in a three-necked flask fitted with reflux condenser and stirrer and protected from atmospheric moisture. To this solution was added dropwise an equimolar amount of ethyl α-alkylacetoacetate. The resultant solution was heated to 70–80° and a slurry containing one-half molar amount of 2-dimethylaminomethylcyclohexanone methiodide in absolute alcohol was added slowly over a period of about one to two hours. After all the methiodide had been added the solution was heated and stirred for four to six hours. One-half of the solvent was removed under reduced pressure and a volume of water equal to the amount of residue was added. The product was isolated by continuous extraction with ether in a liquid–liquid extractor and distilled under reduced pressure.

3-Methyl-1,2,3,4,5,6,7,8-octahydro-2-naphthol.—A solution of 11.2 g. (0.069 mole) of the low-boiling ketone I from the 3-methyl product in 75 ml. of absolute ethanol was hydrogenated over platinum oxide (0.25 g.) at 30 p.s.i. The product was distilled under reduced pressure giving two fractions b.p. 88–91.5 (1.5 mm.), $n^{27}\text{D}$ 1.5025 and b.p. 91.5–93 (1.5 mm.), $n^{27}\text{D}$ 1.5060. After standing for several hours the second fraction solidified, m.p. 40–45°. The solid gave a positive xanthate test, absorbed bromine, and showed an intense absorption band at 3280 cm.$^{-1}$. Since the solid alcohol could not be purified for analysis a *m*-nitrophenylurethan was prepared, m.p. 150–154°.

Anal. Calcd. for $C_{18}H_{22}N_2O_4$: C, 65.44; H, 6.72. Found: C, 65.02; H, 6.62.

The liquid product of fraction one was identified as the ketone described below.

2-Oxo-3-methyldecahydronaphthalene.—A solution of 8.2 g. (0.05 mole) of the higher-boiling ketone II from the 3-methyl product (Table V) in 50 ml. of absolute ethanol was hydrogenated over platinum oxide (0.25 g.) at 30 p.s.i. The ketone absorbed one mole of hydrogen and the product was distilled under reduced pressure, b.p. 83–85° (1.5 mm.), $n^{26}\text{D}$ 1.4840. This material gave a positive phenylhydrazine test and showed strong absorption at 1704 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{18}O$: C, 79.55; H, 10.82. Found: C, 78.97; H, 10.54.

A 2,4-dinitrophenylhydrazone was formed, m.p. 130–138°.

Anal. Calcd. for $C_{17}H_{22}N_4O_4$: C, 58.94; H, 6.43. Found: C, 59.26; H, 6.35.

β-Methylnaphthalene.—A mixture of 0.2 g. of 3-methyl-1,2,3,4,5,6,7,8-octahydro-2-naphthol and 0.1 g. of sulfur was heated for two hours at 250°. Several drops of liquid were collected on a cold finger condenser. A picrate was prepared from the product, m.p. 113–116°. A mixture of this picrate and picric acid melted at 104–109°. The picrate of β-methylnaphthalene is reported[11] to melt at 115°.

2,3-Dimethylnaphthalene.—Two grams (0.012 mole) of 2-oxo-3-methyldecahydronaphthalene was added dropwise to an excess (0.05 mole) of methylmagnesium iodide in dry ether. After being heated for four hours the product was poured onto a mixture of ice and 10% ammonium chloride solution. The organic layer was separated, washed with dilute sodium thiosulfate and dried over Drierite. Part of the crude alcohol (0.2 g.) obtained by this procedure was mixed with 0.1 g. of sulfur and heated at 250° for two hours. A small amount of solid, m.p. 101–102°, collected on the cold finger condenser. A melting point of 102° is reported[12] for 2,3-dimethylnaphthalene. No depression of melting point was observed when the above solid was mixed with an authentic sample of 2,3-dimethylnaphthalene.

Infrared Spectra.—The infrared spectra were measured with a Perkin-Elmer 12C spectrometer remodelled to function as a double-beam continuous recording instrument. Sodium chloride cells were employed and thin films of pure liquids were used.

