Notes

Bridged Polycyclic Compounds. XVI. Bromination of Dihydroaldrin[1]

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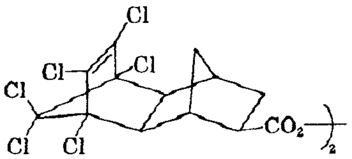
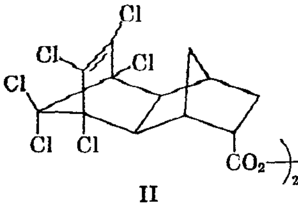
It had previously been noted[2] that bromination by the solvent of the radical V formed by the decomposition of either 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a - octahydro - 1,4 - *exo* - 5,8-*endo*-dimethano-*exo*-2-naphthoyl peroxide (I) or 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a - octahydro - 1,4 - *exo* - 5,8 - *endo* - dimethano - *endo*-2-naphthoyl peroxide (II) in boiling bromotrichloromethane gave only 5,6,7,8,9,9-hexachloro-1,2,3,4-4a,5,8,8a - octahydro - 1,4 - *exo* - 5,8 - *endo* - dimethano-*exo*-2-naphthyl bromide (III). On the other hand, the Hunsdiecker reaction of the acids related to I and II gave a mixture of about 70% of III and 30% of its *endo* isomer IV. These results led the authors[2] to suggest that the Hunsdiecker reaction might not involve a free-radical chain, assuming that the radical V would transfer only on its *exo* side. However, the simple 2-norbornyl radical has been shown[3] to exchange almost entirely on its *exo* side with large halogen donors, such as sulfuryl chloride, carbon tetrachloride, phosphorus pentachloride, and bromotrichloromethane about 70–75% from its *exo* side and 25–30% from its *endo* side with the less bulky reagents, chlorine and bromine. It seemed worth while, therefore, to study the stereochemistry of the radical V in its exchange with molecular bromine.



I



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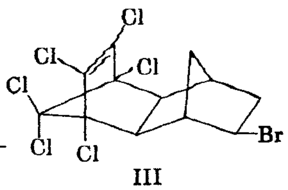

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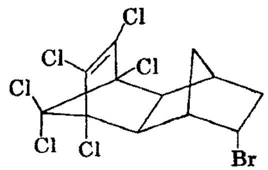

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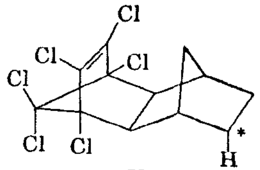
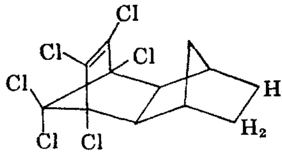


V



VI

Bromination of 1,2,3,4,9,9-hexachloro-1,4,4a,5,6-7,8,8a - octahydro - 1,4 - *exo* - 5,8 - *endo* - dimethanonaphthalene (dihydroaldrin, VI) in chlorobenzene gave a mixture of *exo*-III and *endo*-IV in a 70:30 ratio. The bromination was deliberately carried out only to 3–4% completion to avoid, as much as possible, higher bromination products. In addition it was shown that *exo*-III was not isomerized to *endo*-IV, nor IV to III, under the conditions of the reaction.

It is clear, therefore, that, like the simple norbornyl radical,[3] the radical V may transfer with small reagents from both the *endo* and *exo* sides. The basis of the discussion of the Hunsdiecker reaction[2] must now be abandoned.

