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PART II

STUDIES ON THE ACTION OF SELENIUM DIOXIDE-HYDROGEN PEROXIDE IN TERTIARY BUTANOL ON TRITERPENOIDS HAVING ISO-PROPENYL GROUP.

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CHAPTER I

Oxidation of triterpenoids by hydrogen peroxide with selenium dioxide as catalyst are scanty. The reagents have, however, been used in the oxidation of acrolein[1], cyclo and bicyclo alkanones[2] and steroidal ketones[3,4]. In view of the fact that the succeeding chapter deals with oxidation of some triterpenoids by hydrogen peroxide in presence of selenium dioxide, it is pertinent to present in this chapter a brief account of different oxidative transformation reactions with selenium dioxide hydrogen peroxide and a mixture of selenium dioxide and hydrogen peroxide.

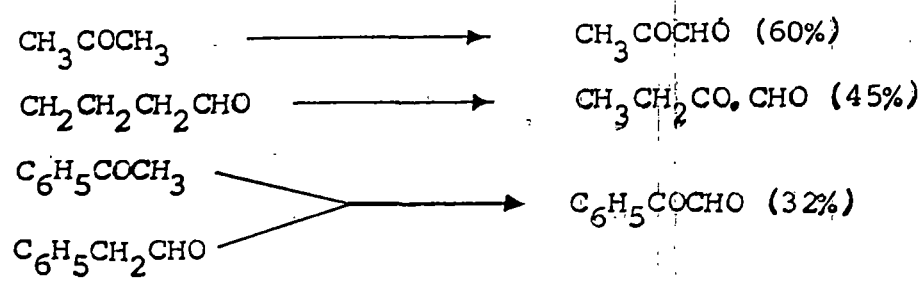
SECTION A: A SHORT REVIEW OF SELECTIVE OXIDATION WITH SELENIUM DIOXIDE

Selenium dioxide has been in use since Riley's pioneering work[5] in which he reported conversion of a monocarbonyl compound having an adjacent methylene unit to an α-dicarbonyl compound. The transformation of a ketone or an aldehyde to an α-dione, allylic oxidation and the conversion of a monoketone or a 1,4 diketone to an α,β-unsaturated ketone or to an ene-dione are the major areas in which the reagent has found rather wide application.

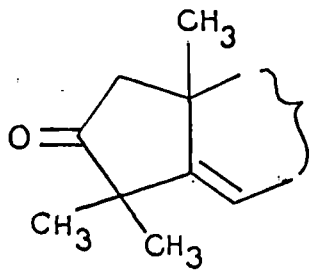
Formation of α-dione

Methylene groups adjacent to the carbonyl group of aldehydes and ketones would react with stoichimetric quantities of selenium dioxide to give α-diketones and keto aldehydes in

reasonable yields as shown below:



Excellent yields can be obtained by preventing the side or competing reaction. So the carbonyl compounds to be oxidised should contain such structural features which reduce or prevent side or competing reactions from occurring. Thus, A-nor allobetulone-3 and A-nor-4,4-dimethyl cholest-5-ene-3-one both of which have the monoketone unit partial structure 1 are oxidised to the diketone 2 in 87% and 92% yield[6]



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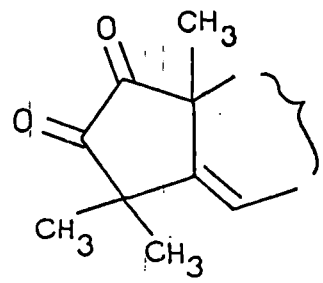

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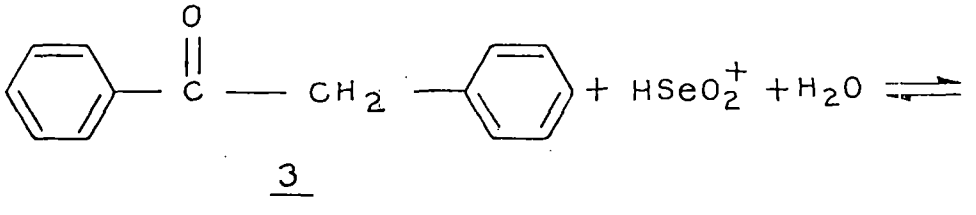
Mechanism:

The critical interpretation of the reaction was given by Corey and Schaefer[7], who studied the oxidation of deoxybenzoin in 70% acetic acid at 89.2°. They found the reaction to be second order; first order in ketone and first order in selenium (IV) reagent and to be catalysed by added strong acid. The presence of two ortho substituents on the ring adjacent to the carbonyl group did not depress the rate of acid catalysed oxidation which eliminated the possibility that carbonyl addition was involved. Replacement of the α-hydrogens of desoxybenzoin 3 by deuterium resulted in a several-fold decrease in rate in the acid catalysed process. On the basis of these and other data it was proposed that the rate determining step in the oxidation of desoxybenzoin 3 was the formation of enol selenite ester 3a directly from the ketone by a process mechanistically related to enolization in which the electrophile-nucleophile pairs were $HSeO_2^+$ or $H_3SeO_3^+$ and H_2O (acid catalysed process). The enol selenite ester 4 rearranges in a series of first steps to an α-selenite (II) keto-ester 5 and finally to benzil 6 (Scheme I).

Scheme I



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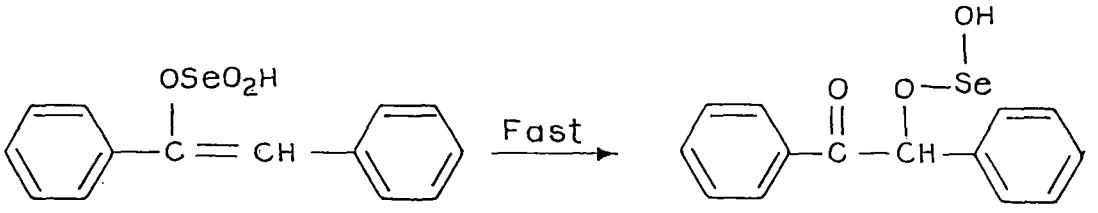

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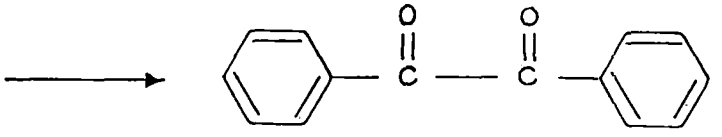

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Allylic oxidation

Guillemonat[8-12] had established that the course of selenium dioxide oxidation of alkenes could be predicted from the following rules:

(i) The oxidation always occurred to alpha to the most substituted end of the double bond.

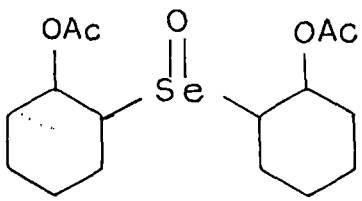
(ii) When the dobule bond was in a ring, whenever possible, oxidation occurred within the ring.

(iii) The order of preference for oxidation was $CH_2 > CH_3 > CH$.

(iv) When the double bond was terminal rather than the expected secondary alcohol or the derivative thereof the primary alcohol was formed with the migration of the double bond.

Though the inadequacy of Guillemonat's had been shown[13-15], the generalization is still valid with respect to site of attack in many cases. Another suggestion made by waters without any experimental support was that the reaction involved neutral radical species[16]. Schaefer, Horvath and Kelvin[17] had shown that the reaction was uneffected by inhibitors and, therefore, could not be radical chain. That no free radical was generated in the system had been pointed out by Trachtenberg et al[18] as the system was incapable of initiating polymerisation of acrylonitrile under conditions of temperature and concentration, where acrylonitrile is rapidly polymerised if a source of free radical is present.

Wiberg[19] established the selenoxides 7, were involved in the oxidation of cyclohexene in acetic acid-acetic anhydride reaction. Schaefer et al[17], however, showed that the analogous compound, 8, violated from the oxidation of 1,3 diphenyl propene, 9, decomposes to 1,3 diphenyl-2-propene-1-ol acetate, 10, at too slow a rate to account for the main course of oxidation. The main pathway must involve solvolysis of an allylic selenite ester, although the structure of the latter has not been vigorously established. They suggested the mechanism shown in Scheme II.



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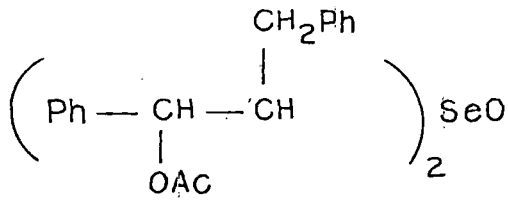

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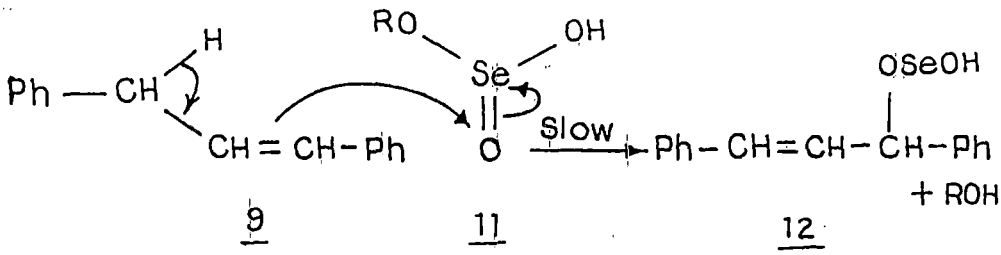
Scheme II



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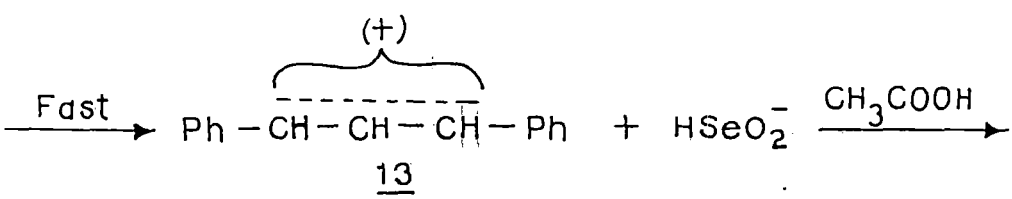

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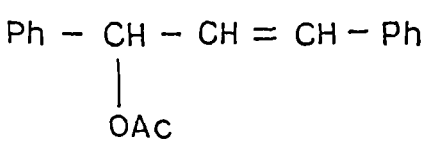

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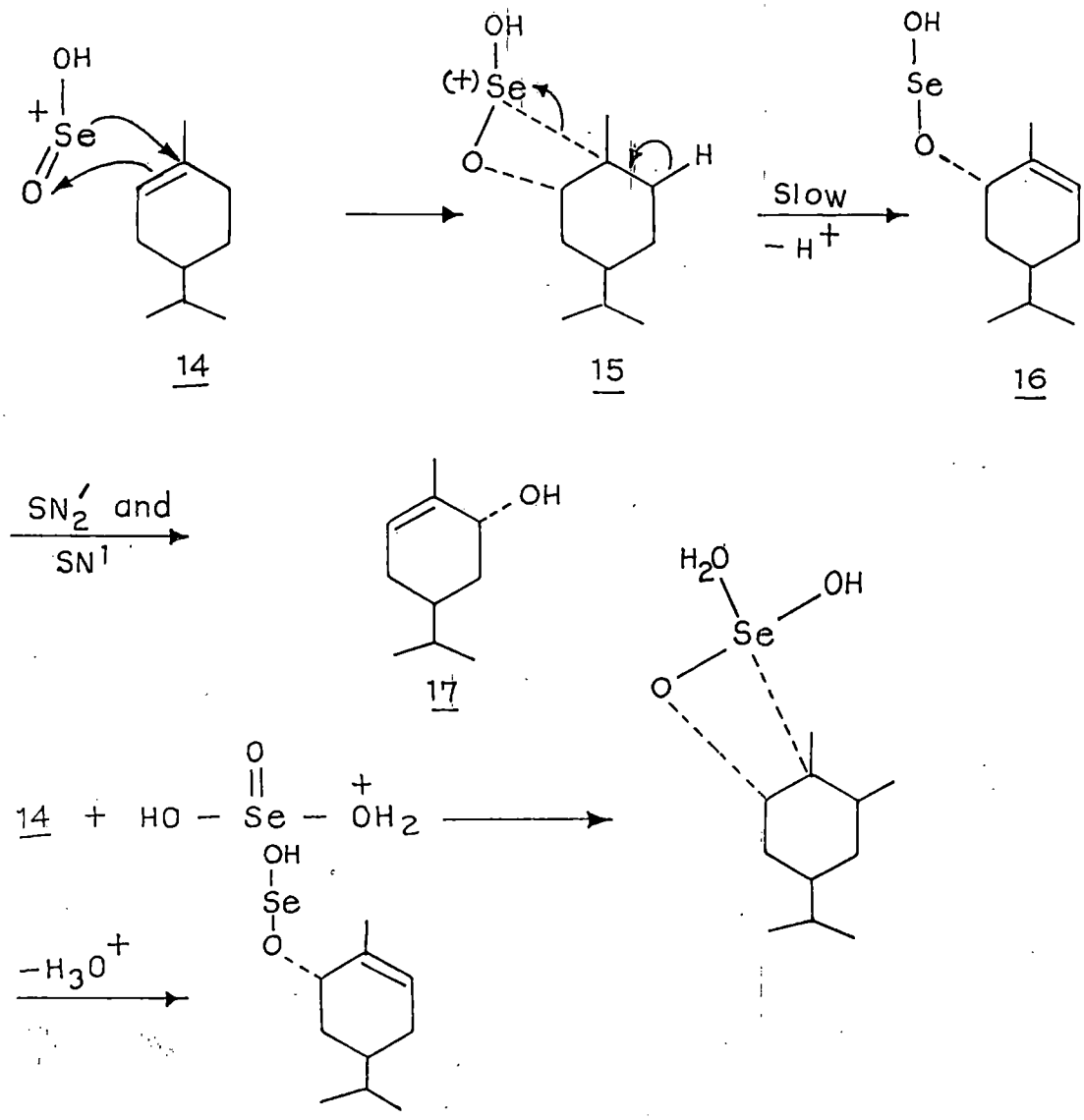
The rapid SN^1 of 12 was in agreement with the observation that 3-deuterium labelled at C-3 showed equilibration of C-1 and C-3. Furthermore the presence of a final solvolytic step was in agreement with observations on many systems. Thus, one obtained alcohols, acetates and ethers when the slenium dioxide oxidation was performed in water, acetic acid and alcohol respectively[13-15].

