Anal. Calcd. for $C_{16}H_{16}N_4O_4$: N, 17.1. Found: N, 17.0.

The **dinitrophenylhydrazone** of V melted at 193.5–195° (deep purple prisms from chloroform). Mixed m.p. with our sample was 194–196°. The ultraviolet spectrum was determined in chloroform and was identical with that of our sample.

The crystallographic investigation[19] gave the following result.

Both samples consisted of birefringent crystal plates bounded, in general, by three pairs of edges of unequal prominence at approximately 120° to each other. Both showed oblique extinction at an angle of about 25° to the longest edge.

The samples were proved to be crystallographically identical by 20-hour Debye–Scherrer photographs of finely powdered specimens with nickel-filtered copper K radiation. The identification was accomplished by visual inspection of the powder diagrams, in which at least eight prominent lines were clearly visible.

TEL-AVIV
REHOVOTH, ISRAEL

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[19] Kindly carried out by Mr. F. Hirshfeld, Laboratory of X-Ray Crystallography, Weizmann Institute of Science, Rehovoth, Israel.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Position of the Double Bond in Pseudosantonin

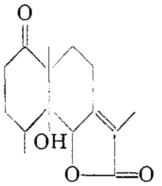
BY WILLIAM G. DAUBEN AND PAUL D. HANCE

RECEIVED FEBRUARY 7, 1953

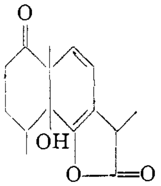
Pseudosantonin and its dihydro and tetrahydro derivatives have been studied spectroscopically and compared with model unsaturated esters and lactones. Examination of the ultraviolet and infrared spectra strongly suggests a β-γ'-type of unsaturation in pseudosantonin and its related compounds.

Since the reported isolation in 1935 of pseudosantonin, a constituent of the sesquiterpenic lactones obtained from *Artemisa maritima*, the structure and the chemistry of the compound has been the subject of considerable investigation.[1–7] On the basis of these researches, three isomeric structures (Ia, Ib, Ic) have been considered and prior to 1952 the structure Ic was thought to offer the most satisfactory explanation of the wide variety of reactions this sesquiterpenic lactone undergoes.

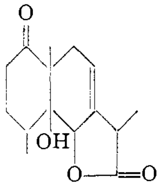
Early in 1952, Cocker, Cross and Hayes[8] reported evidence which led them to favor the alternate structure Ia. They found that pseudosantonin, in the infrared region, possessed an absorption band at 1745 cm.$^{-1}$, a value characteristic for $\Delta^{\alpha,\beta}$-butenolides[9] and, in the ultraviolet region, displayed a maximum of high intensity at 206 mμ, a distinctive feature for an isolated tetrasubstituted olefinic double bond.[10] They also reported that the acidic mixture obtained upon decomposition of the ozonide of pseudosantonin probably contained pyruvic acid, an acid only capable of being formed from a compound of structure Ia. The structure of this sesquiterpenic lactone also has been investigated in this Laboratory and we should like to report a detailed study of the spectra of pseudosantonin and its related hydrogenation products which was undertaken to establish the position of the double bond in the natural product.



Ia

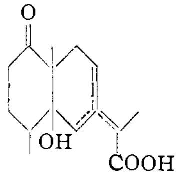


Ib

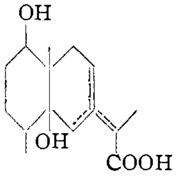


Ic

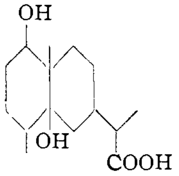
It has been shown[1] that when pseudosantonin (I) is hydrogenated in the presence of palladium in acetic acid the lactone ring undergoes hydrogenolysis and an acid, dihydropseudosantonin (II), is formed. When this dihydro derivative is allowed to react with sodium amalgam, reduction of the carbonyl group occurs and the resulting tetrahydropseudosantonin (III) is obtained. Further reduction of the tetrahydro derivative with platinum in acetic acid yields hexahydropseudosantonin (IV) which can also be obtained directly from pseudosantonin under the same conditions.



II



III



IV

The ultraviolet spectra of pseudosantonin and its hydrogenated derivatives are shown in Fig. 1. It was found that none of these compounds displayed a distinct maxima in the 205–250 mμ region.[11] The value of the extinction coefficients at 210 and 220 mμ are: pseudosantonin, 8300, 3500; dihydropseudosantonin, 4480, 2080; tetrahydropseudosantonin, 3680, 320; hexahydropseudosantonin, 160, 70, respectively.

