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KF Adsorbed on Alumina Effectively Promotes the Epoxidation of Electron Deficient Alkenes by Anhydrous t-BuOOH[!]

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Abstract. KF adsorbed on alumina (KF-Al_2O_3) has been studied in detail for the epoxidation of electron deficient alkenes with anhydrous t-BuOOH. Aqueous base sensitive functional groups survive the reagent. Cyclopentenones are oxidized in decent to quantitative yields without showing any observable aldol products. α,β,γ,δ-Dienones are regioselectively oxidized at the α,β-position. Unlike aqueous alkaline H_2O_2, KF-Al_2O_3 is non-stereospecific and offers a mixture of *cis* and *trans* oxides from most acyclic enones. Except for the oxidation of α,β-unsaturated lactones and for the difference in reaction rates, the present reagent is, in general, similar to the t-BuOOH-DBU combination.

Genesis

Epoxidation of electron deficient alkenes is an often encountered chemical reaction. The resulting oxiranes are readily transformed into various useful materials, e.g., α- and β-hydroxy carbonyl compounds[1], α,β-epoxy alcohols[2], allylic alcohols[3], and 1,3-diols[4]; among others. Nucleophilic α- and β-openings of the oxirane ring enhance their utility further[5]. The α- and β-hydroxy carbonyl groupings are present in various natural products including mevinolins. In connection with a programme directed at the synthesis of mevinolin analogs for their pharmacological evaluations, we became interested in the oxidation of 6-substituted 3,4-dehydro-2-oxotetrahydropyran.

We first attempted the epoxidation of 3,4-dehydro-6-(2-phenylethyl)-2-oxotetrahydropyran (hereinafter refered to as either 'lactenone' or 'enelactone') with alkaline hydrogen peroxide under conditions of Trost[6] and Payne[7a]. The reaction was very slow[8]; lactone ring opening was prominent and methyl 2,3-epoxy-5-hydroxy-7-phenyl-2-heptanoate was the major product. The desired oxirane was formed in only small amounts. Substituting MeOH by other water-miscible and yet non-nucleophilic solvents such as THF and DME were completely ineffective; only the starting enelactone was isolated in each instance. The reaction using Triton-B as base and t-BuOOH as the oxidant in benzene[4] resulted in an intractable products mixture. The reaction, at reflux, with excess m-CPBA (6 equiv) in dichloroethane[9] for 6h furnished a mixture of the desired oxirane and the unreacted lactenone. Although the unreacted m-CPBA was still present, the conversion to oxirane was only 60%. Moreover, product separation from the unreacted lactenone by gravity column chromatography was tedious[10].

We did not use alkylzinc alkylperoxides[11] as they are very chemoselective and bring about the oxidation of enones only. Although no cyclic examples were studied by the original authors, the application of

[!] Dedicated to the sweet memory of Mr. Avaneesh Yadav on the sad occassion of his first death anniversary.

alkyllithiums-TBHP presented a distinct possibility[12]. The procedure, however, suffers from the followings:

(a) low yields; in the closest acyclic example of *cis* t-butyl 3-isopropylacrylate, the conversion was only 20%,
(b) transesterification and hydrolysis to carboxylic acids, and
(c) the requirement of expensive and hazardous alkyllithiums.

A method developed by Still[13] employs potassium hydride in combination with t-BuOOH. Potassium hydride requires careful handling for its inflamable nature and, moreover, it is an specialized chemical and, hence, not so readily available in all parts of the world. We, therefore, looked for alternative methods.

Introduction

Fluoride salts are useful bases that facilitate a variety of synthetic reactions such as alkylations and arylations, esterifications and transesterifications, intermolecular condensations including Michael, aldol, and Knoevenagel, intramolecular cyclizations including carbocycle-, lactone-, and other heterocycle-forming reactions, eliminations comprising dehydrohalogenations and dehydrations, and a host of other important transformations[14]. Clark, Miller, and coworkers[15-17] favored appreciably enhanced nucleophilicity of protic organic compounds, e.g. phenols and carboxylic acids, arising from strong hydrogen bond formation with the fluoride ion; the nucleophilic substitution proceeding with "*hydrogen bond assistance*". The poor solubility of alkali metal fluorides in common organic solvents, however, restricted their broad application in organic synthesis. In partial solution to this problem, the reactions were carried out at high temperatures with preformed hydrogen-bonded complexes or in high boiling solvents, DMF specifically.

