titatively converted to XeF_4. The discharge varied from 1100 volts and 31 milliamp. to 2800 volts and 12 milliamp. while the total pressure varied from 2 to 15 mm. In a typical run of 3.5 hours, 7.10 mmoles of Xe and 14.20 mmoles of F_2 were used and 1.465 g. (7.07 mmoles) of xenon fluoride was produced. The composition of the product, as determined from synthesis, is therefore XeF_4. The advantage of this method over Claassen's[3] thermal method is that it is continuous, quantitative and an excess of fluorine is not required.

The composition of our products was also confirmed by analysis. A 102.3 mg. sample of XeF_4 was hydrolyzed with dilute KOH solution,[3,4] liberating 64.9 ± 1.0% by weight of Xe (theoretical = 63.3 wt. %). The resulting solution contained, by titration with Th$(NO_3)_4$, 35.1 ± 1.0% by weight F^- (theoretical = 36.7 wt. %). In addition, a new analytical method for Xe was used. XeF_4 reacts quantitatively with excess Hg

$$XeF_4 + 4Hg \longrightarrow Xe \uparrow + 2Hg_2F_2 \text{ (or } 2HgF_2)$$
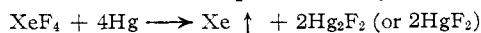
A sample of 136.4 mg. of our XeF_4 gave 87.3 (±0.5) mg. of Xe or 64.0 (±0.5) wt. %.

The product was vacuum sublimed into a glass tube and any trace of SiF_4 or O_2 pumped off; the clear colorless crystals formed were identical in appearance with those described previously.[3]

While these experiments were being completed, one of us (A. V. Grosse)—during a lecture trip in Germany—was shown the production of XeF_2 by the associates of Prof. Hoppe at the University of Münster. The XeF_2 was produced from a mixture of 1 volume of Xe + 1 volume of F_2, by the Ruhmkorff induction coil discharge in a quartz vessel, with quartz sealed electrodes, at $-78°$.

We wish to thank Mr. O. V. Carlson of Union Carbide Corporation for a gift of xenon and Dr. Balcar of the Air Reduction Company for a previous sample of xenon.

THE RESEARCH INSTITUTE   A. D. KIRSHENBAUM
OF TEMPLE UNIVERSITY   L. V. STRENG
4150 HENRY AVENUE   A. G. STRENG
PHILADELPHIA 44, PA.   A. V. GROSSE

THE STRUCTURE OF β-RHOMBOHEDRAL BORON[1]

Sir:

We have determined the structure for β-rhombohedral boron,[2,3] the phase obtained between 1500° and the melting point, where crystallization of a framework requiring a 105-atom unit becomes kinetically feasible.[3] B_{12} icosahedra are linked in a pattern which apparently is energetically superior to that achieved in the tetragonal[4] or, especially, the α-rhombohedral[5] polymorph.

Crystals (*ca.* 99.5% B) from the U. S. Borax Research Corporation give $a = 10.145 ± 0.015$ Å., $\alpha = 65°$ 17' ± 8' for the primitive rhombohedral unit. The 105-atom framework derives from the space group $D_{3d}^5–R\bar{3}m$, and carries (largely substitutional) impurities estimated as 0.11 Mg, 0.04 Al, 0.01 each of Si, Mn, Fe atoms. Three-dimensional intensity data from single crystals were counter-recorded using balanced filters with both Cu $K\alpha$ and Mo $K\alpha$ radiations. Structure determination through analysis of observed in-

(1) Supported by the National Science Foundation and the Advanced Research Projects Agency. We thank also the Cornell Computing Center, Mr. Richard C. Lesser, Director.

(2) D. E. Sands and J. L. Hoard, *J. Am. Chem. Soc.*, **79**, 5582 (1957).

(3) J. L. Hoard and A. E. Newkirk, *ibid.*, **82**, 70 (1960).

(4) J. L. Hoard, R. E. Hughes and D. E. Sands, *ibid.*, **80**, 4507 (1958); *cf.*, J. L. Hoard, S. Geller and R. E. Hughes, *ibid.*, **73**, 1892 (1951).

