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1,2,4-Trioxan-5-ones, a New Class of Endoperoxides: Structures of Three Representative Derivatives

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Abstract. (I): 7,8,15-Trioxadispiro[5.2.5.2]hexadecan-16-one, $C_{13}H_{20}O_4$, m.p. 366–367 K, $M_r = 240{\cdot}3$, monoclinic, $P2_1/c$, $a = 11{\cdot}160$ (2), $b = 11{\cdot}588$ (1), $c = 11{\cdot}169$ (3) Å, $\beta = 118{\cdot}72$ (2)°, $V = 1266{\cdot}7$ (5) Å^3, $Z = 4$, $D_x = 1{\cdot}26$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}086$ mm^{-1}, $F(000) = 520$, room temperature, R (= wR) = 0·089 for 582 observed reflections [$|F_o| > 3\sigma(F_o)$ and $|F_o| > 7{\cdot}0$]. (II): (6*RS*,3*RS*)-6-(Adamant-1-yl)-3-cyclohexyl-1,2,4-trioxan-5-one, $C_{19}H_{28}O_4$, m.p. 395 K, $M_r = 320{\cdot}4$, monoclinic, $P2_1/n$, $a = 12{\cdot}150$ (4), $b = 10{\cdot}693$ (2), $c = 12{\cdot}909$ (2) Å, $\beta = 90{\cdot}78$ (1)°, $V = 1677{\cdot}0$ (7) Å^3, $Z = 4$, $D_x = 1{\cdot}27$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}082$ mm^{-1}, $F(000) = 696$, room temperature, R (= wR) = 0·066 for 1804 observed reflections [$|F_o| > 4\sigma(F_o)$ and $|F_o| > 8{\cdot}0$]. (III): (6*RS*,3*SR*)-6-(Adamant-1-yl)-3-phenyl-1,2,4-trioxan-5-one, $C_{19}H_{22}O_4$, m.p. 372–375 K, $M_r = 314{\cdot}4$, orthorhombic, $P2_12_12_1$, $a = 6{\cdot}5317$ (16), $b = 11{\cdot}316$ (3), $c = 21{\cdot}216$ (3) Å, $V = 1568{\cdot}1$ (6) Å^3, $Z = 4$, $D_x = 1{\cdot}33$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}086$ mm^{-1}, $F(000) = 672$, room temperature, R (= wR) = 0·052 for 1039 observed reflections [$|F_o| > 4\sigma(F_o)$ and $|F_o| > 8{\cdot}0$]. 1,2,4-Trioxan-5-ones are potentially fragile entities with respect to concomitant decarboxylation and scission of the endoperoxide bond. However, they are thermally stable at ambient temperatures. Some are suitably crystalline, thereby permitting their structures to be determined. The trioxane rings in (I) and (II) adopt a flattened half-chair conformation and an envelope in (III). In all three compounds the greatest puckering amplitude is associated with the peroxide bond. None displayed significant antimalarial activity.

Introduction. Our search for new therapeutic compounds related to the antimalarial arteannuin or *Qinghaosu* (Quinghaosu Antimalarial Coordinating Research Group, 1979) has led us to devise methods for the synthesis of simpler analogues of its crucial

