

Fig. 1. Tracé ORTEP (Johnson, 1965) de la molécule de MPP. Les ellipsoïdes sont représentés à 50% de probabilité.

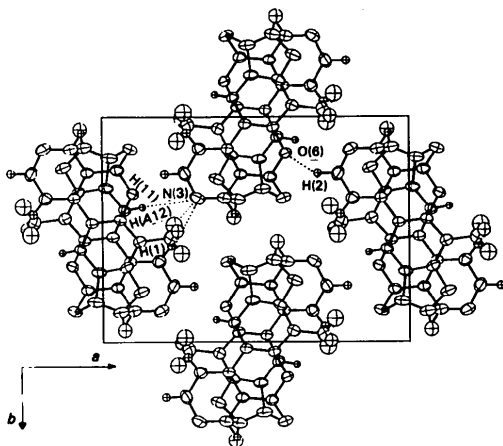


Fig. 2. Projection de la structure parallèlement à l'axe  $Oz$ . Les contacts  $C-H\cdots O$  et  $C-H\cdots N$  sont représentés en pointillés.

1980,*a,b*; Dall'acqua, Benetollo & Bombieri, 1981). La cohésion du cristal est renforcée par des interactions  $CH\cdots O$  et  $CH\cdots N$  [dont l'importance a été mise en évidence par Berkovitch-Yellin & Leiserowitz (1984)], ainsi que par des interactions résultant du recouvrement des orbitales  $\pi$  de molécules parallèles et super-

posées (forces de 'stacking'), la distance entre plans moyens de molécules étant de 3,42 Å (cf. la Fig. 2).

Intéactions  $CH\cdots O$  et  $CH\cdots N$ :  $O(6^i)\cdots H(2^{iv})$ : 2,78;  $N(3^i)\cdots H(1^{ii})$ : 2,735;  $N(3^i)\cdots H(11^{ii})$ : 2,853;  $N(3^i)\cdots H(A12^v)$ : 2,884 Å avec: (i)  $x, y, z$ ; (ii)  $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ ; (iii)  $-x, -y, -z$ ; (iv)  $\frac{3}{2}+x, \frac{3}{2}-y, \frac{3}{2}+z$ ; (v)  $\frac{1}{2}+x, \frac{3}{2}+y, \frac{1}{2}+z$ .

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#### Références

- BERKOVITCH-YELLIN, Z. & LEISEROWITZ, L. (1984). *Acta Cryst.* B40, 159–165.
- BLAIS, J., VIGNY, P., MORON, J. & BISAGNI, E. (1984). *Photochem. Photobiol.* 39, 145–156.
- BRASIC, G. & BIDEAU, J. P. (1978). *Cryst. Struct. Commun.* 7, 633–636.
- BRASIC, G. & BIDEAU, J. P. (1979). *Cryst. Struct. Commun.* 8, 695–698.
- BRASIC, G. & BIDEAU, J. P. (1980a). *Cryst. Struct. Commun.* 9, 243–246.
- BRASIC, G. & BIDEAU, J. P. (1980b). *Cryst. Struct. Commun.* 9, 705–708.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.
- DALL'ACQUA, F. (1977). *Research in Photobiology*, édité par A. CASTELLANI, pp. 245–255. New York et Londres: Plenum.
- DALL'ACQUA, F., BENETOLLO, F. & BOMBIERI, G. (1981). *Cryst. Struct. Commun.* 10, 505–509.
- DELETTRE, J., DELAITRE, M. E., VIGNY, P. & BISAGNI, E. (1986). *Acta Cryst.* C42, 1849–1851.
- DELETTRE, J., MORNON, J. P. & LEPICARD, G. (1980). *Acta Cryst.* B36, 1430–1435.
- DUBERTRET, L., AVERBECK, D., BISAGNI, E., MORON, J., MOUSTACCHI, E., BILLARDON, C., PAPADOPOULOU, D., NOCENTINI, D., VIGNY, P., BLAIS, J., BENSASSON, R., RONFART-HARET, J. C., LAND, E. J., ZAJDELA, F. & LатарJET, R. (1985). *Biochimie*, 67, 417–422.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–376.
- JOHNSON, C. K. (1965). ORTEP. Rapport ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- MORON, J., NGUYEN, C. H. & BISAGNI, E. (1983). *J. Chem. Soc. Perkin. Trans.* 1, pp. 225–229.
- QUEVAL, P. & BISAGNI, E. (1974). *Eur. J. Med. Chem.* 9, 335–340.

