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# 1,8-Diazabicyclo[5.4.0]undec-7-ene : a Remarkable Base in the Epoxidation of $\alpha,\beta$-Unsaturated-$\delta$-Lactones and other Enones with Anhydrous t-BuOOH†

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**Abstract** : 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) has been studied for the epoxidation of electron deficient alkenes with anhydrous t-BuOOH (TBHP) in dichloroethane. Steric demands are higher than that for alkaline $H_2O_2$. DBU is recognised as a remarkable base in these oxidations as other bases such as triethyl amine, diisopropylethyl amine, and 1,4-diazabicyclo[2.2.2]octane (DABCO) are absolutely inefficient. DBU is effective in promoting the oxidation of $\alpha$, $\beta$-unsaturated $\delta$-lactones where most of conventional methods either fail or perform poor.

## Genesis

Epoxidation of electron deficient alkenes is an important reaction. The resulting epoxy materials are readily transformed into various useful targets including, e.g., $\alpha$- and $\beta$-hydroxy carbonyl compounds[1], $\alpha,\beta$-epoxy alcohols[2], allylic alcohols[3], and 1,3-diols[4]. Nucleophilic $\alpha$- and $\beta$-openings of the oxirane ring, whether or not under the influence of suitable additives, enhance their utility further[5]. The $\alpha$- and $\beta$-hydroxy carbonyl groupings are present in various natural products including mevinolins. The bulk activity of mevinolins is due to the $\beta$-hydroxy-$\delta$-lactone unit, the role of the octalin segment is purely that of hydrophobic in nature which provides the necessary guidance for suitable interaction with the active site of 3-hydroxy-3-methylglutaryl coenzyme A (HMG-CoA) reductase[6]. In connection with a programme aimed at the synthesis of mevinolin analogues for their pharmacological evaluations, we happened to be interested in the epoxidation of 6-substituted 3,4-dehydro-2-oxopyran.

## Introduction

Attempted epoxidation of 3,4-dehydro-6-(2-phenylethyl)-2-oxopyran with alkaline hydrogen peroxide under conditions related to those of Trost[7a] and Payne[7b] was very slow. Lactone ring opening[8] was prominent and methyl 2,3-epoxy-5-hydroxy-7-phenyl-2-heptenoate was the major product isolated. The desired oxirane formed the minor constituent. Replacement of MeOH by other water-miscible and yet non-nucleophilic solvents such as THF and DME did not promote any reaction. Biphasic reaction in benzene and water with $H_2O_2$/$NaHCO_3$/n-$Bu_4NI$ was ineffective. The reaction using Triton-B in benzene[4] was very complex. Treatment with excess mCPBA (6 equiv.) in dichloroethane[9] at reflux for 6h furnished

†**Dedicated to Prof. Michael Benn of the University of Calgary who kindly taught few steps of chemistry to one of us (VKY).**

a mixture of the desired oxirane and the unreacted lactenone. Although excess mCPBA was still present, the conversion to oxirane was only 60%. Product separation from unreacted lactenone by gravity column chromatography was difficult[10]. Use of KF-$Al_2O_3$/TBHP[11] returned only the starting material.

Alkylzinc alkylperoxides[12] are very chemoselective and bring about epoxidation of enones only. Although no cyclic examples were studied, the application of alkyllithiums/TBHP presented a decent possibility[13]. The procedure, however, suffers from (a) low yields; in the closest acyclic example of *cis* t-butyl 3-isopropylacrylate, the conversion was 20% only, (b) transesterification and hydrolysis to carboxylic acids, and (c) the requirement of expensive and hazardous alkyllithiums. The last point is also valid for the KH/TBHP method developed by Still[14]. We, therefore, looked for alternative methods.

**Results and discussion**

The above unfortunate failure of the reaction with cyclic esters forced us to look further to other reagents. Given the poor Michael acceptability of cyclic esters, the Micheal donors must be free and uncomplexed unlike the situation with KF-$Al_2O_3$/TBHP above. This guided us to consider still non-aqueous conditions, restricting the choice of the base to non-nucleophilic tertiary amines. This consideration was translated into reality when we discovered DBU promote the much desired epoxidation by TBHP[15] in dichloroethane. The reaction proceeded stereoselectively to furnish, after chromatographic purification, the product oxirane in > 75% yield. Other bases that we examined were DABCO, diisopropylethyl amine, and triethyl amine, and were found ineffective.

