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PREPARATION OF CERTAIN ARYL ALKYL KETONES

DOCTORAL DISSERTATION

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/PDR of Yemen/

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I. INTRODUCTION

The simplest aryl alkyl ketones, acetophenone, benzyl methyl ketone and propiophenone, are important industrial intermediates. The study of their preparations or of methods suitable for their preparations is therefore of importance from an industrial aspect too. This is the fundamental reason why the present theme was chosen.

The aim was to investigate some vapour-phase, heterogeneous catalytic procedures with regard to the preparation of the two isomeric compounds, benzyl methyl ketone and propiophenone. For purposes of comparison, the work connected with the synthesis of benzyl methyl ketone included the study of certain catalysts employed earlier for similar purposes, but now under the continuous flow conditions used in the present investigation. In addition to these, primarily oxide catalysts were examined which have not yet been used in this reaction, i.e. for the preparation of compounds by ketonization.

A second aim was to study the isomerization of 2-methyl-3-phenyloxirane, with the accompanying formation of ketones. This transformation was examined on metal catalysts, with an impulse-microreactor technique.

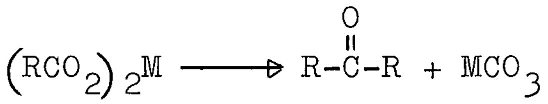
In contrast with the original aims, this dissertation contains only results relating to the preparation of benzyl methyl ketone. The reason for this is that, in the isomerization of the oxirane, it did not prove possible to create reaction conditions that favoured the process leading to propiophenone.

II. REVIEW OF LITERATURE

II.1. Formation of symmetrical and unsymmetrical ketones by thermal decarboxylation over metallic oxide catalysts

II.1.1. Decomposition of monocarboxylic acid salts

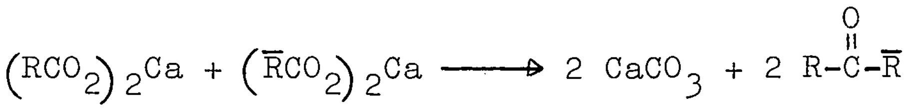
One of the oldest and most often cited methods for the preparation of symmetrical ketones is the pyrolytic decomposition of calcium, magnesium, barium, lead/II/ or other salts of monobasic carboxylic acids /1-3/. Lead salts have been reported to give good results /3/:



$$(RCO_2)_2M \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-R + MCO_3$$

The thermal decarboxylation of iron carboxylates has also been shown to be an excellent method for the preparation of symmetrical straight-chain aliphatic ketones /4/.

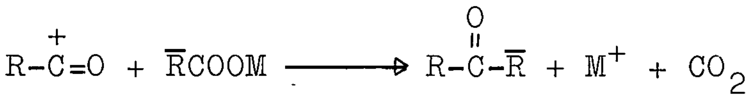
Williamson /5/ long ago showed that the calcination of a mixture of the calcium salts of two fatty acids gave the mixed ketone:



$$(RCO_2)_2Ca + (\bar{R}CO_2)_2Ca \longrightarrow 2\ CaCO_3 + 2\ R-\overset{\overset{\displaystyle O}{\|}}{C}-\bar{R}$$

The mechanism of pyrolysis of calcium salts of carboxylic acids is as follows /6,7/:

$$RCOOM \longrightarrow R-\overset{+}{C}=O + MO^{-} \qquad /M = \tfrac{1}{2}\ Ca/$$

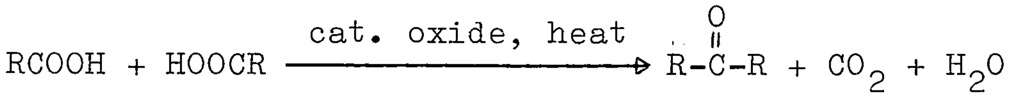


$$R-\overset{+}{C}=O + \bar{R}COOM \longrightarrow R-\overset{\overset{O}{\|}}{C}-\bar{R} + M^{+} + CO_2$$

Alkyl phenyl ketones are generally formed in satisfactory yields when this method is applied to mixtures of the iron salts of benzoic acid and an aliphatic acid /8/. Morgan and Holmes /9/ prepared unsymmetrical ketones by using barium salts. This procedure has been modified by carrying out the reaction in vacuo. Miller et al. /10/ reported that, on decarboxylation, acids which have no α-hydrogen atom may yield unsymmetrical ketones instead of the symmetrical compound.

II.1.2. Catalytic decarboxylation of carboxylic acids

Symmetrical ketones are formed by passing vaporized aliphatic or aromatic carboxylic acids over different types of oxide catalysts at high temperatures:

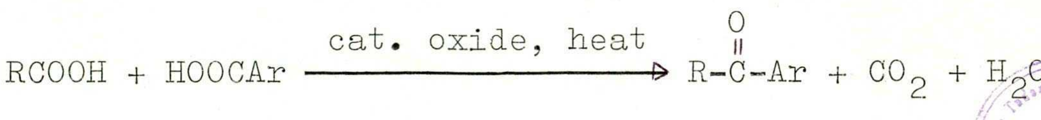


$$RCOOH + HOOCR \xrightarrow{\text{cat. oxide, heat}} R-\overset{\overset{O}{\|}}{C}-R + CO_2 + H_2O$$

This procedure is derived in fact from the old method of preparing symmetrical ketones by calcining the calcium or barium salts of monobasic organic acids at red heat /1,2/. Squibb /2/ conceived the idea of transforming this reaction into a catalytic one, by passing the vapour of acetic acid over barium carbonate heated to about 500°C. Acetone, water and CO_2 were obtained.

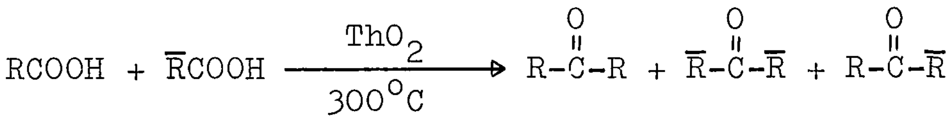
In general, ThO_2, MnO, MnO_2 and ZrO_2 have proved to be the best catalysts for the formation of acetone and diethyl ketone from acetic and propionic acids at 400-450°C, as well as diphenylacetone and benzophenone from phenylacetic and benzoic acids /11,12/. As a better catalyst for this reaction, Swann et al. /13/ used aerogel thoria, which gave a good yield of ketone at temperatures as low as 310°C. Calcium carbonate, zinc oxide, cadmium oxide, alumina and chromic oxide give good results only with acetic acid and lower aliphatic acids /14/.

Studies have been made of the preparation of alkyl phenyl ketones by the thermal decarboxylation of a mixture of two acids /aliphatic and aromatic/ over a metal oxide catalyst. It was found that the catalytic decomposition of a mixture of the two acids by means of oxides, such as CaO, ZnO, Al_2O_3, Cr_2O_3 /14/, MnO, ThO_2 /11/, MgO /15/, CdO, FeO and Fe_2O_3 /16/, gave the unsymmetrical ketone derived from the two acids, rather than the symmetrical ketones:



$$RCOOH + HOOCAr \xrightarrow{\text{cat. oxide, heat}} R\text{-}\overset{\overset{O}{\|}}{C}\text{-}Ar + CO_2 + H_2O$$

Sabatier /17/ states that three ketones are obtained if we start with two aliphatic acids, or with one aliphatic acid and phenylacetic acid, but only two when an aliphatic acid is used with benzoic acid. Bouchoule et al. /18/ reported the kinetic decomposition of mixtures of aliphatic carboxylic acids leading to ketones on ThO_2:



$$RCOOH + \overline{R}COOH \xrightarrow[300^{\circ}C]{ThO_2} R-\overset{O}{\overset{\|}{C}}-R + \overline{R}-\overset{O}{\overset{\|}{C}}-\overline{R} + R-\overset{O}{\overset{\|}{C}}-\overline{R}$$

A simple method for the preparation of unsymmetrical ketones is to pass a mixture of the vapours of the two acids over ThO_2 at about $400^{\circ}C$. For example, this is the best method for the preparation of benzyl methyl ketone, and was used first by Pickard and Kenyon /19/, who obtained the ketone in good yield. Herbst and Manske /20/ employed ThO_2 in pumice at higher temperatures /$420-450^{\circ}C$/, the yield then being around 65%. Martello and Ceccotti /21/ examined the formation of three types of mixed ketones over $ThO_2-Al_2O_3$. The best yields in these reactions are shown in Table 1.

The aromatic acids in which the carboxyl group is in a side-chain, such as phenylacetic and phenylpropionic acids, can be advantageously transformed into the corresponding symmetrical ketones at $430-470^{\circ}C$ /22,23/.

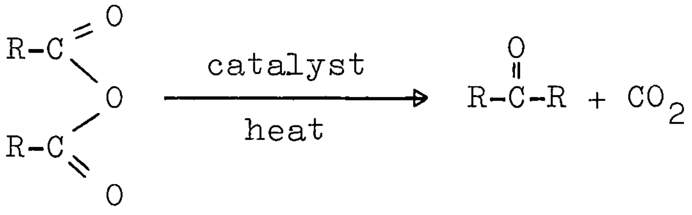
Table 1. Yields of mixed ketones under various reaction conditions

Molar ratio MeCOOH/RCOOH	Yields %		
	Benzyl methyl ketone	Methyl propyl ketone	Acetophenone
1:1	-	44 /460°C/	-
2:1	44 /460°C/	55 /420°C/	-
3:1	68 /420°C/	64 /420°C/	85 /420°C/
4:1	74 /420°C/	70 /420°C/	75-80 /420°C/
5:1	72 /420°C/	-	88 /420°C/

More recently, Thigpen and Trebeilas /24/ pointed out that a mixture of an aliphatic and an aromatic carboxylic acid can be converted into an unsymmetrical ketone with the use of a cobalt compound as catalyst.

II.1.3. Catalytic decomposition of acid anhydrides

Similarly to the carboxylic acids, the acid anhydrides can be decomposed catalytically to form the corresponding symmetrical ketones:



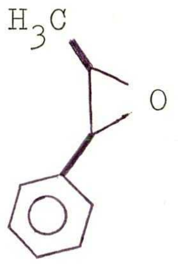
When an acid and the anhydride of another acid are used together, catalytic decomposition gives an unsymmetrical ketone with the two symmetrical ketones /25/. Acylation by means of the decarboxylation of arylacetic acids was described earlier /26,27/.

II.2. Isomerization of 2-methyl-3-phenyloxirane on heterogeneous catalysts

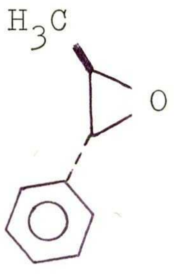
II.2.1. Synthesis of 2-methyl-3-phenyloxirane

The work relating to the synthesis and chemical transformations of the oxiranes has been surveyed by numerous authors /28-40/.

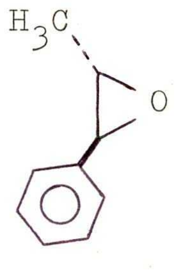
2-Methyl-3-phenyloxirane exists in various stereoisomeric forms, as the *cis* and *trans* isomers and the optical isomers of these:



I



II



III

I: /2R/-*cis*-2-methyl-3-phenyloxirane;

/1S,2R/-1,2-epoxy-1-phenylpropane.

I+mirror image: /±/-*cis*-2-methyl-3-phenyloxirane.

II: /2R/-*trans*-2-methyl-3-phenyloxirane;

/1R,2R/-1,2-epoxy-1-phenylpropane.

III: /2S/-trans-2-methyl-3-phenyloxirane;
/1S,2S/-1,2-epoxy-1-phenylpropane.
II+III: /±/-trans-2-methyl-3-phenyloxirane;
/1RS, 2RS/-1,2-epoxy-1-phenylpropane.

Cis and trans-2-methyl-3-phenyloxiranes have been prepared by various methods /41-52/.

The percentage yields in the formation of 2-methyl-3-phenyloxirane and phenylethylene oxide by the conversions of olefinic compounds via the perbenzoic acid and the bromohydrin /NBS/H_2O/ methods are listed in Table 2.

Table 2. Conversion of olefinic compounds to oxirane via various epoxidation methods

Perbenzoic acid			Bromohydrin /NBS/H_2O/		
Olefinic comp.	Oxirane %	Ref.	Olefinic comp.	Oxirane %	Ref.
styrene	69-75	/49/	styrene	83.3	/41/
allylbenzene	60-80	/50/	allylbenzene	56.3	/41/
cis-propenylbenzene	51.9	/43/			

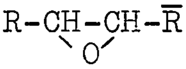
Guss and Rosenthal /41/ reported that the availability and stability of the NBS /N-bromosuccinimide/ reagent simplify the reaction, and the yields obtained make this procedure superior in many instances to alternative methods.

Parker and Rockett /42/ prepared the trans isomer II from α-bromopropiophenone. Cis and trans-2-methyl-3-phenyloxiranes can also be prepared from salts of ephedrine and pseudo-ephedrine /43-48/.

II.2.2. Isomerization of 2-methyl-3-phenyloxirane on the action of heterogeneous catalysts

As a result of the strained ring, the oxiranes are highly reactive compounds and are capable of many kinds of rearrangement reactions. These reactions are dealt with in recent reviews /28,31,53/. The main products of the rearrangement of oxiranes are carbonyl compounds and α,β-unsaturated alcohols. The rearrangements may be classified into: /1/ Base-catalyzed rearrangements. /2/ Acid-catalyzed isomerizations. /3/ Thermal and photochemical isomerizations. /4/ Isomerizations on the action of heterogeneous catalysts.

In the case of the base-catalyzed reaction of benzyloxirane /with $LiNEt_2$/, however, very rapid β-elimination takes place /54/. Isomerization reactions of oxiranes leading to carbonyl compounds can be carried out with both Brønsted and Lewis acids /55-57/. Other publications have appeared on the isomerizations of alkyl and aryl-substituted oxiranes containing various additional functional groups /58,59/.

The isomerization of oxiranes to carbonyl compounds and unsaturated alcohols depends on the surface state of the metal oxide catalyst. The isomerization of olefin oxides has been described in detail in the literature /50,52,60,61/. Catalysts that have been reported for the isomerization of propylene oxide to propionaldehyde include aluminium oxide /62,63/, thorium oxide /64/, tungsten oxide /65/, chromium oxide /65,66/, silica gel and silica /67,68/. Malinovskii /61/ mentioned that the disubstituted ethylene oxides of the type  $R-\underset{\diagdown O \diagup}{CH-CH}-\bar{R}$, where R and $\bar{R}$ are aromatic or aliphatic groups, are isomerized to ketones.

The isomerization of propylene oxides was investigated by many workers, in attempts to confirm the proposed mechanisms of the reactions and the relationships between the selectivity and the acidic and basic characters of the solid acids and bases /69/. The transformations were carried out on silica-magnesia and metal oxides /70/, lithium phosphate /71,72/, metal phosphates /73/, NaX and REX /RE = rare earth metal cations/ /74/, zeolite /75/, and metals supported on silica, metal oxide or metal sulphate /76/.

Studies were recently performed /77-80/ on the isomerization of cycloalkane oxides catalyzed by various solid acids and bases. When Arata and Tanabe /81,82/ examined the isomerization of d-limonone over alumina, the yield of carbonyl compound was 75%. An investigation of the methyldialkyl-substituted oxiranes was reported by Joshi and Dev /83/.

Isomerization resulting in the formation of carbonyl compounds is a characteristic transformation. The mechanism of the catalytic reaction and the isomerizing activities of the catalysts have been examined in the cases of some model compounds /84-90/. Senechal et al. /84/, in investigations relating to the selectivity of splitting of the C-O bond, showed that in the presence of metals this selectivity varied according to the sequence: Pd $<$ Pt $<$ Rh, Cu, Ni. Chernyshkova and Musenko /86/ examined the isomerization of epoxy-cyclodecanone on Pd-Al_2O_3 and Rh-Al_2O_3, and observed only ketone formation.

Catalytic hydrogenation of oxiranes generally yields alcohols. The stereochemistry and mechanism of the hydrogenolysis have been studied /87-95/. Lundsted et al. /96/ made a detailed study of the isomerization of propylene oxide to allyl alcohol. Numerous literature data can be found regarding the catalytic effects of metals and metal oxides. Supported and support-free metal catalysts have proved best /97-99/.

Ni and Pd exhibit opposite selectivities in the hydrogenolysis of certain oxiranes. It has been established that Ni opens the ring on the more sterically-

-hindered, and Pd on the less sterically-hindered side /87,88,100/. Examinations connected with the stereochemistry of hydrogenolysis indicate that the configuration of the alcohol formed is strongly influenced by the catalyst, the reactant and the experimental conditions /98,101/.

The catalytic hydrogenolysis of benzyl-type compounds is an important method for studying the mechanisms of transformations catalyzed by metals /101-105/. Mitsui /98/ dealt with the hydrogenolysis of styrene oxide homologues on Raney Ni, Pd and Pt catalysts. On Raney Ni these styrene oxides gave ethylene /30-50%/ as well as 2-phenylethanols. The differences in the behaviours of cyclopropane, azidine styrene imine and oxirane are ascribed to the differences in their affinities for the catalyst, and the differences in electronegativity of the C, N and O atoms /98,103,106, 107/.

The catalytic cleavage of 4-phenyl-1,3-dioxan and 4-methyl-4-phenyl-1,3-dioxan using Pd or $CuO-Cr_2O_3-BaCrO_4$ catalysts was studied by Cerveny et al. /108/. This cleavage of 4-phenyl-1,3-dioxan in an inert atmosphere produces propiophenone selectively.

III. EXPERIMENTAL

III.1. Synthesis of benzyl methyl ketone with certain heterogeneous metal oxide catalysts

During all preparations of benzyl methyl ketone /20,21/ with different catalysts, two molar ratios of phenylacetic acid - acetic acid were used: 1:2 and 1:4.

III1.1. Description of experimental method

Figure 1 illustrates a diagram of the flow reactor technique applied /109/. Depending on the nature of the catalyst, the quantity of catalyst was 4-8 ml. The mixture of phenylacetic and acetic acids was fed into the reactor tube from the syringe.

