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# X-Ray Structure of (1*RS*, 5*RS*, 7*SR*)-1-Acetoxy-7-cyano-5-methylbicyclo[3.2.0]heptan-2-one, a Photocycloadduct of 2-Acetoxy-3-methyl-2-cyclopenten-1-one and Acrylonitrile

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**Synopsis.** The main product of the photocycloaddition between 2-acetoxy-3-methyl-2-cyclopenten-1-one and acrylonitrile has been found to be (1*RS*, 5*RS*, 7*SR*)-1-acetoxy-7-cyano-5-methylbicyclo[3.2.0]heptan-2-one by means of X-ray crystal structure analysis.

Previously, we reported the synthesis of a sesquiterpene through a process involving the (2+2) photocycloaddition between a 2-acetoxy-3-methyl-2-cyclopenten-1-one (**1**) derivative and 1,1-diethoxyethylene.[1] In the course of studies on the synthesis of a related sesquiterpene, it became necessary to investigate the photoaddition of **1** with acrylonitrile (**2**). Few studies seem to have been made on the photoaddition of cycloalkenones with this electron-deficient olefin since the classical work of Corey *et al.*[2] They showed that the reaction of 2-cyclohexen-1-one with **2** was extremely slow, compared with similar reactions with electron-rich olefins, and suggested that the main products were 8-epimeric 8-cyano-*cis*-bicyclo[4.2.0]octan-2-ones. In order to establish the structure of the main product (**3**, 15.7% yield at 56% conversion) of the photocycloaddition between **1** and **2**, we have now undertaken an X-ray crystal structure analysis.

## Experimental

*Photoaddition.* A solution of **1**[3] (1 g, 6.5 mmol) and freshly-distilled **2** (10.33 g, 195 mmol) in a mixture of THF (21 ml) and EtOH (70 ml) was irradiated with a Hanovia 75-W high-pressure mercury lamp under ice-cooling and $N_2$ atmosphere. A Pyrex filter was used. After 5 h, the mercury lamp was shut off, a white polymeric deposit was removed by filtration, and the filtrate was concentrated *in vacuo*. The residual oil (2.5 g) was chromatographed on silica gel (Kanto, 40 g) using EtOAc–benzene (1 : 9) as the eluent. The first fraction contained the cycloadduct, **3** (98 mg, 7.8%): mp 100.0—101.5 °C; IR (Nujol) 2260 (C≡N), 1752 (ester C=O), 1736 $cm^{-1}$ (cyclopentanone); NMR ($CCl_4$) $\delta$=1.38 (3H, s), 1.90 (2H, m), 2.11 (3H, s), 2.14 (2H, d, $J$=6.5 Hz), 2.58 (2H, m), 3.11 (1H, t, $J$=6.5 Hz). Found: C, 63.39; H, 6.39; N, 6.72%. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32; N, 6.76%. The second fraction was an oily mixture (170 mg) of **3** and an unidentified product, **4** (2 : 1 by NMR). The third fraction was an oil composed of **4** and the other product, **5** (1 : 1 by NMR). From the fourth fraction, 443 mg of **1** was recovered.

*X-Ray Measurement.* A colorless, single crystal with dimensions of about 0.3×0.3×0.4 $mm^3$ was used. The crystal data are as follows: $C_{11}H_{13}NO_3$, mol wt 207.2, monoclinic, space group $P2_1$, $a$=13.852(4), $b$=6.750(3), $c$=13.096(4) Å, $\beta$=116.69(5)°, $Z$=4, $D_c$)=1.258 g $cm^{-3}$. The cell dimensions and diffraction intensities were measured on an automated, four-circle diffractometer with LiF-monochromated Cu $K\alpha$ radiation ($\lambda$=1.5418 Å). The $\theta$—$2\theta$ scan technique was applied at a $\theta$ scan rate of 0.5° $min^{-1}$; the background was measured for 30—60 s at each end of the scan range. Three standard reflections, measured at intervals of every 62 reflections, showed no significant decrease in intensity during the course of data collection. The intensities were corrected for the Lorentz and polarization factors, but not for the absorption or the extinction effect. In the range of $2\theta$ values up to 140°, 2229 unique structure-factor magnitudes above the $\sigma(F)$ level were selected for the structure determination.

## Structure Determination

The structure was solved by the Monte Carlo direct method,[4] using the 30 strongest reflections as the starting set. In order to extend the tentative-phase set derived from random numbers, 12 cycles of the tangent procedure were carried out using 447 $|E|$ values above 1.30. The 21st phase set led to the correct solution; an $E$-map based on 439 phases revealed the locations of all the 30 non-hydrogen atoms. After all the 26 hydrogen atoms had been located in a difference Fourier map, the structure was refined by the block-diagonal least-squares method with anisotropic temperature factors for the non-hydrogen atoms and isotropic ones for the hydrogen atoms. For this refinement, the following weighting scheme was used:

$$w = 1/\{\sigma(F)^2 \exp(AX^2 + BY^2 + CXY + DX + EY)\},$$

where $X=|F_o|$ and $Y=\sin\theta/\lambda$. The $A$, $B$, $C$, $D$, and $E$ coefficients are constants which were determined from the $(\Delta F)^2$ values; $A$=0.001199, $B$=20.61, $C$=1.079, $D$=−0.2608, and $E$=−30.11. The final $R$ value was 0.044. The final atomic parameters are listed in Table 1.†

