[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Further Studies on the Bromination of Bicyclic Olefins. The Bromination of *exo-cis*-3,6-Endomethylene-Δ^4-tetrahydrophthalic Anhydride[1]

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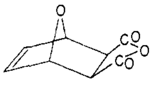
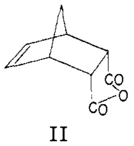
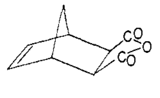
RECEIVED MARCH 25, 1954

The dibromoanhydride, m.p. 184°, obtained from the *exo*-adduct of cyclopentadiene and maleic anhydride is a racemate and consequently has either a *trans*-vicinal or a rearranged structure. The *trans*-vicinal structure is assigned on the basis of the behavior of the corresponding dimethyl ester toward methanolic silver nitrate and of the corresponding dibasic acid in basic solution. Preliminary experiments show that while the *trans*-dibromide is the sole product of bromination in ethyl acetate, a light-catalyzed reaction in carbon tetrachloride gives a complex mixture from which both *cis*- and *trans*-dibromides are isolated.

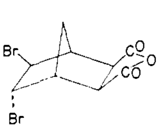
In a previous paper[2] we described the results of the brominations of the bicyclic substances I and II. The product composition in these reactions was shown to be dependent upon reaction conditions, with appreciable amounts of *cis*-dibromide resulting from bromination under free radical conditions. In an extension of this work, we have investigated the bromination of III.

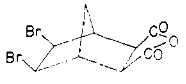

I

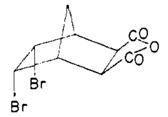

II

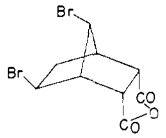

III

Craig[3] has reported a dibromide IV, m.p. 184°, obtained by bromination of III in chloroform and, by analogy to the usual result of simple olefin brominations, has assigned to it the *trans* structure (IVA). This structure has been adopted by Kwart and Kaplan[4] on the basis of dipole moment studies. Because of the occurrence of *cis*-brominations in this series[2] and because of the demonstration[5] that the dipole moment method fails to give the correct structure for at least one dibromide of the series, we have felt it necessary to acquire additional evidence on the structure of the 184° dibromide.


IVA

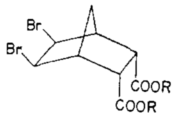

IVB


IVC


IVD

The finding[3] that IV suffers debromination with zinc in acetic acid to the *exo*-unsaturated anhydride III (combined with the fact that the *endo*-unsaturated anhydride II is stable under the conditions of debromination[6]) allows only four reasonable structures for IV: IVA, IVB and IVC, directly derived from III, and the rearranged structure IVD, derived from III by formal Wagner–Meerwein change.

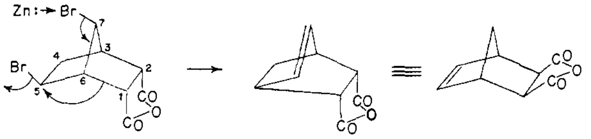
Structure IVB is immediately eliminated since we have already[5] assigned it to the anhydride of m.p. 249° obtained in the pyrolysis of *endo-cis*-3,6-endomethylene-4,5-*exo*-*cis*-dibromohexahydrophthalic acid (Va).



Va, R = H
b, R = CH_3

Structure IVC, inherently improbable on the basis of the rule[7] of *exo*-addition to bicyclic olefins, requires *meso* properties of IV, and can be unequivocally rejected by the finding that the corresponding acid VIa is a racemate. Partial resolution of VIa is readily accomplished *via* the quinine salt. Fractional crystallization of the salt and decomposition of the head fractions give VIa, $[\alpha]_D$ −56.6°. Dextrorotatory VIa, $[\alpha]_D$ +11.3°, is regenerated from the tail fractions. The chemical identity of the active and racemic modifications of VIa is established by comparison of the infrared spectra of the active ($[\alpha]_D$ +27.1°) and racemic dimethyl esters VIb.

