Tetrahedron Vol. 41, No. 3, pp. 569 to 573, 1985
Printed in Great Britain.

0040-4020/85 $3.00 + .00
Pergamon Press Ltd.

STEREOSELECTIVE ALDOL CONDENSATION OF 3,4-DIHYDRO-3-OXO-2H-1,4-BENZOTHIAZINES: X-RAY DETERMINATION OF THE ALDOL STEREOSTRUCTURE

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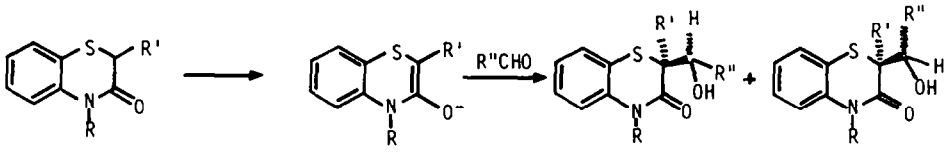
(*Received in UK 20 February* 1984)

Abstract—3,4-Dihydro-2-methyl-3-oxo-2*H*-1,4-benzothiazines (**1**) give *erythro*-stereoselective aldol condensation. The stereochemistry was determined by single crystal X-ray diffraction. The aldol condensation takes place under kinetic control. The reasons for the observed stereoselectivity are discussed.

The mechanistic relationship between the geometry of an enolate and the stereostructure of the aldol it produces on treatment with an aldehyde has been thoroughly investigated, leading to the conclusion that *cis*-enolates give mainly *erythro* products and *trans*-enolates lead predominantly to *threo* isomers for reactions occurring under kinetic control.[1] We have recently reported[2] on the aldol condensation reaction of 3,4-dihydro-4-methyl-3-oxo-2*H*-1,4-benzothiazine (**1a**) which leads to the corresponding aldols with a rather pronounced *erythro*-stereoselection in the case of aliphatic sterically hindered aldehydes, while no significant selectivity was observed with benzaldehydes. In a search for suitable conditions that could favour stereoselective condensation also with aromatic aldehydes, we reasoned that more sterically hindered benzothiazinones might show the desired selectivity in the aldolisation. To test this hypothesis we have investigated the aldol condensation of 3,4-dihydro-2-methyl-3-oxo-2*H*-1,4-benzothiazine **1b** and **1c**.

RESULTS AND DISCUSSION

Enolates **2**, readily generated by lithiation of **1b** (or **1c**) with lithium diisopropylamide (LDA) in tetrahydrofuran at low temperature, were allowed to react with a number of aldehydes to give substantially a mixture of the diasteromeric aldols **3** and **4**, the only contaminants being some starting material **1b** (or **1c**) and aldehyde. No aldol product could be obtained in the case of



3 **4**

1a : R = Me, R'= H
b : R = H, R'= Me
c : R = R'= Me

2a, R = H, R'= Me
b, R = R'= Me

a, R = H, R'= Me, R"= Ph
b, R = R'= Me, R"= Ph
c, R = R'= Me, R"= p-Cl-C_6H_4
d, R = R'= Me, R"=
e, R = R'= Me, R"=
f, R = R'= Me, R"=
g, R = R'= Me,
h, R = R'= Me, R"= $(C_2H_5)_2CH$

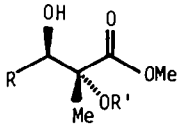
Table 1. Aldols 3 and 4 from the reaction between enolate 2 and aldehydes