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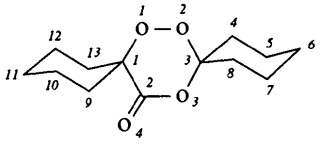
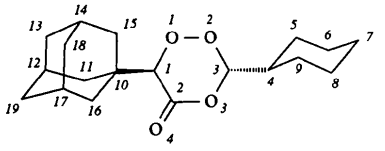
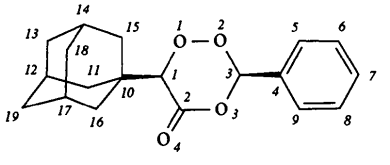
structural feature, the 1,2,4-trioxane ring (Jefford, Ferro, Moulin, Velarde, Jaggi, Kohmoto, Richardson, Godoy, Rossier & Bernardinelli, 1986). Despite the presence of the peroxidic bond, most trioxanes are quite stable. Nevertheless, the additional presence of the carbonyl function in the ring as exemplified by the 1,2,4-trioxan-5-ones would appear to confer fragility. Indeed, these particular entities are essentially unknown. It has been generally thought that they would spontaneously decompose by loss of a molecule of carbon dioxide and two carbonyl fragments. However, exceptions are two bridged bicyclic 1,2,4-trioxan-5-ones which were isolated from the [4 + 2] cyclo-addition of singlet oxygen with α-pyrone (Adam & Erden, 1978). We have recently developed a new method for preparing 3,6-alkylated 1,2,4-trioxan-5-ones which consists of the catalyzed condensation of trimethyl α-trimethylsilylperoxycarboxylates with aldehydes and ketones (Jefford, Rossier & Richardson, 1983). So far, some ten derivatives have been prepared. They behave normally at room temperature, are amenable to chemical modification (Jefford, Rossier & Boukouvalas, 1986), but are air-sensitive and difficult to crystallize. Nonetheless, three of them yielded crystals suitable for X-ray analysis. We now describe the first crystal and molecular structures of trioxanones (I), (II) and (III).



(I)



(II)



(III)

Experimental. Single crystals were grown at room temperature from ether/hexane (1:5) (I) and acetonitrile [(II) and (III)] solutions. All crystals were sealed in Lindemann capillaries under argon and on irradiation showed a loss (4–8%) of the diffracted intensities during the data collection. All reflections are corrected for these drifts. Philips PW1100 diffractometer, graphite-monochromated Mo $K\alpha$ radiation; $\omega/2\theta$ scans; Lorentz–polarization correction; no absorption correction; structure solved by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix least-squares refinement using $|F|$ values. No secondary-extinction correction. Scattering factors from Cromer & Mann (1968). All coordinates of H atoms were calculated. All calculations were performed with a local version of *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). The experimental data and structure refinement are summarized in Table 1.

Table 1. *Summary of crystal data, intensity measurement and structure refinement*

	(I)	(II)	(III)
Crystal size (mm)	0·30 × 0·35 × 0·50	0·20 × 0·30 × 0·45	0·14 × 0·18 × 0·70
Unit-cell determination*			
Number of reflections	24	20	20
2θ range (°)	24–40	29–38	19–34
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0·573	0·550	0·550
h,k,l range	−11,11; 0,13; 0,12	−13,13; 0,11; 0,14	0,7; 0,12; 0,23
Number of measured reflections	2222	2606	1309
Number of observed unique reflections	587	1804	1039
R_{int} for equivalent reflections	0·015	0·011	—
Criterion for observed reflections	$\|F_o\| > 3\sigma(F_o)$ and $\|F_o\| > 7$	$F_o\| > 4\sigma(F_o)$ and $\|F_o^2 > 8$	$F_o^2 > 4\sigma(F_o)$ and $F_o^2 > 8$
Refinement (on F)	Full matrix	Full matrix	Full matrix
Number of parameters	154	208	208
Weighting scheme	$w = 1$	$w = 1$	$w = 1$
Max. and average Δ/σ	0·084, 0·023	0·002, 0·0002	0·008, 0·002
Max. and min. $\Delta\rho$ (e Å^{-3})	0·60, −0·90	0·48, −0·49	0·26, −0·28
S	1·19	8·79	4·15
R ($= wR$)	0·089	0·066	0·052

* Unit cell determined by least-squares fit.

It should be noted that for (I) the unit cell could be described as metrically orthorhombic (maximum $\delta = 0{\cdot}053°$; Le Page, 1982) but the intensities of symmetry-equivalent reflections are actually consistent with a monoclinic system. Moreover, the high values of the atomic displacement parameters and the poor number of observed reflections leads to a relatively high value of the R factor.

Discussion. Final positional parameters (Table 2),* selected bond distances and angles (Table 3), relevant conformational parameters (Table 4) and respective molecular conformations (Fig. 1) were obtained.

