

Fig. 2. Diagram of (II) as determined by X-ray diffraction.

such that two phenyl groups are bonded to adjacent C atoms. The geometry of this cage system is the same as that found in two earlier studies of norbornadiene cage dimers (Neely, van der Helm, Marchand & Hayes, 1976; Chow, Liu & Chao, 1985). The phenyl groups are *cis* to one another (C—C—C—C torsion is -26.9°) and also *cis* to their adjacent ethoxycarbonyl groups (C—C—C—C torsions are -1.7 and -1.6°). In (II), the norbornadiene dimerization occurred involving a carbon monoxide molecule to form an open, rather than caged, fused ring system. The norbornadiene moieties are *trans* to one another across the newly formed central planar five-membered ring. Here, as in (I), the phenyl and ethoxycarbonyl moieties on adjacent C atoms are *cis* to one another (C—C—C—C torsions are -4.6 and -7.1°). However, the phenyl groups are on opposite sides of the fused ring system rather than on adjacent C atoms as in (I). There are no unusually close intermolecular approaches in either molecule where

packing appears influenced solely by van der Waals forces.

APM thanks the Robert A. Welch Foundation (Grant B-963), the Air Force Office of Scientific Research (Grant AFOSR-88-0132) and the University of North Texas, Faculty Research Committee, for financial support of this study. The NRL authors were supported in part by the Office of Naval Research, Mechanics Division.

References

- CHOW, T. J., LIU, L. K. & CHAO, Y. S. (1985). *J. Chem. Soc. Chem. Commun.* pp. 700–701.
- HARGITTAI, I., BRUNVOLL, J., CYVIN, S. J. & MARCHAND, A. P. (1986). *J. Mol. Struct.* **140**, 219–225.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- MARCHAND, A. P. & EARLYWINE, A. D. (1984). *J. Org. Chem.* **50**, 1660–1661.
- MARCHAND, A. P., EARLYWINE, A. D. & HEEG, M. J. (1986). *J. Org. Chem.* **51**, 4096–4100.
- MARCHAND, A. P., GOODIN, D. B., HOSSAIN, M. B. & VAN DER HELM, D. (1984). *J. Org. Chem.* **49**, 2897–2900.
- MARCHAND, A. P. & HAYES, B. R. (1977). *Tetrahedron Lett.* pp. 1027–1031.
- MARCHAND, A. P. & WU, A.-H. (1985). *J. Org. Chem.* **50**, 396–398.
- NEELY, S. C., VAN DER HELM, D., MARCHAND, A. P. & HAYES, B. R. (1976). *Acta Cryst.* **B32**, 561–566.
- SHELDRICK, G. M. (1980). *SHELXTL80*. Minicomputer programs for structure determination. Univ. of Göttingen, Federal Republic of Germany.
- WEISSBERGER, E. & LASZLO, P. (1976). *Acc. Chem. Res.* **9**, 209–217.

Acta Cryst. (1989). **C45**, 1174–1176

Structure of 5-Hydroxy-2,2-dimethyl-4-(*p*-toluenesulfonamido)-3-hexanone

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(Received 8 July 1987; accepted 2 February 1989)

Abstract. C₁₅H₂₃NO₄S, *M_r* = 313.41, monoclinic, *Cc*, *a* = 9.778 (4), *b* = 21.705 (5), *c* = 9.287 (4) Å, β = 121.07 (3)°, *V* = 1688.2 (1) Å³, *Z* = 4, *D_x* = 1.23 g cm⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 1.65 cm⁻¹,

F(000) = 672, *T* = 296 K, *R* = 0.049 for 1028 observed reflections. The S atom has a distorted tetrahedral coordination. A bifurcated hydrogen bond is observed between the amino N atom and the carbonyl O

0108-2701/89/081174-03\$03.00

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atom; the other half is between this amino atom and the hydroxyl atom in the molecule at $x, -y, -\frac{1}{2}+z$. There is a second intermolecular hydrogen bond between this same hydroxyl and one of the sulfonyl O atoms.

Introduction. The stereocontrolled addition of enolates to aldehydes has established itself as a valuable tool in the synthesis of acyclic polyoxygenated compounds (Heathcock *et al.*, 1985).

As part of a program aimed at developing stereocontrolled synthesis of some α -amino- β -hydroxy-carbonyl compounds which incorporate the stereochemical features of natural products such as chloramphenicol (Hahn, 1967) and erythrosphingosine (Shapiro, 1969), we investigated the kinetic deprotonation of some N-protected aminoketones followed by addition of the lithium enolates to aldehydes. Diastereomerically homogeneous α -(*p*-toluenesulfonamido)- β -hydroxyketones were obtained when 3,3-dimethyl-1-(*p*-toluenesulfonamido)-2-butanone was employed but their relative stereochemistry could not be unambiguously assigned from NMR measurements. In this paper the crystal structure of 5-hydroxy-2,2-dimethyl-4-(*p*-toluenesulfonamido)-3-hexanone is described.

