Syntheses, structure analyses, and reactions of 1,3,5-trioxepanes and related compounds

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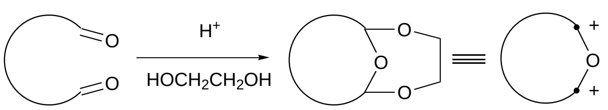
Acid-catalysed condensations of 1,5- or 1,6-dicarbonyl compounds with ethylene glycol give 1,3,5-trioxepane derivatives as a result of neighbouring participation by the adjacent carbonyl group during the acetalization process. With trimethylene glycol, the related 1,3,5-trioxocanes have also been obtained. Reaction of the 1,3,5-trioxepanes with (a) Grignard reagents gives dialkyl-substituted cyclic ethers, (b) titanium tetrachloride–allyltributyltin gives diallyl-substituted cyclic ethers and (c) triethylsilane in the presence of trimethylsilyl triflate provides the corresponding cyclic ethers.

Recent increased use of acetals in cross-coupling reactions with nucleophiles has led to the development of a variety of methods for their activation.[1] In this respect, the acetalization of dicarbonyl compounds, in which the two carbonyl groups lie in close proximity to each other, may proceed by a neighbouring group participation affording bicyclic compounds bearing a 'bis-acetal ether' functionality.[2,3] Since such compounds may behave as potent dication equivalents, they should, in principle, be able to couple with two nucleophiles (Scheme 1) and hence provide new methods for the synthesis of cyclic ethers.[4]

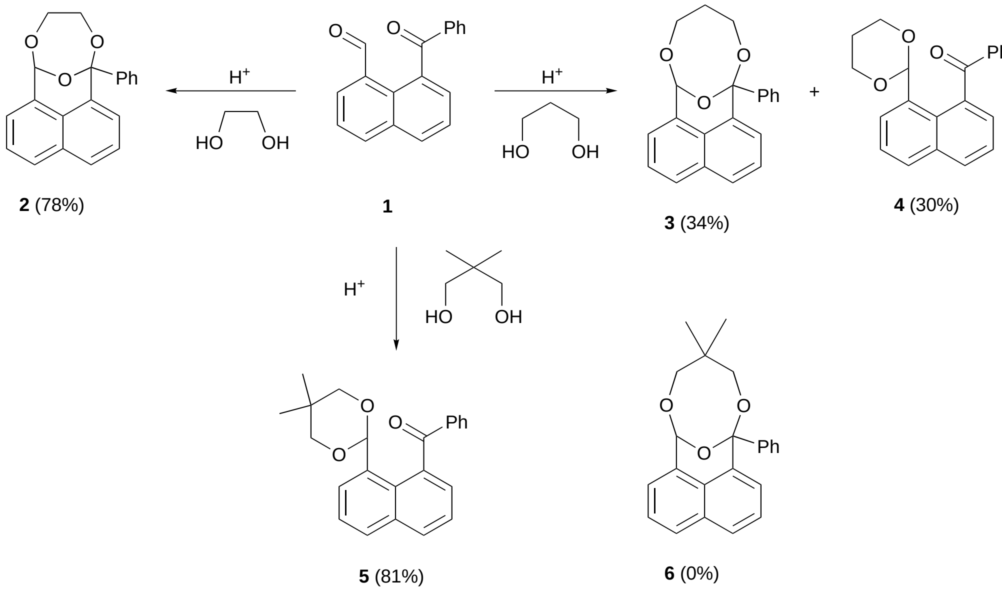


Scheme 1

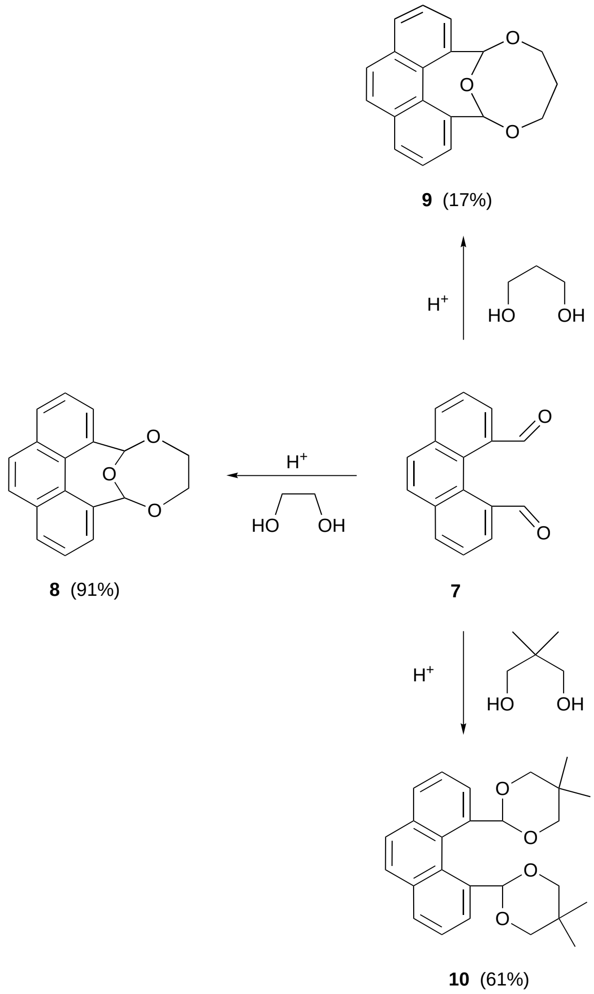
Results and discussion

Acetalization of dicarbonyl compounds

To investigate the possibility of neighbouring group participation during the acetalization of dicarbonyl compounds, a mixture of the keto aldehyde **1** and ethylene glycol was treated with chlorosulfonic acid in dichloromethane (Scheme 2). By column chromatography on silica gel, the expected 1,3,5-trioxepane **2** was isolated in high yield (78%). The analogous reaction between **1** and trimethylene glycol afforded the corresponding 1,3,5-trioxocane **3** along with a roughly similar amount of the keto acetal **4**. With 2,2-dimethylpropane-1,3-diol, however, only the keto acetal **5** was isolated (81%) because the isomeric 1,3,5-trioxocane **6** was not produced in significant quantities. The corresponding condensation reactions involving the structurally rigid 1,6-dialdehyde **7** yielded an analogous range of products **8**–**10** (Scheme 3).



Scheme 2



Scheme 3

The stepwise mechanism outlined in Scheme 4 tentatively accounts for the formation of the trioxepane derivative **2** from the keto aldehyde **1**. Since the 1,3-dioxolane **11** was not formed in significant quantities, it is presumed that the stabilized carbocation *Y* rather than *X* must be the key intermediate in this reaction pathway. When ethylene glycol is replaced by trimethylene glycol, however, there is clearly a finer balance between the analogous competing pathways consistent with the notion that the eight-membered 1,3,5-trioxocane would be less readily formed by cyclization than the corresponding seven-membered 1,3,5-trioxepanes. In the condensation reaction between keto aldehyde **1** and 2,2-dimethylpropane-1,3-diol, the preponderant formation of the 1,3-dioxane derivative **5** possibly reflects the steric effect of the geminal methyl groups which may be more readily accommodated in the six-membered ring than the alternative eight-membered ring.

In a series of acid-catalyzed condensation reactions between 1,5-dicarbonyl compounds **12** and ethylene glycol, the keto aldehydes **12c**–**e** also gave the corresponding trioxepanes **13c**–**e** in good yield (Table 1). In contrast, however, only the isomeric keto acetals **14a,b** were obtained from keto aldehydes **12a**,**b**. Although these results are remarkably clear cut and suggest that the course of the acetalization was influenced by the structures of the dicarbonyl compounds, there is no obvious correlation between the structure of the substrate and that of the product.

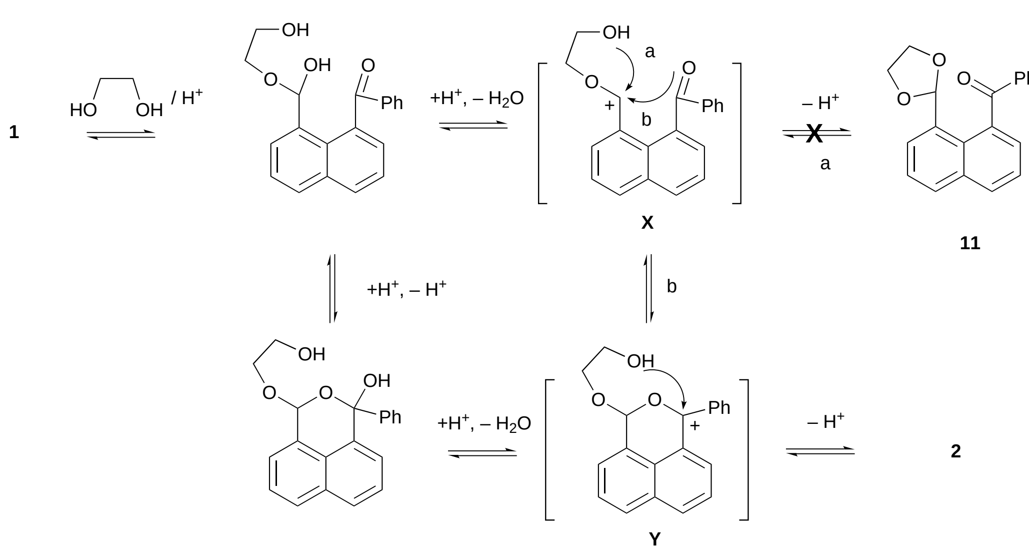
The analogous reactions involving trimethylene glycol give variable results; keto aldehyde **12c** yields the trioxocane derivative **15** whereas **12a** and **12d** are transformed into the mono acetals **16** and **17** respectively. This latter result is surprising given that the reaction of the keto aldehyde **12d** with ethylene glycol resulted in exclusive formation of the trioxepane derivative **13d**. These observations tend to reinforce the view that the neighbouring group participation and cyclization processes leading to the eight-membered trioxocane appear to be less efficient than those related to the formation of the seven-membered trioxepane.

