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# Bridged Polycyclic Compounds. XVII. The Stereochemistry of Conversions of Some Substituted Norbornanecarboxylic Acids to Substituted Norbornyl Bromides[1]

STANLEY J. CRISTOL, JOHN R. DOUGLASS, WILLIAM C. FIRTH, JR., AND ROBERT E. KRALL

*Department of Chemistry, University of Colorado, Boulder, Colo.*

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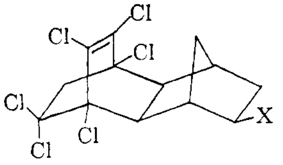
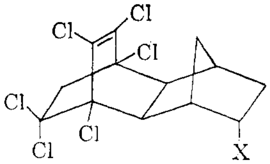
Several methods for the conversion of acids to alkyl halides were studied with the substituted norbornanecarboxylic acids Ib and IIb. These included the Hunsdiecker reaction, the reaction of the acids with mercuric oxide and bromine, and the decomposition of the acyl peroxides in bromine and in bromotrichloromethane. The stereochemical results observed indicate that the alkyl radical intermediate involved in these transformations becomes stereochemically independent of its *endo* or *exo* source before reaction with the halogen donor.

Our interest in the stereochemistry of reactions in boat-form cyclohexane molecules led us in particular to the preparation of a number of norbornane derivatives in which the norbornane ring is fused to another (chlorinated) norbornane ring in an *exo-endo* fashion, as these are readily available by reaction of substituted norbornenes with hexachlorocyclopentadiene.[2] The *exo* (Ia) and *endo* (IIa) bromides were readily available by treatment of hexachlorocyclopentadiene with the mixture obtained from the Diels-Alder reaction[3] of vinyl bromide and cyclopentadiene, and we observed that each of the bromides was substantially inert to silver nitrate in ethanol at room temperature, and was only slightly reactive at reflux temperatures. At the time we began this work, prior studies on the stereochemistry of the Hunsdiecker reaction[4] were complicated by the fact that the products were probably sensitive to epimerization or racemization,[5-8] or to Wagner-Meerwein rearrangements under the reaction conditions.[9] As the bromides Ia and IIa were inert under reaction conditions, these systems seemed ideal for a study of the stereochemistry of the Hunsdiecker reaction.



Ia. X = Br
b. X = $CO_2H$
c. X = COCl
d. X = $CO_2Ag$



IIa. X = Br
b. X = $CO_2H$
c. X = COCl
d. X = $CO_2Ag$

In addition to studying the conversions of the silver salts of the acids Ib and IIb to the bromides (Hunsdiecker reaction), we also looked at a procedure[10] where the acids were treated with mercuric oxide and bromine, as well as those involving treatment of the acyl peroxides (IV and V) with bromine and with bromotrichloromethane.

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(1) (a) Previous paper in series: S. J. Cristol, E. L. Allred, and D. L. Wetzel, *J. Org. Chem.*, **26**, 4672 (1961). (b) from the Ph.D. dissertations of J. R. D., 1951, R. E. K., 1956, and W. C. F., Jr., 1960, in the University of Colorado.

(2) (a) S. B. Soloway, *J. Am. Chem. Soc.*, **74**, 1027 (1952). (b) S. B. Soloway, Ph.D. thesis, University of Colorado, 1955.

(3) (a) J. D. Roberts, E. R. Trumbull, W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950). (b) J. D. Roberts, W. Bennett, and R. Armstrong, *ibid.*, **72**, 3329 (1950).

(4) For pertinent references, see: C. V. Wilson, *Org. Reactions*, **IX**, 332 (1957), R. G. Johnson and R. K. Ingham, *Chem. Rev.*, **56**, 219 (1956).

(5) (a) C. L. Arcus, A. Campbell, and J. Kenyon, *Nature*, **163**, 287 (1949). (b) *J. Chem. Soc.*, 1510 (1949).

(6) F. Bell and I. F. B. Smyth, *ibid.*, 2372 (1949).

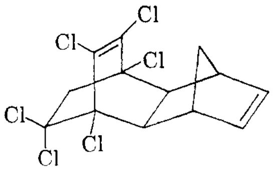
(7) R. T. Arnold and P. Morgan, *J. Am. Chem. Soc.*, **70**, 4248 (1948).

(8) For additional and for later references, see ref. 4.