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[11] E. J. H. Chu and Z. I. Shen, *J. Chinese Chem. Soc.*, **10**, 119 (1943); *cf. C. A.*, **38**, 2951 (1944).

[12] W. Thiele and G. Trautmann, *Ber.*, **68B**, 2245 (1935).

CORVALLIS, OREGON

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

Reactions of Hindered α-Substituted Succinic Acids. IV. Further Reactions Involving the Wagner–Meerwein Rearrangement[1,2]

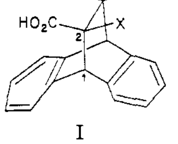
BY WYMAN R. VAUGHAN AND RANDEL Q. LITTLE, JR.[3]

RECEIVED DECEMBER 5, 1953

The rearrangements of 2-bromo- and 2-chloro acids and anhydrides in the dibenzo[2,2,2]bicycloöctadiene-2,3-dicarboxylic acid series to 2-hydroxy derivatives of the 3,4,7,8-dibenzo[3,2,1]bicycloöctadiene-1,6-dicarboxylic acid series by means of silver nitrate or silver oxide are discussed and are compared with the analogous base-induced reactions.

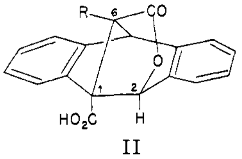
The fact that 2-bromodibenzo[2,2,2]bicycloöctadiene-2,3-*trans*-dicarboxylic acid (IA, Fig. 1) reacts with silver nitrate in part to give the lactone acid IIB[4] (Fig. 2) in a manner completely analogous to the reaction of 2-hydroxy-3-methyldibenzo[2,2,2]bicycloöctadiene-2,3-*trans*-dicarboxylic acid with 48% hydrobromic acid to give the lactone acid IIC[5] (Fig. 2) has led us to investigate the behavior of other haloacids and haloanhydrides in this series with silver nitrate and with silver oxide.

The behavior of IA with silver nitrate is completely analogous to its behavior with alkali, except for the ratio of products[1] (IIIA, Fig. 3, and IIA, Fig. 2) and the fact that the rearranged product is obtained as the lactone acid IIB, instead of the free hydroxyacid. However, certain striking differences were observed with each of the other halo compounds in the series. In particular, the bromoanhydride, IVA (Fig. 4), with silver nitrate affords a rearranged hydroxyacid (VA, Fig. 5) instead of IIIA; the chloroanhydride, IVC (Fig. 4), affords a rearranged hydroxyacid (VB, Fig. 5) *in addition to* IIIB (Fig. 3) and a lactone acid, IIC (Fig. 2), *instead of* IC (Fig. 1), when treated with silver oxide;



I

A, R = H; X = Br
B, R = H; X = OH
C, R = CH_3; X = OH



II

A, R = H (hydroxy acid)
B, R = H
C, R = CH_3

Figs. 1 and 2.

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[1] Preceding paper, W. R. Vaughan and R. Q. Little, Jr., THIS JOURNAL, **76**, 2952 (1954).

[2] Abstracted from a portion of the Ph.D. Dissertation of Randel Q. Little, Jr., University of Michigan, 1953.

[3] American Brake Shoe Company Fellow, 1952–1953.

[4] W. R. Vaughan, M. V. Andersen, Jr., and R. Q. Little, Jr., THIS JOURNAL, **76**, 1748 (1954).

[5] W. R. Vaughan and K. M. Milton, *ibid.*, **74**, 5623 (1952).

and the bromo- and chloroanhydrides, IVA and IVB (Fig. 4), with silver oxide appear to afford traces of the rearranged hydroxyacids IIA and VA (Figs. 2 and 5) *in addition to* IB (Fig. 1) and IIIA (Fig. 3). These reactions are summarized along with the alkali reactions in Table I.

III
A, R = H
B, R = CH_3

IV
A, R = H; X = Br
B, R = H; X = Cl
C, R = CH_3; X = Cl

Figs. 3 and 4.

