Photocaryophyllenes A and D, Products of Photochemical Cyclopropane Formation

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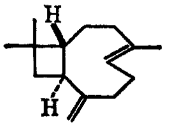
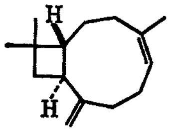
Photocaryophyllenes A and D have been shown to be **2a** and **d** by X-ray analysis of single crystals of the corresponding bromo ketones, **4a** and **d**, obtained by ozonolysis and bromination.

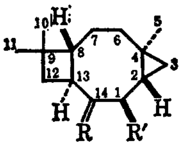
Among the products we have obtained by photolyzing caryophyllene (**1a**) and isocaryophyllene (**1b**) are four substances, termed photocaryophyllenes A–D, all isomeric with starting material, and all retaining the terminal methylene band in the infrared spectrum.[1] From caryophyllene (**1a**), the yields were 27, 5, 2, and 2%, respectively, and from isocaryophyllene (**1b**), 8, 1, 23, and 19%, respectively. It was decided to determine the structure of at least one of these photochemical rearrangement products by X-ray diffraction, and accordingly photocaryophyllene A (**2a**) was ozonized and brominated to give a bromo ketone (**4a**) suitable for crystal structure analysis (Chart I). When the structure of bromo ketone **4a** had been determined, it appeared likely that photocaryophyllenes B, C, and D were stereoisomers of A, but in the absence of an easier method for unambiguously determining the stereochemistry, a second crystal structure analysis was carried out on bromo ketone **4d** from photocaryophyllene D (**2d**). This paper reports the preparation of and X-ray studies on bromo ketones **4a** and **d**.



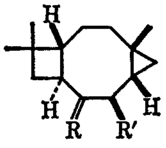
1a



1b



2–4a



2–4d

2, R = CH$_2$; R′ = H
3, R = O; R′ = H
4, R = O; R′ = Br

Experimental Section

Ketone 3a.—A 10-g sample of gas chromatographically pure **2a** ([α]^{20}D −138.8°) dissolved in 50 ml of methylene chloride and 70 ml of methanol was ozonized at −10°. The solvents were removed under reduced pressure (bath temperature <20°), the residue (13 g) was dissolved in 300 ml of methanol, and a solution of 20 g of $Na_2SO_3 \cdot 7H_2O$ in 150 ml of water was slowly added, keeping the temperature below 30°. After 5 hr at 45°, the solution was diluted with 500 ml of water and extracted with ether. Evaporation of the ether gave 8.2 g of crystals, which on recrystallization from hexane gave 5.8 g of **3a**: mp 72°; [α]^{20}D −239° (*c* 10, CHCl$_3$), 1685 cm^{-1} (C=O).

Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.41; H, 10.70.

Bromo Ketone 4a.—To a solution of 5 g of ketone **3a** in 30 ml of carbon tetrachloride while irradiating with a 125-W lamp (Pyrex filter) was slowly added a solution of 4 g of bromine in 40 ml of carbon tetrachloride. After 30 min, solvent and HBr were removed, and the residue partially crystallized on the addition of ether. After filtering and recrystallizing from hexane, 1.4 g of **4a** [mp 146–147°, [α]^{20}D −80.6° (*c* 10, CHCl$_3$), 1710 cm^{-1} (C=O)] was obtained.

Anal. Calcd for $C_{14}H_{21}OBr$: C, 58.95; H, 7.42. Found: C, 59.16; H, 7.33.

Ketone 3d.—According to the above procedure, 3.8 g of 80% pure photocaryophyllene D (**2d**) was ozonized to give 1.2 g of ketone **3d**: mp 56–57°; [α]^{20}D −158.4° (*c* 10, CHCl$_3$), 1696 cm^{-1} (C=O).

Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.37; H, 10.70.

Bromo Ketone 4d.—By the procedure described for the preparation of **4a**, 1.1 g of **3d** gave 120 mg of **4d**, mp 126°.

Anal. Calcd for $C_{14}H_{21}OBr$: C, 58.95; H, 7.42. Found: C, 58.80; H, 7.40.