III.1.2. Analysis

Esterification method

The quantity of unreacted phenylacetic acid remaining after the preparation of benzyl methyl ketone was determined via the following method. 0.1 g of the catalyzate was refluxed for 2 min with 3 ml of boron trifluoride etherate /$BF_3.Et_2O$/ in methanolic solution, and the mixture was then evaporated to dryness /110/. The residue was chromatographed /Fig. 2/. For evaluation of the chromatograms, a calibration curve was prepared /Fig. 3/ after esterifying mixtures of phenylacetic acid and benzyl methyl ketone with known molar ratios by the above procedure.

The gas chromatographic analysis was carried out by Chrom-41 gas chromatograph. The chromatographic conditions were as follows:

Column: 1.2 m long, 4 mm ID; 15% Apiezon-L on K_G-S. Carrier gas: hydrogen, 40 ml/min. Thermostat temperature: 120°C. Sensitivity: 1:1-1:5. Chart speed: 4. Detector current: 100 mA. Sample injected: 3 μl.

III.1.3. Catalysts

III.1.3.1. Properties of catalysts

The catalysts used with their certain characteristics, are listed in Table 3.

Table 3. Properties of certain metal oxide catalysts.

Catalyst	Surface area /m^2/g/	Acidic centres /mmol/g/	Basic centres /mmol/g/
a. 30% ThO_2	-	-	-
b. 30% ThO_2-Al_2O_3	-	-	-
c. MnO	-	-	-
d. Cr_2O_3-ZnO /Leuna-616/	15	0.05	0
e. NiO-MgO /Leuna-9024/	<1	0.013	0.13
f. Bi_2O_3-MoO_3-SiO_2/Leuna-9421/	55	0.27	0
g. Al_2O_3 /Strem/	-	0.2	0.46

All experiments were carried out with fresh catalyst. Before use, the catalysts were activated in a current of air at 500°C for 1 hour.

III.1.3.2. Preparation of 30% ThO_2, 30% ThO_2-Al_2O_3 and MnO catalysts

/a/ 30% ThO_2 /20/

7 g screened pumice /grain size 1-2 mm/ is soaked in 100 ml hot concentrated HNO_3 and then washed thoroughly with hot distilled water. In a porcelain dish the pumice is mixed with a solution of 8 g $Th/NO_3/_4.5H_2O$ /Merck, Germany/ in 20 ml water, and the mixture is evaporated to dryness under vacuum. The impregnated pumice is ignited over a Bunsen burner until decomposition of the nitrate is complete. The pumice carries about 30% /3 g/ ThO_2.

/b/ 30% ThO_2-Al_2O_3 /21/

Excess 25% NH_3 solution is added to 64.4 g $Al/NO_3/_3.9H_2O$ and 10 g $Th/NO_3/_4.5H_2O$ in 700 ml distilled water. The gelatinous precipitate is washed, and dried for 8 hr. It is then crushed and screened.

/c/ MnO /12,17/

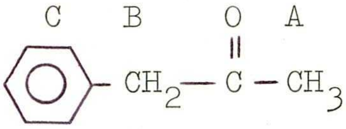
$MnCl_2.4H_2O$ is treated with ammonium carbonate and the carbonate precipitated from solution is put into a reactor tube filled with glass beads, and heated at 150-200°C in methanol vapour /feed rate 6.6 ml/hr^{-1}/. A gentle stream of nitrogen is then passed through at 400-450°C for 8 hr, in order to convert the $MnCO_3$ to MnO, which is allowed to cool to room temperature under nitrogen.

III.1.4. Preparation of benzyl methyl ketone over new heterogeneous metal oxide catalysts

We prepared benzyl methyl ketone on a preparative scale according to the method described by Herbst and Manske /20/ and Martello and Ceccotti /21/. We used new metal oxide catalysts (Cr_2O_3-ZnO, NiO-MgO, Bi_2O_3-MoO_3-SiO_2, Al_2O_3 and MnO /11/) under the same conditions /see Table 5/.

4 ml catalyst /grain size 1-2 mm/ was placed in the reactor, and a mixture of phenylacetic and acetic acid in a molar ratio of 1:2 or 1:4 was fed in at a rate of 6.6 ml/hr at 420-450°C. 50 ml product was collected, neutralized with 50% NaOH, extracted with benzene, and then distilled. Boiling point found: 116-122°C/water suction; literature /20/ boiling point: 110-115°C/21-22 mm Hg. The residue also contained 1,3-diphenylacetone; boiling point: 190-210°C/20 mm Hg.

The NMR data on benzyl methyl ketone are:



A = J = 2.03 ppm; B = δ = 3.55 ppm; C = J = 7.16 ppm.

III.2. Investigation of transformations of 2-methyl-3-phenyloxirane on various heterogeneous catalysts by means of a microreactor

III.2.1. Preparation of 2-methyl-3-phenyloxirane

We chose a suitable method for the preparation of 2-methyl-3-phenyloxirane, previously employed by Goodman et al. /38/ and Guss and Rosenthal /41/, using NBS as reagent.

The amounts of compounds used were: 86.5 g /0,741 mole/ 1-phenylpropene, 132 g /0.74 mole/ N-bromosuccinimide, and 201.7 g 30% /0.52 mole/ aqueous NaOH. A good yield was obtained: 75 g /77%/. The boiling point found: 88-92°C/15 mm Hg; n_D^{24} found: 1.5160. Literature boiling points /44/: trans 87.5°C/15 mm Hg; cis 80-80.5°C/17 mm Hg; literature n_D^{25}: trans 1.5183 /45/, trans 1.5178 /42/; cis 1.5170 /45/.

The conversion of 1-phenylpropene to 2-methyl-3-phenyloxirane may properly be regarded as an oxidative process and constitutes an excellent method for indirect oxiranation:

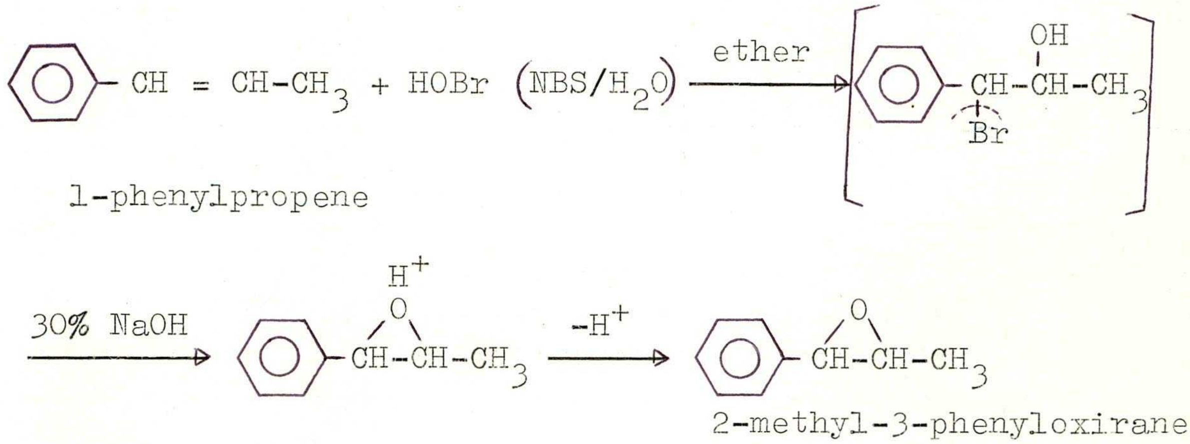


Figure 4 shows the results of gas chromatographic analysis. The conditions were similar to those mentioned in Section III.2.3.

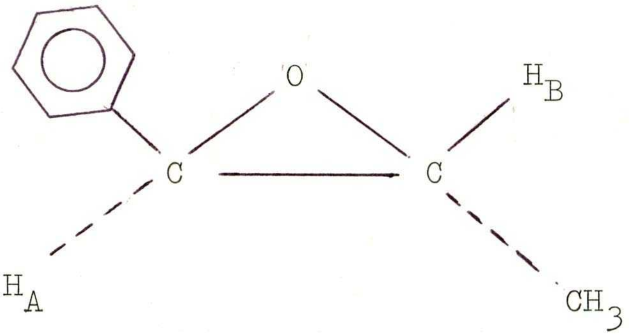
The NMR spectrum /Fig. 5/ reveals that the oxirane obtained contains 95% *trans* isomer and 5% *cis* isomer. Finnegan and Wepplo /39/ too reported that the treatment of olefin with NBS and alkali provides a mixture rich in the *trans* oxirane.

The NMR data collected in Table 4 reveal that the methyl doublet in the *cis* isomer appears at a slightly lower chemical shift than the corresponding doublet in the *trans* isomer.

The characteristic IR bands of 2-methyl-3-phenyloxirane are as follows /Fig. 6/ /44,111/:

ν_{max}^{IR} : 3010, 1700-1695, 1505, 1470, 1430, 1385, 1030, 960, 870, 775, 750, 705 cm^{-1}.

Table 4. NMR data on 2-methyl-3-phenyloxirane prepared from olefin /45/



	CH_3 doublet	C-2H doublet	C-3H octet	phenyl resonance
	δCH_3	δH_A	δH_B	δC_6H_5
Trans	1.29 ppm	3.38 ppm	2.84 ppm	7.15 ppm
Cis	0.95 ppm	3.84 ppm		

Trans isomer 95%; cis isomer 5%.

Proton coupling constants

Trans	Cis
$J_{CH_3/H_B} = 5H_2$	$J_{CH_3/H_B} = 5.5H_2$
$J_{H_A/H_B} = 2\ H_2$	$J_{H_A/H_B} = 4\ H_2$

III.2.2. Description of microreactor technique

The microcatalytic reactor is characterized by the use of a very small quantity of catalyst /usually in the range 0.01-1 g/, with correspondingly small quantities of reactants. The experimental method was the pulse method. An outline of the experimental set-up is shown in Fig. 7. The internal diameter of the reactor was 8 mm. It was coupled to a Chrom-41 gas chromatograph.

III.2.3. Analysis

Column selection

/a/ We had to choose an appropriate column material for the separation of both isomeric ketones /propiophenone, benzyl methyl ketone/, isomeric alcohols /1-phenyl-1-propanol, 1-phenyl-2-propanol/ and 2-methyl-3-phenyloxirane. This material was 15% polydiethylene glycol succinate /PDEGS/ /see Fig. 8/. The gas chromatographic conditions were as follows: Column: 1.2 m long and 4 mm ID, containing 15% PDEGS on a support of silanized Kieselguhr /K_G-S/ with a particle size of 0.2--0.3 mm. Thermostat temperature:140°C. Detector current: 100 mA. Carrier gas: hydrogen, 40 ml/min. Sensitivity: 1:20. Chart speed: 4. Sample injected 5 μl.

/b/ When polyethylene glycol /PEG-20M/ on K_G-S and Carbowax-1500 columns were used, only isomeric alcohols were separated, while a tris-/2-cyanoethoxy/-propane /FRN III/ column could separate only isomeric ketones.

Several different ratios of these partition liquids were used to separate the isomeric ketones and alcohols, but after the test was repeated the column lost its activity. Bartók and Török /89/ and Arata et al. /77,81/ applied these columns in the cases of the isomerizations of unsaturated alcohols and cycloalkene oxides, respectively.

III.2.4. Catalysts

III.2.4.1. Properties of catalysts

γ-Al_2O_3 and SiO_2, with acidic and basic sites, were tested as supports. These catalysts had the following properties:

Catalyst used	Density D%	Surface area S/m^2/g/	Average diameter d/μm/
γ-Al_2O_3 /0.4 mm/	-	100	-
SiO_2/0.2-0.3 mm/	-	-	-
3% Ni/Cab-O-Sil	6.8	45.4	14.8
3% Pd/Cab-O-Sil	15.4	72.2	6.9
3% Pt/Cab-O-Sil	14.0	38.4	7.2

Before investigation, the catalysts were activated in a stream of hydrogen at 350°C for 2 hr.

III.2.4.2. Preparation of 3% Ni, Pd and Pt/Cab-O-Sil catalysts

Numerous literature data deal with the preparation of supported Pt and Ni catalysts /112-116/, while the preparation of 5% Pd on charcoal has been described in paper /117/.

We prepared the catalysts in question by adding an aqueous solution containing the required weight of the substance /H_2PtCl_6, $Ni/NO_3/_2 \cdot 6H_2O$ or $PdCl_2$/ to an aqueous suspension of the support Cab-O-Sil with continuous stirring. The suspended layer was evaporated to dryness and then dried in an air oven at 130°C for 10 hr. Finally, before use the catalysts were activated in a stream of hydrogen at 350°C for 2 hr.

III.2.5. Reaction of 2-methyl-3-phenyloxirane on the heterogeneous catalysts /3% Ni, Pd and Pt/Cab-O-Sil/

The reactions were carried out with a normal pulse microreactor, in hydrogen as carrier gas. The weight of the catalyst was generally 3-10 mg, but in some cases a higher amount was used. The catalysts were activated in hydrogen at 350°C for 2 hr, and then kept at the reaction temperature for 1 hr. The amount of oxirane injected was 1-2 μl. Investigations were performed at temperatures in the range 200-320°C.

The microreactor was coupled with a Chrom-41 gas chromatograph, the gas chromatographic conditions being the same as described in Section III.2.3.

IV. RESULTS AND DISCUSSION

IV.1. Preparation of benzyl methyl ketone

The experimental data on the preparation of benzyl methyl ketone over certain heterogeneous catalysts under various conditions are listed in Table 5. It can be seen that when the reaction conditions are otherwise identical, the amount of ketone formed increases with increase of the proportion of acetic acid. Figure 9 illustrates the percentage yields of benzyl methyl ketone over different metal oxide catalysts, at the 2 different molar ratios and reaction temperatures.

The 30% ThO_2 in pumice catalyst gave 37.6% ketone at 420°C with a flow rate of 6.6 ml/hr. Herbst and Manske /20/ reported a yield of 55-60% with 30% ThO_2 in pumice at 430-450°C. With 15% ThO_2 in pumice, Martello and Ceccotti /21/ obtained yields of 44% and 35% at 460°C. Pickard and Kenyon /19/, however, found a yield of more than 60%. The difference between our yield of ketone and those reported in the literature /19-21/ can be attributed to the lower activity of the catalyst, and the non-uniformity of the feeding of the mixture. Because of this latter, as a consequence of the varying flow rate the periodic longer residence time may have led to decomposition of the ketone product, which showed up in a decreased yield.

Table 5. Percentage yields of benzyl methyl ketone over certain catalysts

Types of catalysts	Catalyst amount g	Best temp. °C	Phenylacetic/ acetic acids molar ratio	Feed rate ml/hr	Yield % in lit.	Yield % found theor	$n_D^{20}=1.5168$	Boiling point water suction °C	Ref.
30% ThO_2- in pumice	5	420	1:2	6.6	55-65	37.6	$n_D^{23}=1.5178$	124	/19,20,21/
			1:4		60	36.0	$n_D^{23}=1.5178$	124	
30% ThO_2- -Al_2O_3	4	420	1:2	6.6	-	45.0	$n_D^{23}=1.5205$	116	/21/
			1:4		74	60.0	$n_D^{22}=1.5319$	120-124	
MnO	2	410	1:2	6.6	-	53.4	$n_D^{18}=1.5158$	116-118	/12,17/ 11
			1:4		-	61.3	$n_D^{18}=1.5162$	118	
	2	420	1:2	6.6	-	46.6	$n_D^{18}=1.5171$	110	
			1:4		-	66.0	$n_D^{18}=1.51161$	112	
	2	450	1:2	6.6	-	48.8	$n_D^{18}=1.5165$	118	
			1:4		-	61.3	$n_D^{18}=1.5166$	120	
Cr_2O_3-ZnO	4.6	420	1:2	11.1	-	60.9	$n_D^{23}=1.5138$	118-120	
			1:4		-	77.5	$n_D^{22}=1.5160$	121-122	
Cr_2O_3-ZnO	4.4	450	1:2	11.1	-	60.0	$n_D^{22}=1.5184$	120-124	
			1:4		-	72.7	$n_D^{23}=1.5162$	118	
NiO-MgO	6.5	420	1:2	11.1	-	60.0	$n_D^{22}=1.5143$	132	
			1:4		-	60.0	$n_D^{22}=1.5157$	134	
NiO-MgO	6.5	450	1:2	11.1	-	62.7	$n_D^{22}=1.5151$	118-120	
			1:4		-	72.7	$n_D^{22}=1.5155$	124	
Bi_2O_3-MoO_3- -SiO_2	4.2	450	1:2	11.1	-	25.5	$n_D^{22}=1.5179$	130	
			1:4		-	42.4	$n_D^{22}=1.5203$	120-122	
Al_2O_3	2.3	420	1:2	11.1	-	48.8	$n_D^{22}=1.5165$	118-122	
			1:4		-	66.6	$n_D^{22}=1.5166$	118-121	
Al_2O_3	2.8	450	1:2	11.1	-	41.0	$n_D^{22}=1.5179$	122	
			1:4		-	62.4	$n_D^{22}=1.5161$	122	

The method of Martello and Ceccotti /21/ with 30% ThO_2-Al_2O_3 gave a yield of 74%, compared with 60% in our experiment. We believe that the difference between the two results was due to decomposition of the compound, because 30% ThO_2-Al_2O_3 is more active than 30% ThO_2 in pumice at 420°C.

The literature data show that the most useful catalysts are ThO_2 and MnO. MnO has high activity, and is as good as ThO_2 for the preparation of unsymmetrical ketones at 400-450°C. It is generally known that the yields of symmetrical ketones are very high at 400-410°C /e.g. 70% in the case of phenylacetic acid/ /11,17/. Our experiment with phenylacetic and acetic acids in a molar ratio of 1:4 at 420°C gave a yield of 66%. The best results were obtained at 420°C. In the investigation of the product obtained on MnO catalyst, it was found that /in contrast to the other catalysts/ this catalyzate did not contain untransformed phenylacetic acid.

The best results obtained with the most active catalysts are to be seen in Table 6.