TABLE I

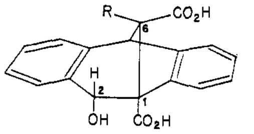
YIELDS OF PRODUCTS

Reactant	Reagent	Relative yields			
		IB	IIIA	VA	IIA or B
IA	$NaHCO_3$[1]	..	11	....	1
	NaOH[5]	..	3	....	2
	$AgNO_3$[4]	..	1	....	5
IVA	$NaHCO_3$[1]	3	2	....	....
	NaOH[5]	2	1	....	....
	$AgNO_3$	8	..	1	....
	Ag_2O	14	1	0.1(?)	....
IVB	Ag_2O[6]	1.4	2	1(?)	0.6(?)
		IC	IIIB	VB	IIC
IVC	Ag_2O[6]	..	2	4	3

An examination of the data in Table I will reveal that, with the noted exceptions, the principal difference between the alkali (or bicarbonate) induced reactions and those effected by silver nitrate (or silver oxide) is encountered in product ratio differences. Thus silver ion with IA favors the rearrangement over dehalogenative decarboxylation, and with IVA the "normal"[5] displacement of halide is favored over dehalogenative decarboxylation.

In the case of IA the dominance of the rearrangement process with silver ion is readily accounted for when one considers that the dehalogenative decarboxylation is generally held to be a reaction of the β-haloacid anion[1,7,8] which cannot be expected to exist to any appreciable extent in an acidic medium of diminishing *p*H. Furthermore it is only reasonable to expect the concerted rearrangement[4,5] to IIB to proceed more smoothly where the removal of bromine is effected by silver ion rather than simple solvation.

Failure to observe any dehalogenative decarboxylation with IVA and silver nitrate where the favorable *trans* disposition of bromine and carboxyl would certainly be expected to facilitate it[1,7,8] leads to the conclusion that the monosilver salt[1] which is formed initially is derived from the 2-carboxyl, and that β-lactone formation by the free 3-carboxyl readily leads to IB and, less readily, to VA by rearrangement. Where the medium is less acidic (silver oxide) the dehalogenative decarboxylation appears, and the "normal" halide displacement[5] *via* the β-lactone is further enhanced by the greater probability of a 2-carboxylate ion. The formation of VA under these conditions is indicated by melting point data.



V
A, R = H
B, R = CH_3–

Fig. 5.

In the reaction of IVA with silver nitrate the separation of the two isomeric reaction products, VA and IB, proved to be difficult because of very similar solubility characteristics and similar melting points. Consequently the relative yields may be appreciably in error. A complete study of the structure of VA was not made, but a comparison of the infrared spectra of the dimethyl esters of VA IB and IIA permits one to conclude that VA more closely resembles IIA than IB. The non-identity of VA and IB in any case, is clear from marked differences in the general shape of their infrared curves, notably between 7 and 10 μ; and the structure of the rearranged product may reasonably be inferred from the nature of the reaction and by analogy with the reaction of IVA with silver nitrate, where the structure of the rearranged product is not in doubt.[4] That VA is not the *cis* acid corresponding to IB is certain from the fact that it is readily obtained as the free acid and does not show the characteristic tendency of the *cis* acids of this series to form anhydrides spontaneously.[5]

In treating IVB, the chloro analog of IVA, with silver oxide the product ratios were found to be rather different. Especially noteworthy is the marked decrease in the amount of IB with respect to IIIA, which suggests that the IVB anhydride itself rather than an "opened" form of IVB is involved (*cf.* the discussion of IVC below). The presence of IIA in the products is suggested by melting point data, but has not been unequivocally confirmed.

The reaction of IVC with silver nitrate was found to be incomplete at best. Even when a dioxane–water solution was heated on the steam-bath, the only identifiable product was the original chloroanhydride (62% recovery), while unreacted silver ion was separated as silver bromide (86%). Consequently it seemed advisable to try the more basic silver oxide. The absence of IC is striking in view of the good yield obtained in the alkali reaction[5] and in view of the good yield of the desmethyl homolog, IB, obtained in reactions of IVA with alkali, silver nitrate and silver oxide.

A possible explanation for the failure to obtain IC may be found in the appreciably greater stability of the anhydride link of IVC compared with that of IVA or IVB, as revealed by the comparative inert-

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(6) The behavior of the chloroanhydride with alkali is similar to that of the analogous bromoanhydride,[5] and so has not been reported independently. Unpublished results, W. R. Vaughan.