Experimental. Colourless prismatic crystals grown from benzene; data collected from a crystal with dimensions $0.50 \times 0.45 \times 0.45$ mm; Enraf-Nonius CAD-4 four-circle diffractometer, cell parameters by least squares from the setting angles of 25 reflections with $9 \leq 2\theta \leq 27^\circ$; graphite-monochromated Mo $K\alpha$ radiation with 2468 integrated reflections collected up to $(\sin\theta)/\lambda = 0.549 \text{ \AA}^{-1}$, ω - 2θ scan technique, scan width $(1.0 + 0.35 \tan\theta)^\circ$, $-10 \leq h \leq 9$, $0 \leq k \leq 23$, $0 \leq l \leq 10$; variable scan rate with max. scan time 20 s per reflection; no significant decline in intensities of two standard reflections ($\bar{4}41$ and 004); Lorentz and polarization but no absorption corrections were applied. Inspection of F_c and F_o values indicated secondary-extinction correction required: $F_{\text{corr}} = F_c / (1 - 10^{-4} x F_c^2 / \sin\theta)$, where x refined to 0.01807 in the final run; 1174 independent reflections, where 1028 reflections with $I \geq 3\sigma(I)$ considered observed after merging with $R_{\text{int}} = 0.016$. Structure solved by direct methods with MULTAN80 (Main *et al.*, 1980); block-diagonal least-squares refinement of 191 parameters with SHELX76 (Sheldrick, 1976) yielded $R = 0.049$, $wR = 0.050$; The weighting scheme chosen was $w = [\sigma^2(F_o) + gF_o^2]^{-1}$, where g was 0.01140, a value which gave the smallest variation of the mean value of $w(F_o - F_c)^2$ as a function of the magnitude of F_o , with (F_o) from counting statistics. Four H atoms of C(4), C(5), N and O(1) were estimated from difference map. The H atoms of five methyl groups were generated from assumed geometries and refined as a rigid group, with C

Table 1. Atomic coordinates and equivalent isotropic temperature factors with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}^* (\AA^2)
S	0.1463	0.1461 (1)	0.2422	4.91 (4)
N	0.1886 (5)	0.0860 (2)	0.3642 (5)	4.0 (1)
O(1)	0.1924 (5)	0.0049 (6)	0.6146 (6)	5.9 (1)
O(2)	0.4453 (5)	0.0121 (2)	0.5110 (6)	6.9 (1)
O(3)	0.0961 (5)	0.1936 (2)	0.3106 (7)	7.1 (2)
O(4)	0.0425 (6)	0.1244 (3)	0.0764 (6)	8.0 (2)
C(1)	0.607 (1)	0.1212 (6)	0.862 (1)	12.5 (5)
C(2)	0.6176 (6)	0.0784 (3)	0.7418 (6)	4.1 (1)
C(3)	0.4560 (6)	0.0569 (2)	0.5934 (7)	4.1 (1)
C(4)	0.3012 (5)	0.0931 (2)	0.5438 (6)	3.5 (1)
C(5)	0.2299 (7)	0.0683 (2)	0.6466 (7)	4.7 (2)
C(6)	0.0788 (9)	0.1041 (3)	0.607 (1)	7.2 (3)
C(7)	0.711 (1)	0.0198 (4)	0.828 (1)	10.9 (3)
C(8)	0.7015 (8)	0.1105 (4)	0.6659 (7)	6.7 (2)
C(9)	0.3249 (5)	0.1712 (2)	0.2580 (5)	3.8 (1)
C(10)	0.4011 (7)	0.1334 (2)	0.1992 (7)	4.7 (1)
C(11)	0.5419 (7)	0.1535 (2)	0.2123 (7)	4.8 (2)
C(12)	0.6054 (6)	0.2096 (2)	0.2808 (7)	4.4 (1)
C(13)	0.5308 (6)	0.2466 (2)	0.3407 (6)	4.7 (1)
C(14)	0.3913 (6)	0.2276 (2)	0.3305 (6)	4.2 (1)
C(15)	0.7591 (8)	0.2306 (3)	0.293 (1)	7.8 (3)

$$* B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j B_{ij} (a_i \cdot a_j) \text{ (Hamilton, 1959).}$$

atoms as the pivot atom. The H atoms of the phenyl ring were placed geometrically but were not refined. The temperature factors of the H atoms are equivalent to those for bonded atoms. At convergence max. $\Delta/\sigma = 0.19$, $S = 0.7$. Residual electron density within $+0.14$ and -0.21 e \AA^{-3} . Scattering factors as in SHELX76. Calculations on a VAX/780 computer using SHELX76.

