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SYNTHESIS OF ALDEHYDES FROM OXIRANES USING SILICA GEL AS REAGENT

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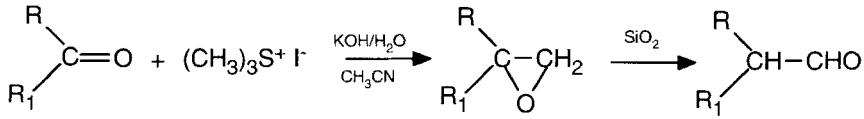
ABSTRACT.- The rearrangement of some 2-aryl monosubstituted and 2-aryl, 2-methyl disubstituted oxiranes to aldehydes using silica gel in very mild conditions is reported.

The transformation of oxiranes into carbonylic compounds like aldehydes and ketones is a useful reaction in the synthesis of numerous compounds.[1] This reactions has been carried out in several ways and by different reagents. The use of Lewis acids as zinc, stannous[2] and magnesium bromides[3] along with BF_3 may be the most common methods for this purposes. Other methods include the use of coordination compounds[4] for the preparation of α,β-unsaturated aldehydes from vinyl oxiranes, and also aluminum oxide has been used to carry out rearrangements in sesquiterpenes containing the oxirane moiety.[1] The aim of the present work is to report the transformation of arylmonosustituted and 2-aryl, 2-methyl disubstituted oxiranes to aldehydes using silica gel as reagent in very mild conditions.

During the course of our investigation on the synthesis of γ-hydroxyamides, compounds with anticonvulsive properties,[5] we required the

oxirane **7** as intermediate. The oxirane was prepared by the reaction of an aromatic aldehyde with trimethylsulfonium or sulfoxonium iodide in basic medium.[6] Usually this reaction proceeds in anhydrous conditions under inert atmosphere, but it can be simplified using acetronitrile as solvent and solid potassium hydroxide as base.[7] When the product was purified by column chromatography using silica gel 60 (70-230 mesh, Merck) as solid support, a rearrangement took place affording the corresponding aldehyde **15**. In order to investigate the scope of this rearrangement, we prepared the oxiranes **1-8**, (Table) by the method described above. The oxiranes were purified by distillation under reduced pressure, some of them with appreciable amount of decomposition during the procedure.



TABLE

OXIRANES			**ALDEHYDES**
Entry	R	R_1	Entry
1	H	Ph	**9**
2	H	p-MeOPh	**10**
3	H	2-Furyl	**11**
4	H	2-Thienyl	**12**
5	CH_3	Ph	**13**
6	CH_3	p-MeOPh	**14**
7	CH_3	2-Thienyl	**15**
8	CH_3	2-Pyridyl	-

The pure oxiranes were allowed to react with silica gel in 1:1 w/w ratio, using ethylacetate or acetone as solvent. The reaction was followed by TLC (the reaction was almost completed in few minutes), and in all cases the only products were the aldehydes, except for oxirane **8**, which was unstable and the transposition did not take place. The aldehydes obtained by this method are shown in the table. The good yields of the rearrangement, the mild conditions and the simple experimental procedure converts this method in a good option for the transformation of 2-monoaryl and 2-aryl, 2-methyl disustituted oxiranes into aldehydes.

EXPERIMENTAL

The IR spectra were recorded on a Nicolet FT-5SX spectrophotometer, the ^{1}H-NMR spectra were obtained on a Varian-Gemini 200 and Varian VXR 300S instruments with TMS as internal standard. Mass spectra were recorded with a Hewlett-Packard 5985-B spectrometer with gc/ms system, compounds were introduced through the direct insertion probe.