* Lists of structure factors, anisotropic thermal parameters, full bond lengths and angles including non-H atoms, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53247 (57 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional coordinates and equivalent isotropic atomic displacement parameters with e.s.d.'s in parentheses for trioxanones* (I), (II) *and* (III)

U_{eq} is the average of the eigenvalues of **U**.

	x	y	z	U_{eq}(Å^2)
Compound (I)				
O(1)	0·2635 (6)	−0·1781 (6)	0·2069 (8)	0·068 (4)
O(2)	0·3195 (6)	−0·0825 (6)	0·2992 (7)	0·072 (4)
O(3)	0·0942 (6)	−0·0414 (5)	0·2504 (8)	0·056 (3)
O(4)	−0·0259 (7)	−0·1855 (6)	0·2579 (9)	0·078 (4)
C(1)	0·1735 (9)	−0·2378 (7)	0·245 (1)	0·051 (5)
C(2)	0·075 (1)	−0·1550 (7)	0·253 (1)	0·051 (6)
C(3)	0·2180 (9)	0·0063 (7)	0·251 (1)	0·049 (5)
C(4)	0·175 (1)	0·0533 (9)	0·114 (1)	0·067 (5)
C(5)	0·293 (1)	0·1179 (9)	0·112 (1)	0·076 (6)
C(6)	0·346 (1)	0·2107 (8)	0·215 (2)	0·094 (8)
C(7)	0·396 (1)	0·161 (1)	0·359 (1)	0·093 (8)
C(8)	0·280 (1)	0·096 (1)	0·367 (1)	0.069 (6)
C(9)	0·2531 (9)	−0·2986 (8)	0·383 (1)	0·059 (5)
C(10)	0·351 (1)	−0·3870 (8)	0·380 (1)	0·070 (6)
C(11)	0·279 (1)	−0·4757 (9)	0·272 (1)	0·079 (7)
C(12)	0·202 (1)	−0·419 (1)	0·133 (1)	0·076 (6)
C(13)	0·104 (1)	−0·3245 (9)	0·133 (1)	0·064 (5)
Compound (II)				
O(1)	0·6952 (2)	0·7308 (3)	0·5385 (2)	0·041 (2)
O(2)	0·6801 (3)	0·7716 (3)	0·4307 (2)	0·039 (2)
O(3)	0·5029 (3)	0·8304 (3)	0·4751 (2)	0·044 (2)
O(4)	0·4069 (3)	0·6743 (5)	0·5367 (3)	0·076 (3)
C(1)	0·6006 (4)	0·6556 (5)	0·5607 (3)	0·036 (3)
C(2)	0·4956 (4)	0·7193 (5)	0·5242 (3)	0·043 (3)
C(3)	0·6086 (4)	0·8732 (4)	0·4367 (4)	0·037 (3)
C(4)	0·5924 (4)	0·9263 (4)	0·3294 (3)	0·035 (3)
C(5)	0·5475 (4)	0·8298 (5)	0·2516 (4)	0·046 (3)
C(6)	0·5327 (5)	0·8895 (6)	0·1438 (4)	0·062 (4)
C(7)	0·6409 (5)	0·9453 (7)	0·1062 (4)	0·068 (4)
C(8)	0·6873 (5)	1·0391 (6)	0·1829 (5)	0·061 (4)
C(9)	0·7009 (4)	0·9835 (5)	0·2920 (4)	0·053 (3)
C(10)	0·6058 (3)	0·6332 (4)	0·6789 (3)	0·029 (2)
C(11)	0·5202 (4)	0·5337 (4)	0·7107 (3)	0·036 (3)
C(12)	0·5291 (4)	0·5110 (5)	0·8288 (4)	0·040 (3)
C(13)	0·6445 (4)	0·4611 (5)	0·8566 (4)	0·044 (3)
C(14)	0·7300 (4)	0·5589 (5)	0·8246 (4)	0·043 (3)
C(15)	0·7222 (4)	0·5826 (5)	0·7074 (4)	0·037 (3)
C(16)	0·5852 (4)	0·7556 (4)	0·7383 (3)	0·035 (3)
C(17)	0·5946 (4)	0·7308 (5)	0·8558 (4)	0·043 (3)
C(18)	0·7100 (4)	0·6822 (5)	0·8826 (4)	0·048 (3)
C(19)	0·5084 (4)	0·6345 (5)	0·8874 (4)	0·044 (3)
Compound (III)				
O(1)	0·2237 (7)	0·2153 (5)	0·4121 (2)	0·062 (3)
O(2)	0·3675 (6)	0·1147 (4)	0·4163 (2)	0·049 (3)
O(3)	0·6260 (7)	0·2489 (4)	0·4370 (2)	0·052 (3)
O(4)	0·6411 (8)	0·4092 (4)	0·3788 (2)	0·065 (3)
C(1)	0·319 (1)	0·3070 (6)	0·3758 (3)	0·045 (4)
C(2)	0·540 (1)	0·3268 (6)	0·3966 (3)	0·048 (4)
C(3)	0·5058 (9)	0·1547 (6)	0·4635 (3)	0·045 (4)
C(4)	0·6426 (9)	0·0529 (6)	0·4814 (3)	0·040 (4)
C(5)	0·839 (1)	0·0408 (6)	0·4582 (3)	0·044 (4)
C(6)	0·961 (1)	−0·0511 (7)	0·4790 (3)	0·059 (4)
C(7)	0·885 (1)	−0·1317 (7)	0·5227 (4)	0·064 (5)
C(8)	0·691 (1)	−0·1200 (7)	0·5455 (3)	0·062 (5)
C(9)	0·567 (1)	−0·0280 (6)	0·5257 (3)	0·053 (4)
C(10)	0·2918 (9)	0·2934 (5)	0·3035 (3)	0·032 (3)
C(11)	0·294 (1)	0·4184 (5)	0·2750 (3)	0·045 (4)
C(12)	0·255 (1)	0·4129 (5)	0·2032 (3)	0·045 (4)
C(13)	0·417 (1)	0·3373 (7)	0·1720 (3)	0·055 (5)
C(14)	0·414 (1)	0·2128 (6)	0·1995 (3)	0·046 (4)
C(15)	0·4547 (9)	0·2171 (5)	0·2714 (3)	0·039 (4)
C(16)	0·079 (1)	0·2376 (6)	0·2913 (3)	0·044 (4)
C(17)	0·037 (1)	0·2323 (6)	0·2203 (3)	0·048 (4)
C(18)	0·037 (1)	0·3567 (6)	0·1923 (3)	0·049 (4)
C(19)	0·202 (1)	0·1573 (6)	0·1881 (3)	0·052 (4)

