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SILICA GEL CATALYSED REARRANGEMENT OF α-EPOXYKETONES TO 1,2-DIKETONES

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ABSTRACT

A convenient and simple method for the preparation of diphenylpropane-1,2-diones is described. The process involves rearrangement of α-epoxyketones on silica gel; an unusual migration of a proton instead of the more common benzoyl migration.

Both silica and alumina are widely employed as catalysts especially in the petrochemical industry.In the laboratory, these adsorbents find use in the chromatographic separation of organic compounds. It is during such an application that an interesting transformation was observed. During the separation and purification of chalcone epoxide on silica gel column, it was noticed that the epoxide rearranged completely to 1,3-diphenylpropane-1,2-dione. Propane-1,2-diones are intermediates in the preparation of furanones

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which are used as flourescent markers of biological materials[1]. These compounds were hitherto prepared by the rearrangement of chalcone epoxides using bases such as potassium t-butoxide[1] or sodium hydroxide[2]. Since silica gel appears to rearrange the epoxides efficiently and completely to the corresponding 1,2-diones with no side products, it is an easy and inexpensive alternative to the present method and as such is of considerable synthetic value.

Epoxides are known to be extremely labile and subject to rearrangements in the presence of heat, light, acids and bases. The subject of rearrangements of both simple epoxides as well as α-epoxyketones has been extensively reviewed[3,4,5]. A survey of literature shows that usually in the presence of heat, light or acids, the epoxides rearrange to give 1,3-diketones or aldehydes[6,7], whereas base catalysed rearrangements lead to 1,2-diketones[8].

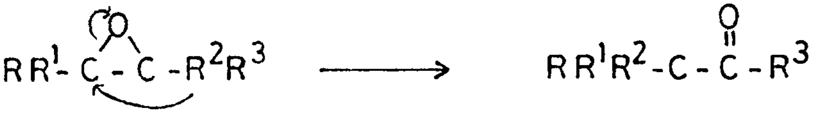
Acid catalysed rearrangements are brought about by the action of Lewis acids e.g. magnesium bromide/ether, boron trifluoride/ether etc. The course of the rearrangement is governed by two main factors viz. the direction of ring opening and the relative migratory aptitudes of the different substituent groups. House and Reif[9] showed that the epoxide opens towards the side with substituents which are together

Table 1. Compounds 2a–e prepared

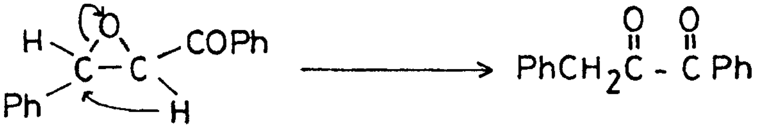
Product 2	Mol. formula[a]	Yield (%)	m.p.(°C)[b]
a	$C_{15}H_{12}O_2$	98	84 (lit.89 ° ref.11)
b	$C_{16}H_{14}O_3$	96	64
c	$C_{17}H_{16}O_4$	98	112
d	$C_{16}H_{14}O_3$	98	62
e	$C_{17}H_{16}O_4$	95	168-170

a - Satisfactory microanalyses obtained: C±0.35 H±0.20
b - uncorrected

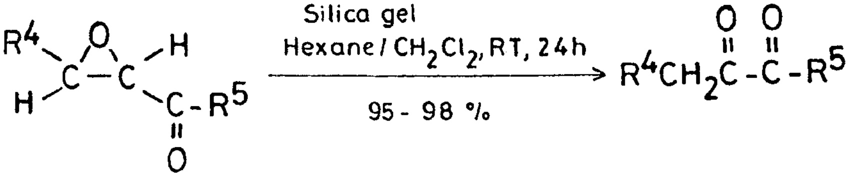
less electron releasing. That is to say, if R and R^1 are together more electron releasing than R^2 and R^3, the epoxide ring opens in the direction shown in Scheme 1. Whether R^2 or R^3 migrates then depends upon their relative migratory aptitudes and it appears that in general that order is aryl > acyl > H > ethyl > methyl[3]. In the present case of chalcone epoxide the ring opens in the direction shown in Scheme 2 followed by a proton migration which results in the 1,2-diketone. This migration of the proton rather than the benzoyl group has not been reported till recently by Bubel et al[10], who achieved this in the presence of a strong lewis acid like $AlCl_3$/RSCN. That