Finally mechanism proposed by Schaefer et al[17] did not explain the stereochemical result.

In order to explain the stereochemical results obtained by oxidation of a number of cyclohexenyl system, Trachtenberg et al[18] proposed the following mechanism as shown in Scheme III with D(+) -1-p-menthene as substrate.

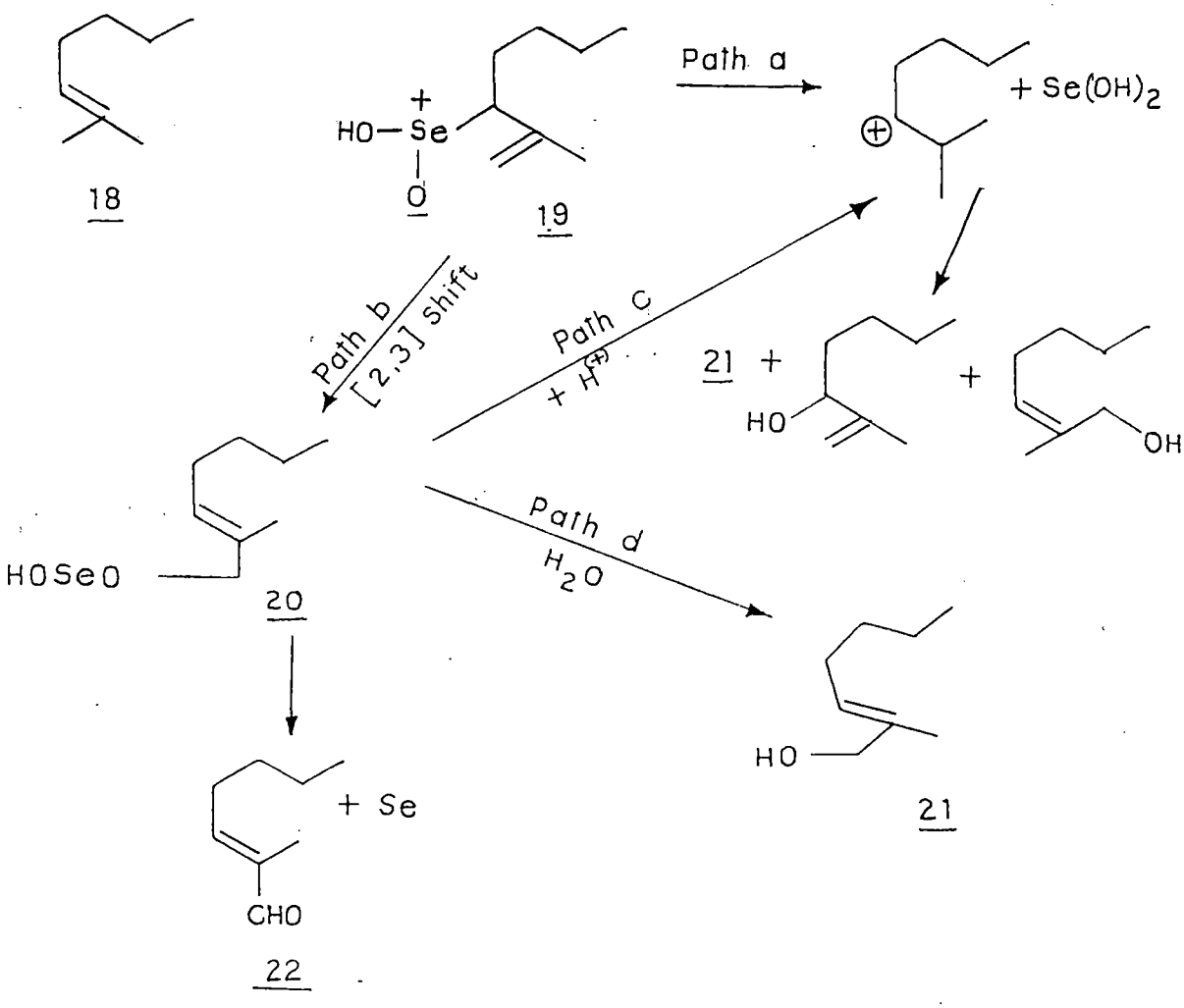
Scheme III



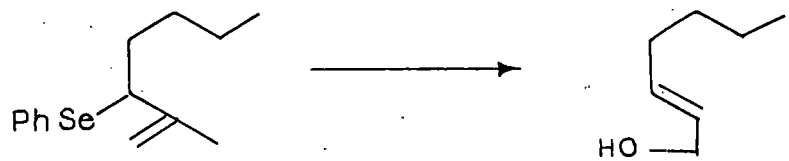
The first step does not imply a concerted 2+2 cycloaddition but rather a typical Markownikoff type electrophilic addition with attack occurring through oxygen to generate positive character at the tertiary carbon followed by cyclization.

Sharpless and Lauer[20] proposed different mechanism for allylic oxidation of olefins by selenium dioxide. As already discussed, Schaefer and Traehtenberg argue against involvement of allylic selenic acid, 19, because of the known inertness of benzylselenic acid to solvolysis. However, a [2,3] sigmatropic rearrangement (path b, Scheme IV) of allyl selenic acid, 19, to a selenium (II) ester, 20, occurred to Sharpless et al[20] as a likely alternative to the solvolysis pathway a. They suggested that the [2,3] sigmatropic shift indicated in the path b is a facile process (Scheme IV).

Scheme IV



The authors had noted that Buchi and Wuest[21] had established that SeO_2 selectively attacks trisubstituted olefins such as, 18, to give only the (E) - alcohol, 21. The allyl selenic acid, 19, must lead stereoselectively to the (E)-ester of 20 if the proposed rearrangement is correct. The mechanism was verified from the conversion of alkyl phenyl selenide 24 to 21.



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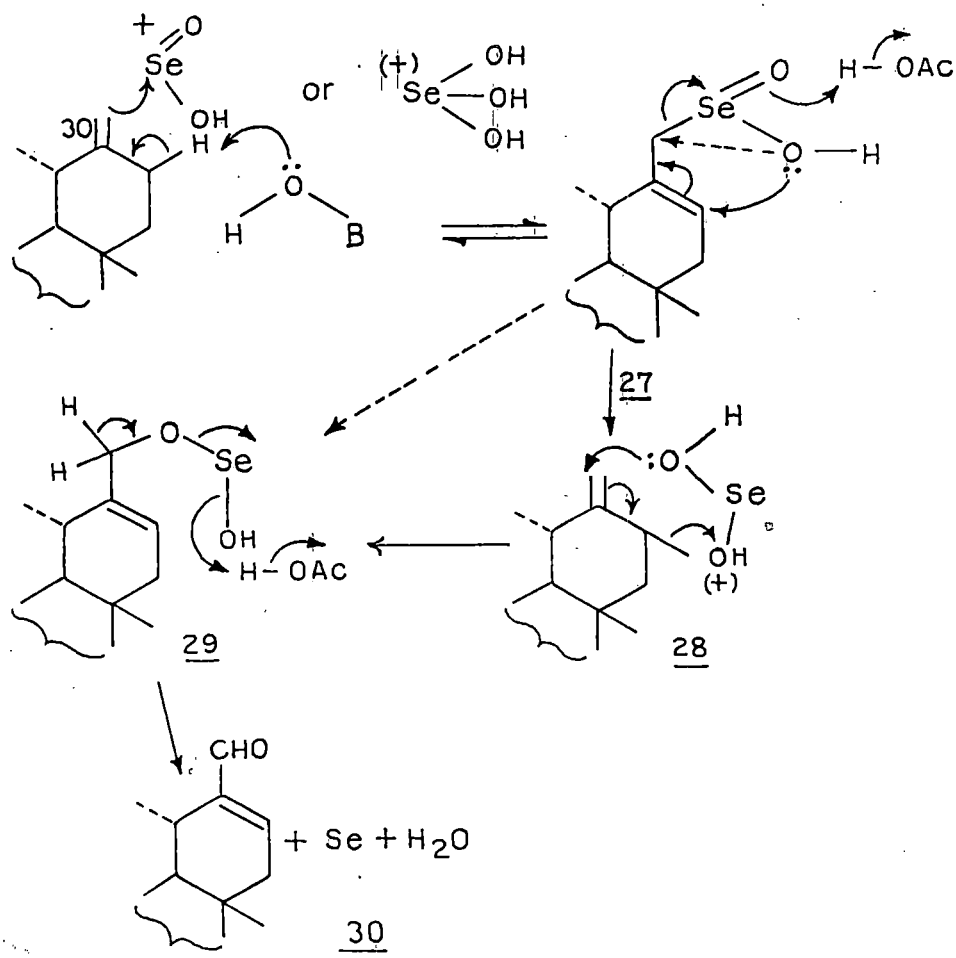
Talapatra et al[22] studied the oxidation of taraxastene 25 and ψ-taraxastene 26 and gave the mechanism for the formation of the corresponding aldehyde[23] shown in Scheme V.

Scheme V



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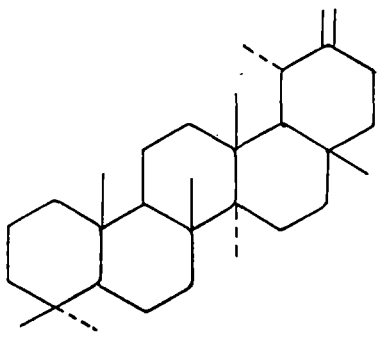
The electrophilic attack of $H\overset{+}{S}eO_2$ or $H_3\overset{+}{S}eO_3$ on the olefinic C-30 with simultaneous or subsequent nucleophilic attack on the allylic C_{21} - H leads to the formation of an unstable Se(IV) complex 27 possessing the more stable double bond parallel to the trans D/E ring juncture. The complex 27 undergoes successive rearrangements, as shown, to form the unstable Se(II) complex intermediate 28 and 29 involving 5 and 6 membered cyclic transition states respectively requiring low activation energies. The intermediate complex 29 could, alternatively, also arise directly from 27 involving a 3-membered transition state, as shown. Intermediate 29 then collapses to form the product 30 by loss of an allylic proton with concomitant deposition of selenium metal as depicted.



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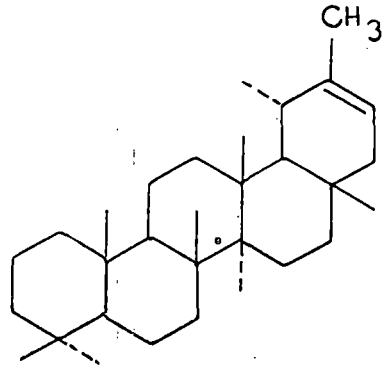

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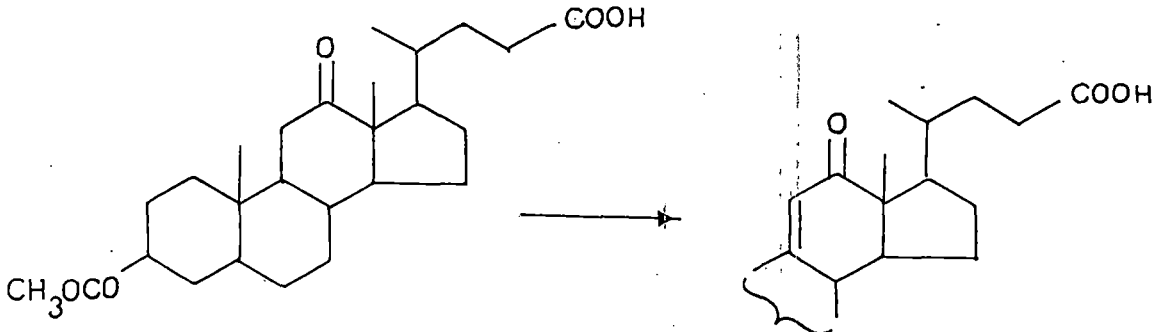
α,β-dehydrogenation of Carbonyl compounds

Riley reported[24] dehydrogenation of diethyl succinate to a mixture of the di and half ester of maleic acid. In 1947 Schwenk and Stahl[25] reported that selenium dioxide oxidation of a 12-keto steroid, 31, produced the $\Delta^{9,11}$-12 ketone of partial structure 32, rather than the 11, 12 diketone[26,27].