General procedure for the preparation of the oxiranes. A slight modification of the original method[7] was used. In a three-necked round bottom flask equipped with magnetic stirrer and nitrogen atmosphere a mixture of 10 mmol of aldehyde or ketone, 10 mmol of trimethylsufonium iodide, 20 mmol of potassium hydroxide, 2.5 mmol of distillate water and acetonitrile was stirred vigorously and heated at 60° for 3 h. After this time the reaction mixture was allowed to cool at room temperature. The solid formed was filtered and the solution was concentrated under reduced pressure. The residue was diluted with anhydrous

ether and more KI precipitated. This action was repeated until no more KI was collected. The filtrate was dried on anhydrous Na_2SO_4 and the solvent evaporated.

Phenyloxirane. (**1**). Prepared in 87% yield (Lit.[7] 96%); this compound decompose and was used without purification for the next reaction. In order to characterize product **1**, its purification was carried out by rapid thin layer chromatography on silica gel protecting the compound from light. The spectroscopic data were compared with those previously reported.[8]

p-Methoxyphenyloxirane. (**2**). Reaction time, 3h; prepared in 85% yield; bp 90°/1 mm Hg (Lit.[9] bp 51°/0.001 mm Hg, mp 20°). IR ($CHCl_3$): 3030, 2820, 1600, 1500, 1240, 823 cm^{-1}, ^{1}H-NMR ($CDCl_3$): δ 2.68 (m, 1H), 3.01 (m, 1H), 3.71 (m, 1H), 3.85 (s, 3H), 6.81 (d, 2H, J=8Hz), 7.11 (d, 2H, J=8Hz); MS: m/z 150 (M^+, 7).

2-Furyloxirane. (**3**). Reaction time, 3h; prepared in 84% yield; bp 65°/1 mm Hg (Lit.[10] bp 56°/14 mm Hg). IR ($CHCl_3$): 3007, 1629, 1366, 1268, 1154, 1015, 980 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.85 (m, 1H), 2.95 (m, 1H), 4.25 (m, 1H), 6.15 (m, 1H), 6.25 (m, 1H), 7.30 (m, 1H); MS: m/z 110 (M^+, 2).

2-Thienyloxirane. (**4**). Reaction time 3h; prepared in 86% yield[7]; bp 63°/1mm Hg. IR (film): 3113, 2915, 1597, 1542, 1475, 1387, 1257, 1139, 962 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 2.97 (dd, 1H, J=6Hz, J=3Hz), 3.15 (dd, 1H, J=6Hz, J=4Hz), 4.08 (dd, 1H, J=4Hz, J=3Hz), 6.90 (m, 1H), 7.15 (m, 2H); MS: m/z 126 (M^+, 10).

2-Methyl, 2-phenyloxirane. (**5**). Reaction time, 24 h; prepared in 54% yield (Lit.[7] 38%); bp 45-47°/1 mm Hg. IR (film): 3075, 2950, 2930, 1610, 1520, 1475, 1257, 1140, 1120, 870 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.55 (s, 3H), 2.70 (b, 2H), 7.31 (m, 5H); MS: m/z 134 (M^+, 13).

2-Methyl, 2(p-methoxyphenyl)oxirane. (**6**). Reaction time, 20 h; prepared in 62% yield; bp 105-109°/1 mm Hg. IR (film): 3040, 2960, 2930, 2840, 1600, 1520,

1460, 1350, 1240, 1170, 1140, 860 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.70 (s, 3H), 2.78 (dd, 2H, J=8Hz), 3.83 (s, 3H), 6.93 (d, 2H, J=7Hz), 7.30 (d, 2H, J=7Hz); MS: m/z 164 (M^+, 11). Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 73.36; H, 7.48.

2-Methyl,2(2-thienyl)oxirane. (**7**). Reaction time, 15 h; prepared in 60% yield; bp 68°/1 mm Hg. IR (film): 3050, 2981, 1550, 1440, 1380, 1360, 1320, 1280, 1230, 1070, 825 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.73 (s, 3H), 2.98 (s, 2H), 6.95 (m, 2H), 7.13 (m, 1H); MS: m/z 140 (M^+, 3). Anal. Calcd for C_7H_8SO: C, 59.97; H, 5.75. Found: C, 59.71; H, 5.54.