Table 3. *Selected interatomic distances* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

	(I)	(II)	(III)
O(1)—O(2)	1·436 (10)	1·468 (4)	1·478 (7)
O(1)—C(1)	1·443 (15)	1·434 (6)	1·434 (8)
O(2)—C(3)	1·430 (11)	1·394 (6)	1·422 (7)
O(3)—C(2)	1·338 (10)	1·350 (6)	1·352 (8)
O(3)—C(3)	1·486 (13)	1·457 (6)	1·439 (8)
O(4)—C(2)	1·201 (15)	1·192 (6)	1·206 (9)
C(1)—C(2)	1·497 (15)	1·516 (7)	1·521 (10)
C(1)—C(9)	1·532 (13)	—	—
C(1)—C(10)	—	1·545 (6)	1·552 (8)
C(1)—C(13)	1·499 (13)	—	—
C(3)—C(4)	1·474 (16)	1·507 (6)	1·507 (9)
C(3)—C(8)	1·539 (14)	—	—
O(2)—O(1)—C(1)	106·3 (8)	105·4 (3)	108·2 (4)
O(1)—O(2)—C(3)	107·0 (5)	104·4 (3)	101·6 (4)
C(2)—O(3)—C(3)	121·8 (8)	120·0 (4)	120·2 (5)
O(1)—C(1)—C(2)	110·4 (7)	111·1 (4)	111·3 (5)
O(3—C(2)—O(4)	117·2 (9)	119·0 (5)	118·3 (6)
O(3)—C(2)—C(1)	119·7 (10)	118·7 (4)	118·8 (6)
O(4)—C(2)—C(1)	123·0 (8)	122·3 (5)	122·9 (6)
O(2)—C(3)—O(3)	107·5 (7)	109·1 (4)	107·9 (5)