The ultraviolet spectra of α,β- and β,γ-unsatu-

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[1] G. R. Clemo and W. Cocker, *J. Chem. Soc.*, 30 (1946).

[2] W. Cocker, *ibid.*, 36 (1946).

[3] W. Cocker and C. Lipman, *ibid.*, 553 (1947); see *ibid.*, 1519 (1950), for correction.

[4] W. Cocker and S. Hornsby, *ibid.*, 1157 (1947).

[5] W. Cocker, B. E. Cross and C. Lipman, *ibid.*, 959 (1949).

[6] W. Cocker and C. Lipman, *ibid.*, 1170 (1949).

[7] W. Cocker, B. E. Cross, A. K. Fateen, C. Lipman, E. R. Stuart, W. H. Thompson and R. R. A. Whyte, *ibid.*, 1781 (1950).

[8] W. Cocker, B. E. Cross and D. H. Hayes, *Chemistry and Industry*, 314 (1952).

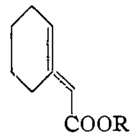
[9] J. F. Grove and H. A. Willis, *J. Chem. Soc.*, 877 (1951).

[10] P. Bladon, H. B. Henbest and G. W. Wood, *ibid.*, 2737 (1952).

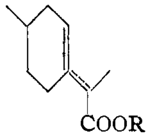
[11] As pointed out by Bladon, Henbest and Wood,[10] the maxima reported in the region of 205 mμ are only "apparent maxima" and are due to the contribution of false-energy factors which will vary with the instrument and the intensity of the light source. The maximum reported by Cocker and his co-workers obviously is such an "apparent maximum" and as such has no real significance.

rated esters[12–15] and lactones[16,17] have been examined by various workers and it has been reported that α,β-unsaturated compounds display a distinct maxima in the region 210–220 mμ with an intensity of about 14,000 whereas the corresponding β,γ-unsaturated compounds show no maxima down to 205 mμ and have a very low extinction coefficient of about 1000. Pseudosantonin also does not possess a maximum in this important region of the spectra and its extinction coefficient is much lower than might be expected for an α,β-isomer. Since the general characteristics of the curves for pseudosantonin and its hydrogenated derivatives were so different from those of simple α,β-unsaturated esters and butenolides and were more like those of a β,γ-isomer, a study with more closely related compounds was undertaken.

A series of model α,β- and β,γ-unsaturated cyclohexenylacetic acid esters[18–20] was synthesized and their ultraviolet spectra are also shown in Fig. 1. The values for the α,β-unsaturated compounds are: V, 218 mμ (ε 13,700) and VII, 225 mμ (ε 8220).[21] The β,γ-isomers again showed only general absorption but with a higher intensity than the acyclic compounds. The extinction coefficients at 210 and 220 mμ are: VI, 2860 and 1900; VIII, 2400 and 1180; IX, 2480 and 1300.

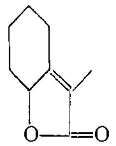


V, VI



VII, VIII

Only one lactone was prepared and investigated. In view of the lower intensity of the 225 mμ maximum of ester VII, the closely related compound, the lactone of 2-(2-hydroxycyclohexylidene)-propionic acid (X) was prepared as described by Cocker and Hornsby.[4] This lactone had a distinct maximum at 217 mμ (ε 14,150) and it is of interest to note that the extinction coefficient is of the normal expected intensity.