IV must then be represented by IVA or IVD. Debromination of IVA to III would be unexceptional,[2] while the rearranged dibromide IVD would have to suffer a formal reversal during debromination of the apparent Wagner–Meerwein change leading to its formation. Although apparent Wagner–Meerwein rearrangements have been observed in halogenations of bicyclic olefins,[8] an example of the reverse of this process has not come to our attention. Nevertheless, such a reaction is conceivable and might proceed under catalysis by zinc bromide or by a concerted (or stepwise) reduction accompanied by rearrangement[5]



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[1] Paper VII of the series "Structure and Stereochemistry of Bicyclic Derivatives."

[2] J. A. Berson and R. Swidler, THIS JOURNAL, **76**, 4060 (1954).

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

[4] H. Kwart and L. Kaplan, *ibid.*, **75**, 3356 (1953).

[5] J. A. Berson, *ibid.*, **76**, 4069 (1954).

[6] (a) K. Alder and G. Stein, *Ann.*, **504**, 247 (1933); (b) P. D. Bartlett and A. Schneider, THIS JOURNAL, **68**, 6 (1946).

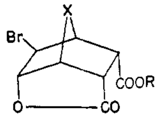
[7] K. Alder and G. Stein, *Ann.*, **515**, 185 (1935); **525**, 183 (1936).

[8] Compare α-pinene → 2,6-dichlorocamphene: (a) O. Aschan, *Ber.*, **61**, 38 (1928); (b) O. Brus, *Compt. rend.*, **180**, 1507 (1925); (c) H. Kwart, THIS JOURNAL, **75**, 5942 (1953).

In contrast to the case previously discussed,[5] the steric disposition of all the atoms here is favorable. The atoms Br, C_7, C_6, C_1 and C=O lie very nearly in a plane, and the bromine at C_5 is favorably situated for rear-side displacement by the C_1–C_6 bonding electrons. Consequently, we do not feel that IVD can be dismissed with confidence at this stage.

A choice between IVA and IVD is based on the behavior of the dibasic acid (VIa) of the 184° anhydride in basic solution and of the corresponding dimethyl ester (VIb) in methanolic silver nitrate. As models, the reactions of the known[2] dibasic acid Va and its dimethyl ester Vb under these conditions are instructive.

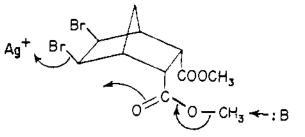
When Va is neutralized with two equivalents of base, one equivalent of bromide ion is rapidly released and the bromolactonic acid (VIIa) is formed in excellent yield.[2]



VIIa, R = H; X = CH_2
b, R = CH_3; X = CH_2
c, R = CH_3; X = O

Lactonization of the second carboxyl group requires much more vigorous conditions.[6a]

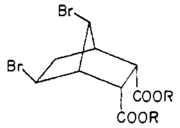
Analogously, Vb reacts rapidly with methanolic silver nitrate to give the *bromolactonic ester*, VIIb, and one equivalent of silver bromide. The reaction is clearly related to the formation of bromolactones in the bromination of γ,δ-unsaturated esters[9] and presumably proceeds by the mechanism VIII, either concerted or stepwise (where B = Br^- or CH_3OH)



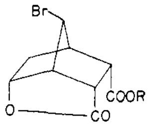
VIII

(No attempt was made to identify methyl bromide or dimethyl ether.) Again closure of the second lactone ring is difficult.[10]

On the basis of the behavior of Va and Vb, the acid IXa and ester IXb derived from the rearranged dibromoanhydride (IVD) should smoothly lactonize to Xa or Xb, respectively.

