## Novel β-Lactams derived from the Photoisomer of *N*-Benzyloxycarbonylmethylene-2-pyridone

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Transformations of the cyclobutene ring in the photoisomer of *N*-benzyloxycarbonylmethylene-2-pyridone gives some novel fused  $\beta$ -lactams.

A SPATE of papers on the photochemistry of 2-pyridones appeared in the early sixties,<sup>1-6</sup> which gave the impression that photodimers were the inevitable products. A notable exception however was a report by Corey and Streith,<sup>7</sup> which showed that *N*-methyl-2-pyridone could be induced photochemically to undergo valence tautomerisation to *N*-methyl-3-oxo-2-azabicyclo[2.2.0]hex-5ene, albeit in low yield. Subsequently further examples of photochemically induced valence tautomerisation of substituted 2-pyridones have been reported.<sup>8-10</sup>

The photoisomers of 2-pyridones are fused  $\beta$ -lactams. With a view to exploring the potential of this form of ring fused  $\beta$ -lactams as novel antibacterial agents and as intermediates for the synthesis of nuclear analogues of the  $\beta$ -lactam antibiotics, the photoisomers of N-benzyl-oxycarbonylmethylene-2-pyridone (3; R = CH<sub>2</sub>Ph) was prepared and its chemistry investigated.

2-Pyridone (1) is alkylated at nitrogen by bromoacetic esters. Both the ethyl and benzyl esters (2; R = Et) and CH<sub>2</sub>Ph) were made in this way in good yield. Photoisomerisation of these N-alkylated-2-pyridones (2; R = Et, and  $CH_2Ph$ ) occurred in 70 and 80% isolated yield respectively, the benzyl ester (3;  $R = CH_2Ph$ ) being crystalline. Selective hydrogenation was achieved over rhodium on alumina catalyst to give the benzyl ester (4). Hydrogenation over palladium on charcoal gave the acid (11). Epoxidation of the olefinic bond of the photoisomer (3;  $R = CH_2Ph$ ) with trifluoroperacetic acid gave a single stereoisomer which was assigned the exo-configuration (5), since the coupling constants between the protons of the epoxide ring and those of the  $\beta$ -lactam ring were less than 1 Hz. Thus, as expected, epoxidation occurs from the least-hindered face of the molecule.



SCHEME Reagents: i, BrCH<sub>2</sub>·CO<sub>2</sub>R, K<sub>2</sub>CO<sub>3</sub>, Me<sub>2</sub>N·CHO; ii,  $h\nu$ ; iii, H<sub>2</sub>-Rh/Al<sub>2</sub>O<sub>3</sub>; iv, H<sub>2</sub>-Pd/C; v, CF<sub>3</sub>·CO<sub>3</sub>H; vi, N-bromo-succinimide-H<sub>2</sub>O; vii, Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, H<sub>2</sub>SO<sub>4</sub>

### TABLE (continued)

Bond lengths (Å) with estimated standard deviations in parentheses

N(1)-C(2)	1.471(9)	C(2) - H(2)	1.07(4)
N(1) - C(6)	1.344(10)	C(3) - H(3)	1.06(4)
N(1) - C(7)	1.450(10)	C(4) - H(4)	1.08(4)
C(2) - C(5)	1.551(11)	O(2) - H(21)	0.97(4)
C(2) - C(3)	1.546(9)	C(5) - H(5)	1.07(4)
C(3) - Br(1)	1.935(7)	C(7) - H(71)	1.08(4)
C(3) - C(4)'	1.537(11)	C(7) - H(72)	1.08(4)
C(4) - O(2)	1,409(9)	C(9)-H(91)	1.07(4)
C(4) - C(5)	1.550(10)	C(9) - H(92)	1.10(4)
C(5) - C(6)	1.529(11)	C(11) - H(11)	1.08(5)
C(6) - O(1)	1.220(10)	C(12) - H(12)	1.08(5)
() ()	( )	C(13) - H(13)	1.08(5)
C(7) - C(8)	1.508(11)	C(14) - H(14)	1.08(5)
$C(8) \sim O(3)$	1.336(9)	C(15) - H(15)	1.10(5)
C(8) - O(4)	1.201(9)	O(1) - H(21)'	1.83(5)
O(3) - C(9)	1.440(10)	(-)	
C(9) - C(10)	1.502(12)		
$C(10) - \dot{C}(11)$	1.376(14)		
C(10) - C(15)	1.354(13)		
C(11) - C(12)	1.437(17)		
C(12) - C(13)	1.323(21)		
C(13) - C(14)	1.316(20)		
C(14) - C(15)	1.353(18)		
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O(1) - O(2)'	2.805(8)		
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The superscripted atoms refer to those generated by the symmetry transformation  $\bar{x}, \bar{y}, \bar{z}$ 