2-Methyl,2(2-pyridyl)oxirane. (**8**). Reaction time, 20 h; prepared in 37% yield; bp 69-75°/1 mm Hg. IR ($CHCl_3$): 3030, 2990, 1590, 1570, 1460, 1440, 1380, 1350, 1080, 1000, 860 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.80 (s, 3H), 2.85 (d, 1H, J=4Hz), 3.0 (d, 1H, J=4Hz), 7.18 (m, 2H), 7.60 (m, 1H), 8.50 (m, 1H); MS: m/z 135 (M^+, 7). Anal. Calcd for C_8H_9NO: C, 71.09; H, 6.71. Found: C, 70.87; H, 6.58.

General Procedure for the conversion of oxiranes into aldehydes. In a three-necked round bottom flask equipped with a magnetic stirrer a solution of 1 g of oxirane in 20 ml of ethylacetate or acetone was placed and, 1 g of silica gel was added. The reaction mixture was stirred vigorously at room temperature until the oxirane disappeared (monitoring by TLC). Most of the reactions were finished within 30 min. When the reaction was completed the silica gel was removed by filtration, the filtrate dried on Na_2SO_4 and the solvent evaporated under reduced pressure.

2(2-Thienyl)propanal. (**15**). Prepared in 78% yield; bp 73°/1 mm Hg. (Lit.[11], 140/6 mm Hg). This compound was identified by comparison of its IR, ^{1}H-NMR and MS data.[11]

Phenylacetaldehyde (**9**). Prepared in 92% yield; bp 80°/15 mm Hg (Lit.[12], 78°/10 mm Hg). IR (film): 3057, 1701, 1598, 1453, 1388, 1310, 984, 876 cm^{-1}. Compared with its reported spectrum.[13]

p-Methoxyphenylacetaldehyde. (**10**). Prepared in 80% yield; bp 87°/1 mm Hg (Lit.[14], 76°/2 mm Hg). IR (film): 3063, 2835, 2730, 1725, 1623, 1583, 1467, 1378, 1280, 937 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 3.21 (d, 2H, J=2Hz), 3.40 (s, 3H), 6.72 (d, 2H, J=7Hz), 6.98 (d, 2H, J=7Hz), 9.40 (t, 1H, J=2Hz); MS: m/z 150 (M^+, 22).

2-Furylacetaldehyde. (**11**). Prepared in 62% yield; bp 63°/1 mm Hg. (Lit.[15], 58°/10 mm Hg). IR ($CHCl_3$): 3007, 2934, 1731, 1629, 1504, 1476, 1380, 1149, 1017, 927 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 3.70 (d, 2H, J=2Hz), 6.25 (m, 1H), 6.45 (m, 1H), 7.30 (m, 1H), 9.65 (t, 1H, J=2Hz); MS: m/z 110 (M^+, 6).

2-Thienylacetaldehyde. (**12**). Prepared in 73% yield; bp 123-125°/1 mm Hg. (Lit.[16], 83-85°/0.01 mm Hg). This compound was identified by comparison with its IR spectrum.[16-18]

2-Phenylpropanal. (**13**). Prepared in 68% yield; bp 72-75°/2 mm Hg. (Lit.[19], 92-92.5°/12 mm Hg). This compound was identified comparing its IR spectrum.[20]

2-(p-Methoxyphenyl)propanal. (**14**). Prepared in 87% yield; bp 77°/1 mm Hg. (Lit.[21], 108-110/5 mm Hg). IR (film): 3028, 2810, 1720, 1610, 1570, 1460, 1320, 1270, 1150, 890 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.38 (d, 3H, J=6Hz), 3.60 (s, 3H), 3.80 (m, 1H), 6.63 (d, 2H, J=7Hz), 7.08 (d, 2H, J=7Hz), 9.55 (d, 1H, J=2Hz); MS: m/z 164 (M^+, 5).

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