X-Ray Studies of 4a and d.—Cell lengths were determined from oscillation and Weissenberg photographs using a traveling microscope. The intensity data were collected on a Supper automatic diffractometer using a fine-focus Cu tube with an Ni filter. A 3° scan at 2°/min was used for each reflection, with 45 sec background counts before and after. Reflections were accepted if the intensity was at least twice the square root of the sum of the scan and background counts. For **4a**, 1013 reflections were accepted on levels 0–5 around the needle axis *c*; for **4d**, 904 reflections were accepted on levels 0–8 around the needle axis *b*.[2] No absorption corrections were made; the needles used for intensity measurements were in both cases about 1 × 0.2 × 0.2 mm.

Results

Both bromo ketones **4a** and **d** crystallize in space group $P2_12_12_1$ with $Z = 4$. For **4a**, $a = 18.95$ (1), $b = 10.90$ (1), $c = 6.78$ (1) Å; $V_{obsd} = 1400$ (4) Å^3 ($V_{calcd} =$ 1420 Å^3 from $d_{obsd} = 1.33$ g cm^{-3}). For **4d**, $a = 14.34$ (1), $b = 9.15$ (1), $c = 10.66$ (1) Å; $V_{obsd} = 1399$ (4) Å^3 ($V_{calcd} = 1400$ Å^3 from $d_{obsd} = 1.35$ g cm^{-3}).

In each case, the three-dimensional Patterson map readily yielded the bromine coordinates, the first Fourier map based on the phases of the bromine showed the approximate positions of all of the carbons and the oxygen atom, and the structure was then refined.[3] For **4a**, *R* with just the bromine was 43.2%. Addition

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[1] The details of the preparation of the photocaryophyllenes will be described in a separate publication.

[2] Lists of structure factors are available in the Ph.D. theses of G. D. Forsythe (photocaryophyllene A), University of Arizona, 1969, and G. A. Wolfe (photocaryophyllene D), University of Arizona, 1968.

[3] Initially, the differential synthesis program of R. Shiono (File No. 7.5.003, Program Information Department, IBM) was used; the final full matrix least squares cycles were carried out using unit weights and form factors obtained by graphical interpolation of those in the International Tables for X-Ray Crystallography, Vol. III, Table 3.3.1A, with the ORFLS program of W. R. Busing, K. O. Martin, and H. A. Levy, ORNL-TM-305, Oak Ridge National Laboratory, 1962.

Table I
Fractional Coordinates

	4a			4d		
	x	*y*	*z*	*x*	*y*	*z*
Br	−0.1347 (1)	0.2969 (2)	0.2404 (5)	0.5199 (2)	0.9728 (3)	−0.0568 (2)
O	−0.2598 (5)	0.4436 (10)	0.1404 (24)	0.3883 (11)	1.0985 (17)	−0.2565 (12)
C1	−0.2235 (7)	0.3133 (16)	0.3959 (27)	0.5270 (13)	0.9599 (19)	−0.2401 (9)
C2	−0.2534 (8)	0.1862 (15)	0.4322 (31)	0.6043 (13)	1.0632 (20)	−0.2875 (14)
C3	−0.2238 (10)	0.0957 (17)	0.5641 (47)	0.7053 (14)	1.0045 (32)	−0.2797 (15)
C4	−0.2934 (10)	0.1610 (15)	0.6255 (37)	0.6577 (12)	1.0283 (27)	−0.4090 (17)
C5	−0.2863 (11)	0.2478 (17)	0.8123 (37)	0.6872 (14)	1.1526 (25)	−0.4877 (17)
C6	−0.3702 (11)	0.1082 (16)	0.5894 (39)	0.6345 (14)	0.8801 (21)	−0.4801 (16)
C7	−0.4225 (9)	0.2065 (18)	0.5419 (43)	0.5570 (13)	0.8994 (20)	−0.5834 (16)
C8	−0.4050 (7)	0.2830 (15)	0.3565 (31)	0.4727 (11)	0.9848 (17)	−0.5387 (11)
C9	−0.4610 (8)	0.3856 (15)	0.2986 (54)	0.3799 (13)	0.9700 (22)	−0.6197 (15)
C10	−0.5108 (11)	0.3410 (20)	0.1182 (42)	0.3637 (17)	1.1083 (26)	−0.7074 (20)
C11	−0.5073 (11)	0.4345 (21)	0.4743 (48)	0.3722 (17)	0.8276 (28)	−0.6893 (19)
C12	−0.4006 (7)	0.4770 (13)	0.2445 (40)	0.3233 (13)	0.9677 (27)	−0.4914 (15)
C13	−0.3484 (7)	0.3984 (13)	0.3725 (32)	0.4158 (13)	0.9259 (16)	−0.4208 (16)
C14	−0.2762 (8)	0.3886 (12)	0.2735 (30)	0.4349 (12)	0.9993 (18)	−0.3005 (12)