Enolate	Aldehyde	Temperature °	Overall yield %	Aldols Relative percentages*	
2a	PhCHO	−55†	54	**3a**(67)	**4a**(33)
2b	PhCHO	−50	74	**3b**(87)	**4b**(13)
2b	PhCHO	−50‡	75	**3b**(86)	**4b**(14)
2b	PhCHO	−50§	74	**3b**(88)	**4b**(12)
2b	PhCHO	−125	75	**3b**(90)	**4b**(10)
2b	PhCHO	−78	77	**3b**(89)	**4b**(11)
2b	PhCHO	−20	70	**3b**(88)	**4b**(12)
2b	PhCHO	−78‖	80	**3b**(50)	**4b**(50)
2b	*p*-Cl—C_6H_4—CHO	−78	85	**3c**(84)	**4c**(16)
2b		−78	84	**3d**(88)	**4d**(12)
2b	*m*-NO_2—C_6H_4—CHO	−78	95	**3e**(87)	**4e**(13)
2b	*p*-NO_2—C_6H_4—CHO	−52	85	**3f**(85)	**4f**(15)
2b	CH_3CHO	−78	78	**3g**(60)	**4g**(40)
2b	$(C_2H_5)_2CHCHO$	−78	80	**3h**(80)	**4h**(20)

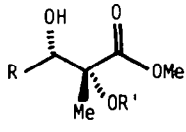
* Percentages determined from isolated and purified aldols.
† Reaction carried out by using 2 mol of LDA.
‡ Reaction carried out in the presence of $ZnBr_2$ (1 mol).
§ Reaction performed by using diisopropylaminomagnesium bromide, generated *in situ* by adding C_2H_5MgBr to diisopropylamine.
‖ Condensation in the presence of tetrabutylammonium fluoride.

condensation with pivaloylaldehyde, likely because of retroaldolisation. The results of the aldol condensation of **2** are summarized in Table 1. As can be seen, with benzaldehydes and α-branched aliphatic aldehydes the reaction shows a quite high diastereoselectivity, while no significant stereoselection occurs with acetaldehyde.

The stereochemistry of the aldols **3** and **4** could not be assigned by NMR spectroscopy. Heathcock's method,[3] which is based on the methyl, carbinol and carbonyl resonances, could not be applied. Indeed, for diastereomeric α-alkoxy-α-methyl-β-hydroxy carbonyl compounds (e.g. **5** and **6**) *threo* carbonyl and *erythro* carbinol resonances appear downfield of the corresponding resonances in their diastereomers and the methyl resonance of the *erythro* adduct lies downfield of that of the *threo* isomer.



5 (*erythro*)



6 (*threo*)

For the aldols derived from the condensation of enolate **2**, the more abundant of the diastereomers shows the carbonyl and the carbinol resonances downfield and the methyl resonances upfield with respect to the corresponding resonances of the less abundant isomer (see Table 2). In the IR spectra (KBr disc) the OH stretching of the major aldol appears much sharper than that of the minor isomer. Considering that aldols **3** and **4** prefer a chair-like conformation in which an intramolecular hydrogen bridge sets up between C=O and OH groups, the IR results might suggest that the major aldols have the *erythro* configuration **3**, in which, for steric reasons, the intramolecular hydrogen bond could be weaker. This is, however, not a reliable way for establishing aldol configuration.

The problem of the structural assignment of the aldols was unequivocally solved by single crystal X-ray diffraction. Details of the analysis are given in the Experimental. Figure 1 depicts a general view of the molecular structure of the major aldol derived from the condensation between enolate **2b** and benzaldehyde. The 6-membered heterocyclic ring has a half-chair conformation with C(10) and C(8) lying −1.0533 and

Table 2. ^{13}C-NMR Resonances for β-hydroxycarbonyl compounds **3** and **4** (in ppm)

		erythro			*threo*		
R	R'	carbonyl	carbinol	methyl	carbonyl	carbinol	methyl
Me	Ph	172.4	76.8	15.7	170.3	75.0	17.8
Me	*p*-Cl—C_6H_4—	170.8	75.1	15.2	168.5	73.5	17.8
Me		171.0	75.5	15.3	168.6	73.7	17.8
Me	*m*-NO_2—C_6H_4—	170.4	74.7	15.3	167.9	73.1	17.4
Me	*p*-NO_2—C_6H_4—	170.4	75.1	15.3	168.1	73.3	17.7
Me	Me	171.3	69.7	16.7	169.3	67.9	17.8
Me	$(C_2H_5)_2CH$—	170.9	74.1	16.6	169.1	71.3	17.8

