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STUDIES ON NUCLEOPHILIC RING OPENING OF SOME EPOXIDES IN POLAR PROTIC SOLVENTS—I†

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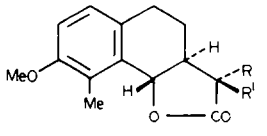
Abstract—The epoxides of the type **4** undergo ring-opening with carbanions; without exception, the nucleophiles attack at C-1 in spite of the increased steric hindrance at the site (as in epoxides **4b** and **4e** having peri-substituents). Interaction of the epoxide **4b** with the anion of diethyl methylmalonate in refluxing t-butanol afforded, besides other products, the novel cyclopropane carboxylic acid **12**. What is more significant is that although the formation of the trans-lactone on the whole is favoured in the ring opening of epoxides **4**, at least in two cases, **4b** and **4c**, there is considerable formation of cis-lactones, a result that remains unexplained. Attempted synthesis of the model cis-lactone **3c** always resulted in the formation of a 1:1 mixture of the cis-**3c** and the trans-lactone **2a**. The stereochemistries of the cis- and the trans-lactones described in this paper have been unambiguously established from the position of the 3a-proton signals of these γ-lactones in their NMR spectra.

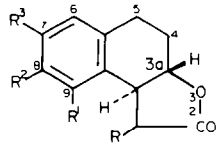
In connection with some synthetic studies of desmotroposantonins and related[1] lactones (as **1**), we synthesised[2] two stereoisomers of cis-1-desmethyldesmotroposantonin methyl ether (as **1a** and **1b** with cis-fused lactone ring). The problem however remains to find ways to synthesise the other two trans-isomers **1a** and **1b**. The epoxides **4** appear to be the most attractive starting materials since on reaction with anions derived from malonic esters, they could in principle give rise to the two series of the trans-lactones **1** and **2** depending on the initial point of attack on the epoxides. A priori one would expect the nucleophilic attack to be directed primarily at the benzylic carbon (C-1) which is ordinarily more reactive towards S_N2 reaction (also towards S_N1); van Tamelen *et al.*[3] synthesised the lactones **2a** and **2b** using the epoxide **4a** and diethyl malonate and methylmalonate respectively. On the other hand, data are available in the literature which indicate that the attack may also be considerably influenced by steric factor,[4,5] particularly if any peri-substituent is present in the epoxide (as **4b**) in which case attack may even be at C-2 instead of C-1 leading to the desired products **1**. Formation of any cis-lactone by S_N2 mechanism is however precluded. A number of epoxides (as **4**) were therefore prepared with or without peri-substituent and their reactions with malonic esters studied. The result unfortunately did not follow any consistent pattern and the main objective, namely, synthesis of I, was never achieved. Nevertheless, some interesting observations were made both regarding the

†A portion of this work has appeared in a preliminary communication (see Ref. 13).



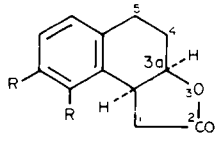
1

a: R = Me; R' = H
b: R = H; R' = Me



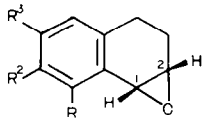
2

a: R = R' = R² = R³ = H
b: R = Me; R' = R² = R³ = H
c: R = R³ = H; R' = Me; R² = OMe
d: R = R' = Me; R² = OMe; R³ = H
e: R = R' = R³ = H, R² = OMe
f: R = R' = R² = H; R³ = OMe
g: R = H; R' = Br; R² = OMe; R³ = Me



3

a: R = Me; R' = OMe
b: R = H; R' = OMe
c: R = R' = H



4

a: R' = R² = R³ = H
b: R' = Me; R² = OMe; R³ = H
c: R² = OMe; R' = R³ = H
d: R³ = OMe; R' = R² = H
e: R' = Br; R² = OMe; R³ = Me

Fig. 1.

preparation of the epoxides as well as in their reactions with malonate. These are presented below under different sections with a discussion of the NMR spectra of the lactones.

Preparation of the epoxides

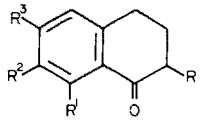
The preparation of the epoxide **4b** was first critically investigated. Halohydrins obtained through sodium borohydride reduction of α-haloketones have been successfully utilised[6] for the preparation of epoxides. Bromination of 7 - methoxy - 8 - methyl - 1 - tetralone[7] **5a** afforded the crystalline α-bromoketone **5b** which on sodium borohydride reduction furnished the undesired cis-bromohydrin **6a**. The preparation of the desired epoxide **4b** through peracid oxidation of the styrene **7a** was next attempted. Sodium borohydride reduction of the ketone **5a** gave the crystalline alcohol **8a** which on dehydration with acid provided the styrene **7a** for oxidation studies. This styrene **7a** on catalytic hydrogenation afforded the known tetralin derivative **8b**,[8] and on oxidation with perbenzoic acid provided only 7 - methoxy - 8 - methyl - 2 - tetralone. The transformation[9] of the trans-dibromide **6b** to the trans-bromohydrin **6c** was then studied in detail. Addition of bromine to the above styrene **7a** gave an oily dibromide which on refluxing with magnesium carbonate in acetone-water mixture gave in moderate yield the desired trans-bromohydrin **6c**. Attempted purification of the above oily dibromide through chromatography† afforded interestingly the trans-bromohydrin **6c** in comparable yield, and this method for the conversion of the dibromide of the type **6b** to the trans-bromohydrin **6c** seems to be more advantageous than the acetone-$MgCO_3$ method described above. An excellent yield of the trans-bromohydrin **6c** was realised when a solution of the above styrene **7a** in DMSO and H_2O was treated with NBS according to the stereospecific procedure of Dalton *et al.*[10] Mild treatment of the trans-bromohydrin **6c** with base provided in nearly quantitative yield the desired epoxide **4b**. The above bromohydrin **6c** on oxidation under non-epimerising[11] condition afforded the aforementioned tetralone derivative **5b**.

The epoxide **4c**, lacking the peri-methyl group was prepared as follows: The crude alcohol obtained through sodium borohydride reduction of 7 - methoxy - 1 - tetralone **5c**, was dehydrated to the styrene **7b**. The crystalline trans-dibromide **6d**, available by the addition of bromine to **7b**, was converted as before to the required trans-bromohydrin **6e** in poor yield. The styrene **7b** was, however, converted to the trans-bromohydrin **6e** in excellent yield following the stereospecific method[10] mentioned above. Mild treatment of **6e** with base gave the desired epoxide **4c**.

The styrene **7c**, required for the epoxide **4d**, was prepared from 6 - methoxy - 1 - tetralone **5d** by the same sequence of reactions reported above. Addition of NBS to a solution of **7c** in DMSO and H_2O as before afforded the desired trans-bromohydrin **6f**, and another crystalline material, m.p. 153–154°; and this was found to be different from the isomeric cis-bromohydrin **6g** available through sodium borohydride reduction of the known 2 - bromo - 6 - methoxy - 1 - tetralone **5e**.[12] It showed no carbonyl absorption in IR, and was recovered unchanged on oxidation with Jones reagent or on treatment with cold methanolic potassium hydroxide. Elemental analysis and especially the mass spectrum of this compound are quite in consistent with the structure **9** assigned to it. The presence of two bromine atoms in **9** follows from its characteristic molecular ion peaks at *m/e* 494, 496 and 498. The epoxide prepared from **6f** was found to be very unstable, and therefore the trans-bromohydrin **6f** was directly used in the condensation reaction described below.

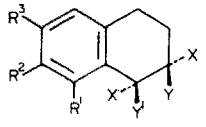
The epoxide **4e** was synthesised as follows: Readily available α-tetralone derivative **5f**[7] was converted to the

†Chromatography was performed during summer (room temp. 32°) when the moisture content of the atmosphere was very high.



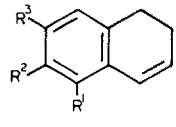
5

a: R¹ = Me; R² = OMe; R = R³ = H
b: R = Br; R¹ = Me; R² = OMe; R³ = H
c: R² = OMe, R = R¹ = R³ = H
d: R¹ = OMe; R = R³ = R² = H
e: R = Br; R¹ = R² = H; R³ = OMe
f: R¹ = Br; R² = OMe; R³ = Me; R = H



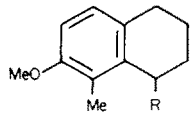
6

a: Y¹ = OH; Y = Br; X = X¹ = R³ = H; R¹ = Me; R² = OMe
b: Y¹ = X = Br, X¹ = Y = R³ = H; R¹ = Me; R² = OMe
c: Y¹ = OH; X = Br; X¹ = Y = R³ = H; R¹ = Me; R² = OMe
d: Y¹ = X = Br; R² = OMe; X¹ = Y = R¹ = R³ = H
e: Y¹ = OH, X = Br; X¹ = Y = R¹ = R³ = H; R² = OMe
f: Y¹ = OH; X = Br; X¹ = Y = R¹ = R² = H; R³ = OMe
g: Y¹ = OH; Y = Br; X = X¹ = R¹ = R² = H; R³ = OMe
h: Y¹ = OH, X = Br; Y = X¹ = H, R¹ = Br; R² = OMe; R³ = Me
i: Y¹ = OEt; X = OH; X¹ = Y = R³ = H; R¹ = Me; R² = OMe
j: Y¹ = OH; X = Br, X¹ = Y = R³ = R² = R¹ = H
k: Y¹ = OEt; X = OH; X¹ = Y = R¹ = R² = R³ = H



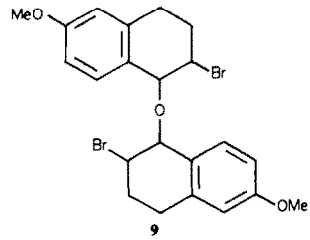
7

a: R¹ = Me; R² = OMe; R³ = H
b: R² = OMe; R¹ = R³ = H
c: R³ = OMe; R¹ = R² = H
d: R¹ = Br; R² = OMe; R³ = Me



8

a: R = OH
b: R = H



9

Fig. 2.

styrene **7d** and then to the trans-bromohydrin **6h** as before. Treatment of **6h** with base finally gave the crystalline epoxide **4e** for ring opening reaction.