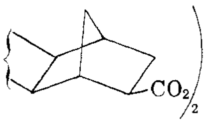
(9) W. v. E. Doering and M. Farber, *ibid.*, **71**, 1514 (1949).

(10) S. J. Cristol and W. C. Firth, Jr., *J. Org. Chem.*, **26**, 280 (1961).

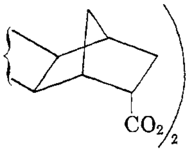
The *exo* and *endo* configurations of the carboxylic acids Ib and IIb and their methyl esters are established from their syntheses from hexachlorocyclopentadiene and 5-norbornene-*exo*-2-carboxylic acid[3] or the methyl ester[3] and the corresponding *endo* compounds,[3,11] respectively. The structures of the bromides, Ia and IIa, need to be considered as well. A mixture of Ia and IIa was formed from hexachlorocyclopentadiene and the 5-bromo-2-norbornene mixture from reaction of vinyl bromide with cyclopentadiene.[3] Although it has been reported[3] that the latter mixture contained less than 15% of the *exo* bromide, in our hands reaction with hexachlorocyclopentadiene gave a yield of about 32% Ia and 48% IIa.[12] The two isomers melted at 179 and 110°. Treatment of each with a solution of sodium $\beta$-ethoxyethoxide in Ethyl Cellosolve gave the same elimination product, aldrin [1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-*endo*-1,4-*exo*-5,8-dimethanonaphthalene (III)], thus demonstrating the stereochemistry of the ring junctions,[2] and showing that the two isomers differ solely in being epimeric at the carbon atom bearing the bromine. The 179° isomer was formed in lesser amount in the Diels-Alder reaction and may be assigned the *exo*(Ia) structure, and the 110° compound is thus the *endo* (IIa) isomer.[3,11,13] This assignment is consistent with the fact that treatment of aldrin (III) with hydrogen bromide in benzene or in acetic acid gives largely the higher melting isomer, in accordance with the Alder rule of *exo* addition to norbornenes,[14] and also with the observation[14f] that dihydroaldrin is brominated to give the higher melting isomer in larger amount. In addition, catalytic hydrogenation of 6-bromoaldrin is reported[2b] to give the lower melting isomer, consistent with *exo* addition of hydrogen.



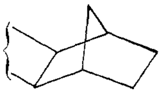
III



IV



V



VI

The acyl peroxides IV and V were prepared by conversion of the acids Ib and IIb to the acid chlorides, and by treatment of these with sodium peroxide. The configurations of these are thus related to the starting acids.

The acids Ib and IIb were converted to the corresponding silver salts Id and IId and could be recovered from them without stereochemical change. Our initial work indicated that the silver salts of both isomeric acids upon treatment with bromine in carbon tetrachloride gave mixtures of both bromides Ia and IIa, and we therefore undertook a study to determine whether there was any stereoselection in the process. The reactions of Id and IId in the dark in refluxing carbon tetrachloride gave mixtures of bromides in erratic yields (40–90%), but with compositions, measured by infrared and isotope-dilution techniques, of 69 ± 4% *exo* Ia and 31 ± 4% *endo* IIa. The configuration of the initial silver salt did not affect the bromide composition, within the limits of our analytical accuracy. Addition of 20–200 mole % of *sym*-trinitrobenzene had remarkably little effect upon either the yield or the composition of the bromide mixture.

Treatment of either the *exo* acid Ib or the *endo* acid IIb with mercuric oxide and bromine in carbon tetrachloride gave yields of bromide mixtures of 93 and 80%, respectively, somewhat better than usually obtained by us in the Hunsdiecker reaction. Again the two mixtures had analyses of 30–31% *endo* isomer IIa.

When the *exo* peroxide IV was decomposed in a solution of bromine and carbon tetrachloride, the bromide mixture that resulted contained 27 ± 4% *endo* isomer IIa. On the other hand, when either peroxide IV or V was decomposed in refluxing bromotrichloromethane, there resulted (in addition to the ester product) a bromide that was *exo* Ia, and within the accuracy of our analyses, free of *endo* isomer IIa.