Selected bond angles (") with estimated standard deviations in parentheses

C(2)-N(1)-C(6)	95.8(6)
C(2) - N(1) - C(7)	130.7(7)
C(6) - N(1) - C(7)	130.5(7)
N(1) - C(2) - C(3)	110.6(6)
N(1) - C(2) - C(5)	86.6(6)
C(3) - C(2) - C(5)	89.7(6)
C(2) - C(3) - C(4)	90.0(6)
C(2) - C(3) - Br(1)	115 6(5)
Br(1) = C(3) = C(4)	114 6(5)
C(3) - C(4) - C(5)	00 1(6)
C(3) - C(4) - O(3)	110 9(6)
O(3) = O(4) = O(2)	119.0(0)
C(4) = C(4) = C(3)	120.1(7)
C(4) = C(5) = C(6)	114.9(6)
C(4) - C(5) - C(2)	89.3(0)
C(2) - C(5) - C(6)	85.4(6)
C(5) - C(6) - O(1)	135.0(8)
C(5)-C(6)-N(1)	92.1(7)
O(1)-C(6)-N(1)	132.8(8)
N) 1) $-C(7)-C(8)$	111.3(7)
C(7)-C(8)-O(4)	125.9(7)
C(7)-C(8)-O(3)	109.0(7)
O(3) - C(8) - O(4)	125.1(7)
C(8) - O(3) - C(9)	115.4(6)
O(3) - C(9) - C(10)	107.7(6)
C(9) - C(10) - C(11)	120.6(1.0)
C(9) - C(10) - C(15)	120.1(9)
C(11) - C(10) - C(15)	119.3(9)
C(10) - C(11) - C(12)	117.4(1.2)
C(11) - C(12) - C(13)	120.5(1.3)
C(12) - C(13) - C(14)	120.2(1.3)
C(13) - C(14) - C(15)	122.1(1.4)
C(14) - C(15) - C(10)	120.6(1.2)
	· · ·
N(1)-C(2)-H(2)	117(5)
C(3) - C(2) - H(2)	119(5)
C(5) - C(2) - H(2)	128(5)
C(2) - C(3) - H(3)	116(5)
C(4) - C(3) - H(3)	116(5)
Br(1) - C(3) - H(3)	106(5)
C(3) - C(4) - H(4)	109(5)
C(5) - C(4) - H(4)	109(4)
O(2) - C(4) - H(4)	109(5)
C(4) - C(5) - H(5)	117(4)
C(2) - C(5) - H(5)	125(5)
C(6) - C(5) - H(5)	118(5)
	(-)



FIGURE The crystal structure of the bromohydrin ester (6), consists of a pair of molecules related by a centre of symmetry and are linked by hydrogen bonds. The atomic co-ordinates, bond lengths, and bond angles are shown in the Table. The numbering scheme is that used in the Table. Numbering of H atoms is only shown when more than one is attached to a carbon atom

### Table

The atomic co-ordinates, bond lengths, and bond angles of the bromohydrin ester (6). The numbering is shown in the Figure