X

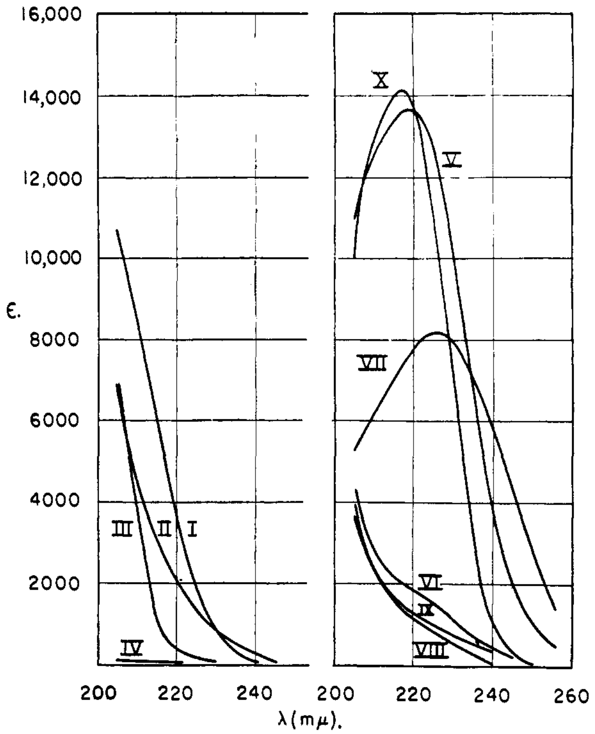


Fig. 1.—Ultraviolet absorption spectra: I, pseudosantonin; II, dihydropseudosantonin; III, tetrahydropseudosantonin; IV, hexahydropseudosantonin; V, ethyl cyclohexylideneacetate; VI, ethyl (1-cyclohexen-1-yl)-acetate; VII, methyl 2-(4-methylcyclohexylidene)-propionate; VIII, ethyl 2-(4-methyl-1-cyclohexen-1-yl)-propionate; IX, ethyl 2-(1-cyclohexen-1-yl)-propionate; X, lactone of 2-(2-hydroxycyclohexylidene)-propionic acid.

Thus, it appears that for all α,β-unsaturated esters and butenolides a strong maximum is found in the 210–225 mμ region while the β,γ-isomers show only weak general absorption in the same region. In general the extinction coefficients of the two isomers at 220 mμ differ by a factor of 5- to 10-fold, the cyclic compounds possessing a higher extinction coefficient. From these data, it is strongly suggested that the pseudosantonin compounds cannot be of the α,β-type of structure but that their spectra are best explained on the basis of a β,γ (Ib) or β,γ′(Ic) type of double bond in the original sesquiterpenic lactone. The reported chemical properties favor Ic for pseudosantonin. Cocker and his co-workers,[8] on the other hand, have concluded that pseudosantonin possesses a tetra-substituted double bond by comparing the extinction coefficient of (I) with the values given by Bladon, Henbest and Wood[10] for isolated olefinic double bonds. Such reasoning is without basis both from examination of the general spectral characteristics of unsaturated esters and lactones mentioned above and from resonance considerations in the α,β-isomers, in particular.

In view of this different conclusion as to the location of the unsaturation in pseudosantonin it became of interest to re-examine the infrared spectra of all of the above compounds since Cocker[8] reported that I possessed a carbonyl absorption which is characteristic of α,β-butenolides. The infrared spectra in the characteristic carbonyl

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(12) W. M. Lauer, W. J. Gensler and E. Miller, THIS JOURNAL, **63**, 1153 (1941).

(13) G. O. Burr and E. S. Miller, *Chem. Revs.*, **29**, 419 (1941).

(14) H. E. Ungnade and F. V. Morriss, THIS JOURNAL, **72**, 2113 (1950).

(15) J. Cason and G. Sumrell, *J. Org. Chem.*, **16**, 1181 (1951).

(16) H. J. Dauben, Jr., and D. W. Goheen, private communication.

(17) W. D. Paist, E. R. Blout, F. C. Uhle and R. C. Elderfield, *J. Org. Chem.*, **6**, 273 (1941).

(18) G. A. R. Kon and R. P. Linstead, *J. Chem. Soc.*, 1269 (1929).

(19) R. L. Frank, private communication.

(20) R. L. Frank and R. E. Berry, THIS JOURNAL, **72**, 2983 (1950); O. Wallach, *Ann.*, **360**, 26 (1908).

(21) The lower extinction coefficient of the substituted propionate can be accounted for on the basis of steric strain. A scale drawing (see E. A. Braude, E. R. H. Jones, H. P. Koch, R. W. Richardson, F. Sondheimer and J. B. Toogood, *J. Chem. Soc.*, 1890 (1949); L. P. Kuhn, R. E. Lutz and C. E. Bauer, THIS JOURNAL, **72**, 5058 (1950)) shows steric interference between the α-methyl group and the ring hydrogen atoms and thus the co-planarity of the olefinic system could be effected. Such an effect is known to lower extinction coefficient values.