Reaction of epoxides **4** *with malonic esters*

Interaction of diethyl sodiomalonate with the epoxide **4b** in dry ethanol under reflux resulted unexpectedly in the isolation of two γ-lactones;† **A** and **B** in 48 and 20% yields respectively. Lactone **A** on heating with a mixture of acetic anhydride and sulphuric acid was recovered unchanged; attempted catalytic hydrogenolysis of **A** also resulted in its quantitative recovery. That the lactone **A** is a cis-lactone **3a** was established from the ease of lactonisation of the hydroxy-acid (isolation impossible) resulting from the alkaline hydrolysis of **A**. Lactone **B** on basic hydrolysis furnished the stable hydroxy-acid **10a**. This acid **10a** on heating under vacuum regenerated the lactone **B**, and on oxidation furnished the 2-keto-acid **11a**. The above transformations suggest that the lactone **B** is a trans-lactone and should be represented by the expression **2c**. The stereostructures **3a** and **2c** for the lactones **A** and **B** respectively were finally secured from their NMR spectra to be discussed in detail at a later stage.

Condensation of the epoxide **4b** with the anion of diethyl methylmalonate under refluxing ethanol afforded in moderate yield a crystalline material, ν_{max} 3584 cm^{-1}; and this was prepared in excellent yield simply by refluxing the epoxide **4b** with ethanolic sodium ethoxide. The structure **6i** for this product was supported through its oxidation to the 2-keto-compound **11b**. The formation of **6i** points out clearly that the peri-methyl group in **4b** definitely hinders the approach of the sterically hindered carbanion to 1-position of the epoxide. Poorer nucleophiles of less steric considerations, such as ethanol or ethoxide ion competes preferentially in ring opening of the epoxide **4b** to furnish the observed product **6i**. Potassium enolate of diethyl methylmalonate was therefore allowed to interact with the epoxide **4b** under refluxing t-butanol, a solvent of greater steric consideration. Processing (see Experimental) of the reaction mixture afforded a crystalline γ-lactone, a hydroxy-acid, m.p. 153–154°, and interestingly the known cyclopropane carboxylic acid‡ **12**.[13,14] The above γ-lactone on alkaline hydrolysis furnished the same hydroxy-acid as mentioned above. This hydroxy-acid on heating under vacuum was quantitatively converted to the above γ-lactone, and on oxidation afforded the 2-keto-acid **11c**. The lactone and the corresponding hydroxy-acid should therefore be represented by the structures **2d** and **10b** respectively.

The isolation of the cis-lactone **3a** as the major product of ring opening of the epoxide **4b** is indeed interesting and deserved further investigations. The studies were therefore extended to a few related epoxides having different substituents in the benzene ring.

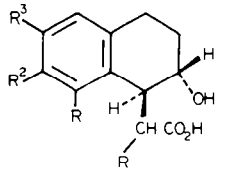
Condensation of the epoxide **4c** with the anion of diethylmalonate under refluxing ethanol gave a γ-lactone which was recovered unchanged in an attempted catalytic hydrogenation. Alkaline hydrolysis of this lactone followed by careful acidification regenerated the original lactone. That the lactone under consideration is a cis-lactone **3b** was finally established from its NMR spectrum, and also from the experiments described below. In another experiment, the above condensation provided a mixture of lactones from which the cis-lactone **3b** and the isomeric trans-lactone **2e** could be separated. This trans-lactone **2e** on alkaline hydrolysis provided the trans-hydroxy-acid **10c** which could be lactonised back to the original lactone. Oxidation of the above hydroxy-acid **10c** unfortunately gave an oily product, characterised as **11d** from its IR absorptions at 1715 and 1725 cm^{-1}. Condensation of the trans-bromohydrin **6e**, the precursor of the epoxide **4c**, with the anion of diethyl malonate again afforded a mixture of lactones from which the pure trans-lactone **2e** could be isolated in reasonable yield.

Interaction of the trans-bromohydrin **6f** with sodium diethyl malonate afforded only the trans-lactone **2f**. Alkaline hydrolysis of this lactone provided the trans-hydroxy-acid **10d** which on relactonisation afforded the trans-lactone **2f**.

Condensation of the epoxide **4e**, having a bulky bromine atom at the peri-position, with the anion of diethyl malonate gave initially a hydroxy-ester which on

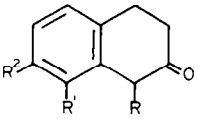
†Repeated experiments gave the same result.

‡This acid is the exclusive product of similar ring opening of the epoxide **4b** under refluxing benzene (see Ref. 13).



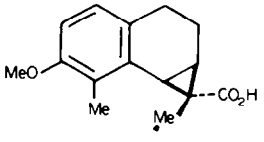
10

a: R = R' = H; R' = Me; R² = OMe
b: R = R' = Me; R² = OMe; R³ = H
c: R = R' = R³ = H; R² = OMe
d: R = R' = R² = H; R' = OMe
e: R = H; R' = Br; R² = OMe; R³ = Me
f: R = R' = R² = R' = H



11

a: R = $CH_2{\cdot}CO_2H$; R' = Me; R² = OMe
b: R = OEt; R' = Me; R² = OMe
c: R = $-CH(Me)-CO_2H$; R' = Me; R² = OMe
d: R = $CH_2{\cdot}CO_2H$; R' = H; R² = OMe
e: R = $CH_2{\cdot}CO_2Et$; R' = R² = H
f: R = $CH_2{\cdot}CO_2H$; R' = R² = H



12

Fig. 3.

hydrolysis furnished the crystalline trans-hydroxy-acid **10e**. Lactonisation of **10e** as before afforded a trans-lactone characterised as **2g** from its elemental analysis and spectral characteristics.

An authentic sample of the known trans-lactone **2a**[3] was prepared through the condensation of the known epoxide **4a** with the anion of diethyl malonate. The trans-nature of this lactone has been unambiguously established both from spectral and chemical evidences.

It may be mentioned here that an attempted condensation of the simplest trans-bromohydrin **6j** with the more sterically hindered carbanion derived from diethyl isopropylmalonate gave only the hydroxy-ether **6k**.

The possibility of the trans-hydroxy-ethers (like **6k**) as the intermediates for the cis-lactones **3a** and **3b** was ruled out by the fact that the hydroxy-ether **6k** was practically recovered unchanged in an attempted condensation with sodium diethyl malonate.

Some of the important results of ring opening of the epoxides are summarised below (Table 1).

The reactions without exception go with the nucleophiles attacking at C-1 in spite of the increased steric hindrance at the site. This is not really unexpected. The aromatic ring and the epoxide linkage make the whole molecule almost planar and if the transition state resembles the ground state as it most probably does, there is very little additional steric hindrance offered by the peri-substituent to the axial approach of the anions to offset the electronic effect favouring the attack at C-1. In one case (entry 2) when the attacking anion is also bulky (diethyl methylmalonate), 1-ethoxy-2-tetralol derivative **6i** is formed. In another (Table 1, entry 3), cyclopropanecarboxylic acid **12** is formed presumably through the mechanism discussed elsewhere[14] for similar system.

What is more significant is that although the formation of the trans-lactone on the whole is favoured in the above reactions, at least in two cases (Table 1, entries 1 and 4), there is considerable formation of cis-lactones. There is no doubt that the products are kinetically controlled since the treatment of the lactones with excess of base or acid does not change their configuration. As can be seen, the cis-lactones are formed with or without peri-substituent and so the effect of the steric interaction if any is inconsequential. The only other explanation, namely the intervention of S_Ni mechanism, also does not appear convincing. For one thing, it is not clear why in S_Ni mechanism there should be preponderance of cis-lactone and secondly, in the epoxide **4d** where the formation of a carbonium ion at C-1 is more congenial (leading to increased S_Ni participation) due to para-methoxyl, the product is a trans-lactone. The results thus remain unexplained at present.

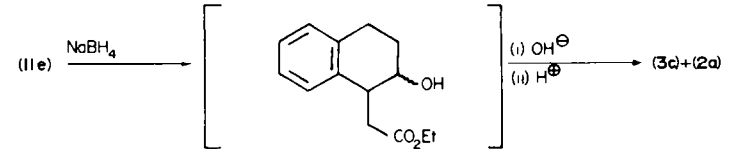
Investigations towards the synthesis of cis-lactones

An unambiguous synthesis of the cis-lactones **3a** and **3b** were required for comparison purposes. Easily available[15] β-tetralone derivative **11e** was first selected for the preparation of the model cis-lactone **3c**. Reduction of **11e** with sodium borohydride and subsequent alkaline hydrolysis and acidification provided an inseparable mixture of the cis-**3c** and the trans-lactone **2a** in a ratio of *ca.* 1:1 (from NMR). Similar reduction of the corresponding keto-acid **11f** gave the same result (Scheme 1).

