0·028 (1) Å]. The other is clearly out of this plane [$d_{Si2}$ = 0·234 (1) Å]. It has been noted (Colvin, 1981) for bis(trimethylsilyl)arylsilanes that, owing to steric acceleration, the first displacement of a silyl group (Si1) occurs 40–400 times more rapidly than does the second (Si2). An explanation of this highly regioselective desilylation could be found in the fact that the Si2 trimethylsilyl group is out of the plane defined by the phenyl ring, so determining the rate of the C—Si bond cleavage.

The *B* ring is in a half-chair conformation in which C4, C5, C8 and C9 are coplanar while C7 and C6 are symmetrically positioned. The *C* ring has a near regular chair conformation.

The *D* ring is in an envelope conformation with C16 at the flap. This conformation leads to some particularities in the $^1$H NMR spectra. Despite its limitations (Karplus, 1963), the Karplus equation, which relates $^3J_{H-H}$ coupling constants and dihedral angles, is a very valuable model for probing molecular geometries (Colucci, Jungk & Gandour, 1985). The structure assignment of (1), made at the same time by two-dimensional NMR techniques, has revealed some surprising vicinal coupling constants especially between H16 and H10 ($J_{calc}$ = 3·8, $J_{obs}$ = 4·7 Hz), H12 and H10 ($J_{calc}$ = 2·3, $J_{obs}$ = 3 Hz) and H15 and H10 ($J_{calc}$ = 1·2, $J_{obs}$ = 0 Hz), which could be explained by the corresponding dihedral angles [H16—C16—C13/H10—C13—C16 = 50 (2); H12—C14—C13/H10—C13—C14 = 61 (2); H15—C16—C13/H10—C13—C16 = 108 (2)°].

J-PG and MM are indebted to Professor K. Peter C. Vollhardt for his continuous interest in this work. This study is part of a collaborative program: Conférences des Grandes Ecoles Françaises–University of California at Berkeley. We thank CNRS, NSF and Roussel-UCLAF for financial support, to J-PG.

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# Structure of 5-Hydroxy-2,2-dimethyl-5-phenyl-2,5-dihydrofuran-3-carbonitrile

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**Abstract.** $C_{13}H_{13}NO_2$, $M_r$ = 215·3, monoclinic, $P2_1/n$, $a$ = 15·299 (4), $b$ = 10·661 (4), $c$ = 14·887 (3) Å, $\beta$ = 90·29 (2)°, $V$ = 2428 (2) Å$^3$, $Z$ = 8, $D_x$ = 1·18 g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71073 Å, $\mu$ = 0·7 cm$^{-1}$, $F$(000) = 912, $T$ = 294 K, $R$ = 0·044 for 1418 observed reflections. The analysis establishes the structure of this reaction product. The two independent molecules in the asymmetric unit differ only in the orientation of the phenyl ring with respect to the furan ring. Molecular dimensions are normal; the molecules are linked by O—H···O hydrogen bonds [O···O 2·767 (5) and 2·957 (5) Å].

**Introduction.** The 3(2*H*)-furanone nucleus (I) occurs in a number of natural products, some of which have antitumour properties. Bullatenone (II) (Brandt & Taylor, 1954; Parker, Raphael & Wilkinson, 1958) is the simplest of these naturally occurring furanones. In an attempt to develop a short synthesis of bullatenone and its derivatives, we examined the

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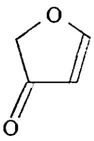
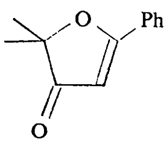
reaction which involved the thermolysis of oxadiazoline (III) in the presence of excess α-chloroacrylonitrile; this gave one product of molecular formula $C_{13}H_{13}NO_2$, for which the cyanohydrin (IV) or hemiketal (V) structures were considered likely. The spectral properties of the compound did not allow us to assign the structure unambiguously but this was clarified by our X-ray analysis which establishes (V) as the correct structure.