The Hunsdiecker reaction is believed[4] to involve the formation of the acyl hypohalite $RCO_2X$ and the subsequent decomposition of this species into carbon dioxide and radical intermediates. In the preliminary description of our results,[15] we assumed that the radical intermediate VI would brominate largely on the *exo* side, as indicated by its reaction with bromotrichloromethane, and suggested that the formation of substantial amounts of *endo* bromide IIa was possible evidence for a process involving cage recombination of alkyl radical and bromine atom. While this may be the correct process,[16] our recent work,[14f] based upon the earlier

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(11) (a) K. Alder, G. Stein, M. Liebmann, and E. Rolland, *Ann.*, **514**, 197 (1934). (b) K. Alder and G. Stein, *Ann.*, **525**, 183 (1936).

(12) Rough solvolysis measurements in 80% aqueous ethanol suggested that our mixture of norbornenyl bromides was about 40% *exo* and 60% *endo*.

(13) (a) K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937). (b) K. Alder, G. Stein, F. v. Buddenbrook, W. Eckardt, W. Frercks, and S. Schneider, *Ann.*, **514**, 1 (1934). (c) K. Alder and R. Rühman, *ibid.*, **566**, 1 (1950).

(14) See, for example: (a) K. Alder and G. Stein, *Ann.*, **504**, 216 (1933). (b) R. B. Woodward and H. Baer, *J. Am. Chem. Soc.*, **70**, 1161 (1948). (c) G. Stork, E. E. van Tamelen, L. J. Friedman, and A. W. Burgstahler, *ibid.*, **75**, 384 (1953). (d) K. Alder and H. Wirtz, *Ann.*, **601**, 138 (1956). (e) S. J. Cristol and R. P. Arganbright, *J. Am. Chem. Soc.*, **79**, 6039 (1957). (f) S. J. Cristol and L. K. Gaston, *J. Org. Chem.*, **26**, 4672 (1961).

(15) S. J. Cristol, J. R. Douglass, W. C. Firth, Jr., and R. E. Krall, *J. Am. Chem. Soc.*, **82**, 1829 (1960).

(16) C. E. Berr, Ph.D. dissertation, University of California at Los Angeles (1952).

work on norbornyl radical itself,[17] showed that in fact the radical VI (produced by attack of bromine atoms on dihydroaldrin) is not stereoselective with small bromine donors (giving, for example, 70:30 *exo:endo* ratio with bromine), although it is increasingly selective with larger reagents, less than 2% of *endo* bromide (IIa) being observed with bromotrichloromethane. It seems clear then that the Hunsdiecker reaction, the reaction of acids with mercuric oxide and bromine,[10] and the decomposition of acyl peroxides all yield radicals with stereochemical proclivities similar to that involved in hydrocarbon bromination. Our experiments lend no support to the concept that any of these reactions have paths leading to selective stereochemical inversion[5] or retention[4] of configuration.

## Experimental

***exo*- and *endo*-6-Bromo-1,2,3,4,10,10-hexachloro-1,4,4a,5,6,7,8,8a - octahydro - *endo* - 1,4 - *exo* - 5,8 - dimethanonaphthalene. (Ia and IIa).**—A mixture (b.p. 36–40° (1.8 mm.), $n^{25}$D 1.5234) of *exo*- and *endo*-5-bromonorbornene was prepared from cyclopentadiene and vinyl bromide substantially as described earlier.[3] A sample of this material was solvolyzed in 80 vol. % ethanol at 87.9°. Plots of log *c. vs.* time indicated that about 40% of this mixture was the more reactive isomer (*exo*) or nortricyclyl bromide and 60% the less reactive one (*endo*).[18–20]

A solution of 18.4 g. (0.106 mole) of the dehydronorbornyl bromide mixture and 28.6 g. (0.106 mole) of hexachlorocyclopentadiene in 25 ml. of xylene was heated for 42 hr. at 145°. Crystals separated from the solution after it had stood for several days. These weighed 12.7 g. and proved to be crude Ia, m.p. 168–173°. The solvent was removed from the filtrate under vacuum. The resulting solid was dissolved in benzene and passed through an activated alumina (Fisher) column to remove colored impurities. Fractional crystallization from acetic acid gave (total) 14.2 g. (30%) of *exo* isomer (Ia), m.p. 178–179°, and 19.0 g. (40%) of *endo* isomer (IIa), m.p. 109.5–110.5°. Isolation of 30% of Ia indicates that most of the rapidly solvolyzing material was *exo*-dehydronorbornyl bromide rather than nortricyclyl bromide.