31 32

Selenium dioxide introduces a double bond at the 1,2 position in either a 5α-3-keto steroid or Δ^4-3-keto steroid[28,29], partial structure being 33 and 34.

33 34

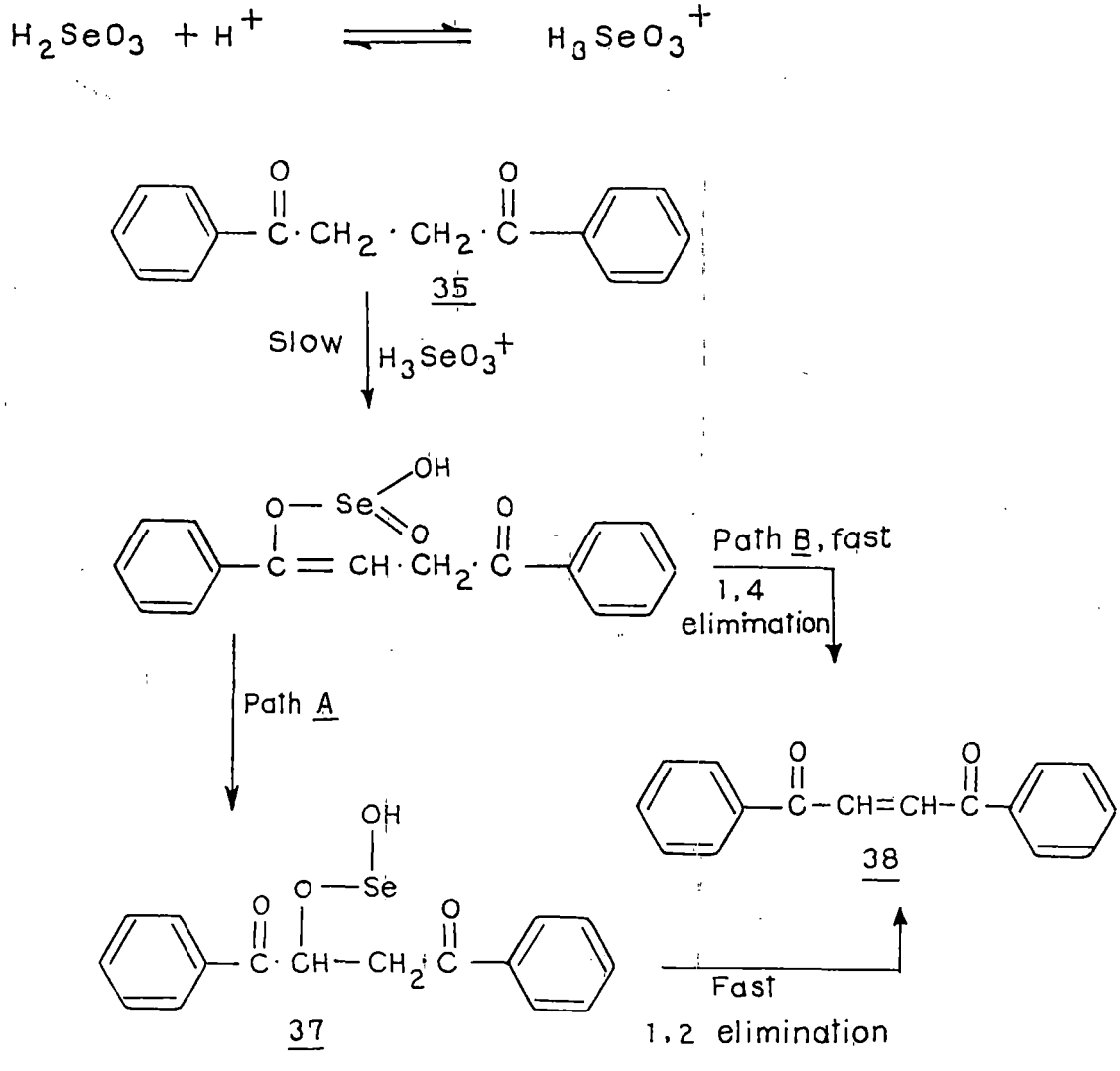
Mechanism of α,β -dehydrogenation

(a) 1,4- diketones

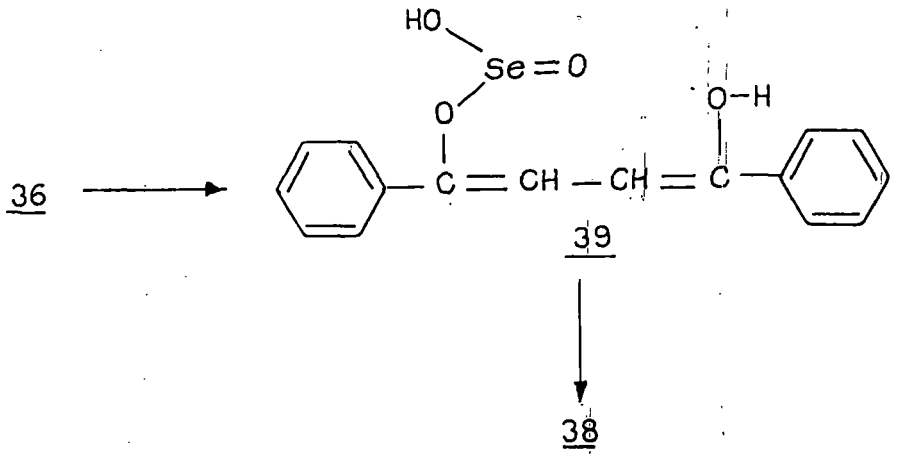
Numerous examples describing the oxidation of organic compounds by selenium dioxide had been reported[30], however, little detailed mechanistic information was available.

To clarify the mechanism of oxidation of 1,4 diketones to 1,4-ene diones, Schaefer et al[31] had carried out a study of the oxidation of 1,2 dibenzoyl ethane 35 to trans-1,2-dibenzoyl ethylene 38. In 80% acetic acid - 20% water as solvent, 38 was obtained in 80-85% yield; no 1,4-diphenyl 1,2,4-butanetrione 36 could be detected. A kinetic study of the reaction was complicated by the fact that 38 also reacted with selenious acid however, the rate of oxidation of 38 was 30 times slower than that of 35. The following mechanism was proposed by Schaefer[32] for the oxidation of 1,2-dibenzoyl ethane 35 to trans-1,2-dibenzoyl ethylene 38, is shown in Scheme VI.

Scheme VI



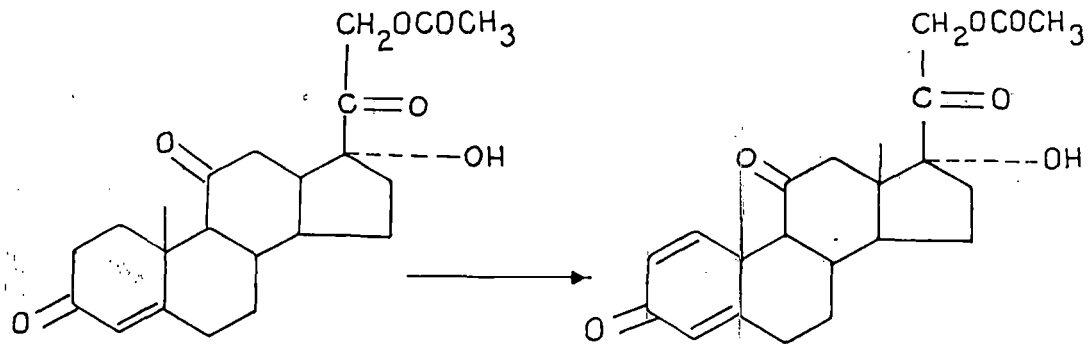
The mechanism involved (i) production of oxidising selenium species, $H_3SeO_3^+$, by protonation of selenious acid, H_2SeO_3 (Scheme VI), (ii) rate determining attack of the oxidising selenium species, $H_3SeO_3^+$ on the substrate, 35, to give an enol selenite ester, 36, and (iii) decomposition of 36 to the product via one of the two pathways. Path A involved rearrangement of 36 to the product α-selenium (II) keto ester, 37, and then to the product 38 by a rapid 1,2 elimination of H_2SeO_2. In path B, 36 was directly converted to 38 by a rapid 1,4 elimination of the elements of H_2SeO_2. Path A is essentially the same mechanism and intermediate already proposed for α-dione formation (Scheme I)[33]. Of the two possibilities the 1,4 elimination from enol selenite ester, 36, was likely since this intermediate contained a doubly activated methylene unit. The latter simply required an enolisation to give the half ester of the dienol, 39, which then decomposed to product 38 via bond migration, the driving force being the reduction of the selenium. The possibility of 1,2 elimination of H_2SeO_2 appeared less likely in view of the fact that the alternative product of its decomposition, 1,4-diphenyl 1,2,3-trioxobutane could not be detected[31]. Either a direct 1,4-elimination from 36 or a rearrangement of 36 to 37 followed by a rapid elimination of the elements of H_2SeO_2 would account for the formation of trans-1,2-dibenzoyl ethylene 38.



36 → 39 → 38

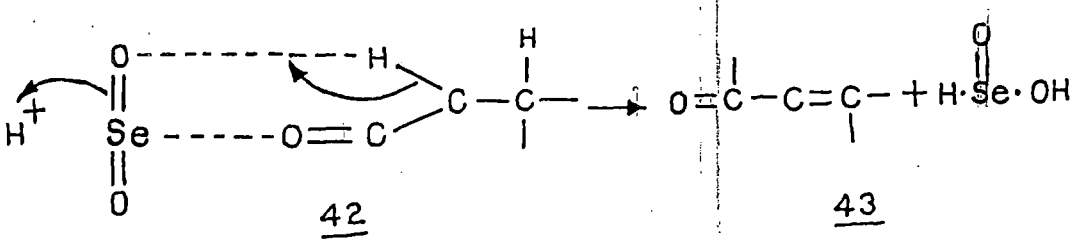
(b) Mono Ketone

Langbein[34] investigated the kinetics of dehydrogenation of an α,β-unsaturated ketones. He obtained a second-order rate constant for the Δ^1-dehydrogenation of cortisone acetate 40 to 41 from a plot which contained the concentration of ketone and selenium dioxide. Langbein[34] proposed a common intermediate, similar to 37, formed by direct attack of the oxidant on the ketone, which decomposed to form all the possible oxidation products.



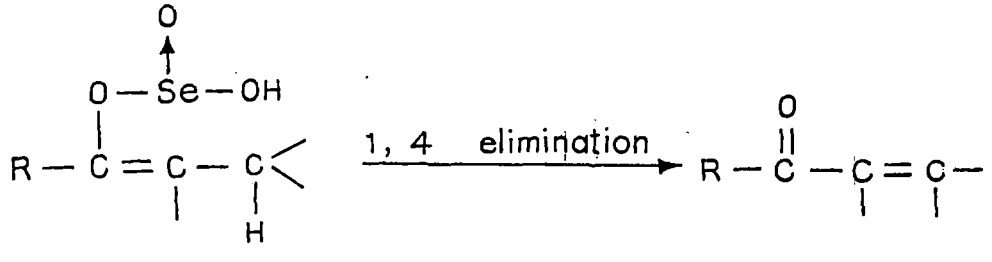
40 41

However, for α,β-dehydrogenation, he[34] considered the more plausible path as one that did not involve carbon-oxygen bond formation as 42.



42 43

The mechanism for this dehydrogenation may involve either concerted 1,4-elimination from the enol ester 44 or concerted 1,2-elimination from Se(II) ester 45. These intermediates were similar to 36 and 37 but without a second carbonyl group to activate the β-position and therefore should be less prone to undergo elimination.