Reactions of the dicarbonyl compounds **1, 6** and **12c** with methanol under acidic conditions gave the corresponding bis-acetal ethers **18, 19** and **20** respectively, albeit in moderate yields.

Structural studies of 1,3,5-trioxepanes and related compounds

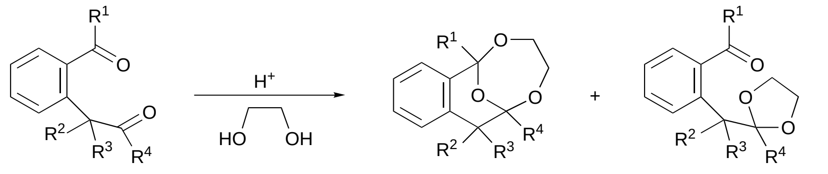
The structures of the bicyclic acetals **2** and **3**, and the keto acetal **4** in the solid state were determined by X-ray crystallographic analysis and are depicted in Figs. 1–3 respectively. Although the observed geometrical parameters for these molecules are unexceptional and lie well within expected ranges, further investigation of their respective overall structures, in particular their preferred conformations, and comparison with structures generated by molecular modelling could offer some rationale for the product selectivities mentioned above.

Molecular modelling of the structure of the bicyclic acetal **2** using molecular mechanics (MM2) combined with a Monte Carlo conformational search procedure reveals that while most of the molecule is rigid and essentially planar, the 1,3,5-trioxepane ring is flexible, being able to adopt several distorted



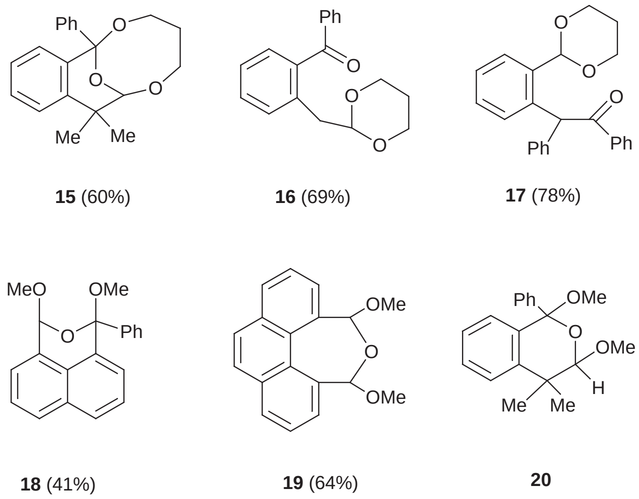
Scheme 4

Table 1 Isolated products from the acid-catalysed condensation reaction between dicarbonyl compound **12** and ethylene glycol



12 **13** **14**

Compound **12**	R^1	R^2	R^3	R^4	Isolated yield (%) **13**	**14**
a	Ph	H	H	H	—	76
b	Ph	Me	H	H	—	83
c	Ph	Me	Me	H	55	—
d	H	Ph	H	Ph	47	—
e	H	$-(CH_2)_4-$		Ph	95	—



Scheme 5

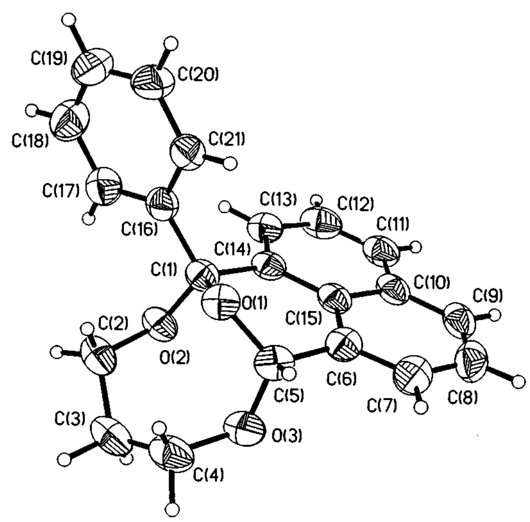


Fig. 2 The solid state structure of one molecule of 1,3,5-trioxocane **3** (ORTEP,[15] the non-hydrogen atoms are represented by 50% probability ellipsoids and hydrogen atoms by spheres of arbitrary radius)

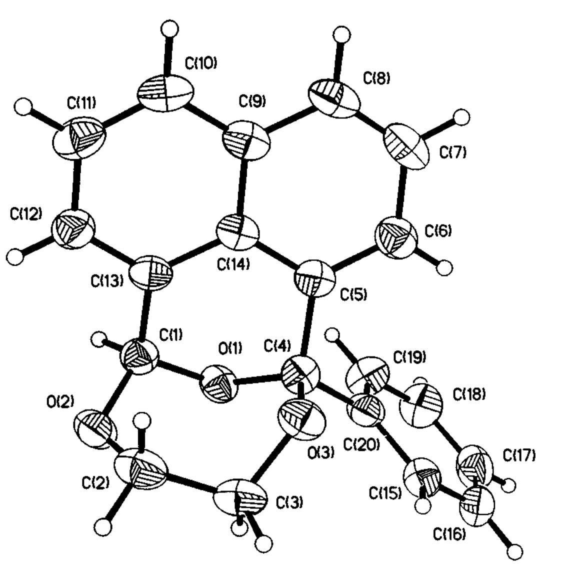


Fig. 1 The solid state structure of one molecule of 1,3,5-trioxepane **2** (ORTEP,[15] the non-hydrogen atoms are represented by 50% probability ellipsoids and hydrogen atoms by spheres of arbitrary radius)

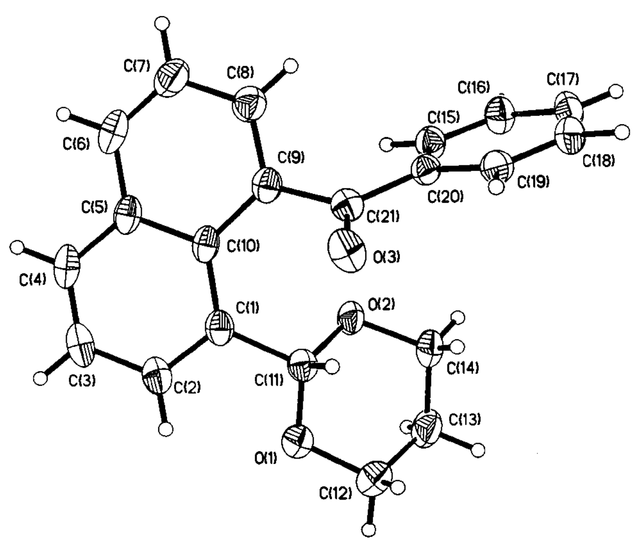


Fig. 3 The solid state structure of one molecule of keto acetal **4** (ORTEP,[15] the non-hydrogen atoms are represented by 50% probability ellipsoids and hydrogen atoms by spheres of arbitrary radius)

Table 2 Summary of the molecular modelling results

Compound	Conformation of 1,3,5-trioxepane/trioxocane ring	Strain energy (MM2)/ kcal mol^{-1}	ΔH_f (MOPAC-PM3)/ kcal mol^{-1}
2	chair	17.764	−34.454
	chair	17.817	−35.725
	chair	18.584	−35.006
3	boat-chair	18.058	−37.678
	twist-chair-chair	22.000	−37.625
	crown	22.691	−39.473
4	—	17.701	−35.902
5	—	18.639	−47.445
6	boat-chair	19.445	−47.232
11	—	18.518	−32.214

chair conformations with shallow minima. The two lowest energy conformations were found to have similar strain energies and heats of formation and a third, having a 1,3,5-trioxepane ring with mirror plane symmetry, was less favoured than the other two by about 1 kcal mol^{-1} (Table 2). The lowest energy structure calculated for **2** is comparable to that determined by X-ray crystallography (Fig. 1). The heat of formation (MOPAC93-PM3) for the unobserved keto acetal **11** was estimated to be about 2 kcal mol^{-1} higher than that of **2**.

Structural modelling of the bicyclic acetal **3** indicates that the 1,3,5-trioxocane ring adopts three well-defined, recognizable conformations: a boat-chair, a twist-chair-chair and a crown. The structure of molecule **3** in the solid state (Fig. 2) corresponds to a boat-chair conformation, essentially the same as the global minimum identified by molecular mechanics.