ThO_2 has no acidic properties, but is slightly basic; hence, the bonds in ThO_2 can be expected to be less covalent than in Al_2O_3. Al_2O_3, which is a typical Lewis acid catalyst, exhibited almost the same activity as those of Cr_2O_3-ZnO, NiO-MgO and MnO. On the other hand, MgO, which has a basic character, was almost inactive, while Bi_2O_3-

-MoO_3-SiO_2 had only poor activity. These results seem to indicate that the activity and selectivity do not depend directly on the acidic or basic natures of the catalysts. The data relating to the numbers of acidic and basic centres of some of the catalysts we used have been listed in Table 3, from which it can be seen that the corresponding data on the two best catalysts /NiO-MgO and Cr_2O_3-ZnO/ differ considerably.

Table 6. Optimum yields of benzyl methyl ketone on various catalysts under different experimental conditions.

Catalyst	Temp.:420°C Molar ratio:1:4 phenyl-acetic/acetic acids		Temp.:450°C Molar ratio:1:4 phenyl-acetic/acetic acids	
	Feed rate ml/hr	Yield %	Feed rate ml/hr	Yield %
30%ThO_2-Al_2O_3	6.6	60	-	-
Cr_2O_3-ZnO	11.1	78	11.1	73
NiO-MgO	11.1	60	11.1	73
Al_2O_3	11.1	67	11.1	62
MnO	6.6	66	6.6	61

To summarize, it may be stated that NiO-MgO and Cr_2O_3-ZnO proved the most suitable catalysts for the preparation of benzyl methyl ketone from a mixture of phenylacetic and acetic acids.

IV.2. Examination of transformation of 2-methyl-3-phenyloxirane on various heterogeneous catalysts

IV.2.1. γ-Al_2O_3 and SiO_2

Not many reports have been made on the isomerization of epoxides as catalyzed by solid acids and bases, and little work has been done on the relationship between the selectivities and the acidic and basic properties of the catalysts /69/.

The isomerization of 2-methyl-3-phenyloxirane over γ-Al_2O_3 and SiO_2 catalysts produces benzyl methyl ketone. Table 7 contains the results of the transformations observed on γ-Al_2O_3 and on SiO_2, based on the chromatographic analysis data /Fig. 10/. It can be seen that SiO_2 catalyzed the transformation to the isomeric epoxide /cis-2-methyl-3-phenyloxirane/ and isomerization with ketone formation, while on γ-Al_2O_3 a third process too could be observed.

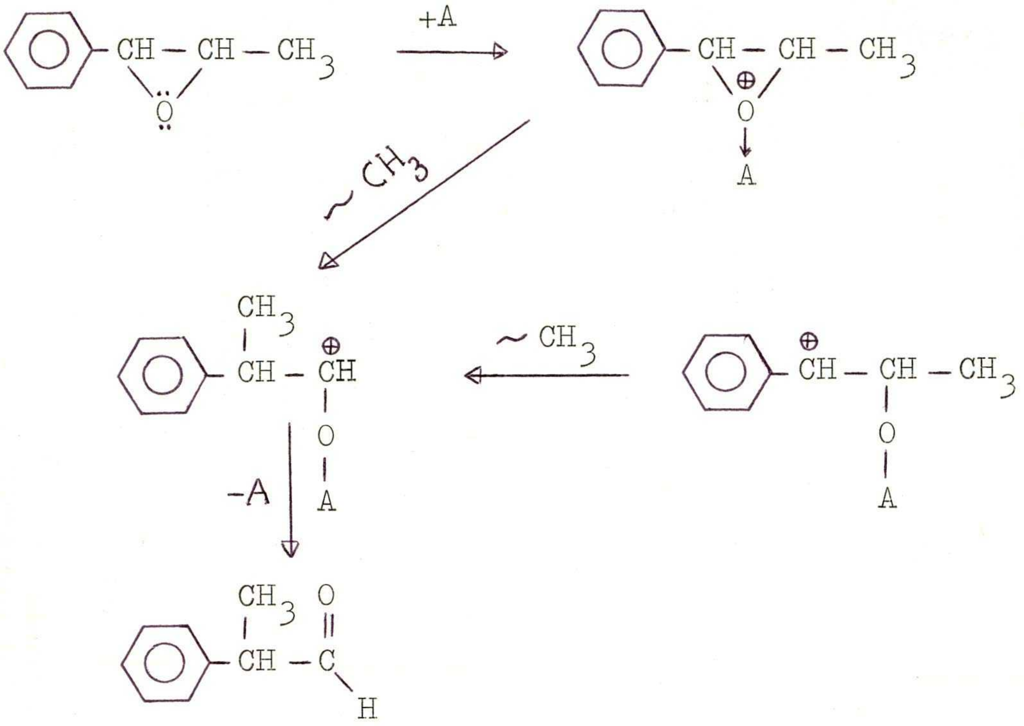
Numerous literature reports have described the isomerization and rearrangement of oxiranes over Al_2O_3 and other acidic and basic catalysts /77-83,86, 118-120/. Carbonyl compounds are generally formed over Al_2O_3 and Al_2O_3-SiO_2.

Table 7. Catalytic activities and selectivities in transformations of 2-methyl-3-phenyloxirane

Reaction temp. °C	SiO_2 /10 mg/ Conversion %	Selectivity % I	II	γ-Al_2O_3 /5 mg/ Conversion %	Selectivity % I	II	III
250	15.31	57.87	42.06	60.64	6.18	30.5	63.4
300	22.17	46.28	53.72	78.52	2.43	28.3	69.3
350	27.38	41.45	58.55	86.09	3.46	36.9	59.6
400	29.42	46.26	53.77	76.19	4.08	31.4	64.5

I, cis isomer of 2-methyl-3-phenyloxirane; II, benzyl methyl ketone; III, 2-phenyl-propionaldehyde.

The NMR and IR spectra /Figs. 11 and 12/ of the product obtained in our preparative-scale reaction over γ-Al_2O_3 revealed that this was 2-phenylpropionaldehyde; that is, besides the isomerization leading to benzyl methyl ketone, the isomerization epoxide ⟶ oxo compound, accompanied by substituent migration, occurs as a fundamental process on this catalyst. This process is probably a transformation commencing with splitting of the benzyl C-O bond, proceeding via a carbonium cation, or by means of a concerted mechanism, with methyl group migration /Scheme 1/.



Scheme 1.

IV.2.2. Experimental data on transformations over supparted Ni, Pd and Pt/Cab-O-Sil

The transformations of 2-methyl-3-phenyloxirane over Ni, Pd and Pt/Cab-O-Sil catalysts were studied by an impulse technique in the presence of hydrogen at 200-320°C. The main products of isomerization were benzyl methyl ketone and 1-phenyl-2-propanol. Analysis was performed by gas chromatography, as illustrated in Fig. 13.

Catalytic activities and selectivities in the isomerizations of 2-methyl-3-phenyloxirane over the supported metal catalysts are presented in Figs. 14-23, together with the experimental data.

The ratio of ketone formation increases with increasing reaction temperature, while at the same time the quantity of alcohol decreases. This means that the first reaction is the formation of alcohol, this reaction being followed by dehydration leading to the formation of ketone. The stereochemistry of hydrogenolysis indicates that the configuration of the alcohol formed is strongly influenced by the catalyst, the reactant and the experimental conditions /98,101/. The investigated catalysts display the following sequence of activity on the isomerization of 2-methyl-3-phenyloxirane: 3% Pt/Cab-O-Sil > 3% Pd/Cab-O-Sil > 3% Ni/Cab-O-Sil.

In all investigations over the Pd catalyst, the cis isomer was nearly unchanged, as shown in Fig. 19. On the Pt and Ni catalysts the quantity of the isomer varied. It decreased as the reaction temperature was raised. The greatest change was observed on the Pt catalyst /5-20%/. At higher temperatures, small amounts of 1-phenylpropane and 1-phenylpropene were also produced over Pd and Pt/Cab-O-Sil catalysts. On Ni/Cab-O-Sil, however, these two compounds were the principle products /see Fig. 20/.

Figure 14 shows the catalytic activity and the conversion of 2-methyl-3-phenyloxirane as functions of temperature when 10 mg Pt/Cab-O-Sil catalyst was used. The conversion values relating to the two curves were determined on the same catalyst sample on two consecutive days. A difference in activity was observed between the first day and the next day. In the course of these investigations, an interesting phenomenon was noted, which is unexplained up to now: the conversion decreased between 260 and 280°C on a deactivated catalyst. This phenomenon was observed in the course of several other measurements too, carried out on new catalysts.

The variations of the product compositions as a function of temperature for the first and second activations in the transformation of the oxirane are depicted in Fig. 15. On each day, 10 mg catalyst was used for the first and second activations. It can be observed that the conversion of the reactant was higher in the first and second activations as compared with those in Fig. 14. Figure 16 illustrates the variation in the product composition as a function of temperature on 10 mg Pt/Cab-O-Sil catalyst, without activation at 350°C for 2 hr. There was no difference in conversion and selectivity as compared with Fig. 15.

The results of investigations with 5 mg Pt/Cab-O-Sil catalyst are given in Fig. 17. The quantity of the <u>cis</u> isomer varies between 5 and 20%. Its amount decreases with increasing temperature. As regards the catalysts we examined, the Pt catalyst exhibits a high activity with respect to the isomerization of the oxirane to the ketone.

The variation of the product composition as a function of temperature when 3,5 and 7 mg Pd/Cab-O-Sil catalyst was used is shown in Figs. 18 and 19. The selectivity and conversion increase as the amount of catalyst is increased. The isomerization accompanied by ketone formation is catalyzed to a similar extent by the Pd catalyst as by the Pt catalyst /Figs. 17 and 19a/. However, since the Pd catalyst is much more stable as regards its activity, it is preferable to use this rather than the Pt catalyst. The phenomenon that the conversion decreases with the increase of temperature between 200 and 210^{o}C is due to the fact that this temperature is lower than the boiling point of the oxirane, and hence the evaluation of the chromatographic peaks is inaccurate because of the evaporation.

Figure 20 gives the results on Ni/Cab-O-Sil. The principal products in addition to benzyl methyl ketone and 1-phenyl-2-propanol are 1-phenylpropane and 1-phenylpropene. The percentage yield of 1-phenylpropane is 42--56% and 68-75% on 2.5 and 5 mg, respectively, of catalyst. The quantity of 1-phenylpropene varies between 8 and 24%. The amount of 1-phenylpropane increases as the temperature is raised, while the quantities of benzyl methyl ketone and 1-phenyl-2-propanol decrease. This fact, that the saturated and unsaturated hydrocarbons are formed with higher selectivities than the ketone and the alcohol, is due to the strong affinity of the catalyst for the oxygen atom.

The results obtained on the three catalysts /Ni, Pd and Pt/ and the variation of the conversion of the oxirane as a function of temperature are outlined in Fig. 21 /catalyst amount 5 mg/. Figures 22 and 23 show the variation of the product composition as a function of the catalyst amount at constant temperature over Pt and Pd/Cab-O-Sil. The selectivity of ketone formation and the conversion increase with increase of the amount of catalyst, while the yield of alcohol decreases. On large quantities of catalysts /25 and 30 mg/, the conversion is as high as 100%, but some hydrocarbons are also formed in increasing amounts.

On the basis of our experimental work, it can be stated that the Pd and Pt/Cab-O-Sil catalysts are suitable for the vapour-phase transformation of the oxirane for preparative purposes too. We believe that more research work is necessary to explain the interesting phenomenon that the conversion decreased between 260 and 280°C on deactivated Pt/Cab-O-Sil catalyst.

IV.2.3. Interpretation of the transformations

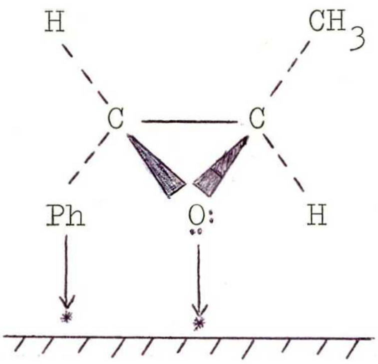
The mechanisms of transformation of oxiranes to alcohols in solution in the presence of heterogeneous catalysts /Ni, Pd, Pt/ are discussed in the literature /98,104/. The stereoselectivity of the hydrogenolysis of benzyl-type compounds is affected by many factors, such as the structures of the compound, the natures of the catalyst and the solvent, the additives, etc. /106/.

In the present work, only benzyl methyl ketone and 1-phenyl-2-propanol were detected in the gas phase for all of the different heterogeneous catalysts. The ratio of the alcohol and ketone formed varies, depending on the hydrogenation and dehydrogenation processes.

IV.2.3.1. Adsorption of 2-methyl-3-phenyloxirane

A. Nickel/Cab-O-Sil catalyst

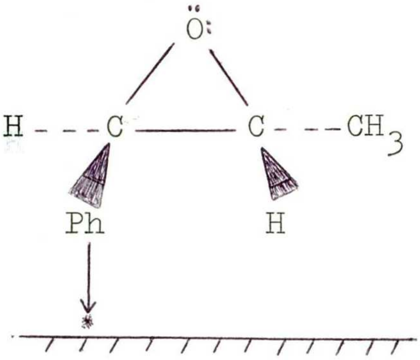
The oxygen atom in the oxiranes possesses two lone-pairs; this gives a possibility for the reactant molecule to bind to the surface of the catalyst via its oxygen atom. On the Ni catalyst, therefore, 2-methyl--3-phenyloxirane is probably transformed via I. The homobenzyl carbon in I can not approach so closely to the catalyst surface, and scarcely any attack on this carbon will occur. Accordingly, the hydrogenolysis of 2-methyl-3-phenyloxirane occurs predominantly with retention of configuration over the Ni catalyst.



I

B. Palladium and platinum/Cab-O-Sil catalysts

The results of transformation of the oxirane over different catalysts depend on the affinity of the oxygen lone-pair and on the structure of the reactant molecule. Since Pd does not have such a strong affinity for the oxygen lone-pair, over the Pd catalyst the oxirane is more probably transformed via II.



II

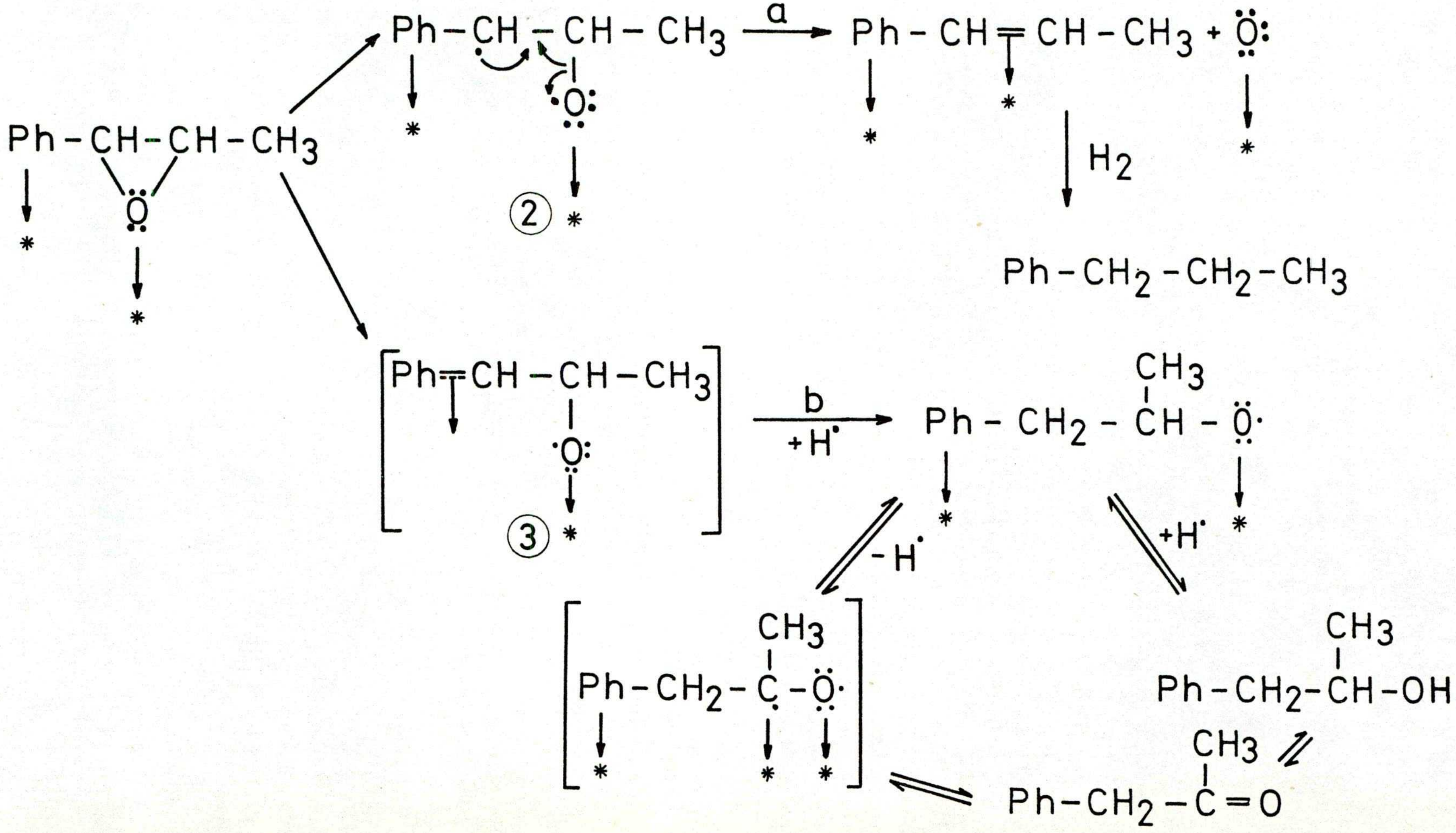
However, the hydrogenolysis over the Pt catalyst definitely favours the path via II, because Pt is less sensitive to the catalyst hindrance than Ni and Pd. Hence, the hydrogenolysis of 2-methyl-3-phenyloxirane over the Pd and

Pt catalysts takes place predominantly with inversion of configuration.