Discussion. The structure was originally solved and refined in the space group $P1$ [$a = 9.287$ (4), $b = 9.778$ (3), $c = 11.903$ (5) \AA , $\alpha = 65.73$ (3), $\beta = 77.81$ (3), $\gamma = 58.93$ (3) $^\circ$] with two independent molecules per asymmetric unit. However, following the suggestion of the referees, it was possible to verify that the true space group is Cc .

Table 1* gives the final atomic coordinates and equivalent isotropic temperature factors. Bond lengths and angles are given in Table 2. Fig. 1 illustrates the geometry and labelling of the molecule drawn with ORTEP (Johnson, 1965). The torsion angles are given in Table 3.

The S atom shows a distorted tetrahedral coordination with bond-angle range 105.2 – 121.0° and mean angle 110.2° . The distances S–N and S–C(9) are 1.636 (4) and 1.762 (5) \AA . These values agree with those found by Germain, Declercq, Castresana, Elizalde & Arrieta (1983) in the structure of 4-methyl-*N*-(8-quinolyl)benzenesulfonamide. The atoms

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51790 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (Å) and angles (°) with e.s.d.'s in parentheses

S—N	1.636 (4)	C(4)—N	1.457 (6)
S—O(3)	1.425 (6)	C(4)—C(5)	1.54 (1)
S—O(4)	1.418 (4)	C(5)—O(1)	1.416 (6)
S—C(9)	1.762 (5)	C(5)—C(6)	1.54 (1)
C(2)—C(1)	1.50 (1)	C(9)—C(10)	1.396 (9)
C(2)—C(3)	1.538 (7)	C(10)—C(11)	1.389 (9)
C(2)—C(7)	1.53 (1)	C(11)—C(12)	1.367 (7)
C(2)—C(8)	1.50 (1)	C(12)—C(15)	1.51 (1)
C(3)—O(2)	1.208 (8)	C(12)—C(13)	1.388 (9)
C(3)—C(4)	1.550 (7)	C(13)—C(14)	1.381 (9)
		C(14)—C(9)	1.386 (6)
N—S—O(3)	106.9 (3)	C(3)—C(2)—C(1)	115.1 (6)
N—S—O(4)	105.7 (3)	C(3)—C(2)—C(7)	106.1 (5)
N—S—C(9)	107.7 (2)	C(3)—C(2)—C(8)	106.2 (5)
O(3)—S—O(4)	120.5 (3)	C(2)—C(3)—O(2)	121.6 (5)
O(3)—S—C(9)	107.7 (2)	C(4)—C(3)—O(2)	117.9 (4)
O(4)—S—C(9)	108.5 (3)	C(2)—C(3)—C(4)	120.5 (5)
S—N—C(4)	118.7 (3)	C(4)—C(5)—C(6)	111.2 (5)
S—C(9)—C(10)	119.4 (3)	C(4)—C(5)—O(1)	111.2 (6)
S—C(9)—C(14)	120.6 (4)	C(6)—C(5)—O(1)	109.2 (5)
C(14)—C(9)—C(10)	120.0 (5)	C(9)—C(10)—C(11)	119.0 (4)
N—C(4)—C(3)	109.3 (5)	C(10)—C(11)—C(12)	121.3 (6)
N—C(4)—C(5)	110.8 (4)	C(11)—C(12)—C(13)	119.3 (6)
C(3)—C(4)—C(5)	108.8 (4)	C(11)—C(12)—C(15)	120.3 (6)
C(1)—C(2)—C(7)	112.1 (7)	C(15)—C(12)—C(13)	120.4 (5)
C(1)—C(2)—C(8)	109.1 (7)	C(12)—C(13)—C(14)	121.8 (4)
C(7)—C(2)—C(8)	108.0 (7)	C(13)—C(14)—C(9)	119.7 (5)