Atomic co-ordinates

		A	
Atom	x/a	y/b	z/c
Br(1)	$0.439\ 76(9)$	$-0.086\ 66(7)$	0.617 56(4)
N(Ì)	$0.202 \ 1(7)$	0.137 0(6)	$0.525\ 5(2)$
O(1)	-0.0385(6)	0.124 1(4)	$0.518\ 2(2)$
O(2)	$0.049\ 6(7)$	-0.1310(5)	0.588 1(2)
O(3)	$0.267 \ 2(5)$	0.255 4(4)	$0.401\ 0(2)$
O(4)	0.142 9(6)	0.332 6(5)	$0.465\ 2(2)$
C(2)	$0.265 \ 0(8)$	0.103 8(6)	0.574 3(3)
C(3)	$0.284 \ 1(8)$	-0.0332(6)	0.577 8(3)
C(4)	$0.144\ 3(9)$	-0.0440(6)	0.604 7(3)
C(5)	$0.116\ 1(8)$	0.090 3(7)	$0.594\ 7(3)$
C(6)	$0.071\ 3(10)$	$0.120\ 1(5)$	$0.540\ 5(3)$
C(7)	0.260 8(9)	0.143 9(7)	$0.475\ 0(3)$
C(8)	$0.215 \ 3(8)$	$0.255\ 8(7)$	$0.447 \ 9(3)$
C(9)	$0.234\ 6(11)$	$0.358\ 7(8)$	0.370 6(3)
C(10)	$0.283\ 5(6)$	0.334 6(8)	$0.317\ 6(3)$
C(11)	$0.366\ 2(8)$	0.415 6(10)	0.292 8(4)
C(12)	$0.401\ 6(9)$	$0.390\ 2(15)$	$0.241\ 0(5)$
C(13)	$0.355\ 5(14)$	$0.292\ 2(18)$	$0.218\ 6(5)$
C(14)	$0.276\ 6(12)$	0.217 1(13)	$0.243\ 7(6)$
C(15)	0.239 8(8)	0.236 0(10)	$0.292\ 5(4)$
H(21)	0.048 8(102)	$-0.130\ 5(75)$	$0.551\ 1(17)$
H(2)	$0.345\ 3(70)$	0.160 8(64)	$0.588\ 0(32)$
H(3)	$0.292\ 2(87)$	0.078 7(67)	$0.542\ 5(21)$
H(4)	0.162 3(92)	0.056 3(71)	$0.644\ 7(18)$
H(5)	0.073 5(88)	0.141 8(66)	$0.625\ 2(24)$
H(71)	$0.371\ 7(47)$	0.147 6(45)	$0.476\ 5(22)$
H(72)	$0.227 \ 2(45)$	0.069 8(46)	$0.452\ 2(22)$
H(91)	$0.125\ 7(48)$	$0.371\ 1(42)$	$0.371\ 5(24)$
H(92)	$0.287 \ 6(46)$	0.436 5(43)	$0.386\ 6(24)$
H(11)	$0.403\ 1(26)$	$0.495\ 1(37)$	$0.311 \ 4(15)$
H(12)	$0.466\ 2(30)$	$0.452\ 7(38)$	$0.221\ 1(16)$
H(13)	$0.382\ 2(29)$	$0.273\ 3(37)$	$0.179\ 6(18)$
H(14)	0.239 8(29)	0.137 5(39)	$0.225\ 0(16)$
H(15)	0.173 8(30)	0.170 9(35)	0.311 9(15)

Treatment of the photoisomer (3;  $R = CH_{a}Ph$ ) with *N*-bromosuccinimide in aqueous dimethylethyleneglycol gave as the major product the bromohydrin (6). The structure of this product was established by X-ray crystallography. The computer drawing is shown in the Figure, and the atomic co-ordinates, bond lengths, and bond angles are shown in the Table. This structure shows that the electrophilic attack by bromine occurs from the least-hindered face of the molecule. The regioselectivity of the attack of water on the intermediate bromonium ion is more difficult to rationalise, but it may well be that the stereoisomer derived by attack at the alternative carbon atom is a minor product. Oxidation of the bromohydrin (6) with chromic acid to the bromo-ketone (7) was achieved in good yield.

Each of the benzyl esters, that is (3), (5), (6), and (7) were hydrogenolysed to the corresponding acids (8)—(11) which were tested as their sodium salts for antibacterial activity against a wide range of gram positive and gram negative bacteria at 1 mg/ml, but were ineffective.