The calculations were performed on FACOM 230-75 and HITAC M-200H computers at the Hokkaido University Computing Center, using our own programs. The atomic scattering factors were taken from the International Tables.[5]

## Results and Discussion

The two crystallographically-independent molecules, A and B, have almost the same geometries, except that their absolute configurations are opposite. The skeleton of the B molecule is drawn in Fig. 1(a); the structure of **3** has thus been established as shown in Fig. 1(b). The position of the cyano group agrees with that predicted by the frontier-orbital theory.[6] The torsion angles for the bicyclic system are given in Fig. 2. The

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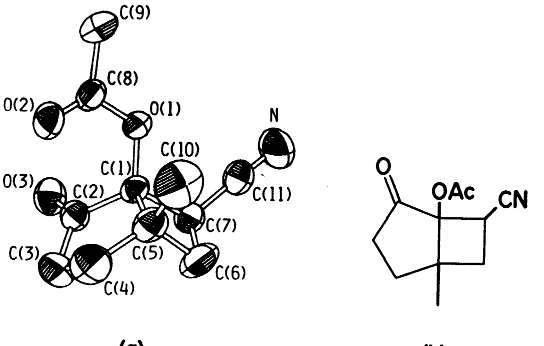
† The tables of the anisotropic temperature factors and hydrogen parameters, and the $F_o-F_c$ table are kept at the Chemical Society of Japan (Document No. 8217).

Table 1. The final atomic parameters and estimated standard deviations
The atomic coordinates are multiplied by $10^4$.

| Atom | $x$ | $y$ | $z$ | $B_{eq}$ $^{a)}$/Å$^2$ | Atom | $x$ | $y$ | $z$ | $B_{eq}$/Å$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| O(A1) | 2814(2) | 3225(4) | 4074(2) | 3.26 | O(B1) | 3076(2) | 475(4) | −556(2) | 3.71 |
| O(A2) | 2413(2) | 693(4) | 4921(2) | 4.16 | O(B2) | 1892(2) | 2069(6) | −2108(2) | 5.07 |
| O(A3) | 1038(2) | 1101(4) | 2301(2) | 4.37 | O(B3) | 943(2) | −114(6) | −716(3) | 5.22 |
| N(A) | 3179(3) | 7762(6) | 3238(4) | 4.99 | N(B) | 5118(4) | −735(11) | 2023(4) | 7.88 |
| C(A1) | 1715(2) | 3818(4) | 3638(2) | 2.86 | C(B1) | 2680(2) | 1562(5) | 104(2) | 3.25 |
| C(A2) | 919(2) | 2163(5) | 2962(3) | 3.26 | C(B2) | 1442(3) | 1391(6) | −350(3) | 3.81 |
| C(A3) | −19(3) | 2228(6) | 3258(4) | 4.10 | C(B3) | 1019(4) | 3367(9) | −216(4) | 5.71 |
| C(A4) | 384(3) | 3350(6) | 4394(3) | 4.11 | C(B4) | 1870(5) | 4884(7) | −123(4) | 5.95 |
| C(A5) | 1279(2) | 4739(5) | 4439(3) | 3.20 | C(B5) | 2948(3) | 3809(6) | 360(3) | 4.45 |
| C(A6) | 866(3) | 6540(5) | 3610(3) | 3.67 | C(B6) | 3395(5) | 3302(9) | 1645(4) | 6.18 |
| C(A7) | 1471(2) | 5774(5) | 2932(3) | 3.30 | C(B7) | 3294(3) | 1054(7) | 1394(3) | 4.23 |
| C(A8) | 3074(3) | 1607(5) | 4759(3) | 3.69 | C(B8) | 2609(3) | 909(7) | −1685(3) | 4.10 |
| C(A9) | 4254(3) | 1165(8) | 5262(5) | 5.86 | C(B9) | 3118(4) | −251(11) | −2286(4) | 6.27 |
| C(A10) | 2104(3) | 5314(7) | 5629(3) | 4.52 | C(B10) | 3796(5) | 4640(10) | 33(6) | 7.21 |
| C(A11) | 2434(3) | 6896(5) | 3109(3) | 3.59 | C(B11) | 4321(3) | 19(9) | 1736(3) | 5.20 |

a) $B_{eq}=8\pi^2(u_1^2+u_2^2+u_3^2)/3$, where $u_i$ is the root-mean-square deviation in the $i$th principal axis of the thermal ellipsoid.



(a) (b)

Fig. 1. A perspective view of the **3** molecule, and the corresponding structural formula.

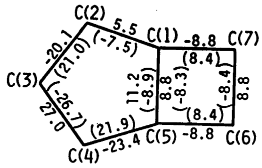


Fig. 2. The torsion angles ($\phi$/°) for the bicyclic system. The values for the B molecule are given in parentheses.

cyclopentanone ring takes a half-chair form; the C(4) and C(3) atoms deviate from the C(2)–C(1)–C(5) plane onto the side of the acetyl group and the opposite side, respectively. It should be noted that the acetyl oxygen atom, O(2), approaches closely the ketonic carbon atom, C(2); their distance is 2.661(3) and 2.682(5) Å for the A and B molecules respectively. In this connection, the C(2) atom deviates slightly from the plane through the C(1), C(3), and O(3) atoms onto the side of the O(2) atom; this deviation is 0.018 and 0.011 Å for the A and B molecules respectively. The cyclobutane ring is somewhat puckered; the puckering angle is about 12° for both molecules.

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