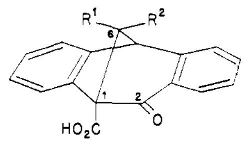
(7) S. J. Cristol and W. P. Norris, THIS JOURNAL, **75**, 632, 2645 (1953).

(8) E. Grovenstein, Jr., and D. E. Lee, *ibid.*, **75**, 2639 (1953).

ness to silver nitrate.[9] If one accepts this condition, it becomes obvious that a reaction proceeding through a β-lactonic intermediate to IC cannot occur. The dehalogenative decarboxylation of IVC may be pictured as a concerted process in which an "opened" form of the anhydride is not involved, water (or hydroxyl) attacking the 2-carbonyl as silver ion removes the chlorine while the 3-carbonyl and anhydride oxygen are eliminated as carbon dioxide. The reaction is analogous to that suggested for IVB, above. The production of VB and IIC may be similarly pictured, as described in the sequel where consideration of the configurations of these products is discussed. Failure to observe the analogous rearrangement of IVA or IVB to IIB under similar conditions may be attributed to the greater ease with which the anhydride system of IVA and IVB is opened, thus permitting other reactions to occur.

Owing to the difficulty of obtaining sufficiently large quantities of VA in a state of purity suitable for further study, it was decided to concentrate upon establishing the structure of its methyl homolog, VB, obtained from IVC and silver oxide. In order to do this with reasonable certainty, it seemed advisable first to establish a general structural relationship between VB and the isomeric lactone acid IIC, whose structure has been established[4] and which is produced simultaneously in the same reaction.

Like the unisolable dibasic hydroxyacid derived from IIC, VB is readily oxidized to a ketoacid (VI, Fig. 7) which is isomeric but not identical with the ketoacid from IIC (VII, Fig. 6). The infrared spectra for the dimethyl esters of VA and VII are very similar, with differences comparable to those observed between the spectra of the dimethyl esters of VA and IIA. Furthermore, like VII, VI dissolves in concentrated sulfuric acid to produce an intensely yellow solution from which the unchanged ketoacid is precipitated upon dilution with water. The ultraviolet spectra of VI in alcohol and concentrated sulfuric acid (Fig. 7) closely resemble those of VII.[4] However, the ultraviolet spectra of VI and VII are not superimposable as are those of VII (Fig. 6) and VIII[4] where the only difference in structure is the methyl group on carbon-6 of VII. This is in keeping with a distinct difference in configuration but a clearly similar gross structure. Arguments as to the nature of the band shifts in the ultraviolet spectra have been presented in support of the aromatic ketonic structure for VII and VIII,[4] and the same arguments are applicable in the present case. Final evidence for the structural relationship between VI and VII is found in the fact that, like VII,[4] VI can be oxidized to 3,3′-spirobiphthalide.



VI, $R^1 = CO_2H$; $R^2 = CH_3$
VII, $R^1 = CH_3$; $R^2 = CO_2H$
VIII, $R^1 = H$; $R^2 = CO_2H$

Fig. 6.

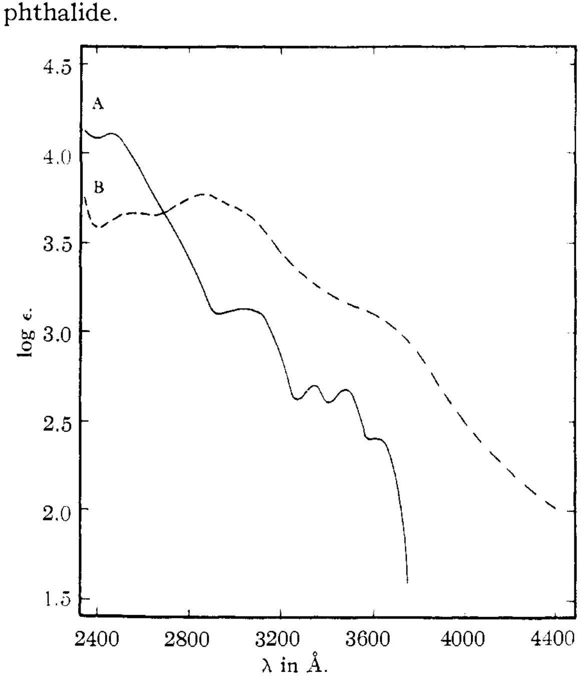


Fig. 7.—Ultraviolet spectra of VI; solvent: A, 95% ethanol; B, concd. sulfuric acid.