*Anal.* Calcd. for $C_{12}H_9BrCl_6$: C, 32.32; H, 2.03. Found (for Ia): C, 32.39; H, 2.18. Found (for IIa): C, 32.15; H, 2.19. Analysis by a cryoscopic procedure[21] of a similar preparation indicated a yield of 32% *exo* isomer and 48% *endo* isomer. Each pure bromide could be passed onto and eluted from alumina with benzene without loss or change in melting point.

Dry hydrogen bromide gas was bubbled slowly for 5 hr. through a stirred solution of 6.20 g. (0.017 mole) of aldrin in 100 ml. of dry benzene at 55–60°. The benzene and hydrogen bromide were removed by evaporation; the residue was taken up in benzene again, decolorized on an alumina column, and concentrated by evaporation. Addition of a small amount of methanol precipitated nearly pure 1a, m.p. 173–178° (5.41 g., 72%). Recrystallization gave pure Ia, m.p. 178–179.2°.

A solution of 600 mg. of Ia in Ethyl Cellosolve containing a large excess of sodium β-ethoxyethoxide was heated at reflux for 2 hr. The reaction mixture was allowed to cool and was then filtered. The solvent was removed by evaporation at room temperature and the residue was washed repeatedly with petroleum ether. This solution was passed through alumina and the pentane was then distilled. The residual solid, impure III, weighed 417 mg. (85%), m.p. 74–90°. One recrystallization from glacial acetic acid gave 368 mg. of III, m.p. 96–101.5°. A mixture with aldrin, m.p. 102–103°, melted at 101.5–103°.

A similar experiment with 502 mg. of IIa gave 389 mg. (95%) of impure III, m.p. 84–98°. Recrystallization gave a product, m.p. and mixed m.p. with pure III, 99–100°.

A solution of 617 mg., (1.38 mmoles) of IIa and 500 mg. (2.93 mmoles) of silver nitrate in 50 ml. of absolute ethanol was heated at reflux for 48 hr. Volhard titration indicated that 6.6% of the bromide had reacted. A similar experiment with Ia gave 8.8% of the theoretical bromide ion. Neither isomer liberated as much as 1% of halide ion when heated at reflux in acetic acid for 3 days. Neither isomer was isomerized when treated with silver bromide in the presence or absence of hydrogen bromide in refluxing carbon tetrachloride solution for 1 hr.

**5,6,7,8,9,9-Hexachloro-1,2,3,4,4a,5,8,8a-octahydro-*exo*-1,4-*endo*-5,8-dimethano-*endo*-2-naphthoic Acid (IIb).**—A mixture of 34.7 g. (0.25 mole) of somewhat impure 5-norbornene-*endo*-2-carboxylic acid,[3a,22] 75.0 g. (0.275 mole) of hexachlorocyclopentadiene, and 25 ml. of glacial acetic acid was heated at reflux for 42 hr. Cooling of this solution gave a 48 g. (47%) crop of crystals, m.p. 204–210° and a second crop (34.2 g., 33%) was obtained from aqueous acetic acid, m.p. 130–190°. Several recrystallizations from acetic acid gave pure IIb, m.p. 216–217°. Recrystallization from benzene gave m.p. 223–224°. When pure *endo*-norbornenecarboxylic acid, m.p. 43.8–44.6°[3a] was used in the Diels-Alder reaction, the product melted at 211–214° and did not depress the m.p. of the other sample. Thus it is clear that the product is *endo*.

*Anal.* Calcd. for $C_{13}H_{10}Cl_6O_2$: C, 37.99; H, 2.45, neut. equiv., 411. Found: C, 38.01; H, 2.45; neut. equiv., 409, 413.

The **methyl ester** of IIb was prepared by heating a mixture of 9.11 g. (0.0176 mole) of the silver salt of IIb, 5.00 g. (0.0352 mole) of methyl iodide, and 50 g. of acetone at reflux for 1 hr. After the silver iodide had been removed by filtration, the ester was recovered by distillation of the acetone. Recrystallization from aqueous acetone gave 5.60 g. (75%) of methyl 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-*exo*-1,4-*endo*-5,8-dimethano-*endo*-2-naphthoate, m.p. 92–93.5°. This ester could also be prepared by a Diels-Alder synthesis with methyl *endo*-norbornenecarboxylate[3a] and hexachlorocyclopentadiene at 105° for 36 hr.

*Anal.* Calcd. for $C_{14}H_{12}Cl_6O_2$: C, 39.56; H, 2.85. Found: C, 39.66; H, 2.92.