(I)



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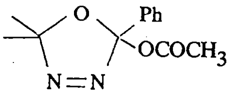

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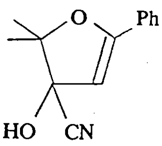

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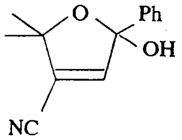

(V)

**Experimental.** 5-Acetoxy-2,2-dimethyl-5-phenyl-2,5-dihydro-1,3,4-oxadiazole (III) (Yeung, MacAlpine & Warkentin, 1978) and α-chloroacrylonitrile were refluxed in dry benzene (50 ml) for 10 min. Evaporation of the solvent and radial chromatography of the residue on silica using a petroleum spirit–ethyl acetate gradient (7·5–20%) as eluant, gave a white solid (0·75 g, 41%) thought to be (IV) or (V); m.p. 355·5–356·5 K (found: C 72·6, H 5·95, N 6·6; $C_{13}H_{13}NO_2$ requires C 72·6, H 6·0, N 6·5%).

Table 1. *Positional and thermal parameters with e.s.d.'s in parentheses*

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameters defined as:

$$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

| | *x* | *y* | *z* | *B* |
|---|---|---|---|---|
| O1*A* | 0·4876 (2) | 0·1052 (3) | 0·1825 (3) | 4·22 (9) |
| O2*A* | 0·5242 (3) | 0·2014 (3) | 0·0488 (2) | 4·55 (9) |
| N*A* | 0·7681 (4) | −0·0353 (6) | 0·2776 (4) | 8·3 (2) |
| C2*A* | 0·5449 (4) | 0·0170 (5) | 0·2281 (4) | 3·7 (1) |
| C3*A* | 0·6334 (3) | 0·0745 (5) | 0·2145 (4) | 3·6 (1) |
| C4*A* | 0·6285 (3) | 0·1818 (5) | 0·1696 (4) | 3·6 (1) |
| C5*A* | 0·5354 (4) | 0·2058 (5) | 0·1417 (4) | 3·7 (1) |
| C6*A* | 0·5193 (4) | 0·0103 (6) | 0·3254 (4) | 5·7 (2) |
| C7*A* | 0·5364 (4) | −0·1112 (5) | 0·1821 (4) | 4·9 (2) |
| C8*A* | 0·7095 (4) | 0·0162 (5) | 0·2485 (4) | 5·1 (2) |
| C9*A* | 0·4997 (3) | 0·3318 (5) | 0·1746 (4) | 3·4 (1) |
| C10*A* | 0·4584 (4) | 0·3427 (5) | 0·2555 (4) | 5·9 (2) |
| C11*A* | 0·4298 (5) | 0·4584 (6) | 0·2855 (5) | 7·5 (2) |
| C12*A* | 0·4390 (4) | 0·5613 (5) | 0·2329 (5) | 6·4 (2) |
| C13*A* | 0·4794 (4) | 0·5523 (5) | 0·1528 (4) | 6·3 (2) |
| C14*A* | 0·5087 (4) | 0·4375 (5) | 0·1225 (4) | 5·3 (2) |
| O1*B* | 0·7237 (2) | −0·1049 (3) | 0·0357 (2) | 4·16 (9) |
| O2*B* | 0·6148 (2) | 0·0101 (3) | −0·0352 (2) | 4·18 (9) |
| N*B* | 0·7981 (4) | −0·3885 (5) | −0·2005 (3) | 6·5 (1) |
| C2*B* | 0·7505 (4) | −0·2276 (5) | 0·0040 (4) | 4·2 (1) |
| C3*B* | 0·7513 (3) | −0·2073 (5) | −0·0961 (3) | 3·5 (1) |
| C4*B* | 0·7263 (3) | −0·0932 (5) | −0·1194 (3) | 3·5 (1) |
| C5*B* | 0·7044 (3) | −0·0210 (4) | −0·0359 (3) | 3·3 (1) |
| C6*B* | 0·6841 (5) | −0·3246 (6) | 0·0327 (4) | 6·3 (2) |
| C7*B* | 0·8408 (4) | −0·2537 (7) | 0·0413 (4) | 6·7 (2) |
| C8*B* | 0·7760 (4) | −0·3086 (5) | −0·1559 (4) | 4·7 (1) |
| C9*B* | 0·7558 (3) | 0·0997 (5) | −0·0249 (3) | 3·9 (1) |
| C10*B* | 0·8265 (4) | 0·1058 (6) | 0·0318 (4) | 5·6 (2) |
| C11*B* | 0·8749 (5) | 0·2154 (7) | 0·0384 (5) | 8·2 (2) |
| C12*B* | 0·8528 (5) | 0·3155 (7) | −0·0142 (5) | 8·8 (2) |
| C13*B* | 0·7830 (6) | 0·3110 (6) | −0·0701 (5) | 8·4 (2) |
| C14*B* | 0·7329 (5) | 0·2025 (6) | −0·0770 (4) | 5·7 (2) |