(5) B. F. Decker and J. S. Kasper, *Acta Cryst.*, **12**, 503 (1959).

equalities and statistical relations connecting unitary structure factors, although demonstrably feasible, was short-circuited when one of us (R. E. H.) independently devised a model for the 84-atom subunit described below. The complete structure, free of interpretive ambiguity, then was obtained by Fourier synthesis in successive approximation. Presently R is 0.15 for all reflections of $(\sin \theta)/\lambda < 0.71$ and bond lengths are 1.65–1.87 Å., averaging 1.79 Å.

Excepting one atom at $1/2, 1/2, 1/2$, the structural unit is contained within a larger aggregate, itself recognizable in the crystal, of $13B_{12}$ icosahedra linked in a pattern retaining maximum symmetry. Take $r \cong 1.71$ Å. and $e \cong 1.80$ Å. as radius and edge of a regular B_{12} icosahedron, $l \cong 1.70$ Å. for a direct intericosahedral link. Consider a central B_{12} icosahedron radially linked to twelve others, with each secondary icosahedron derived from the central B_{12} through translation of $2r + l$ along the common fivefold axis and rotation of $2\pi/10$ about this axis. (This "eclipsed" configuration for linked B_{12} pairs is observed throughout.) Centers of the secondary icosahedra lie upon the surface of a sphere of diameter $4r + 2l \cong a = 10.145$ Å. Within this sphere are 84 atoms comprising the central B_{12} radially joined to 12 half-icosahedra or pentagonal pyramids; the 60 peripheral atoms occupy vertices of a truncated icosahedron (12 pentagonal, 20 hexagonal faces) in which the 30 edges connecting B_5 pentagons in pairs are also links connecting secondary B_{12} icosahedra in pairs nearly along (within 5° of) *quasi*-fivefold axes. Some compression of the central B_{12} with accompanying expansion of the attached icosahedra is observed: averaged edge lengths for the respective B_{12} types presently are 1.75 and 1.83 Å., intericosahedral links range from 1.65 to 1.75 Å. with, interestingly, the twelve radial links longest. When centered at a lattice point with symmetry $\bar{3}m$, the 84-atom subunit has six of its *quasi*-fivefold radii essentially along rhombohedral axes. Lattice translations generate an approximately cubic closest-packed assemblage of these subunits which are joined in an elegant three-dimensional framework through completion of B_{12} icosahedra centered at the midpoints of all rhombohedral edges. Thus, the 84-atom complex plays a role somewhat analogous to that of a B_{12} icosahedron in the simple α-rhombohedral structure.[5]

Each subunit has still six pentagonal pyramids with axes inclined alternatively ±10° to the equatorial plane; these are capped, using just 20 atoms, to complete B_{12} icosahedra within partially condensed aggregates of symmetry $3m$. Three icosahedra, from three subunits, terminate in a single atom on the threefold axis. This atom has nine neighbors at the vertices of a polyhedron $(3m)$ having three pentagonal and five triangular faces. Six of these nine atoms are shared between icosahedra and display eight-coördination; the remaining three retain six-coördination by forming each a bond with the 105th atom at the cell center $(\bar{3}m)$. This last atom displays *octahedral* coördination in tying together the two sets of condensed icosahedra "centered" at $\pm(uuu)$ with $u = 0.385$. Bond distances of 1.72–1.86 Å., averaging 1.79 Å., characterize the internal crosslinking. (In the α structure, three center bonding provides the crosslinking.[5]) Over-all, the coördination number for 91 atoms is six, for 12 atoms, eight, for the final pair, nine. Two holes of modest size at $\pm(vvv)$, $v \cong 0.22$, carry no appreciable electron density. Preferential substitution by magnesium and aluminum (probably as Mg^{++}, Al^{+++}) in the octahedral or nine-coördinate positions seems probable, but is not proven.