Table 4. *Endocyclic torsional angles* (°), *ring-puckering parameters* (Q, φ_2, θ_2) *and asymmetry parameters* (ΔC_s, ΔC_2) *of trioxane rings*

Ring-puckering parameters (Q, φ_2, θ_2) according to Cremer & Pople (1975); asymmetry parameters (ΔC_s, ΔC_2) according to Nardelli (1983). The starting position and direction for ring-puckering calculations are: O(1)—O(2)—C(3)—O(3)—C(2)—C(1).

	(I)	(II)	(III)
Conformation	Flattened half-chair	Flattened half-chair	Envelope
O(1)—O(2)	−79·7 (9)	81·3 (4)	78·1 (5)
O(2)—C(3)	59·7 (10)	−64·2 (4)	−70·6 (5)
C(3)—O(3)	−18·6 (12)	18·0 (5)	36·9 (7)
O(3)—C(2)	−5·3 (13)	14·2 (6)	−5·0 (8)
C(2)—C(1)	−11·8 (12)	2·0 (6)	10·0 (8)
C(1)—O(1)	51·7 (8)	−46·6 (4)	45·7 (6)
Q	0·595	0·643	0·622
φ_2	36·0	−138·9	−127·6
θ_2	53·7	120·3	130·3
ΔC_s	O(2): 0·145	O(2): 0·133	O(2): 0·046
ΔC_2	O(1)—O(2): 0·030	O(1)—O(2): 0·066	O(1)—O(2): 0·109

Most 1,2,4-trioxane rings adopt chair conformations (Bernardinelli, Jefford, Boukouvalas, Jaggi & Kohmoto, 1987 and references therein). However, the biological activity of arteannuin seems to be associated with a boat form, which is not easy to attain when the rings are neither bridged nor fused. The trioxanes under study all posses different substitution patterns. (I) is unique in being doubly spirocyclic at C(3) and C(6) positions, while (II) is characterized by *trans*-3,6-disposed bulky substituents and (III) by *cis*-3,6 substituents. Although none of them display significant antimalarial activity *in vitro* against *Plasmodium falciparum*, their conformational preferences are of structural interest. Conformational inversion in (I) should be easy and would, of course, merely generate its enantiomer. On

the other hand, (II) would be constrained by its equatorially disposed substituents on the assumption that they are attached to a chair, and would therefore exists as a racemate. In fact, (I) and (II) adopt a flattened half-chair conformation with a minimum value of the asymmetry parameter (Nardelli, 1983) associated with a C_2 symmetry axis passing through the peroxide bond.

For (III), the *cis*-disposed substituents, again on the assumption that they are attached to a chair conformation, will present an opportunity for conformational inversion. In principle, the adamantyl and the phenyl substituents could adopt either equatorial and axial, or conversely, axial and equatorial positions respectively. Each alternative further exists as a racemate. In reality, it is seen that the constraint of the axial substituent, at least in the solid state, obliges the trioxane ring to assume an envelope conformation of C_s symmetry in which the O(2) atom lies out of the plane. Despite the possibility of the aforementioned two conformational choices for the substituents, a net preference is expressed; the phenyl group occupies the equatorial-like position, whereas the bulky adamantyl group paradoxically takes up an axial arrangement. Clearly, the balance of non-bonded interactions is responsible. A consequence of this conformational preference is that the C(3)—O(3) bond length [1·439 (8) Å], owing to the aligned phenyl substituent, is somewhat shortened compared with that found in (I) and (II) [1·486 (13) and 1·457 (6) Å respectively].

