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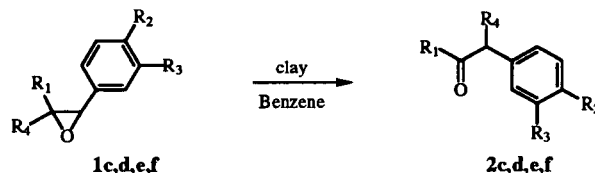
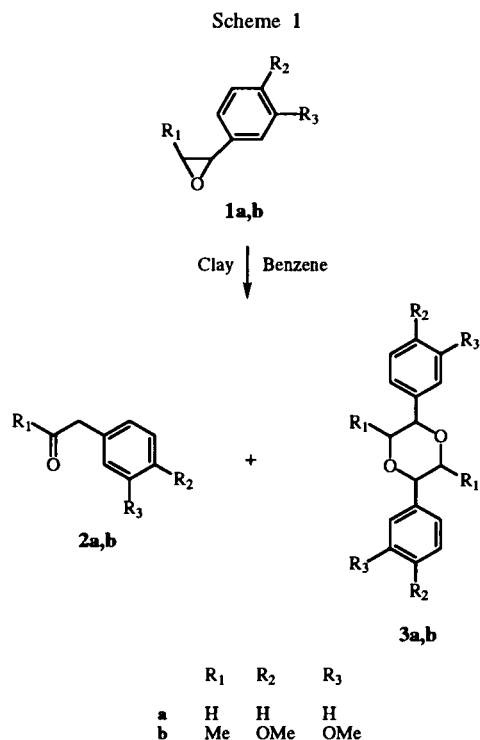
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The reaction of phenylloxiranes with a clay produces aldehydes, ketones and cyclic ethers. This method has the advantage that experimental conditions are simple and the reagents used are cheaper.

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The extensive use of oxiranes in organic synthesis as precursors for a variety of molecules has been described in the literature. Oxiranes ring has been opened by different reagents such as magnesium bromide [3], boron trifluoride [4], a group VI transition metal tetramethylazide [5], cobalt(0) octacarbonyl [6], sodium iodide/dimethyl sulfoxide [7], sodium borohydride [8], a nickel complex [9], a rhodium complex [10] and palladium(0) [11], affording aldehydes and ketones. In this regard it has been reported that solvolytic ring oxirane opening with a clay afforded only monomeric products [12]. As a part of a program directed toward the synthesis and reactivity of heterocyclic derivatives with possible pharmacological activity we report here the reaction of phenylloxiranes **1a-f** with a clay [13] in benzene. Our key intermediates **1a-f** were prepared similarly to literature methods [14]. The structure of compounds **1a,b,c,d,f** was supported by physical and spectral data and they agree with the literature data.



	R ₁	R ₂	R ₃	R ₄
c	Me	OMe	H	H
d	Ph	H	H	H
e	Me	OH	OMe	H
f	Me	H	H	NO ₂

In a typical procedure phenylloxirane **1a**, clay and potassium bromide were stirred in benzene at room temperature to give **2a** and **3a** (Scheme 1). Structural assignment of **2a** and **3a** was made on spectroscopic grounds and they agree with the literature data [15,16]. When the phenylloxirane **1b** was treated as was compound **1a** it also afforded the ketone **2b** and the 1,4-dioxane **3b**. The identity of **2b** was confirmed by ¹H-nmr, ir and mass spectra and it agree with the literature data [17]. The general run of this reaction was tested with the phenylloxiranes **1c,d,e,f** that were treated as was compound **1a** and they only afforded the ketones **2c,d,e,f** (Scheme 2). The identity of these compounds was also confirmed by ¹H-nmr, ir and mass spectra and comparison with the literature data [18,19,17,20]. In conclusion the isomerization of phenylloxiranes to carbonyl and ether compounds with this method has the advantage that experimental conditions are simple and the reagent used is inexpensive.

EXPERIMENTAL

All melting points are uncorrected. The ir spectra were recorded on a Nicolet FT-55X spectrophotometer. The ¹H-nmr spectra were determined in Varian Gemini 200 and Varian-VXR-300S spectrometers. All nmr spectra were obtained with the pulse sequence as part of the spectrometer's software and were determined in deuteriochloroform solution containing tetramethylsilane as the internal standard with chemical shifts (δ) expressed downfield from tetramethylsilane. Mass spectra were obtained with a Jeol SX-100 mass spectrometer.

Compounds **1a-f** have been prepared following a reported procedure. The structure of compounds **1a-f** was supported by ir, ¹H-nmr

and mass spectral data which are similar to those reported. Compound **1e** is new and its physical and spectroscopic data is below.