Noted for subsequent elaboration are the following: The β-rhombohedral structure probably is thermodynamically preferred (for ordinary pressures) at every temperature below the melting point. Establishment of the partial framework having 84-atom subunits, but with a different internal crosslinking (probably influenced by foreign atoms), is the obvious, if inconclusive, interpretation of X-ray powder data from some boron samples crystallized too far below the melting point. At still lower temperatures kinetic mechanism determines the choice of framework.[3]

(6) Author to whom correspondence should be addressed.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF PENNSYLVANIA   R. E. HUGHES
PHILADELPHIA, PENNSYLVANIA

     C. H. L. KENNARD
     D. B. SULLENGER
DEPARTMENT OF CHEMISTRY   H. A. WEAKLIEM
CORNELL UNIVERSITY   D. E. SANDS
ITHACA, NEW YORK   J. L. HOARD[6]

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TOTAL SYNTHESIS OF d,l-CARYOPHYLLENE AND d,l-ISOCARYOPHYLLENE

Sir:

The hydrocarbons known as the caryophyllenes have occupied a unique position in the terpene field for more than a century because of the unusual array of difficulties which have been encountered during their study.[1] We describe here the total synthesis of XI and XV, now commonly known as isocaryophyllene and caryophyllene, respectively, as the racemates.

The ketone I, one of the compounds which appeared suitable as a starting material, was obtained by a new and remarkable reaction, the photochemical addition of 2-cyclohexenone to isobutylene at *ca.* $-40°$. This process affords *ca.* 58% of 7,7-dimethylbicyclo[4.2.0]-octanone-2 (I) and *none* of the isomeric 8,8-dimethylbicyclo[4.2.0]octanone-2.[2] Further, *both cis* and *trans* isomers of the bicyclic ketone I are formed, with *trans* predominating by a factor of about four. These isomers are readily distinguished by n.m.r.; two sharp peaks due to methyl protons occur at 0.97 and 1.15 δ[3] in the spectrum of the *cis* ketone and at 1.07 and 1.15 δ for the *trans* ketone. The configurations indicated are assigned from the fact that the predominating ketone in the photoreaction is completely isomerized to the minor isomer by treatment with dilute base.[4-6] The α-proton at C_1 in the *cis* photo adduct, infrared max. 5.84 μ, b.p. 72° (1 mm.), (C, 78.78; H, 10.50), gives rise to six sharp peaks in the n.m.r. spectrum (a pair of triplets downfield from the remaining peaks) which disappear on base-catalyzed deuteration.

The *cis* ketone I was further transformed according to the sequence: to II (methyl carbonate–sodium hydride–dioxane), b.p. 82–83° (0.3 mm.), infrared

(1) For a recent review see P. de Mayo, "Mono- and Sesquiterpenes," Interscience Publishers, Inc., New York, N. Y., 1959, p. 286.

(2) In addition *ca.* 30% of a non-distillable resin and 12% of a C_{10} unsaturated ketone are produced.

(3) All n.m.r. data were obtained at 60 Mc. and are expressed as p.p.m. shift from tetramethylsilane as internal standard.

(4) *trans*-I is not produced by irradiation of *cis*-I under preparative conditions (experiment by Dr. J. D. Bass).

(5) For related studies see (a) G. Büchi and I. Goldman, *J. Am. Chem. Soc.*, **79**, 4741 (1957); (b) R. C. Cookson and E. Crundwell, *Chem. and Ind.*, 1004 (1958); (c) P. deMayo, H. Takeshita and A. B. Sattar, *Proc. Chem. Soc.*, 119 (1962); (d) P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2344, 2554 (1962). It is clear that the photoaddition of 2-cyclohexenone to isobutylene does not proceed as might have been anticipated from previous results and discussions. We are presently investigating the factors which control orientation and stereochemistry in such addition processes.