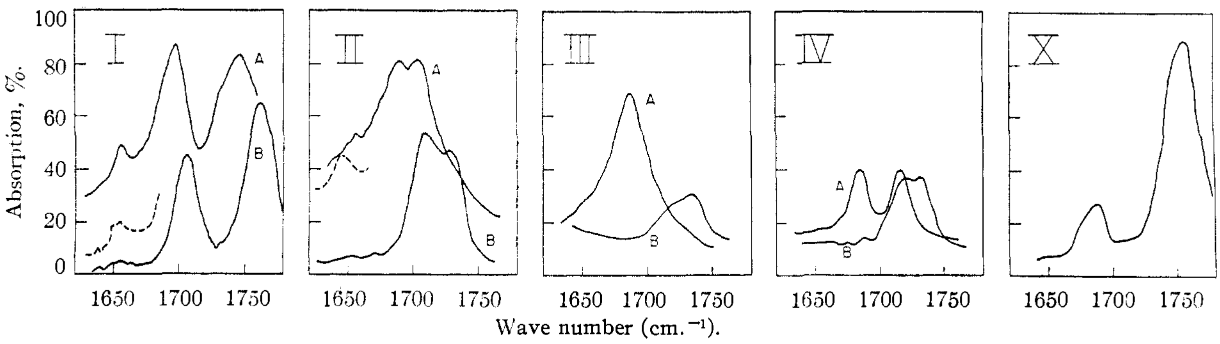

Fig. 2.—Infrared absorption spectra: IA, pseudosantonin in mineral oil mull; IB, pseudosantonin in 0.1 M methylene chloride solution (dotted line 1 M solution); IIA, dihydropseudosantonin in mineral oil mull; IIB, methyl ester of dihydropseudosantonin in 0.1 M carbon disulfide solution (dotted line 1 M solution); IIIA, tetrahydropseudosantonin in mineral oil mull; IIIB, methyl ester of tetrahydropseudosantonin in 0.1 M carbon disulfide solution; IVA, hexahydropseudosantonin in mineral oil mull; IVB, methyl ester of hexahydropseudosantonin in 0.1 M carbon disulfide solution; X, lactone of 2-(2-hydroxycyclohexylidene)-propionic acid in 0.1 M carbon tetrachloride solution.

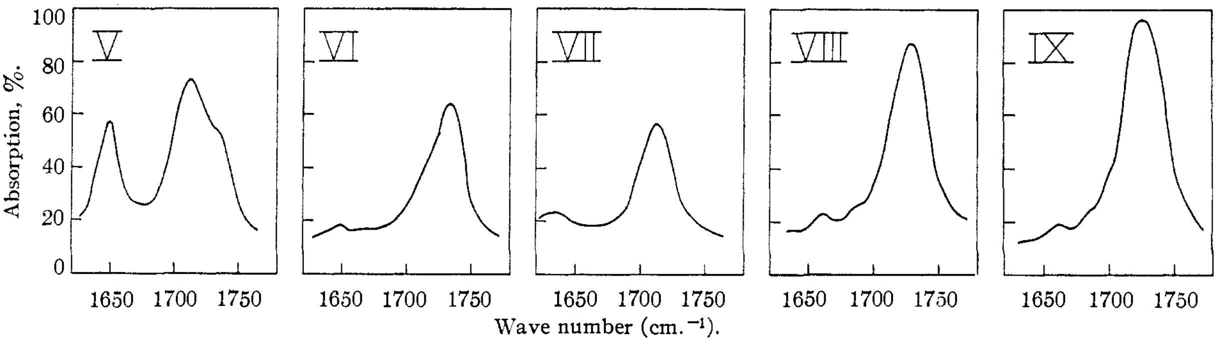

Fig. 3.—Infrared absorption spectra: V, ethyl cyclohexylideneacetate (film); VI, ethyl (1-cyclohexen-1-yl)-acetate (film); VII, methyl 2-(4-methylcyclohexylidene)-propionate (film); VIII, ethyl 2-(4-methyl-1-cyclohexen-1-yl)-propionate (film); IX, ethyl 2-(1-cyclohexen-1-yl)-propionate in 0.1 M carbon tetrachloride solution.

and olefinic double bond stretching region of these compounds are given in Figs. 2 and 3.