Reagents supported on inorganic and organic solids are attractive as these offer potential advantages in:

(a) simple workup and product purification,
(b) enhanced or reduced reactivity of functional groups, and
(c) selectivity that may be different from that in solution.

To lay some emphasis on the last of these points, let us consider Ono's report[18] on the regiospecific N-methylation of 4(5)-methylimidazole with MeOH over zeolites. The Y-zeolites were found more active than others. A solution of the 4(5)-methylimidazole in MeOH (molar ratio = 1:3) was fed to a fixed bed reactor under atmospheric pressure at 230-320 °C to receive 1,5-dimethylimidazole almost exclusively (1,5- : 1,4- = 94 : 6) with 32% conversion. This must be compared with the results of 20% aqueous NaOH-promoted alkylation[19a] with Me_2SO_4 and also the results of the self-promoted alkylation[19b] with MeI; the ratio of 1,4- and 1,5-dimethylimidazoles was 2:1. Clearly, with the use of the zeolite, higher regioselectivity was in force. Further, Yadav and Kirthivasan[20] have recently studied the O-alkylation of alcohols and discovered the effective usage of dodecatungustophosphoric acid supported on K-10 clay as an efficient catalyst in the O-methylation of t-BuOH with MeOH. Finally, Reddy and Sayari[21] have found Ti-β zeolites as effective catalysts in the epoxidation of simple olefins such as 1-hexene and norbornylene by aqueous H_2O_2.

Ando and Yamawaki[22] found KF supported on celite more efficient than unsupported KF in alkylations of protic compounds. In another study[23], several alkali metal fluorides were adsorbed on alumina and their activities compared in promoting alkylation of phenols and alcohols. Acetonitrile was discovered the best

solvent for optimum reaction rates; the possible role of acetonitrile in these reactions was, however, not discussed. Though CsF was the most effective, the authors preferred KF for its nonhygroscopic nature and the relatively much lower cost. Optimization of reagent preparation and elucidation of the active species were investigated by Ando et al[24] subsequently. The understanding which emerged from all this resulted in enhanced research activity and KF-Al_2O_3 witnessed renewed interest; almost all the reactions that were performed earlier with unsupported fluoride salts[25] were reinvestigated with this supported material and improved results obtained.

We too became interested in the above Al_2O_3-supported KF and reasoned it, in combination with t-BuOOH, suitable for the epoxidation of electron-depleted alkenes. Though this reagent system was ineffective in the oxidation of the lactenone in question, various other substrates reacted very well. Since our communication[26] on t-BuOOH/KF-Al_2O_3 as an efficient oxidant, we have continued to explore other substrates to widen the scope and, in the event, discovered interesting results. In a parallel study, we have found t-BuOOH-DBU also promote epoxidations of electron-deficient olefins including the lactenone in question[27]. For the purposes of comparison and, thus, help us determine the preferred reagent from these two for a given olefin, we have chosen an almost identical set of olefins representing broad structural types. Herein, we present a detailed account of our work.

Results and Discussion

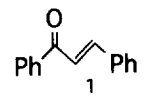
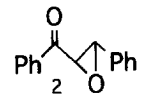
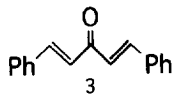
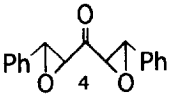
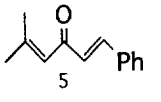
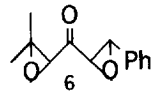
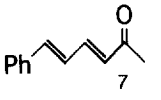
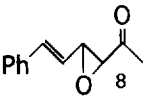
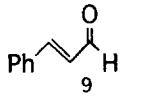
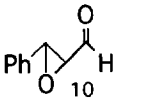
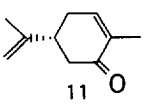
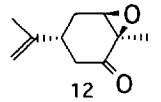
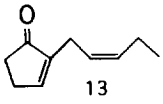
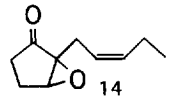
A wide range of olefins reacted smoothly. The examples are collected in the Table. The following points may be discerned:

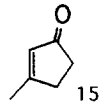
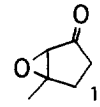
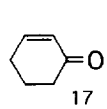
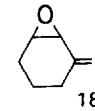
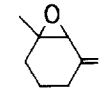
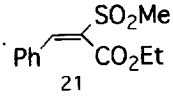
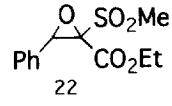
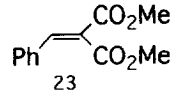
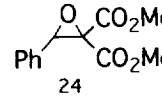
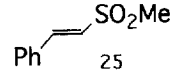
(a) chalcone and dibenzalacetone furnished the epoxy products in almost quantitative yields. The result with chalcone is to be contrasted with that of Julia et al[28] who noticed no reaction when chalcone was treated in toluene with a solution of NaOH in 30% H_2O_2 for 48h. We ourselves have confirmed this result. The same reactions with t-BuOOH-DBU take almost 10h for completion.