The potential of photoisomers of *N*-substituted-2pyridones as intermediate for the synthesis of analogues of the  $\beta$ -lactam antibiotics is being explored.

### EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were determined with a Perkin-Elmer 257 grating spectrometer and <sup>1</sup>H n.m.r. spectra with a Perkin-Elmer R32 or Bruker WH90 spectrometer. Mass spectra were determined on an A.E.I. MS9 or Varian MAT CH7 spectrometer. Preparative layer chromatography (p.l.c.) was carried out on Merck  $HF_{254}$  silica gel. Light petroleum refers to the fraction of b.p. 60—80 °C.

N-Benzyloxycarbonylmethylene-2-pyridone (2; R = Ph- $CH_2$ ).—Pyridone (4.21 g), benzyl bromoacetate (9.64 g), and potassium carbonate in dimethylformamide (80 ml) were stirred at 20  $^\circ\text{C}$  for 16 h. The dimethylformamide was removed under reduced pressure and the residue partitioned between water (50 ml) and methylene chloride (50 ml); the aqueous layer was extracted with methylene chloride. The combined extracts were dried  $(MgSO_4)$  and the solvent removed. The residual solid was recrystallised from benzene-light petroleum to give the benzyl ester as needles (6.5 g, 67%), m.p. 100—101 °C,  $\delta_{\text{H}}$  (CDCl<sub>3</sub>), 7.35 (s, 5 H, Ph), 7.30 (m, 2 H, pyr), 6.60 (d, 1 H, pyr), 6.20 (t, 1 H, pyr), 5.22 (s, 2 H,  $CH_2Ph$ ), and 4.70 (s, 2 H, N-CH<sub>2</sub>);  $v_{max}$  (CHCl<sub>3</sub>) 1 750 (ester), and 1 668 and 1 595 cm<sup>-1</sup> (amide); m/z: 243(20), 136(5), 109(100), 108(37), 91(95), and 80(47) (M, 243) (Found: C, 69.2; H, 5.1; N, 5.7. C<sub>14</sub>H<sub>13</sub>NO<sub>3</sub> requires C. 69.1; H. 5.4; N. 5.7%).

N-Ethoxycarbonylmethylene-2-pyridone (2; R = Et).— The ethyl ester (2; R = Et) was prepared similarly in 77% yield using ethyl bromoacetate.

N-Benzyloxy carbonylmethylene-3-oxo-2-azabicyclo [2.2.0]-

hex-5-ene (3;  $R = PhCH_2$ ).—The pyridone (2;  $R = Ph-CH_2$ ) (8.0 g) was photolysed  $[4 \times 2$ -g batches in benzene (2 l)] for 65 h. The solvent was removed and the residue taken up in methylene chloride and pre-adsorbed onto Florisil and then chromatographed on silica gel under medium pressure (10 lb in<sup>-2</sup>). The impurities were eluted with ether-light petroleum (1:1) and the product with

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ether-light petroleum (7:3). Recrystallisation of the *photoisomer* from ethyl acetate-light petroleum gave prisms (5.6 g, 70%), m.p. 74 °C,  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 7.35 (s, 5 H, Ph), 6.55 (bs, 2 H, CH=CH), 5.18 (s, 2 H, CH<sub>2</sub>Ph), 4.55 (t, *J* 2 Hz, 1 H, CH·CH), 4.22 (m, 1 H, CH·CH), and 6.00 (ABq, *J* 18 Hz, 2 H, NCH<sub>2</sub>CO<sub>2</sub>R);  $\nu_{\rm max.}$  (CHCl<sub>3</sub>) 1 740 (CO<sub>2</sub>R) and 1 750 cm<sup>-1</sup> (β-lactam); *m/z* 243(1), 108(2), 91(100), and 52(73) (*M* 243) (Found: C, 69.3; H, 5.4; N, 5.9. C<sub>14</sub>H<sub>13</sub>-NO<sub>3</sub> requires C, 69.1; H, 5.4; N, 5.8%).

The ethyl ester (2; R = Et) gave the photoisomer (3; R = Et) as an oil in 80% yield.