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## An Unexpected Product from the Oxidation of Uric Acid in Anhydrous Methanol

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**Abstract.** 5-Ureido-5-methoxybarbituric acid,  $C_6H_8N_4O_5$ ,  $M_r = 216.2$ , orthorhombic,  $P_{can}$ ,  $a = 7.907(2)$ ,  $b = 17.686(4)$ ,  $c = 12.207(2)$  Å,  $V = 1707(1)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.68$  Mg m<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu(Mo K\alpha) = 0.1592$  mm<sup>-1</sup>,  $F(000) = 896$ ,  $T = 293$  K,  $R = 0.0565$ , 1092 unique reflections. The

molecule is a methoxy- and urea-C(5)-substituted barbituric acid and has approximate mirror symmetry. Bond lengths and bond angles are normal.

**Introduction.** Kozluk & Spenser (1985) were attempting to add two hydroxyl groups to the C(4)=C(5) double bond in uric acid by oxidation with chlorine in methanol and were interested in knowing the structure of the product, particularly with respect to the configuration of the hydroxyl groups. We have examined the product of the reaction by X-ray crystallography and shown that it is not the desired product. Instead ring opening has occurred at the N(9)–C(5) bond, yielding the compound whose structure is described in this paper.

**Experimental.** Prepared by the reaction of uric acid with chlorine in anhydrous methanol (Kozluk & Spenser, 1985), colourless plates recrystallized from methanol. Cut to give right parallelepiped 0.3 × 0.3 × 0.06 mm. Nicolet P3 automatic diffractometer. Unit-cell parameters from 15 well centred reflections 30 > 2θ > 19°. No absorption correction, maximum error in  $F_o$  < 1.5%. Intensity measurement 2θ:θ scan, minimum rate 5° min<sup>-1</sup>, maximum rate 29.3° min<sup>-1</sup>.  $2(\sin\theta)/\lambda_{\max} = 0.5385 \text{ \AA}^{-1}$ ,  $hk\pm l$ ,  $h$ , 0 to 8,  $k$ , 0 to 19,  $l$ , -13 to 13. 2550 reflections measured, 1132 unique reflections,  $R_{\text{int}} = 0.0233$ , 1092 with  $I > 0$  classified as observed, used in refinement.

Intensity variation of two standards (072, 133) < 1.2%. Structure solved by direct methods with *SHELX76* (Sheldrick, 1976). Structure refined by full-matrix least squares (*SHELX76*) on  $F$ . Final refinement cycles included anisotropic temperature factors for all non-hydrogen atoms. H atoms were located and refined isotropically. Final  $R = 0.0565$ ,  $wR = 0.0535$ ,  $S = 1.3885$ ,  $w = (\sigma^2)^{-1}$ ; maximum and minimum heights in final difference Fourier map 0.320 and  $-0.287 \text{ e \AA}^{-3}$  at  $x = 0.3311$ ,  $y = 0.3621$ ,  $z = 0.2989$  and  $x = 0.3400$ ,  $y = 0.800$ ,  $z = 0.200$  respectively.