(b) β-unsubstituted cyclic enones such as cyclohexenone and R-(-)-carvone reacted at moderate rates to provide high yields of the products; carvone reacted relatively much slower, possibly owing to a combination of the steric interference imposed by the isopropenyl substituent and the reduced electrophilicity of the π-bond due the electron-releasing α-methyl substituent. The reaction with carvone was highly stereoselective; there was only one oxirane formed which was confirmed from ^1H nmr analysis. While carvone reacted at a rate comparable to that with t-BuOOH-DBU, the reaction with cyclohexenone was much faster.

(c) β-substituted cyclic enones are much less reactive, e.g. isophorone and testosterone (not shown in the Table) did not participate in the reaction and were recovered unchanged even after 20h; 3-methyl-2-cyclohexenone and 3-Methyl-2-cyclopentenone, however, reacted to the extents of 40 and 65% conversions, respectively, after 20h. These conversions were computed from ^1H nmr integrals. The results of epoxidation of 3-methyl-2-cyclohexenone with t-BuOOH-DBU are slightly superior; the conversion being 65% after 24h as against only 40% with t-BuOOH-KF in 20h.

TABLE

Entry	Substrate	Product	Time/h	Yield[a]
1.	 1	 2	$\frac{1}{6}$	100
2.	 3	 4	$\frac{1}{6}$	100[b]
3.	 5	 6	12	87[b]
4.	 7	 8	56	45[b]
5.	 9	 10	5	75[c]
6.	 11	 12	10	85
7.	 13	 14	30	100

Entry	Substrate	Product	Time/h	Yield[a]
8.	 15	 16	20	65[d]
9.	 17	 18	1	85
10.	 19	 20	20	40
11.	 21	 22	20	34
12.	 23	 24	20	35[e]
13.	 25	— — —	32	NR
14.	p-$MeC_6H_4SO_2N$=CHPh 26		DECOMPOSITION[f]	

NR = NO REACTION

[a] yields given are the isolated yields in percentage, unless indicated otherwise.

[b] mix of *cis* and *trans* epoxides.

[c] mix of *trans* and *cis* epoxides in the ratio 3:1 (^{1}H nmr).

[d] the conversion to the product after 20h was only 65% (*cf.* entry 7).

[e] represents the extent of conversion. It must be noted that this reaction with DBU as base (see ref. 27) is much faster, giving a complete reaction in only 2 hours. Also, the reaction with DBU as base is extremely clean as no other product could be detected from the ^{1}H nmr spectrum.

[f] only p-toluenesulphonamide and benzaldehyde were noticed from tlc; also the ^{1}H nmr of the crude did not show any of the desired epoxide.

(d) in contrast to 3-methyl-2-cyclopenten-1-one (above), the 2-substituted cyclopentenone derivative at entry 7 reacted rapidly and quantitatively, indicating the steric demand of the present reagent.

(e) the dienone at entry 4 reacted with remarkably very high regioselectivity and furnished only the α,β-epoxy material; a reaction with H_2O_2/$NaHCO_3$/MeOH (12h) under conditions of Danishefsky et al[7b] failed and the starting material was recovered intact. 1,6-Addition of the t-butylperoxy anion following double bond isomerization and subsequent colllapse of the resultant enolate on the peroxy oxygen may be expected to furnish furan products. Such a material was not detected in the present study. However, a reaction with cycloheptatrienone should be interesting; we did not attempt this reaction due to the unavailability of the ketone with us. It must be noted that a reaction with m-CPBA will be expected to furnish the γ,δ-epoxy isomer[29] in preference to the above α,β-epoxy species. The present reagent system, therefore, is complementary to the peracid method. Moreover, a comparison with the DBU-based reagent quickly establishes a faster reaction rate with the present KF-based oxidant.