Table II
Anisotropic Thermal Parameters[a]

	4a						4d					
	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	0.0032 (1)	0.0210 (3)	0.0295 (8)	0.0024 (1)	0.0043 (3)	0.0059 (6)	0.0136 (2)	0.0195 (4)	0.0077 (2)	−0.0021 (3)	0.0014 (2)	0.0005 (3)
O	0.003 (0)	0.012 (1)	0.017 (5)	0.000 (1)	0.002 (1)	0.004 (2)	0.009 (1)	0.021 (3)	0.011 (1)	0.004 (2)	0.001 (1)	−0.010 (2)
C1	0.002 (0)	0.012 (2)	0.006 (5)	0.001 (1)	0.002 (1)	−0.002 (3)	0.009 (1)	0.011 (2)	0.000 (1)[b]	0.003 (2)	−0.001 (1)	−0.001 (1)
C2	0.003 (1)	0.010 (2)	0.005 (6)	0.001 (1)	0.003 (2)	−0.002 (3)	0.006 (1)	0.010 (3)	0.006 (1)	−0.001 (2)	0.001 (1)	0.002 (2)
C3	0.005 (1)	0.011 (2)	0.038 (11)	0.003 (1)	−0.001 (3)	0.000 (5)	0.008 (1)	0.027 (6)	0.008 (2)	−0.001 (3)	−0.001 (1)	−0.003 (3)
C4	0.005 (1)	0.008 (2)	0.019 (8)	0.000 (1)	0.002 (2)	0.002 (4)	0.005 (1)	0.019 (4)	0.012 (2)	0.001 (2)	−0.001 (1)	0.000 (3)
C5	0.006 (1)	0.011 (2)	0.020 (9)	−0.001 (1)	−0.004 (2)	0.001 (4)	0.007 (2)	0.017 (4)	0.010 (2)	−0.003 (2)	0.004 (1)	−0.001 (2)
C6	0.006 (1)	0.010 (2)	0.029 (9)	−0.004 (1)	0.005 (3)	0.000 (4)	0.008 (1)	0.008 (3)	0.010 (2)	0.004 (2)	0.001 (1)	−0.005 (2)
C7	0.003 (1)	0.012 (2)	0.038 (10)	−0.002 (1)	0.001 (2)	0.002 (5)	0.006 (1)	0.009 (3)	0.010 (2)	0.002 (1)	0.002 (1)	−0.004 (2)
C8	0.002 (0)	0.010 (2)	0.017 (6)	−0.002 (1)	−0.001 (2)	0.005 (4)	0.006 (1)	0.008 (3)	0.004 (1)	−0.004 (2)	0.000 (1)	0.004 (1)
C9	0.002 (0)	0.010 (2)	0.064 (16)	0.000 (1)	−0.001 (3)	0.013 (6)	0.007 (1)	0.007 (3)	0.011 (2)	−0.002 (2)	−0.001 (1)	0.001 (2)
C10	0.005 (1)	0.015 (3)	0.028 (10)	−0.001 (1)	−0.007 (3)	0.004 (5)	0.008 (2)	0.014 (4)	0.014 (3)	0.001 (2)	−0.002 (2)	0.004 (3)
C11	0.004 (1)	0.018 (3)	0.036 (11)	0.002 (1)	0.003 (3)	0.009 (6)	0.010 (2)	0.020 (5)	0.010 (2)	−0.003 (2)	−0.002 (2)	−0.008 (3)
C12	0.003 (0)	0.009 (2)	0.020 (6)	0.000 (1)	0.002 (2)	0.000 (4)	0.006 (1)	0.018 (4)	0.009 (2)	−0.001 (2)	−0.001 (1)	0.004 (3)
C13	0.003 (0)	0.006 (1)	0.014 (6)	−0.001 (1)	0.002 (2)	0.002 (3)	0.007 (1)	0.002 (3)	0.010 (2)	−0.001 (1)	0.003 (1)	−0.000 (2)
C14	0.004 (1)	0.006 (1)	0.004 (5)	−0.001 (1)	0.001 (2)	−0.003 (3)	0.008 (1)	0.003 (3)	0.005 (1)	−0.001 (2)	0.002 (1)	0.001 (2)