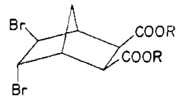


IXa, R = H
b, R = CH_3

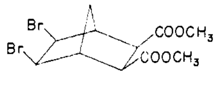


Xa, R = H
b, R = CH_3

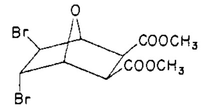
By contrast, neither the acid VIa nor the ester VIb of IVA could lactonize without rearrangement or epimerization. Experimentally, the dibasic acid of the 184° anhydride is inert under the same conditions which rapidly cause lactonization of Va. No bromide ion is produced and the starting material is quantitatively recovered. The dimethyl ester of this acid is also essentially inert. After 22 hours in boiling methanolic silver nitrate only 0.01 equivalent of bromide ion is produced and the starting material is recovered in 86% yield. The behavior of the ester parallels that of the inert dibromides XI,[5] XII[11] and XIII.[11] Accordingly, we formulate the 184° anhydride as IVA and its acid and derived ester as VIa and VIb, respectively.[12]



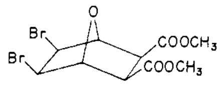
VIa, R = H
b, R = CH_3



XI



XII



XIII

On the Stereochemistry of Bicyclic Olefin Brominations.—Preliminary experiments on the effect of reaction conditions on the course of the bromination of III reveal at least a superficial similarity to the bromination of I. In ethyl acetate, the only product we are able to isolate (92% yield) is the *trans*-dibromide IVA. In carbon tetrachloride, the reaction is very sensitive to light catalysis. The light-catalyzed reaction gives a mixture of products from which, by either fractional crystallization or chromatography, are isolated both the *trans*-dibromide IVA and the *cis*-dibromide[5] IVB. The problem of isolation is made somewhat more difficult in this case than in those we have previously studied[5] by the relatively small differences in solubility of the isomers. Also, indirect evidence (see the Experimental section) indicates that a third product is present in the reaction mixture. So far as we are aware, the occurrence of *cis*-addition of bromine in the present case and in those we have previously reported[2] are the first such examples in which the steric outcome of the reaction is not subject to complication by rotational isomerization of starting materials or intermediates during the reaction.[13] The observations[2] that *cis*-addition is markedly favored by light catalysis and non-polar media and is suppressed or eliminated by darkness, oxygen and polar media provide at least presumptive evidence that a major portion of the *cis*-dibromide

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[9] (a) R. Fittig and E. Hjelt, *Ann.*, **216**, 52 (1883); (b) P. N. Craig and I. H. Witt, THIS JOURNAL, **72**, 4925 (1950); (c) P. N. Craig, *ibid.*, **74**, 129 (1952); (d) R. T. Arnold, M. de Moura Campos and K. L. Lindsay, *ibid.*, **75**, 1044 (1953).

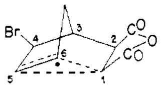
[10] We attribute this to the strong dipole–dipole repulsion in the dilactone, a part of which will be felt in the transition state for cyclization of the second lactone ring.

[11] J. A. Berson and R. Swidler, THIS JOURNAL, **76**, 4057 (1954).

[12] It is of interest that the melting points of the dibromoendomethylenehexahydrophthalic acid derivatives follow the pattern of those of the endoxo series. Thus in the endoxo series the 4,5-*trans*-dibromo derivatives invariably melt at lower temperatures than the corresponding *cis*-dibromides (see Table I of reference 2). In the endomethylene series, the *trans*-derivatives are anhydride, m.p. 188°, acid (hydrate), m.p. 161°, dimethyl ester, m.p. 59°. The corresponding *cis* derivatives[5] are anhydride, m.p. 258°, acid, m.p. 258°, dimethyl ester, m.p. 175°.