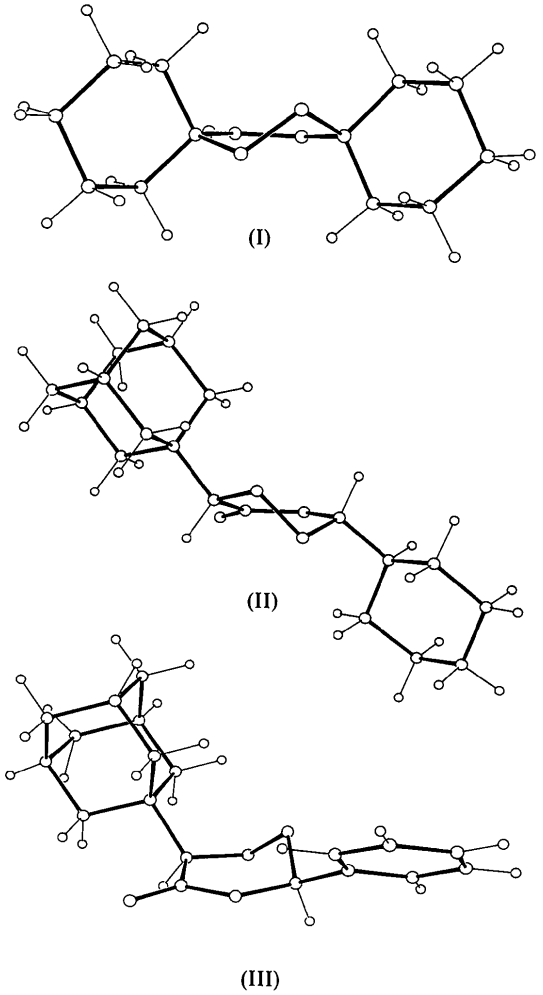


Fig. 1. Perspective view of 1,2,4-trioxane-5-ones (I), (II) and (III) showing the conformation of the trioxane rings.

In all three cases it is worth noting that the final conformation is largely dictated by the geometrical constraint imposed by the trigonal planarity of the carbonyl function.

As the barrier to rotation about the O—O bond is small, the peroxide bond shows the greatest puckering amplitude (torsion angle range 78–81°). A corollary is that such puckering decreases the C—O—O valence angles, which exhibit an observed mean value of 105·3°. This value is particularly low about the O(2) atom (101·6°) in (III).

The C—O bond lengths fall between 1·394 and 1·478 Å in keeping with those found in other 1,2,4-trioxanes. The O—O bond lengths (mean value of 1·461 Å) may be regarded as being in good agreement with the mean value of 1·470 (2) Å which is usually observed for cyclic fragments C(sp^3)—O—O—C(sp^3) (Allen, Bellard, Brice, Cartwright, Doubleday, Higgs, Hummelink, Hummelink-Peters, Kennard, Motherwell, Rodgers & Watson, 1979).

Finally, for (I), (II) and (III), no intermolecular distances significantly shorter than normal values were found.

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Structures of Three Products Derived from the Tin- and Aluminium-Mediated Coupling of Aldehydes and Cinnamyl Chloride