From examination of the absorption spectra of the ester groupings of the unsaturated acids, it is seen that the absorption due to carbonyl stretching vibration was found to occur between 1708–1712 cm.$^{-1}$ (V, 1708; VII, 1712) for α,β-unsaturated isomers as compared to 1726–1734 cm.$^{-1}$ (VI, 1734; VIII, 1726; IX, 1728) for the β,γ-isomers. These values are in agreement with those reported by Cason, Freeman and Sumrell[22] for the 3-methylnonenoic acids. Methyl dihydropseudosantonin (II, curve B) showed a band at 1728 cm.$^{-1}$ whereas methyl tetrahydropseudosantonin (III, curve B) absorbed at 1735 cm.$^{-1}$. Such results strongly indicate a β,γ-structure for these latter compounds. Examination of the characteristics of the olefinic double bond absorption added further agreement to this conclusion. It is seen that the α,β-unsaturated ester showed a relatively strong band in the 1635–1650 cm.$^{-1}$ region whereas in all of the β,γ-isomers the band was either very weak or not observable.

Examination of the spectra of the lactones did not lead to any such clear result. As has been previously reported,[8,9] $\Delta^{\alpha,\beta}$-butenolides show a carbonyl band around 1750 cm.$^{-1}$ whereas the $\Delta^{\beta,\gamma}$-isomers absorb at 1800 cm.$^{-1}$. For example, lactone X showed a carbonyl absorption at 1757 cm.$^{-1}$ in carbon tetrachloride solution (as compared to 1750 cm.$^{-1}$ reported by Cocker[8] with no conditions stated). Pseudosantonin in methylene chloride solution (I, curve B) showed two strong bands at 1706 and 1762 cm.$^{-1}$. The former was established as being due to the six membered ring ketone[9] since it also appeared in the dihydro derivative. The absorption at 1762 cm.$^{-1}$ thus must be assigned to that of the lactone. When pseudosantonin was run in a Nujol mull (curve A), slight shift in bands occurred and maxima were found at 1692 and 1746 cm.$^{-1}$, this latter value being in agreement with a value previously reported by Cocker.[8] Again, olefinic double bond absorption was strong in lactone X (1688 cm.$^{-1}$) while in pseudosantonin it was only weakly absorbing in very concentrated solution (I, dotted line) and in the mull (1656 cm.$^{-1}$). This shift occurring in a mull of a solid suggests hydrogen bonding and/or association interactions of the molecule. From these results, it would appear certain that the classical β,γ-structure (Ib) which should absorb at 1800 cm.$^{-1}$ range can be ruled out. Unfortunately, no model compounds related to a β,γ'-type of structure (Ic) have been prepared but, as a first approximation to a structure such as Ic, a saturated five membered lactone, such as γ-butyrolactone, might be considered. Such lactones show carbonyl absorption at 1770 cm.$^{-1}$.[9] Thus, an absorption of 1762 cm.$^{-1}$ in solution for the sesquiterpenic lactone lies between the value for an

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[22] J. Cason, N. K. Freeman and G. Sumrell, *J. Biol. Chem.*, **192**, 415 (1951).

$\Delta^{\alpha,\beta}$-butenolide and a saturated γ-lactone. With such small differences between model compounds and since pseudosantonin shows hydrogen bond and/or association interaction, any direct inference as to its structure on the above infrared data is inconclusive.

To date, no chemical evidence has been obtained to establish the fact that the position of the carbon–carbon double bond in the hydrogenated derivatives is the same as in the parent lactone. Some insight can be gained on this matter, however, by examination of the 2950–3150 cm.$^{-1}$ region using a lithium fluoride prism.[23] In this range, olefinic carbon–hydrogen stretching bands appear. It was found that 1-methylcyclohex-1-ene had a band at 2994 cm.$^{-1}$ which was missing in its saturated analog 1-methylcyclohexane. Ethyl 2-(4-methylcyclohexen-1-yl)-propionate (VIII) has a corresponding band at 2978 cm.$^{-1}$ which its $\Delta^{\alpha,\beta}$-isomer (VII) containing a tetra-substituted double bond lacks. Pseudosantonin (I) and the esters of its di- and tetrahydro derivatives (II and III) show absorption at 2967, 2972 and 2974 cm.$^{-1}$, respectively. Such a constancy would suggest that the carbon–carbon double bond has not been affected in the formation of compounds II and III. Since structures Ia and Ib for pseudosantonin and the corresponding $\Delta^{\alpha,\beta}$-structure for II and III of the hydrogenated pseudosantonins lack olefinic carbon hydrogen bonds, further confirmatory evidence of structure Ic is at hand.