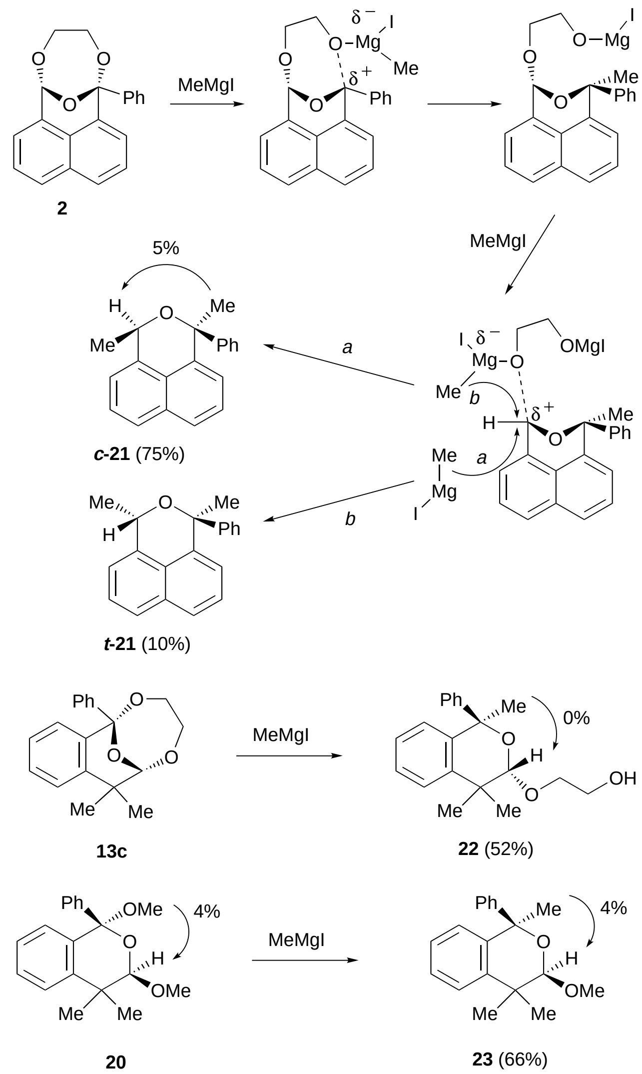
Cursory inspection of the calculated and solid state molecular structures of keto acetal **4** reveals marked differences in the orientations of the 1,3-dioxanyl and benzoyl groups. Since the substituents in keto acetal **4** would be expected to have a degree of conformational freedom, the observed conformation of **4** in the solid state will probably be determined by crystal packing forces. From heats of formation calculated for minimised structures, the bicyclic acetal **3** is more stable than the keto acetal **4** by about 1.7 kcal mol^{-1}.

Structural modelling of the mono-acetal **5** and the isomeric gem-dimethyl 1,3,5-trioxocane derivative **6** indicate that the strain energy or heats of formation of these molecules differ by less than 1 kcal mol^{-1} which would not readily account for the high degree of selectivity observed in the reaction.

In summary, molecular modelling studies using molecular mechanics (MM2) have accurately reproduced the preferred conformations of the bicyclic acetals **2** and **3** observed in the solid state. The heats of formation estimated by semi-empirical calculations are less reliable in this respect and the differences in heats of formation between the pairs of isomeric mono- and bi-cyclic acetals do not correlate particularly well with the observed product distributions.

Reaction of 1,3,5-trioxepanes

Reaction with Grignard reagents. Acetals are reported to react with Grignard reagents to provide the alkyl-substituted ethers.[5] By analogy, the reaction of the trioxepane **2** with methylmagnesium iodide afforded the dimethyl-substituted cyclic ether as a mixture of diastereoisomers ***c*-21** and ***t*-21**.† On the basis of ^{1}H NMR NOE studies, the major product was found to be stereoisomer ***c*-21** (Scheme 5). In contrast, the reaction of the trioxepane **13c** with methylmagnesium iodide gave only the mono-methylated compound **22**; similarly the bis-acetal **20** was transformed into **23**. These latter results imply that the magnesium ion of the Grignard reagent must selectively coordinate

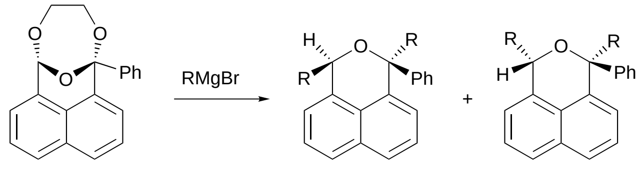


Scheme 5

to the more hindered oxygen atom in **13c** and **20** resulting in cleavage of the C–O bond with concomitant development of a significant degree of electrophilic character at the highly substituted carbon centre. The nucleophilic methyl group would then be subsequently delivered to the incipient carbocationic centre. ^{1}H NMR NOE Measurements on **22** and **23** are consistent with the methyl group having been delivered *syn* to the displaced oxygen. Further methylation of either **22** or **23** does not occur because the required carbocation, formed on heterolytic cleavage of the C–O bond, cannot be sufficiently stabilised. The mono-methylated product from **2** does, however, undergo a second methylation predominantly *via* an intermolecular displacement to yield ***c*-21** as illustrated in Scheme 5.

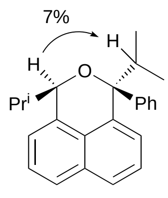
† Nomenclature based on the fiducial substituent system proposed by L. C. Cross and W. Klyne, *Pure Appl. Chem.*, 1976, **45**, 11; see also E. L. Eliel and S. H. Wilen in 'Stereochemistry of Organic Compounds', Wiley, New York, 1994, pp. 665–666.

Table 3 Products from the reaction of Grignard reagents with compound **2**



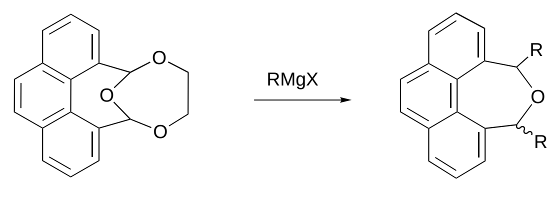
2 *c*-**24** *t*-**24**

Product	R	Yield (%)	*c* : *t*
24a	Et	56	86 : 14
24b	Pr^i	28	100 : 0
24c	Ph	34	n.a.
24d	allyl	46	100 : 0



c-**24b**

Table 4 Products obtained from the reaction between Grignard reagents and 1,3,5-trioxepane **8**



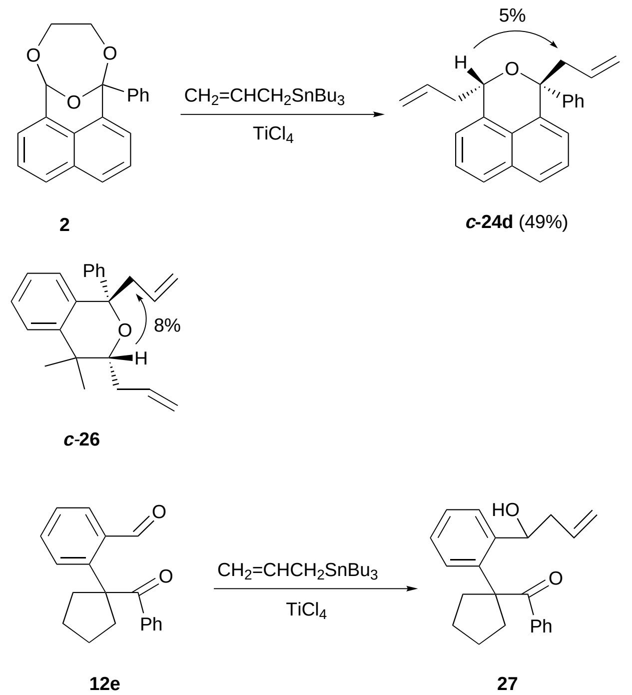
8 **25**

Product	RMgX	Yield (%)	*cis* : *trans*
25a	MeMgI	74	42.58
25b	EtMgBr	69	50 : 50
25c	PhMgBr	82	29 : 71
25d	allyl MgBr	73	50 : 50

Treatment of the trioxepane **2** with a series of Grignard reagents gave in each case the corresponding dialkyl-substituted cyclic ethers **24a**–**d** respectively (Table 3). The reaction was highly stereoselective affording the *c*-isomer as the predominant or exclusive product. Product stereochemistry was assigned on the basis of ^{1}H NMR NOE measurements as for *c*-**24b**. Surprisingly, the analogous reactions involving trioxepane **8** were non-stereoselective; roughly 1 : 1 mixtures of *cis*- and *trans*-**25** were obtained (Table 4). These observed differences in stereoselectivity between the two trioxepanes, **2** and **8**, would be consistent with the formation of discrete carbocations from **8** which could subsequently undergo intermolecular nucleophilic attack on either face in a relatively unselective fashion.

$TiCl_4$-Catalyzed reaction of the trioxepanes with allyltributyltin

Since treatment of acetals with allyltributyltin–titanium tetrachloride has been shown to provide allyl-substituted ethers,[6] the analgous reaction with 1,3,5-trioxepanes was examined as an alternative route to the corresponding diallyl-substituted cyclic ethers. Thus, the diallyl-substituted cyclic ethers **24d**, **25d** (83%) and **26** (73%) were obtained in acceptable yield from the corresponding trioxepanes **2**, **8** and **13c** respectively (Scheme 6). ^{1}H NOE NMR Measurements suggest that compounds **24d** and **26** were each formed stereoselectively as the *c*-isomer in which the allyl groups have been delivered to opposite faces of the molecule in each case (*cf*. the reaction of **2** with allylmagnesium bromide).



Scheme 6

Diallyl-substituted compounds such as **24d** are also potentially available directly from their corresponding dicarbonyl precursors using the allyltributyltin–titanium tetrachloride method.[7] Thus, the desired products, **24d** (51%), **25d** (50%) and **26** (25%), were obtained from the corresponding dicarbonyl compounds **1**, **7** and **12c** respectively though the yields were generally lower than above. Moreover, in the case of the keto aldehyde **12e** the reaction stopped at the stage of the mono-allylation and the alcohol **27** was isolated in 71% yield (Scheme 6).