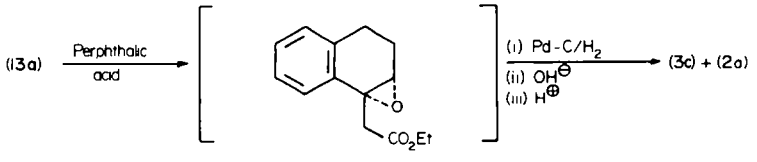
Catalytic hydrogenolysis of epoxides[16] and related compounds[17] are known to proceed predominantly and sometimes exclusively by trans-opening. A stereoselective pathway for the synthesis of the cis-lactone **3c** through epoxide opening was next investigated (Scheme 2). The crude epoxide, available through perphthalic acid oxidation of the known β,γ-unsaturated ester[18] **13a**, was directly hydrogenolysed (Pd–C), and the resulting product on alkaline hydrolysis and subsequent acidification afforded again a 1:1 mixture of the lactones **3c** and **2a**.

Table 1.

No.	Epoxide	Reactant	Solvent	Lactones (%) cis	trans
1	**4b**	Diethyl-malonate	EtOH	48	20
2	**4b**	Diethyl methylmalonate	EtOH	—	–only **6i**
3	**4b**	Diethyl methylmalonate	t-BuOH	—	22 + **12**
4	**4c**	Diethyl-malonate	EtOH	48	—
5	**4d**	Diethyl-malonate	EtOH	—	50
6	**4e**	Diethyl-malonate	EtOH	—	70 (as hydroxy-acid)



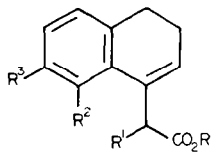
Scheme 1.



Scheme 2.

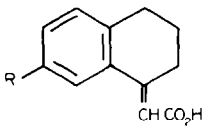
The enol lactone **15**, prepared from the keto-acid **11f**, on catalytic hydrogenation also gave a 1:1 mixture of the cis-**3c** and the trans-lactone **2a**.

Attempted lactonisation of the known β,γ-unsaturated acids **13b**[18] and **13c**[19] with concentrated sulphuric acid under controlled condition afforded only the corresponding exo-acids **14a** and **14b** respectively. Acid-catalysed lactonisation of the unsaturated acids **13d** and **13e**, prepared through Reformatsky reaction of the tetralone derivative **5a** with α-haloesters, was therefore not investigated further.



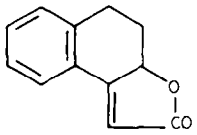
13

a: R = Et; R¹ = R² = R³ = H
b: R = R¹ = R² = R³ = H
c: R = R¹ = R² = H; R³ = OMe
d: R = R¹ = H; R² = Me; R³ = OMe
e: R = H; R¹ = R² = Me; R³ = OMe



14

a: R = H
b: R = OMe



15

Fig. 4.

Halogenolactonisation[20] of the β,γ-unsaturated acid **13c** was next briefly investigated. Bromolactonisation of **13c** according to the procedure of Barnett *et al.*[20d] gave a neutral product containing bromine. This product showed no carbonyl absorption in the infrared. The UV absorption maxima at 229 and 264 nm, and especially its NMR spectrum (see Experimental) indicated it to be a mixture† of **16** and **17**. This assignment is also in consistent with the mass spectrum which showed characteristic doublet for the molecular ion at *m/e* 252 and 254. The formation of these products may possibly be rationalised by the mechanism shown in Scheme 3.

†The presence of a trace amount of completely aromatised product in this mixture can not be ruled out altogether.

NMR spectra of the cis-and trans-lactones **3** *and* **2**

The position of the 3a-proton signals is found to be characteristic of the stereochemistry of the lactone ring. Thus the protons of the trans-lactones appear at τ 5.76–6.16 whereas those of the cis-lactones appear at τ 4.96–5.02 (Table 2) and there is hardly any overlap of the peaks in a mixture. Inspection of a Dreiding model reveals that the 3a-hydrogen in trans-isomer is much more shielded by the ring current of benzene ring than that in the cis-isomer. This difference may therefore be utilised (and in fact has been utilised in the present case) for establishing the stereochemistries of the γ-lactones of the type tabulated in Table 2.

Table 2. NMR signals for the C-3a hydrogen atom of cis- and trans-lactones

Lactones	Stereochemistry of the lactone ring fusion	Signal for C-3a hydrogen multiplet (τ)	Multiplet centred at (τ)
3a } Stereo	cis	4.82–5.10	4.96
2c } isomers	trans	5.61–6.04	5.82
3b } Stereo	cis	4.92–5.20	5.06
2e } isomers	trans	5.66–6.10	5.88
3c } Stereo-	cis	4.89–5.13	5.02
2a } isomers	trans	6.00–6.33	6.16
2f	trans	5.68–6.16	5.92
2g	trans	5.44–6.06	5.75

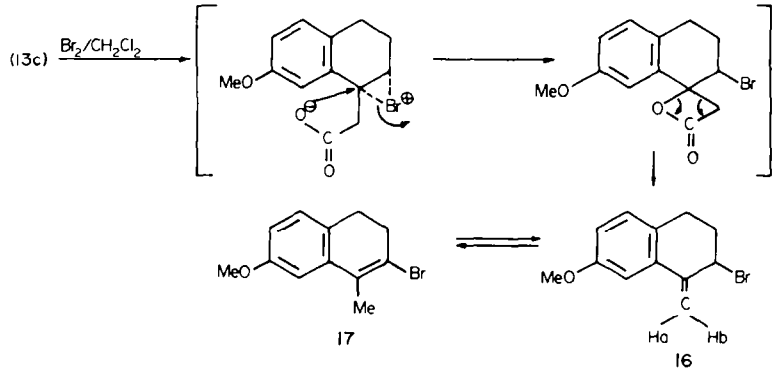
EXPERIMENTAL

The compounds described are racemic. The same experimental procedures and instruments were used as described[2] previously. In addition some spectral measurements were performed on a Varian T-60 NMR spectrometer. Ethanol used was dried over magnesium.

7 - *Methoxy* - 8 - *methyl* - 1 - *tetralone* **5a** was prepared by the reported procedure.[7]

2 - *Bromo* - 7 - *methoxy* - 8 - *methyl* - 1 - *tetralone* **5b**

(a) *From the α-tetralone derivative* **5a**. To a stirred soln of **5a**[7] (900 mg) in dry ether (200 ml) was added one drop of Br_2 at room temp (28°). The colour of Br_2 was discharged instantaneously. To this soln, maintained at 10° was then added dropwise a soln of Br_2 (850 mg) in dry ether (20 ml) over a period of 0.5 h allowing each drop of Br_2 to decolourise before another was added. The reaction mixture was further stirred for 0.5 h at 10°, and 3–4 h at room temp. Usual processing of the solvent gave the bromo-ketone **5b** (950 mg, 59%) as violet-coloured solid, m.p. 77–78° (ether-light petroleum). Sublimation of this product at 125–130° (bath)/0.2 mm afforded analytically pure sample of **5b** as colourless needles, m.p. 77–78°, λ_{max} 260 and 343 nm (ϵ 10,000 and 2,692), ν_{max} 1670 cm^{-1}



Scheme 3.

(keto C=O). (Found: C, 53.27; H, 4.95; OMe, 11.58. $C_{12}H_{13}BrO_2$ requires: C, 53.57; H, 4.83; OMe 11.51%).

(b) *From the trans-bromohydrin* **6c**. To a stirred soln of **6c** (100 mg) in pure acetone (30 ml), maintained at 5° was added Jones reagent[21] (0.1 ml). The reaction mixture was stirred for 5 min and then diluted heavily with water. The product was then extracted with ether (2 × 25 ml). The solvent was washed with water, dried and evaporated to give the bromo-ketone **5b** (70 mg, 71%), m.p. 75–77°.

cis - 2 - *Bromo* - 7 - *methoxy* - 8 - *methyl* - 1,2,3,4 - *tetrahydronaphthalene* - 1 - *ol* **6a**. To an ice-cold stirred soln of the above α - bromo - ketone **5b** (710 mg) in acetone free MeOH (8 ml) was added $NaBH_4$ (240 mg) in two equal portions. The resulting homogeneous reaction mixture was stirred under ice-cold condition for 4 h and then left at room temp. for 16 h. The reaction mixture was then decomposed with dil AcOH and the product was extracted with ether (3 × 50 ml). The solvent was washed repeatedly with water to free from acid. Evaporation of the dry solvent and sublimation of the solid residue gave **6a** (650 mg, 91%), m.p. 110–114°. Recrystallisation of this product provided analytical sample of **6a**, m.p. 116–117° (ether-light petroleum), λ_{max} 280 nm (ε 1,995) (Found: C, 52.73; H, 5.49. $C_{12}H_{15}O_2Br$ requires: C, 53.09; H, 5.53%). The bromohydrin **6a** was practically recovered unchanged by treatment with methanolic KOH at room temp. or at 50° for 15 min.

7 - *Methoxy* - 8 *methyl* - 1,2,3,4 - *tetrahydronaphthalene* - 1 - *ol* **8a**. The α-tetralone derivative **5a** (1.0 g) was reduced with $NaBH_4$ (400 mg) as above to give the crystalline alcohol **8a** (1.0 g, 98%), m.p. 74° (light petroleum), λ_{max} 280 nm (ε 2,042) (Found: C, 74.70; H, 8.22. $C_{12}H_{16}O_2$ requires: C, 74.97; H, 8.39%).

7 - *Methoxy* - 8 - *methyl* - 3,4 - *dihydronaphthalene* **7a**. An intimate mixture of the above alcohol **8a** (1.0 g) and freshly ignited $KHSO_4$ (1.0 g) was heated in an oil bath maintained at 170° for 7 min. The residue on distillation afforded **7a** (700 mg, 79%) as colourless oil, b.p. 100° (bath)/0.4 mm, λ_{max} 227 and 264 nm (ε 34,800 and 8941) (Found: C, 82.50; H, 8.33. $C_{12}H_{14}O$ requires: C, 82.72; H, 8.10%).