(f) the tetrasubstituted acyclic enones such as 2-cyclopentylidene cyclopentanone (not shown) are completely inert. This result, when taken with the relatively sluggish reaction of 3-methyl cyclohex-2-en-1-one and also of 3-methylcyclopent-2-en-1-one, reflects on the reagent's high steric requirement. The testosterone example, although only trisubstituted, is further complicated by the nearby angular methyl group which is believed to prevent the approach of the reagent through its steric effects. Likewise, the accessibility of the enone function in isophorone, another trisubstituted variant, by the reagent is completely prevented by the *gem*-dimethyl substituent. In contrast to testosterone and isophorone, the reaction with 3-methyl-2-cyclohexenone offers a 40% conversion after 20h; the reaction is undoubtedly very slow.

(g) whereas acyclic and cyclic α,β-unsaturated esters and sulphones such as methyl cinnamate, 3,4-dehydro-6-(2-phenylethyl)-2-oxopyran, and *trans* methyl (2-phenylvinyl)sulphone **25** did not react, the doubly activated esters such as **21** and **23** reacted. The reactions were much slow in stark contrast to the reactions with the t-BuOOH-DBU system; with the latter oxidant the product oxiranes were obtained in quantitative yields after 30 min and 2h, respectively. The best yield of the product oxirane from the sulphone derivative **21** which we could achieve with t-BuOOH-KF was mere 34% with no unreacted starting sulphone left; the contributory factor to such a low yield was the decomposition of the epoxy product under the reaction conditions which we have established from a separate experiment. The product(s) of decomposition were, however, not investigated. The extent of conversion of the diester **23** after 20h was only 35%, the rest being the unreacted starting material. The reason(s) as to why there is such a large rate difference in reactions of **21** and **23** with KF- and DBU-based reagents is not clear to us. This, however, does not undermine the synthetic utility of the present oxidation system.

We have also reacted the acetate derived from testosterone with the present reagent system. Although there was no oxidation of the double bond, the acetate function remained intact. This result is noteworthy as an acetate function shall be expected to be labile to aqueous alkaline H_2O_2 under other known conditions. The DBU-based reagent behaves similarly. The failure of simple acyclic esters and sulfones, and the good to excellent reactivity

of the doubly activated analogs in the above reactions are clear indications as to the poor Michael acceptability of the former category of materials and, hence, their diminished reactivity.

Cyclopentanones are notorious for base-catalyzed self-condensation of aldol-type. It is remarkable that in the above KF-Al_2O_3 promoted oxidations of species **13** and **15**, there were no aldol products noticed. These results, including the reaction rate, with **13** are similar to those obtained from the use of t-BuOOH-DBU. Both the oxidation systems are, therefore, suitable to complex organic molecules consisting of functionalities that are otherwise labile to basic conditions.

Whereas the reaction with chalcone furnishes only the *trans* oxirane, other acyclic materials such as cinnamaldehyde, dibenzal acetone, and 5-methyl-1-phenyl-1,4-hexadien-3-one gave a mixture of *trans* and *cis* oxides. The reactions with KF-Al_2O_3 are, therefore, not stereospecific. These results are akin to those obtained from t-BuOOK-t-BuOOH (see below) and at variance from those achieved with alkaline H_2O_2[30].

The oxidation of α,β-unsaturated sulphones is an important reaction. A limited number of methods are available to achieve this transformation[31]. Zwanenburg-Weil conditions[31b] are stereospecific and transform both *trans* and *cis* alkenes into only the *trans* oxirane by alkaline aqueous H_2O_2. The combination of t-BuOOK and t-BuOOH is non-stereospecific and transforms alkenes of either configuration into a *cis/trans* mixture. The alkyllithiums/t-BuOOH method of O.M.-Cohn[12] is an excellent solution; the yields of the requisite oxiranes are very high and, moreover, the initial stereointegrity of the alkene is retained in the product. Unsubstituted vinyl sulphones may also be very conveniently oxidised by this method. We explored the possibility of preparing a,b-epoxy sulfone from the oxirane **22** by dealkyldecarboxylation. In the event, LiCl in DMF at 160±5 °C was very effective and the desired epoxide was received in >70% yield after rapid chromatographic purification. The dealkyldecarboxylation was very rapid and it was complete within 35 min. This, therefore, accomplishes a new indirect method for the preparation of α,β-epoxysulphones and may be useful in select cases.