[13] *Cf. inter alia*, G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 298, for a discussion of this point.

arises by a free radical reaction. We have proposed[2] that the stereochemistry of the addition under these conditions may be in part controlled by the intervention of a "non-classical" bridged radical, *e.g.*, XIV. This formulation is consistent with the qualitative trend of all our results so far,

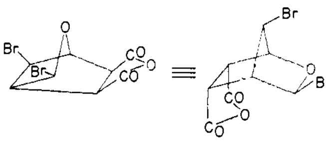


XIV

but it should be borne in mind that radicals of the type of XIV need not determine the reaction course in all cases of radical additions to bicyclic systems. Thus, in the bromination of the *endo*-anhydride II, the occurrence under radical conditions of essentially exclusive *cis*-bromination[2] as contrasted to roughly equal amounts of *cis*- and *trans*-addition in the radical bromination of I[2] implies an important effect of the *endo*-anhydride function, exerted either by steric blocking of the *endo* side of the double bond or by electronic interaction with a developing p-orbital during attack by a bromine atom, or both. Further, a carbonyl group at C_1 would be expected to stabilize the mesomeric radical more than would an alkyl or hydrogen substituent *via* its stabilizing effect[14] on the contributing canonical structure XV

XV

A corollary to the proposal of the bridged radical intermediate is the possibility that rearranged dibromide (*e.g.*, IVD), may be observed as a product. This possibility is being investigated.[15]



XVI

NOTE ADDED IN PROOF.—Dr. S. B. Soloway has pointed out to us that certain dibromides derived from partially hydrogenated di- and tricyclopentadienes very probably have *cis* configurations of the bromines [*cf.* H. L. Donle, *Z. physik. Chem.*, **18B**, 146 (1932)]. Models reveal that the steric shielding of one side of the olefinic bond in these cases is so severe as to make *trans*-addition energetically unfavorable, regardless of mechanism.

Experimental[16]

Optical Resolution of the Dibasic Acid VIa.—The racemic acid was prepared (95% yield) by boiling the anhydride IVA in 50% acetonitrile for 2.5 hours. It melted sharply at 159–160° with evolution of gas, resolidified as the temperature was raised and remelted at 184–185°, reported[3] m.p. 160–161° dec. The over-all material balance in the resolution of this acid was poor, principally because of the pronounced solubility of the optically active acid in water and organic solvents. A hot solution of 3.94 g. of VIa in 20 cc. of acetone was treated with a hot, filtered solution of 4.15 g. of quinine trihydrate in 100 cc. of acetone. The salt (7.28 g.) precipitated immediately. The mother liquor A was preserved. The salt was recrystallized from 250 cc. of methanol and the mother liquor B was preserved. The precipitate, 3.0 g. of a microcrystalline powder, was treated with 10 cc. of ice-cold 15% hydrochloric acid, whereupon it dissolved. The organic acid failed to crystallize from this solution. The solution was made basic with ammonia and extracted successively with chloroform, methylene chloride and ether. When the aqueous phase was acidified with hydrochloric acid and chilled, 0.23 g. of a colorless solid separated. The mother liquor C was preserved. The solid contained inorganic salt which was removed during recrystallization from ethyl acetate–ligroin. The resulting acid D was preserved. The aqueous mother liquor C was evaporated to dryness on the steam-bath *in vacuo* and the residue leached successively with boiling ethyl acetate and chloroform. The salt residue E was preserved. The extract was combined with D and the whole evaporated to dryness. The residue was recrystallized from ethyl acetate–ligroin to give 0.105 g. of the dibasic acid, sintering at 155° and melting at 183–184°. This material showed $[\alpha]_D$ −23.1° (*c* 1.05 in acetone, *l* = 4). The organic mother liquor F was preserved.

An additional 0.04 g. of material was obtained by leaching the salt residue E with methylene chloride. This was combined with the residue obtained by evaporation of the solvent from F and the whole recrystallized from ethyl acetate–ligroin to give 0.085 g. of sharply defined triangular plates. This material melted at 146–147° to a turbid liquid which became clear at 160°; in acetone, $[\alpha]_D$ −56.6° (*c* 0.48, *l* = 4).

Anal. Calcd. for $C_9H_{10}O_4Br_2$: C, 31.61; H, 2.95. Found: C, 31.72; H, 2.79.