IV.2.3.2. Mechanisms of the transformations

A. Nickel/Cab-O-Sil catalyst

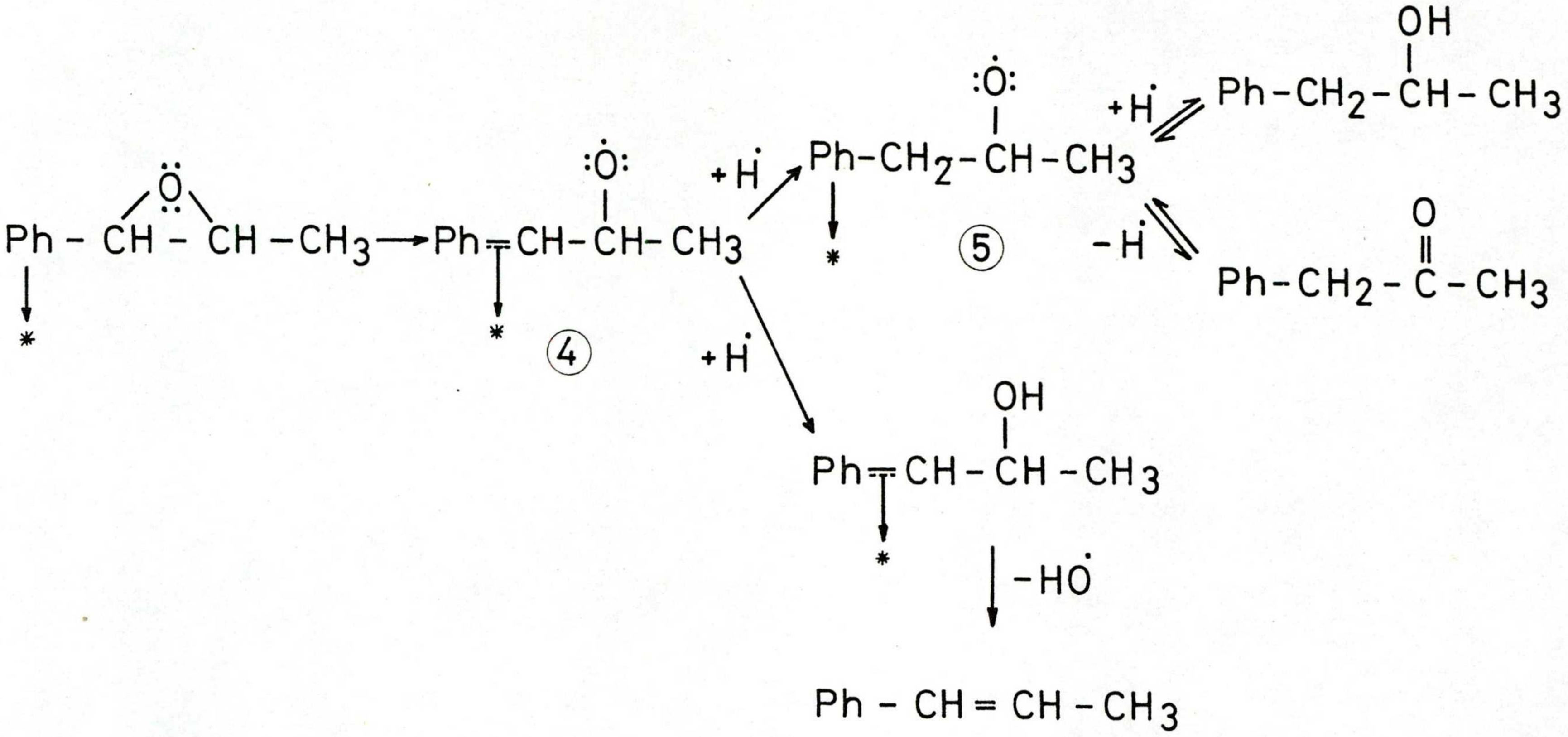
As a consequence of the strong affinity of Ni for the lone-pairs of the oxirane oxygen atom, the transformation may be interpreted in that the surface adsorption of the substrate in form I makes possible the radical cleavage of the oxirane ring /105/. The surface binding /the strong chemisorption of the oxygen atom and the phenyl group, and the resulting increase in the oxirane ring strain/, and also the well-known ready splitting of the benzyl C-O bond, explain the ring-opening possibility illustrated in Scheme 2, i.e. the formation of the surface-bound radicals ② and ③. The two-point surface sorption of the starting compound inhibits the close approach of the benzyl carbon atom to the surface, and consequently ③ is formed in a slow reaction, with lower probability than ②. This can explain why the products 1-phenylpropane and 1-phenylpropene are dominated by those which are formed in the further reactions of ②, that is the 1-phenylpropane will be formed via olefin directly from the corresponding 2-methyl-3-phenyloxirane, but not from 1-phenyl-2-propanol /98/.


Ph-CH-CH-CH3
Ö
*
Ph-CH-CH-CH3
Ö:
②
a
Ph-CH=CH-CH3 + Ö:
H2
Ph-CH2-CH2-CH3
[Ph=CH-CH-CH3
Ö:]
③
b
+H·
CH3
Ph-CH2-CH-Ö·
-H·
+H·
[Ph-CH2-C-Ö·]
CH3
Ph-CH2-CH-OH
CH3
Ph-CH2-C=O

Scheme 2.

B. Palladium and platinum/Cab-O-Sil catalysts

In contrast with Ni, an O-M bond is not produced on Pd and Pt; only the phenyl ring is sorbed. Accordingly, since the arrangement of the oxirane molecule on the surface favours the approach of the benzyl carbon atom to the surface, the possibility is given for the formation of the π-benzyl complex ④ /Scheme 3/. In connection with the discussion of this question, it was pointed out by Smith and Roth /121/ that the complete overlaping of the benzyl carbon atom and the surface atom of the metal can not occur, because of the more favoured π-complex formation; at the same time, the rate of hydrogen addition to this complex also increases. The oxygen is very distant from the surface of the catalyst in the resulting structure, and therefore the splitting-off of oxygen from the molecule is not favoured. Thus, the oxygen-containing compounds, the alcohol and the ketone, are obtained as the final products, via the intermediate ⑤.


Ph - CH - CH - CH3
Ph=CH-CH-CH3
④
+H
Ph-CH2-CH-CH3
⑤
+H
Ph-CH2-CH-CH3
OH
-H
Ph-CH2-C-CH3
O
+H
Ph=CH-CH-CH3
OH
-HO
Ph - CH = CH - CH3
*

Scheme 3.

V. SUMMARY

1. Preparation of benzyl methyl ketone by ketonization on oxide catalysts; best conditions for the preparation of the compound:
   temperature: 450°C
   phenylacetic acid - acetic acid molar ratio: 1:4
   feed rate: 11.1 ml/hr
   catalyst: Cr_2O_3-ZnO or NiO-MgO
   Yield: 73%
2. Study of the isomerization of 2-methyl-3-phenyloxirane:
   /a/ For synthesis of the compound, epoxidation via the bromohydrin was used, which has proved suitable in other cases. A yield of 77% was attained. The NMR spectrum and gas chromatographic data showed that the product contained the <u>trans</u> and the <u>cis</u> isomers in a ratio of 95:5.
   /b/ On γ-Al_2O_3 as catalyst, the main process was the formation of 2-phenylpropionaldehyde, produced by substituent migration.
   /c/ On Pd and Pt/Cab-O-Sil catalysts, under the conditions of the pulse technique, the main reaction is isomerization leading to benzyl methyl ketone. The yield of this compound varies, depending on the amount of catalyst and the reaction temperature; the best value was 78% /10 mg Pt/Cab-O-Sil,

320°C/. 1-Phenyl-2-propanol is formed as side-product.

/d/ On Ni/Cab-O-Sil catalyst, primarily 1-phenylpropane and 1-phenylpropene are formed by hydrogenolysis.

/e/ With the increase of the temperature and the catalyst amount, the ketone - alcohol ratio is shifted in favour of the former.

/f/ On the Pd catalysts the quantity of the *cis* isomer is nearly constant, but on the Pt and Ni catalysts at low temperature isomerization to the *cis*-epoxide was observed.

/g/ Under the experimental conditions employed, the formation of the isomeric ketone and alcohol, and the cyclohexanone derivatives produced by hydrogenation, was not observed.

/h/ Between 260 and 290°C, a decrease of the conversion was observed with increase of the temperature on deactivated Pt catalyst.

/i/ The difference in product composition can be interpreted by different adsorption of oxirane molecule.

/j/ The Pd and Pt catalysts are suitable for the preparation of benzyl methyl ketone.

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FIGURES

LIST OF FIGURES

Fig. 13. Analysis of transformation products over 3% Ni/Cab-O-Sil /a/, 3% Pd/Cab-O-Sil /b/ and 3% Pt/Cab-O-Sil /c/. Temperature: 260°C.

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Fig. 22. Variation of the product composition as a function of the catalyst amount at a constant temperature of 230°C over Pd/Cab-O-Sil.

23. Variation of the product composition as a function of the catalyst amount at a constant temperature of 250°C over Pt/Cab-O-Sil.

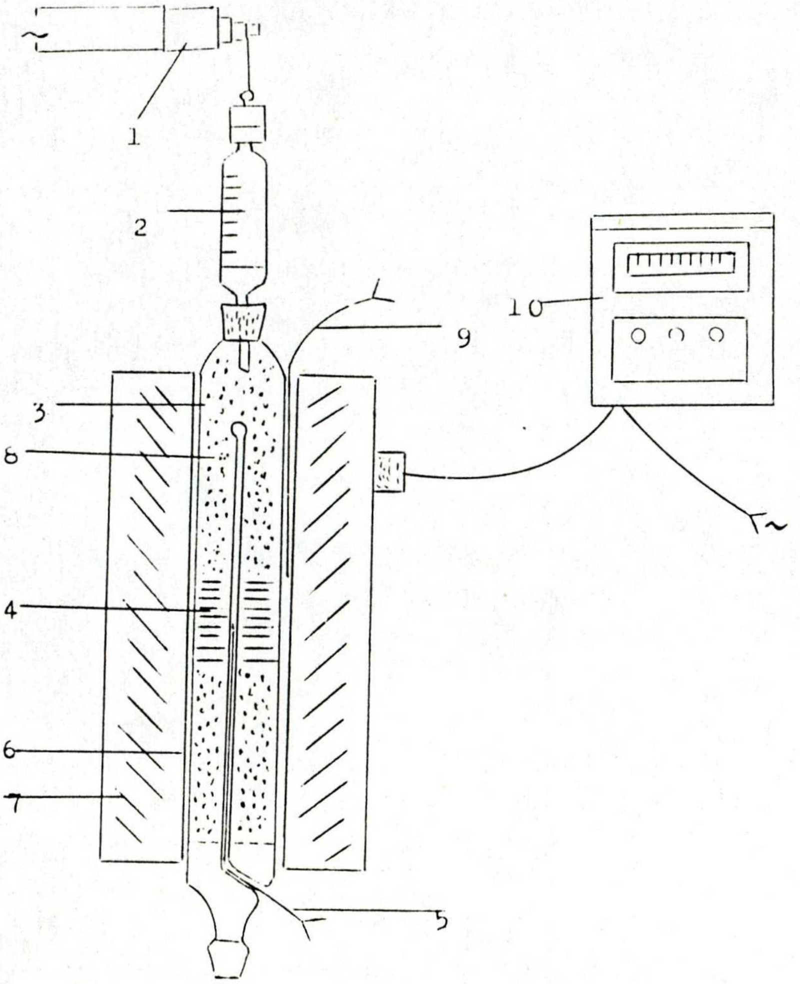


Fig. 1. Flow reactor technique

1. Feeder machine, 2. Syringe, 3. Reactor tube /20 mm ID, 160 mm/, 4. Catalyst, 5. Thermocouple of temperature controller, 6. Covering iron, 7. Heat insulator cotton-wool, 8. Glass beads, 9. Thermocouple of temperature regulator, 10. Temperature regulator PID.

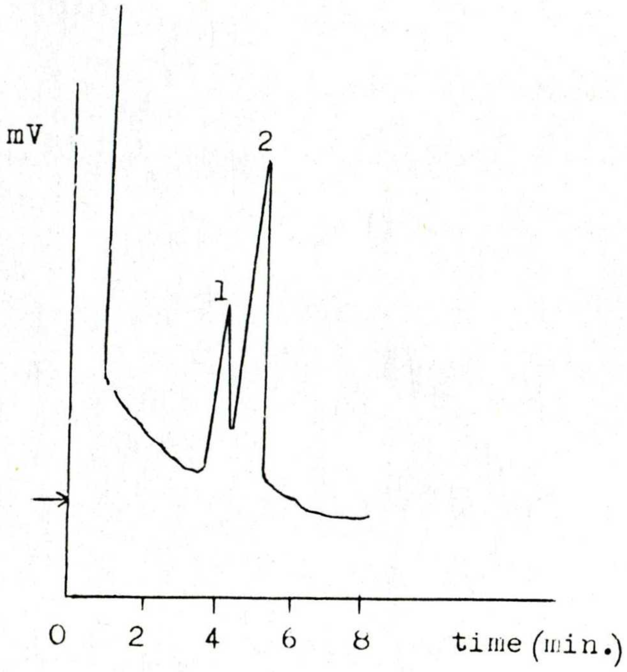


Fig. 2. Gas chromatographic analysis of the esterified reaction product from a 1:1 mixture of phenylacetic acid and benzyl methyl ketone.

1. benzyl methyl ketone
2. methyl phenylacetic acid

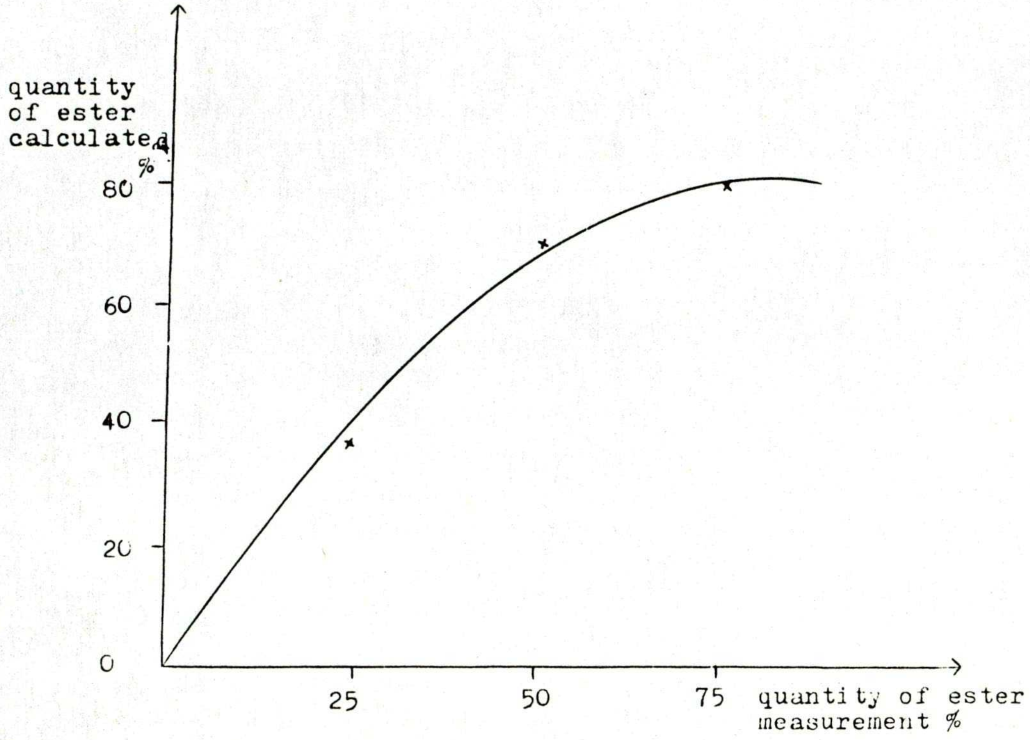


Fig. 3. Calibration curve after esterification of various ratios of phenylacetic acid and benzyl methyl ketone.