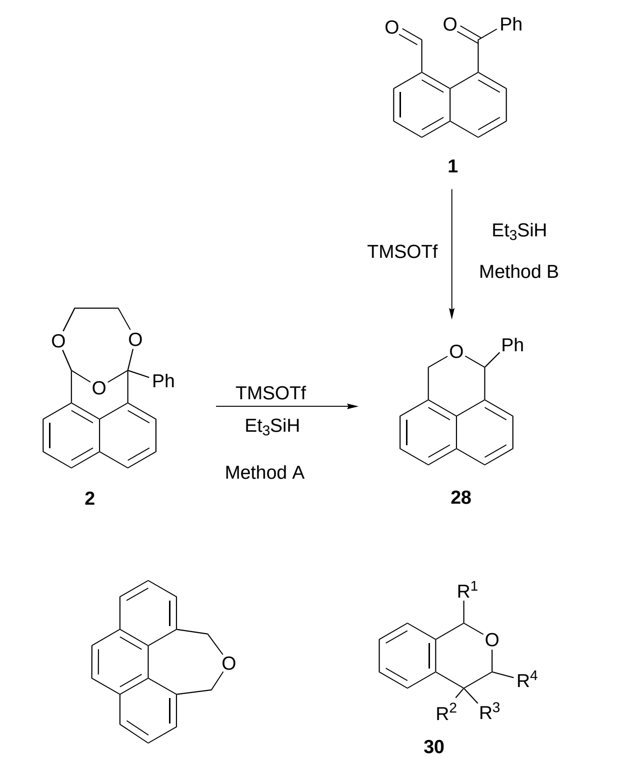
Reaction of the trioxepane with triethylsilane in the presence of trimethylsilyl triflate

Treatment of the trioxepane **2** with triethylsilane in the presence of trimethylsilyl triflate (TMSOTf) gave the expected cyclic ether **28** in good yield (Scheme 7).[8] In a similar fashion, the trioxepanes **8**,**13c**–**e** were smoothly reduced to the cyclic ethers **29**,**30c**–**e** respectively (Table 5). However, the cyclic ethers **28**–**30** were found to be more conveniently prepared by reduction of dicarbonyl compounds with triethylsilane. The yields were generally superior to those obtained from the reactions of the corresponding trioxepanes. Since under similar conditions, aliphatic and aromatic carbonyl compounds are easily reduced to give the corresponding alcohols,[9] and ω-hydroxy-substituted ketones give the corresponding cyclic ethers,[10] the formation of cyclic ethers **28**–**30** from dicarbonyl compounds is most likely to proceed *via* the corresponding diols.

Experimental

General

^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ with $SiMe_4$ as standard, using a JEOL JNM-EX-270 spectrometer; *J* values are given in Hz. IR Spectra were recorded on a Hitachi 260 spectrometer. 8-Benzoylnaphthalene-1-carbaldehyde **1**, phenanthrene-4,5-dicarbaldehyde **7**, 2-(*o*-benzoylphenyl)acetalde-



	R1	R2	R3	R4
a	Ph	H	H	H
b	Ph	Me	H	H
c	Ph	Me	Me	H
d	H	Ph	H	Ph
e	H	-(CH2)4-		Ph

Scheme 7

Table 5 Cyclic ethers from the reaction of trioxepanes (Method A) or dicarbonyl compounds (Method B) with triethylsilane–trimethylsilyl triflate

	Method A		Method B	
Product	Substrate	Yield (%)	Substrate	Yield (%)
28	**2**	97	**1**	98
29	**8**	89	**7**	92
30a	—	—	**12a**	71
30b	—	—	**12b**	63
30c	**13c**	57	**12c**	82
30d	**13d**	53	**12d**	59
30e	**13e**	42	**12e**	69

hyde **12a**, 2-(*o*-benzoylphenyl)propanal **12b**, and *o*-(1,2-diphenyl-2-oxoethyl)benzaldehyde **12d** were prepared by the reported methods.[11]

Preparation of 2-(*o*-benzoylphenyl)-2-methylpropanal 12c and *o*-(1-benzoylcyclopentyl)benzaldehyde 12e

The preparation of the dialdehyde **12c** is representative. Into a solution of 1,1-dimethyl-3-phenylindene (3.31 g, 15 mmol) in dichloromethane, was passed a slow stream of ozone (1.5 equiv.). After evaporation of the solvent, the residue was dissolved in benzene, and treated with triphenylphosphine (1 equiv.) for 15 h. After concentration, the crude product was purified by column chromatography on silica gel. Elution with diethyl ether–benzene (3:97) gave the keto aldehyde **12c** (2.76 g, 73%).

2-(*o*-Benzoylphenyl)-2-methylpropanal 12c. Pale yellow liquid (Found: C, 81.2; H, 6.2. $C_{17}H_{16}O_2$ requires: C, 81.0; H, 6.3%); δ_H 1.30 (6 H, s), 7.2–7.8 (9 H, m) and 9.38 (1 H, s); ν_{max}/cm^{-1} 1670 and 1730.

***o*-(1-Benzoylcyclopentyl)benzaldehyde 12e.** (85%) Mp 75–76 °C (from hexane) (Found: C, 82.2; H, 6.6. $C_{19}H_{18}O_2$ requires: C, 82.0; H, 6.5%); δ_H 1.7–2.0 (m, 4 H), 2.2–2.4 (m, 2 H), 2.6–2.8 (m, 2 H), 7.1–7.8 (m, 9 H), 10.06 (s, 1 H); ν_{max}/cm^{-1} 1770, 1680, 1450, 1235, 755 and 705.

Reaction of dicarbonyl compounds with ethylene glycol in the presence of chlorosulfonic acid

The reaction of the keto aldehyde **1** is representative. A solution of keto aldehyde **1** (542 mg, 2.08 mmol), ethylene glycol (10 cm^3) and chlorosulfonic acid (281 mg, 2.41 mmol) in dichloromethane (40 cm^3) was stirred at room temperature for 15 h. After addition of diethyl ether (100 cm^3), the organic layer was washed with aqueous $NaHCO_3$, saturated brine, and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel. Elution with diethyl ether–hexane (3:97) gave the trioxepane derivative **2** (493 mg, 78%).

3,4-Dihydro-1-phenyl-1,6-epoxy-1*H*,6*H*-naphtho[1,8-*fg*][1,4]-dioxonine 2. Mp. 159–161 °C (from ethyl acetate–hexane) (Found: C, 78.8; H, 5.2. $C_{20}H_{16}O_3$ requires: C, 78.9; H, 5.3%); δ_H 3.6–4.4 (4 H, m), 6.50 (1 H, s) and 6.8–8.0 (11 H, m); δ_C 66.47, 66.92, 96.01, 97.10, 122.20, 123.02, 124.33, 125.53, 125.95, 127.29, 128.01, 128.16, 128.43, 128.53, 128.61, 130.40, 132.02, 132.18, 132.43 and 135.50.

1,3,4,6-Tetrahydro-1,6-epoxy-phenanthro[4,5-*fgh*][1,4]-dioxecine 8. Mp 114–116 °C (from methanol) (Found: C, 77.8; H, 5.0. $C_{18}H_{14}O_3$ requires: C, 77.8; H, 5.1%); δ_H 3.93 (4 H, s), 6.17 (2 H, s) and 7.2–7.9 (8 H, m); δ_C 66.84, 102.27, 126.03, 126.67, 127.60, 128.03, 129.83, 134.52 and 137.71.

3,4,6,7-Tetrahydro-7,7-dimethyl-1-phenyl-1,6-epoxy-1*H*-benzo[1,4]dioxonine 13c. Colourless oil (Found: C, 77.3; H, 7.0. $C_{19}H_{20}O_3$ requires: C, 77.0; H, 6.8%); δ_H 1.30 (3 H, s), 1.40 (3 H, s), 3.4–3.7 (2 H, m), 3.87 (1 H, d, *J* 12), 4.29 (1 H, dd, *J* 12 and 10), 5.0 (1 H, s) and 7.1–7.5 (9 H, m); δ_C 23.29, 28.25, 38.24, 66.45, 66.76, 100.86, 102.66, 125.12, 125.80, 126.04, 126.27, 127.44, 127.92, 128.10, 128.52, 128.63, 133.21, 143.49 and 144.91.

3,4,6,7-Tetrahydro-6,7-diphenyl-1,6-epoxy-1*H*-benzo[1,4]-dioxonine 13d. Mp 170–172 °C (from diethyl ether–hexane) (Found: C, 79.9; H, 5.8. $C_{23}H_{20}O_3$ requires: C, 80.2; H, 5.9%); δ_H 3.3–3.8 (4 H, m), 4.13 (1 H, s), 6.47 (1 H, s) and 6.6–7.5 (14 H, m); δ_C 55.14, 65.23, 95.76, 102.80, 125.87, 126.93, 127.05, 127.38, 127.50, 127.63, 127.80, 127.92, 128.30, 128.66, 128.97, 129.71, 130.02, 131.73, 138.45, 139.42 and 140.08.