EXPERIMENTAL

Bromination of dihydroaldrin **(VI).** Dihydroaldrin, 1.835 g. (5.00 mmoles), was dissolved in 50 ml. of chlorobenzene which contained 79 mg. (0.5 mmole) of bromine in a 100-ml. Pyrex flask. The air above the solution was replaced with nitrogen, the flask was stoppered, and the solution was irradiated with a 100-watt light bulb for 13 hr. The excess bromine was removed with sodium thiosulfate, and the solution was then dried. The solvent was removed under reduced pressure. The residue was chromatographed on 160 g. of neutral, activity I alumina (1.8 × 65 cm), 100-ml. fractions of eluent being collected.[4] The first fraction of pentane was empty. Fractions 2 through 6, which were developed with pentane, contained 1.763 g. (96.1%) of unchanged starting material, VI. Fractions 7 through 9 were empty; fraction 9 eluent being 4% ether in pentane. Fractions 10 through 20, developed with 4% ether in pentane, contained 71.3 mg. (3.2%) of a mixture of III and IV, m.p. 91–166°, remelted, 95–158°. A mixture containing 66% of III and 34% of IV is reported to melt at 158°.[5] The bromide fraction was analyzed in a Perkin-Elmer Model 137 infrared spectrophotometer fitted with potassium bromide optics using a differential method[6] which gave 30 ±

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[1] Previous paper in series: S. J. Cristol and P. K. Freeman, *J. Am. Chem. Soc.*, **83**, 4427 (1961).

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

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

[4] H. Brockmann and H. Schodder, *Ber.*, **74B**, 73 (1941).

[5] R. E. Krall, Ph.D. thesis, University of Colorado, 1956.

[6] I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis*, 3rd ed., The Macmillan Co., New York, 1952, p. 632.

3% of IV. Analytical absorption bands for *endo*-IV were found at 613 and 622 cm.$^{-1}$, while those for *exo*-III were at 506, 521, 598, 622, and 651 cm.$^{-1}$ Solutions of the bromides in tetrachloroethylene were used. This procedure was much more satisfactory than that described earlier.[3] The infrared spectrum of the mixture, both in the sodium chloride and potassium bromide regions, was essentially identical to that of a synthetic mixture which contained 31% IV and 69% III. *exo*-Bromide III was found not to isomerize to *endo*-bromide IV under the bromination conditions. (The solvent was saturated with hydrogen bromide at the start.)

Bromination of a mixture of dihydroaldrin (VI) *and endo-*(IV) *or exo-*(III) *aldrin hydrobromide.* A mixture of 1.835 g. (5.00 mmoles) of VI and 21.2 mg. (0.050 mmole) of IV was brominated as described above for VI. There was recovered 1.802 g. (98.2%) of VI and 77.2 mg. of aldrin hydrobromides. The latter corresponds to an increment of 56.0 mg. (2.5%) of bromination product plus 21.2 mg. of added IV. The mixture gave an analysis corresponding to 46% *endo* product (calcd., 49%) indicating that *endo* material IV survived further bromination (within experimental error). A similar experiment with *exo* bromide gave similar results (found: 11% *endo;* calcd.: 10% *endo*).

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Steroids and Related Natural Products. IX. Selective Osmium Tetroxide Oxidation of Olefins[1,2]