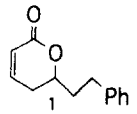
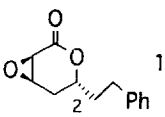
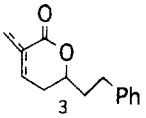
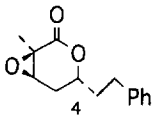
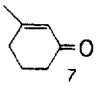
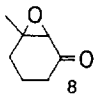
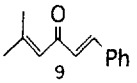
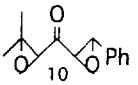
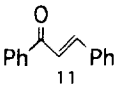
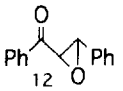
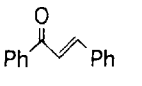
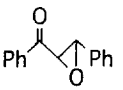
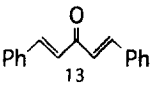
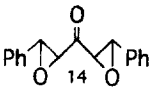
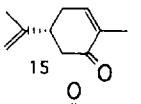
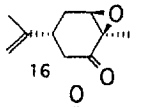
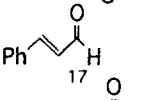
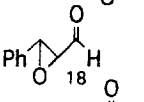
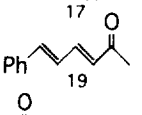
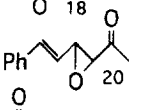
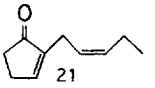
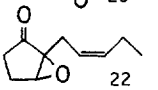
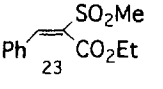
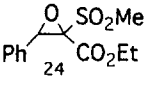
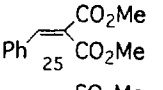
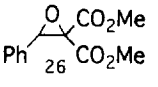
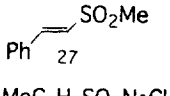
Encouraged from the above findings, we set to explore the scope and reacted other substrates. The results are collected in the Table. Reaction on a mixture of the *endo* and the *exo* δ-lactenones **3** at entry 2 furnished a mixture consisting of the *endo* lactenone and the oxirane **4** derived from it. None of the *exo* oxirane was noticed from the $^1H$ nmr spectrum of the crude material. Apparently, the *exo* lactenone isomerizes to the *endo* counterpart which undergoes slow oxidation to the product. A separate experiment on pure *endo* δ-lactenone furnished the same products mixture. In an nmr tube experiment in which a mixture of the two lactenones was treated with 1.0 equiv. of DBU in $CDCl_3$, pure *endo* lactenone was detected after 10 hrs.

Recognizing the potency of the DBU/TBHP reagent system, we wished to explore its versatility and, therefore, reacted enones of differing substitution patterns. Certain observations are noteworthy:

(a) whereas 2-cyclohexenone reacted completely in 10h, 3-methyl-2-cyclohexenone was much slow to offer only 65% conversion even after 24 h; raising, therefore, the possibility of regioselective oxidations,

(b) interestingly, the mono epoxide from 5-methyl-1-phenyl-1,4-hexadien-3-one (entry 5) reacts faster than the starting dienone itself; in an experiment in which the dienone was reacted with 0.6 mol equiv. of TBHP and 0.55 mol equiv. of DBU, the products mixture consisted of a 1:1 mixture[16] of the starting dienone and the *bis* epoxy derivative only,

**TABLE**

| Entry | Substrate | Product | Time/h | Yield[a] |
|---|---|---|---|---|
| 1. |  |  | 12 | 75 |
| 2. |  |  | 18 | 35[b] |
| 3. |  |  | 10 | 92 |
| 4. |  |  | 24 | 65[c] |
| 5. |  |  | 10 | 80[d] |
| 6. |  |  | 10 | 100[e] |
| 7. |  |  | 28 | 100[f] |
| 8. |  |  | 10 | 100[d] |
| 9. |  |  | 12 | 90 |
| 10. |  |  | 10 | 70[g] |
| 11. |  |  | 96 | 35[h] |
| 12. |  |  | 30 | 100 |
| 13. |  |  | $\frac{1}{2}$ | 100 |
| 14. |  |  | 2 | 100[i] |
| 15. |  | NO REACTION | 32 | |
| 16. | $MeC_6H_4SO_2N{=}CHPh$ (28) | $MeC_6H_4SO_2NHCOPh$ (29) | | |

[a] yields given are the isolated yields in percentage unless indicated otherwise.
[b] the ratio of the endo lactenone and the endo epoxide was 60:40 ($^1$H nmr).
[c] contrast this result with Wynberg, H.; Marsman, B. *J. Org. Chem.* **1980**, *45*, 158 where the reaction fails.
[d] mixture of *cis* and *trans* epoxides were obtained.
[e] contrast this result with Julia, S.; Masana, J.; Vega, J.C. *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 929 where the reaction in toluene with a solution of NaOH in 30% $H_2O_2$ for 48h did not give any of the desired oxirane. We ourselves have confirmed this.
[f] this reaction was performed with 10 mol% of DBU wrt substrate and 2.0 equiv. of t-BuOOH.
[g] the reaction was non-stereospecific as a mix of both cis and trans oxiranes were obtained.
[h] from a very clean reaction, the conversion to the product was only 35%.
[i] this is to be noted that this *bis* ester reacted slower than the sulfone derivative at entry 13.