The non-identity of VI and VII now becomes conclusive evidence for a configurational difference involving the 6-carboxyl group; thus since the 6-carboxyl in VII and (IIC) is *cis* with respect to the oxygen function on carbon-2,[4] in VI (and VB) it must be *trans*. Presumably the same relationship holds in VA.

The configuration of the hydroxyl on carbon-2 of VB (and presumably VA) is less definite. A strong objection to the introduction of this hydroxyl in intermolecular nucleophilic displacement during the rearrangement is possible on the ground that carbon-1 of the original compound (IVC, or IVA or IVB) is equally if not more inaccessible to intermolecular nucleophilic attack than carbon-2 of the original compound. The inaccessibility of the latter has been abundantly demonstrated.[5] Thus to counter this objection it is suggested that the 2-hydroxyl of VB (and VA) is introduced by attack of the 2-carboxyl of IVC (IVA or IVB) which becomes favorably situated as the rearrangement progresses. Thus lactone formation analogous to that encountered in reaction of IA with silver nitrate[4] accomplishes intramolecular displacement. The highly strained nature of the β-lactone which would be so produced militates against its survival; hence it is opened at once, the configuration of the hydroxyl becoming *endo* both on steric grounds (hindered approach from above) and on mechanistic[4] grounds, since the cleavage must occur either in the acidic medium of the silver nitrate reaction or the mildly basic medium of the silver oxide reaction. The formation of IIC instead of IC is attributable to the non-involvement of a "free" β-halo carboxylate ion, as suggested above, and consequent in-

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(9) This inertness asserts itself in another instance: a comprehensive series of attempts to prepare the dimethyl and diethyl esters of IVC by all of the more obvious methods which would not lead at once to involvement of the intramolecular displacements and rearrangements common to this system afforded no success whatever. On the other hand, the desmethyl analog, IVB, readily formed the dimethyl ester on refluxing in methanol with sulfuric acid.

volvement of intermediates favoring rearrangement, *e.g.*, an α-lactonic structure dependent upon C-2.

Experimental[10]

2-Chloro-3-methyldibenzo[2,2,2]bicycloöctadiene-*cis*-2,3-dicarboxylic Anhydride (IVC).—A solution of 5.00 g. (0.0341 mole) of chlorocitraconic anhydride[11] and 6.03 g. (0.0338 mole) of anthracene in 25 ml. of xylene was refluxed for 5 days. After cooling, the mixture was warmed on the steam-bath to dissolve the anthracene which precipitated, and it was then filtered. The residue was washed with two 10-ml. portions of hot benzene, leaving 5.88 g. (53.5%) of crude IVC, m.p. 220.5–221.0°. After recrystallization from benzene and then from nitromethane IVC melted at 222.0–222.5°.

Anal. Calcd. for $C_{19}H_{13}ClO_3$: C, 70.27; H, 4.03; Cl, 10.92. Found[12]: C, 70.43; H, 4.13; Cl, 10.96.

The filtrate from the reaction mixture was distilled to remove the benzene from the washings and then was refluxed for an additional 2 days. After cooling and rewarming to redissolve separated anthracene it was filtered and the residue was washed with two 5-ml. portions of hot benzene. In this manner there was obtained an additional 1.64 g. of IVC (14.9%), m.p. 216.5–218.5°. The total yield was thus 68.4%.