7 - *Methoxy* - 8 - *methyl* - 1,2,3,4 - *tetrahydronaphthalene* **8b**. A soln of the styrene **7a** (300 mg) in 95% EtOH (10 ml) was hydrogenated over Pd-C (50 mg, 10%) at room temp. and atmosphere pressure. Theoretical amount of H_2 was absorbed within 10 min. Usual work-up gave a product which on sublimation at 100–110° (bath)/0.6 mm furnished the tetralin derivative **8b** (200 mg, 70%), m.p. and m.m.p. 47–49° (reported[8] m.p. 52°).

7 - *Methoxy* - 8 - *methyl* - 2 - *tetralone*. To an ice-cold soln of perbenzoic acid (610 mg) in chloroform (40 ml) was added a soln of the above styrene **7a** (700 mg) in chloroform (4 ml) at 0°. After 24 h at 0°, the styrene consumed the theoretical amount of the per-acid (from blank). Usual processing of the reaction mixture gave 7 - methoxy - 8 - methyl - 2 - tetralone (430 mg, 56%), b.p. 140° (bath)/0.2 mm. The analytical material solidified on standing, m.p. 78–80°, λ_{max} 282 nm (ε 1,820), ν_{max} 1710 cm^{-1} (keto C=O) (Found: C, 75.37; H, 7.37. $C_{12}H_{14}O_2$ requires: C, 75.76; H, 7.42%).

trans - 2 - *Bromo* - 7 - *methoxy* - 8 - *methyl* - 1,2,3,4 - *tetrahydronaphthalene* - 1 - *ol* **6c**

(a) *From the trans-dibromide* **6b**. To an ice-cold stirred soln of the styrene **7a** (700 mg, 0.004 mole) in alcohol free $CHCl_3$ (10 ml) was added dropwise a soln of Br_2 in $CHCl_3$ (7.03 ml containing 0.0044 mole of Br_2). Each drop of bromine soln was added after decolourisation of the previous one. Temperature of the reaction mixture during addition of Br_2soln was kept between 0 and 10°. After complete addition, the resulting clear soln was stirred at 0–10° for 2 h, and then left in the refrigerator for 16 h. Removal of the solvent under reduced pressure furnished the crude dibromocompound **6b** (1.6 g) as viscous oil. A mixture of **6b** (1.0 g), $MgCO_3$ (500 mg), acetone (7.5 ml) and water (1.2 ml) was heated under reflux for 6 h. $MgCO_3$ was then filtered and the residue was washed repeatedly with ether. The combined solvent was washed with H_2O, dried and evaporated to furnish a semisolid material (720 mg) which was chromatographed over Florisil (30 g). Elution of the chromatogram with ether-light petroleum (10:90) provided the crystalline trans-bromohydrin **6c** (390 mg, 58%), m.p. 128° (ether–light petroleum), λ_{max} 280 nm (ε 1950) (Found: C, 52.75; H, 5.66. $C_{12}H_{15}O_2Br$ requires: C, 53.09; H, 5.53%). Direct chromatography of the crude dibromide **6b** (500 mg) over florisil (15 g), and elution of the chromatogram as above afforded the bromohydrin **6c** (210 mg, 59%), m.p. 125–127°. Use of silica gel in place of Florisil gave the same bromohydrin **6c** in comparable yield.

(b) *Directly from the styrene* **7a** *following the procedure of Dalton* et al.[10a]

A typical procedure is described below for the preparation of **6c** from **7a**. The styrene **7a** (700 mg) was dissolved in dry DMSO (17 ml) and the soln was cooled in ice bath. To this cold soln water (0.18 g) was added and the mixture was stirred under N_2. N-Bromosuccinimide (1.2 g) was then carefully added under N_2 so that the temp. of the reaction mixture was not allowed to rise above 10°. The resulting pale yellow soln was stirred further for 1 h at 5–10°. The reaction mixture was then diluted with large volume of H_2O and the separated product was extracted with ether (3 × 50 ml). Usual processing of the solvent furnished the bromohydrin **6c** (800 mg, 74%), m.p. 126–128° (ether-light petroleum).

7 - *Methoxy* - 8 - *methyl* - 3,4 - *dihydronaphthalene* - 1,2 - *oxide* **4b**. To an ice-cold stirred soln of the above bromohydrin **6c** (1.0 g) in absolute ethanol (16 ml) was added dropwise a soln of KOH in dry MeOH (3.5 ml containing 0.35 g of KOH). During the addition, KBr began to separate, and after the addition was complete, the reaction mixture was stirred for 1 h to complete the reaction. The reaction mixture was then diluted with H_2O and the product was extracted with ether (3 × 50 ml). The solvent was washed with water, dried, and evaporated to give the crystalline epoxide **4b** (610 mg, 85%), m.p. 77° (ether–light petroleum) λ_{max} 215 and 280 nm (ε 14,791 and 1995) (Found: C, 75.60; H, 7.54. $C_{12}H_{14}O_2$ requires: C, 75.76; H, 7.42%).

Interaction of sodiomalonic ester with the epoxide **4b**. *Formation of cis* - 3a,4,5,9b - *tetrahydro* - 8 - *methoxy* - 9 - *methylnaphtho*[2,1 - b]*furan* - 2(1H) - *one* **3a**, *the corresponding trans-lactone* **2c**, *and the trans-hydroxy acid* **10a**. To a stirred and refluxing soln of sodiomalonic ester, prepared from Na (250 mg), dry EtOH (56 ml) and diethyl malonate (1.6 g), was added dropwise under N_2 a soln of the crystalline epoxide **4b** (600 mg) in dry EtOH (10 ml) over a period of 1 h. The reaction mixture, after stirring and refluxing for a further period of 4 h, was diluted with ice-water and the product was extracted with ether (3 × 50 ml). The solvent was washed with H_2O, dried and evaporated. Excess malonic ester was removed under vacuum and the resulting residue on treatment with ether-light petroleum partially solidified to give the cis-lactone **3a** (350 mg, 48%), m.p. 109° (ether-light petroleum) λ_{max} 279 nm (ε 1,998), ν_{max} 1775 cm^{-1} (lactone C=O), τ 7.83 (3H, s), 6.63–7.72 (7H, m), 6.14 (3H, s), 4.82–5.10 (1H, m), 3.08 (2H, qu, J 8.0 Hz). On TLC (MeOH-benzene, 10:90) it gave a bright single spot. (Found: C, 72.16; H, 7.02. $C_{14}H_{16}O_3$ requires: C, 72.39; H, 6.94%).

The oily material (1.1 g), ν_{max} 1776 and 1722 cm^{-1} obtained after separation of the cis-lactone **3a**, was hydrolysed by heating under reflux for 1 h with a soln of NaOH (2.4 g) in EtOH (140 ml) and H_2O (120 ml). Usual processing of the alkaline soln furnished an acidic material (800 mg) which was decarboxylated by heating for 25 min in an oil bath maintained at 140°. The resulting residue was dissolved in ether, and the acidic product was extracted with sat aq $NaHCO_3$. The neutral ether on evaporation furnished an oily solid material (450 mg) which on several recrystallisations from ether–light petroleum provided the trans-lactone **2c** (170 mg, 20%) as silky needles, m.p. 186–187°, λ_{max} 280 nm (ε 1,995), ν_{max} 1789 cm^{-1} (lactone C=O), τ 7.85 (3H,s), 6.55–7.67 (7H,m), 6.20 (3H,s), 5.61–6.04 (1H,m), 3.12 (2H, qu, J 8.4 Hz). On TLC (MeOH–benzene, 10:90) it showed a bright single spot. (Found: C, 72.21; H, 6.82%). Mother liquors of the crystallisations of the trans-lactone **2c** afforded a solid material (60 mg), m.p. 113–150° (mixture of cis and trans lactone), and an oil (180 mg).

The above $NaHCO_3$ extract on acidification and subsequent ether extraction provided an acidic material (300 mg), m.p. 135–140° which on several recrystallisations provided a pure sample of the trans-hydroxy-acid **10a** (18 mg), m.p. 149°

(ether–light petroleum), λ_{max} 279 nm (ϵ 1,995), ν_{max} 1712 (carboxy C=O) and 3550 cm^{-1} (OH) (Found: C, 67.53; H, 7.14. $C_{14}H_{18}O_4$ requires: C, 67.18; H, 7.25%).

Alkaline hydrolysis of the cis **3a**, *and the trans-lactone* **2c**. The cis-lactone **3a** (110 mg) was hydrolysed by heating under reflux for 5 h with a soln of methanolic NaOH (5 ml, 10%). Methanol was then removed and the cold aqueous alkaline soln was cautiously acidified with dil HCl. The product was immediately extracted with ether (2 × 25 ml). The solvent was washed with water, dried and evaporated to furnish the recovered cis-lactone **3a** (80 mg), m.p. 108–109°. Alkaline hydrolysis of the above trans-lactone **2c** (30 mg) as above afforded 2 - hydroxy - 7 - methoxy - 8 - methyl - 1,2,3,4 - tetrahydro - 1 - naphthylacetic acid **10a** (30 mg), m.p. 148–149°.

Treatment of the cis-lactone **3a**

(a) Attempted catalytic hydrogenation of the cis-lactone **3a** (80 mg) in presence of Pd-C (50 mg, 10%) in ethanol (15 ml) gave only the starting material **3a** (70 mg).

(b) Attempted isomerisation of the cis-lactone **3a** by heating a mixture of **3a** (200 mg), acetic anhydride (3.5 ml) and a drop of conc. H_2SO_4 on the steam bath for 20 min regenerated the lactone **3a** (170 mg).

Lactonisation of the trans-hydroxy-acid **10a**

Sublimation of the hydroxy-acid **10a** (25 mg) at 160°/0.3 mm afforded the trans-lactone **2c** (15 mg), m.p. 186–187°.