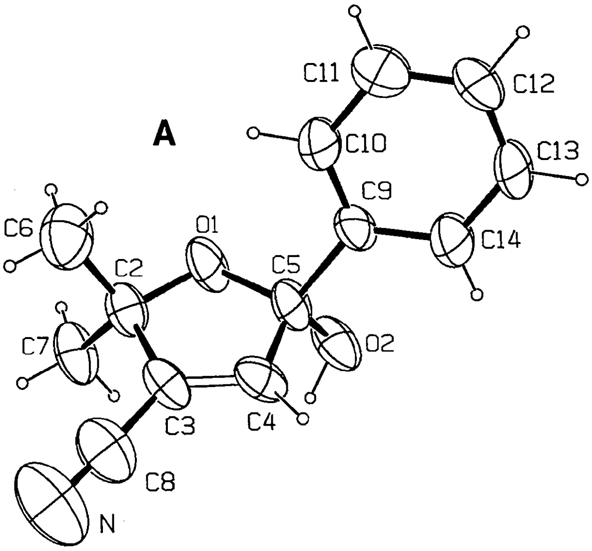

Fig. 1. A view of molecule *A* with the atomic numbering scheme. Ellipsoids are at the 50% probability level.

Colourless plate-shaped crystals were grown from 5% ethyl acetate in hexane over *ca* ten days in a freezer at 253 K. Accurate cell dimensions and crystal orientation matrix were determined on a CAD-4 diffractometer by a least-squares treatment of the setting angles of 25 reflections in the range $8 < \theta < 14°$. Crystal dimensions 0·10 × 0·25 × 0·30 mm; intensities of reflections with indices *h* −14 to 14, *k* 0 to 10, *l* 0 to 14, with $2 < 2\theta < 40°$ measured; $\omega$–$2\theta$ scans, $\omega$-scan width $(0{\cdot}7 + 0{\cdot}35 \tan\theta)°$; graphite-monochromated Mo $K\alpha$ radiation; intensities of three reflections measured every 2 h showed no evidence of crystal decay. 2612 reflections measured, 2262 unique ($R_{int}$ 0·022) and 1418 with $I > 3\sigma(I)$ labelled observed and used in structure solution and refinement. Data corrected for Lorentz and polarization effects. No correction for absorption required. Space group $P2_1/n$ uniquely from the systematic absences ($h0l$ absent if $h + l = 2n + 1$; $0k0$ absent if $k = 2n + 1$). There are two independent molecules in the asymmetric unit, and the structure was solved with the aid of *MULTAN*82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Refinement was by full-matrix least-squares calculations on $F$, initially with isotropic and then with anisotropic thermal parameters. Difference maps showed maxima in positions consistent with the expected locations of the H atoms; in the final rounds of calculations, the H atoms were positioned on geometrical grounds (C—H, O—H 0·95 Å) and included (as riding atoms) in the structure-factor calculations with an overall $B_{\rm iso}$ of 7·0 Å$^2$. The final cycle of refinement included 289 variable parameters, $R = 0{\cdot}044$, $wR = 0{\cdot}053$, goodness of fit 1·43, $w = 1/[\sigma^2(F_o) + 0{\cdot}055(F_o)^2]$. Max. shift/e.s.d. 0·03; density in final difference map ± 0·43 e Å$^{-3}$; there were no chemically significant features. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All calculations were performed on a PDP11/73 computer using *SDP-Plus* (B. A. Frenz & Associates Inc., 1983). Atomic coordinates† and details of molecular geometry are given in Tables 1 and 2. Fig. 1 is a view of one of the two independent molecules prepared using *ORTEP*II (Johnson 1976).