Dextrorotatory material was obtained from the tail fractions (A and B). These solutions were combined and concentrated by evaporation to a volume of 100 cc. The solution was allowed to stand in the refrigerator for three days. The precipitated quinine salt (3.94 g.) was filtered off, treated with 10 cc. of concentrated ammonia water and the mixture was washed with chloroform. The aqueous phase was acidified with concentrated hydrochloric acid and exhaustively extracted with ethyl acetate. The organic solution was dried with sodium sulfate, evaporated and the residue (2.1 g.) recrystallized from ethyl acetate–ligroin. The acid, 0.60 g., melted at 184–186° and was virtually optically inactive. The mother liquor was concentrated and the resulting crystalline product collected. It weighed 1.25 g., sintered at 138° and melted at 185–186°; in acetone, $[\alpha]_D$ +11.3° (*c* 2.13, *l* = 4). The greater solubility of the enantiomeric modification compared to that of the racemate parallels our experience with the previous members of the series.[2,5]

The Dimethyl Ester VIb. A. Racemic Form.—A solution of 0.38 g. of the racemic dibasic acid[3] in 10 cc. of methanol was added to an excess of ethereal diazomethane. After one hour, a few drops of acetic acid were added, the solvents evaporated and the residue (0.39 g.) crystallized from methanol and recrystallized from carbon tetrachloride–ligroin to give the ester, m.p. 57.5–59°. The ester can also be obtained from the anhydride IVA with methanol and sulfuric acid.

Anal. Calcd. for $C_{11}H_{14}O_4Br_2$: C, 35.70; H, 3.81. Found: C, 35.33; H, 3.73.

B. Dextrorotatory Form.—Four-tenths of a gram of the (+)-acid, $[\alpha]_D$ +11.3° was treated with excess diazomethane as above. The residue (0.44 g.) after evaporation of the solvent was recrystallized from carbon tetrachloride–ligroin to give 0.15 g. of hemispherical aggregates, m.p. 55–57°. This material showed virtually no optical activity. The mother liquor from the above recrystallization of the crude product was evaporated, leaving a mixture of crystals and a clear oil. The infrared spectrum of a chloroform solution of this material was identical with that of racemic dimethyl ester. In acetone, the crude (+)-ester showed $[\alpha]_D$ +27.1° (*c* 0.67, *l* = 1). Fractionation of racemate and enantiomer is again apparent.

The *endo-cis*-Dimethyl Ester Vb.—This substance was prepared from *endo-cis*-3,6-endomethylene-4,5-*exo-cis*-di-

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(14) *Cf.* (a) F. R. Mayo and C. Walling, *Chem. Revs.*, **27**, 351 (1940); (b) F. R. Mayo, F. M. Lewis and C. Walling, *Discs. Faraday Soc.*, **2**, 285 (1947); (c) M. J. S. Dewar, THIS JOURNAL, **74**, 3353 (1952); (d) "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 243.

(15) Failure to find rearranged material XVI in the bromination of I[2] is not unexpected, since XVI, an α-bromoether, would be expected to rearrange to *cis*-(vicinal)-dibromide or suffer other decomposition.[2]

(16) Melting points are corrected. The analyses are by Mr. W. J. Schenck.

bromohexahydrophthalic acid[2,6] (Va) by boiling 10 g. of the acid with 50 cc. of methanol and 4 cc. of fuming sulfuric acid for three hours. It was recrystallized from benzene–ligroin as glistening, transparent staves, m.p. 80.5–81.5°.

Anal. Calcd. for $C_{11}H_{14}O_4Br_2$: C, 35.70; H, 3.86. Found: C, 35.78; H, 3.61.

Reaction of Vb with Silver Nitrate.—A solution of 0.70 g. of Vb and 1.0 g. of silver nitrate in 25 cc. of methanol was heated at reflux. In a few minutes, a heavy pale-yellow precipitate of silver bromide had appeared. After five hours, the mixture was filtered and the precipitate washed with methanol. The filtrate and washings were preserved. The silver bromide was washed with hot water and hot acetone and dried. It weighed 0.37 g. (1.04 equivalents). The methanol filtrate and washings were evaporated to a volume of 10 cc., diluted with water, extracted with ethyl acetate and the extract after being washed with water and dried over sodium sulfate was evaporated. The oily residue crystallized upon being triturated. It weighed 0.37 g. and melted at 65–68°. Recrystallization from dilute methanol raised the m.p. to 71–72°. A mixed m.p. with an authentic sample of the bromolactonic ester[6] VIIb, reported m.p. 77°, was not depressed. A mixed m.p. with the starting material Vb was depressed about 20°.