2 - *Keto* - 7 - *methoxy* - 8 - *methyl* - 1,2,3,4 - *tetrahydro* - 1 - *napthylacetic acid* **11a**. The oxidation of the trans-hydroxy-acid **10a** (180 mg) with Jones reagent[21] (0.5 ml) as before afforded a semisolid material (130 mg) which was chromatographed over silica gel (5 g). Elution of the chromatogram with ether–light petroleum (15:85) furnished the keto-acid **11a** (80 mg), m.p. 161–162° (ether–light petroleum), λ_{max} 230 and 285 nm (ϵ 19,950 and 2,512), ν_{max} 1739 (carboxy C=O) and 1705 cm^{-1} (keto C=O) (Found: C, 67.62; H, 6.34. $C_{14}H_{16}O_4$ requires: C, 67.73; H, 6.50%).

trans - 1 - *Ethoxy* - 2 - *hydroxy* - 7 - *methoxy* - 8 - *methyl* - 1,2,3,4 - *tetrahydronaphthalene* **6i**

(a) *By condensation of the anion of diethyl methylmalonate with the epoxide* **4b**. To a stirred and refluxing soln of sodiomethylmalonate, prepared from Na (250 mg), absolute EtOH (56 ml) and diethyl methylmalonate (1.8 g), was added dropwise under N_2 a soln of the epoxide **4b** (1.26 g) in EtOH (15 ml) over a period of 2 h. After stirring and refluxing for a period of 28 h, the reaction mixture was cooled and diluted with water. The separated product was extracted with ether (3 × 75 ml) and after usual processing of the solvent as before, the residue was distilled under vacuum to furnish the hydroxy-ether **6i** (700 mg, 45%) b.p. 155–160°/0.2 mm, m.p. 122° (ether–light petroleum), λ_{max} 278 nm (ϵ 1,950), ν_{max} 3585 cm^{-1} (OH) (Found: C, 71.07; H, 8.36. $C_{14}H_{20}O_3$ requires: C, 71.16; H, 8.53%).

(b) *By reaction of the epoxide* **4b** *with sodium ethoxide under refluxing ethanol.* The epoxide **4b** (1.0 g) was refluxed for 20 h with a soln of NaOEt prepared from Na (230 mg) and dry EtOH (20 ml). Working up of the reaction mixture as above afforded the crystalline hydroxy-ether **6i** (1.10 g, 88%), m.p. 122° (ether–light petroleum).

1 - *Ethoxy* - 2 - *keto* - 7 - *methoxy* - 8 - *methyl* - 1,2,3,4 - *tetrahydronaphthalene* **11b**. The above hydroxy-ether **6i** (400 mg) was oxidised by Jones reagent[21] (0.65 ml) as before. The keto-ether (320 mg) obtained as an oil was purified through chromatography over silica gel (10 g). Elution of the chromatogram with light petroleum afforded **11b** (250 mg), b.p. 100° (bath)/0.4 mm, λ_{max} 221 and 279 nm (ϵ 12,020 and 2,148), ν_{max} 1710 cm^{-1} (keto C=O) (Found: C, 71.37; H, 7.60. $C_{14}H_{18}O_3$ requires: C, 71.77; H, 7.74%). Semicarbazone separated from MeOH and had m.p. 210–211° (d) (dil MeOH) (Found: C, 61.91; H, 7.27; N, 14.54. $C_{15}H_{21}N_3O_3$ requires: C, 61.84; H, 7.27; N, 14.42%).

Interaction of potassium diethyl methylmalonate with the epoxide **4b** *in t-butanol*

Formation of trans - 3a,4,5,9b - *tetrahydro* - 1 - *methyl* - 8 - *methoxy* - 9 - *methylnaphtho*[2,1 - b]*furan* - 2(1H) - *one* **2d**; *the corresponding trans* - *hydroxy* - *acid* **10b**, *and the cyclopropane carboxylic acid* **12**. To a stirred and refluxing soln of the potassium enolate of diethylmethylmalonate, prepared from K (220 mg), dry t-butanol (15 ml) and diethyl methylmalonate (1.8 g), was added dropwise under N_2 a soln of the epoxide **4b** (1.0 g) in dry t-butanol (8 ml) over a period of 1 h. After stirring and refluxing for a further period of 36 h, excess t-butanol was removed under reduced pressure. The residue was diluted with H_2O and the neutral product was extracted with ether (3 × 75 ml). The aq alkaline soln on acidification and subsequent ether extraction afforded the trans-hydroxy-acid **10b** (70 mg, 2.6%) as needles, m.p. 153–154° (ether–light petroleum), λ_{max} 279 nm (ϵ 2,045), ν_{max} 3775 (OH) and 1705 cm^{-1} (carboxy C=O). (Found: C, 68.25; H, 7.46. $C_{15}H_{20}O_4$ requires: C, 68.16; H, 7.63%).

The above neutral ether soln was washed with H_2O, dried and evaporated. The residue thus obtained on distillation afforded the unreacted epoxide **4b** (100 mg), b.p. 110° (bath)/0.3 mm; and a viscous oil (730 mg) b.p. 155° (bath)/0.3 mm, ν_{max} 1774 and 1722 cm^{-1}. This higher boiling product on trituration with ether–light petroleum gave the trans-lactone **2d** (120 mg), m.p. 133–134° (ether–light petroleum), λ_{max} 220 and 280 nm (ϵ 10,000 and 1998), ν_{max} 1785 cm^{-1} (lactone C=O). (Found: C, 73.23; H, 7.20. $C_{15}H_{16}O_3$ requires: C, 73.15; H, 7.37%).

The oil (600 mg) remaining after separation of the above trans-lactone **2d** was hydrolysed with alkali as before, and the resulting acid on heating furnished an additional amount of the above trans-lactone **2d** (100 mg), and the known[13] cyclopropane carboxylic acid **12** (123 mg, 9.5%), m.p. 199–200° (ether–light petroleum) (reported[13] m.p. 200–201°). The overall yield of the trans-lactone **2d** was (220 mg, 22%).

Alkaline hydrolysis of the trans-lactone **2d**

Formation of trans - 2 - *hydroxy* - 7 - *methoxy* - 8 - *methyl* - 1,2,3,4 - *tetrahydro* - 1 - *naphthyl* - *α* - *propionic acid* **10b**

The above trans-lactone **2d** (100 mg) on alkaline hydrolysis as described before gave the trans - hydroxy - acid **10b** (80 mg), m.p. 152–153° reported above.

Lactonisation of the trans - *hydroxy* - *acid* **10b**

The hydroxy-acid **10b** (50 mg) m.p. 152° was lactonised by sublimation at 160° (bath)/0.1 mm to give the crystalline trans-lactone **2d** (30 mg), m.p. 133°.

2 - *Keto* - 7 - *methoxy* - 8 - *methyl* - 1,2,3,4 - *tetrahydro* - 1 - *naphthyl* - *α* - *propionic acid* **11c**. To an ice-cold soln of the hydroxy-acid **10b** (150 mg) in acetone (30 ml) was added Jones' reagent[21] (0.1 ml). The reaction mixture was stirred for 45 min and was worked up as before to furnish the crystalline keto-acid **11c** (100 mg), m.p. 188–189° (ether–light petroleum), λ_{max} 286 nm (ϵ 2,799), ν_{max} 1753 (carboxy C=O) and 1706 cm^{-1} (keto C=O). (Found: C, 68.51; H, 7.17. $C_{15}H_{18}O_4$ requires: C, 68.69; H, 6.97%).

7 - *Methoxy* - 3,4 - *dihydronaphthalene* **7b**. 7 - Methoxy - 1 - tetralone[22] **5c** (2.0 g) was reduced with $NaBH_4$ (800 mg) as before to give a crude alcohol (2.0 g). Dehydration of this alcohol with $KHSO_4$ afforded the desired styrene **7b** (1.2 g, 57%) as colourless oil, b.p. 100° (bath)/0.4 mm, λ_{max} 217 and 260 nm (ϵ 24,550 and 8751) (Found: C, 82.36; H, 7.54. $C_{11}H_{12}O$ requires: C, 82.46; H, 7.55%).

trans - 1,2 - *Dibromo* - 7 - *methoxy* - 1,2,3,4 - *tetrahydronaphthalene* **6d**. Addition of Br_2 to the above styrene **7b** (1.0 g) as before afforded the trans-dibromide **6d** (1.4 g, 70%), m.p. 75–76° (ether–light petroleum), λ_{max} 298 nm (ϵ 2512) (Found: C, 41.51; H, 3.97. $C_{11}H_{12}Br_2O$ requires: C, 41.27; H, 3.75%).

trans - 2 - *Bromo* - 7 - *methoxy* - 1,2,3,4 - *tetrahydronaphthalene* - 1 - *ol* **6e**

(a) *From the trans-dibromide* **6d**. The above dibromo-compound **6d** (750 mg) without purification was refluxed in acetone soln with $MgCO_3$ and H_2O as before to give the desired trans-bromohydrin **6e** (230 mg, 38%), m.p. 95–96° (ether–light petroleum), λ_{max} 280 nm (ϵ 2098) (Found: C, 51.37; H, 5.34. $C_{11}H_{13}O_2Br$ requires: C, 51.36; H, 5.04%). Chromatography of the crude dibromo-compound **6d** (1.2 g) over florisil or silica gel (32 g)

as before afforded directly the trans-bromohydrin **6e** (480 mg), m.p. 94–96°.

(b) *Directly from the styrene* **7b**. A soln of the styrene **7b** (500 mg) in dry DMSO (15 ml) and 3 drops of water was treated with NBS as described earlier to furnish the desired bromohydrin **6e** (620 mg, 74%), m.p. 94–96°. The yield of **6e** was much reduced if the internal temp. of the reaction mixture during NBS addition was allowed to rise above 20°.