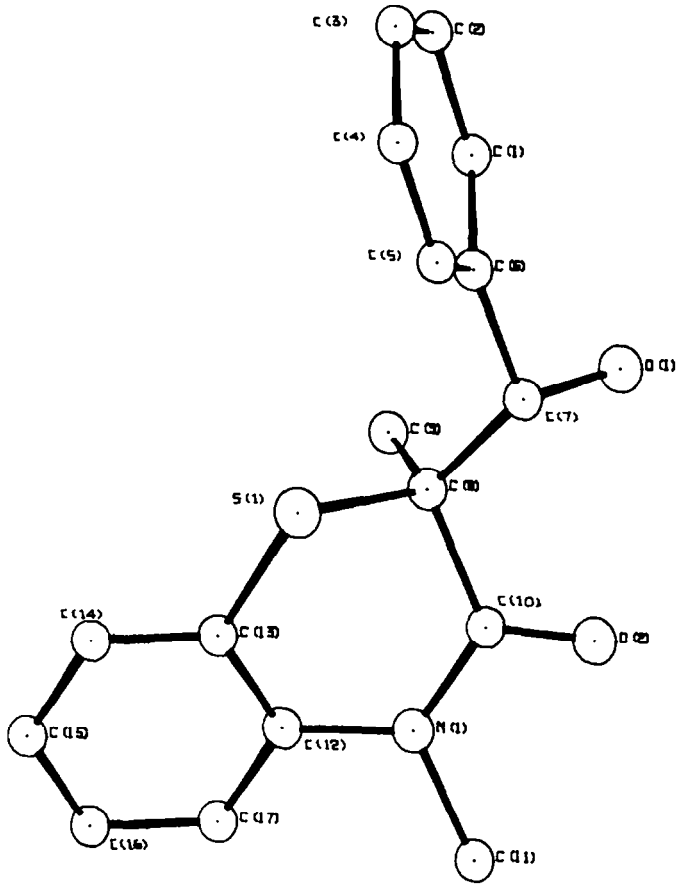
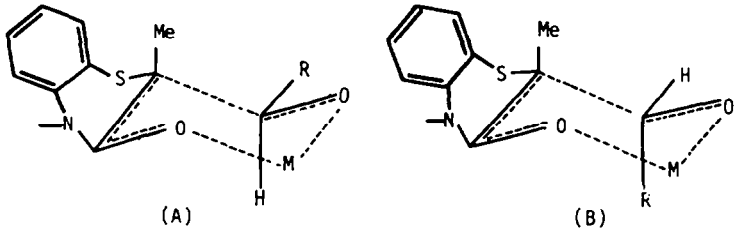


Fig. 1.

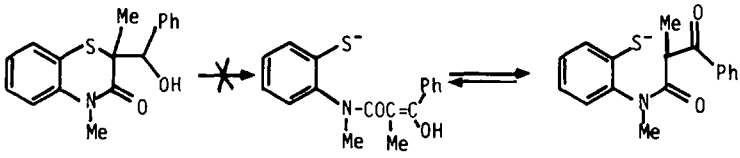
−0.3362 respectively out of the quasi-planar arrangement of the other four atoms S(1)-C(13)-C(12)-N(1). The hydroxybenzyl group has an equatorial orientation and is (−) synclinal with respect to the C=O group [O(2)-C(10)-C(8)-C(7) = −15.03°]. The methyl group has an axial orientation. A hydrogen bridge exists between the carbonyl and OH groups [O(1)—H(01)···O(2) = 2.764(3)Å]. Therefore, the more abundant diastereomer of the reaction between enolate **2b** and benzaldehyde has an *erythro* configuration according to Heathcock's nomenclature.[1]