(c) the dienone at entry 11 reacted, although slow but with complete regioselection, to furnish only the $\alpha$, $\beta$-epoxy derivative; it is important to note here that a reaction with alkaline hydrogen peroxide in MeOH for 12h was ineffective and returned only the starting material,

(d) the oxidation of the cyclopentenone derivative at entry 12 is quantitative, and

(e) reaction with acyclic $\alpha$, $\beta$-unsaturated esters (not shown in Table) fails, but with the doubly activated esters such as **23** and **25** (entries 13 and 14, respectively) the reaction is very rapid and complete conversions are achieved.

Theoretically, it is possible to conduct the reaction with only catalytic amounts of DBU, the reactions shall be expected to take longer time. This was put to experimental verification and chalcone was preferred as the substrate for reasons of visual colour change monitor. Whereas the use of only 10 mol% DBU did promote the oxidation, the duration for complete conversion was 28h (entry 7); to be compared against only 10h with 1.2 equiv. of DBU (entry 6) under identical conditions.

Testosterone, teststerone-acetate, isophorone, and acyclic $\alpha,\beta$-unsaturated esters did not react (not shown) with DBU/TBHP and, in each case, the substrate was recovered intact. These failures are due, probably, to the steric interference offered by the angular methyls in the steroid series, the axial methyl in isophorone, and low Michael accepability in acyclic unsaturated esters. The success with the cyclic esters (the lactenones) is due, probably, to the strain in the rings.

Success in achieving the oxidation of the 2-cyclopentenone derivative is remarkable. These materials are notorious for base catalyzed self condensation of aldol-type; no aldol products were noticed in the present study. Also, although the acetate derived from testosterone was unreceptive to oxidation by either of the reagents, the recovered material retained the acetoxy function; such a survival of the acetoxy group would be unexpected of other methods making use of aqueous bases[7]. Further, this functionality is likely to be touched in methods employing alkyllithiums/TBHP[13] and KH[14].

Whereas the DBU-TBHP system furnished, on reaction with chalcone, only the *trans* oxirane, other acyclic materials such as dibenzal acetone and 5-methyl-1-phenyl-1,4-hexadien-3-one gave a mixture of *trans* and *cis* oxides [16]; showing that the present reaction is not stereospecific with these systems. Why then with chalcone the reaction is so stereospecific is not clear. The present oxidation system is also successful with aldehydes such as cinnamaldehyde (entry 10) where, again, a mixture of *cis* and *trans* oxides is received. This last result is at variance from that achieved with alkaline $H_2O_2$[17].

The oxidation of $\alpha,\beta$-unsaturated sulphones is an important reaction. A limited number of methods are available[18,19]. Phenyl $\beta$-phenylvinyl sulphones under Weitz-Scheffer conditions undergo stereospecific epoxidation to give the *trans* epoxides from both the *cis* and the *trans* alkenes[19]. Potassium t-butylhydroperoxide is non-stereospecific and transforms *cis* phenyl $\beta$-phenylvinyl sulphone into a *cis/trans* (= 2/3) mixture of the corresponding oxiranes. The alkyllithiums/TBHP method of O. M.-Cohn et al[13] provides an excellent stereospecific solution; the yields of the requisite oxiranes are very high and, moreover, the initial stereo-integrity of the olefinic bond is retained in the product epoxide.

We looked at the possibility of entry to epoxy sulphones by either direct oxidation of $\alpha,\beta$-unsaturated sulphones or performing dealkyldecarboxylation of the epoxy material **24** (entry 13). Whereas the direct oxidation of methyl vinyl sulphone **27** failed, the further activated sulphones **23** reacted very fast and quantitatively to generate the requisite oxirane. This, when reacted with LiCl in DMF at 160 $\pm$ 5 °C, we were delighted to observe a very rapid reaction and procured the desired epoxide **33**, after chromatographic purification, in ~70% yields. The dealkyldecarboxylation was complete within 35 min. This accomplishes a new indirect method for the preparation of $\alpha,\beta$-epoxy sulphones.