2-Bromodibenzo[2,2,2]bicycloöctadiene-2,3-*cis*-dicarboxylic Anhydride[5] (IVA) with Silver Nitrate.—A solution of 0.5 *M* silver nitrate (2.9 ml.) was added to 0.502 g. (0.00141 mole) of IVA in 5 ml. of acetone. After a short time a grayish white precipitate appeared,[1] and upon standing in the dark for three hours, with occasional shaking, the initial precipitate gave way to a yellow precipitate of silver bromide (0.268 g., 101%). After filtration 2 ml. of 5% potassium bromide solution was added to the filtrate, and after shaking and standing for a short time a slight additional quantity of silver bromide was separated. Then the filtrate was evaporated to a volume of about 5 ml. in order to remove the acetone, and upon cooling 0.358 g. (81.8%) of crude IB separated; m.p. 222.0–223.5° dec. (reported 236.4–236.7° dec.[5]). After one recrystallization from water there was obtained 0.302 g. (69.0%) of IB which failed to depress the melting point of an authentic sample of IB.[5]

Upon concentration of the original mother liquor there was obtained a second crop of white crystals; 0.048 g. (11%) of VA, m.p. 229.0–232.5° dec. When mixed with an authentic sample of IB the melting point was depressed to 225–226° dec. After two recrystallizations from water the melting point was raised to 237.0–238.5° dec.; mixed with IB, m.p. 233–235° dec.

Anal. Calcd. for $C_{18}H_{14}O_5$: C, 69.66; H, 4.55. Found[13]: C, 69.58; H, 4.49.

The dimethyl ester of VA was prepared by means of diazomethane and was recrystallized from methanol, m.p. 160.5–161.8°. (The dimethyl ester of IB melts at 199.0–199.6° cor.[5]).

Anal. Calcd. for $C_{20}H_{18}O_5$: C, 70.99; H, 5.36. Found[13]: C, 71.02; H, 5.35.

IVA[5] with Silver Oxide.—A mixture of 1.000 g. (0.00282 mole) of IVA and 0.327 g. (0.00141 mole) of silver oxide with 10 ml. of dioxane and 10 ml. of water was heated with stirring on the steam-bath for 1 hr. in the dark. The yellow precipitate of silver bromide was removed by filtration; 0.524 g. (99.0%). After evaporation of the filtrate to dryness the residue was dried overnight *in vacuo* and then was further dried by treatment with 5 ml. of benzene, which was distilled off. The residue was next extracted with 5 ml. of boiling benzene, leaving 0.740 g. (84.8%) of crude IB, m.p. 222.0–224.5° dec. Recrystallization from 10% dioxane–water solution afforded low-melting IB (first crop 232–233° dec.; second crop 226–230° dec.), 0.663 g. (75.8%). Admixture with authentic IB[5] raised the melting points slightly; 233–234° dec., 227.0–229.5° dec. for the first and second crops, respectively. A third crop (VA) was obtained (0.007 g.) which melted at 227.5–230.0° dec., but this material upon admixture with authentic IB showed a depression, 225.5–226.5° dec.

The benzene extract was evaporated to dryness, and the residue was extracted several times with a total of about 150 ml. of boiling water. The residue weighed 0.075 g., m.p. 225.0–237.5°. Upon recrystallization from acetic acid–water there was obtained 0.038 g. (5.4%) of IIIA, m.p. 245.0–247.5° dec., which was undepressed upon admixture with authentic III.[5]

IVB[14] with Silver Oxide.—A 1.000-g. sample of IVB (0.00322 mole) was treated with 0.373 g. (0.00161 mole) of silver oxide in 10 ml. of dioxane and 10 ml. of water as for IVA above. A 98.5% (0.455 g.) yield of silver chloride was obtained. The reaction mixture was worked up as for IVA, and the benzene-insoluble residue (IB) weighed 0.752 g. (75.4%), m.p. 222.0–223.5° dec. Recrystallization from dioxane–water afforded results comparable to those obtained above with IVA.

Careful evaporation of the benzene extract afforded a 0.053-g. precipitate of white solid which melted at 217–223° dec. and at 214–218° dec. upon being mixed with authentic IB. When placed in the melting point bath at 125°, the sample softened and then resolidified with melting at 217–223° dec. (VA?).