Maximum least-squares  $\Delta/\sigma$  0.044 for all atoms. Atomic scattering factors from Cromer & Waber (1974). All crystallographic calculations performed on a Cyber 170/815. Initial data treatment used *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), diagrams prepared with *ORTEPII* (Johnson, 1976). Least-squares planes, dihedral and torsional angles by *NRC22* (Ahmed & Pippy, 1978). Atomic positional parameters are given in Table 1.\*

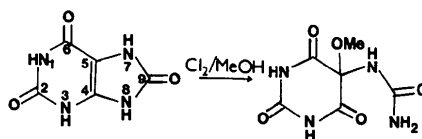
\* Lists of structure factors, anisotropic thermal parameters, H atom parameters, best least-squares-planes data, torsion angles and a proposed reaction scheme have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43248 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ( $\times 10^4$ , H atoms  $\times 10^3$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ )

	x	y	z	$U_{\text{eq}}$ or $U_{\text{iso}}$
N(1)	5322 (3)	4504 (2)	1156 (2)	30 (2)*
C(2)	6477 (4)	3972 (2)	840 (2)	28 (2)*
N(3)	5842 (3)	3309 (2)	407 (2)	30 (2)*
C(4)	4177 (4)	3136 (2)	258 (2)	28 (2)*
C(5)	2872 (3)	3681 (2)	743 (3)	29 (2)*
C(6)	3608 (4)	4452 (2)	1063 (2)	30 (2)*
N(7)	1492 (3)	3778 (2)	-11 (2)	34 (2)*
C(8)	1828 (4)	3997 (2)	-1048 (3)	29 (2)*
N(9)	506 (4)	4129 (2)	-1700 (3)	46 (2)*
O(2)	7991 (3)	4071 (1)	933 (2)	41 (2)*
O(4)	4756 (3)	2538 (1)	-156 (2)	36 (2)*
O(5)	2107 (3)	3337 (1)	1659 (2)	41 (2)*
C(5')	3223 (6)	3095 (3)	2511 (4)	64 (3)*
O(6)	2712 (3)	4990 (1)	1245 (2)	51 (2)*
O(8)	3326 (2)	4055 (1)	-1353 (2)	33 (1)*
H(1)	575 (4)	492 (2)	133 (3)	3 (1)
H(3)	662 (5)	295 (3)	152 (4)	8 (1)
H(51)	247 (5)	286 (2)	305 (3)	6 (1)
H(52)	433 (9)	328 (4)	267 (6)	16 (3)
H(53)	416 (6)	269 (3)	240 (4)	8 (1)
H(7)	49 (5)	374 (2)	23 (3)	4 (1)
H(91)	83 (5)	421 (2)	-232 (4)	5 (1)
H(92)	-51 (5)	416 (2)	-135 (3)	5 (1)

$$* U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

**Discussion.** The reaction of chlorine in methanol with uric acid has caused methoxy addition at C(5) and has opened up the five-membered ring of the purine by breaking the N(9)–C(4) bond with concomitant addition of oxygen at C(4) as shown.



The resultant molecule is a barbituric acid, urea- and methoxy-substituted at C(5).

The molecule is shown in Fig. 1 and the bond lengths and angles are given in Table 2. The molecule has pseudo-mirror symmetry; equivalent bond lengths and angles agree very well except N(1)–C(2), C(2)–N(3); C(4)–O(4), C(6)–O(6); and N(1)–C(2)–O(2), N(3)–C(2)–O(2) (see below). Bond lengths and angles within the barbituric acid moiety are generally within  $2\sigma$  [ $\sigma = (\sigma_1^2 + \sigma_2^2)^{1/2}$ ] of the corresponding average parameters in barbituric acids (Voet, 1972; Craven, Vizzini & Rodriguez, 1969; Craven & Vizzini, 1969; McMullan, Fox & Craven, 1978; Williams, 1974; Gartland & Craven, 1974; Hsu & Craven, 1974). Exceptions are C(4)–C(5) and C(5)–C(6) which are both larger by  $2.2\sigma$  and N(1)–C(5)–O(6), which is larger by  $2.6\sigma$  than the average. In addition, all distances and angles lie within the range observed previously except C(4)–C(5), C(5)–C(6), C(6)–N(1) and N(3)–C(4)–C(5).