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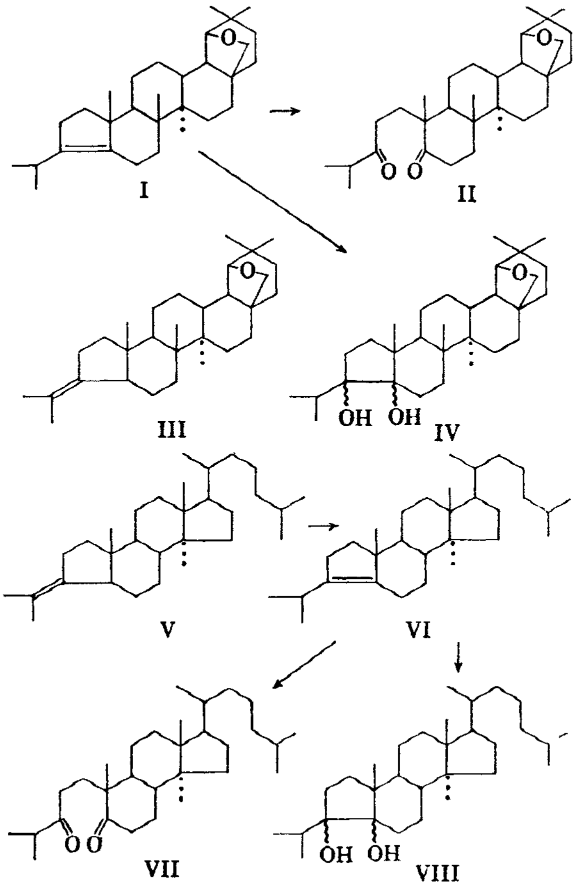
Addition of osmium tetroxide to an olefin usually yields a cyclic osmium ester and this reaction may be accelerated by employing solvents such as pyridine.[3,4] A *cis*-glycol derivative of the original olefin can be prepared by treating the osmic acid ester with one of several reagents. Hydrogen sulfide or sodium sulfite in aqueous ethanol are commonly used for this purpose.[3,5] Recently, Baran has recommended an osmium tetroxide hydroxylation procedure utilizing pyridine as solvent for the initial reaction and sodium bisulfite in aqueous pyridine for generating the *cis*-glycol.[6,7]

During a previous study concerned with the structure of α-apoallobetulin (I)[8] we found that oxidation of this substance using the osmium tetroxide-pyridine-sodium bisulfite technique[6] yields diketone II. When exocyclic olefin III was oxidized under the same conditions only a glycol derivative was obtained. Similarly, glycol IV was readily prepared from the endocyclic isomer (I) using an osmium tetroxide (benzene solution)–hydrogen sulfide procedure.



Information derived from these experiments suggested that the Baran procedure[6] might provide a method for selectively oxidizing certain tetrasubstituted olefins. Several transformations of the A-norsteroid (V)[9] arising from phosphorus pentachloride dehydration of 3β-hydroxy-5α-lanostane

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[1] The preceding contribution in this series was prepared by G. R. Pettit and T. R. Kasturi, *J. Org. Chem.*, **26**, 4557 (1961).

[2] This investigation was supported by PHS Research Grants CY-4074(C1) and CY-4074(C2) from the National Cancer Institute, Public Health Service.

[3] A recent review of this reaction has been prepared by F. D. Gunstone, *Advances in Organic Chemistry: Methods and Results*, Vol. I, R. A. Raphael, E. C. Taylor, and H. Wynberg, eds., Interscience, New York, 1960, p. 110.

[4] Compare the observations of: G. Cooley, B. Ellis, F. Hartley, and V. Petrow, *J. Chem. Soc.*, 4377 (1955); J. A. Zderic, H. Carpio, and C. Djerassi, *J. Org. Chem.*, **24**, 909 (1959); and E. Bunnenberg and C. Djerassi, *J. Am. Chem. Soc.*, **82**, 5953 (1960).

[5] Alternatively, the osmium intermediate may be oxidized with periodate to a dicarbonyl derivative of the original olefin. *Cf.* R. Pappo, D. S. Allan, Jr., R. U. Lemieux, and W. S. Johnson, *J. Org. Chem.*, **21**, 478 (1956); and N. A. Nelson and R. B. Garland, *J. Am. Chem. Soc.*, **79**, 6313 (1957).

[6] J. S. Baran, *J. Org. Chem.*, **25**, 257 (1960).

[7] *Cf.* also, B. J. Magerlein and J. A. Hogg, *J. Am. Chem. Soc.*, **80**, 2226 (1958).

[8] Evidence in support of this structure has been summarized by G. R. Pettit, B. Green, and W. J. Bowyer, *J. Org. Chem.*, **26**, 2879 (1961). The NMR spectrum of α-apoallobetulin is also consistent with formulation I. We are indebted to Dr. George Slomp, Research Division, the Upjohn Company, for providing this information.

[9] D. H. R. Barton, D. A. J. Ives, and B. R. Thomas, *J. Chem. Soc.*, 903 (1954).