Finally, the oxirane derived from N-(p-toluenesulphonyl)benzyl imine **28** (entry 16) is an useful material for the convenient introduction of a hydroxyl function $\alpha$ to a carbonyl group[20]. This material has been prepared by the mCPBA oxidation of the above imine[21]. We considered applying the present methodology. The reaction with DBU-based reagent offered the rearranged product **29** (entry 16) in near quantitative yields. Obviously, the requisite epoxide is first formed which then quickly rearranges, under the reaction conditions, to the observed product.

1,4-Addition of t-butylperoxy anion following attack of the resultant enolate on the *per* oxygen accounts for product(s) formation. In an experiment in which benzaldehyde was substituted for TBHP and chalcone used as the reacting substrate, PhCH:C(CHOH)COPh was not received. Likewise, in another experiment in which the TBHP was replaced by MeI, PHCH:C(Me)COPh was not isolated. In each case, chalcone was recovered intact. These observations argue against a reaction pathway which may be considered to initiate by conjugate addition of DBU following (a) attack of the resultant enolate on the *per* oxygen of TBHP giving an $\alpha$-hydroxy intermediate, which subsequently (b) undergoes an intramolecular ring closure to furnish the observed oxiranes and the DBU is regenerated.

In summary, we have presented an economical and much less hazardous reagent system useful in the epoxidation of electron deficient alkenes, including 3,4-dehydro-$\delta$-lactones. The reagent is sensitive to steric effects and could, therefore, be useful in regioselective oxidations (*cf.* ref 13). The reaction with 2,4-dienones is highly regioselective to furnish only the $\alpha,\beta$-epoxy material. This could be expected to have good synthetic potential. Because the aqueous base sensitive functional groups survive the present reagent system, this is likely to find applications in the oxidation of other substrates possessing functional groups that are, otherwise, labile. The yields, in general, are attractive and, hence, likely to find broader applications in synthetic endeavours.

**Experimental**

**General :** All chromatographic separations were performed over silica gel (100-200 mesh) using petroleum ether (60-80) and ethyl acetate mixtures as eluant. Ether, wherever used, stands for diethyl ether. The organic extracts were dried over anhydrous $Na_2SO_4$ and the solvents were removed under reduced pressure on rotovap. Commonly used abbreviations are used throughout: rt for room temperature, mix for mixture, and min for minutes. 0 °C refers to ice-water slush temperature. Solvents used in this study were

dried as per established procedures.

IR and mass spectra were recorded, respectively, on Perkin Elmer 1320 and Jeol D-300 series of instruments. $^1$H nmr spectra were recorded on either Bruker WM-400 ($CDCl_3$) or Bruker WP-80 ($CDCl_3$) or Varian EM-360L ($CCl_4$) series of spectrometers. $^1$H chemical shifts are reported in parts per million (ppm or $\delta$) from either $CHCl_3$ or tetramethyl silane.

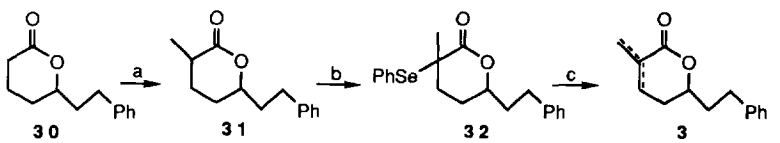
**General method for the oxidation with t-BuOOH and DBU :** A dichloroethane solution (2.0 ml) of the substrate (1.0 mmol) was added to a solution of DBU (1.2 mmol)) and anhydrous t-BuOOH (2.0 mmol, 850 $\mu$L of a 2.35 M solution in dichloroethan ) in dichloroethane (2.0 ml) at 0 °C. The anhydrous t-BuOOH in dichloroethane was prepared very simply following the procedure of Sharpless and Verhoeven[22].

The reaction mixture is stirred at rt and the progress monitored by tlc. The workup involved dilution with $CHCl_3$ (5.0 ml), addition of water (1.0 ml) following solid sodium metasulphite and stirring for 15 min in that order, separation of the organic layer, drying, filtration, solvent evaporation, and chromatography (if necessary).

**3,4-Dehydro-6-(2-Phenylethyl)tetrahydropyran-2-one (1):** $^1$H nmr (60Mz, $CCl_4$)) $\delta$ 7.3 (5H, s), 7.0-6.6 (1H, m), 5.9 (1H, qd, J = 12.5 Hz), 4.35 (1H, m); IR (CCl4) 1720, 1610 cm$^{-1}$. Calculated m/z for $C_{13}H_{14}O_2$ = 202.0993; observed m/z = 202.0964.