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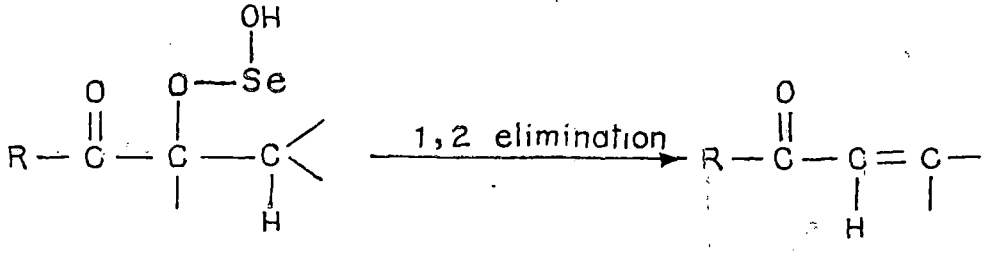

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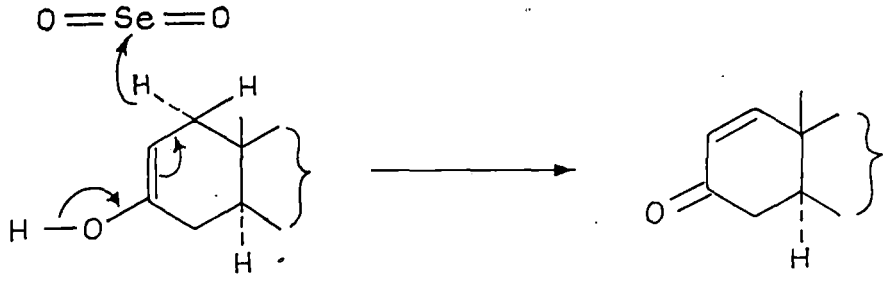
Another path, which circumvented the difficulty inherent in 44, would be direct attack of the selenium dioxide on the allylic position in the enol to remove hydride ion.



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Why do some mono ketones give α -diones and others α,β-unsaturated ketones remain unanswered. This is assumed to be due partially to solvent effect. Tertiary alcohols are normally used to carry out dehydrogenation reaction[28], but the reaction can be effected in acetic acid[35] or in aromatic solvents[36] α -diones are generally produced using ethyl alcohol or dioxan[37]. Again shielding of α -CH_2 (methylene) group by nearby bulky substituents often favours the formation of α,β -unsaturated ketone.

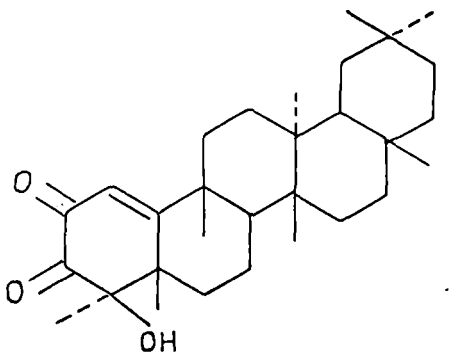
Stephenson et al[38] investigated both regio-chemical and stereochemical aspects of the allylic hydroxylation reactions of selenium dioxide. The principle findings are as follows:

i) In tert-butyl alcohol the mechanism is more complex than predicted by using the ene-[2,3] sigmatropic shift scheme proposed by Sharpless et al[20].

ii) The stereochemical complexities appear to derive from ionic intermediates and can be suppressed in more basic media e.g. tert-butyl alcohol/pyridine.

iii) The strong preference for trans allylic alcohol products in the reaction is due to steric preference in the [2,3] sigmatropic migration. The ene step is non-selective.

Pradhan et al[39] carried out oxidation of friedelin 47 with selenium dioxide in tertiary butanol and obtained two products to which they assigned the structure of friedel-1(10)-en-4β-ol-2,3-dione 49 and 3α-acetyl-4-nor-friedel-1(10)-en-3β-ol-2-one 48.



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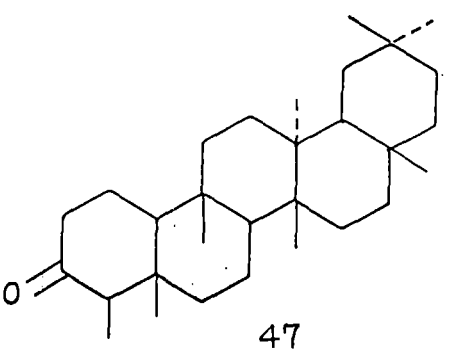

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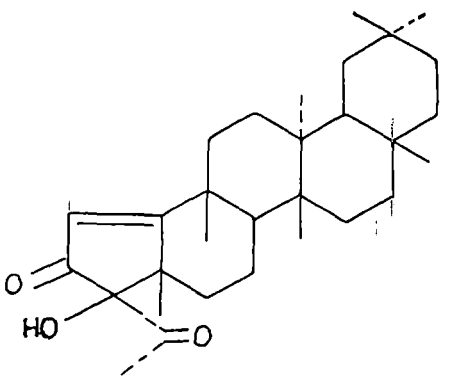
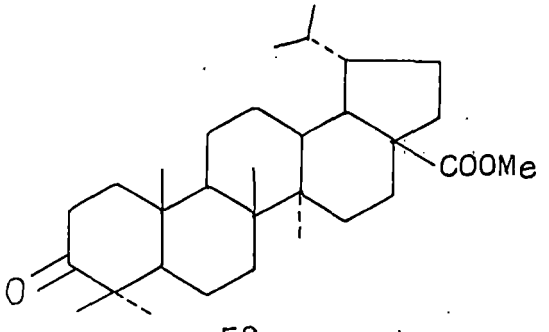


48

They[40] also reported that the 4-gem dimethyl-3-keto triterpenoid, methyl dihydrobetulonate 50 on prolonged heating with selenium dioxide in tertiary butanol gave lup-28-carbomethoxy-1(2)-en-3-one-2-selenide 51 and A-nor-lup-28-carbomethoxy-2-carb⟶1-olide-3α-ol 52 and suggested the following mechanism (Scheme VII) for their formation.



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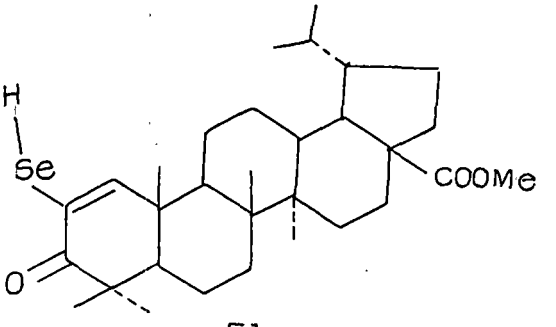

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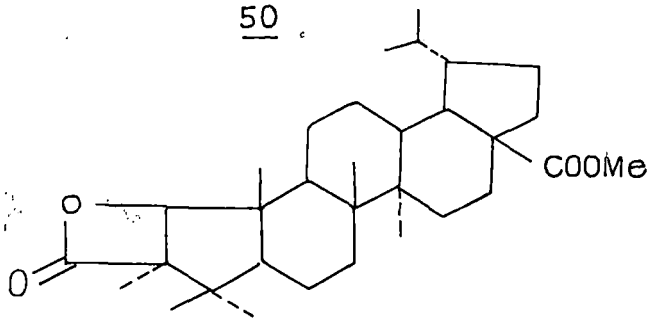

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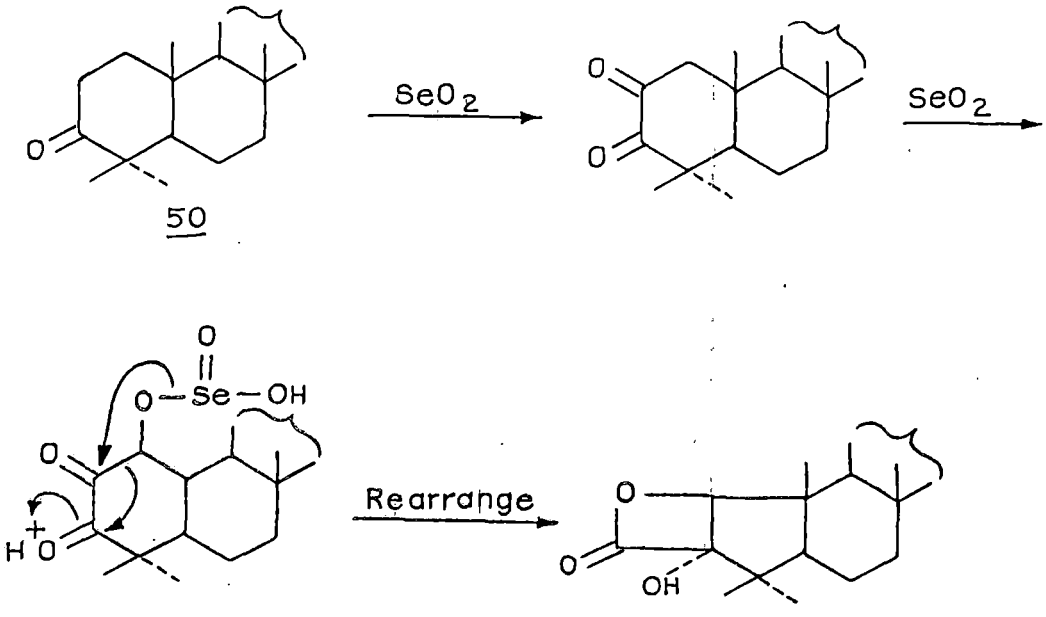
Scheme VII



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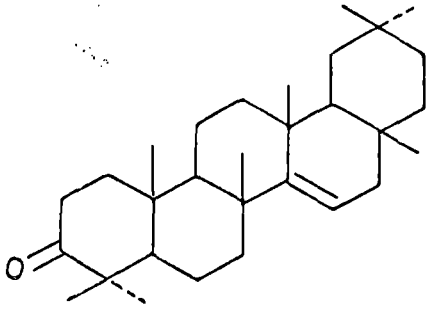
52

Pradhan et al[41] also carried out the same reaction on taraxerone 53 which resulted in the formation of five products, viz. 1(2)-dehydro taraxerone 54, 1(2)-dehydro taraxerone-2-selenide 55, 2-nor-tarxer-1,3-dione 56, 1(2)-dehydrotaraxerone-2,2'-seleno-taraxer-1',3'-dione 57 and 1β, 3α-dihydroxy-3-carboxy-A-nor-taraxerone 58.



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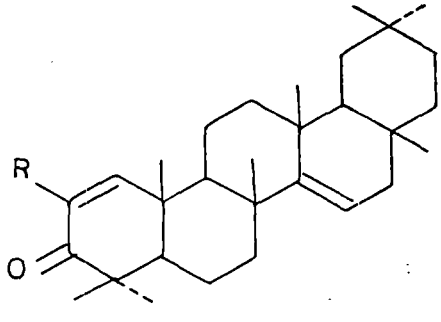
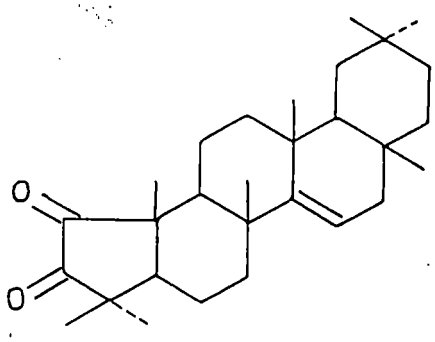


54 , R = H

55 , R = SeH



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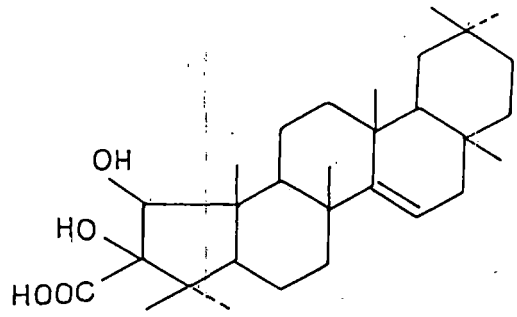

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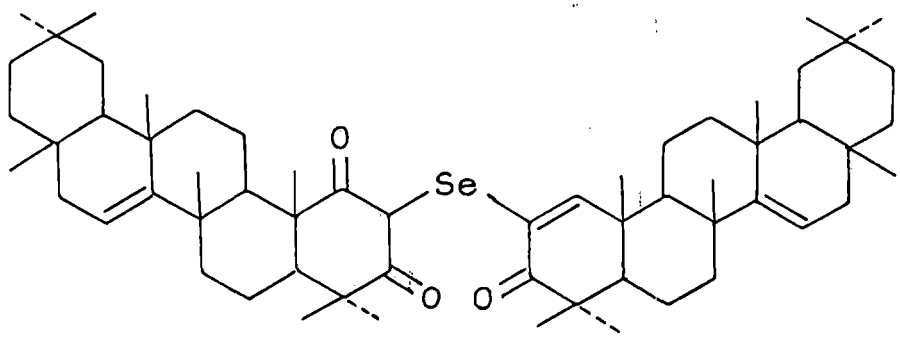
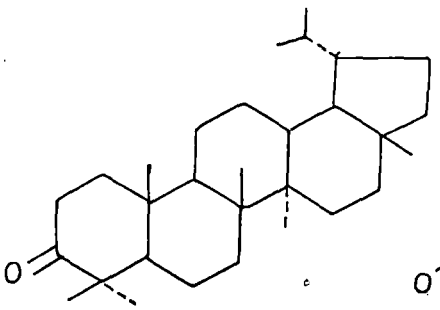


57

Lupanone 59 on similar treatment with selenium dioxide in tertiary butanol afforded seven products[42] designated as lup-1-en-3-one 59a, lup-1(2)-en-3-one-2-selenide 59b, lup-1-(2)-en-3-one-2 bis selenide 59c, 1β, 3α-dihydroxy-3β-carboxy-A-nor-lupane 59d, A-nor-lupan anhydride 59e , 1-hydroxy-lupan anhydride 59f and 1-hydroxy-A-nor lup-2-carb ⟶ 4 olide 59g.