The remaining benzene solution was treated with Norit and then was evaporated to dryness, the residue being taken up in 5% sodium hydroxide. The solution was filtered and then acidified, and the precipitate was extracted with eight 10-ml. portions of boiling water leaving a white solid; 0.092 g. (11.5%), m.p. 233.0–236.5° dec. Upon recrystallization from acetic acid–water there was obtained 0.052 g. of IIIA, m.p. 242–244° dec., which upon admixture with authentic IIIA melted at 242–245.3° dec. (reported[5] 247.1–248.6° dec., cor.).

The aqueous extracts, upon standing deposited 0.032 g. of material melting at 175–182° dec. (IIA?). The melting point was raised to 180–185° dec. upon admixture with authentic IIA. In view of the very small quantity no complete identification was attempted.

IVC with Silver Oxide.—A 1.000-g. sample of IVC (0.00308 mole) was treated with the appropriate quantity of silver oxide as in the preceding experiments, and 0.449 g. (102%) of silver chloride was obtained. The product was processed as in the preceding experiments, and after the hot benzene extraction there remained 0.417 g. (41.8%) of VB, m.p. 197.0–198.5° dec. When mixed with authentic IIC (203.4–204.0° dec., cor.[5]) the melting point was 187–188° dec. The product is soluble in 5% sodium bicarbonate and decolorizes neutral permanganate only after 30–40 min. The absence of halogen was shown by a negative Beilstein test. One recrystallization from nitromethane and one from toluene gave a constant melting point 200.0–200.5° dec.

Anal. Calcd. for $C_{19}H_{16}O_5$: C, 70.30; H, 4.97. Found[13]: C, 69.93; H, 5.04.

The dimethyl ester was prepared by means of diazomethane and was recrystallized from methanol, m.p. 154.5–156.0°.

Anal. Calcd. for $C_{21}H_{20}O_5$: C, 71.58; H, 5.72. Found[13]: C, 71.45; H, 5.93.

The benzene extract was evaporated to give an oily solid which was extracted with a total of 175 ml. of boiling water in 10- to 25-ml. portions. The water-insoluble powdery residue weighed 0.159 g. (19.7% calculated as IIIB), m.p. 257–262° dec. An authentic sample of IIIB, whose melting point has been shown to be very sensitive to the temperature of placement in the bath and rate of heating,[5] melted at 266.5–267.0° dec. when placed in the bath at 250° with the temperature rising at 5° per min. Upon recrystallization from acetonitrile of IIIB from this reaction, under identical conditions the melting point and mixed melting point with authentic IIIB were 262.5–264.0° dec. and 265–266° dec., respectively.

The combined aqueous extracts were evaporated to a volume of about 25 ml. and cooled, whereupon 0.290 g. (30.8%) of crude IIC separated, m.p. 214.5–220.0° dec. Recrystallization from acetic acid–water followed by chlorobenzene afforded 0.169 g. (17.9%) of IIC, m.p. 228.5–229.5° dec. No depression was observed on admixture with authentic IIC[5] (233–234° dec., cor.). Because of the slight discrepancy in melting points, the methyl ester was prepared

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(10) Melting points are uncorrected.

(11) T. Zincke and O. Fuchs, *Ber.*, **26**, 512 (1893).

(12) Microanalysis by Clark Microanalytical Laboratory, Urbana, Illinois.

(13) Microanalysis by Goji Kodama, University of Michigan.

(14) M. E. Synerholm, THIS JOURNAL, **67**, 1229 (1945).

and proved to be identical in all respects with the methyl ester of authentic IIC,[4] m.p. and mixed m.p. 153.0–154.5°.

Oxidation of VB to VI.—A 0.502-g. sample of VB (0.00155 mole) was heated on the steam-bath for 6 hr. in a solution of 20 ml. of 1% potassium permanganate, 0.5 ml. of 20% sodium hydroxide and 40 ml. of water and the manganese dioxide was filtered from the hot solution. The pink filtrate was acidified with hydrochloric acid and treated with a little sodium sulfite to decolorize it. A white solid separated and was filtered off; 0.309 g. (61.8%), m.p. 259.5–269.0° dec. After three recrystallizations from acetone-benzene, and one recrystallization from nitromethane VI melted at 268–270° dec. A distinct depression in the melting point of a sample mixed with authentic VII (267–268°[4] dec.) was observed.