**3,4-Epoxy-6-(2-phenylethyl)tetrahydropyran-2-one (2):** $^1$H nmr (400 MHz, $CDCl_3$) $\delta$ 7.35-7.15 (5H, m), 4.53 (1H, m), 3.62 (1H, m), 2.9-2.8 (1H, m), 2.8-2.55 (1H, m), 2.35 (1H, td, J = 12, 3 Hz), 2.0-1.8 (4H, m); IR 1705 cm$^{-1}$. Calculated m/z for $C_{13}H_{14}O_3$ = 218.0942; observed m/z = 218.0928. Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.56; H, 6.42. Found: C, 71.48; H, 6.49.

**3-Methylidene-6-(2-phenylethyl)tetrahydropyran-2-one and 3,4-dehydro-3-methyl-6-(2-phenylethyl)tetrahydropyran-2-one (3):** A mixture of these two materials was prepared as per the following sequence:




(a) LDA, MeI, -80 °C- rt, 67% (b) LDA, PhSeBr, -80 °C - rt , 78%
(c) $H_2O_2$, pyridine, 0 °C - rt, 100%

Synthesis of 6-(2-phenylethyl)tetrahydropyran-2-one (**30**) is described elswhere. Please see Yadav, V.K.; Kapoor, K.K. *J. Org. Chem.* **1995** (submitted).

**3-Methyl-6-(2-phenylethyl)tetrahydropyran-2-one (31):** A solution of 6-(2-phenylethyl)tetrahydropyran-2-one (0.34g, 1.67 mmol) in dry THF (4 ml) was added at -80 °C to lithium diisopropylamide (2.17 mmol) in THF (4 ml). After 30 min, the yellow coloured enolate was reacted with a solution of MeI (2.17 mmol)

in THF (2 ml) containing HMPA (2.17 mmol). The resultant reaction mixture was allowed to stirr at -80 °C for 10 min and then let come to rt (3 hrs). This was poured into 5% aqueous HCl (7 ml) covered with ether (20 ml). The layers were separated and the aqueous phase extracted with ether (1 x 10 ml). The combined organic solution was washed with brine (1 x 10 ml) and freed of the volatiles to furnish, after chromatography, the desired product, 0.244g, 67% yield.

$^1$H nmr (60 MHz, $CCl_4$) $\delta$ 7.2 (5H, s), 4.4-3.9 (1H, m), 3.0-2.6 (2H, m), 2.5-1.4 (7H, m), 1.4-1.0 (3H, 2d, J = 5 Hz); IR 1720, 1205, 1190, 1075 cm$^{-1}$. From the $^1$H nmr characteristics, the product is a mixture of two diastereomers. The *bis* equatorial isomer constitutes the major component. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.06; H, 8.26. Found: C, 76.92; H, 8.39.

**3-methyl-3-phenylselenenyl-6-(2-phenylethyl)tetrahydropyran-2-one (32):** A solution of 3-methyl-6-(2-phenylethyl)tetrahydropyran-2-one (0.230g, 1.05 mmol) in THF (3.0 ml) was added to lithium diisopropylamide (1.36 mmol) in THF (3.0 ml) at -80 °C. To this was added, after 20 min, a dark THF (2.0 ml) solution of benzeneselenenyl bromide (1.36 mmol) in one lot. The colour disappeared immediately. The reaction mix was stirred at -80 °C for 30 min and then allowed to come to rt (4 hrs). This was poured into a cold 5% aqueous HCl (5.0 ml) covered with a mix of petroleum ether and ether (1:1, 10 ml). The organic layer was separated and the aqueous phase extracted with 1:1 ether and petroleum ether (3 x 10 ml). The combined organic extracts was washed with brine (1 x 15 ml). This was dried, filtered, and stripped of the volatiles. Chromatography furnished the product, 0.308g, 78% yield.

$^1$H nmr (60MHz, $CCl_4$) $\delta$ 7.8-7.1 (5H, m), 7.2 (5H, s), 4.6-4.0 (1H, m), 3.0-2.6 (2H, m), 1.6 (3H, s); IR 1710, 1265, 1105 cm$^{-1}$. A single singlet for the methyl ($\delta$ 1.6) is indicative of a single diastereomer being obtained. Calcd m/z for $C_{20}H_{22}O_2Se$ = 373.0784; observed m/z = 373.0768.

