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The Relative Configuration of 8-[(2,2-Dimethyl-3-oxocyclohexyl)methoxymethyl]-1-methylbicyclo[4.2.0]octan-7-one

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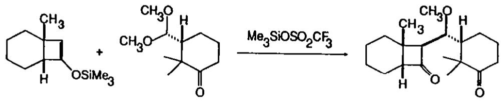
Abstract. $C_{19}H_{30}O_3$, $M_r = 306\cdot45$, triclinic, $P\bar{1}$, $a = 10\cdot902\,(2)$, $b = 11\cdot251\,(2)$, $c = 7\cdot924\,(2)$ Å, $\alpha = 105\cdot69\,(2)$, $\beta = 106\cdot63\,(2)$, $\gamma = 75\cdot70\,(2)°$, $V = 881\cdot2\,(3)$ Å^3, $Z = 2$, $D_x = 1\cdot155\,(1)$ g cm^{-3}, Mo $K\alpha$ ($\lambda = 0\cdot7107$ Å), $\mu = 0\cdot71$ cm^{-1}, $F(000) = 336$, $T = 295\,(1)$ K, final discrepancy factor $R_F = 3\cdot9\%$ for 1550 unique reflections above $2\sigma(I)$ in the range $4 < 2\theta < 45°$. The title compound is the methyl ether of a *threo* aldol; the methyl group of the 8-methylbicyclo[4.2.0]octan-6-one ring system and the chain attached to C3 of the 2,2-dimethylcyclohexan-1-one are equatorial to their respective cyclohexane rings. The puckering of the cyclobutanone ring is indicated by the dihedral angle of 29·9 (2)° between the planes defined by the atoms C5—C6—C7 and C5—C8—C7 of the 8-methylbicyclo[4.2.0]octan-6-one ring system. The bond angles and distances are normal.

Introduction. The single-crystal X-ray diffraction study reported herein demonstrates that the principal crystalline product of the trimethylsilyl triflate-mediated condensation (Murata, Suzuki & Noyori, 1980) of the cyclobutanone silyl enol ether (2) with the aldehyde dimethyl acetal (3) results from mutual kinetic resolution in the *same* sense, *via* a transition state of the *same* relative topicity (Prelog & Helmchen, 1982; Seebach & Prelog, 1982; Seebach & Golinski, 1981), as that observed in the reaction of the enolate with the aldehyde in the presence of zinc chloride (Fair, Clark & Nikaido, 1985).



(2) (3) (1)

The cyclobutanone silyl enol ether (2) was prepared by trapping the corresponding enolate with chlorotrimethylsilane. The starting material was the known 7,7-dichloro-1-methylbicyclo[4.2.0]octan-6-one (Krepski & Hassner, 1978; Bak & Brady, 1979), which was reductively monodechlorinated using zinc in acetic acid following the procedure of Fleming (Fleming & Au-Yeung, 1981) to provide the α-chlorocyclobutanone 7-chloro-1-methylbicyclo[4.2.0]octan-6-one. Reduction of the α-chlorocyclobutanone with dimethyl(copper)lithium in ether (Clark, Lin & Nikaido, 1984) followed by trapping with chlorotrimethylsilane (Stork & Hudrlik, 1968; House, Czuba, Gall & Olmstead, 1969) in the presence of hexamethylphosphoric triamide produced the silyl enol ether (2) (74%).

The dimethyl acetal (3) was prepared from the corresponding aldehyde. Thus, the copper-catalyzed 1,4-addition of vinylmagnesium bromide (House, Chu, Phillips, Sayer & Yau, 1977) to 2-methyl-2-cyclo-

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hexen-1-one was followed by *in situ* trapping of the enolate with methyl iodide in the presence of hexamethylphosphoric triamide to produce 3-ethenyl-2,2-dimethylcyclohexanone in 60% yield. Ozonolysis in methanol followed by reduction with dimethyl sulfide afforded 3-formyl-2,2-dimethylcyclohexanone, and stirring the aldehyde with cerium trichloride in a solution of methanol and trimethyl orthoformate (Luche & Gemal, 1978; Gemal & Luche, 1979) gave the aldehyde dimethyl acetal (3) (65% for two steps).

The silyl enol ether and the acetal were mixed in methylene chloride at 195 K in the presence of trimethylsilyl triflate, following the procedure of Noyori (Murata, Suzuki & Noyori, 1980), to give the product (1) (55% based on starting material not recovered).