Scheme 1



Scheme 2



1a - e

2a - e

	R^4	R^5
a	Ph	Ph
b	Ph	4-OMe C_6H_4
c	4-OMeC_6H_4	4-OMe C_6H_4
d	4-OMeC_6H_4	Ph
e	4- OMeC_6H_4	3- OMe C_6H_4

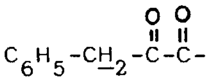
Scheme 3

Table 2. Spectroscopic data of 1,3-diphenylpropane-1,2-diones

Product 2	IR(KBr)[a] ν(cm^{-1})	^{1}HNMR(CDCl$_3$/TMS)[b] δ,J(Hz)	MS(70 ev) m/z (%)
a	3062,1692,1601,1587,1551, 1500,1457,1414,1356,1324, 1298, 1241	7.9(dd,2H),7.5-7.0(m,8H), 3.9(s,2H)	-
b	3035,2952,2854,1666,1605, 1575,1515,1462,1424,1308, 1255,1183,1104,1063	7.8(d,2H,J=9),7.65(s, 5H),6.75(d,2H,J=9), 3.9(s,2H),3.75(s,3H)	254(M$^+$ 98.8), 197(17.2),135(100), 136(25),120(8.8), 97(11),91(12.2), 92(14.4),77(16)
c	2952,2854,1666,1609,1583, 1522,1458,1424,1315,1293, 1255,1180,1111,1063	7.8(dd,2H),6.1-7.1(m, 6H),3.7(s,3H), 3.8(s, 3H),3.85(s,2H)	284(M$^+$ 30),228(9.6), 135(100),121(64.67), 120(20),107(15), 105(16),92(60),91(44), 78(42),77(53)
d	3450,2952,2854,1696,1672, 1609,1582,1515,1478,1466, 1402,1310,1264,1180,1111	7.8(dd,2H),7.0-6.6(m, 7H),3.85(s,3H), 3.8(s,2H)	254(M$^+$ 1.8),165(8), 152(13.3),135(100), 121(13.3),105(50), 107(9),92(18),77(56),
e	2952,2854,1666,1602,1583, 1515,1492,1466,1432,1293, 1262,1173	6.7-7.8(m,8H), 3.85(s,6H),3.8(s,2H)	-

a - Recorded on Perkin Elmer 882 Infrared Spectrophotometer

b - Recorded on R24B 60 MHz Hitachi High Resolution NMR Spectrometer a mild acid like silica gel could bring about this migration is therefore interesting.

The rearrangement was carried out with five substituted chalcones to confirm the general applicability of the reaction (**Scheme 3**). The chalcone epoxides were left over silica gel in hexane/methylene chloride solution overnight. On work up NMR showed that the epoxides rearranged to the corresponding 1,2-diones. The doublet of doublet at δ4.1 disappeared and instead a singlet corresponding to  $C_6H_5\text{-}\underline{CH_2}\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}$ appeared at $\simeq$δ3.8 (Table 2).

EXPERIMENTAL

General Procedure

4'-Methoxy chalcone epoxide (**1b**, 50mg, 0.21 mmol) was left over silica gel (60-120 mesh, 1g) in 4:1 hexane: CH_2Cl_2 (10 ml) for 24 h. The solution was then filtered off and the silica gel washed several times with CH_2Cl_2. The solvent was removed to give 48 mg (96%) of 1-(4'-methoxyphenyl)-3-phenylpropane-1,2-dione (<u>**2b**</u>, Tables 1&2). The diketones were further purified by recrystallisation from hexane: CH_2Cl_2 solution.

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