**5,6,7,8,9,9-Hexachloro-1,2,3,4,4a,5,8,8a-octahydro-*exo*-1,4-*endo*-5,8-dimethano-*exo*-2-naphthoic Acid (Ib).**—To a solution of 0.45 g. (0.020 mole) of sodium in 40 ml. of absolute methanol was added 5.40 g. (0.0127 mole) of the *endo* methyl ester of IIb. The solution was heated at reflux for 24 hr., with addition of 10 ml. of dry benzene at the tenth hour to bring more ester into solution. Thirty milliliters of methanol was then distilled, and 20 ml. of water was added, followed by 18 hr. of reflux to effect hydrolysis of the ester. The solution was acidified with 20% sulfuric acid while hot and the product Ib crystallized. One recrystallization from ethanol gave 3.28 g. (61%) of acid, m.p. 211–214°. Recrystallization from benzene gave pure Ib, m.p. 220–221°. A mixed melting point with IIb was depressed to 172–175°.

*Anal.* Calcd. for $C_{13}H_{10}Cl_6O_2$: C, 37.99; H, 2.45. Found: C, 38.15; H, 2.24.

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[17] E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958).

[18] These results agree with the suggestion[19] that earlier reports[3] of the *exo* isomer content in this mixture were incorrect.

[19] J. D. Roberts and W. Bennett, *J. Am. Chem. Soc.*, **76**, 4623 (1954).

[20] (a) S. Winstein, H. M. Walborsky, and K. Schreiber, *ibid.*, **72**, 5795 (1950). (b) S. Winstein and D. Trifan, *ibid.*, **71**, 2953 (1949); **74**, 1147, 1152 (1952).

[21] Details of cryoscopic analyses of mixtures of Ia and IIa are described in the Ph.D. dissertation of R.E.K.[1b] These are not described here as we now prefer an infrared technique.[14f]

[22] K. Alder and G. Stein, *Ann.*, **514**, 197 (1934).

This product was also prepared by a diene synthesis using *exo*-norbornenecarboxylic acid[8a] and hexachlorocyclopentadiene.

**Methyl 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-*exo*-1,4-*endo*-5,8-dimethano-*exo*-2-naphthoate.**—A solution of 15.0 g. (0.099 mole) of methyl *exo*-norbornene-2-carboxylate[8a] and 26.8 g. (0.099 mole) of hexachlorocyclopentadiene in 40 ml. of xylene was heated at 130° for 42 hr. Xylene and other volatiles were removed by steam distillation. Crystallization of the remaining oil from petroleum ether, b.p. 60–70°, gave two crops: 7.7 g., m.p. 118–135°, and 19.0 g., m.p. 86–116° (64%). Recrystallization from methanol gave 8.9 g. (21%) of the methyl ester of Ib, m.p. 142–143°.

*Anal.* Calcd. for $C_{14}H_{12}Cl_6O_2$: C, 39.56; H, 2.85; sapon. equiv., 425. Found: C, 39.74; H, 2.83; sapon. equiv., 418. Saponification of this material in aqueous methanol gave Ib.

**Preparation of Silver Salts (Id and IId).**—The ammonium salts were prepared by stirring a suspension of the acid in a large excess of liquid ammonia until the acid dissolved. The excess ammonia was then allowed to evaporate. An aqueous solution of the ammonium salt was run into a well stirred aqueous solution of silver nitrate. The crystalline silver salts were filtered, dried, and stored in a vacuum desiccator for several days over phosphorus pentoxide. The salt was then ground to a fine powder, washed with warm carbon tetrachloride, filtered, and pumped dry. Samples were nearly colorless and were kept in the dark in vacuum desiccators over phosphorus pentoxide for several weeks to ensure dryness.[4]

Treatment of each of these salts with dilute nitric acid liberated the corresponding acid. Over 90% of each acid was recovered with rather high purity.

**5,6,7,8,9,9-Hexachloro-1,2,3,4,4a,5,8,8a-octahydro-*exo*-1,4-*endo*-5,8-dimethano-*endo*-2-naphthoyl Chloride (IIc).**—The *endo* (IIb) acid (111 g., 0.27 mole) was heated at reflux for 1.5 hr. with 222 g. (1.87 mole) of thionyl chloride. A calcium chloride drying tube protected the reaction from atmospheric moisture. After an additional 2.5 hr. at room temperature, the thionyl chloride was partially removed by vacuum distillation. A mixture of dry benzene–petroleum ether (b.p. 60–70°) (2:1, 150 ml.) was added and removed by vacuum distillation. This procedure was repeated and the residue dried under vacuum.