**2-Methylidene-6-(2-phenylethyl)tetrahydropyran-2-one and 3,4-dehydro-3-methyl-6-(2-phenylethyl)tetrahydropyran-2-one (3):** To a solution of the above seleno material **32** (0.221g, 0.59 mmol) in dichloromethane (3 ml) was added pyridine (0.094g, 1.18 mmol) and the solution cooled to 0 °C. To this was added aqueous 10% $H_2O_2$ (600 $\mu$L, 0.060g $H_2O_2$, 1.78 mmol) dropwise over a period of 5 min. The resultant mix was vigorously stirred at 0 °C for 20 min and then at rt for 20 min. The reaction mixture was poured into a well stirred mix of aqueous 5% $NaHCO_3$ (12 ml) and dichloromethane (12 ml). The layers were separated and the aqueous. solution extracted with dichloromethane (2 x 10 ml). The combined organic extracts was washed with brine (1 x 15 ml) and dried. Concentration and chromatography furnished the product olefins, 0.128g, quantitative yield.

$^1$H nmr **[3,4-dehydro-3-methyl-6-(2-phenylethyl) tetrahydropyran-2-one]** (80 MHz, $CDCl_3$) $\delta$. 7.3 (5H, s), 6.6 (1H, m), 4.6-4.1 (1H, m), 3.0-2.6 (2H, m), 2.5-1.7 (4H, m), 1.9 (3H, bs); IR 1705 cm$^{-1}$. Calculated m/z for $C_{14}H_{16}O_2$ = 216.1149; observed m/z = 216.1124.

$^1$H nmr **[3-methylidene-6-(2-phenylethyl) tetrahydropyran-2-one]** (80 MHz, $CDCl_3$) $\delta$ 7.3 (5H, s), 6.5 (1H, q, J = 2 Hz), 5.6 (1H, q, J = 2 Hz), 4.3 (1H, m); IR 1715 cm$^{-1}$.

**3,4-epoxy-3-methyl-6-(2-phenylethyl)tetrahydropyran-2-one (4)**: $^1$H nmr (80 MHz, $CDCl_3$) $\delta$ 7.2 (5H, m), 4.5 (1H, m), 3.4 (1H, d, J = 3 Hz), 2.9-2.5 (2H, m), 2.2-1.6 (4H, m), 1.56 (3H, s). IR 1720 cm-1. Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.41; H, 6.89. Found: C, 72.12; H, 6.57.

**2,3-Epoxy-2-cyclohexenone (6):** $^1$H nmr (60 MHz, $CCl_4$) $\delta$ 3.7 (1H, m), 3.2 (1H, d, J = 4 Hz), 2.9-1.4 (6H, m); IR 1700 $cm^{-1}$.

**2,3-Epoxy-3-methyl-2-cyclohexenone (8):** $^1$H nmr (60 MHz,$CCl_4$) $\delta$ 2.9 (1H, s), 2.3-1.5 (6H, m), 1.4 (3H, s); IR 1700 $cm^{-1}$. Calcd m/z for $C_7H_{10}O_2$ = 126.0680; observed m/z = 126.0664.

**5-Methyl-1-phenyl-1,4-hexadien-3-one (9):** To a solution of mesityl oxide (0.98g, 10.0 mmol) and benzaldehyde (1.06g, 10.0 mmol) in ethanol (25 ml) was added a solution of NaOH (0.80g, 20.0 mmol) in a 2:1 mix of EtOH and water (15 ml) at 0 °C under nitrogen. The reaction solution was allowed to come to rt and the stirring continued. After 4 hrs, most of the EtOH was removed on rotovap, the residue diluted with water (20 ml), and extracted with ether (3 x 20 ml). The combined extract was washed with brine (1 x 20 ml), dried, and concentrated. The residue was chromatographed to furnish the desired product; 1.02g, 55%.

$^1$H nmr (60 MHz, $CCl_4$) $\delta$ 7.8 (1H, d, J = 16 Hz), 7.7-7.3 (5H, m), 6.8 (1H, d, J = 16 Hz), 6.4 (1H, m), 2.3 (3H, s), 2.0 (3H, s); IR 1700, 1665, 1620, 1590, 1570, 1445, 1115 $cm^{-1}$. Calcd m/z for $C_{13}H_{14}O$ = 186.1044; observed m/z = 186.1036.

**The bis epoxides from 5-methyl-1-phenyl-1,4-hexadien-3-one (10):** $^1$H nmr (80 MHz, $CDCl_3$) $\delta$ 7.5 (5H, bs), 4.2-3.6 [3H, d 4.19 (d), 4.0 (d), 3.84 (d), 3.75 (d), 3.70 (s), 3.53 (s)], 1.50-1.34 [6H, d 1.50 (s), 1.40 (s), 1.34 (s)]; IR 1705, 1665, 1615, 1440, 1110 $cm^{-1}$. Anal. calcd for $C_{13}H_{14}O_3$: C, 71.56; H, 6.42. Found: C, 71.63; H, 6.51.