As a further test to rule out a normal β,γ-structure (Ib), the reaction of aniline with pseudosantonin was tried. Linstead and his co-workers[24] found that this reaction was quite definitive for differentiating the α,β- and β,γ-butenolide; the β,γ-isomer reacts while the α,β does not. No reaction was found to occur with pseudosantonin. Thus, again, a structure such as Ib appears unlikely. The reactivity of a structure such as Ic is not known.

Since investigation of the 205–250 mμ region of the ultraviolet spectra and the 1600–1800 cm.$^{-1}$ of the infrared spectra of II and III yields data best correlated with a β,γ-type of structure and since studies in the 2950–3100 cm.$^{-1}$ region strongly suggest that no bond migration has occurred in the preparation of these compounds from I, structure Ic appears to warrant consideration in further chemical degradative studies.

Finally, it should be noted that in the infrared spectrum of hexahydropseudosantonin (IV) a splitting of the carbonyl absorption occurs (1717 and 1685 cm.$^{-1}$) and a similar but not so marked split is found in the ester of IV (curve B, 1718 and 1732 cm.$^{-1}$). No explanation of this splitting appears reasonable at this time but it is being further investigated.

Acknowledgment.—The authors wish to thank Messrs. T. and H. Smith, Ltd., Edinburgh, Scotland, for kindly supplying the pseudosantonin used in this work. They are also indebted to Dr. Robert L. Frank for his interest and coöperation. One of the authors (Paul D. Hance) is the holder of the Shell Research Fellowship in Chemistry.

Experimental

All boiling points are uncorrected and all melting points are corrected. All distillations unless otherwise stated, were conducted in a 30-plate column. Ultraviolet absorption spectra were determined in 95% ethanol with a Beckman Model DU quartz spectrophotometer as described by Cason and Sumrell.[25] Infrared spectra were obtained with Models 12C and 21 Perkin–Elmer recording spectrophotometers.

Pseudosantonin (I).—A sample obtained from T. and H. Smith, Ltd., Edinburgh, was recrystallized from ethanol, m.p. 182.8–185.8° (lit.[1] 183–184°).

Dihydropseudosantonin (II).—Hydrogenation of (I) according to the method of Clemo and Cocker[1] and recrystallization from methanol yielded (II), m.p. 187.0–189.0° (lit.[1] 188–189°). The methyl ester was prepared with diazomethane and recrystallized from methylene chloride, m.p. 76.3–78.0° (lit.[1] 77°).

Tetrahydropseudosantonin (III).—Reduction of (II) with sodium amalgam, following the published procedure,[1] and recrystallization from water yielded III, m.p. 192.0–192.5° (lit.[1] 189–190°). The ester was prepared with diazomethane and recrystallized from chloroform, m.p. 91.0–93.7°.

Anal. Calcd. for $C_{16}H_{26}O_4$: C, 68.05; H, 9.28. Found: C, 67.78; H, 9.27.

Hexahydropseudosantonin (IV).—Hydrogenation of (I) according to Clemo and Cocker[1] gave a viscous oil after removal of the solvent under reduced pressure. Trituration with chloroform gave a white solvated solid, m.p. 163–168°. Recrystallization twice from water gave white needles, m.p. 182.0–182.5° (lit.[1] 191–192°).

Anal. Calcd. for $C_{15}H_{26}O_4$: C, 66.63; H, 9.69. Found: C, 66.65; H, 10.05.

Esterification of (IV) with diazomethane and recrystallization from diethyl ether yielded ester melting from 95.1–96.2°.[26]

Anal. Calcd. for $C_{16}H_{28}O_4$: C, 67.57; H, 9.93. Found: C, 67.67; H, 10.15.

Ethyl Cyclohexylideneacetate (V) and Ethyl (1-Cyclohexen-1-yl)-acetate (VI).—The crude mixture of isomeric esters was prepared by dehydration of ethyl (1-hydroxycyclohexan-1-yl)-acetate and the pure isomers obtained by fractional distillation.[18] The β,γ-ester boils 104–105.5° (15 mm.), n^{25}_{D} 1.4617 (lit.[18] n^{18}_{D} 1.4639) and the α,β-isomer boils 110–114° (15 mm.), n^{25}_{D} 1.4722 (lit.[18] n^{18}_{D} 1.4768).