The residue was dissolved in 400 ml. of hot, dry petroleum ether (trace of solid failed to dissolve) and the solution was filtered. The filtrate was stored overnight at −34°. The solid was filtered, washed with petroleum ether, and dried under vacuum over sodium hydroxide and paraffin chips. The yield of acid chloride was 105 g. (89%), m.p. 110–112.5°.

*Anal.* Calcd. for $C_{13}H_9Cl_7O$: C, 36.36; H, 2.11. Found: C, 36.14; H, 2.35.

The infrared spectrum of this material (in potassium bromide) indicated that no detectable amount of the *exo* (Ic) acid chloride was present.

**5,6,7,8,9,9-Hexachloro-1,2,3,4,4a,5,8,8a-octahydro-*exo*-1,4-*endo*-5,8-dimethano-*exo*-2-naphthoyl Chloride (Ic).**—The *exo* acid Ib (15 g., 0.036 mole) was heated at reflux for 2.25 hr. with 30 g. (0.25 mole) of reagent grade thionyl chloride. A drying tube kept the reactants from contact with atmospheric moisture. After an additional 2 hr., the excess thionyl chloride was removed under vacuum. Seventy milliliters of a 2:1 mixture of dry benzene–petroleum ether was then added in two portions and removed under vacuum. The residue was dissolved in 40 ml. of redistilled petroleum ether and the hot solution was filtered. The filtrate was kept in a refrigerator overnight before the crystals were filtered and dried over potassium hydroxide under vacuum. The yield was 10.4 g. (67%), m.p. 99.5–101.5°.

*Anal.* Calcd. for $C_{13}H_9Cl_7O$: C, 36.36; H, 2.11. Found: C, 36.16; H, 2.35.

The infrared spectrum of this material (in potassium bromide) indicated that no detectable amount of the *endo* (IIc) acid chloride was present.

**Bis(5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-*exo*-1,4-endo-5,8-dimethano-*endo*-2-naphthoyl) Peroxide (V).**—Five milliliters of distilled water in a 50-ml. flask was cooled to 0° in a brine bath. Sodium peroxide (0.63 g., 0.0081 mole), followed by a solution of 6.8 g. (0.016 mole) of *endo* (IIc) acid chloride in 22 ml. of redistilled xylene were added with mechanical stirring. The addition took 13 min.; the temperature remained between 2–4°. After an additional 1.5 hr. of stirring the solvents were removed under vacuum and the solid residue leached with four 50-ml. portions of boiling redistilled acetone (the residue then dissolved easily in water). The acetone solution was filtered and 200 ml. of distilled water was added to precipitate the peroxide. After 7 hr., the peroxide was filtered, washed twice with 20 ml. of distilled water, and dried under vacuum over sodium hydroxide. The yield was 3.4 g. (51%), m.p. 133–135° dec.

This peroxide was apparently contaminated with acid (IIb), since its infrared spectrum (in potassium bromide, taken after about 25 days at room temperature) had some carbonyl absorption at 5.87 $\mu$. Strong peroxide absorptions[23] at 5.53 and 5.63 $\mu$ were also present. Several precipitations with water from acetone solution gave V, m.p. 132.5–134° dec.

*Anal.* Calcd. for $C_{26}H_{18}Cl_{12}O_4$: C, 38.09; H, 2.21. Found: C, 37.97; H, 2.41.

This peroxide had carbonyl absorptions at 5.54 and 5.62 $\mu$ (more intense). Seven aliphatic diacyl peroxides absorb at 5.49–5.52 $\mu$ and 5.57–5.60 $\mu$.[23]

The infrared spectrum of this material (in potassium bromide) indicated the absence of the *exo* (IV) peroxide.

**Bis(5,6,7,8,9,9-Hexachloro-1,2,3,4,4a,5,8,8a-octahydro-*exo*-1,4-*endo*-5,8-dimethano-*exo*-2-naphthoyl) Peroxide (IV).**—Five milliliters of distilled water was cooled in an ice–alcohol bath to 0–1° and sodium peroxide (0.80 g., 0.011 mole) was added with stirring. The acid chloride (Ic) (7.5 g., 0.018 mole) in 24 ml. of redistilled xylene was added dropwise during 0.5 hr. to the stirred solution of sodium peroxide (maintained at 0–4°) and the reaction mixture was stirred for an additional 1.5 hr. with cooling.