In the aldol condensation of **2** the *erythro/threo* ratio does not depend on the experimental conditions, as it does not change appreciably for reactions carried out under a wide range of temperatures (−125° → −20°). Diastereomeric aldols **3** and **4** do not isomerize. Treatment of **3c** or **4c** with methanolic sodium methoxide did not cause any isomerization. Moreover, the *erythro* and *threo* aldolates generated by adding the *erythro* aldol **3c** and *threo* isomer **4c** to LDA at −78°, when allowed to stand at this temperature for 2 hr, did not equilibrate to the corresponding diastereomers; only retroaldolisation was observed over a longer reaction time (overnight at room temp). The *erythro/threo* ratio is also independent of the cation, as it remains practically unaltered using lithium, zinc or magnesium enolates of **1c**. These results clearly indicate that the aldol condensation of **2** occurs under kinetic control and the *erythro*-diastereoselectivity observed may be rationalized by assuming a cyclic transition state. The energy of the six-center chair-like transition state (A) that precedes the *erythro* isomer formation should be lower than that of transition state (B) which produces the *threo* aldol. The evidence that the condensation of **2** with benzaldehyde carried out in the presence of tetrabutylammonium fluoride affords the two diastereoisomers **3b** and **4b** in a 1 : 1 ratio allows us to rule out the possibility of an acyclic transition state.[4] That transition state (A) is energetically more stable than (B) may be ascribed to the fact that in (A) the aldehyde substituent R may adopt an equatorial orientation.

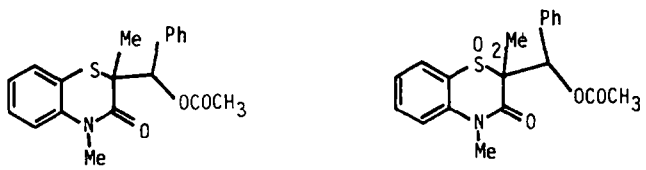


It is worthy mentioning that in all cases the *erythro* isomer forms preferentially notwithstanding the fact that the precursor enolate **2** is fixed in an E configuration. Evidently, when the enolate approaches the aldehyde (RCHO) it attacks to place the R group equatorial in the transition state.

Having in hand the diastereomeric aldols **3** and **4**, we hoped to ring-open the dihydrobenzothiazine moiety to produce β-ketobenzamides like **7**, as a β-elimination involving the carbinol hydrogen and the ring sulfur was expected to take place. Rather surprisingly, however, all attempts were unsuccessful; indeed, treatment of the aldol **3b** with sodium methoxide in methanol or in dimethylformamide gave substantial retroaldolisation. Moreover, no ring cleavage was observed on reacting both the ester **8** and the sulfone **9** with t-BuOK or NaH in THF and with Et_3N in CH_2Cl_2 at room temp.



3b **7**



8 **9**

The present results thus indicate that the aldol condensation of dihydrobenzothiazinones with benzaldehydes occurs stereoselectively also when an alkyl group is introduced into the 2-position of the heterocyclic ring. The stereostructure of the resulting aldols cannot be assigned following Heathcock's ^{13}C-NMR method, suggesting that this method is not general. The crystal data here reported may aid understanding of the correlation between the potential antiinflammatory activity[5] of aldols such as **3** and **4** and their structure.

EXPERIMENTAL

^1H-NMR spectra were recorded on Varian EM360A or EM390 spectrometers. ^{13}C-NMR spectra were performed with a Varian XL200 spectrometer. Chemical shifts (δ) in $CDCl_3$ are expressed in ppm downfield from internal Me_4Si. IR Spectra were recorded on a Perkin–Elmer 681 spectrometer. Thin-layer chromatography (TLC) was performed on silica gel sheets with fluorescent indicator (stratocrom SIF, Carlo Erba). Column chromatography was carried out by using 70-230 mesh silica gel (Merck). Elemental analyses were performed on a Perkin–Elmer analyser. Reactions requiring anhydrous conditions were performed in oven-dried glassware under a nitrogen atmosphere. Tetrahydrofuran from a commercial source (RS, Carlo Erba) was purified by distillation (twice) from sodium wire in a N_2 atmosphere. Diisopropylamine (Carlo Erba) was freshly distilled and stored under N_2. Standardised n-butyllithium in hexane was from Aldrich Chemical Co. All other chemicals were commercial grade and were purified by distillation or crystallisation prior to use. Petroleum ether refers to the 40–70° boiling fraction. 3,4-Dihydro-2-methyl-3-oxo-2*H*-1,4-benzothiazine (**1b**)[6] and 3,4-dihydro-2,4-dimethyl-3-oxo-2*H*-1,4-benzothiazine (**1c**)[7] were prepared according to the reported procedures.