**Chalcone-epoxide (12):** $^1$H nmr (80 MHz, $CDCl_3$) $\delta$ 8.3-7.1 (10H, m), 4.3 (1H, d, J = 2 Hz), 4.1 (1H, d, J = 2 Hz); IR 1680, 1445, 1410, 1235 $cm^{-1}$. Anal. calcd for $C_{15}H_{12}O_2$: C, 80.36; H, 5.36. Found: C, 80.26; H, 5.42.

**Dibenzal acetone epoxide (14):** $^1$H nmr (60 MHz, $CCl_4$) $\delta$ 7.4 (10H, s), 4.1 (2H, m), 3.6 (2H, m); IR 1710 $cm^{-1}$. Anal. calcd for $C_{17}H_{14}O_3$: C, 76.69; H, 5.26. Found: C, 76.58; H, 5.13.

**2,3-Epoxy-5-isopropenyl-2-methyl-2-cyclohexenone [R-(-)-carvone epoxide] (16):** $^1$H nmr (60 MHz, $CCl_4$) $\delta$ 4.8 (2H, m), 3.4 (1H, m), 3.0-1.5 (5H, m), 1.8 (3H, s), 1.4 (3H, s); IR 1700, 1660,1435, 1115, 885 $cm^{-1}$. Calcd m/z for $C_{10}H_{14}O_2$ = 166.0993; observed m/z = 166.0980.

*Trans* **2,3-epoxy cinnamaldehyde (18):** $^1$H nmr (60 MHz, $CCl_4$) $\delta$ 9.3 (1H, d, J = 6 Hz), 7.4 (5H, s), 4.1 (1H, d, J = 2 Hz), 3.4-3.2 (1H, dd, J = 6, 2 Hz).

*Cis* **2,3-epoxy cinnamaldehyde (18):** $^1$H nmr (60 MHz, $CCl_4$) $\delta$ 9.2 (1H, d, J = 6 Hz), 7.3 (5H, s), 4.4 (1H, d, J = 4.5 Hz), 3.6-3.3 (1H, dd, J = 6, 4.5 Hz).

**6-Phenyl-3,5-hexadien-2-one (19):** To a well stirred slurry of KF-$Al_2O_3$ (1.42g, 9.0 mmol of KF) in dry acetonitrile (10 ml) at 5 °C was added a mixed solution of cinnamaldehyde (0.792g, 6.0 mmol) and acetone (1.16g, 20.0 mmol) in dry acetonitrile (10 ml) dropwise over a period of 30 min. The reaction mix was allowed to come to rt when the solution turned dark orange in colour from the initial yellow. After 2.5h, KF-$Al_2O_3$ was removed by filtration, the filtrate freed of solvent, and residue chromatographed to furnish the product; 0.30g, 30% yield.

$^1$H nmr (60 MHz, $CCl_4$) $\delta$ 7.7-7.1 (6H, m), 7.1-6.6 (2H, m), 6.3-6.0 (1H, dd, J = 15 and 2 Hz), 2.2 (3H,s). IR 1650, 1610, 1350, 1250 cm$^{-1}$. Anal. calcd for $C_{12}H_{12}O$: C, 83.72; H, 6.98. Found: C, 83.58; H, 6.81.

**3,4-Epoxy-6-phenyl-3,5-hexadien-2-one (20):** This epoxide was inseparable from the parent dienone by gravity column chromatography. The $^1$H nmr (60 MHz, $CCl_4$) of the mixture consists of the following signals that are characteristics of the trans epoxide: $\delta$ 3.6 (dd, J = 7, 2 Hz), 3.3 (d, J = 2 Hz), 2.0 (s); IR 1705 cm$^{-1}$.
**2,3-Epoxy-2-(*cis/trans* 2-pentenyl)-2-cyclopenten-1-one (22):** $^1$H nmr (60 MHz, $CCl_4$) $\delta$ 5.8-5.0 (2H, m), 3.7 (1H, s), 3.0-1.7 (8H, m), 1.0 (3H, t, J = 7 Hz); IR 1730, 1050 cm$^{-1}$. Anal. calcd for $C_{12}H_{12}O_2$: C, 76.59; H, 6.38. Found: C, 76.50; H, 6.26.