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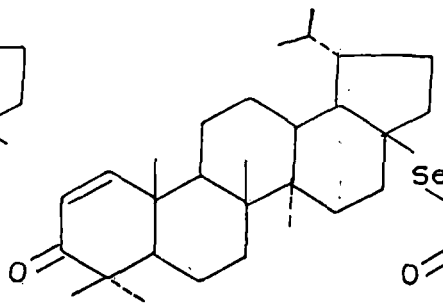

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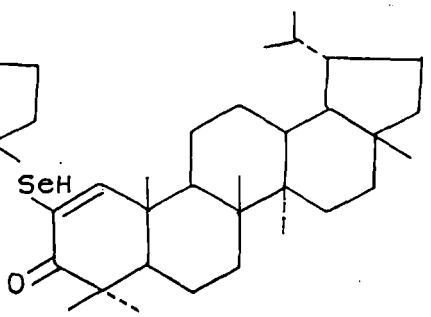

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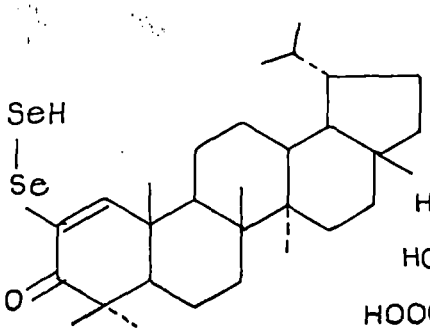

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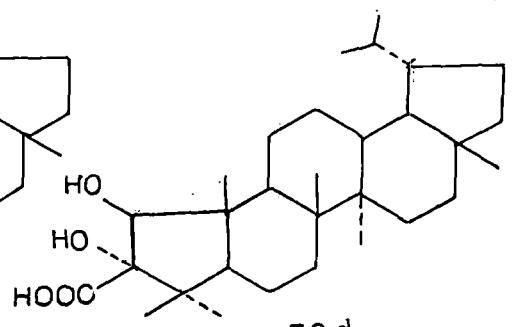

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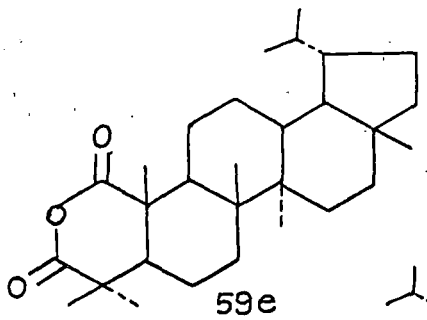

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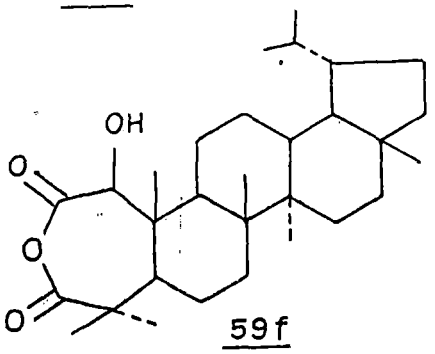

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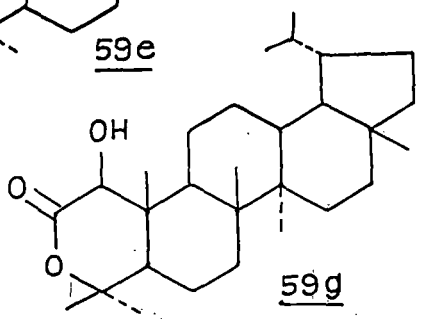


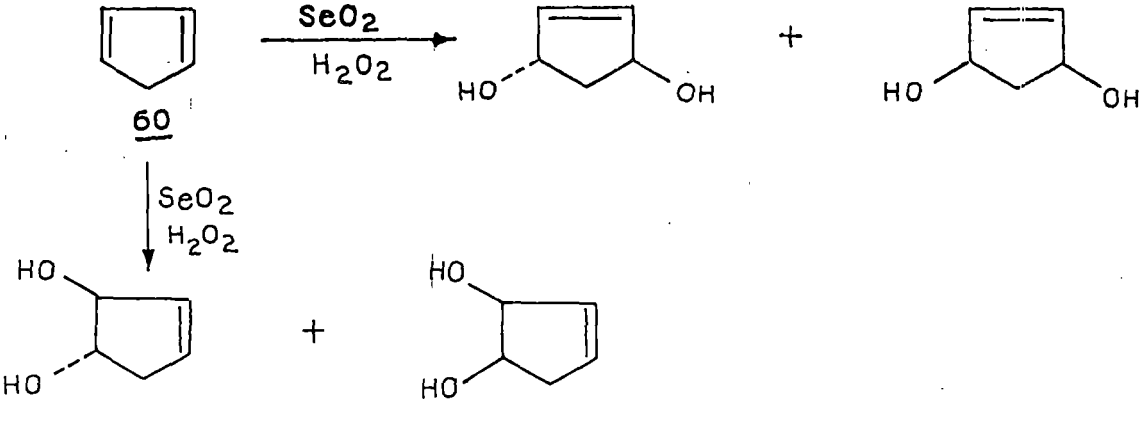
59g

The structures of the compounds have been established on the basis of analytical and spectral data.

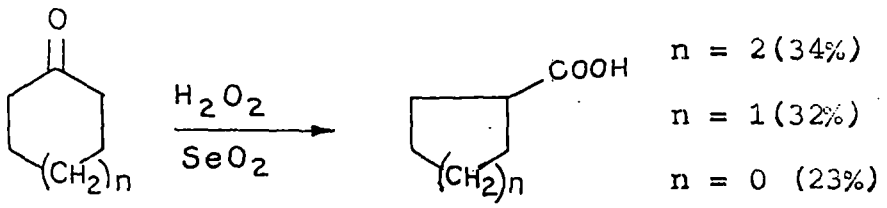
SECTION B: A SHORT REVIEW ON REACTIONS OF HYDROGEN PEROXIDE IN PRESENCE OF SELENIUM DIOXIDE.

It is evident from discussion in the preceeding section that selenium dioxide and hydrogen peroxide have separately found wide application. This section deals with the short review on the products obtained on combined oxidation with hydrogen peroxide and selenium dioxide.

Seguin et al[43] prepared trans cyclohexane-diol free of cis-compound from cyclohexane using hydrogen peroxide in presence of SeO_2 and also prepared 1,2-diols of cyclopentadiene from cyclopentadiene. Curtis et al[1] used selenium dioxide, as catalyst in presence of hydrogen peroxide to oxidise acrolein and metacrylic to monomeric acrylic and metacrylic acids and suggested that at first selenious acid oxidised to selenenic acid with hydrogen peroxide then that seleninic acid reacted with acrolein to give acrylic acid and selenious acid. In another obviously different case[44], the reagents have been used for hydroxylation of cyclpentane and cyclopentadiene 60. The catalyst in this case is probably perselenic acid.

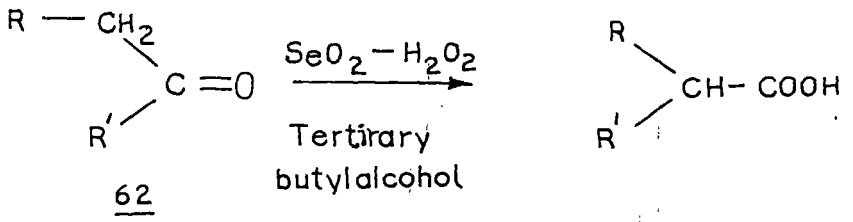


Oxidation of methylene groups adjacent to carbonyl groups with stoichimetric quantity of selenium dioxide to give α-diketones or keto aldehydes are well known. Payne et al[45] investigated oxidation of cycloheptanone, cyclohexanone and cyclopentanone with selenium dioxide in presence of hydrogen peroxide and anticipated that the cyclic ketones might undergo the well known reaction with selenium dioxide giving α-diketone with hydrogen-peroxide serving merely to oxidise selenium metal back to the dioxide. They[45] observed that along with other competing reactions, all three ketones underwent oxidative ring contraction to cyclohexane, cyclopentane and cyclobutane carboxylic acids in 34, 32 and 23% yields respectively.



61

Sonoda et al[46] studied oxidation of aliphatic ketones, RCH_2COR' 62 with hydrogen peroxide in presence of selenium dioxide (solvent-tertiary butanol) and got carboxylic acids, RR'CHCOOH accompanied by rearrangement of alkyl groups.



62

where R = H, R' = alkyl group

R = R' = alkyl group

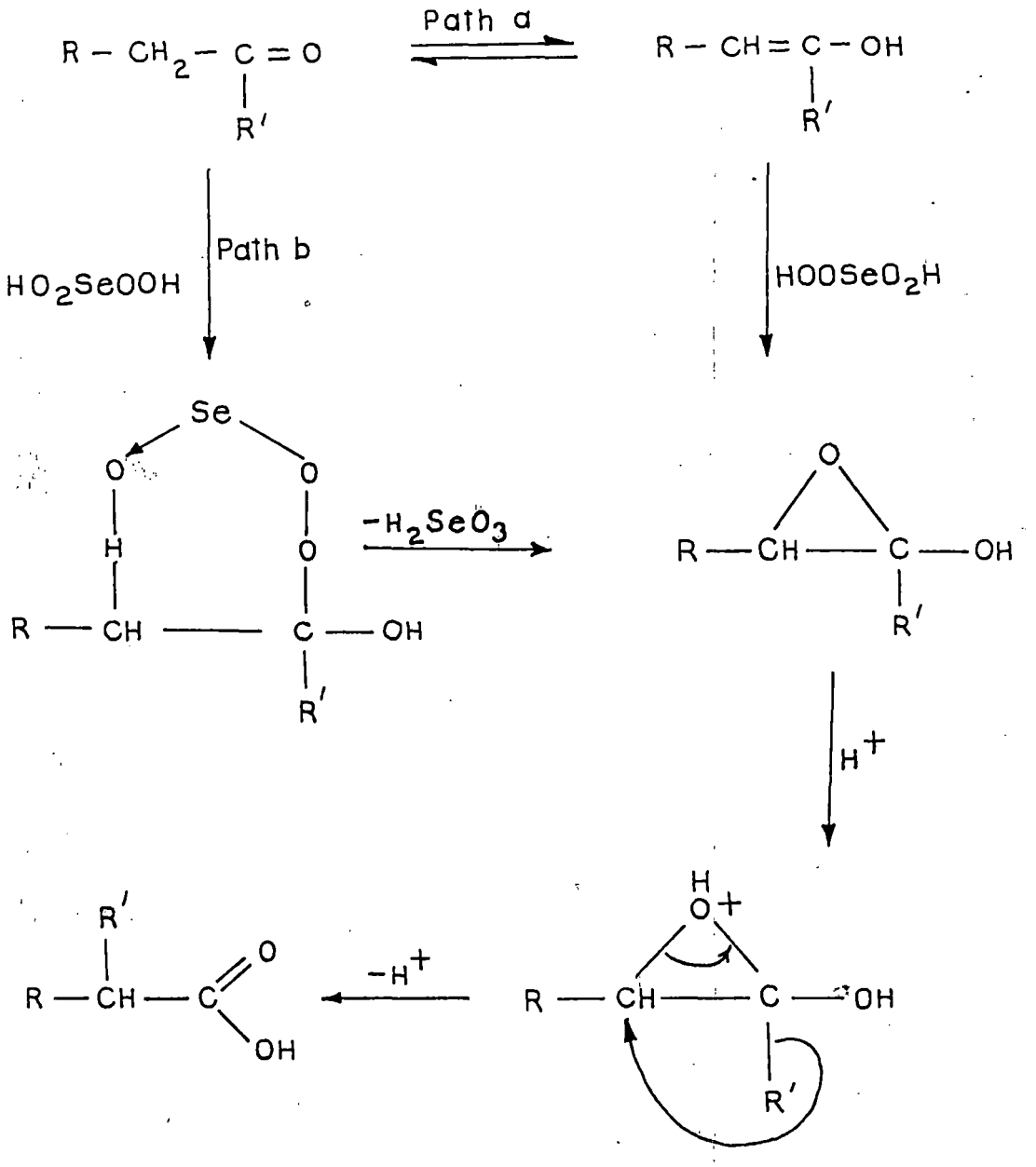
Acetone, methyl ethyl ketone, methyl n-propyl ketone and diethyl ketone were selected as starting materials. They[46] suggested that the main rearrangement observed was due to migration of the alkyl group having a smaller number of carbon atoms to the α-carbon atom of the larger alkyl group and the migration of the alkyl group with a larger number of carbon atoms to the smaller one also occurred in some degree. These workers[46] shared the view of Hughes and Martin[47] who proposed the formation of peroxy selenious acid, 63, from the selenium dioxide by the action of hydrogen peroxide.