Table 2. Bond lengths (Å) and angles (°)

N(1)—C(2)	1.367 (4)	C(8)—O(8)	1.246 (4)
C(4)—C(5)	1.533 (5)	O(5)—C(5')	1.430 (5)
C(2)—O(2)	1.215 (4)	N(3)—O(4)	1.364 (4)
N(7)—C(8)	1.350 (4)	C(6)—N(1)	1.363 (4)
O(5)—O(5)	1.409 (4)	C(5)—N(7)	1.438 (4)
C(2)—N(3)	1.381 (4)	C(8)—N(9)	1.334 (5)
C(5)—C(6)	1.533 (4)	C(6)—O(6)	1.207 (4)
C(4)—O(4)	1.218 (4)		
C(6)—N(1)—C(2)	126.4 (3)	C(4)—C(5)—N(7)	109.8 (3)
N(3)—C(4)—C(5)	117.2 (3)	C(5)—N(7)—C(8)	119.0 (3)
N(1)—C(2)—O(2)	122.2 (3)	O(8)—C(8)—N(9)	123.5 (3)
C(5)—C(4)—O(4)	121.6 (3)	C(5)—O(5)—C(5')	116.2 (3)
O(5)—C(5)—N(7)	103.5 (2)	C(2)—N(3)—C(4)	126.4 (3)
N(7)—C(8)—O(8)	119.4 (3)	C(5)—C(6)—N(1)	117.4 (3)
C(6)—C(5)—O(5)	110.2 (3)	N(3)—C(4)—O(4)	121.0 (3)
N(1)—C(6)—O(6)	121.0 (3)	C(6)—C(5)—N(7)	110.3 (3)
N(1)—C(2)—N(3)	116.7 (3)	N(7)—C(8)—N(9)	117.1 (3)
C(4)—C(5)—C(6)	113.8 (2)	C(4)—C(5)—O(5)	108.9 (3)
N(3)—C(2)—O(2)	121.1 (2)	C(5)—C(6)—O(6)	121.7 (3)

## Hydrogen bonds

N—H...O	N...O	N—H	H...O	N—H...O
N(1)—H(1)...O(8)	2.773 (4)	0.84 (4)	1.95 (3)	160 (3)
N(3)—H(3)...O(4)	2.833 (3)	0.94 (4)	1.93 (4)	160 (4)
N(7)—H(7)...O(2)	3.043 (3)	0.85 (4)	2.23 (4)	160 (3)
N(9)—H(91)...O(2)	3.126 (5)	0.81 (5)	2.34 (5)	164 (4)
N(9)—H(92)...O(6)	3.035 (4)	0.92 (4)	2.30 (4)	137 (3)

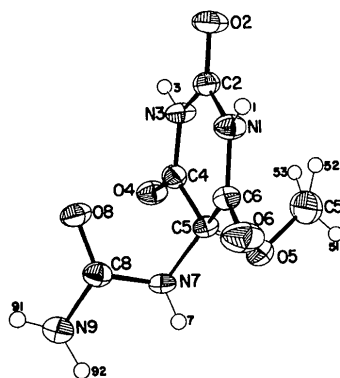
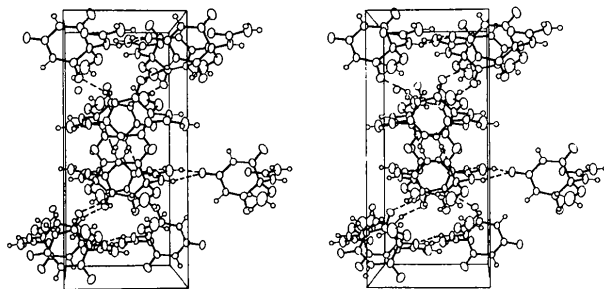


Fig. 1. The molecule showing the atom numbering. Hydrogen atoms are labelled by affixes only in smaller print.

Fig. 2. The packing within the unit cell. **a** and **b** are parallel to the bottom and sides of the page respectively and the view is down **c**. Hydrogen bonds are shown by dotted lines.