The solvent was removed under vacuum and the residue leached with 250 ml. of boiling, redistilled acetone. The hot acetone solution was filtered and the peroxide precipitated with 250 ml. of distilled water. After the mixture stood overnight the peroxide was filtered and washed with water. It was dried for 2 days under vacuum at room temperature over sodium hydroxide and paraffin.

The peroxide (4.5 g., 61%) had a m.p. between 105–111° (dec.) which apparently depended upon the rate of heating. It absorbed strongly at 5.51 $\mu$ and 5.63 $\mu$.[23] There was a shoulder at 5.82 $\mu$ on the peroxide band, probably due to acid. The band at 13.35 $\mu$ of the *endo* (V) peroxide was not observed in the spectrum.

The analytical sample of the *exo* peroxide was prepared in much the same manner as the analytical sample of the *endo* peroxide.

*Anal.* Calcd. for $C_{26}H_{18}Cl_{12}O_4$: C, 38.09; H, 2.21. Found: C, 38.23; H, 2.36.

The peroxides IV and V decomposed on standing at room temperature and lost their oxidizing power.

**Analytical Procedures.**—The mixtures of bromides Ia and IIa resulting from the various conversions were analyzed by three procedures. We first used cryoscopic techniques,[21] but switched to infrared techniques, using potassium bromide disks and wave lengths at 7.62 and 7.67 $\mu$ to determine the composition of the mixtures.[24] These compositions were

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(23) W. H. T. Davison, *J. Chem. Soc.*, 2456 (1951).

(24) We now prefer infrared analysis using a spectrophotometer with potassium bromide optics.[14f] Details of the procedures with sodium chloride optics and the isotope-dilution procedures are given in the Ph.D. thesis of W. C. F.[1b]

checked using an isotope-dilution technique with tritium-labeled Ia (prepared by addition of tritium bromide to aldrin).[24]

**Reaction of Silver Salts Id and IId with Bromine (Hunsdiecker Reaction). A. Preparative Scale.**—Ten grams (0.019 mole) of the *endo* silver salt IId was suspended in 100 ml. of dry carbon tetrachloride in a flask equipped with a stirrer, a dropping funnel, and a condenser. The stirrer was started and 2 ml. (6.2 g., 0.039 mole) of dry bromine was added through the dropping funnel. The solution warmed up rapidly and bubbling indicated that decarboxylation was proceeding. After the bromine was added, the solution was heated at reflux for 1 hr. The mixture was cooled and the silver bromide precipitate was filtered and washed with three 25-ml. portions of carbon tetrachloride. Treatment of the silver bromide precipitate with 4 *N* nitric acid and extraction with benzene gave no organic product.

The carbon tetrachloride solution was washed successively with: (1) 30 ml. of 10% sodium hydroxide–30 ml. of methanol; (2) 10 ml. of water–10 ml. of methanol; (3) 20 ml. of saturated sodium chloride solution. Acidification of the basic solution gave 0.517 g. (6.5% recovery) of acid, m.p. 210.5–213.5°. There was no depression of melting point when a mixture of this acid and an authentic sample of IIb was used.

After the solvent had been removed from the carbon tetrachloride solution, the residue was taken up in boiling glacial acetic acid and allowed to crystallize slowly. Fractional crystallization gave 4.5 g. (52%) of *exo* bromide Ia, m.p. 177–177.5°, and 2.3 g. (27%) of *endo* bromide IIa, m.p. 105–110°.

A similar experiment with *exo* acid Ib gave a 3.5% recovery of *exo* acid and a bromide mixture from which 59% of Ia and 14% of IIa were isolated.