Anal. Calcd. for $C_{19}H_{14}O_5$: C, 70.80; H, 4.38. Found[13]: C, 70.45; H, 4.38.

The dimethyl ester was prepared by means of diazomethane and was recrystallized from methanol, m.p. 188–191°.

Anal. Calcd. for $C_{21}H_{18}O_5$: C, 71.99; H, 5.18. Found[13]: C, 71.61; H, 5.09.

A 10-mg. sample of VI was oxidized in boiling 70% sulfuric acid[4] to give a few mg. of 3,3′-spirobiphthalide, identified by mixed m.p. with an authentic sample,[4] m.p. 205.5–207.0°, which was undepressed. Upon solution of VI in concd. sulfuric acid an intense yellow color was produced, and VI was reprecipitated unchanged on dilution of the solution with water.

ANN ARBOR, MICHIGAN

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New Types of Thermochromic Substances. The Stereochemical Aspect of Thermochromism; Thermochromism and Vinylogy

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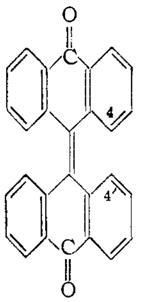
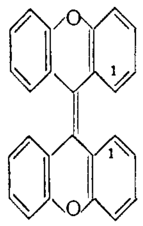
The discovery of thermochromic organic substances has been accidental. A working hypothesis, based on the connection between thermochromism and stereochemistry has led to the discovery of the thermochromic properties of the compounds listed in Table I. The relationship between vinylogy and thermochromism is discussed.

It is known that the color of solutions of colored organic substances in inert solvents changes with temperature and that these changes are strictly reversible provided that no reactions occur during heating and cooling; these changes of color are usually slight. However, some substances exhibit in solution striking changes observable with the naked eye; the term "thermochromism" in this paper is limited to such striking changes occurring between 0° and higher temperatures.

Thermochromism and Changes in Planarity of the Molecules of Thermochromic Substances.—This relationship has been discussed previously in connection with spirans,[1] bianthrones[2] (I) and dixanthylenes[3] (II); in all three cases substances which were colorless at low temperatures developed vivid colors with a rise of temperature. The chemical evidence suggested: (a) that thermochromism is due to a change of planarity of the molecules, the "colored molecules" having a greater degree of planarity, and (b) that since the thermochromic substances are thermostable, the phenomenon is not due to the formation of radicals or biradicals. The yellow color exhibited by the melt of 9,10-diphenylanthracene (m.p. 249–250°), a thermostable compound, cannot be explained by the formation of biradicals. On the other hand, when the solutions of many thermochromic substances are exposed to light, photo-activated molecules are formed which behave chemically like biradicals (disproportionation)[4]; thus I undergoes dehydrogenation with the loss of the two hydrogen atoms attached to positions 4 and 4′ and the formation of a new linkage.



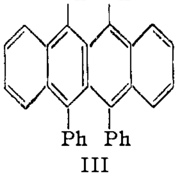
I



II

New Thermochromic Substances.—Up to now the discovery of thermochromic organic substances has been accidental. On the basis of the relationship between thermochromism and changes of planarity shown by the spirans, I and II, we have attempted to develop a general theory, by which the thermochromism of substances could be predicted. The value of our hypothesis has been proved by the discovery that the substances listed in Table I have thermochromic properties; the molecules of these substances are overcrowded to such a degree that planarity is hindered.

This working hypothesis may be formulated as follows: In overcrowded molecules in which planarity is hindered, the degree of non-planarity changes with temperature. This is associated with change of color, one reason being that resonance is related to planarity. If the molecules absorb in the visible region, thermochromism may be observed with the naked eye.



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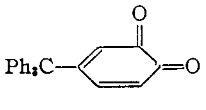

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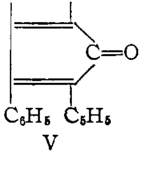

V

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