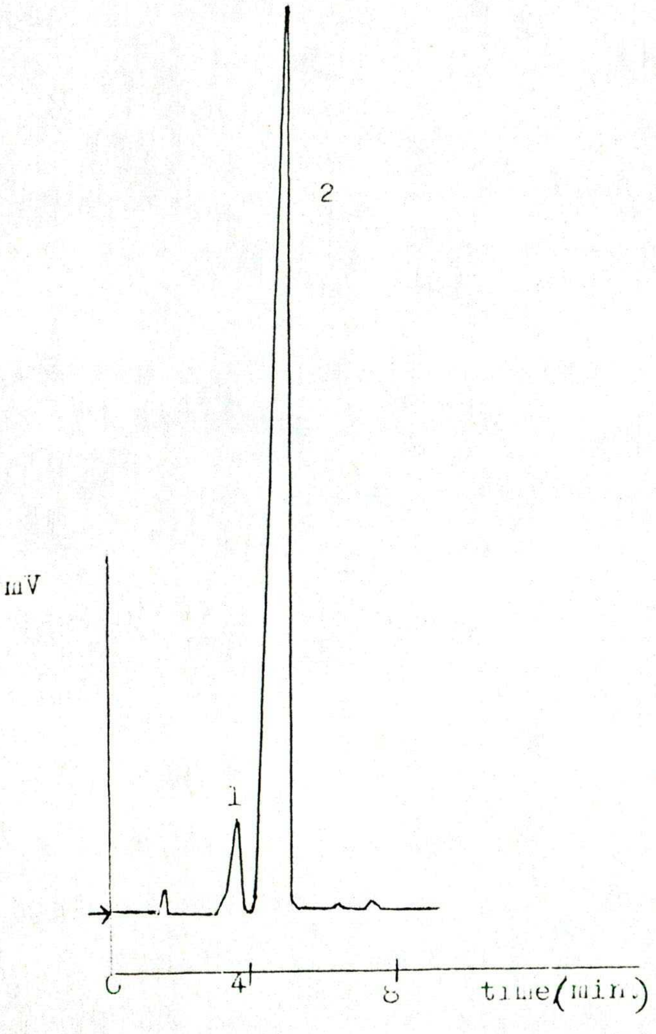


Fig. 4. Gas chromatographic analysis of 2-methyl-3--phenyloxirane

1. <u>cis</u>-2-methyl-3-phenyloxirane
2. <u>trans</u>-2-methyl-3-phenyloxirane

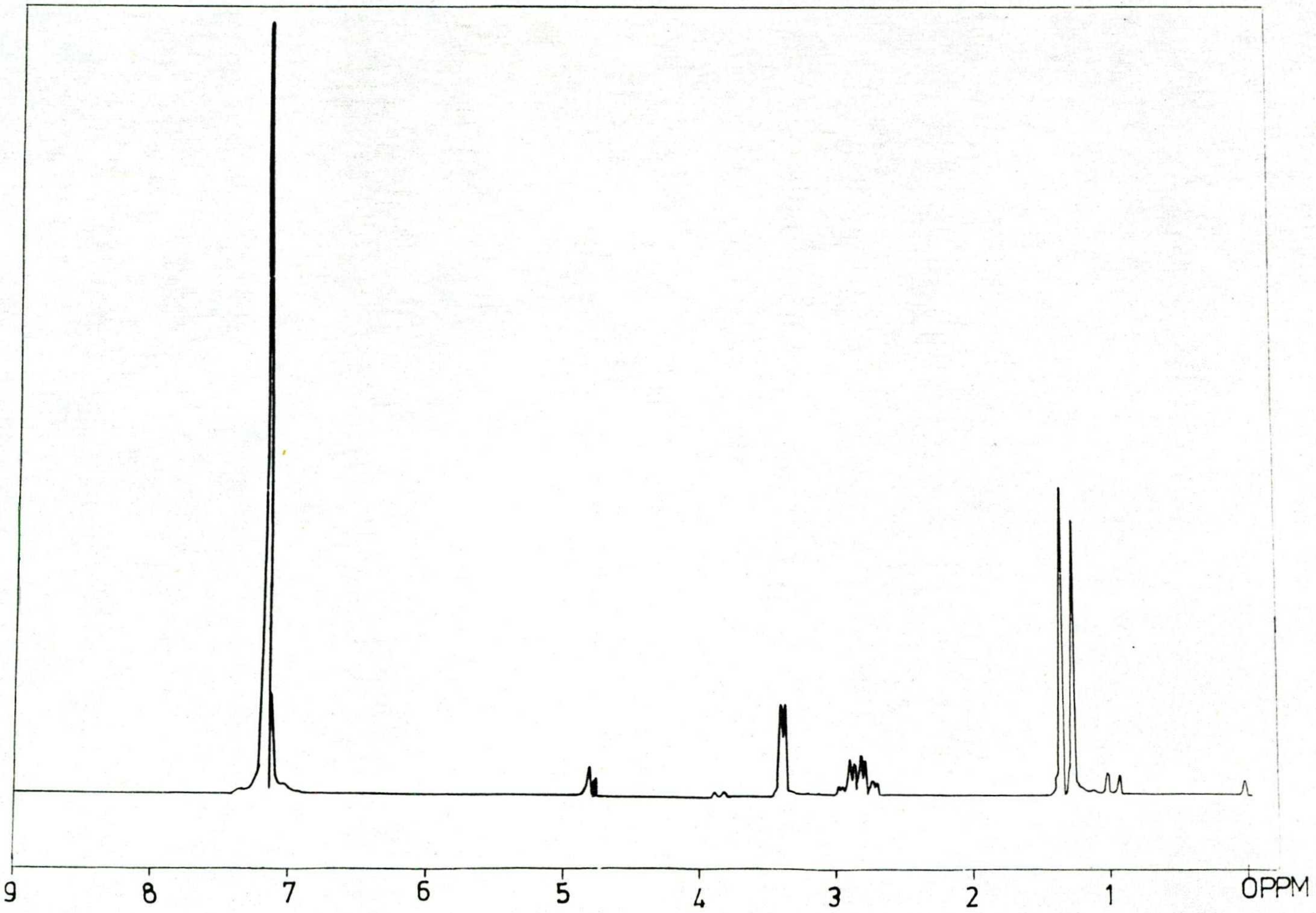


Fig. 5. NMR spectrum of 2-methyl-3-phenyloxirane

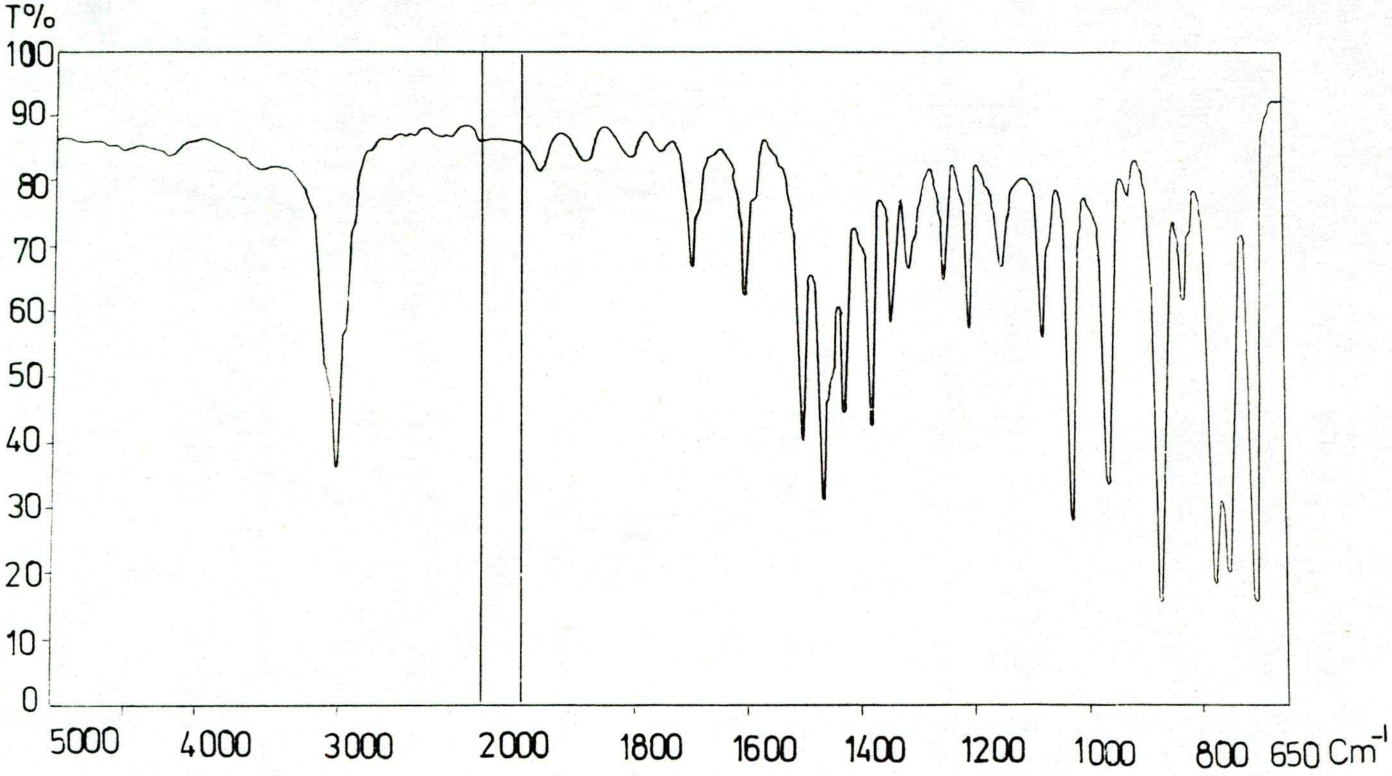


Fig. 6. IR spectrum of 2-methyl-3-phenyloxirane

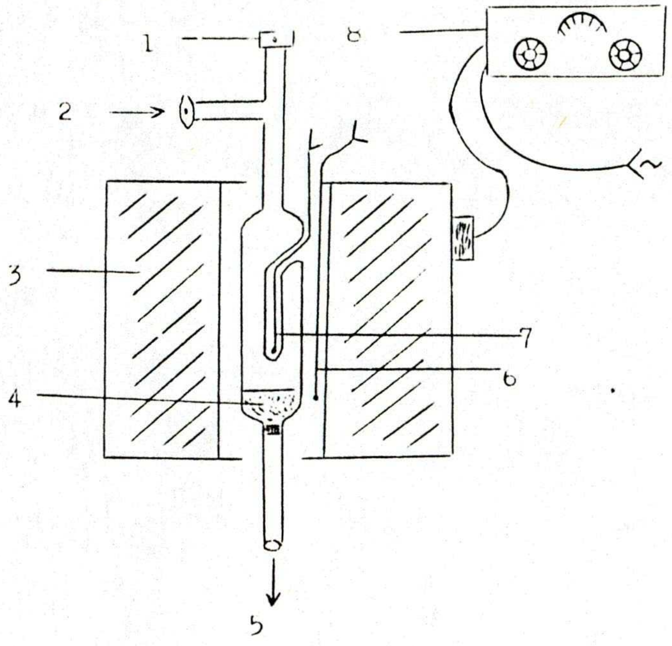


Fig. 7. Outline scheme of microreactor

1. Injector port, 2. Carrier gas, 3. Heater, 4. Catalyst, 5. To GLC column, 6. Thermocouple of temperature controller, 7. Thermocouple for measuring of temperature, 8. Temperature regulator PID.

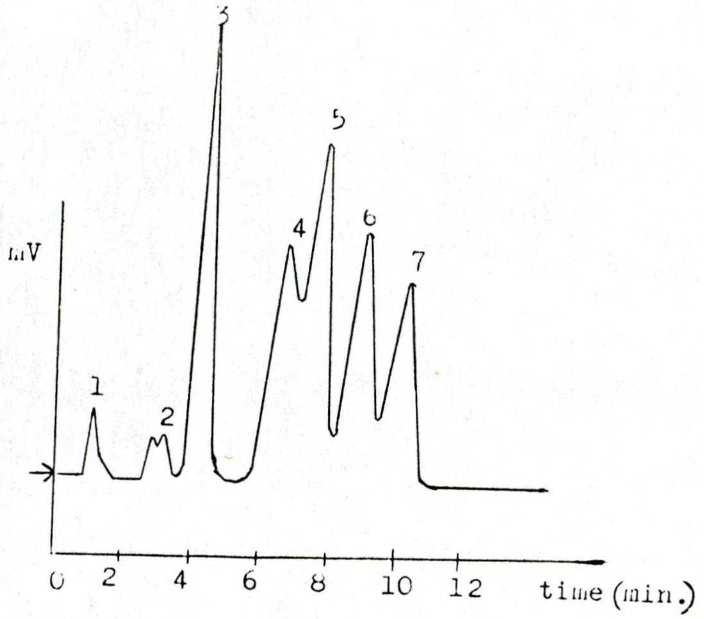


Fig. 8. Chromatogram of the possible products of 2-methyl-3-phenyloxirane and its catalytic transformation isomers.

1. 1-phenylpropene, 2. Cis-isomer of oxirane, 3. Trans-isomer of oxirane, 4. Propiophenone, 5. Benzyl methyl ketone, 6. 1-phenyl-2-propanol, 7. 1-phenyl-1-propanol.

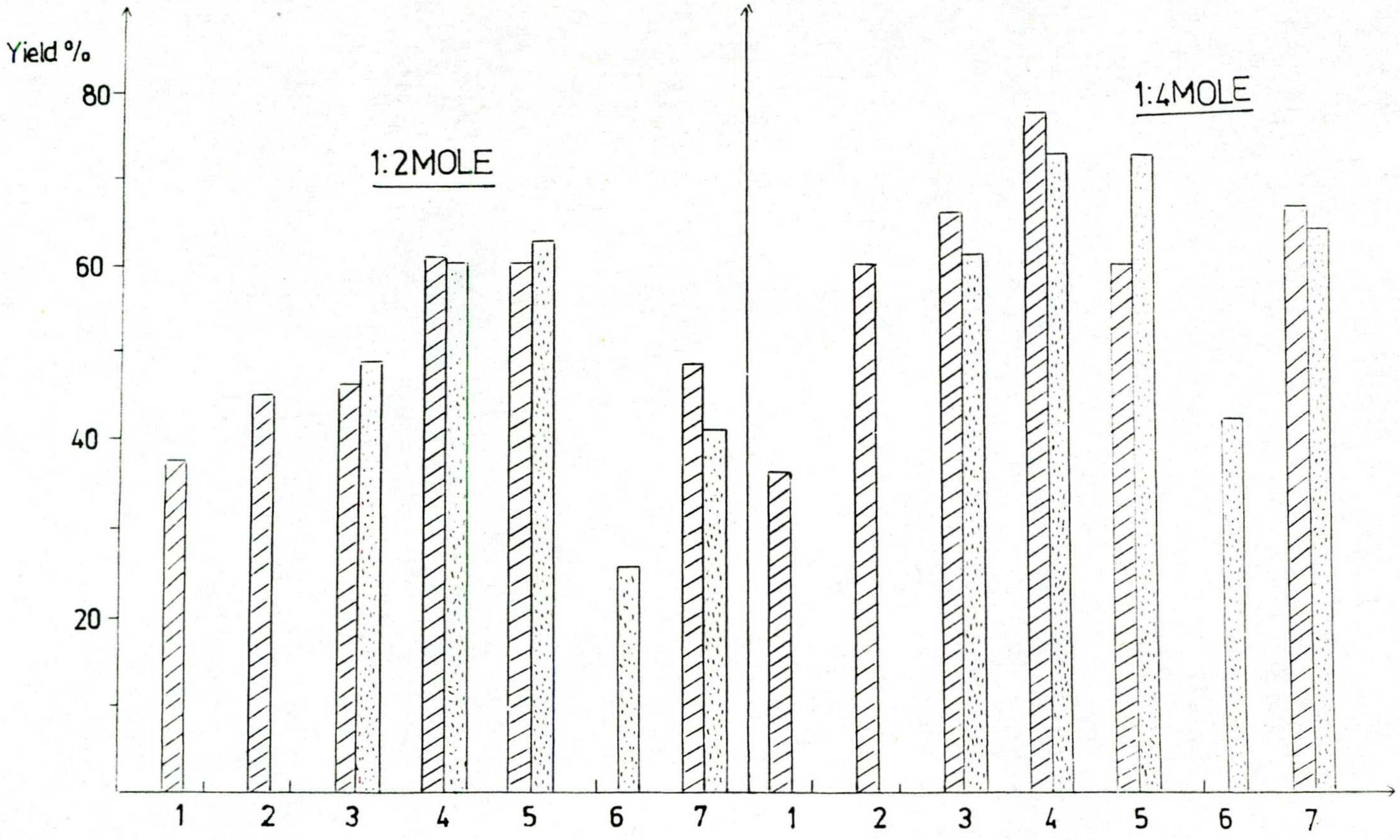
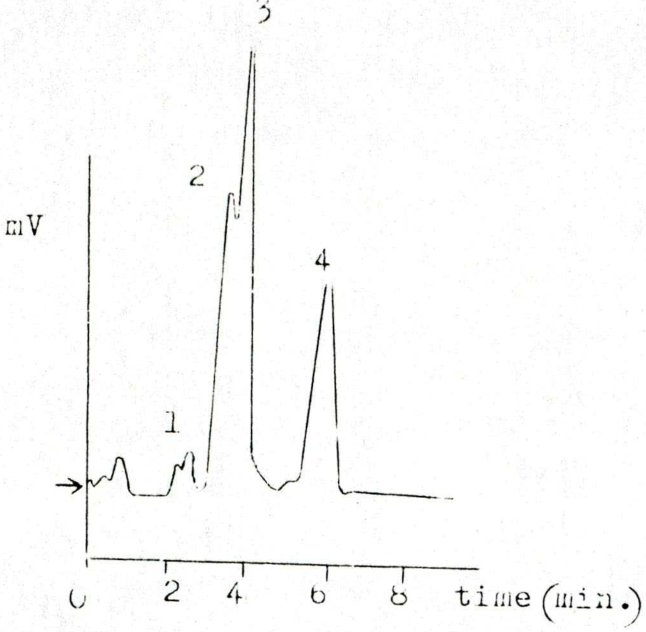


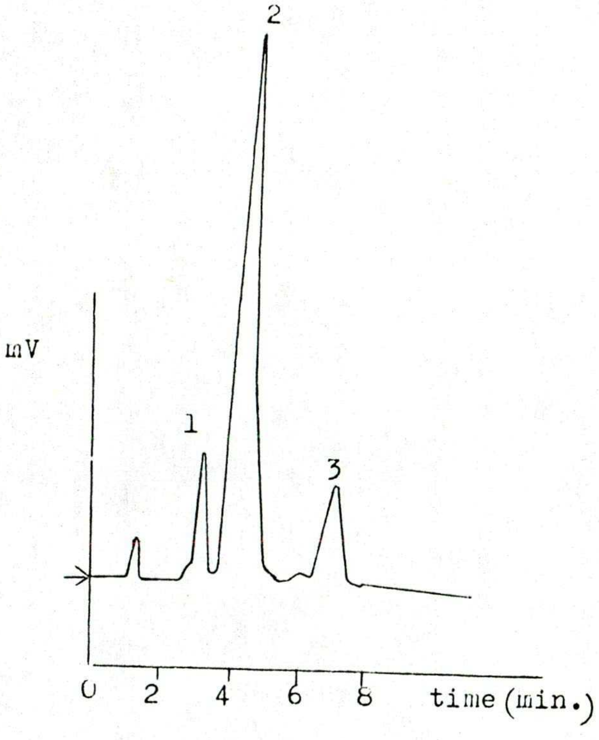
Fig. 9. Percentage yields of benzyl methyl ketone over different metal oxide catalysts, at two different molar ratios temperatures

▨ at 420°C   1. 30% ThO_2-pumice, 2. 30% ThO_2-Al_2O_3, 3. MnO,
░ at 450°C   4. Cr_2O_3-ZnO, 5. NiO-MgO, 6. Bi_2O_3-MoO_3-SiO_2,
7. Al_2O_3.