**Discussion.** Our analysis establishes that the principal product from the reaction of the oxadiazole (III) with α-chloroacrylonitrile has structure (V), the wrong one for bullatenone syntheses. There are two independent molecules in the asymmetric unit (one is shown in Fig. 1); they differ in their mode of hydrogen bonding and slightly in conformation. The dihydrofuran ring is approximately planar in each molecule; in molecule *A*, the interplanar angle between the phenyl- and furan-ring planes is 69·3° (64·5° for molecule *B*). The molecules are linked to form centrosymmetric tetramers by O—H···O hydrogen bonds [O2*A*—H···O2*B* 2·767 (5) Å, O2*B*—H···O1*A** 2·957 (5) Å].

The molecular dimensions are mostly unexceptional; the only angle which differs significantly from the usual values associated with five-membered ring systems or unstrained $sp^2$ or $sp^3$ hybridization is found in both molecules with C4—C3—C8 [127·2 (5) in *A* and 126·9 (5)° in *B*]; this probably arises to accommodate *cis* steric interaction of the cyano carbon C8 with the hydrogen on the neighbouring atom C4 [the C2—C3—C8 angles are 121·0 (5) and 120·2 (5)° in *A* and *B* respectively]. Apart from the hydrogen bonds noted above, there are no untoward intermolecular contacts.

Table 2. *Bond lengths* (Å), *bond angles* (°) *and hydrogen-bond lengths* (Å)