*Epoxy-ester* (5).—The photoisomer (3;  $R = PhCH_2$ ) (0.5 g) was dissolved in methylene chloride (20 ml) and disodium hydrogen phosphate (1.5 g) added. An equivalent of trifluoroperacetic acid in methylene chloride (3 ml) was added dropwise to the stirred mixture at 0 °C. When addition was complete the solution was stirred for 12 h at 20 °C. The solution was filtered and the insoluble product dissolved in water and extracted with methylene chloride. The combined methylene chloride solutions were washed with saturated sodium hydrogen carbonate solution (2  $\times$  20 ml), dried (MgSO<sub>4</sub>), and the solvent removed. The residue was chromatographed on Fluorisil with ether-light pettroleum as eluant. Ether-light petroleum (1:1) eluted the epoxide (0.30 g, 57%) which crystallised from ethyl acetatelight petroleum as prisms, m.p. 56–57 °C,  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 7.35 (s, 5 H, Ph), 5.20 (s, 2 H,  $CH_2Ph$ ), 4.38 (dd, 1 H, J 3.2 and 0.5 Hz,  $\beta$ -lactam CH·N), 3.82 (dd, 1 H, J 3.2 and 0.8 β-lactam CH·CO), 4.20 and 4.19 (ABq, 2 H, epoxide 2 H), and 4.14 (ABq, 2 H, N-CH<sub>2</sub>CO<sub>2</sub>R);  $\nu_{\text{max}}$  (CHCl<sub>3</sub>) 1 760 (β-lactam) and 1 750 cm<sup>-1</sup> (CO<sub>2</sub>CH<sub>2</sub>Ph); m/z 259(1), 124(7), 107(3), 97(19), 92(17), 91(100), 77(4), 69(11), 68(100), 65(17), and 41(24) (Found: C, 64.7; H, 5.2; N, 5.6. C<sub>14</sub>H<sub>13</sub>NO<sub>4</sub> requires C, 64.9; H, 5.1; N, 5.4%).

Bromohydrin Ester (6).--A solution of the photoisomer (3;  $R = PhCH_{2}$  (1.0 g) and N-bromosuccinimide (0.877 g) in dimethylethylene glycol-water (2:1:45 ml) was stirred at 20 °C for 1 h. The solvent was removed and the residue taken up in methylene chloride (20 ml) and applied to p.l.c. plates and eluted with ethyl acetate. The band containing the bromohydrin was extracted with ethyl acetate and recrystallised from ethyl acetate-light petroleum to give the bromohydrin (0.86 g, 61%) as prisms, m.p. 103—105 °C,  $\delta_{\rm H}$ (CDCl<sub>3</sub>) 7.38 (s, 5 H, Ph), 5.21 (s, 2 H, CH<sub>2</sub>Ph), 4.66 (bs, 1 H, OH), 4.28 (d, 1 H, CH•CH•N), and 4.2-4.0 (complex due to  $NCH_2CO_2CH_2Ph$ , CH•OH and CH•Br);  $\delta_C$  (CDCl<sub>3</sub>) 168.259 and 166.244 (2s, CO of  $\beta$ -lactam and ester), 134.789 (s, quarternary Ph), 128.745 and 128.615 (CH of Ph), 73.243 (d, CH·OH), 67.719 (t, CH<sub>2</sub>Ph), 56.671 and 54.786 (2d, CH·CH bridgehead), 46.922 (d CHBr), and 42.828 (t,  $\rm NCH_2\text{-}CO_2CH_2Ph)$ ;  $\nu_{max}$  (CHCl\_3) 3 600 and 3 450 (OH, free and H bonded), 1 765 (β-lactam), and 1 750 cm^{-1} (CO\_2CH\_2-Ph); m/z M<sup>+</sup> 339/341 (Found: C, 49.4; H, 4.0; Br, 23.7; N, 4.1. C<sub>14</sub>H<sub>14</sub>BrNO<sub>4</sub> requires C, 49.4; H, 4.1; Br, 23.5; N, 4.1%).