7 - *Methoxy* - 3,4 - *dihydronaphthalene* - 1,2 - *oxide* **4c**

Treatment of the above bromohydrin **6e** (1.0 g) with alcoholic KOH as before gave the epoxide **4c** (480 mg, 62%), b.p. 85–90° (bath)/0.3 mm, λ_{max} 227 and 281 nm (ϵ 6,607 and 1995) (Found: C, 74.81; H, 7.11. $C_{11}H_{12}O_2$ requires: C, 74.98; H, 6.86%).

cis - 3a,4,5,9b - *tetrahydro* - 8 - *methoxynaphtho*[2,1-b]*furan* - 2(1H) - *one* **3b** *and the corresponding trans-lactone* **2e**

(a) *From the epoxide* **4c**. The epoxide **4c** (970 mg) was condensed with sodiomalonic ester under refluxing ethanol as before to give a high-boiling viscous liquid (1.15 g), b.p. 172–175°/0.2 mm, ν_{max} 1720 and 1774 cm^{-1}. This material on trituration with ether–light petroleum partially solidified to provide the cis-lactone **3b** (380 mg), m.p. 93° (light petroleum), λ_{max} 224 and 281 nm (ϵ 14, 450 and 2,238), ν_{max} 1772 cm^{-1} (lactone C=O), τ 6.70–7.89 (7H,m), 6.21 (3H,s), 4.92–5.2 (1H,m), 2.83–3.36 (3H,m) (Found: C, 71.43; H, 6.33. $C_{13}H_{14}O_3$ requires: C, 71.54; H, 6.47%). The oily material (600 mg), left after separation of the cis-lactone **3b** on alkaline hydrolysis gave an acid which on heating as before afforded an additional amount of the cis-lactone **3b** (160 mg). The total yield of the lactone **3b** was (540 mg, 48%).

In another experiment, the condensation of the epoxide **4c** (2.0 g) with sodiomalonic ester gave a mixture of products which on alkaline hydrolysis followed by decarboxylation furnished a mixture of cis **3b** and the trans-lactone **2e** (800 mg), m.p. 60–140°. Repeated fractional crystallisations of this product gave a pure sample of trans - 3a,4,5,9b - tetrahydro - 8 - methoxynaphtho[2,1-b]furan - 2(1H) - one **2e**, m.p. 141° (acetone–light petroleum), λ_{max} 227 and 278 nm (ϵ 8,318 and 2,139), ν_{max} 1778 cm^{-1} (lactone C=O), τ 6.81–8.02 (7H,m), 6.21 (3H,s), 5.66–6.1 (1H,m), 2.85–3.5 (3H,m) (Found: C, 71.34; H, 6.64%). Mother liquors of the above crystallisations gave an oil (200 mg) which on chromatography over silica gel provided the cis-lactone **3b** (90 mg), m.p. 93°.

(b) *From the trans-bromohydrin* **6e**. Interaction of the trans-bromohydrin **6e** (4.0 g) with three equivalents of sodium diethylmalonate under refluxing ethanol (6 h reflux) afforded a mixture from which the pure trans-lactone **2e** (1.1 g, 33%), m.p. 141° (acetone–light petroleum) could be isolated. (Found: C, 71.53; H, 6.41%).

*Treatment of the cis-***3b** *and the trans-lactone* **2e** *with alkali.* The cis-lactone **3b** (60 mg) was hydrolysed by heating under reflux with methanolic KOH (5 ml, 10%). Usual processing of the reaction mixture afforded the recovered cis-lactone **3b** (quantitative), m.p. 92–93°.

The above trans-isomer **2e** (100 mg) on similar alkaline hydrolysis provided *trans* - 2 - *hydroxy* - 7 - *methoxy* - 1,2,3,4 - *tetrahydro* - 1 - *naphthylacetic acid* **10c** (80 mg), m.p. 103–104° (ether–light petroleum), λ_{max} 279 nm (ϵ 2,512), ν_{max} 1712 cm^{-1}. (Found: C, 66.13; H, 6.41. $C_{13}H_{16}O_4$ requires: C, 66.09; H, 6.83%).

Sublimation of the above hydroxy-acid **10c** (20 mg) at 130° (bath)/0.01 mm afforded the trans-lactone **2e** (15 mg).

Oxidation of the above hydroxy-acid **10c** (20 mg) with Jones reagent[21] gave a 2-keto acid as an oil, ν_{max} 1725 and 1715 cm^{-1}.

6 - *Methoxy* - 3,4 - *dihydronaphthalene* **7c**. 6 - Methoxy - 1 - tetralone[23] **5d** (2.0 g) was reduced with $NaBH_4$ (83 mg) as before to give a crude alcohol (1.93 g). This alcohol was dehydrated by $KHSO_4$ by heating the mixture at 170° for 10 min. Distillation of the residue afforded the desired styrene **7c** (1.3 g, 72%) as colourless oil, b.p. 95° (bath)/0.2 mm (reported[24] b.p. 110–118°/3 mm), λ_{max} 269 nm (ϵ 13,760) (Found: C, 82.18; H, 7.65. $C_{11}H_{12}O$ requires: C, 82.46; H, 7.55%).

trans - 6 - *Methoxy* - 2 - *bromo* - 1,2,3,4 - *tetrahydronaphthalene* - 1 - *ol* **6f**, *and bis* - (2 - *bromo* - 6 - *methoxy* - 1,2,3,4 - *tetrahydro* - 1 - *naphthyl*) *ether* **9**. A soln of the above styrene **7c** (2.28 g) in DMSO and H_2O was treated with NBS as described before to give the desired trans-bromohydrin **6f** (2.05, 48%), m.p. 89–90° (ether–light petroleum), ν_{max} 3230 cm^{-1} (OH). (Found: C, 51.35; H, 5.07. $C_{11}H_{13}O_2Br$ requires: C, 51.36; H, 5.06%).

Mother liquors after separation of the trans-bromohydrin **6f** on keeping for several days provided a crystalline material (400 mg), m.p. 151–153°. Chromatography of this product over silica gel and elution with ether–light petroleum (25:75) gave pure bromo–ether **9** (320 mg), m.p. 152–153° (acetone–light petroleum), λ_{max} 234, 275 and 283 nm (ϵ 9,550, 1,493 and 1,445) ν_{max} 1613, 1126, 1112 and 1096 cm^{-1}, *m/e* 494, 496, 498 (due to M^+), the other peaks of medium intensities are at *m/e* 415 and 417 (M^+–Br); 334 (M^+–2HBr), 239, 241 and 160. (Found: C, 53.37; H, 5.09; Br, 31.92. $C_{22}H_{24}O_3Br_2$ requires: C, 53.22; H, 4.84; Br, 32.26%).

cis - 2 - *Bromo* - 6 - *methoxy* - 1,2,3,4 - *tetrahydronaphthalene* - 1 - *ol* **6g**. Reduction of the known α - bromo - ketone **5e**[12] (730 mg) with $NaBH_4$ as before afforded the cis-bromohydrin **6g** (530 mg, 79%) as fine needles, m.p. 118–120° (ether–light petroleum) (Found: C, 51.23; H, 5.09. $C_{11}H_{13}O_2Br$ requires: C, 51.36; H, 5.06%).

Attempted preparation of 6 - *methoxy* - 3,4 - *dihydronaphthalene* 1,2 - *oxide* **6d**. The above trans-bromohydrin **6f** (1.8 g) was treated with alcoholic KOH as before to give an yellow oil (730 mg, 59%), b.p. 120–125° (bath)/0.3 mm. This oil gradually turned deep brown in colour and full characterisation was not possible.

trans - 3a,4,5,9b - *tetrahydro* - 7 - *methoxynaphtho*[2,1-b]*furan* - 2(1H) - *one* **2f**. To a stirred and refluxing soln of sodium diethylmalonate prepared from Na (550 mg), absolute EtOH (14 ml) and diethylmalonate (3.84 g), was added dropwise under N_2 a soln of the trans-bromohydrin **6f** (3.02 g) in EtOH (30 ml) over a period of 3 h. After complete addition, the reaction mixture was refluxed for 3 h more, and worked up as before to furnish the trans-lactone **2f** (1.17 g) as silky needles, m.p. 120–122°, ν_{max} 1766 cm^{-1} (lactone C=O), τ 6.73–8.3 (7H,m), 6.25 (3H,s), 5.68–6.16 (1H,m), 3.0–3.37 (3H,m) (Found: C, 71.30; H, 6.89. $C_{13}H_{14}O_3$ requires: C, 71.54; H, 6.47%). The oily material (350 mg), obtained after separation of the crystalline lactone **2f**, on alkaline hydrolysis furnished an acid which on heating as before provided an additional amount of the lactone **2f** (60 mg). The overall yield of the lactone **2f** was (1.23 g, 50%).

Formation and lactonisation of trans - 2 - *hydroxy* - 6 - *methoxy* - 1,2,3,4 - *tetrahydro* - 1 - *naphthylacetic acid* **10d**. Alkaline hydrolysis of the above trans-lactone **2f** (500 mg) by the usual procedure gave the trans - hydroxy - acid **10d** (360 mg, 66%) as short needles, m.p. 147° (acetone–light petroleum) (Found: C, 65.90; H, 6.68. $C_{13}H_{16}O_4$ requires: C, 66.09; H, 6.83%). The above hydroxy-acid **10d** (90 mg) was sublimed at 150–160° (bath)/0.1 mm to afford the above mentioned trans-lactone **2f** (60 mg) as needles, m.p. 122°.