Experimental. Crystals obtained by recrystallization from hexane; prismatic, 0·1 × 0·2 × 0·3 mm; Enraf–Nonius CAD-4 diffractometer; unit-cell parameters from 25 centered reflections ($2\theta = 15–30°$); no absorption correction; *hkl* range: $h = -11$ to 11, $k = -12$ to 12, $l = 0$ to 8; 2506 reflections with $2\theta < 45°$. Three standards measured after every 2 h of X-ray exposure, less than 1% decay. 2305 unique reflections [$R_{\rm int}$(merging) = 2·1%]; 755 reflections [$I < 2\sigma(I)$] considered unobserved. Structure solved by direct methods; hydrogens located by difference Fourier methods and calculation. Positional parameters refined for all H atoms. Isotropic temperature factors for H atoms fixed at $1·3B_{\rm eq}$ for attached nonhydrogen atom. 290 variables refined {$x,y,z,6\beta$ nonhydrogen and isotropic extinction parameter [$g = 1·95\,(5) \times 10^{-6}$]}. $\sum w(|F_o| - |F_c|)^2$ minimized, $w^{-1} = [\sigma^2_{\rm counting}(F_o^2) + (0·05F_o^2)^2]/4F_o^2$. $R = 3·9$, $wR = 4·7\%$, $S = 1·86$. Max. Δ/σ in last cycle 0·02. $\Delta\rho_{\max}$ ($\Delta\rho_{\min}$) on final difference Fourier map = 0·2 (−0·15) e Å^{-3}. Scattering factors including *f′* and *f″* values from *International Tables for X-ray Crystallography* (1974). Computations on PDP 11/34 computer using Enraf–Nonius (1983) *SDP-Plus* programs. The positional parameters for the nonhydrogen atoms are listed in Table 1.[*]

Table 1. *Positional and equivalent isotropic thermal parameters and their e.s.d.'s*

	x	y	z	$B_{\rm eq}$(Å^2)
O1	0·9758 (2)	0·034 (2)	0·8066 (2)	5·13 (5)
O2	1·0015 (1)	−0·2923 (1)	0·6865 (2)	4·07 (4)
O3	1·4177 (2)	−0·6130 (2)	1·0126 (3)	7·29 (6)
C1	1·4005 (2)	−0·1511 (2)	0·7540 (3)	4·64 (6)
C2	1·3840 (3)	−0·1196 (2)	0·5736 (4)	5·71 (7)
C3	1·3381 (3)	0·0206 (2)	0·5828 (3)	5·49 (7)
C4	1·2038 (3)	0·0622 (2)	0·6257 (3)	4·93 (7)
C5	1·2043 (2)	0·0327 (2)	0·8040 (3)	3·84 (6)
C6	1·0835 (2)	−0·0179 (2)	0·7856 (3)	3·94 (6)
C7	1·1540 (2)	−0·1543 (2)	0·7428 (3)	3·36 (5)
C8	1·2830 (2)	−0·0992 (2)	0·8365 (3)	3·59 (6)
C8′	1·3211 (2)	−0·0952 (2)	1·0389 (3)	4·64 (7)
C9	1·1223 (2)	−0·2600 (2)	0·8009 (3)	3·44 (6)
C10	1·2292 (2)	−0·3771 (2)	0·7893 (3)	3·33 (5)
C11	1·2251 (2)	−0·4740 (2)	0·8957 (3)	3·92 (6)
C12	1·3448 (2)	−0·5779 (2)	0·8809 (3)	4·61 (7)
C13	1·3688 (3)	−0·6369 (2)	0·6966 (4)	5·07 (7)
C14	1·3622 (2)	−0·5389 (2)	0·5918 (3)	4·72 (6)
C15	1·2389 (2)	−0·4400 (2)	0·5950 (3)	4·08 (6)
C16	1·2306 (3)	−0·4137 (3)	1·0947 (3)	5·50 (7)
C17	1·1051 (2)	−0·5393 (2)	0·8160 (4)	5·18 (7)
C18	0·8918 (2)	−0·2381 (3)	0·7617 (4)	5·26 (7)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $\frac{4}{3}[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Discussion. The structure of (1) is shown in Fig. 1 and the bond distances and angles are given in Table 2. The puckering of the cyclobutane ring is indicated by the dihedral angle of 29·9 (2)° between the planes defined by the atoms C5—C6—C7 and C5—C8—C7. The structure shows that the cation generated by the action of the triflate approaches the silyl ether from the least-hindered *exo* face, thereby setting the configuration at C7 as *β*. The adjacent center, C9, bears a methoxy group, and the relative configuration of the methoxy group to the C7 center is *threo*, following the usage introduced by Dubois & Dubois (1967).

The bond distances are in good agreement with those in the previous aldol. Again the longest C—C distances are C5—C8, C7—C8, and C10—C11. These distances average 1·569 Å in the present compound and 1·553 Å in the parent compound. There are some major changes in bond angles. Those changes greater than 2° are included in Table 2. Thus there is a greater planarity of the fused rings at C7 and C8 in the present compound but correspondingly more puckering at C5.