Methyl 2-(4-Methylcyclohexylidene)-propionate (VII).—This pure acid was prepared according to the procedure of Frank.[19] Ethyl 2-(4-methyl-1-hydroxycyclohexan-1-yl)-propionate was refluxed with a methanolic solution of potassium hydroxide for three hours. The solvent was removed under reduced pressure, the product acidified and extracted with ether. Evaporation of the ether gave a quantitative yield of crude hydroxy acid which was dehydrated by refluxing for three hours with acetic anhydride. The excess anhydride was hydrolyzed and the acid solution extracted with ether. The product was distilled, b.p. 123–126° (3.5 mm.), yield 64%.

The crude acid from the above distillation was purified by partial esterification with ethanol and sulfuric acid and from 12.5 g. of crude material, 9.0 g. of solid $\Delta^{\alpha,\beta}$-acid was obtained. The acid was recrystallized from acetone, m.p. 52.8–54.4° (lit.[19] 50–51°). The acid was esterified with diazomethane b.p. 100–102° (10 mm.), n^{25}_{D} 1.4778.

Ethyl 2-(4-Methyl-1-cyclohexen-1-yl)-acetate (VIII).—The corresponding hydroxy ester, prepared from 4-methylcyclohexanone and ethyl 2-bromopropionate,[20] was dehydrated with phosphorus pentoxide and the resulting unsaturated ester carefully fractionated, b.p. 106.5–108.5° (10 mm.), n^{25}_{D} 1.4566 (lit.[20] 114–116° (13 mm.), 62–70° (0.6 mm.), n^{21}_{D} 1.4583).

Ethyl 2-(1-Cyclohexen-1-yl)-propionate (IX).—The hydroxy ester was prepared from ethyl 2-bromopropionate and

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[23] N. Sheppard and D. M. Simpson, *Quart. Rev.* (*London*), **6**, 1 (1952).

[24] F. A. Kuehl, Jr., R. P. Linstead and B. A. Orkin, *J. Chem. Soc.*, 2213 (1950).

[25] J. Cason and G. Sumrell, *J. Org. Chem.*, **16**, 1177 (1951).

[26] The degree of drying affected the melting point and material melting sharply but in the range 91–96° could be obtained. Analysis showed solvation with ether and a correct analysis could only be obtained on a sublimed sample which was glassy.

cyclohexanone[20] and dehydrated with thionyl chloride and pyridine.[27] The unsaturated ester was distilled, b.p. 122.5–123° (30 mm.), n^{26}_{D} 1.4600 (lit.[20] 108–112° (12 mm.)).

Lactone of 2-(2-Hydroxycyclohexylidene)-propionic Acid (X).—The lactone was prepared from 2-(2-ketocyclohexyl)-propionic acid according to the procedure of Cocker and Hornsby.[4] The material boils 121–124° (3 mm.), n^{25}_{D} 1.5060 (lit.[4] 133–134° (3 mm.)).

Attempted Reaction of Aniline and Pseudosantonin.—Following the general procedure of Kuehl, Linstead and Orkin,[25] 1.0 g. of pseudosantonin was allowed to stand for four days at room temperature with 1 g. of aniline. The reaction mixture was diluted with methylene chloride, the solution extracted with dilute hydrochloric acid and the solvent evaporated. The residue was recrystallized from methylene chloride to yield 0.8 g. of pseudosantonin, m.p. 188.0–190.4°.

BERKELEY 4, CALIFORNIA

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[27] This experiment was performed by Mr. Thomas Colby.

[CONTRIBUTION FROM THE H. FLETCHER BROWN LABORATORIES OF THE UNIVERSITY OF DELAWARE]

Isomerism in the Diels–Alder Reaction. II. The Bromination of Diels–Alder Adducts[1]