3,4,6,7-Tetrahydro-6-phenyl-1,6-epoxy-1*H*-benzo[1,4]-dioxonine-7-spirocyclopentane 13e. Mp 165–167 °C (Found: C, 77.8; H, 6.85. $C_{21}H_{22}O_3$ requires: C, 78.2; H, 6.9%); δ_H 0.7–2.3 (8 H, m), 3.2–3.9 (4 H, m), 6.23 (1 H, s) and 7.2–7.8 (9 H, m); δ_C 25.52, 27.38, 33.43, 38.47, 54.10, 64.75, 65.33, 95.42, 105.17, 125.56, 125.64, 127.52, 127.61, 128.09, 128.75, 128.91, 128.99, 129.19, 130.62, 138.83, 146.90.

Phenyl *o*-(1,3-dioxolan-2-ylmethyl)phenyl ketone 14a. Colorless oil (Found: C, 76.0; H, 6.1. $C_{17}H_{16}O_3$ requires: C, 76.1; H, 6.0%); δ_H 3.14 (2 H, d, *J* 4.5), 3.6–3.8 (4 H, m), 5.05 (1 H, t, *J* 4.5) and 7.2–7.9 (9 H, m); δ_C 37.27, 64.51, 103.97, 125.73, 127.08, 128.73, 129.79, 129.88, 131.84, 132.79, 134.97, 137.66, 139.17 and 197.96.

Phenyl *o*-[1-(1,3(dioxolan-2-yl)ethyl]phenyl ketone 14b. Oil (Found: C, 76.5; H, 6.5. $C_{18}H_{18}O_3$ requires: C, 76.6; H, 6.4%); δ_H 1.25 (3 H, d, *J* 6), 2.8–3.8 (5 H, m), 4.87 (1 H, d, *J* 4) and 6.7–8.1 (9 H, m); ν_{max}/cm^{-1} 710, 930, 1100, 1460, 1670 and 2950.

Reaction of dicarbonyl compounds with trimethylene glycol in the presence of chlorosulfonic acid

The reaction of the keto aldehyde **1** is representative. A solution of keto aldehyde **1** (194 mg, 0.75 mmol), trimethylene glycol (573 mg, 7.5 mmol) and chlorosulfonic acid (144 mg, 1.24 mmol) in dichloromethane (40 cm^3) was stirred at room temperature for 15 h. After the work-up as described above, the crude products were isolated by column chromatography on silica gel. The first fraction (elution with diethyl ether–hexane, 3:97) afforded the 1,3-dioxane derivative **4** (72 mg, 30%). From the second fraction (diethyl ether–hexane, 10:90) was obtained the trioxepane derivative **3** (80 mg, 34%).

4,5-Dihydro-1-phenyl-1,7-epoxy-1*H*,3*H*,7*H*-naphtho[1,8-*gh*]-[1,5]dioxocine 3. Mp 178–179 °C (Found: C, 79.1; H, 5.6. $C_{21}H_{18}O_3$ requires: C, 79.3; H, 5.7%); δ_H 1.47 (1 H, m), 2.17 (1 H, m), 4.10 (4 H, m), 6.29 (1 H, s), 7.1–7.9 (11 H, m); δ_C 30.87, 64.84, 66.60, 97.06, 101.21, 123.58, 123.85, 125.49, 125.87, 125.98, 127.12, 127.80, 128.04, 128.19, 128.29, 128.60, 129.51, 132.54, 133.41 and 142.88.

Phenyl 8-(1,3-dioxan-2-yl)-1-naphthyl ketone 4. Mp 122–124 °C (Found: C, 79.05; H, 5.8. $C_{21}H_{18}O_3$ requires: C, 79.3; H, 5.7%); δ_H 1.12 (1 H, m), 1.82 (1 H, m), 3.6–3.8 (4 H, m), 5.62 (1 H, s), 7.3–8.0 (11 H, m); δ_C 25.39, 65.79, 98.98, 123.13, 125.54, 127.35, 128.00, 128.27, 128.50, 130.19, 130.93, 132.00, 132.47, 134.11, 135.11, 136.87, 137.83 and 195.99; ν_{max}/cm^{-1} 1100, 1290, 1660 and 2850.

1,7-Epoxy-1,4,5,7-tetrahydro-3*H*-phenanthro[4,5-*ghi*]-[1,5]dioxacycloundecine 9. Mp 110–112°C (Found: C, 77.6; H, 5.1. $C_{19}H_{16}O_3$ requires: C, 77.8; H, 5.1%); δ_H 1.9–2.2 (2 H, m), 3.8–4.3 (4 H, m), 5.94 (1 H, s), 6.45 (1 H, s) and 7.5–7.9 (8 H, m); δ_C 14.11, 15.28, 32.60, 65.84, 67.30, 67.76, 68.20, 90.24, 99.32, 101.60, 121.02, 124.78, 125.70, 125.91, 127.58, 128.05, 128.28, 128.88, 130.01, 133.78, 134.47, 138.72 and 139.41.

4,5,7,8-Tetrahydro-1-phenyl-8,8-dimethyl-1,7-epoxy-1*H*,3*H*-benzo[1,5]dioxecine 15. Colourless oil (Found: C, 77.9; H, 7.1. $C_{20}H_{22}O_3$ requires C, 77.4; H, 7.1%); δ_H 1.40 (6 H, s), 1.4–1.6 (1 H, m), 2.0–2.2 (1 H, m), 3.8–4.2 (4 H, m), 4.84 (1 H, s) and 7.1–7.5 (9 H, m); δ_C 23.38, 30.93, 31.54, 36.73, 62.45, 68.93, 99.52, 105.32, 124.83, 124.93, 126.09, 126.85, 127.80, 127.94, 128.09, 128.16, 128.27, 135.22, 139.32 and 144.08.

Phenyl *o*-(1,3-dioxan-2-ylmethyl)phenyl ketone 16. Colourless oil (Found: C, 76.2; H, 6.55. $C_{18}H_{18}O_3$ requires: C, 76.6; H, 6.4%); δ_H 1.1–1.3 (1 H, m), 1.7–1.9 (1 H, m), 2.9 (2 H, d, *J* 7), 3.4–3.6 (2 H, m), 3.7–3.9 (2 H, m), 4.57 (1 H, t, *J* 7) and 7.1–7.8 (9 H, m); δ_C 25.45, 38.78, 66.52, 101.78, 125.64, 128.09, 128.39, 129.88, 130.25, 132.13, 132.83, 135.29, 137.75, 139.26 and 198.31.

1,2-Diphenyl-2-[*o*-(1,3-dioxan-2-yl)phenyl]ethan-1-one 17. Mp 162–163 °C (Found: C, 80.3; H, 6.2. $C_{24}H_{22}O_3$ requires C, 80.4; H, 6.2%); δ_H 1.3 (1 H, d, *J* 14), 2.0–2.2 (1 H, m), 3.7–4.0 (3 H, m), 4.15 (1 H, dd, *J* 12 and 5), 5.48 (1 H, s), 6.77 (1 H, s), 7.0–7.6 (12 H, m) and 8.00 (2 H, d, *J* 7); δ_C 25.48, 55.17, 67.23, 67.40, 101.96, 126.86, 126.99, 127.24, 128.39, 128.95, 129.51, 130.58, 132.54, 135.53, 136.95, 137.39, 138.80 and 198.35.

Reaction of dicarbonyl compounds with 2,2-dimethylpropane-1,3-diol in the presence of chlorosulfonic acid

The reaction of the dialdehyde **7** is representative. A solution of dialdehyde **7** (200 mg, 0.87 mmol), 2,2-dimethylpropane-1,3-diol (1.4 g, 13 mmol) and chlorosulfonic acid (100 mg, 0.87 mmol) in dichloromethane (40 cm^3) was stirred at room temperature for 15 h. After the work-up as above, the crude products were separated by column chromatography on silica gel. Elution with benzene gave the keto acetal **10** (214 mg, 61%).

Phenyl 8-(5,5-dimethyl-1,3-dioxan-2-yl)-1-naphthyl ketone 5. Mp 170–175 °C (from ethyl acetate–hexane) (Found: C, 79.6; H, 6.45. $C_{23}H_{22}O_3$ requires: C, 79.7; H, 6.4%); δ_H 0.75 (3 H, s), 1.00 (3 H, s), 2.8–4.1 (4 H, m), 5.67 (1 H, s) and 7.3–8.2 (11 H, m); δ_C 21.72, 23.11, 30.04, 99.13, 123.19, 125.53, 125.70, 125.86, 127.48, 128.04, 128.46, 128.67, 130.25, 130.95, 132.08, 132.55, 133.99, 135.21, 136.90, 137.84 and 196.12; ν_{max}/cm^{-1} 730, 790, 840, 1110, 1290, 1670, 2980.

4,5-Bis(5,5-dimethyl-1,3-dioxan-2-yl)phenanthrene 10. Mp 245–250 °C (from methanol) (Found: C, 76.5; H, 7.45. $C_{26}H_{30}O_4$ requires: C, 76.8; H, 7.45%); δ_H 0.67 (6 H, s), 1.67 (6 H, s), 3.67 (4 H, s), 3.90 (4 H, s), 6.23 (2 H, s) and 7.2–8.2 (8 H, m); δ_C 21.71, 23.13, 30.26, 100.66, 125.87, 126.10, 126.54, 127.09, 128.46, 133.67 and 136.96; ν_{max}/cm^{-1} 840, 1040 and 1300.