10.a.

1. Cis-oxirane
2. Trans-oxirane
3. 2-phenylpropionaldehyde
4. Benzyl methyl ketone



10.b.

1. Cis-oxirane
2. Trans-oxirane
3. Benzyl methyl ketone

Fig. 10. Chromatographic analysis of 2-methyl-3-phenyloxirane and its transformation products over γ-Al_2O_3 /a/ and SiO_2 /b/. Temperature: 400°C. Sample injected 2 μl.

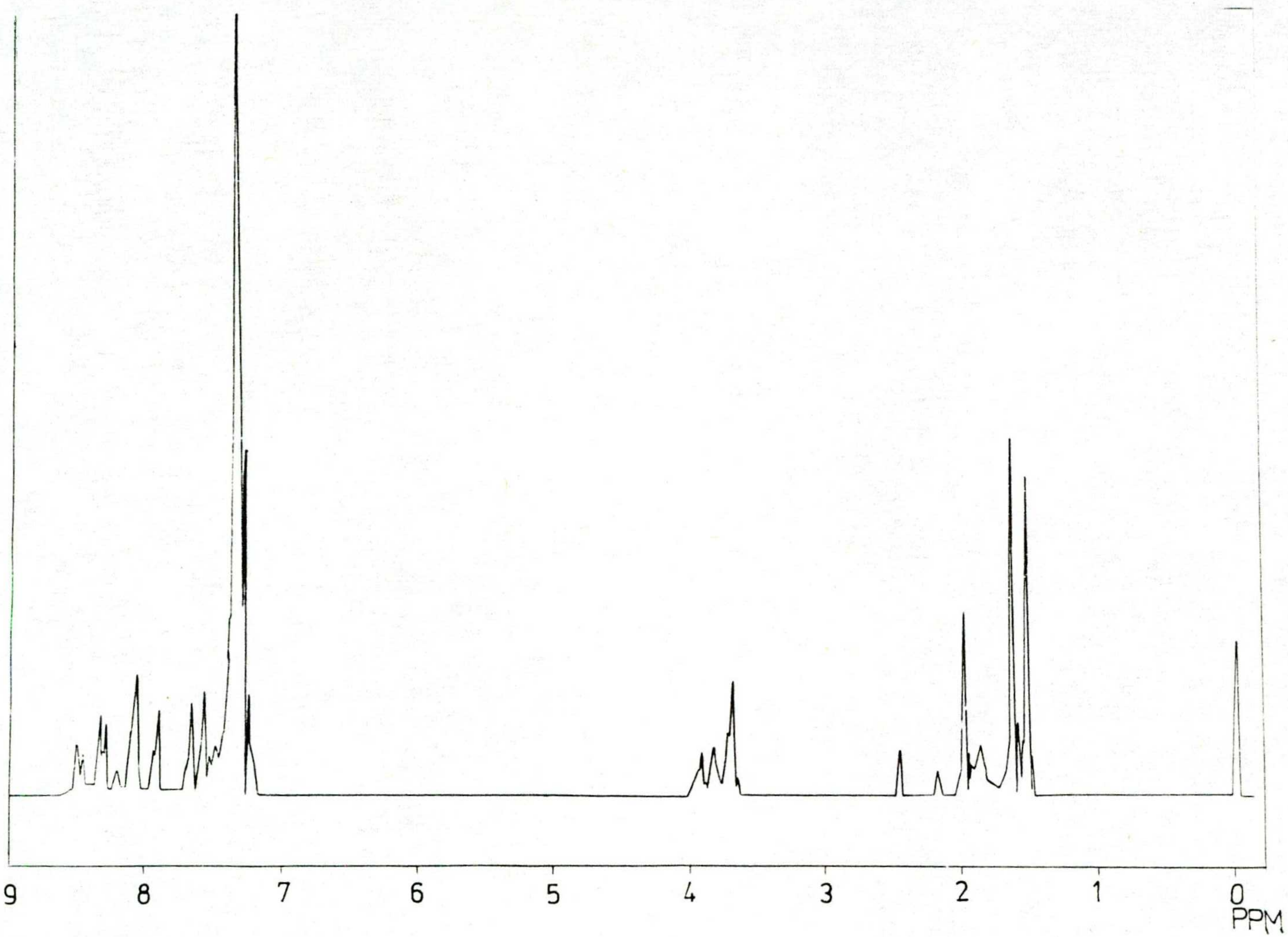


Fig. 11. NMR spectrum of reaction product

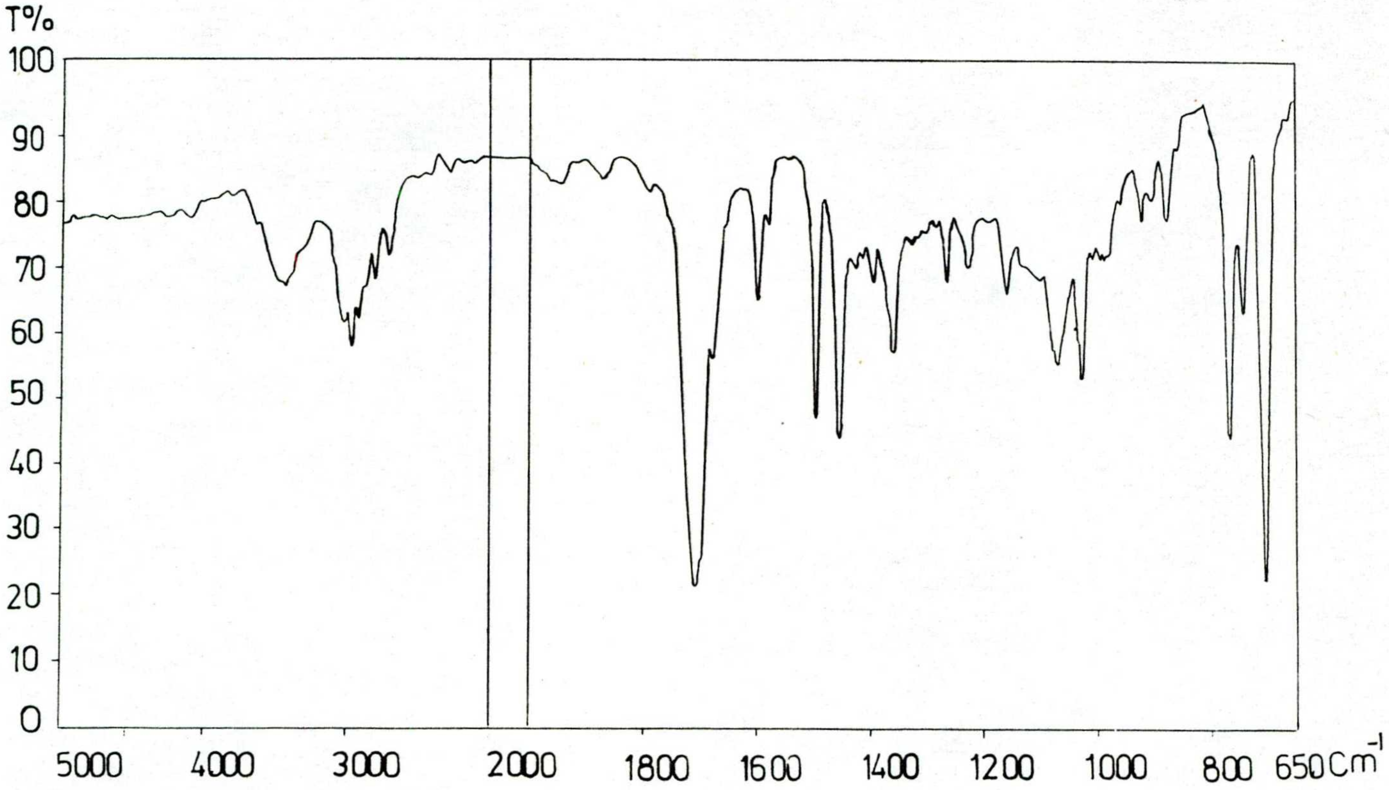


Fig. 12. IR spectrum of reaction product

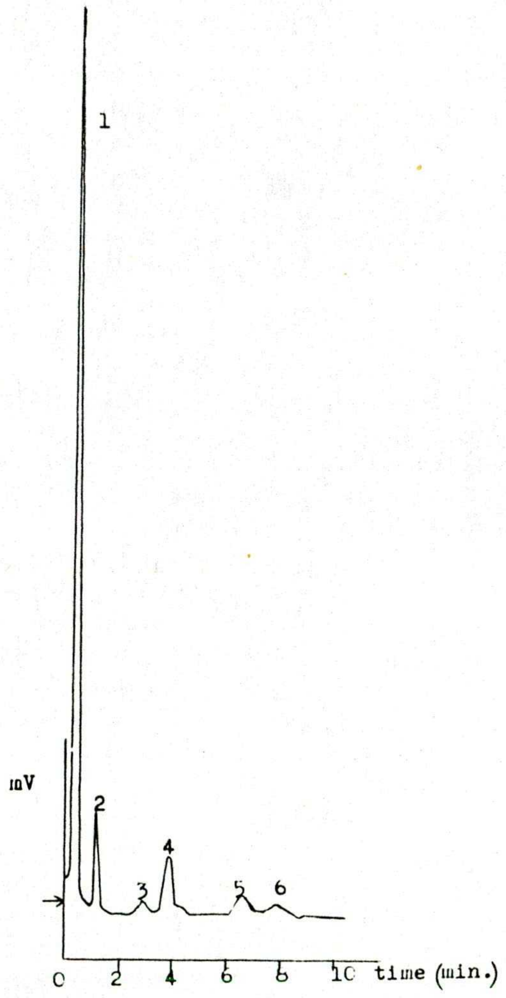
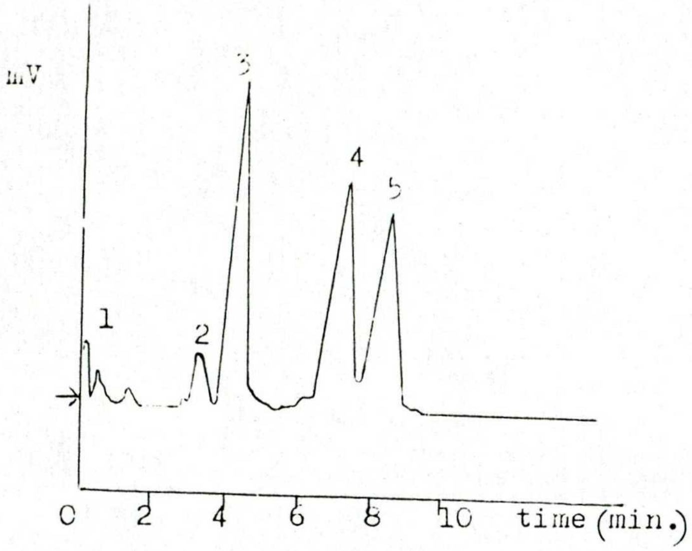
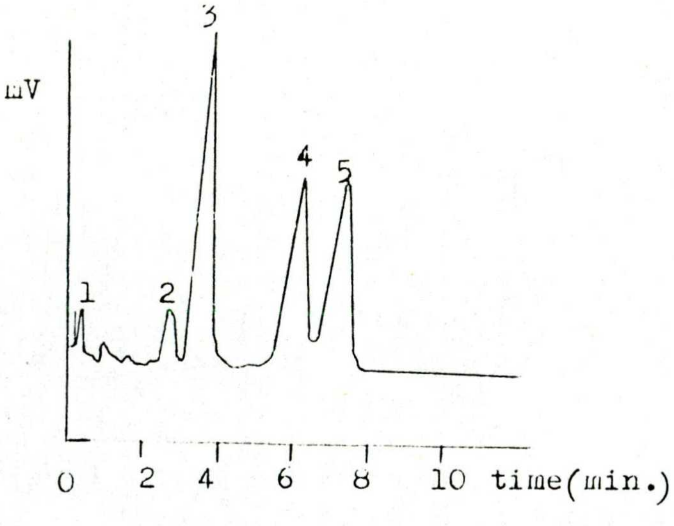


Fig. 13.a. Analysis of transformation products over 3% Ni/Cab-O-Sil. Temperature: 260°C, Sample injected: 1 μl.
1. 1-phenylpropane, 2. 1-phenylpropene, 3. _cis_-oxirane, 4. _trans_-oxirane, 5. benzyl methyl ketone, 6. 1-phenyl-2-propanol.



13.b.



13.c.

Fig. 13.b.c. Analysis of transformation products over 3% Pd/Cab-O-Sil /b/ and 3% Pt/Cab-O-Sil /c/. Temperature: 260°C. Sample injected: 2 µl. 1. 1-phenylpropane and 1-phenylpropene, 2. cis-oxirane, 3. trans-oxirane, 4. benzyl methyl ketone, 5. 1-phenyl-2-propanol.

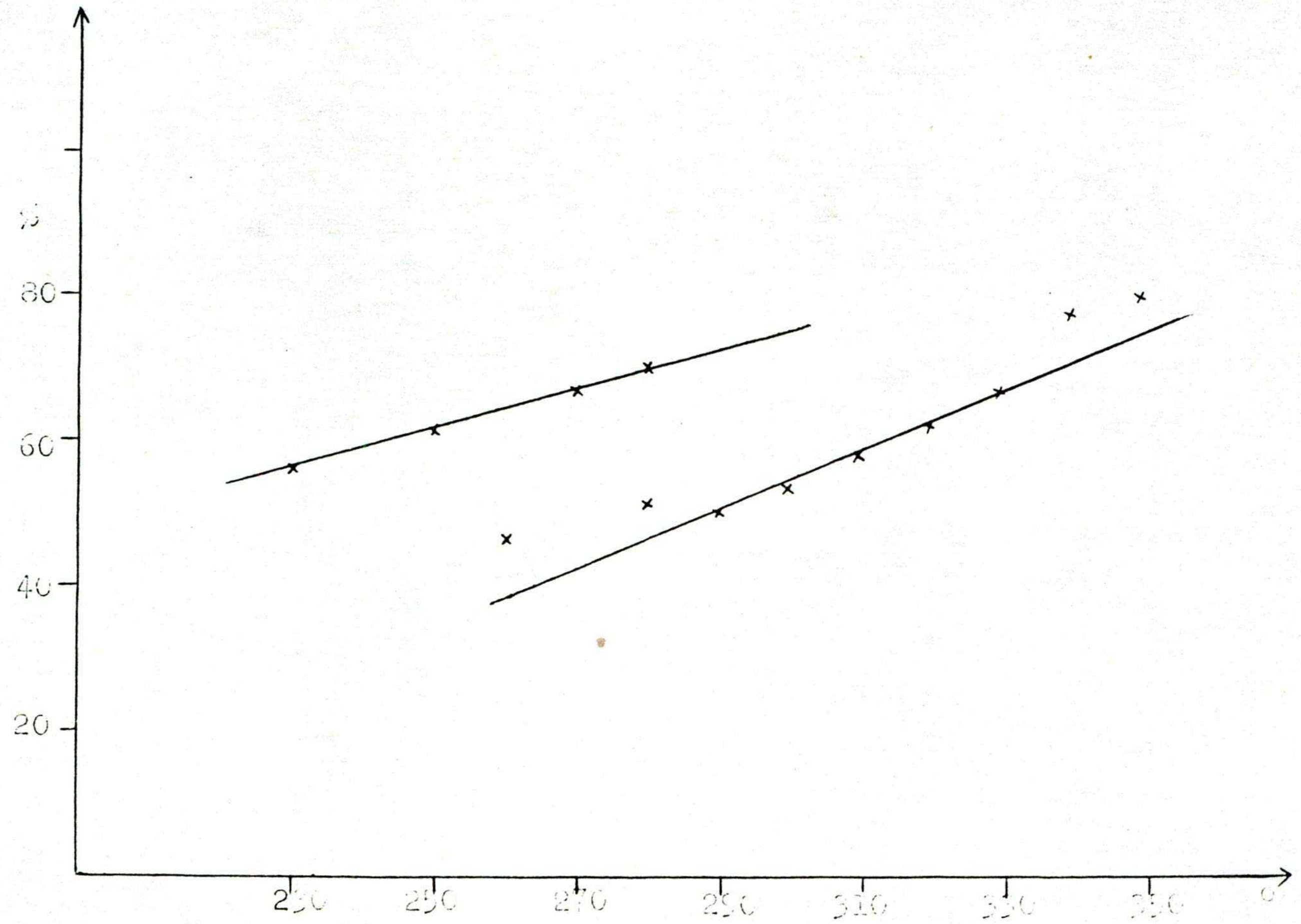


Fig. 14. The catalytic activity and conversion of 2-methyl-3-phenyl-oxirane as functions of temperature /Pt/Cab-O-Sil, 10mg/.