**Ethyl 2-methylsulphonyl-3-phenylacrylate (23):** This material was prepared as per the procedure of Happer and Steenson[23]; 97% yield. $^1$H nmr (60 MHz, $CCl_4$) $\delta$ 7.7 (1H, s), 7.5 (5H, s), 4.3 (2H, q, J = 7 Hz), 3.1 (3H, s), 1.3 (3H, t, J = 7 Hz); IR 1715, 1615 1310, 1220, 1140 cm$^{-1}$. Calculated m/z for $C_{12}H_{14}O_4S$ = 254.0612; observed m/z = 254.0590.
**Ethyl 2,3-epoxy-2-methylsulphonyl-3-phenylacrylate (24):** $^1$H nmr (60 MHz, $CCl_4$) $\delta$ 7.8 (5H, s), 4.8 (1H, s), 4.2 (2H, q, J = 7 Hz), 3.2 (3H, s), 1.0 (3H, t, J = 7 Hz); IR 1730, 1320 cm$^{-1}$. Calculated m/z for $C_{12}H_{14}O_5S$ = 270.0561; observed m/z = 270. 0536. Anal. calcd for $C_{12}H_{14}O_5S$: C, 53.33; H, 5.18; S, 11.85. found: C, 53.25; H, 5.26; S, 11.76.

**Methyl 2-phenylvinylsulphone (27):** The above Ethyl 2-methylsulphonyl-3-phenylacrylate was subjected to dealkyldecarboxylation as per the procedure of Happer and Steenson[23] to receive the product. $^1$H nmr (60 MHz, $CCl_4$) $\delta$ 7.7 (1H, d, J = 16 Hz), 7.5 (5H, s), 7.0 (1H, d, J = 16 Hz), 3.0 (3H, s); IR 1610, 1565, 1485, 1440, 1130, 960 cm$^{-1}$. Calcd m/z for $C_9H_{10}O_2S$ = 182.0400; observed m/z = 188.0384.

**Methyl (1,2-epoxy-2-phenylvinyl) sulphone (33):** The epoxide of ethyl 2-methylsulphonyl-3-phenylacrylate **24** (0.181g, 0.67 mmol) and LiCl (0.57g, 1.34 mmol) were taken in DMF (6.0 ml) and the resultant heated to 160 $\pm$ 5 °C for 35 min. The reaction mix was allowed to cool to rt and poured into cold water (25 ml). This was extracted with ether (3 x 10 ml) and the combined extracts washed with cold water (2 x 10 ml) and brine (1 x 15 ml). Drying and solvent removal furnished a residue that was chromatographed to afford the desired product, 0.80g, 70% yield.

$^1$H nmr (60 MHz, $CCl_4$) $\delta$ 7.6 (5H, s), 4.4 (2H, s), 2.8 (3H, s); IR 1300, 1115 cm$^{-1}$. Anal. calcd for $C_9H_{10}O_3S$: C, 54.54; H, 5.05; S, 16.16. Found: C, 54.40; H, 4.90; S, 16.10.

**Benzylidene dimethylmalonate (25):** Dimethyl malonate (1.32g, 10.0 mmol), benzaldehyde (1.27g, 12.0 mmol) and piperidine (0.086g, 1.0 mmol) were taken in benzene (50 ml) and refluxed under nitrogen with azeotropic removal of water formed during the reaction using Dean-Stark apparatus. After 9 hrs, the reaction mix was cooled to rt and poured into a well stirred cold aqeous 5% HCl (10 ml) covered with ether (20 ml). The layers were separated and the aqeous phase extracted with ether (2 x 15 ml). The combined ether extracts were washed successively with water (1 x 20 ml) and brine (1 x 20 ml). Drying, filtration and solvent removal furnished a residue which was chromatographed to isolate the desired product, 2.1g, 95% yield.

$^1$H nmr (60 MHz, $CCl_4$) $\delta$ 7.9 (1H, s), 7.5 (5H, s), 3.9 (3H, s), 3.85 (3H, s); IR 1730, 1630 cm$^{-1}$. Calcd m/z for $C_{12}H_{12}O_4$ = 220.0735; observed m/z = 220.0720.

**The epoxide from benzylidene dimethylmalonate (26):** $^1$H nmr (60 MHz, $CCl_4$) $\delta$ 7.3 (5H, s), 4.5 (1H, s), 3.9 (3H, s), 3.6 (3H, s); IR (neat) 1745, 1255 cm$^{-1}$. Calcd m/z for $C_{12}H_{12}O_5$ = 236.0684; observed m/z = 236.0672.

**N-(p-Toluenesulphonyl)benzamide :** $^1$H nmr (60 MHz, $CCl_4$) $\delta$ 8.1-7.6 (4H, m), 7.6-7.0 (5H, m), 5.6-5.0 (1H, bs), 2.4 (3H, s); IR 3300, 1700, 1600, 1180 cm$^{-1}$. Anal. calcd for $C_{14}H_{13}O_3NS$: C, 61.09; H, 4.73; N, 5.09; S, 11.64. Found: C, 61.15; H, 4.79; N, 5.16; S, 11.60.

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