2-(4-Hydroxy-3-methoxy)phenyl-3-methyloxirane **1e**.

This compound was obtained as colorless oil (75%), 145-147°, 5 mm Hg; ir (neat): δ 3520 (OH) cm^{-1} ; ^1H nmr (deuteriochloroform): δ 7.41 (m, 3H, Ar-H), 6.92 (d, $J = 3.8$ Hz, 1H, H-2), 4.15 (m, 1H, H-3), 3.95 (s, 3H, OMe), 2.05 (bs, 1H, OH), 1.20 (bs, 3H, CH_3 -C3); ms: M^+ at m/z 180.

Anal. Calcd. for $\text{C}_{10}\text{H}_{12}\text{O}_3$: C, 66.65; H, 6.71; Found: C, 66.69; H, 6.70.

General Procedure for the Reaction of Phenylloxiranes **1a-f** with the Clay ($\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{H}$).

To a suspension of the clay (0.5 g) and potassium bromide (0.5 g) in dry benzene (25 ml) was added 1.2 g (10 mmoles) of **1a** and the mixture was stirred at room temperature for 15 minutes. After the reaction mixture was filtered on celite and washed with benzene, the filtrate was evaporated to dryness. The oil obtained was then separated by column chromatography (silica gel, hexane/ethyl acetate, 90/10) into **2a** (0.6 g, 50%) and **3a** (0.96 g, 40%).

2-Phenylethanaldehyde **2a**.

This compound was obtained as colorless oil, bp 86-88°, 10 mm Hg (lit [15] 85-86°, 10 mm Hg); ms: m/z 120 (M^{++})

2,5-Diphenyl-1,4-dioxane **3a**.

This compound was obtained as colourless needlesh, mp 179-181°, (lit [16] 177-178°); ms: m/z 240 (M^{++})

Compound **1b** (1.94 g, 10 mmoles) was allowed to react with the clay (0.5 g) and potassium bromide (0.5 g) according to the procedure described above. It gave **2b** in 40% (0.78 g) and **3b** in 50% (1.94 g) yields, respectively.

1-(3,4-Dimethoxyphenyl)-2-propanone **2b**.

This compound was obtained as colorless needles(hexane), mp 72-73° (lit. [17] 71-72°); ms: m/z 194 (M^{++})

2, 5-Dimethyl-3,6-bis(3, 4-dimethoxyphenyl)-1, 4-dioxane **3b**.

This compound was obtained as colourless needlesh, mp 189-191°; ^1H nmr (deuteriochloroform): δ 7.5 (m, 6H, Ar-H), 5.72 (d, $J = 10.4$ Hz, 2H, H-2), 4.2 (m, 2H, H-3), 3.9 (s, 6H, OCH_3), 3.8 (s, 6H, OCH_3) 1.25 (d, $J = 11.2$ Hz, 6H, CH_3 -C3, CH_3 -C6); ms: M^+ at m/z 388 (M^{++})

Anal. Calcd. for $\text{C}_{22}\text{H}_{28}\text{O}_6$: C, 68.02; H, 7.26. Found: C, 68.08; H, 7.23.

Compound **1c** (1.64 g, 10 mmoles) was allowed to react with the clay (0.5 g) and potassium bromide (0.5 g) according to the procedure described above. It gave **2c** in 61% (1 g) yield.

1-(4-Methoxyphenyl)-2-propanone **2c**.

This compound was obtained as colorless oil, bp 118-120°, 5 mm Hg (lit [18] 117-119°, 5 mm Hg); ms: m/z 164 (M^{++})

Compound **1d** (1.96 g, 10 mmoles) was allowed to react with the clay (0.5 g) and potassium bromide (0.5 g) according to the procedure described above. It gave **2d** in 70% (1.37 g) yield.

1,2-Diphenylethanone **2d**.

This compound was obtained as colorless needles, mp 61-63° (lit [19] 60-62°); ms: m/z 196(M^{++})

Compound **1e** (1.8 g, 10 mmoles) was allowed to react with the clay (0.5 g) and potassium bromide (0.5 g) according to the procedure described above. It gave **2e** in 80% (1.44 g) yield.

1-(4-Hydroxy-3-methoxyphenyl)-2-propanone **2e**.

This compound was obtained as colorless needles, mp 102-104° (lit [17] 101-102); ms: m/z 180 (M^{++})

Compound **1f** (1.8 g, 10 mmoles) was allowed to react with the clay (0.5 g) and potassium bromide (0.5 g) according to the procedure described above. It gave **2f** in 60% (1.07 g) yield.

1-Nitro-1-phenyl-2-propanone **2f**.

This compound was obtained as colorless oil, bp 104-105° (lit. [20] 104-107°); ms: m/z 179(M^{++})

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