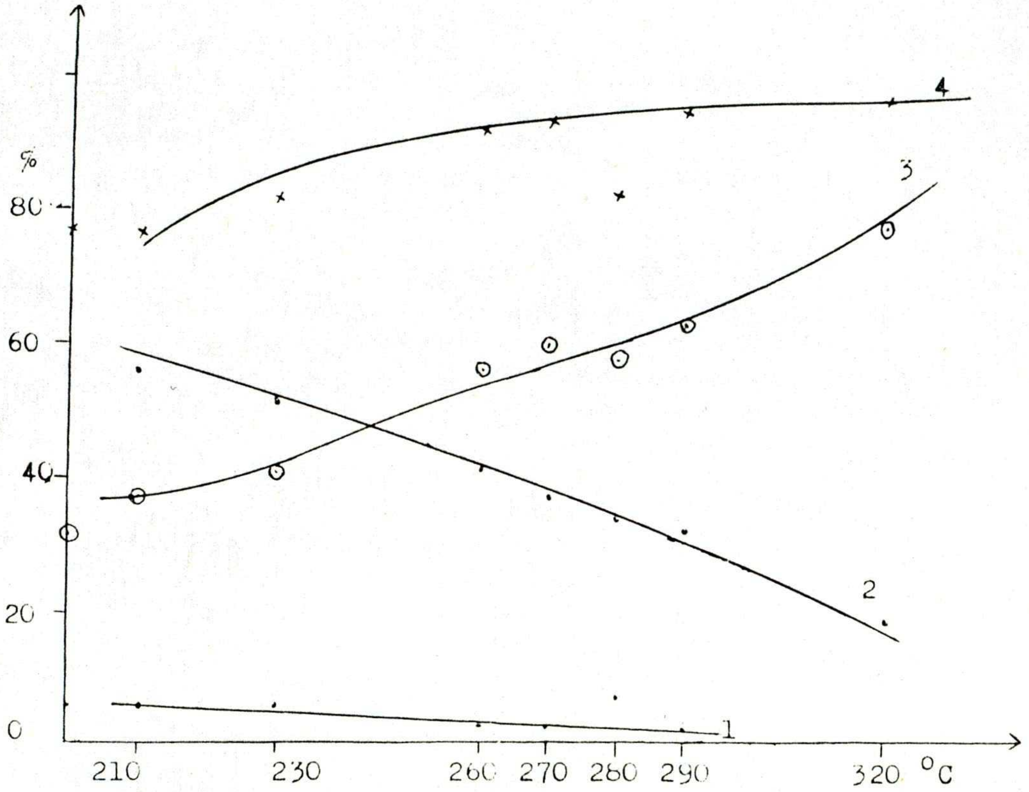


Fig. 15.a. Variation of the product composition as a function of temperature in a/First activation, /Pt/Cab-O-Sil, 10 mg/.

1. <u>cis</u>-oxirane, 2. 1-phenyl-2-propanol, 3. benzyl methyl ketone, 4. <u>trans</u>-oxirane.

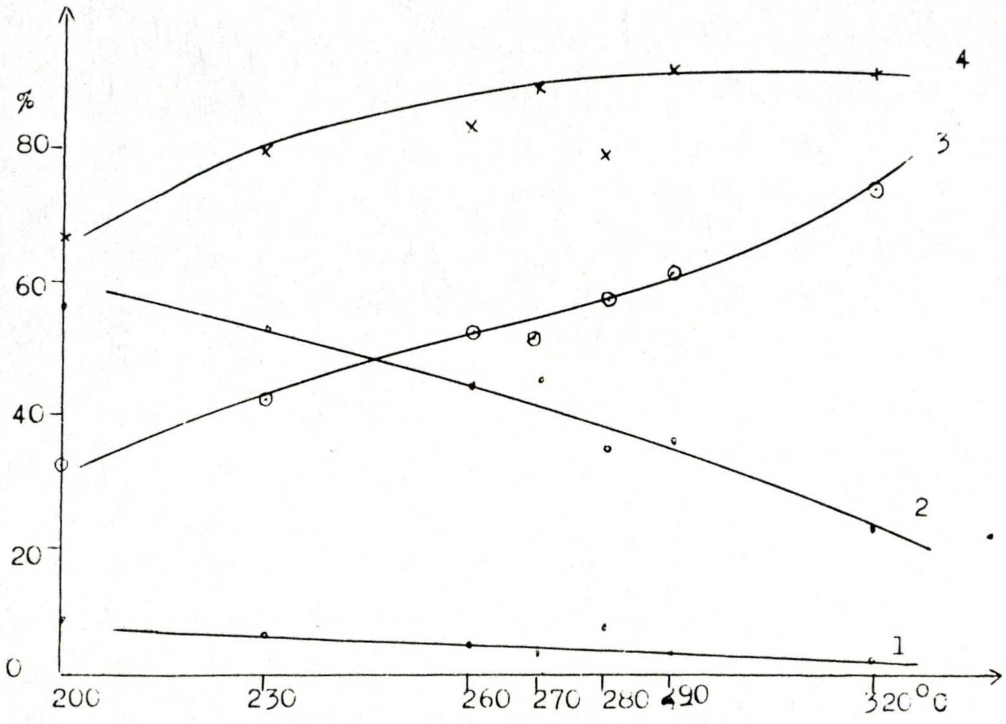


Fig. 15.b. Variation of the product composition as a function of temperature in /b/ Second activation /Pt/Cab-O-Sil, 10mg/.

1. cis-oxirane, 2. 1-phenyl-2-propanol, 3. benzyl methyl ketone. 4. trans-oxirane.

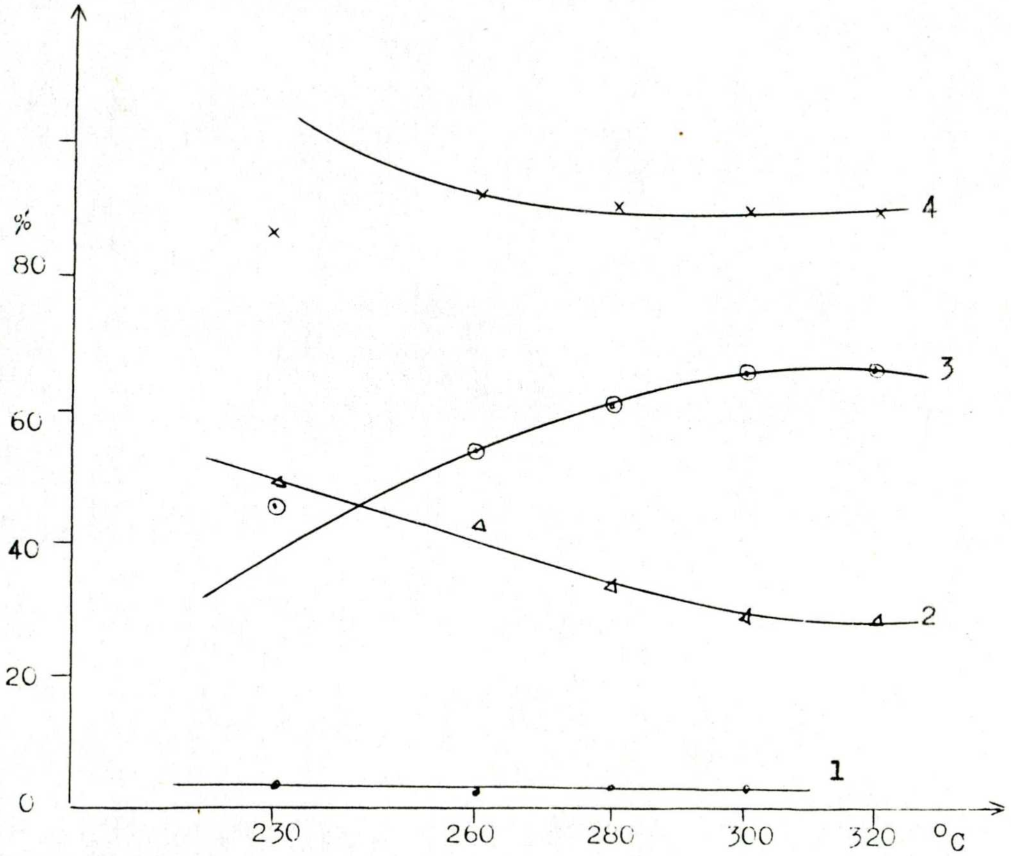


Fig. 16. Variation of the product composition as a function of temperature without activation /Pt/Cab-O-Sil, 10 mg/.

1. *cis*-oxirane, 2. 1-phenyl-2-propanol, 3. benzyl methyl ketone, 4. *trans*-oxirane.

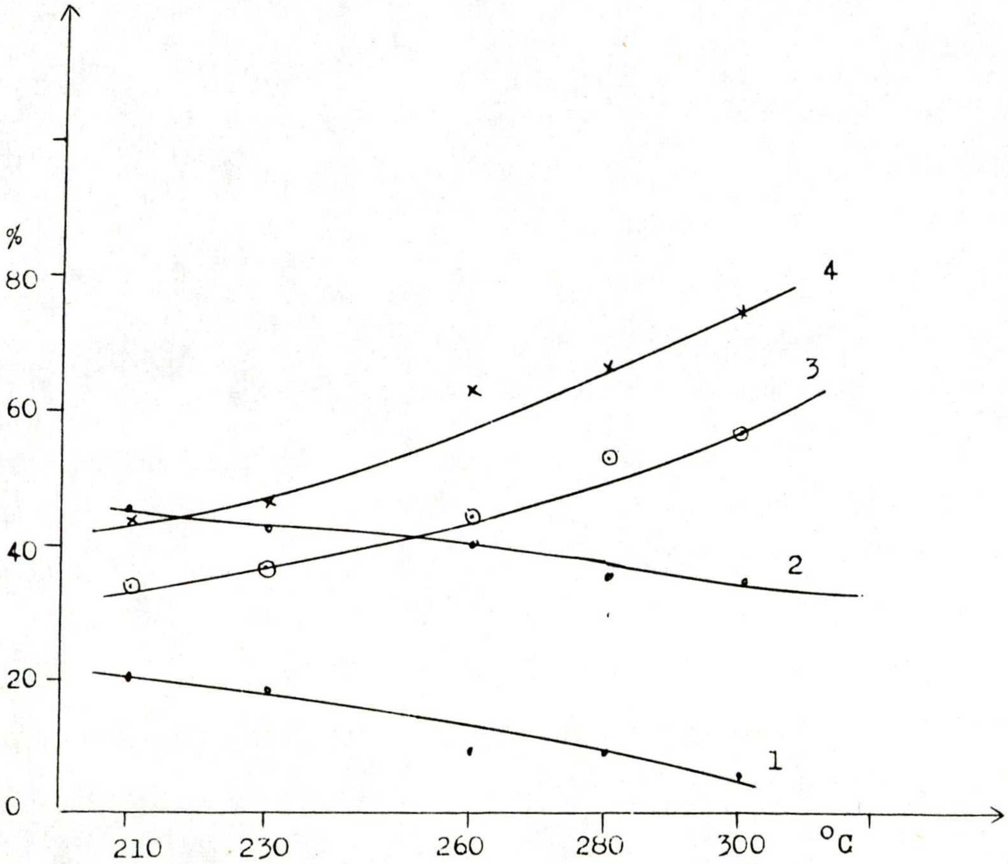


Fig. 17. Variation of the product composition as a function of temperature /Pt/Cab-O-Sil, 5 mg/.

1. cis-oxirane, 2. 1-phenyl-2-propanol,
3. benzyl methyl ketone, 4. trans-oxirane.

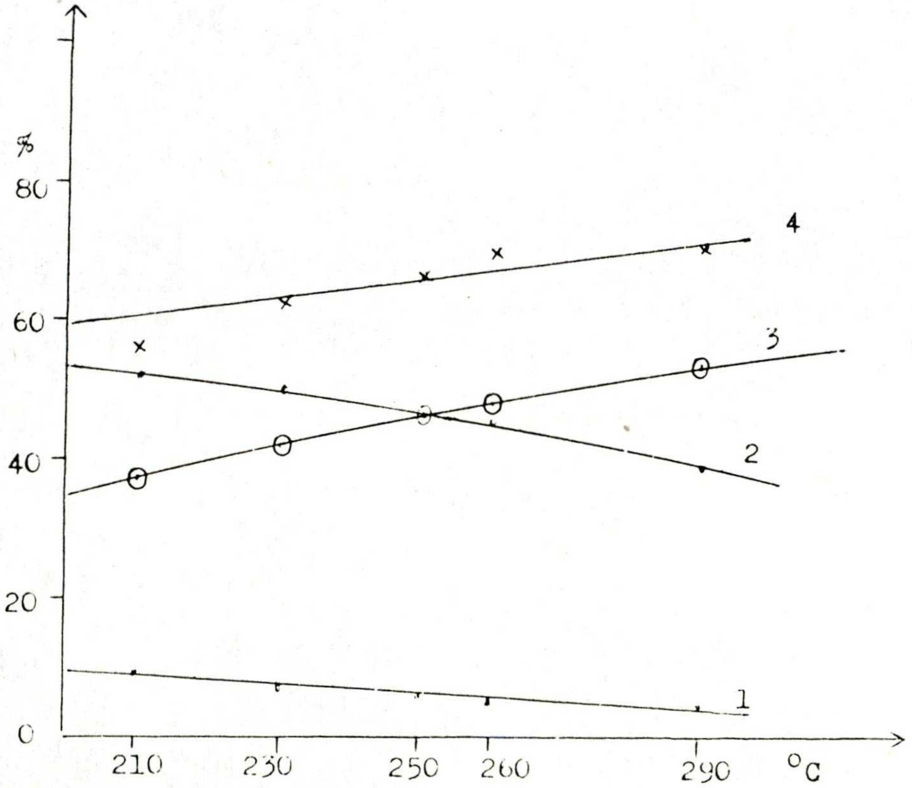


Fig. 18.a. Variation of the product composition as a function of temperature /Pd/Cab-O-Sil, 3 mg/.

1. cis-oxirane, 2. 1-phenyl-2-propanol,
3. benzyl methyl ketone, 4. trans-oxirane.

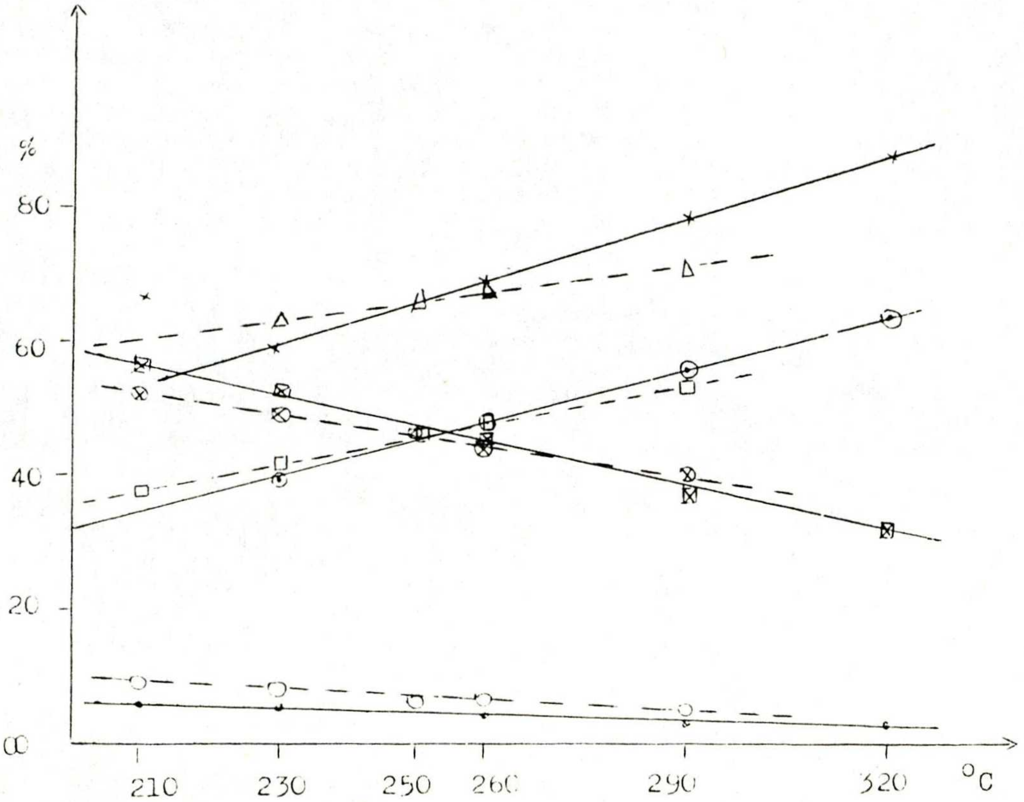


Fig. 18.b. Variation of the product composition as a function of temperature /Pd/Cab-O-Sil, 3 and 5 mg/.

•,O = *cis*-oxirane ---- = 3 mg
⊠,⊗ = 1-phenyl-2-propanol —— = 5 mg
⊙,□ = benzyl methyl ketone
X,Δ = *trans*-oxirane

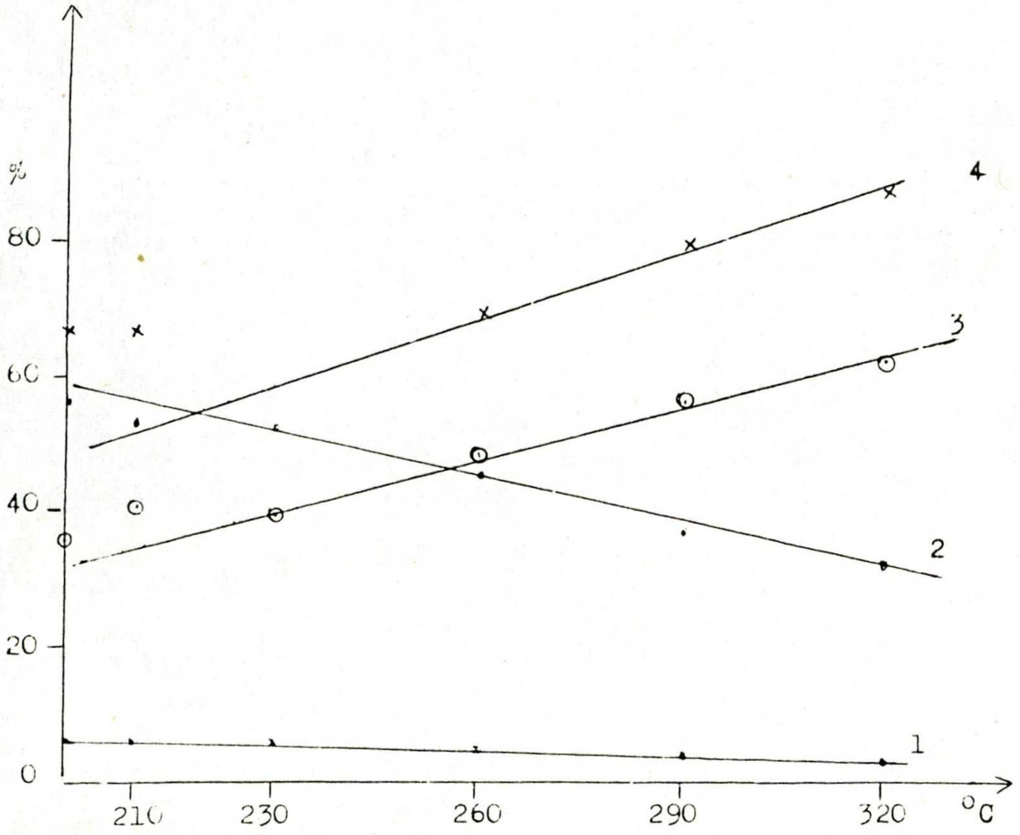


Fig. 19.a. Variation of the product composition as a function of temperature /Pd/Cab-O-Sil, 5 mg/.