**B. Analytical Scale.**—A 100-ml. round-bottom flask containing the silver salt of the acid (0.5–1.2 mmoles) and 70 ml. of dry carbon tetrachloride was equipped with a reflux condenser (both flask and condenser were covered with aluminum foil to exclude light). The suspension was heated at reflux (carbon tetrachloride, b.p. 70–71° (630 mm.) and stirred vigorously. A solution of bromine (0.5–1.0 mmoles) in carbon tetrachloride was pipetted into the condenser. The mixture was heated at reflux for 2 hr. and then cooled. The solution was concentrated almost to dryness then extracted with benzene (five 25-ml. portions). These extracts were run *seriatim* through a column of 100 g. of activated alumina. An additional 75 ml. of benzene was run through the column. This procedure was shown to elute halogenated hydrocarbons, but not the oxygen-containing by-products. The benzene solutions were combined and the solvent removed finally *in vacuo*. The residual bromides were dried *in vacuo* for 24 hr. in preparation for the analytical procedures. Yields of bromides varied in an erratic fashion from 42–89% with *endo* acid in general giving somewhat better yields than *exo*. Addition of *sym*-trinitrobenzene did not affect the analyses. Five runs with the *exo* acid Ib gave 30 ± 4% *endo* bromide IIa and 70 ± 4% *exo* bromide Ia and four with *endo* acid IIa gave 31 ± 4% *endo* bromide IIa and 69 ± 4% *exo* bromide with all results (by infrared or isotope dilution analysis) falling within the indicated limits.

**Reaction of Acids Ib and IIb with Mercuric Oxide and Bromine.**[10]—A suspension of 2.0 g. (4.9 mmole) of *endo* acid IIb and 2.0 g. (9.2 mmoles) of mercuric oxide in 35 ml. of carbon tetrachloride was heated to reflux, and 1.09 g. (6.8 mmoles) of bromine in 15 ml. of carbon tetrachloride was added. The reaction flask was wrapped in foil to exclude light. The reaction mixture was heated at reflux and stirred for 2 hr. The solid was removed from the mixture by filtration; the residue was extracted with carbon tetrachloride. Evaporation of the solvent from the filtrates gave an oil which solidified on trituration with methanol. Evaporation of the methanol gave 1.88 g. of crude bromide, m.p. 91–170°. Chromatography of 1.67 g. of this material on 100 g. of alumina gave 1.55 g. (80%) of bromide eluted by carbon tetrachloride, m.p. 84–168°.

*Anal.* Calcd. for $C_{12}H_9BrCl_6$: Br, 17.92. Found: Br, 18.24.

This material indicated 70% *exo* bromide Ia by isotope dilution.

A similar experiment with the *exo* acid Ib gave 1.86 g. (93%) of chromatographed bromide, m.p. 93–163°.

*Anal.* Calcd. for $C_{12}H_9BrCl_6$: Br, 17.92. Found: Br, 18.30.

Isotope dilution analysis indicated that this bromide mixture contained 72% *exo* bromide Ia.

**Decomposition of the *exo* Acid Peroxide (IV) in a Solution of Bromine in Carbon Tetrachloride.**—A solution of 0.485 g. of impure peroxide IV (titrating for 73% peroxide by iodimetry, 0.43 mmole) and 69 mg. (0.43 mmole) of bromine in 11 ml. of carbon tetrachloride under anhydrous air-free conditions was heated at reflux for 3 hr. The bromine color disappeared in about 20 min. Chromatography gave 70% of bromide fraction (*Anal.* Calcd. for $C_{12}H_9BrCl_6$: Br, 17.92. Found Br, 15.67) corresponding to 87% bromide. Infrared analysis indicated a content of 27% *endo* IIa–60% *exo* Ia while isotope dilution indicated 67% *exo* Ia. These determinations normalized to 100% indicate that this process gives 27 ± 4% *endo* Ia product.

**Decomposition of the Acid Peroxides IV and V in Bromotrichloromethane.**—A solution of 2.49 g. (3.04 mmoles) of *endo* peroxide V in 75 ml. of dry bromotrichloromethane was heated at reflux for 18 hr. in an air-free atmosphere. The bromotrichloromethane was removed by distillation and a small amount of hexachloroethane, m.p. 180°, was removed by vacuum distillation. The residue weighed 2.23 g., m.p. 105–172°, contained no peroxide (iodide test) and contained carbonyl compounds and bromide (infrared data). Chromatography to isolate the halogenated hydrocarbon fraction gave a fraction representing a 27% yield of bromide and 5% unknowns. Isotope dilution analysis and infrared analysis indicated that the bromide mixture contained less than 2% *endo* isomer IIa.

A similar experiment with the *exo* peroxide IV gave a yield of about 23% of the bromide. Again the infrared spectrum was similar to *exo* bromide (mixtures containing 7% *endo* isomer IIa could be analyzed) and isotope-dilution experiments also indicated that the bromide was substantially all *exo* isomer Ib.

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