General procedure for generation of anions **2**

To a nitrogen-flushed 100 ml three-necked flask, equipped with magnetic stirrer and nitrogen inlet and containing anhydrous THF (20 ml), was added 0.9 g (9 mmol) of diisopropylamine. The solution was cooled at −78° and 1.3 M n-butyllithium solution in hexane (7.8 ml, 9 mmol) was added via a dropping funnel. The mixture was stirred for 30 min and then a 15 ml THF solution of **1b** (or **1c**) (8.2 mmol) was added. The resulting yellow solution of **2** was used in the reactions described below.

General procedure for reactions of enolates **2** *with aldehydes*

To a stirred solution of anion (**2b** or **2c**) (1 mmol) prepared as above, a 10 ml THF solution of the aldehyde (1 mmol) was added at low temperature (see Table 1). The mixture was kept at this temperature for 1 hr, then allowed to warm to room temp, stirred there for further 1 hr and quenched with sat NH_4Cl. Extraction with ether (3 × 20 ml), drying (Na_2SO_4) and removal of the solvent under reduced pressure gave a mixture of the diasteromeric aldols **3** and **4**, which were separated by column chromatography on silica gel, using ether-petroleum/ether 1/1 as the eluent. Overall yields and realtive percentages are summarised in Table 1.

3,4-*Dihydro*-2(α-*hydroxybenzyl*)-4H-2-*methyl*-3-*oxo*-2H-1,4-*benzothiazine* **3a**, **4a**. *Erythro*-form **3a**, m.p. 171–172° (MeOH). ^1H-NMR ($CDCl_3$, D_2O): δ 1.35 (s, 3H), 5.0 (s, 1H) 6.5–7.3 (m, 9H). *Threo*-form **4a**, thick oil. ^1H-NMR ($CDCl_3$, D_2O): δ 1.4 (s, 3H), 4,5 (s, 1H), 6.5–7.4 (m, 9H).

3,4-*Dihydro*-2(α-*hydroxybenzyl*)-2,4-*dimethyl*-3-*oxo*-2H-1,4-*benzothiazine* **3b**, **4b**. *Erythro*-form **3b**, m.p. 141–142° (EtOH); IR (KBr): ν_{max} 3480 (sharp) and 1630 cm^{-1}. ^1H-NMR ($CDCl_3$, D_2O): δ 1.3 (s, 3H), 3.4 (s, 3H), 4.9 (s, 1H), 6.7–7.6 (m, 9H). *Threo* form **4b**, m.p. 138–139° (MeOH). IR (KBr): ν_{max} 3540 (broad) and 1650 cm^{-1}. ^1H-NMR ($CDCl_3$, D_2O): δ 1.3 (s, 3H), 3.45 (s, 3H), 5.0 (s, 1H), 6.7–7.6 (m, 9H).

2-(p-*Chloro*-α-*hydroxybenzyl*)-3,4-*dihydro*-2,4-*dimethyl*-3-*oxo*-2H-1,4-*benzothiazine* **3c**, **4c**. *Erythro*-form **3c**, m.p. 133–134° (EtOH). IR (KBr): ν_{max} 3400 (sharp) and 1640 cm^{-1}. ^1H-NMR ($CDCl_3$, D_2O): δ 1.2 (s, 3H), 3.45 (s, 3H), 5.0 (s, 1H), 6.6–7.4 (m, 8H). *Threo*-form **4c**, m.p. 165–167° (MeOH). IR (KBr): ν_{max} 3430 (broad) and 1660 cm^{-1}. ^1H-NMR ($CDCl_3$, D_2O): δ 1.2 (s, 3H), 3.4 (s, 3H), 4.8 (s, 1H), 6.7–7.6 (m, 8H).