(6) A subsequent paper will deal with another approach to the ring system of I, the photolysis of 2-*t*-butylcyclohexanone which produces 7,7-dimethylbicyclo[4.2.0]octanol-1.
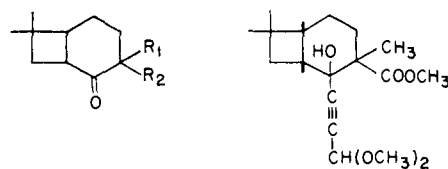
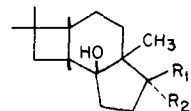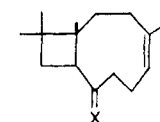I, $R_1 = R_2 = H$
II, $R_1 = H$, $R_2 = COOCH_3$
III, $R_1 = CH_3$, $R_2 = COOCH_3$

IV
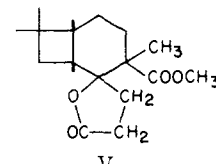
V

VI, $R = COOCH_3$
VII, $R = H$

VIII, $R_1 = H_1$, $R_2 = OH$
IX, $R_1 = OH$, $R_2 = H$

X, $X = O$
XI, $X = CH_2$
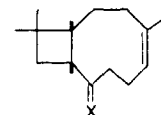
XII, $X = O$
XIII, $X = CH_2$
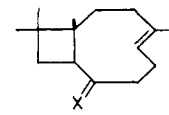
XIV, $X = O$
XV, $X = CH_2$

max. at 5.70, 5.86, 6.05 and 6.19 μ (C, 68.84; H, 8.55); then to III (methyl iodide–base), b.p. 80–85° (0.3 mm.), infrared max. 5.84 and 5.74 μ (C, 69.98; H, 9.19), as a 3:1 mixture of isomers (v.p.c. analysis); further to the acetylene IV (propargyl aldehyde dimethyl acetal lithio derivative in tetrahydrofuran) and beyond to the ester lactone V (hydrogenation with Pd–C catalyst in methanol followed by oxidation with chromic acid in aqueous acetic acid), b.p. *ca.* 120–130° (bath) (0.08 mm.), infrared max. at 5.63 and 5.78 μ (C, 68.51; H, 8.86); additionally to the keto ester VI (methylsulfinylcarbanion in dimethyl sulfoxide[7]) infrared max. 5.67 and 5.77 μ, purple color with ferric ion; then to the hydroxy ketone VII (by hydrolysis with cold aqueous base and decarboxylation at 115° in pyridine), m.p. 126–127°, infrared max. 2.7–2.9 and 5.76 μ (C, 75.57; H, 9.96), sharp n.m.r. peaks at 0.93, 1.10 and 1.21 δ (three methyl groups).[8]

Reduction of the hydroxy ketone VII with either sodium borohydride in methanol, lithium aluminum hydride, lithium aluminum tri-*t*-butoxyhydride or sodium–moist ether produced a crystalline diol (VIII, methyl and OH *trans*), m.p. 122.5–124° (C, 73.90 (low); H, 10.90), which was transformed readily into a mono *p*-toluenesulfonate. Generation of the fused 4-9 ring fusion of the caryophyllenes was accompanied by internal elimination *via* the γ-oxide anion[9] derived from the toluenesulfonate. Thus, treatment of the hydroxy *p*-toluenesulfonate with methylsulfinylcarbanion[7] (3 equivalents) at 25° in dimethyl sulfoxide for 30 minutes followed by addition of several equivalents of *t*-butyl alcohol and a further 2 hours for isomerization of the 4-9 ring fusion afforded the ketone X, infrared max. 5.90 μ (C, 81.65; H, 10.90). Reaction of this ketone with methylenetriphenylphosphorane–dimethyl sulfox-

(7) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962).

(8) The stereochemistry of this hydroxy ketone may be either (starting from the 4-6 fusion) (1) *cis,anti,cis* or (2) *cis,anti,trans*.

(9) See (a) A. Eschenmoser and A. Frey, *Helv. Chim. Acta*, **35**, 1660 (1952); (b) R. B. Clayton, H. B. Henbest and M. Smith, *J. Chem. Soc.*, 1983 (1957); also *Chem. and Ind.*, 1315 (1953); (c) P. S. Wharton, *J. Org. Chem.* **26**, 4781 (1961).