$$SeO_2 + H_2O_2 \rightleftharpoons HOOSeO_2H$$

63

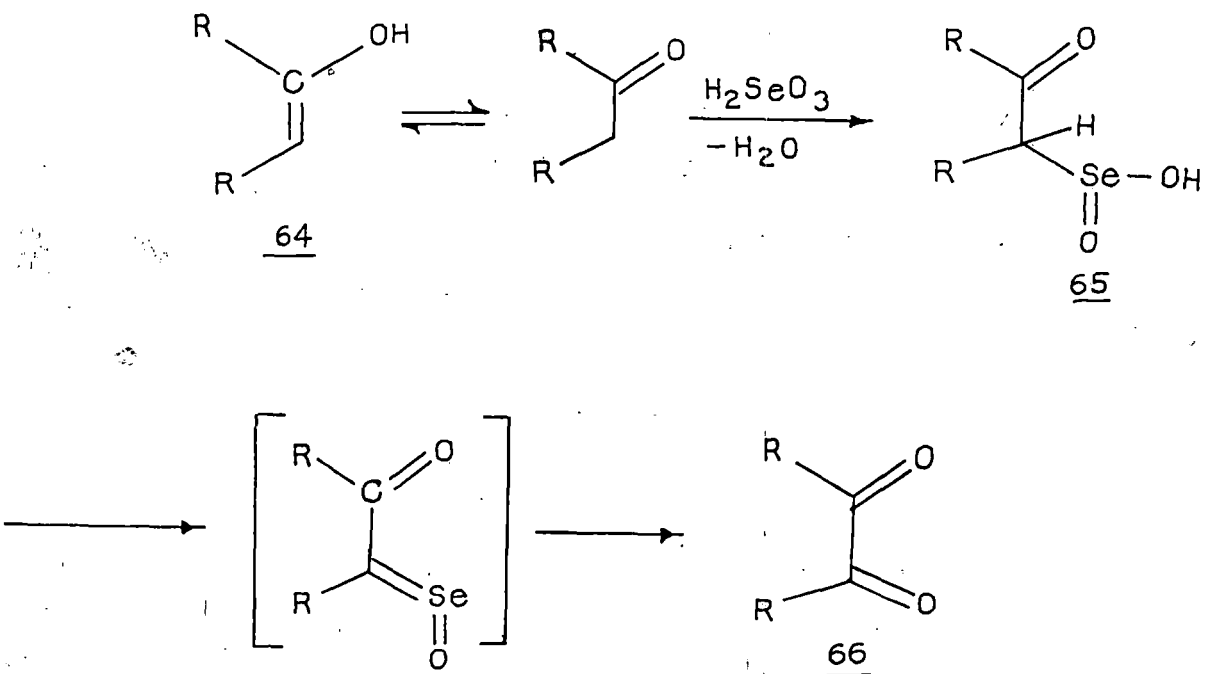
The following mechanism as shown in Scheme VIII was presumed by the workers.

SCHEME VIII

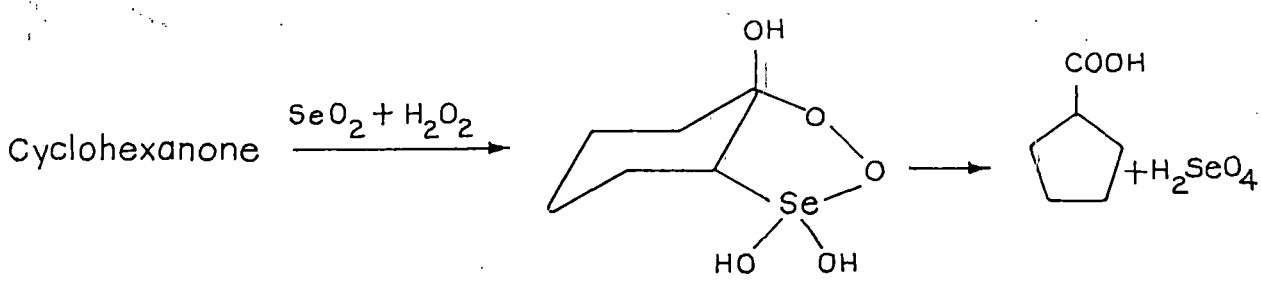


Sharpless et al[48] reported that selenium dioxide oxidation of ketones and aldehydes to α-diketone and glycols involved an organo-selenium species. They proposed that the key intermediate (Scheme IX) in this sequence was the β-keto seleninic acid 65 formed by the electrophilic attack of selenous acid on the enol 64 which after rearrangement[49] afforded 66. They[48] also suggested that this β-keto seleninic acid intermediate was responsible for the unusual oxidative rearrangement, observed during SeO_2 oxidation of ketones in the presence of H_2O_2 (Scheme X).

Scheme IX

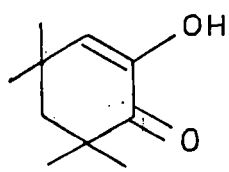


Scheme X



T. Laitalainen[50] and co-workers had reported the isolation and structure determination of two new organo selenium compounds 69 and 70.

Diosphenol 67 on treatment with an equimolar amount of SeO_2 in boiling dioxane for 1.5 hour gave a compound, which was assigned the structure 69, bis (2-hydroxy-4,4,6,6-tetramethyl-1-cyclohexen-3-one) selenide, on the basis of the analytical and spectroscopic evidence, whereas the same reaction with longer reaction times (4-6h) gave 70 together with the diketone 68 and traces of 69.



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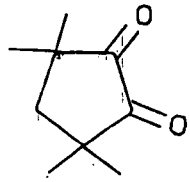

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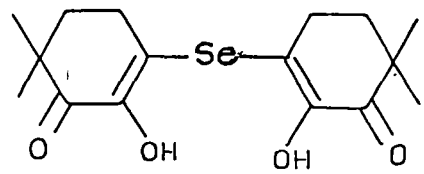

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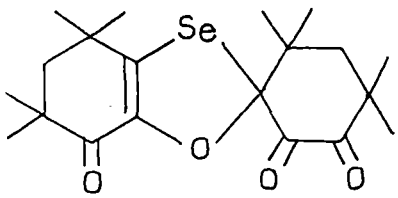
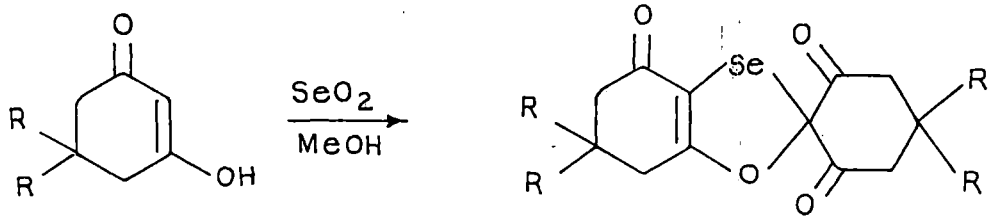


70

They[51] also described the SeO_2 oxidations of 1,2 and 1,3 diketones. They prepared 1,3-oxaselenoles 73 and 74 by the reaction of cyclohexane 1,3-dione derivatives 71 and 72 with SeO_2. The reaction of the trione 75 with 0.5 mol equiv. of selenium dioxide in methanol[52] afforded a new member of this series to which the structure 76 was assigned (Scheme XI). when the same reaction was carried out in boiling acetic acid with 2.5 mol. equivalent of selenium dioxide, 3,3,5,5-tetramethyl cyclopentane-1,2,4-trione was formed along with 76. They[51] also isolated the bis selenide 78 and the 1,3-oxaselenole 79 along with the ring-contraction products 80 and 81 (Scheme XII) by oxidising the diketone 77 with an equimolecular amount of SeO_2 in 1,4-dioxan. Conducted in methanol with 0.5 mol. equivalent of selenium dioxide the reaction yielded 78, 79, 80, 81 and 82.

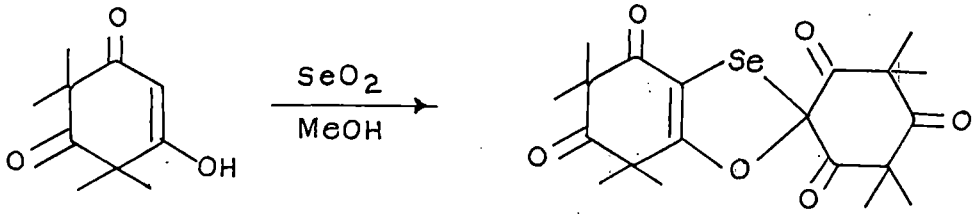
They[51] also carried out the oxidation of 3,5,5-trimethyl cyclohexane-1,2-dione 83 in dioxan and reported the formation of bridge selenide 84[52] together with the elimination product 85. Postulating 19[48] as a probable intermediate they suggested the following mechanism as shown in scheme XIII. The intervention of the intermediate 88 was further supported by metaperiodate oxidation of 90 to 74.

Scheme XI



71 , R = H
72 , R = Me

73 , R = H
74 , R = Me



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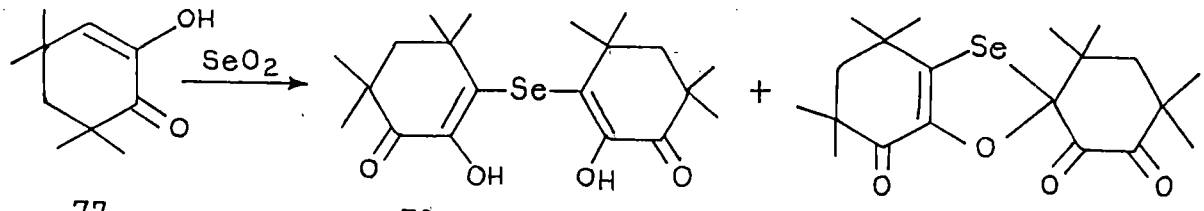
76