8 - *Bromo* - 7 - *methoxy* - 6 - *methyl* - 3,4 - *dihydronaphthalene* **7d**. Reduction of 8 - bromo - 7 - methoxy - 6 - methyl - 1 - tetralone[7] **5f** (2.0 g) with $NaBH_4$ as before gave an oily alcohol (2.1 g). Dehydration of this material with $KHSO_4$ afforded the desired styrene **7d** (1.43 g, 71%) as viscous oil, b.p. 125–130° (bath)/0.2 mm, λ_{max} 225 and 268 nm (ϵ 19,950 and 9,333) (Found: C, 56.75; H, 5.30. $C_{12}H_{13}OBr$ requires: C, 56.92; H, 5.14%).

trans - 2,8 - *Dibromo* - 7 - *methoxy* - 6 - *methyl* - 1,2,3,4 - *tetrahydronaphthalene* - 1 - *ol* **6h**. A soln of the above styrene **7d** (1.34 g) in DMSO and water was treated with NBS as described before to give the desired trans-bromohydrin **6h** (1.1 g, 61%) as needles, m.p. 125–127° (ether–light petroleum) (Found: C, 41.01; H, 4.23. $C_{12}H_{14}O_2Br_2$ requires: C, 41.14; H, 4.00%).

8 - *Bromo* - 7 - *methoxy* - 6 - *methyl* - 3,4 - *dihydronaphthalene* - 1,2 - *oxide* **4e**. Treatment of the above trans-bromohydrin **6h** (780 mg) with alcoholic KOH as before gave the epoxide **4e** (480 mg, 80%), m.p. 56–58° (petroleum ether, b.p. 40–60°), λ_{max} 226, 272, 277 and 285 nm (ϵ 7,943; 645,708 and 758), ν_{max} 1286, 1088, 998 and 864 cm^{-1}; τ 7.99–8.45 (2H,m), 7.75 (3H,s), 7.31–7.61 (2H,m), 6.28–6.68 (1H,m), 6.28 (3H,s), 5.59 (1H, d, J 4.4 Hz), 3.21 (1H,s) (Found: C, 53.48; H, 5.02. $C_{12}H_{13}O_2Br$ requires: C, 53.53; H, 4.83%).

trans - 8 - *Bromo* - 2 - *hydroxy* - 7 - *methoxy* - 6 - *methyl* - 1,2,3,4 - *tetrahydro* - 1 - *naphthylacetic acid* **10e**. Condensation of the above epoxide **4e** (1.8 g) with the anion of diethyl malonate

was performed as before but the refluxing time was 7 h. Usual processing of the reaction mixture afforded a hydroxy-ester (2.3 g), ν_{max} 1725 and 3430 cm^{-1}. This material was hydrolysed by heating under reflux for 1 h with a soln of NaOH (3.84 g) in EtOH (232 ml) and H_2O (174 ml). Alcohol was removed under reduced pressure and the alkaline soln on usual work-up provided the trans - hydroxy-acid **10e** (1.55 g, 70%), m.p. 158–159° (ether–light petroleum), ν_{max}^{KBr} 1695 (acid C=O) and 3320 cm^{-1} (OH) (Found: C, 50.80; H, 5.26. $C_{14}H_{17}O_4Br$ requires: C, 51.07; H, 5.10%).

trans - 3a,4,5,9b - *tetrahydro* - 9 - *bromo* - 8 - *methoxy* - 7 - *methylnaphtho*[2,1-*b*]*furan* - 2(1H) - *one* **2g**. Sublimation of the above trans-hydroxy - acid **10e** (500 mg), at 180–185° (bath)/0.1 mm afforded the desired trans-lactone **2g** (350 mg, 80%), m.p. 156–159° (ether–light petroleum) ν_{max} (KBr) 1772 cm^{-1} (lactone C=O), τ 7.62 (3H,s), 6.23–7.5 (7H,m), 6.11 (3H,s), 5.44–6.06 (1H,m), 2.85 (1H,s) (Found: C, 53.96; H, 5.01. $C_{14}H_{15}O_3Br$ requires: C, 54.02; H, 4.82%).

3,4 - *Dihydronaphthalene* - 1,2 - *oxide* **4a**. Reduction of 1-tetralone (2.0 g) with $NaBH_4$ (1.06 g) as before gave a crude alcohol (2.02 g) which on dehydration with $KHSO_4$ afforded 3,4 - *dihydronaphthalene* (1.1 g, 71%) as colourless oil, b.p. 90° (bath)/2 mm (reported[25] b.p. 86°/13 mm). Treatment of a soln of the above styrene (1.1 g) in DMSO (30 ml) and H_2O (0.3 ml) with NBS as before (temp. 10–15°) gave trans - 2 - bromo - 1,2,3,4 - tetrahydronaphthalene - 1 - ol **6j** (1.3 g, 71%), m.p. 110–111° (ether–light petroleum) (reported[9] m.p. 111–112°) (Found: C, 52.80; H, 4.85. $C_{10}H_{11}OBr$ requires: C, 52.86; H, 4.84%). The above trans-bromohydrin **6j** (2.0 g) on treatment with alcoholic KOH as described before provided the desired epoxide **4a** (1.2 g, 92%), b.p. 100° (bath)/2 mm (reported[9] b.p. 124–125°/13 mm).

Interaction of the epoxide **4a** *with sodium diethyl malonate. Formation of trans* - 3a,4,5,9b - *tetrahydronaphtho*[2,1-b]*furan* - 2(1H) - *one* **2a**, *and trans* - 2 - *hydroxy* - 1,2,3,4 - *tetrahydro* - 1 - *naphthylacetic acid* **10f**

Condensation of the epoxide **4a** (1.64 g) with the anion of diethyl malonate as before afforded a viscous material (1.77 g) b.p. 152–155°/0.2 mm. Alkaline hydrolysis of this material and decarboxylation of the resulting acid provided the trans-lactone **2a** (600 mg, 28%), m.p. 146–147° (benzene–light petroleum) (reported[3] m.p. 147°), ν_{max}^{KBr} 1785 cm^{-1} (lactone C=O), τ 6.41–8.24 (7H,m), 5.6–6.03 (1H,m) and 2.22–3.07 (4H,m); and the trans - hydroxy - acid **10f** (116 mg), m.p. 116–117° (ether–light petroleum), ν_{max}^{KBr} 1725 (acid C=O) and 3450 cm^{-1} (OH) (Found: C, 69.82; H, 7.01. $C_{12}H_{14}O_3$ requires: C, 69.89; H, 6.84%).

Alkaline hydrolysis of the trans-lactone **2a**, *and lactonisation of the trans-hydroxy-acid* **10f**. The above-lactone **2a** (550 mg) on hydrolysis with methanolic KOH (10 ml, 7%) afforded the trans - hydroxy - acid **10f** (550 mg, 86%), m.p. 115–116°.

Sublimation of the aboe hydroxy-acid **10f** (86 mg) at 140–142° (bath)/0.2 mm gave the trans-lactone **2a** (50 mg, 60%), m.p. 146°.

trans - 1 - *Ethoxy* - 2 - *hydroxy* - 1,2,3,4 - *tetrahydronaphthalene* **6k**

(a) *By condensation of the trans-bromohydrin* **6j** *with sodium diethyl isopropylmalonate.* Condensation of the bromohydrin **6j** (3.6 g) with sodium diethyl isopropylmalonate in refluxing EtOH (4 h reflux) gave no lactonic product (from IR). The only product isolated was the trans - hydroxy - ether **6k** (1.64 g, 54%), b.p. 118–120°/0.4 mm, ν_{max} 3450 cm^{-1} (OH) (Found: C, 74.83; H, 8.16. $C_{12}H_{16}O_2$ requires: C, 74.97; H, 8.39%).

(b) *By opening of the epoxide* **2a** *with sodium ethoxide in refluxing ethanol.* A soln of the epoxide **2a** (1.7 g) in dry ethanol (9 ml) was added to a refluxing soln of NaOEt (from 530 mg Na) in dry EtOH (35 ml) over a period of 1 h. After heating under reflux for 20 h, the reaction mixture was worked up as before to give the trans - hydroxy - ether **6k** (1.78 g, 79%).

Attempted condensation of the above hydroxy–ether **6k** (1.78 g) with sodium diethylmalonate under refluxing ethanol gave mainly the recovered material **6k** (1.2 g, 86%), b.p. 115–120°/0.2 mm, ν_{max} 3375 cm^{-1}.

Attempted synthesis of cis - 3a,4,5,9b - *tetrahydronaphtho*[2,1-*b*]*furan* - 2(1H) - *one* **3c**

Formation of a mixture of the cis - **3c** *and the isomeric trans-lactone* **2a**

(a) *By* $NaBH_4$ *redn of ethyl* 1,2,3,4 - *tetrahydro* - 2 - *oxo* - 1 - *naphthylacetate* **11e**. To a cold and stirred soln of the known[15] keto-ester **11e** (500 mg) in MeOH (15 ml) and H_2O (0.4 ml) was added $NaBH_4$ (167 mg). The reaction mixture was stirred at the cold condition for 2 h and worked-up as before to furnish a neutral material as oily solid (430 mg), ν_{max} 1768 and 1724 cm^{-1}. Chromatography of this material over neutral alumina and elution with benzene-light petroleum (1:1) gave a solid material (60 mg), m.p. 72–78°. Repeated crystallisations of this product afforded an eutectic mixture of the cis-**3c** and the trans-lactone **2a**, m.p. 78–79° (ether–light petroleum), ν_{max} 1772 (lactone C=O, broad), τ 6.69–8.21 (6H,m), 6.00–6.33 (1H,m), 4.89–5.13 (1H,m), 2.60–2.88 (4H,m). The integration curves for the two C-3a hydrogen multiplets show that the cis-**3c** and the trans-lactone **2a** are present in a ratio of *ca.* 1:1 in the mixture. (Found: C, 76.48; H, 6.58. $C_{12}H_{12}O_2$ requires: C, 76.57; H, 6.43%).