Reaction of dicarbonyl compounds with methanol in the presence of chlorosulfonic acid

The reaction of the keto aldehyde **1** is representative. A solution of keto aldehyde **1** (300 mg, 1.15 mmol), methanol (10 cm^3) and a few drops of conc. HCl in dichloromethane (40 cm^3) was stirred at room temperature for 15 h. After the work-up as above, the crude products were separated by column chromatography on silica gel. Elution with benzene–hexane (1:9) gave the dihydropyran **12a** (143 mg, 41%).

1,3-Dimethoxy-1-phenyl-1*H*,3*H*-naphtho[1,8-*cd*]pyran 18. Mp 152–154 °C (Found: C, 78.4; H, 5.9. $C_{20}H_{18}O_3$ requires: C, 78.4; H, 5.9%); δ_H 3.50 (3 H, s), 3.67 (3 H, s), 6.30 (1 H, s) and 7.2–8.0 (m, 11 H).

1,3-Dimethoxy-1,3-dihydrophenanthro[4,5-*cde*]oxepine 19. Colourless oil (Found: C, 76.8; H, 5.75. $C_{18}H_{16}O_3$ requires: C, 77.1; H, 5.75%); δ_H 3.67 (6 H, s), 5.64 (2 H, s) and 7.3–7.9 (8 H, m).

3,4-Dihydro-1,3-dimethoxy-4,4-dimethyl-1-phenyl-1*H*-benzo[*c*]pyran 20. Colourless oil (Found: C, 76.7; H, 7.8. $C_{19}H_{22}O_3$ requires: C, 76.5; H, 7.4%); δ_H 1.40 (6 H, s), 3.41 (3 H, s), 3.62 (3 H, s), 4.87 (1 H, s) and 7.1–7.8 (9 H, m); δ_C 23.40, 23.60, 38.24, 50.53, 57.50, 101.96, 102.53, 125.48, 126.11, 127.22, 127.67, 127.94, 128.27, 128.37, 135.67, 141.19 and 142.34.

Reaction of 1,3,5-trioxepanes with Grignard reagents

The reaction of keto aldehyde **1** with isopropylmagnesium bromide is representative. To a solution of isopropylmagnesium bromide, prepared from isopropyl bromide (1234 mg, 10.04 mmol) and magnesium (244 mg, 10.04 mmol) in diethyl ether (50 cm^3), was added a solution of the trioxepane **2** (304 mg, 1.00 mmol) in benzene (50 cm^3) and the resulting mixture was heated at reflux for 4 h. The reaction mixture was poured into ice-cold aqueous HCl, and the organic layer was washed with aqueous $NaHCO_3$, saturated brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the dihydropyran **24b** (94 mg, 28%) was isolated from the crude product mixture by column chromatography on silica gel eluting with benzene–hexane (3:7).

1,3-Dimethyl-1-phenyl-1*H*,3*H*-naphtho[1,8-*cd*]pyran 21. A mixture of *cis*- and *trans*-isomers 88:12, colourless oil (Found: C, 87.5; H, 6.7. $C_{20}H_{18}O$ requires C, 87.6; H, 6.6%); δ_H (major) 1.72 (3 H, d, *J* 7.5), 1.94 (3 H, s), 5.40 (1 H, q, *J* 7.5) and 7.2–7.8 (11 H, m); δ_C 20.92, 25.02, 66.74, 78.13, 119.78, 122.61, 125.27, 125.34, 126.07, 126.38, 127.08, 127.33, 127.91, 128.18, 131.86, 132.00, 132.67, 136.57, 140.63 and 146.34; δ_H (minor) 1.66 (3 H, d, *J* 7.5), 2.00 (3 H, s), 4.68 (1 H, q, *J* 7.5) and 7.2–7.8 (11 H, m); δ_C 19.75, 31.23, 66.96, 79.12, 119.67, 125.00, 125.43, 125.73, 126.67, 126.94, 127.49, 128.09, 128.28, 128.46, 128.66, 131.41, 132.94, 137.02, 137.36 and 144.96.

1,3-Dimethyl-1,3-dihydrophenanthro[4,5-*cde*]oxepine 25a. A mixture of *cis*- and *trans*-isomers 42:58, mp 94–102 °C (Found: C, 86.8; H, 6.6. $C_{18}H_{16}O$ requires C, 87.1; H, 6.5%); δ_H (major isomer) 1.65 (6 H, d, *J* 7.5), 4.63 (2 H, q, *J* 7.5) and 7.5–7.9 (8 H, m); δ_C 19.28, 71.77, 124.31, 126.34, 126.47, 127.13, 129.43, 132.00, 132.24 and 138.67; δ_H (minor one) 1.40 (6 H, d, *J* 7.5), 5.27 (2 H, q, *J* 7.5) and 7.5–7.9 (8 H, m); δ_C 22.61, 76.25, 123.95, 126.04, 126.97, 127.55, 128.27, 133.59 and 142.57.

1,3-Diethyl-1-phenyl-1*H*,3*H*-naphtho[1,8-*cd*]pyran 24a. A mixture of *cis*- and *trans*-isomers 86:14, colourless oil (Found: C, 87.6; H, 7.4. $C_{22}H_{22}O$ requires: C, 87.4; H, 7.3%); δ_H (major isomer) 1.01 (3 H, t, *J* 7.3), 1.12 (3 H, t, *J* 7.3), 2.0–2.4 (4 H, m), 5.22 (1 H, dd, *J* 6.6 and 3.6) and 7.0–7.8 (11 H, m); δ_C 8.30, 9.29, 27.37, 29.47, 70.24, 80.20, 119.84, 122.39, 125.27, 125.30, 126.15, 126.24, 126.33, 126.94, 127.33, 128.00, 128.05, 128.28, 133.10, 134.97, 140.61 and 143.86; δ_H (minor isomer) 0.96 (3 H, t, *J* 7.3), 1.13 (3 H, t, *J* 7.3), 1.9–2.2 (4 H, m), 4.61 (1 H, dd, *J* 6.6 and 3.6) and 7.0–7.8 (11 H, m); δ_C 8.68, 14.13, 26.38, 36.80, 70.56, 81.37, 119.50, 123.11, 124.82, 125.48, 126.67, 126.79, 127.46, 127.80, 133.44 and 134.66.

1,3-Diethyl-1,3-dihydrophenanthro[4,5-*cde*]oxepine 25b. A 1:1 mixture of *cis*- and *trans*-isomers, mp 88–91 °C (Found: C, 86.4; H, 7.3. $C_{20}H_{20}O$ requires C, 86.9; H, 7.3%); δ_H 0.6–0.8 (6 H, m), 1.6–2.1 (4 H, m), 4.40 (1 H, t, *J* 6.9), 4.88 (1 H, dd, *J* 8.4 and 4.2) and 7.4–7.8 (m, 8 H); δ_C 10.59, 11.18, 26.90, 29.44, 78.51, 82.01, 124.12, 125.01, 125.82, 126.29, 126.51, 126.99, 127.10, 127.40, 129.83, 131.57, 132.51, 133.44, 138.96 and 141.80.

1,*c*-3-Diisopropyl-*r*-1-phenyl-1*H*,3*H*-naphtho[1,8-*cd*]pyran 24b. Colourless oil (Found: C, 86.7; H, 8.1. $C_{24}H_{26}O$ requires C, 87.2; H, 7.9%); δ_H 0.91 (3 H, d, *J* 7.2), 0.94 (3 H, d, *J* 6.9), 1.16 (3 H, d, *J* 6.9), 1.29 (3 H, d, *J* 6.9), 2.6–2.7 (1 H, m), 2.8–2.9 (1 H, m), 5.37 (1 H, s) and 6.9–7.8 (11 H, m); δ_C 15.24, 17.84, 19.37, 20.31, 32.42, 36.30, 75.54, 81.67, 119.80, 123.52, 125.14, 125.30, 125.98, 126.20, 126.50, 127.11, 127.62, 127.71, 128.28, 128.34, 132.81, 134.43, 138.74 and 146.63.

1,1,3-Triphenyl-1*H*,3*H*-naphtho[1,8-*cd*]pyran 24c. Colourless oil (Found: C, 90.4; H, 6.2. $C_{30}H_{22}O$ requires: C, 90.5; H, 6.1%); δ_H 5.74 (1 H, s) and 6.7–7.5 (21 H, m); δ_C 75.62, 85.45, 122.75, 124.91, 125.34, 125.82, 127.80, 128.14, 128.30, 128.50, 128.70, 128.79, 128.91, 129.63, 132.83, 136.35, 136.87, 141.49, 142.97 and 147.04.

1,3-Diphenyl-1,3-dihydrophenanthro[4,5-*cde*]oxepine 25c. A mixture of *cis*- and *trans*-isomers 29:71, mp 194–196 °C (Found: C, 89.9; H, 5.5. $C_{28}H_{20}O$ requires C, 90.3; H, 5.4%); δ_H (major isomer) 6.34 (2 H, s) and 7.5–8.2 (18 H, m); δ_C 82.75, 126.02, 126.51, 126.76, 127.15, 127.44, 127.66, 127.78, 127.91, 128.00, 128.27, 129.87, 133.48, 141.44 and 142.16; δ_H (minor one) 6.82 (2 H, s) and 7.5–8.2 (18 H, m,); δ_C 79.12, 132.00, 132.11, 138.85 and 140.61.