| | | | |
|---|---|---|---|
| O1*A*—C2*A* | 1·451 (6) | O1*B*—C2*B* | 1·451 (6) |
| O1*A*—C5*A* | 1·435 (6) | O1*B*—C5*B* | 1·423 (6) |
| O2*A*—C5*A* | 1·393 (6) | O2*B*—C5*B* | 1·411 (6) |
| N*A*—C8*A* | 1·135 (8) | N*B*—C8*B* | 1·132 (8) |
| C2*A*—C3*A* | 1·501 (7) | C2*B*—C3*B* | 1·506 (8) |
| C2*A*—C6*A* | 1·504 (8) | C2*B*—C6*B* | 1·511 (9) |
| C2*A*—C7*A* | 1·534 (7) | C2*B*—C7*B* | 1·513 (9) |
| C3*A*—C4*A* | 1·327 (7) | C3*B*—C4*B* | 1·321 (7) |
| C3*A*—C8*A* | 1·412 (8) | C3*B*—C8*B* | 1·451 (8) |
| C4*A*—C5*A* | 1·504 (7) | C4*B*—C5*B* | 1·502 (7) |
| C5*A*—C9*A* | 1·533 (7) | C5*B*—C9*B* | 1·516 (7) |
| C9*A*—C10*A* | 1·368 (8) | C9*B*—C10*B* | 1·371 (8) |
| C9*A*—C14*A* | 1·376 (8) | C9*B*—C14*B* | 1·387 (8) |
| C10*A*—C11*A* | 1·384 (9) | C10*B*—C11*B* | 1·387 (10) |
| C11*A*—C12*A* | 1·355 (9) | C11*B*—C12*B* | 1·366 (10) |
| C12*A*—C13*A* | 1·348 (10) | C12*B*—*C13B* | 1·350 (11) |
| C13*A*—C14*A* | 1·380 (8) | C13*B*—C14*B* | 1·392 (9) |
| | | | |
| C2*A*—O1*A*—C5*A* | 112·0 (4) | C2*B*—O1*B*—C5*B* | 112·4 (4) |
| O1*A*—C2*A*—C3*A* | 102·4 (4) | O1*B*—C2*B*—C3*B* | 101·3 (4) |
| O1*A*—C2*A*—C6*A* | 108·8 (4) | O1*B*—C2*B*—C6*B* | 107·8 (5) |
| O1*A*—C2*A*—C7*A* | 108·6 (4) | O1*B*—C2*B*—C7*B* | 109·4 (5) |
| C3*A*—C2*A*—C6*A* | 112·8 (5) | C3*B*—C2*B*—C6*B* | 112·3 (5) |
| C3*A*—C2*A*—C7*A* | 112·2 (4) | C3*B*—C2*B*—C7*B* | 112·7 (5) |
| C6*A*—C2*A*—C7*A* | 111·5 (5) | C6*B*—C2*B*—C7*B* | 112·6 (5) |
| C2*A*—C3*A*—C4*A* | 111·8 (5) | C2*B*—C3*B*—C4*B* | 112·9 (5) |
| C2*A*—C3*A*—C8*A* | 121·0 (5) | C2*B*—C3*B*—C8*B* | 120·2 (5) |
| C4*A*—C3*A*—C8*A* | 127·2 (5) | C4*B*—C3*B*—C8*B* | 126·9 (5) |
| C3*A*—C4*A*—C5*A* | 109·7 (4) | C3*B*—C4*B*—C5*B* | 108·7 (4) |
| O1*A*—C5*A*—O2*A* | 109·5 (4) | O1*B*—C5*B*—O2*B* | 109·8 (4) |
| O1*A*—C5*A*—C4*A* | 103·9 (4) | O1*B*—C5*B*—C4*B* | 104·6 (4) |
| O1*A*—C5*A*—C9*A* | 109·6 (4) | O1*B*—C5*B*—C9*B* | 110·3 (4) |
| O2*A*—C5*A*—C4*A* | 112·4 (4) | O2*B*—C5*B*—C4*B* | 110·4 (4) |
| O2*A*—C5*A*—C9*A* | 107·8 (4) | O2*B*—C5*B*—C9*B* | 107·7 (4) |
| C4*A*—C5*A*—C9*A* | 113·6 (4) | C4*B*—C5*B*—C9*B* | 114·0 (4) |
| N*A*—C8*A*—C3*A* | 176·5 (6) | N*B*—C8*B*—C3*B* | 177·3 (6) |
| C5*A*—C9*A*—C10*A* | 121·6 (5) | C5*B*—C9*B*—C10*B* | 120·9 (5) |
| C5*A*—C9*A*—C14*A* | 120·0 (5) | C5*B*—C9*B*—C14*B* | 118·7 (5) |
| C10*A*—C9*A*—C14*A* | 118·4 (5) | C10*B*—C9*B*—C14*B* | 120·2 (5) |
| C9*A*—C10*A*—C11*A* | 120·5 (6) | C9*B*—C10*B*—C11*B* | 120·2 (6) |
| C10*A*—C11*A*—C12*A* | 120·1 (6) | C10*B*—C11*B*—C12*B* | 119·2 (7) |
| C11*A*—C12*A*—C13*A* | 120·2 (6) | C11*B*—C12*B*—C13*B* | 121·3 (7) |
| C12*A*—C13*A*—C14*A* | 120·2 (6) | C12*B*—C13*B*—C14*B* | 120·6 (6) |
| C9*A*—C14*A*—C13*A* | 120·5 (6) | C9*B*—C14*B*—C13*B* | 118·5 (6) |
| | | | |
| O2*A*—H···O2*B* | 2·767 (5) | | |
| O2*B*—H···O1*A** | 2·957 (5) | | |

* Refers to equivalent position: $1 - x$, $-y$, $-z$.

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† Lists of structure factors, thermal parameters, calculated H-atom coordinates and mean planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52647 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.