(b) *By* $NaBH_4$ *redn of* 2 - *oxo* - 1,2,3,4 - *tetrahydro* - 1 - *naphthylacetic acid* **11f**. Hydrolysis of the keto-ester **11e**[15] (1.0 g) by heating under reflux for 0.5 h with a soln of Na_2CO_3 (800 mg) in MeOH (7.3 ml) and H_2O (10 ml) afforded the keto-acid **11f** (800 mg), ν_{max} 1753 and 1716 cm^{-1}. To an ice-cold stirred soln of the above keto-acid **11f** (800 mg) in EtOH (5 ml) was added a soln of $NaBH_4$ (304 mg) and NaOH (352 mg) in water (7.5 ml). The reaction mixture was stirred for 4 h under cold condition and left at room temp for 16 h. Usual work-up of the reaction mixture gave a neutral fraction (80 mg) and an acidic fraction (500 mg). This acid was again dissolved in ether and after usual separation with sat $NaHCO_3$ soln provided a neutral (260 mg) and an oily acidic material (200 mg). The above two neutral fractions (80 mg + 260 mg) on repeated crystallisations afforded a mixture of lactones (300 mg, 46%), m.p. 78–79° (ether–light petroleum), ν_{max} 1772 cm^{-1} (lactone C=O, broad), τ 6.56–8.26 (6H,m), 5.83–6.25 (1H,m), 4.71–4.99 (1H,m), 2.57–2.79 (4H,m). Integration curves for C-3a hydrogen atoms indicate 1:1 mixture of **3c** and **2a**. (Found: C, 76.47; H, 6.39%).

(c) *From ethyl* 3,4 - *dihydro* - 1 - *naphthylacetate* **13a**. To an ice-cold soln of the β,γ-unsaturated ester **13a**[18] (760 mg) in ether (7 ml) was added a soln of monoperphthalic acid (760 mg) in ether (19 ml). The reaction mixture was kept in the refrigerator for 66 hr to complete the reaction (blank). Precipitated phthalic acid was filtered and washed thoroughly with ether. The combined solvent was washed with aq NaOH (2%) to free from acid. Usual processing of the solvent afforded an epoxy-ester as colourless oil (600 mg), b.p. 145–150° (bath)/0.2 mm, λ_{max} 274 nm (ϵ 2,489), ν_{max} 1735, 1250 and 1160 cm^{-1}.

The above crude epoxy-ester (1.9 g) was hydrogenated over Pd-C (200 mg, 10%) at room temp. (31°) and atmospheric pressure to give an oily product (1.9 g) which on alkaline hydrolysis and subsequent acidification provided a neutral product as a 1:1 mixture (from NMR) of lactones **3c** and **2a** (720 mg, 47%), m.p. 77–78° (ether–light petroleum), ν_{max} 1778 cm^{-1} (lactone C=O), τ 6.64–8.22 (6H,m), 5.98–6.37 (1H,m), 4.84–5.15 (1H,m), 2.72–2.90 (4H,m) (Found: C, 76.60; H, 6.67%).

(d) *Through catalytic hydrogenation of the enol-lactone* **15**. The keto-acid **11f** (600 mg) was refluxed with a mixture of Ac_2O and AcONa according to the prescribed procedure[26] to give a semi-solid neutral material (320 mg), b.p. 170–175° (bath)/0.6 mm. This product on crystallisation from acetone–light petroleum provided 3a,4,5 - trihydronaphtho - [2,1-b]furan - 2 - one **15** (98 mg), m.p. 114–116°, ν_{max} 1748 and 1633 cm^{-1} (Found: C, 76.97; H, 5.63. $C_{12}H_{10}O_2$ requires: C, 77.40; H, 5.41%); and an oil (200 mg); ν_{max} 1800 (hump), 1744 and 1633 cm^{-1} (strong).

Catalytic hydrogenation of a soln of **15** (80 mg) in EtOH (12 ml) with Pd-C (40 mg, 10%) afforded a 1:1 mixture of **3c** and **2a** as an oil (65 mg), b.p. 145–150° (bath)/0.2 mm, ν_{max} 1772 cm^{-1}, NMR identical as above. Similar reduction of the above oily product (200 mg) also gave a 1:1 mixture (from NMR) of **3c** and **2a**.

7 - *Methoxy* - 8 - *methyl* - 3,4 - *dihydro* - 1 - *naphthyl* - α - *propionic acid* **13e**. To a soln of 7 - methoxy - 8 - methyl - 1 -

tetralone[7] **5a** (1.0 g) in dry benzene (50 ml) was added zinc metal (350 mg). Some benzene (15 ml) was distilled off to remove moisture. Ethyl α-bromopropionate (900 mg) and a crystal of iodine was then added and the reaction mixture was refluxed for 6 h. After every 2 h of refluxing, a further quantity of zinc metal (350 mg) and ethyl α-bromopropionate (900 mg) was added for completion of the reaction. After complete addition, the reaction mixture was refluxed for a further period of 3 h. Usual processing of the reaction mixture gave the unreacted ketone **5a**[7] (450 mg), and a high boiling residue which was dehydrated by heating with $KHSO_4$ at 170° for 7 min, and the product was distilled under vacuum to give an unsaturated ester (600 mg), b.p. 145° (bath)/0.3 mm, λ_{max} 217 and 259 nm (ε 19,950 and 7244). This ester (600 mg) on alkaline hydrolysis and acidification provided the β,γ-unsaturated acid **13e** (310 mg), m.p. 144–145° (ether–light petroleum), λ_{max} 218 and 260 nm (ε 19,950 and 7943), ν_{max} 1711 cm^{-1} (acid C=O) (Found: C, 73.36; H, 7.37. $C_{15}H_{18}O_3$ requires: C, 73.15; H, 7.37%).

7 - *Methoxy* - 8 - *methyl* - 3,4 - *dihydro* - 1 - *naphthylacetic acid* **13d**. Reformatsky reaction of the α-tetralone derivative[7] **5a** (1.0 g) with ethyl bromoacetate as above afforded the unreacted ketone **5a** (110 mg), and a high boiling residue which on dehydration as before gave an unsaturated ester (700 mg), b.p. 140° (bath)/0.3 mm, λ_{max} 220 and 259 nm (ε 22,390 and 9120). Basic hydrolysis of this ester as before furnished the β,γ-unsaturated acid **13d** (280 mg), m.p. 112° (ether–light petroleum), λ_{max} 218 and 261 nm (ε 19,950 and 7762), ν_{max} 1711 cm^{-1} (carboxy C=O) (Found: C, 72.43; H, 7.22. $C_{14}H_{16}O_3$ requires: C, 72.39; H, 6.94%).

Attempted acid-catalysed lactonisation of 3,4 - *dihydro* - 1 - *naphthylacetic acid* **13b**, *and its* 7 - *methoxy* - *derivative* **13c**

Formation of 1,2,3,4 - *tetrahydro* - 1 - *naphthylideneacetic acid* **14a** *and its* 7 - *methoxy derivative* **14b**. To well-stirred conc H_2SO_4 (12 ml), cooled in an ice-salt bath (−10 to −5°) was added dropwise during 15 min a soln of the β,γ-unsaturated acid **13b**[18] (400 mg), m.p. 104–106° in dry $CHCl_3$ (24 ml). The reaction mixture was stirred at −10° to −5° for 1 h more, and then diluted with large volume of H_2O. $CHCl_3$ layer separated and the aqueous layer was extracted with ether (3 × 50 ml). The combined solvent was extracted with aq KOH (2%) and then washed with H_2O. Evaporation of the neutral solvent gave no product. The above alkaline extract on acidification and subsequent ether extraction afforded 1,2,3,4 - tetrahydro - 1 - naphthylideneacetic acid[18] **14a** (210 mg), m.p. 160–161° (ether–light petroleum) (reported[18] m.p. 162–163°), ν_{max} 1684 cm^{-1} (acid C=O) (Found: C, 76.28; H, 6.79. $C_{12}H_{12}O_2$ requires: C, 76.57; H, 6.43%).

Similar acid-catalysed cyclisation of the β,γ-unsaturated acid[19] **13c** (300 mg), m.p. 139° afforded 7 - methoxy - 1,2,3,4 - tetrahydro - 1 - naphthylideneacetic acid **14b** (140 mg), m.p. 167–168° (ether–light petroleum), ν_{max} 1678 cm^{-1} (acid C=O) (Found: C, 71.31; H, 6.55. $C_{13}H_{14}O_3$ requires: C, 71.54; H, 6.47%).

Attempted bromolactonisation of 7 - *methoxy* - 3,4 - *dihydro* - 1 - *naphthylacetic acid* **13c**

Formation of the dihydronaphthalene derivative **16** *and* **17**. Bromolactonisation of the β,γ-unsaturated acid **13c** (720 mg) according to the procedure of Barnett *et al.*[20d] gave a neutral product (600 mg) containing bromine. This product showed no characteristic band for C=O in IR. A fraction was distilled to give yellow oil, b.p. 150–155° (bath)/0.2 mm, λ_{max} 229 and 264 nm (ε 27,960 and 6,486), τ 8.6–8.8 (m), 7.78 (s, Me attached to olefinic carbon), 7.16–7.54 (m), 6.23 (s, OMe), 6.20 (s, OMe), 6.07 (s, olefinic H_b), 5.70(m), 5.50 (s, olefinic H_a), 2.4–3.43 (m, aromatic H), *m/e* 254 and 252 (M^+), 173 (M^+–Br), 172 (M^+–HBr, base peak).

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