[a] From $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$. [b] The value obtained for this parameter on refinement, −0.00005 (80), was physically meaningless, and 0.004 was used for the ORTEP plot.

of the carbons and oxygen gave a value of 26.7, dropped through isotropic and later anisotropic refinement to 10.9%. For **4d**, the *R* of 39.9% based on bromine dropped to 28.3% with the first placement of the carbons and oxygen, and on three cycles of anisotropic refinement, to 13.2%. Refinement of the interlayer scale factors and coordinates followed by refinement of the temperature factors gave a final *R* of 10.0%. No attempt was made in either case to locate the hydrogens.

The final atomic parameters with their standard deviations are given in Tables I and II. Figure 1 shows ORTEP[4] plots of both structures. Bond lengths and angles calculated with ORFFE[5] are given in Tables III and IV, respectively; their relatively poor quality is probably due largely to absorption errors and decomposition. No attempt was made to determine the absolute configurations crystallographically; since inversion at C8 seems unlikely, they are assumed to be as in caryophyllene (**1a**).[6]

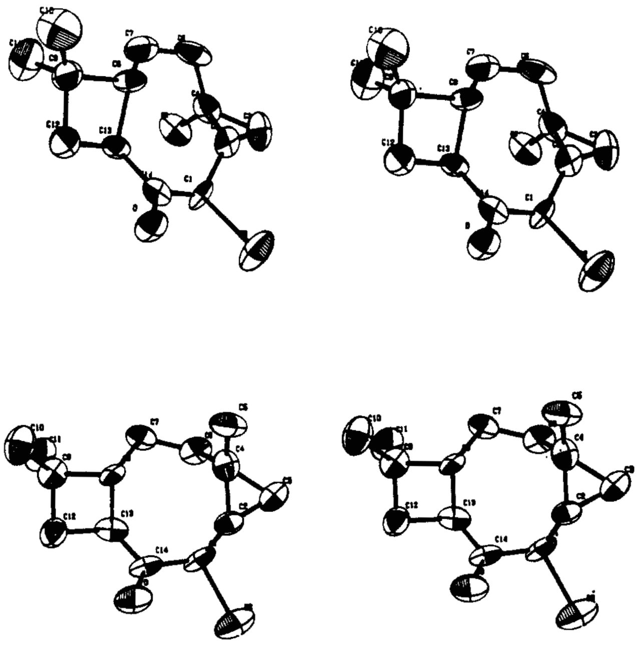

Figure 1.—ORTEP plots of **4a** (top) and **d**. Thermal ellipsoids enclose 50% probability.

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(4) C. K. Johnson, ORNL-3794.

(5) W. R. Busing, K. O. Martin, and H. A. Levy, ORNL-TM-306, Oak Ridge National Laboratory, 1964.

(6) D. H. R. Barton and A. Nickon, *J. Chem. Soc.*, 4665 (1954); J. M. Robertson and G. Todd, *ibid.*, 1254 (1955).

TABLE III

BOND DISTANCES IN ÅNGSTRÖMS

Bond	4a	4d
Br–C1	1.99 (1)	1.96 (1)
O–C14	1.13 (2)	1.22 (2)
C1–C2	1.52 (2)	1.54 (2)
C1–C14	1.54 (2)	1.51 (2)
C2–C3	1.44 (3)	1.55 (3)
C2–C4	1.54 (3)	1.54 (2)
C3–C4	1.55 (3)	1.55 (2)
C4–C5	1.59 (3)	1.48 (3)
C4–C6	1.58 (3)	1.59 (3)
C6–C7	1.49 (3)	1.57 (2)
C7–C8	1.55 (3)	1.52 (2)
C8–C9	1.59 (2)	1.59 (2)
C8–C13	1.66 (2)	1.59 (2)
C9–C10	1.62 (4)	1.57 (3)
C9–C11	1.57 (4)	1.50 (3)
C9–C12	1.56 (2)	1.59 (2)
C12–C13	1.57 (3)	1.57 (2)
C13–C14	1.53 (2)	1.47 (2)