Reaction of the dihydropyrans, 13c and 20, with methylmagnesium iodide

The reaction of **20** is representative. A solution of the dihydropyran **20** (168 mg, 0.54 mmol) and methylmagnesium iodide [prepared from methyl iodide (775 mg, 5.6 mmol) and magnesium (132 mg, 5.4 mmol)], in diethyl ether–benzene (50 cm^3, 1:1) was heated at reflux for 4 h. After work-up as described above, the acetal **23** (115 mg, 66%) was isolated by column chromatography on silica gel, eluting with benzene–diethyl ether (9:1).

3,4-Dihydro-3-(2-hydroxyethyloxy)-1-phenyl-1,4,4-trimethyl-1*H*-benzo[*c*]pyran 22. Reaction of **13c** gave **22** as a colourless oil (Found: C, 77.3; H, 8.0. $C_{20}H_{24}O_3$ requires C, 76.9; H, 7.7%); δ_H 1.37 (6 H, s), 1.98 (3 H, s), 2.40 (1 H, br s), 3.4–3.7 (4 H, m), 4.73 (1 H, s) and 6.8–7.5 (9 H, m); δ_C 23.99, 26.22, 28.39, 31.57, 61.91, 71.57, 79.25, 103.27, 125.59, 126.94, 127.12, 127.26, 127.42, 127.49, 127.76, 127.96, 128.30, 138.92, 141.74 and 146.77; ν_{max}/cm^{-1} 3200–3650.

3,4-Dihydro-3-methoxy-1-phenyl-1,4,4-trimethyl-1*H*-benzo[*c*]pyran 23. Reaction of **20** gave **23** as a colourless oil (Found: C, 80.6; H, 7.8. $C_{19}H_{22}O_2$ requires C, 80.8; H, 7.8%); δ_H 1.35 (6 H, s), 2.00 (3 H, s), 3.15 (3 H, s), 4.60 (1 H, s) and 6.8–7.5 (9 H, m); δ_C 23.83, 26.47, 28.45, 38.21, 56.19, 78.74, 104.15, 125.46, 125.54, 126.92, 127.03, 127.22, 127.30, 127.85, 139.34, 141.94 and 147.13.

Reaction of 1,3,5-trioxepanes with allyltributyltin in the presence of titanium tetrachloride

The reaction of the trioxepane **2** is representative. To a solution of the trioxepane **2** (255 mg, 0.84 mmol) in dichloromethane (20 cm^3) was added $TiCl_4$ (172 mg, 0.91 mmol), and then allyltributyltin (805 mg, 2.43 mmol) at −70 °C under nitrogen. After 1 h, diethyl ether (50 cm^3) was added, and the mixture was washed with aqueous $NaHCO_3$, saturated brine, and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the crude products were separated by column chromatography on silica gel. Elution with benzene–hexane (3:7) gave the dihydropyran ***c*-24d** (134 mg, 49%).

1,*c*-3-Diallyl-*r*-1-phenyl-1*H*,3*H*-naphtho[1,8-*cd*]pyran *c*-24d. Colourless oil (Found: C, 88.4; H, 7.2. $C_{24}H_{22}O$ requires C, 88.3; H, 6.8%); δ_H 2.8–3.2 (4 H, m), 5.0–5.2 (4 H, m), 5.41 (1 H, t, *J* 6.3), 5.8–6.1 (2 H, m) and 6.8–7.8 (11 H, m); δ_C 39.00, 41.13, 69.74, 79.66, 117.05, 117.72, 120.38, 122.66, 125.28, 125.32, 125.55, 126.00, 126.43, 126.54, 127.17, 127.57, 128.00, 133.03, 133.71, 134.39, 134.50, 134.83, 139.44 and 143.86.

1,3-Dihydro-1,3-diallylphenanthro[4,5-*cde*]oxepine 25d. A 1:1 mixture of *cis*- and *trans*-isomers, colourless oil (Found: C, 87.7; H, 6.65. $C_{22}H_{20}O$ requires C, 88.0; H, 6.7%); δ_H 2.3–2.9 (4 H, m), 4.70 (1 H, t, *J* 6.3), 4.8–5.0 (4 H, m), 5.16 (1 H, t, *J* 6.3), 5.6–5.8 (2 H, m) and 7.5–7.9 (8 H, m); δ_C 38.35, 40.61, 76.91, 80.15, 116.50, 116.60, 124.58, 125.32, 126.00, 126.38, 126.61, 127.10, 127.31, 127.66, 133.41, 135.20, 135.54, 138.26 and 140.74.

3,4-Dihydro-1,*c*-3-diallyl-4,4-dimethyl-*r*-1-phenyl-1*H*-benzo[*c*]pyran *c*-26. Colourless oil (Found: C, 86.35; H, 8.2. $C_{23}H_{26}O$ requires C, 86.75; H, 8.2%); δ_H 1.33 (3 H, s) 1.34 (3 H, s), 2.3–2.5 (2 H, m), 3.15 (2 H, d, *J* 1.7), 3.85 (1 H, dd, *J* 9.2 and 2.5), 5.0–5.2 (4 H, m), 5.8–6.1 (2 H, m) and 6.8–7.6 (9 H, m); δ_C 24.85, 25.32, 34.95, 36.62, 41.67, 76.46, 80.06, 115.72, 117.47, 125.48, 125.77, 126.45, 126.79, 127.39, 127.96, 134.39, 137.34, 140.31, 142.88 and 145.44.

Reaction of the keto aldehyde 12e with allyltributyltin in the presence of titanium tetrachloride

To a solution of the keto aldehyde **12e** (279 mg, 1.00 mmol) in dichloromethane (20 cm^3) was added $TiCl_4$ (202 mg, 1.06 mmol), and then allyltributyltin (1030 mg, 3.11 mmol) at −70 °C under nitrogen. After 1 h, diethyl ether (50 cm^3) was added, and the mixture was washed with aqueous $NaHCO_3$, saturated brine, and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel. Elution with diethyl ether–hexane (13:87) gave the keto-alcohol **27** (249 mg, 78%).

Phenyl 1-[*o*-(1-hydroxybut-3-enyl)phenyl]cyclohexyl ketone 27. Colourless oil (Found: C, 82.0; H, 7.8. $C_{22}H_{24}O_2$ requires: C, 82.5; H, 7.55%); δ_H 0.7–1.4 (8 H, m), 2.0–2.6 (2 H, m), 3.18 (1 H, dd, *J* 6.8 and 0.5), 5.0–5.2 (2 H, m), 5.71 (1 H, br s), 5.9–6.1 (1 H, m) and 7.2–7.8 (9 H, m); δ_C 12.31, 14.04, 14.29, 28.65, 40.13, 70.91, 78.38, 116.17, 125.61, 128.70, 130.08, 130.35, 130.96, 133.46, 134.09, 136.35, 137.38, 139.08, 141.99 and 199.24.

Reaction of the trioxepane 2 with triethylsilane in the presence of TMSOTf

The reaction of the trioxepane **2** is representative. To a solution of the trioxepane **2** (304 mg, 1.00 mmol) in dichloromethane (30 cm^3) was added triethylsilane (931 mg, 8.01 mmol) and then TMSOTf (457 mg, 2.06 mmol) at −70 °C and the mixture was stirred at room temperature for 45 min. After the work-up as described above, the dihydropyran derivative **28** (239 mg, 97%) was isolated by column chromatography [silica gel, eluting with benzene–hexane (1:1)].

1-Phenyl-1*H*,3*H*-naphtho[1,8-*cd*]pyran 28. Mp 96–98 °C (from ethyl acetate–hexane) (Found: C, 87.6; H, 5.75. $C_{18}H_{14}O$

requires C, 87.8; H, 5.7%); δ_H 5.17 (2 H, s), 5.97 (1 H, s), 6.8–7.8 (11 H, m); δ_C 67.07, 80.21, 120.11, 122.48, 125.42, 125.49, 125.53, 126.39, 126.75, 127.05, 128.25, 128.55, 128.59, 128.71, 132.60, 132.81, 134.97 and 140.42.

1,3-Dihydrophenanthro[4,5-*cde*]oxepine 29. Mp 55–57 °C (Found: C, 87.6; H, 5.5. $C_{16}H_{12}O$ requires C, 87.35; H, 5.5%); δ_H 4.83 (4 H, s) and 7.3–8.0 (8 H, m); δ_C 71.93, 126.33, 126.43, 126.95, 127.49, 127.85, 131.65, 132.95 and 136.88.

3,4-Dihydro-4,4-dimethyl-1-phenyl-1*H*-benzo[*c*]pyran 30c. Colourless oil (Found: C, 85.5; H, 7.7. $C_{17}H_{18}O$ requires C, 85.7; H, 7.6%); δ_H 1.28 (3 H, s), 1.44 (3 H, s), 3.68 (1 H, s), 3.72 (1 H, s), 5.72 (1 H, s) and 6.6–7.4 (9 H, m); δ_C 25.82, 29.42, 33.68, 75.26, 80.72, 122.26, 125.36, 125.88, 126.13, 127.58, 127.71, 127.98, 128.52, 128.77, 135.87, 142.23 and 143.40.

3,4-Dihydro-3,4-diphenyl-1*H*-benzo[*c*]pyran 30d. Colourless oil (Found; C, 87.8; H, 6.4. $C_{21}H_{18}O$ requires C, 88.1; H, 6.3%); δ_H 4.00 (1 H, d, *J* 3), 4.95 (1 H, d, *J* 3), 5.05 (1 H, d, *J* 19), 5.10 (1 H, d, *J* 19) and 6.6–7.2 (14 H, m); δ_C 50.19, 69.04, 79.93, 124.00, 125.88, 126.60, 126.81, 126.85, 127.21, 127.58, 130.05, 134.14, 137.07, 140.14 and 140.67.