Crystal Data. M = 340.2, Orthorhombic, a = 9.717(2), b = 11.189(2), c = 26.363(4) Å, V = 2866.3 Å<sup>3</sup>,  $D_c = 1.58$ g cm<sup>-3</sup>, Z = 8. Mo- $K_{\alpha}$  radiation,  $\lambda = 0.710$  69 Å,  $\mu = 30.5$ cm<sup>-1</sup>.

A sample consisting of well formed plates was obtained on crystallisation from ethyl acetate-light petroleum. A selected crystal (ca.  $0.25 \times 0.13 \times 0.11$  mm) was mounted in air and set up on an Enraf-Nonius CAD-4F diffractometer. The above unit cell and the orientation matrix were optimised by least-squares based on the angular co-ordinates of 25 reflections with  $15 < \theta < 18^{\circ}$ . Each independent reflection with  $\theta < 25^{\circ}$  and some equivalents were then measured in bisecting geometry using  $\omega - n\theta$  scans (n = 1.33). Intensity and orientation checks on selected reflections were performed frequently throughout data collection. Two azimuthal scans were also recorded, but a correction for absorption was found to be unnecessary. The systematic absences which were apparent, hk0; h =2n + 1, h0l; l = 2n + 1 and 0kl; k = 2n + 1, determine the space group unambiguously as Pbca.

Lorentz and polarisation corrections were applied to the 3 972 measured intensities and the data were merged to yield 1 068 independent structure factor amplitudes with  $I > 3\sigma(I)$  where, for a given reflection, I is the weighted average of the corrected intensities and  $\sigma(I)$  is the weighted average of the standard deviations as derived from the counting statistics. The location of the bromine atom was deduced from a Patterson synthesis and, after refinement, approximate co-ordinates for the other non-hydrogen atoms were determined in a  $|F|_{obs}$  Fourier synthesis. This atomic model was improved by full-matrix least-squares techniques. After anisotropic temperature factors had been introduced, a difference Fourier synthesis was computed in a search for the hydrogen atoms. These were all well-defined except for those of the phenyl substituent [C(10)-C(15)], although after further refinement, electron density was apparent close to the expected positions for H(11) and H(13)-H(15). H(12)was placed geometrically.

The hydrogen co-ordinates were included as variable parameters, subject to a series of Waser-type constraints on their bond lengths and angles,<sup>11, 12</sup> although the temperature factors were fixed at  $U_{iso} = 0.05 [0.10 \text{ for } H(11)-H(15)]$ . The phenyl substituent sits in a relatively large pocket in the crystal structure and it is subject to large amplitude thermal vibration. This is evidenced by the  $U_{ii}$  components of C(10)-C(15). The co-ordinates of these atoms are, as a result, imprecisely defined and the phenyl ring was therefore constrained to be planar. In addition, the  $U_{11}$  components of C(11)-C(15) were constrained to be 0.15(3), but this latter restriction was removed when, after refinement, the respective components for C(12)-C(15) had values of greater than 0.18 indicating that the constraint was invalid.

In the final cycles of refinement in which there were 223 variables with 41 constraints, a three-term Chebyshev series was employed as the weighting scheme.13 The final residuals were R = 0.0399 and  $R_w = 0.0449$ . All the aforementioned calculations were performed using the CRYSTALS system 12 with atomic scattering factors taken from Cromer and Mann<sup>14</sup> and Spagna<sup>15</sup> (H only). The final atomic co-ordinates are presented in the Table. A list of the anisotropic temperature factors and observed and calculated structure factors is available as Supplementary Publication number 23095 (11 pages.).\*

The crystal structure consists of pairs of molecules, related by a centre of symmetry, which are linked by hydrogen bonds O(2)-H(21) · · · O(1) as displayed in the Figure. The long axis of the molecule lies approximately parallel with the crystallographic z-axis.

Bromoketo-ester (7).-To the bromohydrin (6) (0.15 g) in ether (15 ml) at 0 °C was added dropwise a solution of chromic acid [2 ml of a solution made from Na2Cr2O72H2-O (2g), conc. sulphuric acid (1.5 ml) and water (6 ml)].