Action of Silver Nitrate on the Dimethyl Ester VIb.—A solution of 0.52 g. of VIb and 0.7 g. of silver nitrate in 20 cc. of methanol was heated at reflux. After six hours, the presence of silver bromide was undetectable. The solution remained perfectly clear and even a faint opalescence was not observed. After 22 hours, the solution was cooled, filtered and the filtrate preserved. The precipitate, after being washed with nitric acid, methanol, acetone and ether and dried weighed 3 mg. (0.01 equivalent).

The methanol filtrate was diluted with water, extracted with ethyl acetate and the extract washed with water, dried with sodium sulfate and evaporated to give 0.45 g. (86%) of the starting material, m.p. 54–55°, mixed m.p. 56–58°.

Action of Silver Nitrate on the Bromolactonic Esters VIIb and VIIc.[17]—A solution of 1.4 g. of VIIb[6a] and 1.0 g. of silver nitrate in 40 cc. of methanol was heated at reflux for 21 days. The clear solution was concentrated to a volume of 10 cc., diluted with water and the resulting oil brought into solution by warming the mixture. Upon cooling the solution, 0.9 g. of the starting material, m.p. 73–75°, was recovered.

A solution of 2.8 g. of VIIc[18] and 2.0 g. of silver nitrate in 60 cc. of methanol was heated at reflux for seven days. The clear solution was treated with 100 cc. of water, the precipitated solid was collected and recrystallized from dilute acetone to give 2.4 g. of the starting material, m.p. 170–172°, reported[18] m.p. 175°.

Stability of the Salt of VIa.—A suspension of 0.50 g. of VIa in 5 cc. of water was treated with 3 *N* aqueous sodium hydroxide to a phenolphthalein end-point and the reaction mixture was allowed to stand at room temperature for five hours. It was then acidified with concentrated nitric acid whereupon a colorless oil separated. This material crystallized when it was cooled and scratched. The reaction mixture was filtered. The precipitate weighed 0.50 g. and melted at 150° with evolution of gas, resolidified and remelted at 184–185°, alone or mixed with the starting material VIa. The filtrate gave only a faint opalescence when treated with an excess of aqueous silver nitrate.

Under the same conditions, Va gave 0.98 equivalent of silver bromide and a 75% yield of the bromolactonic acid VIIa in two hours.[2]

Bromination of III. A. Ethyl Acetate.—A solution of 1.0 g. of the *exo*-anhydride III in 10 cc. of ethyl acetate was treated with 1.0 g. of bromine in 5 cc. of ethyl acetate. Heat was evolved and the bromine color faded immediately. The solution was concentrated to a small volume and chilled in ice to give 1.82 g. (92%) of the *trans*-dibromide, m.p. 184–185°, reported m.p. 184°. Recrystallization from benzene–ligroin gave material melting at 187–188°.

B. Dark Reaction in Carbon Tetrachloride.—A solution of 1.0 g. of III in 35 cc. of carbon tetrachloride was treated in the dark in a light-tight room with a solution of 1.0 g. of bromine in 5 cc. of carbon tetrachloride. The solution was kept in the dark except for brief periods of a few seconds each while the course of the reaction was being observed. A precipitate of platelets gradually accumulated during five hours, but the reaction was still incomplete, as evidenced by the persistence of a strong bromine color. The reaction mixture was chilled in ice and filtered to give 1.22 g. (62%) of the *trans*-dibromide IVA, m.p. 183–185°. The mother liquor yielded 0.52 g. of a solid which instantaneously decolorized potassium permanganate in acetone, again indicating incomplete reaction.

