the starting compound. The elegant synthesis[2] described for this substance made this choice attractive. Benzoylation with an equimolar amount of benzoyl chloride gave the crystalline 3-*O*-benzoate (46%). The equivalence of the two open positions precludes any isomeric product.

(1) J. K. N. Jones, THIS JOURNAL, **78**, 2855 (1956).

(2) E. Baer and H. O. L. Fischer, *J. Biol. Chem.*, **128**, 463 (1939).