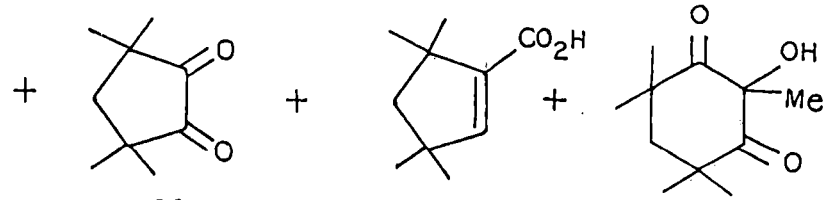
Scheme XII



77

78

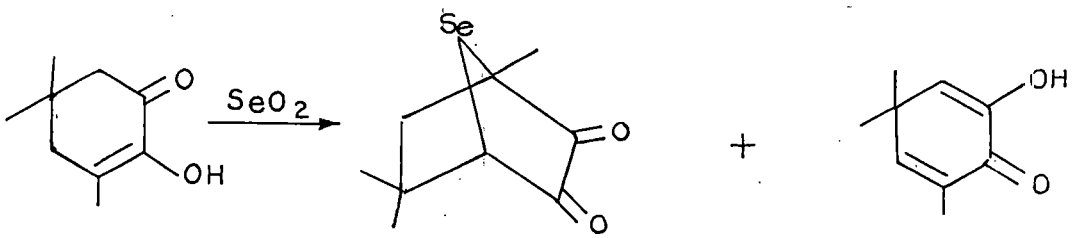
79



80

81

82

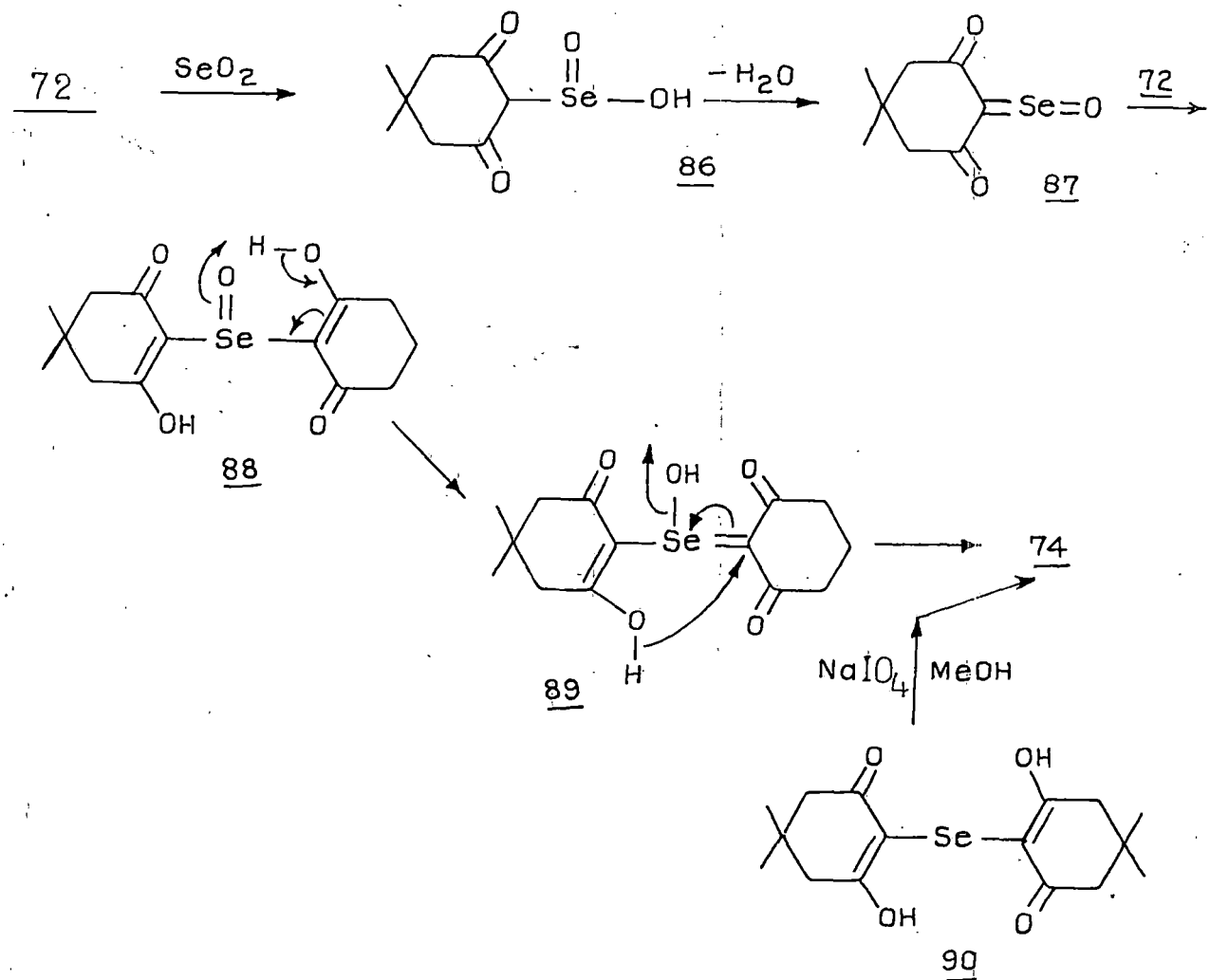


83

84

85

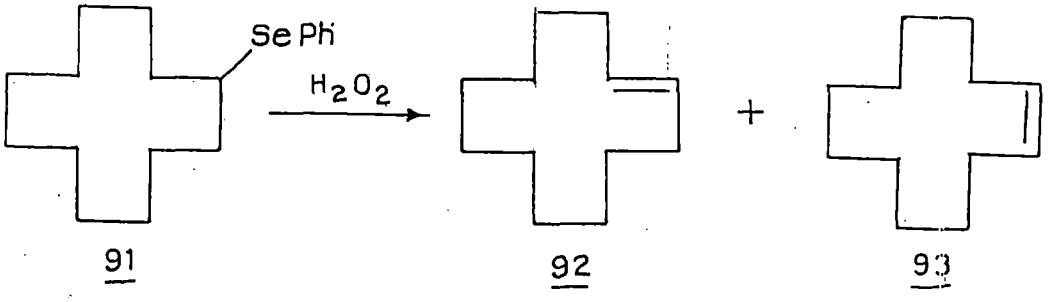
Scheme XIII



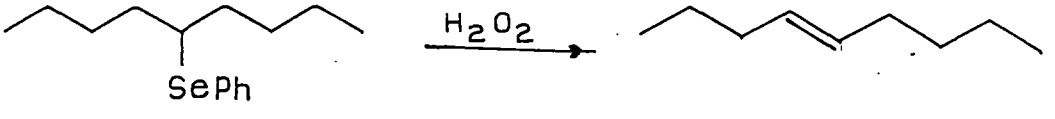
However, Uemura et al[53] reported that the treatment of secondary-alkyl phenyl selenides with various oxidants (H_2O_2, m-chloroperbenzoic acid, $NaIO_4$) afforded the corresponding trans alkene highly selective irrespective of the amount of oxidant.

They reexamined the experiment by Sharpless et al[54] on the oxidation of 91 with hydrogen peroxide (70%) and isolated 92 as main product together with a small amount of 93 in a sharp contrast to their[53] result of a quantitative yield of a 1:1 mixture of 92 and 93.

A similar phenomenon was also observed in the oxidation of 5-nonyl phenyl selenide 94 which afforded the corresponding trans alkene (trans-non-4-ene) 95.

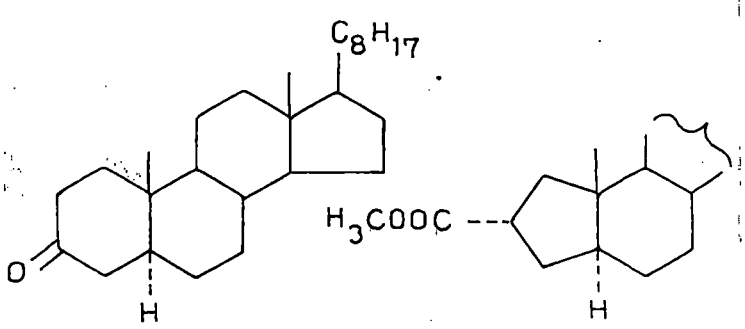


91 92 93

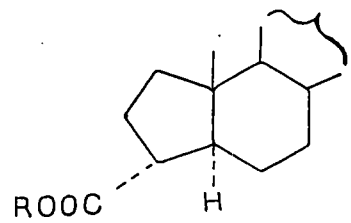


94 95

The reaction was also applied to several keto steroids with 5α-cholestan-3-one, 96, a mixture of acid was obtained[55]. The acids after esterification were separated and characterised as 97 and 98. The yields were 25% and 19.5% respectively.



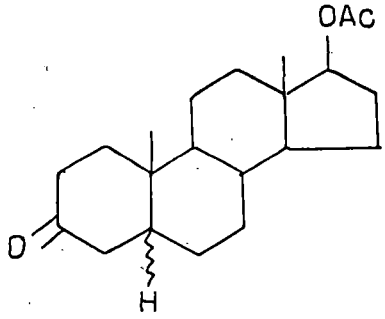
96 97



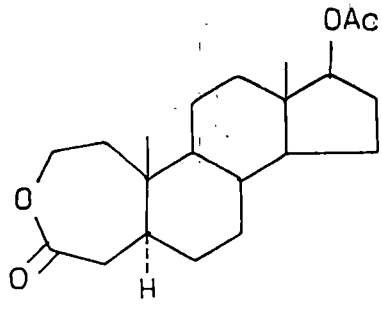
98 (a) R = CH_3
(b) R = H

Caspi et al[56] studied the reaction for steroidal 3-ketones of 5α-and 5β series and found that the major reaction was not ring contraction but Baeyer-Villiger oxidation.

The compound with A/B trans juncture, 17β-acetoxy-5α-androstran-3-one, 99a, gave a lactone, 100 and carboxylic acids, 101 and 102 . The oxidation of 17β-acetoxy-5β-androstan-3-one, 99b gave the lactone 103 as a single product.



99 a = 5α-H
b = 5β-H



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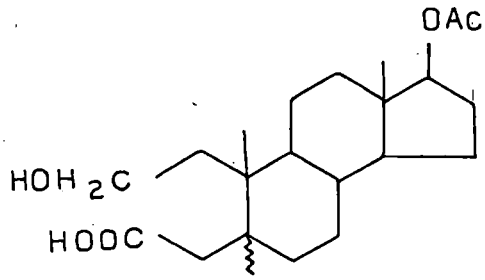

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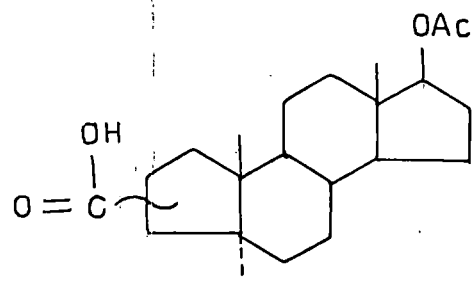

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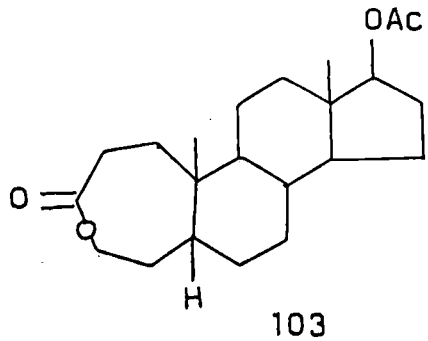
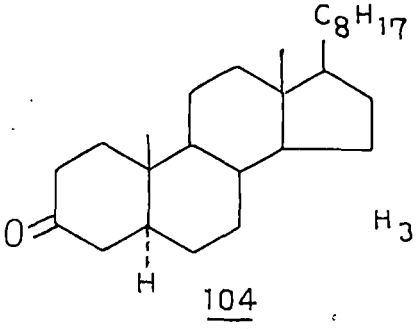


103

Hara et al[57] had shown that perbenzoic acid oxidation of 5α and 5β-3 ketones yielded mixture of lactones with an oxygen atom inserted in either side of the 3-oxo group. With the commonly used peracids it would seen that the reaction proceeds in a rather indiscriminate manner[58]. Capsi et al[56] employed nearly neutral condition and concluded that the direction of attack was more substrate dependent, and hence led to the formation mainly of single compound. For example, for A/B trans junction the 2,3 bond and for A/B cis junction the 3,4 bonds are cleaved. In their experiment Capsi et al[59] observed that no directional influence of ring A/B junction on the course of the reaction occurs. However, the same reaction[60] on 17β-acetoxy-5α-cholestan-3-one gave products which were different from those previously published.[61,62]

Jerussi et al[60] carried out the reaction of 104, with selenic acid and 30% H_2O_2 in tert-butyl alcohol and the reaction yielded a complex mixture of acids. Esterification of the crude product with diazomethane followed by chromatography and several times crystallisation yielded 2α-carbomethoxy-A-nor-5α-cholestane, 105 and 2,3-seco-5α-cholestane, 2,3 dioate 108a and 107a, compound 106 was, however, not found.



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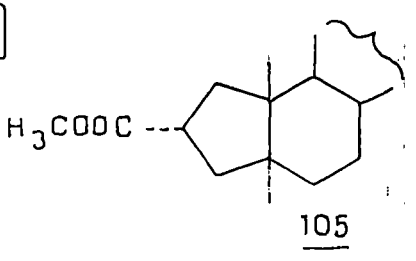

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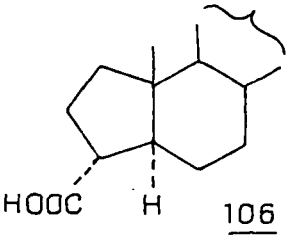

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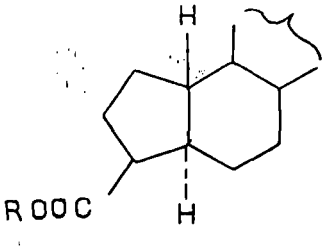
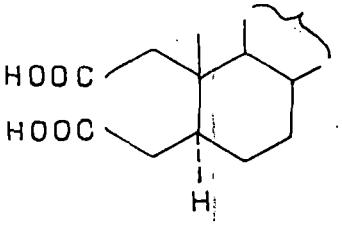