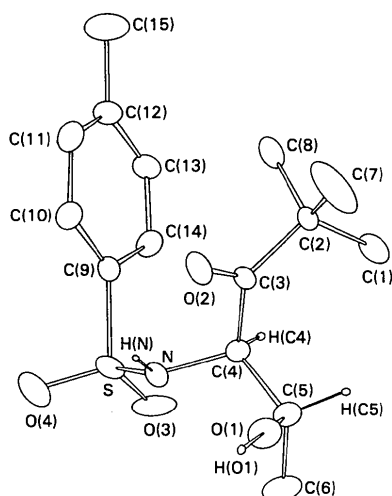


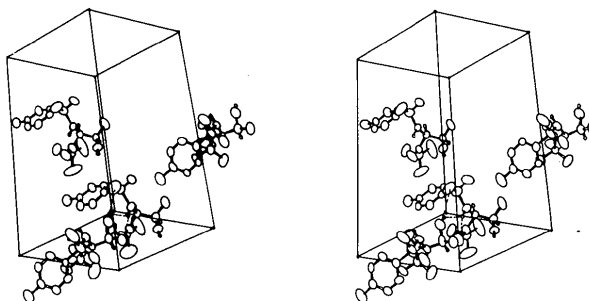
Fig. 1. Perspective view of the title molecule with the atom numbering. H atoms of C(4), C(5), O(1) and N are given arbitrarily small spheres for clarity. Thermal ellipsoids are depicted at the 20% probability level.

of the phenyl ring and the C(15), O(3) and S atoms are planar to within 0.02 Å from their least-squares plane.

A bifurcated hydrogen bond is observed with $H(N)\cdots O(2) = 2.331$, $N-H(N)\cdots O(2) = 2.683$ (5) Å, $N-H(N)\cdots O(2) = 104.4$ (7)° as a strong intramolecular bond, and $H(N)\cdots O(1^i) = 2.303$, $N-H(N)\cdots O(1^i) = 3.057$ (5) Å, $N-H(N)\cdots O(1^i) = 145.3$ (6)° (with $i = x, -y, -\frac{1}{2} + z$) as a weak intermolecular bond. There is a second weak intermolecular hydrogen bond from the O(1ⁱ) hydroxyl to O(4), with

Table 3. Torsion angles (°)

E.s.d.'s $\approx 0.7^\circ$.			
C(1)—C(2)—C(3)—O(2)	162.0	O(1)—C(5)—C(4)—N	-60.3
C(1)—C(2)—C(3)—C(4)	-18.8	C(5)—C(4)—N—S	-127.9
C(7)—C(2)—C(3)—O(2)	37.4	C(3)—C(4)—N—S	112.0
C(7)—C(2)—C(3)—C(4)	-143.4	C(4)—N—S—O(4)	-176.8
C(8)—C(2)—C(3)—O(2)	-77.3	C(4)—N—S—O(3)	53.8
C(8)—C(2)—C(3)—C(4)	101.9	C(4)—N—S—C(9)	-61.0
C(2)—C(3)—C(4)—N	-150.8	N—S—C(9)—C(10)	-65.6
O(2)—C(3)—C(4)—N	28.5	N—S—C(9)—C(14)	113.4
C(2)—C(3)—C(4)—C(5)	88.0	O(3)—S—C(9)—C(10)	179.8
O(2)—C(3)—C(4)—C(5)	-92.8	O(3)—S—C(9)—C(14)	-1.2
C(3)—C(4)—C(5)—O(1)	60.1	O(4)—S—C(9)—C(10)	48.4
C(3)—C(4)—C(5)—C(6)	-178.0	O(4)—S—C(9)—C(14)	-132.6
C(6)—C(5)—C(4)—N	61.5		

Fig. 2. Stereodrawing of the molecular packing with the hydrogen bonds shown by broken lines. The *b* axis is upwards, the *a* axis is down to the left and the *c* axis is down to the right.

$H(O1^i)\cdots O(4) = 2.034$, $O(1^i)-H(O1^i)\cdots O(4) = 3.099$ (5) Å, $O(1^i)-H(O1^i)\cdots O(4) = 158.8^\circ$. The angle $O(2)\cdots H(N)\cdots O(1^i)$ is 88.2° , and the atoms N, H(N), O(2), O(1ⁱ), H(O1ⁱ) and O(4) are within 0.5 Å from their least-squares plane. An ORTEP stereoscopic view of the molecular packing and hydrogen bonding is shown in Fig. 2.

Financial support was received from CNPq, FINEP, FAPESP, CAPES and IFS (International Foundation for Science).

References

- GERMAIN, G., DECLERCQ, J.-P., CASTRESANA, J. M., ELIZALDE, M. P. & ARRIETA, J. M. (1983). *Acta Cryst.* C39, 230–232.
- HAHN, F. (1967). In *Antibiotics*, Vol. 1, edited by D. GOTTLIEB & P. D. SHAW, New York: Springer-Verlag.
- HAMILTON, W. E. (1959). *Acta Cryst.* 12, 609–610.
- HEATHCOCK, C. H., HAGEN, J. P., YOUNG, S. D., PILLI, R., BAL, D., MARKI, H., KEES, K. & BADERTSCHER, M. (1985). *Chem. Scr.* 25, 39–43.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- SHAPIRO, D. (1969). In *Chemistry of Sphingolipids*. Paris: Hermann.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.