3,4 - *Dihydro* - 2(α - *hydroxy* - 3,4 - *methylenedioxybenzyl*) - 2,4 - *dimethyl* - 3 - *oxo* - 2H - 1,4 - *benzothiazine* **3d, 4d**—*Erythro*-form **3d**, m.p. 157–158° (EtOH). IR (KBr): ν_{max} 3440 (sh) and 1630 cm^{-1}. ^{1}H-NMR ($CDCl_3$, D_2O): δ 1.3 (s, 3H), 3.5 (s, 3H), 5.0 (s, 1H), 5.9 (s, 2H), 6.6–7.4 (m, 7H). *Threo*-form **4d**, oil. IR (CCl_4): ν_{max} 3540 (br) and 1650 cm^{-1}. ^{1}H-NMR ($CDCl_3$, D_2O): δ 1.25 (s, 3H), 3.4 (s, 3H), 4.7 (s, 1H), 5.8 (s, 2H), 6.4–7.3 (m, 7H).

3,4 - *Dihydro* - 2(α - *hydroxy* - m - *nitrobenzyl*) - 2,4 - *dimethyl* - 3 - *oxo* - 2H - 1,4 - *benzothiazine* **3e, 4e**—*Erythro*-form **3e**, m.p. 195–196° (MeOH). IR (KBr): ν_{max} 3380 (sh) and 1635 cm^{-1}. ^{1}H-NMR (DMSO-d_6, D_2O): δ 1.3 (s, 3H), 3.4 (s, 3H), 4.65 (s, 1H), 7.0–8.2 (m, 8H). *Threo*-form **4e**, m.p. 160–162° (EtOH). IR (KBr): ν_{max} 3400 (br) and 1640 cm^{-1}. ^{1}H-NMR (DMSO-d_6, D_2O): δ 1.3 (s, 3H), 3.45 (s, 3H), 4.9 (s, 1H), 6.9–8.2 (m, 8H).

3,4 - *Dihydro* - 2(α - *hydroxy* - p - *nitrobenzyl*) - 2,4 - *dimethyl* - 3 - *oxo* - 2H - 1,4 - *benzothiazine* **3f, 4f**—*Erythro*-form **3f**, m.p. 135–136° (EtOH). IR (KBr): ν_{max} 3460 and 1640 cm^{-1}. ^{1}H-NMR ($CDCl_3$, D_2O): δ 1.3 (s, 3H), 3.45 (s, 3H), 5.2 (s, 1H), 6.8–8.3 (m, 8H). *Threo*-form **4f**, m.p. 149–150° (EtOH). IR (KBr): ν_{max} 3520 and 1660 cm^{-1}. ^{1}H-NMR ($CDCl_3$, D_2O): 1.3 (s, 3H), 3.5 (s, 3H), 4.95 (s, 1H), 6.8–8.2 (m, 8H).

3,4 - *Dihydro* - 2(α - *hydroxyethyl*) - 2,4 - *dimethyl* - 3 - *oxo* - 2H - 1,4 - *benzothiazine* **3g, 4g**—*Erythro*-form **3g**, thick oil. IR (CCl_4): ν_{max} 3510 and 1650 cm^{-1}. ^{1}H-NMR ($CDCl_3$, D_2O): δ 1.2 (d, 3H, J = 7Hz), 1.25 (s, 3H), 3.4 (s, 3H), 4.2 (q, 1H, J = 7Hz), 6.7–7.4 (m, 4H). *Threo*-form **4g**, thick oil. IR (CCl_4): ν_{max} 3560 and 1660 cm^{-1}. ^{1}H-NMR ($CDCl_3$, D_2O): δ 1.25 (d, 3H, J = 7Hz), 1.33 (s, 3H), 3.4 (s, 3H), 3.9 (q, 1H, J = 7Hz), 6.8–7.3 (m, 4H).