TABLE IV

BOND ANGLES IN DEGREES

Angle	4a	4d
Br–C1–C2	108.6 (10)	109.0 (10)
Br–C1–C14	108.2 (12)	111.4 (10)
C2–C1–C14	109.5 (13)	110.0 (12)
C1–C2–C3	125.5 (17)	116.3 (17)
C1–C2–C4	119.1 (16)	120.4 (15)
C3–C2–C4	62.7 (15)	60.5 (11)
C2–C3–C4	61.6 (13)	59.5 (11)
C2–C4–C3	55.7 (14)	60.0 (12)
C2–C4–C5	122.1 (15)	117.5 (18)
C2–C4–C6	112.7 (19)	118.3 (17)
C3–C4–C5	114.5 (19)	119.1 (19)
C3–C4–C6	124.9 (17)	113.3 (20)
C5–C4–C6	114.7 (18)	116.5 (16)
C4–C6–C7	112.5 (14)	112.7 (15)
C6–C7–C8	114.9 (18)	113.6 (12)
C7–C8–C9	115.9 (16)	116.9 (12)
C7–C8–C13	119.7 (16)	118.8 (14)
C9–C8–C13	85.1 (11)	88.3 (11)
C8–C9–C10	111.3 (18)	111.5 (15)
C8–C9–C11	115.0 (24)	113.7 (17)
C8–C9–C12	91.0 (11)	87.7 (11)
C10–C9–C11	110.3 (15)	113.7 (15)
C10–C9–C12	116.3 (25)	115.5 (17)
C11–C9–C12	111.8 (20)	112.0 (17)
C9–C12–C13	89.0 (14)	89.1 (13)
C8–C13–C12	88.3 (11)	88.4 (12)
C8–C13–C14	119.9 (13)	115.9 (13)
C12–C13–C14	111.0 (16)	117.5 (15)
O–C14–C1	122.5 (15)	119.4 (14)
O–C14–C13	124.2 (16)	124.9 (16)
C1–C14–C13	112.5 (15)	115.1 (14)

Discussion

As can be seen in Figure 1, the bromo ketones from photocaryophyllenes A (**4a**) and D (**4d**) are stereoisomeric cyclopropane derivatives, differing only in configuration at C4. This difference changes the conformation of the eight-membered ring considerably; in **4a**, it approximates a crown. The dihedral angles in the cyclobutane rings of **4a** and **d** have normal values of 27 (3)° and 27 (2)°, respectively. The dihedral angle between the Br–C1–C14 and C1–C14–O planes in **4a** is only 15 (2)°, putting the oxygen and bromine only 2.94 (1) Å apart. In **4d**, this angle is 38 (2)°, and the oxygen–bromine distance is 3.07 (1) A.

Although the cell volumes are nearly identical and the compounds crystallize in the same space group, the packing arrangements differ considerably, as suggested by the large difference in cell shapes. In **4a**, the closest intermolecular distance is 3.16 (3) Å, between oxygen and carbonyl carbon. A different dipole–dipole interaction appears to govern the packing in **4d**, in which the closest intermolecular approach [3.52 (3) Å] is between oxygen and C1.

From the structures of bromo ketones **4a** and **d** it is very likely that photocaryophyllenes A and D have structures **2a** and **d**, respectively. It is conceivable but unlikely that the configuration at C13 changes during the photoreaction, and changes back during the conversion to the bromo ketone.

Several reasonable mechanisms for the photoreactions can be written, including a hydrogen shift mechanism analogous to that proposed for a corresponding reaction of *cis*-1,4-polyisoprene,[7] and a carbon shift mechanism involving opening of the nine-membered ring of caryophyllene (**1a**) with the formation of two allylic radicals, one of which rearranges to a cyclopropyl radical and recouples to photocaryophyllenes **4a–d**.[8] Elucidation of the mechanism awaits further experimental results, including the determination of the configurations of photocaryophyllenes B and C.

Registry No.—**2a**, 18,755-92-5; **2d**, 18,755-93-6; **3a**, 18,755-94-7; **3d**, 18,755-95-8; **4a**, 18,755-96-9; **4d**, 18,755-97-0.

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(7) M. A. Golub and C. L. Stephens, *J. Polym. Sci., Part A-1*, **6**, 763 (1968).

(8) This sequence is similar to one implied by H. Kristinsson and G. S. Hammond, *J. Amer. Chem. Soc.*, **89**, 5970 (1967), for the conversion of i into ii