1. cis-oxirane, 2. 1-phenyl-2-propanol, 3. benzyl methyl ketone, 4. trans-oxirane.

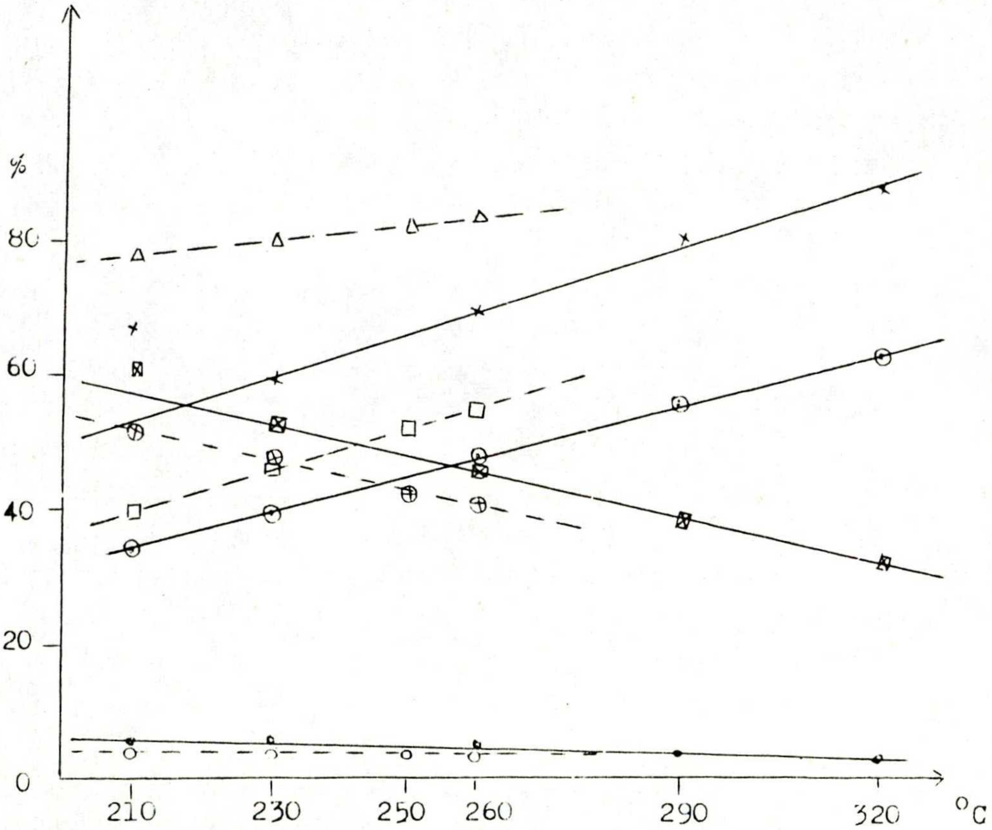


Fig. 19.b. Variation of the product composition as a function of temperature /Pd/Cab-O-Sil, 5 and 7 mg/.

•,○ = cis-oxirane
⊠,⊗ = 1-phenyl-2-propanol
⊙,□ = benzyl methyl ketone
x,△ = trans-oxirane

——— = 5 mg
- - - - - = 7 mg

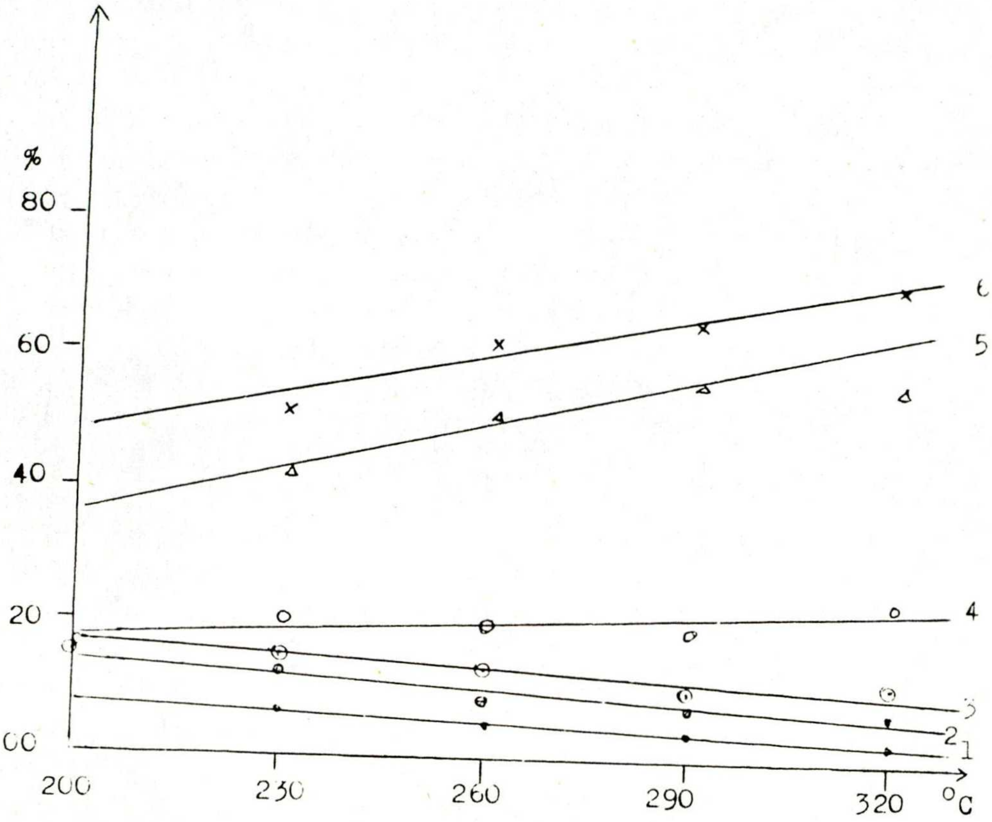


Fig. 20.a. Variation of the product composition as a function of temperature /Ni/Cab-O-Sil, 2.5 mg/.

1. 1-phenyl-2-propanol, 2. cis-oxirane,
3. benzyl methyl ketone, 4. 1-phenylpropene,
5. 1-phenylpropene, 6. trans-oxirane.

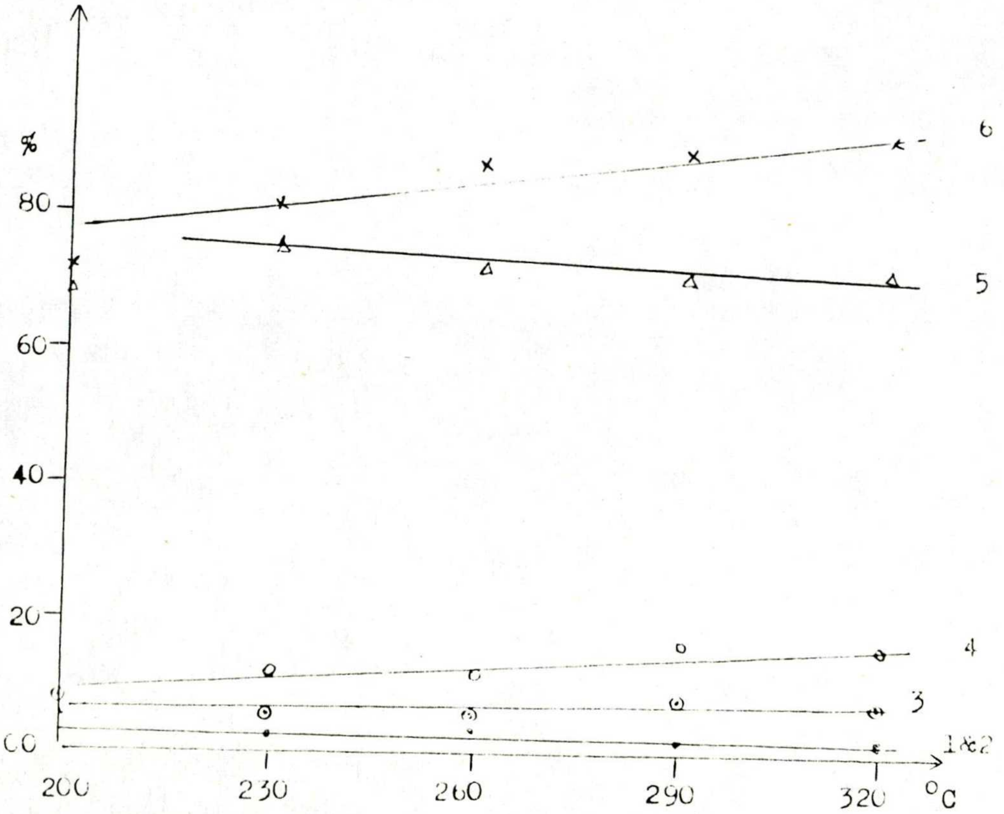


Fig. 20.b. Variation of the product composition as a function of temperature /Ni/Cab-O-Sil, 5 mg/.

1.& 2. 1-phenyl-2-propanol and <u>cis</u>-oxirane, 3. benzyl methyl ketone, 4. 1-phenylpropene, 5. 1-phenylpropane, 6. <u>trans</u>-oxirane.

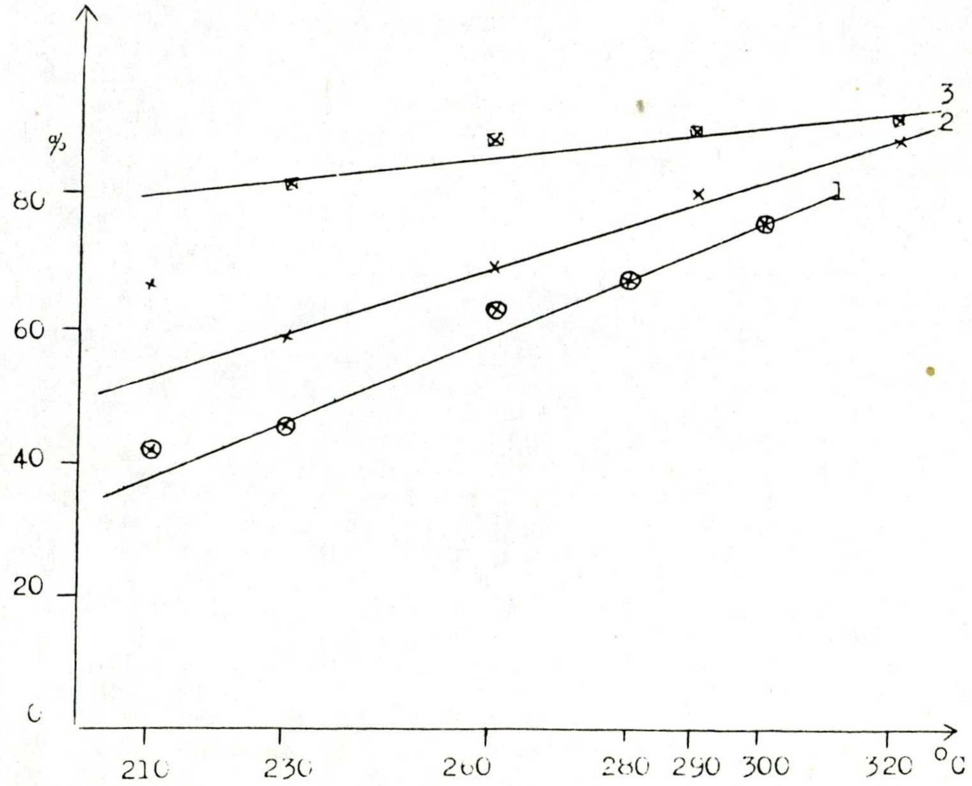


Fig. 21. Variation of the conversion of 2-methyl-3-phenyloxirane as a function of temperature over the three catalysts /5 mg/.

1. Pt/Cab-O-Sil, 2. Pd/Cab-O-Sil, 3. Ni/Cab-O-Sil.

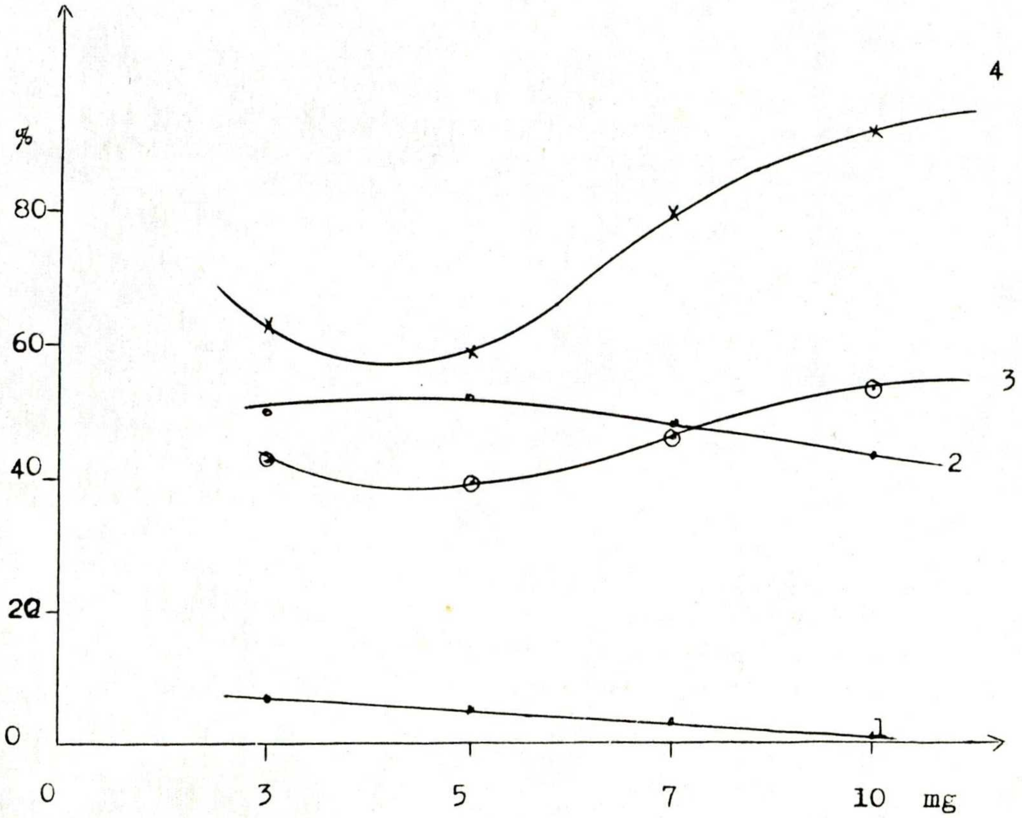


Fig. 22. Variation of the product composition as a function of the catalyst amount at a constant temperature of 230°C over Pd/Cab-O-Sil.

1. <u>cis</u>-oxirane, 2. 1-phenyl-2-propanol, 3. benzyl methyl ketone, 4. <u>trans</u>-oxirane.

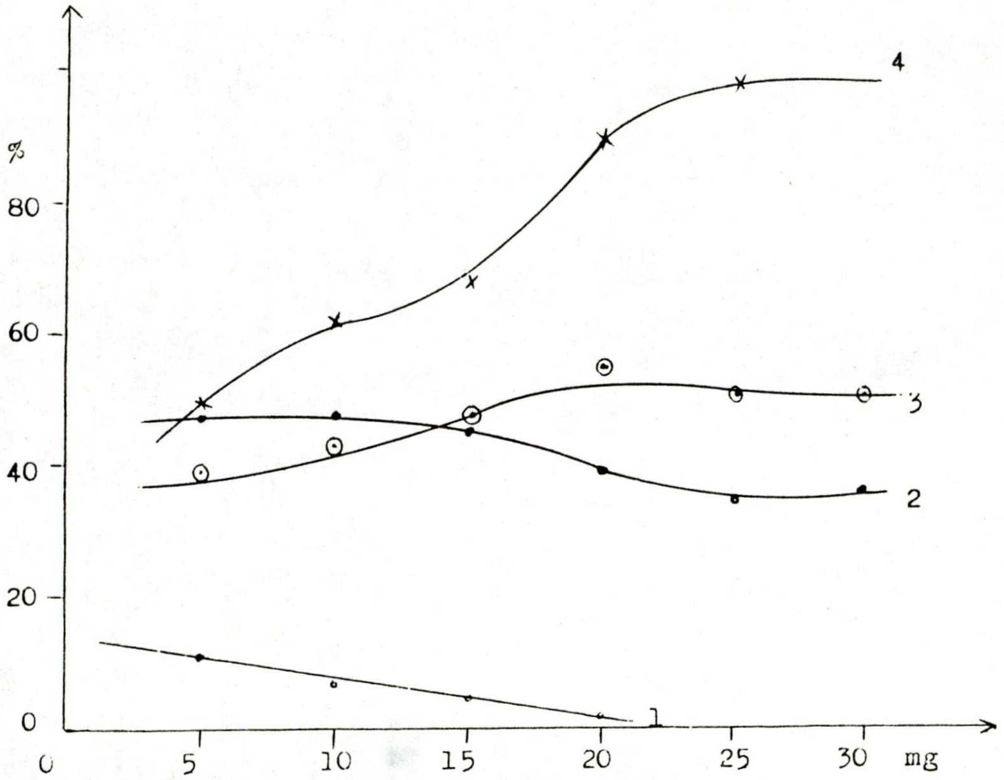


Fig. 23. Variation of the product composition as a function of the catalyst amount at a constant temperature of 250°C over Pt/Cab-O-Sil.

1. <u>cis</u>-oxirane, 2. 1-phenyl-2-propanol, 3. benzyl methyl ketone, 4. <u>trans</u>-oxirane.