The most noticeable differences between the crystal structure of the methyl ether of the aldol reported herein and that of the parent aldol reported previously (Fair, Clark & Nikaido, 1985) are that the cyclobutane pucker angle is different, C9 is equatorial in the present structure and axial in the previous one, and the methoxy group in the present structure is incapable of hydrogen bonding whereas the hydroxyl in the previous structure (O2) was engaged in intermolecular hydrogen bonding with O3. It is interesting to note that the loci of greatest geometrical difference are near the atoms involved in the hydrogen bonding.

Mutual kinetic resolution in the aldol reaction, first observed by Heathcock and co-workers (Heathcock, Pirrung, Lampe, Buse & Young, 1981), relies on a larger rate of reaction for what Masamune, Choy, Peterson & Sita (1985) refer to as the 'matched pair' than for the 'unmatched pair'. The relative topicity of the aldehyde, the relative topicity of the transition state,

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[*] Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43942 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

and the relative topicity of the enolate are the three factors which combine to determine the products of the aldol reaction between racemic modifications of a chiral enolate and a chiral aldehyde. If we use the proposal of Prelog and Seebach (Prelog & Helmchen, 1982; Seebach & Prelog, 1982; Seebach & Golinski, 1981) for specifying relative topicity, the descriptor *Lk* refers to the juxtaposition of *R* or *Re* with *R* or with *Re*, or of *S* or *Si* with *S* or *Si*. The descriptor *Ul* refers to the juxtaposition of *R* or *Re* with *S* or *Si*.

An 'extended' transition-state structure for the aldol reaction should lead to an *erythro* aldol adduct (resulting from a transition state of *Ul* relative topicity) regardless of enolate geometry (Murata, Suzuki & Noyori, 1980), while the cyclic transition-state structure proposed first by Zimmerman & Traxler (1957) should give a *threo* adduct (resulting from a transition state of *Lk* relative topicity) from an *E* enolate and an *erythro* adduct from a *Z* enolate. Since the cyclobutanone enolate (2) has the *E* configuration, an extended transition state should give the *erythro* (*Ul*) adduct, while the Zimmerman–Traxler transition state should give the *threo* (*Lk*) adduct. Carbocation formation through the reaction of trimethylsilyl triflate with an aldehyde dimethyl acetal permits carbon–carbon bond formation with a silyl enol ether in a cationic analogue of the aldol reaction. The extended transition state has been proposed to account for the observed relative stereochemistry, which results from a transition state of *Ul* relative topicity (Murata, Suzuki & Noyori, 1980).

Therefore, it is most surprising to find that the principal crystalline product of the trimethylsilyl triflate-mediated condensation of the cyclobutanone silyl enol ether (2) with the aldehyde dimethyl acetal (3) results from mutual kinetic resolution in the *same* sense, *via* a transition state of the *same* relative topicity, as that observed in the reaction of the enolate with the aldehyde in the presence of zinc chloride (Fair, Clark, & Nikaido, 1985).

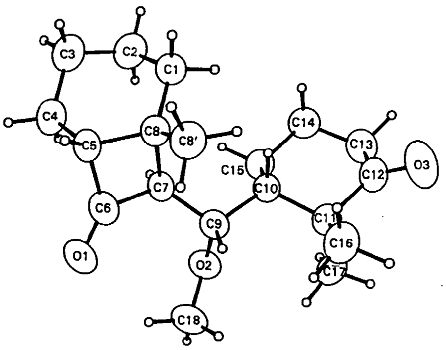

Fig. 1. View of one molecule showing thermal ellipsoids (50% probability level) and the conformation in the crystal.

Table 2. *Bond distances* (Å) *and angles* (°) *involving non-hydrogen atoms*

Selected bond angles in the parent aldol (Fair *et al.*, 1985) are shown to the right of values for the present compound