3,4-Dihydro-3-phenyl-1*H*-benzo[*c*]pyran-4-spirocyclopentane 30e. Mp 41–45 °C (Found: C, 86.1; H, 7.6. $C_{19}H_{20}O$ requires C, 86.3; H, 7.6%); δ_H 0.8–2.1 (8 H, m), 4.52 (1 H, s), 4.68 (1 H, d, *J* 19), 4.78 (1 H, d, *J* 19) and 6.8–7.3 (9 H, m); δ_C 26.90, 31.52, 37.50, 39.14, 48.43, 67.15, 83.51, 123.45, 125.32, 126.07, 126.61, 127.42, 127.71, 127.94, 128.30, 128.68, 133.12, 138.81 and 145.53.

Reaction of dicarbonyl compounds with triethylsilane in the presence of TMSOTf

The reaction of the keto aldehyde **12a** is representative. To a solution of the keto aldehyde **12a** (221 mg, 0.99 mmol) in dichloromethane (30 cm^3) was added triethylsilane (929 mg, 7.99 mmol) and then TMSOTf (223 mg, 1.00 mmol) at −70 °C and the mixture was stirred at room temperature for 45 min. After the work-up as described above, the crude products were separated by column chromatography on silica gel. Elution with benzene–hexane (1 : 1) gave the dihydropyran derivative **30a** (147 mg, 71%).

3,4-Dihydro-1-phenyl-1*H*-benzo[*c*]pyran 30a.[12] Mp 88–90 °C (Found: C, 85.3; H, 6.7. $C_{15}H_{14}O$ requires C, 85.7; H, 6.7%); δ_H 2.7–2.9 (1 H, m), 3.0–3.2 (1 H, m), 3.8–4.0 (1 H, m), 4.2–4.3 (1 H, m), 5.73 (1 H, s) and 6.7–7.4 (9 H, m); δ_C 28.79, 63.90, 79.64, 125.89, 126.57, 126.88, 128.07, 128.39, 128.70, 128.86, 133.80, 137.32 and 142.15.

3,4-Dihydro-4-methyl-1-phenyl-1*H*-benzo[*c*]pyran 30b.[13] Colourless oil (Found: C, 85.4; H, 7.1. $C_{16}H_{16}O$ requires C, 85.7; H, 7.2%); δ_H 1.35 (3 H, d, *J* 7.5), 3.01 (1 H, qt, *J* 7.5 and 7.5), 3.41 (1 H, dd, *J* 12.0 and 7.5), 3.95 (1 H, dd, *J* 12.0 and 7.5), 5.57 (1 H, s) and 6.6–7.3 (9 H, m); δ_C 21.64, 32.69, 69.92, 80.20, 125.88, 126.69, 127.35, 128.00, 128.07, 128.39, 128.66, 128.84, 136.80, 139.35 and 132.14.

Molecular modelling studies on 1,3,5-trioxepane 2 and related compounds

The molecular modelling studies were performed on a Power Computing Power Centre Pro computer equipped with 210 MHz 604e RISC processor, 64 Mb of RAM, 1 Mb L2 cache and 60 MHz system bus.

Initial structures for the Monte Carlo conformational searches were generated by a custom written Applescript which allowed the rotation of the torsional angles of selected molecular segments by up to 35°. Molecular Mechanics minimizations were then performed using the modified MM2 force field implemented in Chem 3D Pro (ver. 3.5.1). Semi-empirical calculations were performed with MOPAC93 using PM3 potential functions.

Chem3D Pro and MOPAC93 were purchased from CambridgeSoft as part of ChemOffice.

Crystal structure determination of the 1,3,5-trioxepane 2

The crystal of **2** used for X-ray data collection (approx. dimensions 0.2 × 0.3 × 0.4 mm) was grown by slow evaporation from an ethyl acetate–hexane solution and mounted in a sealed Lindemann capillary tube.

Crystal data. $C_{20}H_{16}O_3$, $M = 304.3$, colourless prisms, monoclinic, space group $P2_1/n$ (alternative setting of No. 14), $a = 8.4715$ (8), $b = 22.608$ (3), $c = 8.7042$ (9) Å, $\beta = 117.481$ (7)°, $V = 1478.9$ (3) Å^3, $Z = 4$, $D_c = 1.367$ g cm^{-3}, $F(000) = 640$, μ(Mo-Kα) = 0.091 mm^{-1}.

Data collection. The intensity data were collected on Siemens P4 four-circle diffractometer [temperature 293(2) K; θ range: 1.80 to 25.0°; $-1 \leqslant h \leqslant 10$, $-1 \leqslant k \leqslant 26$, $-10 \leqslant l \leqslant 9$] using graphite monochromated Mo-Kα X-radiation (λ 0.710 73 Å) and ω-scanning. Of the 2578 unique data [R(int) = 0.037] measured, 1454 had $F_o > 4\sigma(F_o)$. The data were corrected for Lorentz and polarisation effects, but not for absorption.

Structure solution and refinement. The approximate positions of the non-hydrogen atoms were determined by direct methods [SHELXS-86] (ref. 14). The structure was refined by full-matrix least-squares methods on F^2 (SHELXTL/PC[15]) using all F_o^2 data and anisotropic temperature factors for all the non-hydrogen atoms. All the hydrogen atoms were located on difference Fourier maps and included in the refinement process at idealised positions with isotropic temperature factors (1.5 times U_{iso} of the bonded heavy atom). At convergence, the discrepancy factors R and wR^2 were 0.052 and 0.101 respectively. The weighting scheme, $w = 1/[\sigma^2(F_o^2) + (0.0487\ P)^2]$ where $P = (F_o^2+2F_c^2)/3$, was found to give satisfactory analyses of variance. The final difference Fourier map was essentially featureless (general noise level less than ±0.10 e Å^{-3}) with largest difference peak and hole of 0.18 and −0.19 e Å^{-3} respectively.‡

Crystal structure determination of the 1,3,5-trioxocane 3

The general experimental procedures were as described above for **2**.

Crystal data. $C_{21}H_{18}O_3$, $M = 318.4$, colourless prisms (approx. dimensions 0.30 × 0.34 × 0.81 mm from diethyl ether–hexane), monoclinic, space group P2$_1$/c (No. 14), $a = 8.5324$ (9), $b = 11.1349$ (11), $c = 16.9196$ (13) Å, $\beta = 100.699$ (7)°, $V = 1579.5$ (3) Å^3, $Z = 4$, $D_c = 1.339$ g cm^{-3}, $F(000) = 672$, μ(Mo-Kα) = 0.089 mm^{-1}. The 2758 unique data [R(int) = 0.034]) were measured on a Siemens P4 four-circle diffractometer [temperature 293(2) K; θ range: 2.20 to 25.0°; $-1 \leqslant h \leqslant 10$, $-1 \leqslant k \leqslant 13$, $-20 \leqslant l \leqslant 20$; Mo-Kα X-radiation ($\lambda$ 0.710 73 Å); ω–scanning). The structure was solved by direct methods [SHELXS-86 (ref. 14)] and refined by full-matrix least-squares methods on F^2 (SHELXTL/PC[15]). At convergence, the discrepancy factors R and wR^2 ($w = 1/[\sigma^2(F_o^2) + (0.0433\ P)^2]$) where $P = (F_o^2 + 2F_c^2)/3$), were 0.052 and 0.101 respectively for 1739 data with [$F_o > 4\sigma(F_o)$]. The final difference Fourier map was essentially featureless (general noise level less than ±0.10 e Å^{-3}) with largest difference peak and hole of 0.15 and −0.15 e Å^{-3} respectively.‡

Crystal structure determination of the keto acetal 4

The general experimental procedures were as described above for **2**.

Crystal data. $C_{21}H_{18}O_3$, M = 318.4, colourless prisms (approx. dimensions 0.42 × 0.46 × 0.63 mm from diethyl ether–hexane), orthorhombic, space group *Pbca* (No. 61), $a = 8.5902$ (14), $b = 11.4363$ (13), $c = 34.025$ (5) Å, $V = 3342.6$ (8) Å^3,

‡ Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc.*, *Perkin Trans. 1*, available *via* the RSC Web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/229.

$Z = 8$, $D_c = 1.265$ g cm^{-3}, $F(000) = 1344$, μ(Mo-Kα) = 0.084 mm^{-1}. The 2888 unique data [R(int) = 0.038]) were measured on Siemens P4 four-circle diffractometer (temperature 293(2) K; θ range: 1.20 to 25.0°; $-1 \leqslant h \leqslant 10$, $-1 \leqslant k \leqslant 13$, $-1 \leqslant l \leqslant 40$; Mo-K$\alpha$ X-radiation (λ 0.710 73 Å); ω–scanning). The structure was solved by direct methods [SHELXS-86 (ref. 14)] and refined by full-matrix least-squares methods on F^2 (SHELXTL/PC[15]). At convergence, the discrepancy factors R and wR^2 ($w = 1/[\sigma^2(F_o^2) + (0.0504\ P)^2 + 0.06\ P]$) where $P = (F_o^2 + 2F_c^2)/3$), were 0.058 and 0.110 respectively for 1215 data with [$F_o > 4\sigma(F_o)$]. The final difference Fourier map was essentially featureless (general noise level less than ±0.10 e Å^{-3}) with largest difference peak and hole of 0.18 and −0.17 e Å^{-3} respectively.‡

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