Light-catalyzed Reaction in Carbon Tetrachloride.—The solvent was carefully degassed by passing a vigorous stream of nitrogen through a stirred sample for 20 minutes. The reagents, 1.0 g. of III in 30 cc. of carbon tetrachloride and 1.0 g. of bromine in 5 cc. of carbon tetrachloride, were mixed under an atmosphere of nitrogen in a Vycor flask under illumination by a General Electric Type AH-4 lamp. The color of bromine had faded in one minute. The reaction mixture was chilled and filtered to give 1.78 g. (first crop) of material melting at 159–162°. A second crop of crystals, obtained by evaporation of the filtrate, weighed 0.11 g., melted at 128–170° and was saturated to permanganate. The total yield was thus 95%.

Use of the degassing technique seemed to have little effect on the gross result as compared to that obtained using ordinary reagent-grade carbon tetrachloride. With the latter solvent, two independent illuminated runs gave: (i) from 1.0 g. of III, 1.60 g. of material melting at 159–166°, and (ii) from 2.0 g. of III, 3.62 g. of material melting at 157–164° and 0.15 g. of a second crop, m.p. 113–137°.

Direct recrystallization of the first crop of dibromide material from the illuminated runs failed to yield readily a pure substance. Thus, recrystallization of 2.4 g. from ethyl acetate–ligroin gave 1.42 g. of a mixture, m.p. 167–175°.

The mother liquor from this recrystallization gave upon evaporation 0.87 g. of a sticky solid. This material was chromatographed in chloroform–benzene 2:1 on a 15 × 0.5 inch column of 28 × 200 mesh Davison silica gel. The following fractions were obtained (in order of ease of elution): (1) 0.13 g. of crude *trans*-dibromide IVA, m.p. 180–183°; (2) 0.35 g. of a thick oil; (3) 0.28 g. of a solid, m.p. 155–239°; (4) 0.02 g. of oil. The total recovery was 90%.

Fraction 2 crystallized from benzene, m.p. 142–165°. Fraction 3 was recrystallized from acetonitrile–ligroin to give 0.1 g. of bold, centimeter-long spears, m.p. 254–256°, alone or mixed with authentic[5,6] *cis*-dibromide IVB.

Isolation of IVA and IVB was also accomplished by fractional crystallization of the crude bromination product. The first crop from an illuminated run (1.78 g.) was triturated with 25 cc. of chloroform at room temperature and filtered. The filtrate was preserved. The insoluble material, 0.31 g., m.p. 185–245°, was recrystallized from acetonitrile to give 0.14 g. of the *cis*-dibromide IVB, m.p. 254–256°. A second crop of material from this recrystallization melted over a wide range above 180°. The chloroform filtrate was evaporated and the residue recrystallized from ethyl acetate–ligroin to yield 0.5 g. of material, m.p. 179–180°. The mother liquor was preserved. The solid, upon recrystallization from benzene–Skellysolve B, gave 0.32 g. of the pure *trans*-dibromide (IVA), m.p. 187–188°. The ethyl acetate–ligroin mother liquor gave 0.71 g. of an oil which slowly crystallized. This material is being investigated.

The presence of at least one more product in the reaction mixtures in addition to IVA and IVB is inferred from the melting point of some of the crude fractions. The melting points of a series of synthetic mixtures of IVA and IVB over the entire composition range were determined. Designating the melting point of these mixtures as the temperature at which the last crystal disappeared, the melting point *vs.* composition curve failed to show a definite minimum, although each of the mixtures melted over a wide range of temperatures. Thus the occurrence of fractions of the reaction mixture melting well below the melting point of the lower-melting pure substance (188°) implies the presence of appreciable quantities of contaminants.

LOS ANGELES 7, CALIFORNIA

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(17) Observations of Dr. Ronald Swidler.

(18) O. Diels and K. Alder, *Ann.*, **490**, 243 (1931).