Craven, Cusatis, Gartland & Vizzini (1973) have examined how small differences in distances and angles within barbituric acids differ with hydrogen bonding to the ketonic groups. Although the C—O groups in our compound probably do not differ significantly in length  $\{[C(4)—O(4)] - [C(6)—O(6)] = 1.94\sigma\}$  the lengths are as expected for the hydrogen bonding  $[C(4)—O(4)$ , one medium H bond  $> C(2)—O(2)$ , two weak H bonds  $> C(6)—O(6)$ , one weak H bond]. The difference in the  $N(1)—C(2)$ ,  $C(2)—N(3)$  distances is in the direction observed by Craven *et al.* (1973), although the expected differences in  $C(6)—N(1)$ ,  $C(4)—N(3)$  and  $C(5)—C(4)$ ,  $C(4)—C(6)$  were not observed. Craven *et al.* (1973) did not examine differences in  $N(1)—C(2)—O(2)$ ,  $N(3)—C(2)—O(2)$ .

The barbiturate ring is not quite planar, but is distorted nearly symmetrically with respect to the  $C(2)\cdots C(5)$  line. The distortions are much greater than in other structures examined by Craven *et al.* (1973) and, in contrast to these structures, one of the amide groups differs significantly from planarity  $[C(5)C(4)N(3)O(4): C(5), -0.011(4) \text{ \AA}, C(4), 0.035(3) \text{ \AA}, N(3), -0.009(3) \text{ \AA}, O(4), -0.007(2) \text{ \AA}]$ . Bond lengths and angles within the urea moiety agree reasonably well with previous results (Kobelt & Paulus, 1972; Wawrzak, Grochulski, Karniewicz, Galdecki & Glowka, 1981; Prout, Fail, Hernandez-Casson & Miao, 1982).

The packing is shown in Fig. 2. Most interactions are van der Waals, although there is a three-dimensional hydrogen-bonding network. The fairly strong hydrogen bond  $N(1)—H(1)\cdots O(8)$  joins molecules in the **b** direction, weak  $N(7)—H(7)\cdots O(2)$  and  $N(9)—H(92)\cdots O(6)$  in the **a** direction, very weak  $N(9)—H(91)\cdots O(2)$  in the **c** direction and medium  $N(3)—H\cdots O(4)$  in the **b** and **c** directions.

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## References

- AHMED, F. R. & PIPPY, M. E. (1978) *NRC-22*. National Research Council of Canada, Ottawa, Canada.
- CRAVEN, B. M., CUSATIS, C., GARTLAND, G. L. & VIZZINI, E. A. (1973). *J. Mol. Struct.* **16**, 331–342.
- CRAVEN, B. M. & VIZZINI, E. A. (1969). *Acta Cryst.* **B25**, 1994–2009.
- CRAVEN, B. M., VIZZINI, E. A. & RODRIGUEZ, M. M. (1969). *Acta Cryst.* **B25**, 1978–1993.
- CROMER, D. J. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B, pp. 99–101. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- GARTLAND, G. L. & CRAVEN, B. M. (1974). *Acta Cryst.* **B30**, 980–987.
- Hsu, I.-N. & CRAVEN, B. M. (1974). *Acta Cryst.* **B30**, 988–993.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
- KOBELT, D. & PAULUS, E. F. (1972). *Acta Cryst.* **B28**, 3452–3457.

- KOZLUK, T. & SPENSER, I. D. (1985). Private communication.  
 McMULLAN, R. K., FOX, R. O. & CRAVEN, B. M. (1978). *Acta Cryst.* B34, 3719–3722.  
 PROUT, K., FAIL, J., HERNANDEZ-CASSON, S. & MIAO, F. M. (1982). *Acta Cryst.* B38, 2176–2181.  
 SHELDRICK, G. M. (1976) *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976) The *XRAY76* system. Tech. Rep. TR-446. Univ. of Maryland, College Park, Maryland.  
 VOET, D. (1972). *J. Am. Chem. Soc.* 94, 8213–8222.  
 WAWRZAK, Z., GROCHULSKI, P., KARNIEWICZ, J., GALDECKI, Z. & GLOWKA, M. L. (1981). *Ferroelectrics*, 34, 157–159.  
 WILLIAMS, P. P. (1974). *Acta Cryst.* B30, 12–17.