We have also explored the oxidation of nitro-olefins with a view to making the corresponding nitro-susbtituted oxiranes for potential use in organic synthesis. In the event, nitrostyrene was reacted with the KF-Al_2O_3 reagent under standard conditions. The monitoring of the reaction by tlc indicated a fast disappearence (within 5 min) of the reactant olefin. However, the products distribution was complex. ^1H nmr analysis of the crude mixture indicated presence of some aldehydic material. Nitro group is reported to be labile to KF-Al_2O_3 reagent by earlier workers in the area[15-17]; this, therefore, may be contributing to the very complex nature of the products mixture in the present case.

Finally, we considered oxidation of the imine derived from the condensation of benzaldehyde and p-toluenesulfonamide. The expected oxirane, called Davis' reagent, is an useful entity in the one step introduction of a hydroxyl function α to a carbonyl group[32]. This oxirane has earlier been prepared by oxidation of the above imine with m-CPBA using lipophilic phase transfer catalysts such as benzyltriethylammonium chloride[33]. The requisite oxidation with the present reagent, however, failed and only the products of hydrolysis were received. This result is at variance with that reported from t-BuOOH-DBU where the first formed requisite oxirane undergoes, under the reaction condition, rapid rearrangement to provide N-benzoylsulfonamide[27].

All the reactions presented in the Table were carried out in dry acetonitrile. In order to ascertain the role of the solvent, we undertook to study various other common solvents and have discovered that acetonitrile as such does not play any role. We chose R-(-)-carvone as substrate for this study and used benzene, diglyme, dimethoxyethane (glyme), n-hexane and tetrahydrofuran as solvents. All the reactions were carried out for 10 h

to be compared with the reaction in acetonitrile at entry 6 in the Table. Whereas there was no reaction in diglyme, glyme is quite comparable to acetonitrile; both exhibiting almost the same extent of reaction (~ 85%) and hence similar reaction rates. Benzene, n-hexane and tetrahydrofuran appear better than both acetonitrile and glyme as they lead to faster reaction rates. With each of these latter solvents, complete conversion of carvone to the expected oxirane was noticed.

1,4-Addition of t-butylperoxy anion followed by attack of the resultant enolate on the *per* oxygen accounts for product formation. In an experiment with chalcone where t-BuOOH was replaced by MeI, chalcone was recovered unchanged. Absence of PhCH(F)CH(Me)COPh rules out the halohydrin pathway that one may envisage arising from conjugate addition of fluoride ion followed by capture of the resulting enolate with t-BuOOH. '*Hydrogen bond-assisted ring closure*' of the halohydrin would then furnish the observed epoxide.

Ando, Clark, and Miller and their coworkers[2-4] have reported that KF-Al_2O_3 owes its efficient and versatile reactivity as a heterogeneous base to at least three possible mechanisms:

(a) dispersion and increased surface area of KF giving coordinately unsaturated fluoride ions,

(b) liberation of strong base during preparation, and

(c) the cooperative action of fluoride ions and the hydrated alumina surface.

KF adsorbed on other solid surfaces is not so active. Possible strong bases believed to have generated during the preparation stage do not work alone so well either. These lend much credit to the cooperative action argument above and indicate an unique role of alumina. Relying upon this ideology, these authors[2-4] have suggested a mechanism for the alkylation of alcohols with alkyl halides. The fluoride ion is hydrogen bonded to the OH groups[3-4] on the surface of the alumina and is, thus, in close proximity to it. In the event of a reaction, this fluoride ion attacks the aluminum atom in the surface and releases HO^-; the latter brings about the necessary deprotonation of the alcohol to have the resultant alkoxide attack the alkyl halide to complete the reaction. The HO^- generated above should not leave the alumina surface for their strong mutual affinity and, thus, the subsequent reactions must also take place at the alumina surface only. Must the generated HO^- leave the alumina surface and diffuse into the solution, it shall be expected to transform an acetate function to an alcohol. This, however, does not happen in the reaction of testosterone acetate; testosterone was not detected by tlc. We, therefore, tend to favour a model analogous to that proposed earlier[2-4] for the present epoxidation process. This is only meant to provide for a working hypothesis and not to reflect on the reaction mechanism in absolute terms; the actual reaction pathway is likely to be more complicated for the heterogeneous nature of the mixture.