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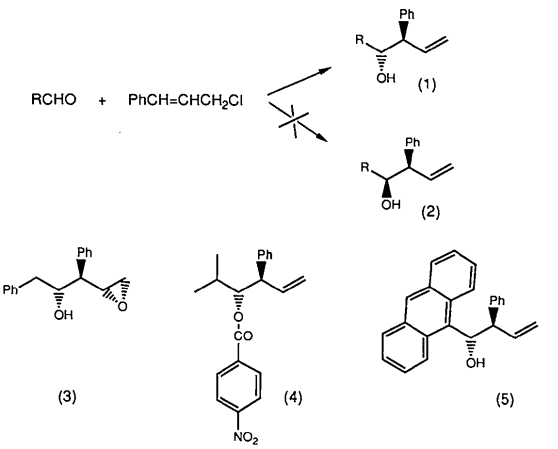
Abstract. (3) (2*RS*,3*RS*,4*RS*)-1,3-Diphenyl-4,5-epoxy-2-pentanol, $C_{17}H_{18}O_2$, $M_r = 254{\cdot}3$, monoclinic, $P2_1/n$, $a = 15{\cdot}243\ (4)$, $b = 9{\cdot}736\ (2)$, $c = 19{\cdot}066\ (4)$ Å, $\beta = 103{\cdot}03\ (2)°$, $V = 2757$ Å^3, $Z = 8$, $D_x = 1{\cdot}23$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}07$ mm^{-1}, $F(000) = 1088$, $T = 150$ K, $R = 0{\cdot}047$ for 2339 independent observed reflections. (4) (3*RS*,4*RS*)-2-Methyl-4-phenyl-5-hexen-3-yl 4-nitrobenzoate, $C_{20}H_{21}NO_4$, $M_r = 339{\cdot}4$, monoclinic, $P2_1/c$, $a = 19{\cdot}521\ (6)$, $b = 6{\cdot}014\ (2)$, $c = 15{\cdot}454\ (5)$ Å, $\beta = 96{\cdot}78\ (3)°$, $V = 1802$ Å^3, $Z = 4$, $D_x = 1{\cdot}25$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}08$ mm^{-1}, $F(000) = 720$, $T = 170$ K, $R = 0{\cdot}044$ for 1182 independent observed reflections. (5) (1*RS*,2*SR*)-1-(9-Anthryl)-2-phenyl-3-buten-1-ol, $C_{24}H_{20}O$, $M_r = 324{\cdot}4$, tetragonal, $P4_22_12$, $a = b = 19{\cdot}920\ (4)$, $c = 9{\cdot}095\ (5)$ Å, $V = 3609$ Å^3, $Z = 8$, $D_m = 1{\cdot}17$, $D_x = 1{\cdot}19$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}08$ mm^{-1}, $F(000) = 1376$, $T = 295$ K, $R = 0{\cdot}046$ for 1756 independent observed reflections. The three structures confirm the stereoselective preference for formation of the *threo* diastereoisomer in Sn/Al-mediated coupling of aldehydes and cinnamyl chloride.

Introduction. We have recently reported the regioselective and diastereoselective coupling of a variety of aldehydes with cinnamyl chloride mediated by tin and aluminium (Coxon, van Eyk & Steel, 1989). A key feature of these reactions is the highly selective formation of the *threo* diastereoisomer (1) in preference to the *erythro* isomer (2). Distinction between the two isomers could not always be made by spectroscopic methods and it was necessary to carry out X-ray structure determinations on a number of the products. Here we report the crystal structures of the major products from reaction of cinnamyl chloride with phenylacetaldehyde (and subsequent epoxidation), with methylpropanal (and subsequent conversion to its 4-nitrobenzoate) and with 9-anthraldehyde.



Experimental. The three compounds (3)–(5) were prepared as previously reported (Coxon, van Eyk & Steel, 1989). Crystal sizes $0{\cdot}49 \times 0{\cdot}23 \times 0{\cdot}08$ mm for (3), $0{\cdot}65 \times 0{\cdot}26 \times 0{\cdot}07$ mm for (4), $0{\cdot}72 \times 0{\cdot}68 \times 0{\cdot}24$ mm for (5). Measured density by flotation in aqueous potassium iodide solution. Nicolet *R3m* diffractometer; lattice parameters from 25 reflections with $2\theta > 25°$. $\theta/2\theta$ data collection to 50 and 55° for (3) and (5) respectively and ω collection to 48° for (4). Standard reflections (and intensity variations) 008, 031, 600 (4·0%) for (3), 004, 031, 500 (2·1%) for (4), 006, 080, 12,0,0 (2·2%) for (5) monitored every

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