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## 9-(2,2-Dimethylpropionyloxy)-9-(9-borabicyclo[3.3.1]nonanyl)-9-borabicyclo[3.3.1]nonane

BY GERHARD MÜLLER\* AND CARL KRÜGER

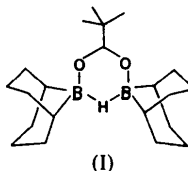
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**Abstract.** C<sub>21</sub>H<sub>38</sub>B<sub>2</sub>O<sub>7</sub>, *M<sub>r</sub>* = 344.16, monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 18.167 (1), *b* = 10.089 (1), *c* = 23.198 (1) Å, β = 97.64 (1)°, *V* = 4214.32 Å<sup>3</sup>, *Z* = 8, *D<sub>x</sub>* = 1.085 g cm<sup>-3</sup>, λ(Cu Kα) = 1.54178 Å (Ni filter), μ(Cu Kα) = 4.66 cm<sup>-1</sup>, *F*(000) = 1520, *T* = 294 K, *R* = 0.075 for 4050 unique observed reflections and 459 parameters. The title compound forms a cyclic carboxylic acid–diorganoborane adduct in which two 9-borabicyclo[3.3.1]nonanyl groups are connected by a bridging carboxylate and an additional three-centre–two-electron BHB bond. The six-membered rings OCOBHB are slightly puckered with a maximum deviation from their best plane of 0.14 Å for one ring atom. The average B–C bond length is 1.582 (9) Å and the average B–O bond length 1.52 (1) Å. The non-bonding B···B intramolecular distance is 2.496 (7) Å; the B–H bond is 1.33 (3) Å (average values). The B–H–B angle is 141 (3)° (average).

**Introduction.** In recent investigations of the dialkylhydroborane reduction of carboxylic acids, especially glucuronic acid (Köster, Idelmann & Dahlhoff, 1982), reaction intermediates with characteristic IR absorption of B–(μ-H)–B groups could be observed. Subsequent studies showed that these intermediates also occur in the reduction of simple monocarboxylic acids and established them as novel cyclic adducts of diorgano(acyloxy)boranes with diorgano(hydro)boranes. Upon substitution of the reactants with suitably bulky substituents some of these intermediates could be sufficiently stabilized to be isolable in the solid

state. Thus the reaction of pivalic acid with bis-9-borabicyclo[3.3.1]nonane (9-BBN) (Köster, 1960; Köster & Binger, 1974) in non-etheral solvents afforded 9-(2,2-dimethylpropionyloxy)-9-(9-borabicyclo[3.3.1]nonanyl)-9-borabicyclo[3.3.1]nonane (I) in quantitative yield (Idelmann, Müller, Scheidt, Schübler, Seevogel & Köster, 1984).



The novel character of this boron heterocycle as well as its alleged general role as intermediate in the reduction of carboxylic acids by boranes (Brown, 1972, 1980) prompted us to determine its crystal and molecular structure. Further impetus came from the observation that upon heating to 373 K the adduct disproportionates with elimination of bis(octane-1,5-diyl)diboroxane to give the unreduced acid and the corresponding alcohol, both as their 9-borabicyclo[3.3.1]nonanyl compounds. The disproportionation also occurs in the solid state, thereby suggesting an intermolecular reaction mechanism (Idelmann *et al.*, 1984). Thus, it was hoped that an investigation of the packing mode of these molecules in the crystal would give further insight into the mechanism leading to the observed products.

**Experimental.** Platelike crystals (0.8 × 0.2 × 0.4 mm), grown from heptane; Enraf–Nonius CAD-4 diffractometer; cell dimensions and their e.s.d.'s by least-

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