In summary, KF-Al_2O_3 in combination with t-BuOOH is an economical oxidising reagent, useful in the epoxidation of various structural types of electrophilic alkenes. The t-BuOOH-DBU method is complementary to the present t-BuOOH-KF-Al_2O_3 method in the oxidation of α,β-unsaturated lactones. Alongwith numerous similarities with the t-BuOOH-DBU reagent in reaction results, the reagent based on KF-Al_2O_3 possesses some very distinct characteristics; some of which we have highlighted above in the 'Results and Discussion' segment. This reagent's sensitiveness to steric effects makes regioselective oxidations possible. The reactions with 2,4-dienones are highly regioselective to furnish only the α,β-epoxy materials which could be envisioned to have good synthetic potentials. In this respect, the present oxidation reagent is complementary to peracids which shall provide the γ,δ-epoxy substrates and similar to the t-BuOOH-DBU reagent. Because the aqueous base sensitive functional groups including cyclopentanones survive the reagent well, the present reagent holds promise for more meaningful applications in complex situations.

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, refers to 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, e.g. aq for aqueous, rt for room temperature, mix for mixture, and min for minutes. 0 °C refers to ice-water slush temperature. Dry solvents used in this study were prepared from commercial samples as per established procedures. The anhydrous t-BuOOH in dichloroethane was prepared following the procedure of Sharpless and Verhoeven[35].

IR and mass spectra were recorded, respectively, on Perkin Elmer 1320 and Jeol D-300 series of instruments. ^1H 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. ^1H chemical shifts are reported in parts per million (ppm) from either $CHCl_3$ or tetramethylsilane.

Preparation of KF-Al_2O_3 reagent : Anhydrous potassium fluoride (58.0 g, 1.0 mol) was dissolved in distilled water (100 ml) and mixed with neutral alumina (100g, LR, "s.d. fine-chem ltd", Bombay; batch no. s/0193/892/301211). The water was removed at 45-50 °C on a rotovap under reduced pressure and dried further at 75 °C for 30h in a vacuum drying oven. The free-flowing material, thus obtained, was used throughout the present study.

General method for the oxidation with t-BuOOH and KF-Al_2O_3 : A reacting olefin (2.0 mmol) dissolved in dry acetonitrile (1.0 ml) was added to a stirred suspension of KF-Al_2O_3 (0.48g, 3.0 mmol of KF) in acetonitrile (6.0 ml) containing dichloroethane solution of t-BuOOH (1.7 ml, 4.0 mmol). The resultant mixture was stirred at rt and monitored by tlc for completion. Simple filtration and evaporation of the volatiles furnished the product(s) which, when necessary, was filtered through a short silica gel column. The reaction times for either full conversion or partial transformations are given in the Table.

For the preparation, full spectral (^1H NMR and IR) data, and elemental analyses on 5-methyl-1-phenyl-1,4-hexadien-3-one **5**, 6-phenyl-3,5-hexadien-2-one **7**, ethyl 2-methylsulphonyl-3-phenylacrylate **21**, benzylidene dimethylmalonate **23**, and methyl (2-phenylvinyl)sulphone **25**, please see ref 27.

For ^1H NMR, IR, high resolution mass, and elemental analysis data on chalcone-epoxide **2**, dibenzal acetone epoxide **4**, the bis epoxides from 5-methyl-1-phenyl-1,4-hexadien-3-one **6**, 3,4-epoxy-6-phenyl-3,5-hexadien-2-one **8**, *trans* 2,3-epoxy cinnamaldehyde **10**, *cis* 2,3-epoxy cinnamaldehyde **10**, 2,3-Epoxy-5-isopropenyl-2-methyl-2-cyclohexenone [R-(-)-carvone epoxide] **12**, 2,3-Epoxy-2-(*cis/trans* 2-pentenyl)-2-cyclopentenone **14**, 2,3-epoxy-2-cyclohexenone **18**, 2,3-epoxy-3-methyl-2-cyclohexenone **20**, ethyl 2,3-epoxy-2-methylsulphonyl-3-phenylacrylate **22**, the oxirane from benzylidene dimethylmalonate **24**, and methyl (1,2-epoxy-2-phenylvinyl) sulphone, please see ref 27.

2,3-Epoxy-3-methylcyclopentanone (**16**): ^{1}H NMR (60 MHz) ppm 3.1 (1H, s), 1.6 (3H, s); IR 1730 cm^{-1}. Calculated m/z for $C_6H_8O_2$ = 112.0524; observed m/z = 112. 0518.

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