BY HAROLD KWART AND LLOYD KAPLAN

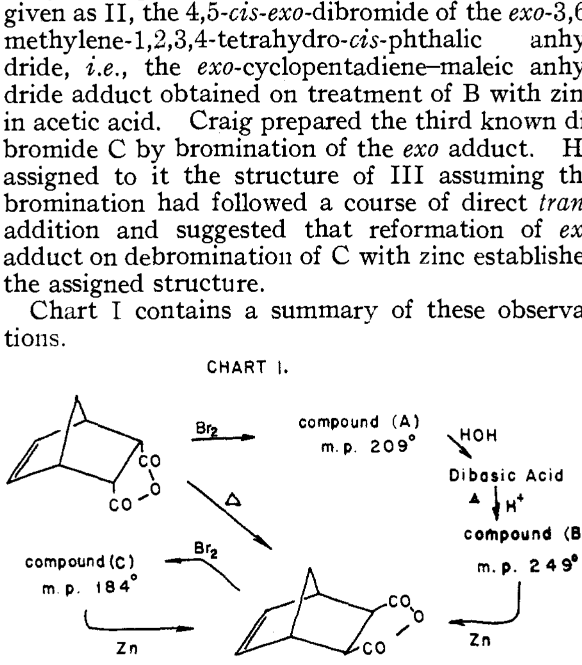
RECEIVED NOVEMBER 24, 1952

The steric course of bromination of the Diels–Alder adducts of cyclopentadiene and maleic anhydride has been examined. The previously reported structures of two of the three known dibromides in this series are found to be inconsistent with the measured dipole moments. Structural assignments are revised to bring all three structures into line with the dipole moment data and with modern concept on the steric course of addition and rearrangement reactions in related bicyclic systems.

Craig[2] has examined the reaction mechanism of the thermally induced transformation of the *endo* into the *exo* adduct of cyclopentadiene and maleic anhydride. Among other considerations taken into account in his examination, he discusses the nature of the products obtainable on bromination of the residual double bond. Earlier, Alder and Stein[3] had brominated the *endo* adduct and assigned to the resulting compound A the structure I on the basis of an assumed course of direct *trans* addition of the elements of bromine to the double bond. Alder and Stein also prepared an isomeric dibromide by careful hydrolysis of A to a dibromo acid and thermal rearrangement and dehydration of the latter to an anhydride product B. The structure of B was given as II, the 4,5-*cis*-*exo*-dibromide of the *exo*-3,6-methylene-1,2,3,4-tetrahydro-*cis*-phthalic anhydride, *i.e.*, the *exo*-cyclopentadiene–maleic anhydride adduct obtained on treatment of B with zinc in acetic acid. Craig prepared the third known dibromide C by bromination of the *exo* adduct. He assigned to it the structure of III assuming the bromination had followed a course of direct *trans* addition and suggested that reformation of *exo* adduct on debromination of C with zinc establishes the assigned structure.

Chart I contains a summary of these observations.

CHART I.



In the course of our work with this system it appeared that the structures of A, B and C previously assigned may be in error for two reasons; the experimental evidence did not seem to be complete or conclusive in some instances and the assumed reaction course for bromination of the double bond ignored the possibilities of rearrangement previously identified in other double bond addition reactions of this system.[4]

It seemed apparent also that a quick test of the validity of the assigned structure was obtainable through a comparison of the computed dipole moments of I, II and III with the experimental values we have determined and are reporting here for compounds A, B and C. Table I affords this comparison.

It is to be noted that a large discrepancy exists between the calculated and observed values in the cases of compounds A and B whereas good agreement is demonstrated for compound C. On this basis it is clear that the structure of compound C has been properly assigned, but the structures previously assigned for A and B are seriously in error.

What structures do accord with the observed dipole moments and how could these structures arise in the procedure used for their preparation? A tabulation of all other possible dibromo anhydrides that would possess the observed reactions[2,3] of the three isomers is contained in Table I together with their calculated dipole moments.

The limits of inaccuracy in our dipole moment measurement is estimated to be ±0.1 *D*. The structure dipole moment values (Table I) calculated from individual bond moments are not corrected in all cases for mutual polarizability of the bonds and internal field interaction effects.[5] We estimate from the magnitude of such effects that we have encountered in similar molecules[10b] a maximum correction of ±0.3 *D*. It is seen, therefore, that the upper limit of discrepancy between calculated and observed moments is ±0.4 *D*.

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[1] The research work being reported here has been supported by the Office of Naval Research under contract N-onr-567(00). *Cf.* previous paper in this series—THIS JOURNAL, **74**, 3094 (1952).

[2] D. Craig, *ibid.*, **73**, 4889 (1951).

[3] K. Alder and G. Stein, *Ann.*, **504**, 247 (1933).

[4] P. D. Bartlett and A. Schneider, THIS JOURNAL, **68**, 6 (1946); R. B. Woodward and H. Baer, *ibid.*, **70**, 1161 (1948).

[5] I. F. Halverstadt and W. D. Kumler, *ibid.*, **64**, 2988 (1942); R. J. W. LeFèvre, "Dipole Moments," Methuen and Co., London, 1948, Chap. III.