After 3 h the ethereal layer was washed with water, and sodium carbonate solution and then dried  $(MgSO_4)$  and the solvent removed. The bromo-ketone recrystallised from benzene-light petroleum as prisms, m.p. 101-102 °C, δ<sub>H</sub> (CDCl<sub>3</sub>) 7.40 (s, 5 H, Ph), 5.20 (s, 2 H, CH<sub>2</sub>Ph), 5.08, 4.90, and 4.52 (three multiplets each 1 H, CH·CH·CHBr), and 4.15 (s, 2 H, NCH<sub>2</sub>);  $\nu_{max}$  1810 ( $\alpha$ -bromo-ketone), 1770 ( $\beta$ -lactam), and 1750 cm<sup>-1</sup> (CO<sub>2</sub>CH<sub>2</sub>Ph) (Found: C, 49.9; H, 3.6; Br, 23.5; N, 4.2. C<sub>14</sub>H<sub>12</sub>BrNO<sub>4</sub> requires C, 49.7; H, 3.6; Br, 23.6; N, 4.1%).

N-Benzyloxycarbonylmethylene-3-oxo-2-azabicyclo[2.2.0]hexane (4).—The photoisomer (3;  $R = PhCH_2$ ) (0.10 g) in ethyl acetate (10 ml) was hydrogenated at atmospheric pressure and 20 °C over 5% rhodium on alumina catalyst (30 mg). The theoretical volume (10 ml) was rapidly con-The catalyst was filtered off and removal of the sumed. solvent gave the hydrogenation product  $M^+ m/z$  245.105 35. Calc. for C<sub>14</sub>H<sub>15</sub>NO<sub>3</sub> 245.105 19).

N-Carboxymethylene-3-oxo-2-azabicyclo[2.2.0]hexane (11). -The photoisomer (3;  $R = PhCH_2$ ) (0.50 g) in ethyl acetate (20 ml) was hydrogenated at atmospheric pressure and 20 °C over 10% Pd on charcoal catalyst. Exactly 2 molar equiv. of hydrogen were consumed. The catalyst was filtered off and the solvent removed from the filtrate. The residue was dissolved in water (25 ml) containing sodium carbonate (0.11 g) and the solution lyophilised to give the sodium salt;  $\delta_{\rm H}$  (D<sub>2</sub>O) 4.12 (m, CHCH), 4.02 and 3.62 (q, 2 H,  $J_{AB}$  18 Hz, NCH<sub>2</sub>CO<sub>2</sub><sup>-</sup>), 3.55 (m, 1 H, CH·CH), and 2.6-1.7 p.p.m. (m, 4 H, CH<sub>2</sub>·CH<sub>2</sub>).

Epoxy-acid (10).—The epoxy-ester (5) (0.30 g) in ethyl acetate (15 ml) was hydrogenated over 5% palladium on charcoal (50 mg) at atmospheric pressure and 20 °C. The theoretical amount of hydrogen (28 ml) was taken up in less than 1 h. The catalyst was filtered off and the solvent removed from the filtrate. The residue,  $v_{max.}$  (CHCl<sub>3</sub>) 3 000 (broad  $CO_2H$ ), 1 760 ( $\beta$ -lactam), and 1 730 cm<sup>-1</sup>  $(CO_2H)$ , was dissolved in water (20 ml) containing sodium carbonate (62 mg). The solution was lyophilised to give a quantitative yield of the sodium salt.

Bromohydrin Acid (9).—The bromohydrin ester (6) (0.10 g) in ethyl acetate (10 ml) was hydrogenated over 5% palladium on charcoal catalyst (20 mg) at atmospheric pressure and 20 °C. The theoretical amount of hydrogen (7 ml) was consumed in less than 1 h. The catalyst was filtered off and the solvent removed. The residue was dissolved in water (10 ml) containing sodium carbonate (16 mg). The solution was lyophilised to give the sodium salt quantitatively.

Bromoketo-acid (8).—The bromoketo-ester (7) was hydrogenated as described for the bromohydrin acid and converted into its sodium salt. The yield was quantitative.

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