2 - (2 - *Ethyl* - 1 - *hydroxybutyl*) - 3,4 - *dihydro* - 2,4 - *dimethyl* - 3 - *oxo* - 2H - 1,4 - *benzothiazine* **3h, 4h**—*Erythro*-form **3h**, m.p. 125–127° (EtOH). IR (KBr): ν_{max} 3540 (sh) and 1640 cm^{-1}. ^{1}H-NMR ($CDCl_3$, D_2O): δ 0.98 (t, 6H), 1.4 (cm, 8H), 3.45 (s, 3H), 3.9 (s, 1H), 6.8–7.4 (m, 4H). *Threo*-form **4h**, m.p. 108–109° (EtOH). IR (KBr): ν_{max} 3450 (br) and 1640 cm^{-1}. ^{1}H-NMR ($CDCl_3$, D_2O): δ 0.7–1.5 (m, 14H), 3.4 (s, 3H), 3.6 (s, 1H), 6.8–7.4 (m, 4H).

2 - (α - *Acetoxybenzyl*) - 3,4 - *dihydro* - 2,4 - *dimethyl* - 3 - *oxo* - 2H - 1,4 - *benzothiazine* **8**—This compound was prepared by acetylation of **3b** with Ac_2O in pyridine at room temp. Thick oil. ^{1}H-NMR ($CDCl_3$): δ 1.4 (s, 3H), 2.0 (s, 3H), 3.4 (s, 3H), 5.8 (s, 1H), 6.9–7.4 (m, 9H).

2 - (α - *Acetoxybenzyl*) - 3,4 - *dihydro* - 2,4 - *dimethyl* - 3 - *oxo* - 2H - 1,4 - *benzothiazine* - 1,1 - *dioxide* **9**—Sulfone **9** was prepared by oxidation of sulfide **8** with *m*-chloroperbenzoic acid in CH_2Cl_2 at 0°, m.p. 165–167° (EtOH). ^{1}H-NMR ($CDCl_3$): δ 1.8 (s, 3H), 2.0 (s, 3H), 3.2 (s, 3H), 5.9 (s, 1H), 6.7–7.9 (m, 9H). Satisfactory analytical data were obtained for all new compounds.[10]

Crystal structure of aldol **3b**

Crystal data—$C_{17}H_{17}SNO_2$, M = 299. Crystal dimensions: 0.7 × 0.4 × 0.24 mm. Monoclinic, $P2_1/c$, a = 12.609, b = 12.054, c = 10.218, β = 106.15, V = 1491.8Å,[3] Z = 4, D_c = 1.33 g cm^{-3}, F(000) = 632. MoKα radiation, λ = 0.71069 Å.

3419 independent intensity data were recorded with a Nonius CAD-4 diffractometer by $\omega/2\theta$ scan and $\theta \geq 28°$, 2579 reflections with $I > 3\sigma$ (I), Lp correction, absorption ignored, no correction for secondary extinction.

Solution and refinement. The structure was solved by direct methods using the package of programs SIR.[8] The favourable space group symmetry allowed us to estimate with high accuracy the following 9 one-phase structure seminvariants via their second representation.[9]

$$\phi_{14,0,\bar{6}} = \pi; \quad \phi_{14,0,2} = \pi; \quad \phi_{12,0,2} = 2\pi;$$

$$\phi_{0,0,10} = 2\pi; \quad \phi_{10,0,\bar{6}} = 2\pi; \quad \phi_{10,0,\overline{10}} = \pi;$$

$$\phi_{10,10,\bar{6}} = \pi; \quad \phi_{2,0,0} = \pi; \quad \phi_{0,10,0} = \pi$$

Thus the phasing procedure started with 16 known reflections (3 for origin definition and 4 as symbolic phases). The most probable E-map showed the positions of all non-hydrogen atoms. The atomic positions were refined through several cycles of least squares calculations. After the refinement of the anisotropic thermal parameters the Fourier difference showed the position of all the hydrogen atoms. These atoms were given the thermal factors of the connected atoms. The final residual value was R = 0.05 for the 2579 reflexions having $I > 3\sigma$ (I).

Tables of fractional coordinates, equivalent isotropic thermal parameters, bond distances and angles, are available on request.[10]

Acknowledgement—We thank CNR and Ministero Pubblica Istruzione (Rome) for financial support and Istituto di Chimica (University, Genova) for the use of a Nonius CAD-4 diffractometer.

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[10] Supplementary data (analyses) available: see Notice to Authors, *Tetrahedron* **40**(2), ii (1984). X-ray data are obtainable on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.