O1–C6	1·208 (2)	C7–C8	1·580 (3)
O2–C9	1·437 (2)	C7–C9	1·529 (3)
O2–C18	1·417 (2)	C8–C8′	1·528 (3)
O3–C12	1·212 (2)	C9–C10	1·529 (2)
C1–C2	1·515 (3)	C10–C11	1·563 (3)
C1–C8	1·521 (3)	C10–C15	1·533 (3)
C2–C3	1·521 (3)	C11–C12	1·530 (3)
C3–C4	1·528 (3)	C11–C16	1·529 (4)
C4–C5	1·535 (3)	C11–C17	1·550 (3)
C5–C6	1·515 (3)	C12–C13	1·500 (3)
C5–C8	1·566 (3)	C13–C14	1·527 (4)
C6–C7	1·532 (3)	C14–C15	1·521 (3)
C9–O2–C18	114·5 (2)	C7–C8–C8′	111·1 (2) 118·7 (2)
C2–C1–C8	114·7 (2)	O2–C9–C7	109·3 (1)
C1–C2–C3	111·2 (3)	O2–C9–C10	109·0 (1)
C2–C3–C4	109·9 (2)	C7–C9–C10	111·7 (1)
C3–C4–C5	112·0 (2)	C9–C10–C11	114·6 (1) 111·3 (2)
C4–C5–C6	110·7 (2) 121·4 (2)	C9–C10–C15	112·8 (2)
C4–C5–C8	115·5 (2) 121·1 (2)	C11–C10–C15	118·2 (2)
C6–C5–C8	86·4 (1)	C10–C11–C12	106·9 (1) 109·9 (2)
O1–C6–C5	132·9 (2)	C10–C11–C16	111·6 (2) 109·3 (2)
O1–C6–C7	134·8 (2)	C10–C11–C17	113·8 (2)
C5–C6–C7	92·3 (2)	C12–C11–C16	109·1 (2) 106·4 (2)
C6–C7–C8	85·3 (1)	C12–C11–C17	106·3 (2) 111·6 (2)
C6–C7–C9	122·4 (2) 116·3 (2)	C16–C11–C17	109·0 (2)
C8–C7–C9	122·6 (1) 118·6 (2)	O3–C12–C11	121·7 (2)
C1–C8–C5	116·2 (2) 109·8 (2)	O3–C12–C13	120·5 (3)
C1–C8–C7	119·0 (2) 109·2 (2)	C11–C12–C13	117·8 (2)
C1–C8–C8′	111·1 (2)	C12–C13–C14	112·2 (2)
C5–C8–C7	88·6 (1)	C13–C14–C15	111·2 (2)
C5–C8–C8′	108·9 (2) 115·9 (2)	C10–C15–C14	110·9 (2)

Numbers in parentheses are estimated standard deviations in the least significant digits.

A model for predicting the direction of approach of a nucleophile to a carbonyl carbon was put forward by Cram & Elhafez (1952), and has enjoyed widespread operational success; the works of Cherest, Felkin & Prudent (1968), Ahn (1980) and Houk *et al.* (1986) place the reasons for the success of the model on firm theoretical grounds. The results herein indicate that an incipient oxonium ion with an α-chiral center also enjoys the same directional specificity as the neutral carbonyl. This may be seen as follows. For the enantiomer depicted in Fig. 1, the absolute configuration of C10 is *R* and the C7–C9 bond was formed by the attack by C7 on the *Re* face of C9. Therefore, with the descriptors proposed by Prelog and Seebach (Prelog & Helmchen, 1982; Seebach & Prelog, 1982; Seebach & Golinski, 1981), the relative topicity displayed by the aldehyde dimethyl acetal during the formation of the C7–C9 bond is *Lk*-1,2. This is the same relative topicity as the rule proposed by Cram & Elhafez (1952) predicts (Seebach & Prelog, 1982). The option of using *Lk* and *Ul* rather than *lk* and *ul* as descriptors (Prelog & Helmchen, 1982) is to emphasize that the underlying assigned absolute stereochemistry is reflection-variant, although the descriptors themselves are not.

Since the *Re* face of C7 was attacked by the *Re* face of C9, the relative topicity of the transition state is *Lk*. Finally, since the absolute configuration of C8 is *R* and the *Re* face of C7 was attacked, the relative topicity of the enolate is *Lk*-1,2. The relative topicity of the reaction is therefore characterized by the descriptors *Lk*-1,2, *Lk*, *Lk*-1,2 (*aldehyde, transition state, enolate*) for the centers of *R, Re, Re, R* absolute stereochemistry. If the relative topicity of the transition state had been inverted, the *Re* face of the aldehyde would have been joined to the *Si* face of the enolate, and the descriptor would be *Ul*. The descriptors for the reaction would then be *Lk*-1,2, *Ul*, *Lk*-1,2, for centers of *R, Re, Si, S* absolute stereochemistry. Note that if the relative stereochemistry of C9 and C7 had been inverted, one would also expect that the relative stereochemistry of C10 and C8 would be inverted. This would give rise to mutual kinetic resolution in the *opposite* sense. Efforts along these lines are continuing.

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Méthanesulfonate de Péfloxacinium (Péflacine DCI)

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(*Reçu le* 10 *février* 1987, *accepté le* 16 *avril* 1987)

Abstract. 4-(3-Carboxy-1-ethyl-6-fluoro-1,4-dihydro-4-oxo-7-quinolyl)-1-methylpiperazinium methanesulfonate dihydrate, $C_{17}H_{21}FN_3O_3^+.CH_3O_3S^-.2H_2O$, M_r = 465·5, triclinic, $P\bar{1}$, $a = 16·737\ (2)$, $b = 9·621\ (2)$, $c = 6·988\ (1)$ Å, $\alpha = 108·44\ (2)$, $\beta = 98·11\ (1)$, $\gamma = 94·27\ (1)$°, $V = 1048·2$ Å^3, $Z = 2$, $D_x =$

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