107a R = CH_3

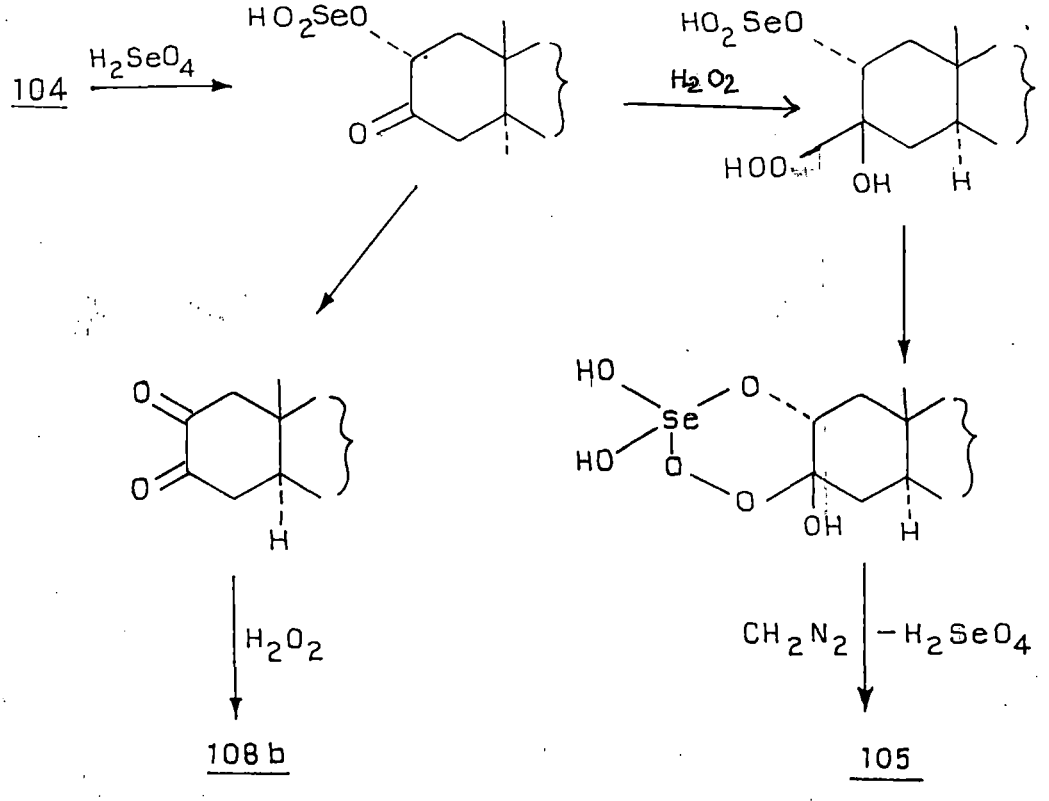
107b R = H

108a R = CH_3

108b R = H

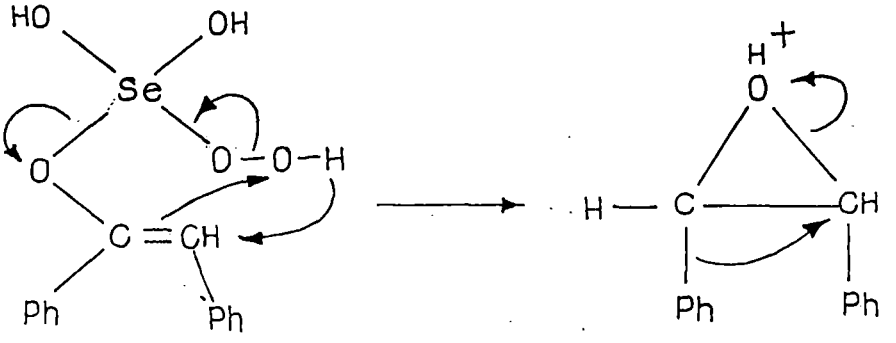
The mechanism proposed by Jerussi et al[60] are summarized in the Scheme XIV.

Scheme XIV

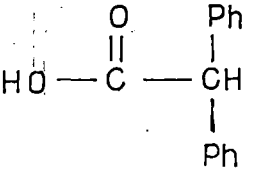


The mechanism had been proposed by Sonoda and Tsutsumi[63] for the rearrangement of desoxybenzoin, in which a peroxy-selenious enol ester 109, was postulated as an intermediate. This then undergoes intramolecular epoxidation to give the enol epoxide, 110 which rearranges as shown to give diphenyl acetic acid, 111.

Opening of the epoxide, 110, in the manner proposed appears unlikely in view of the course of epoxide reactions in the acidic solution[64].



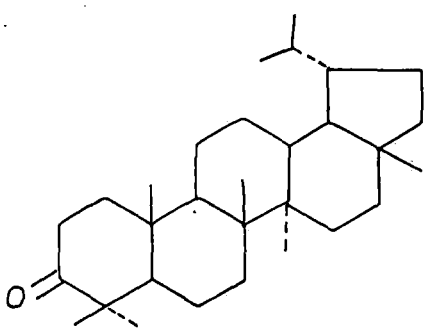
109 → 110



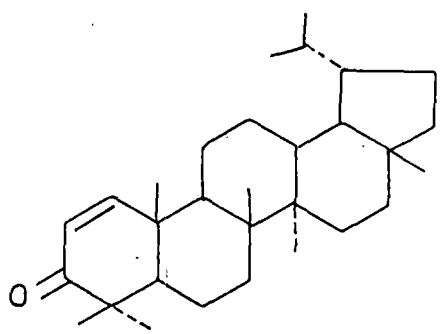
111

All examples of oxidative rearrangements of ketones using H_2O_2 and selenic acid or SeO_2 have involved enolised ketone. Non enolizable ketones, even those having α-hydrogen atoms fail to give the reaction[65]. Hence, it is plausible to assume that with steroid ketones also enolisation or enol ester formation is an essential step. An enol selenite ester, which rearranges to an α-keto selenium ester, has been proposed by Corey and Schaefer as an intermediate in the selenious acid oxidation of desoxy benzoin[28].

The selenium dioxide catalysed reaction of hydrogen peroxide on pentacyclic triterpene-3-ketone was studied by Pradhan et al[66]. They observed that lupanone 59 on oxidation with molar proportion of H_2O_2 and catalytic amount of SeO_2 in tertiary butanol afforded lup-1-ene-3-one[67] 112, 2∝ - carbonyl-A-nor-lupane[68] 113 and 2,3-seco lupane dicarboxylic acid 114 ; with excess of H_2O_2 59 furnished 4, 23, 24-tri-nor-lupane-3 ⟶ 5 olide, a δ -lactone 115 together with[69] 114. The following mechanism was suggested for the formation of δ -lactone 115 shown in Scheme X. V.



59



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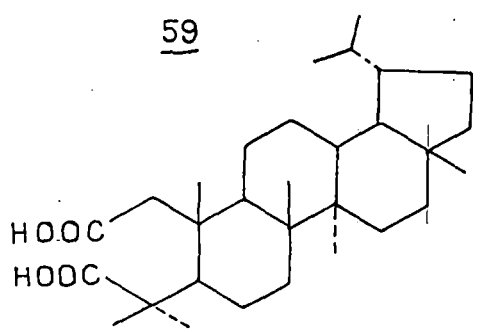

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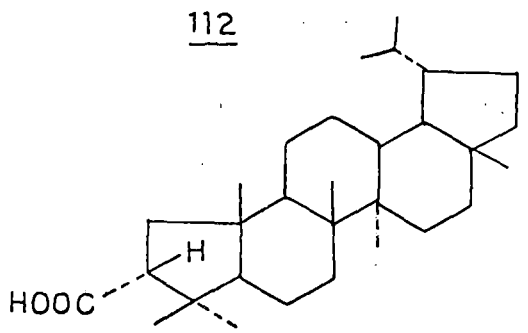
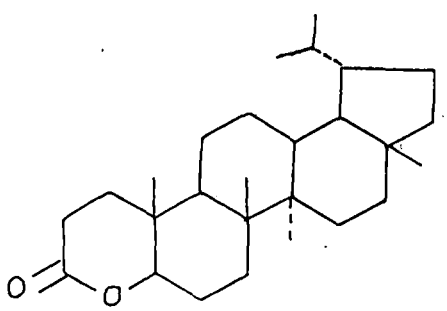
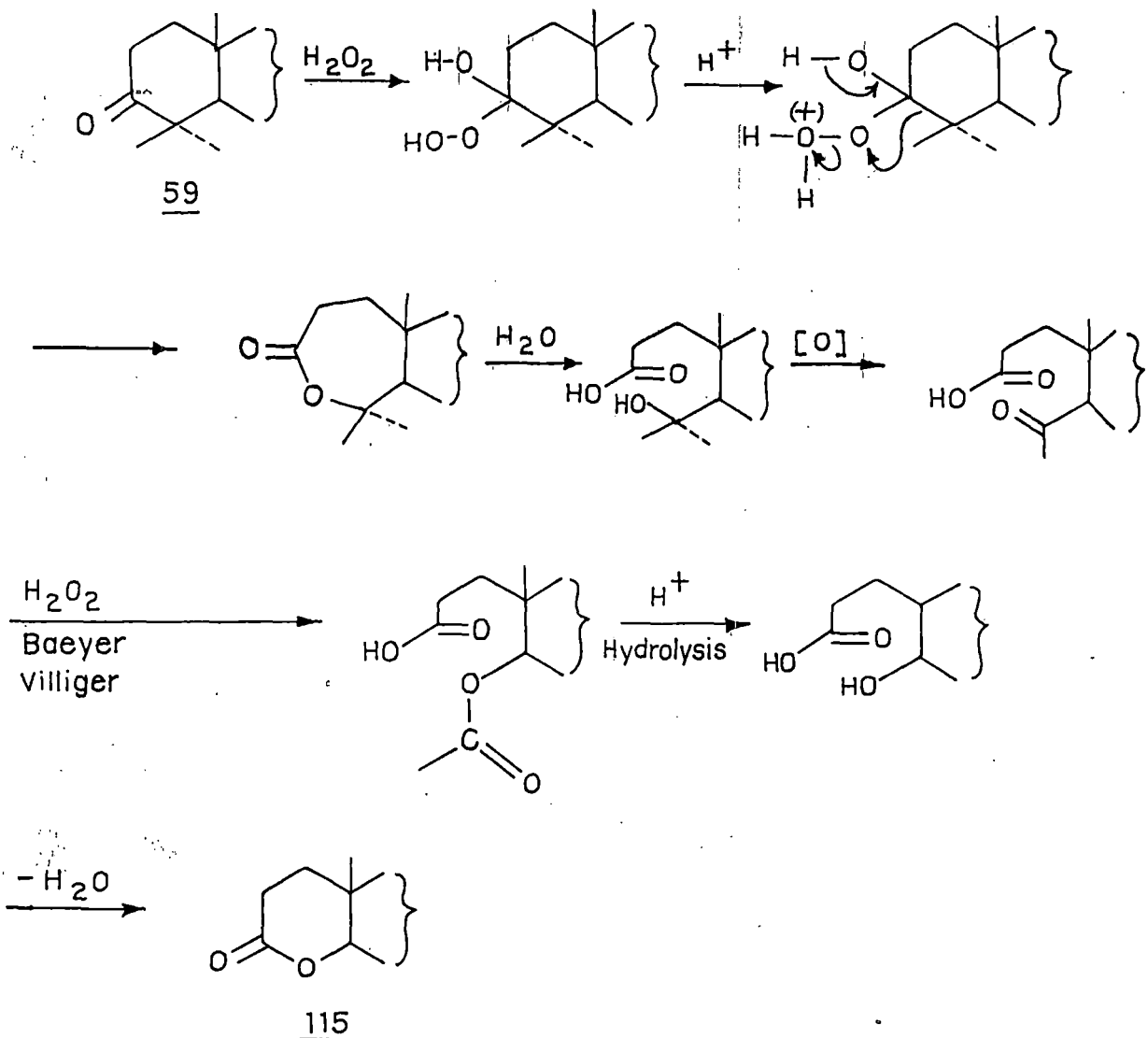


113



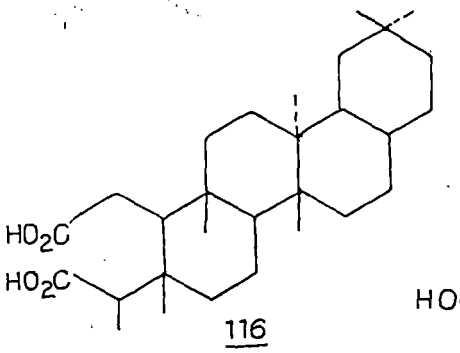
115

Scheme X. V



Pradhan et al[70] carried out similar reaction of hydrogen peroxide-selenium dioxide in t-butanol on friedelin 47 and reported the isolation of 2,3 seco friedelinic acid 116,

2∝-carboxy-A-nor-friedelin 117 and a δ-lactone 118



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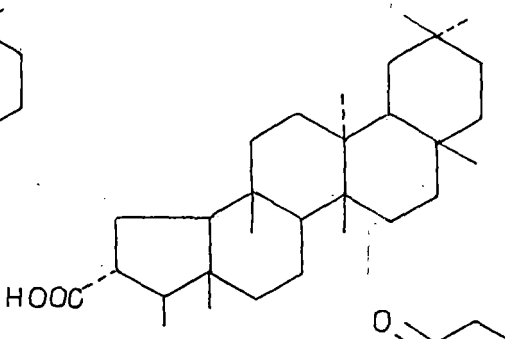

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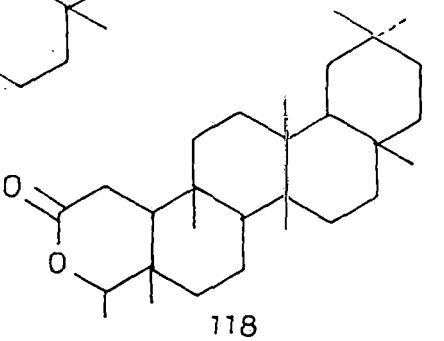
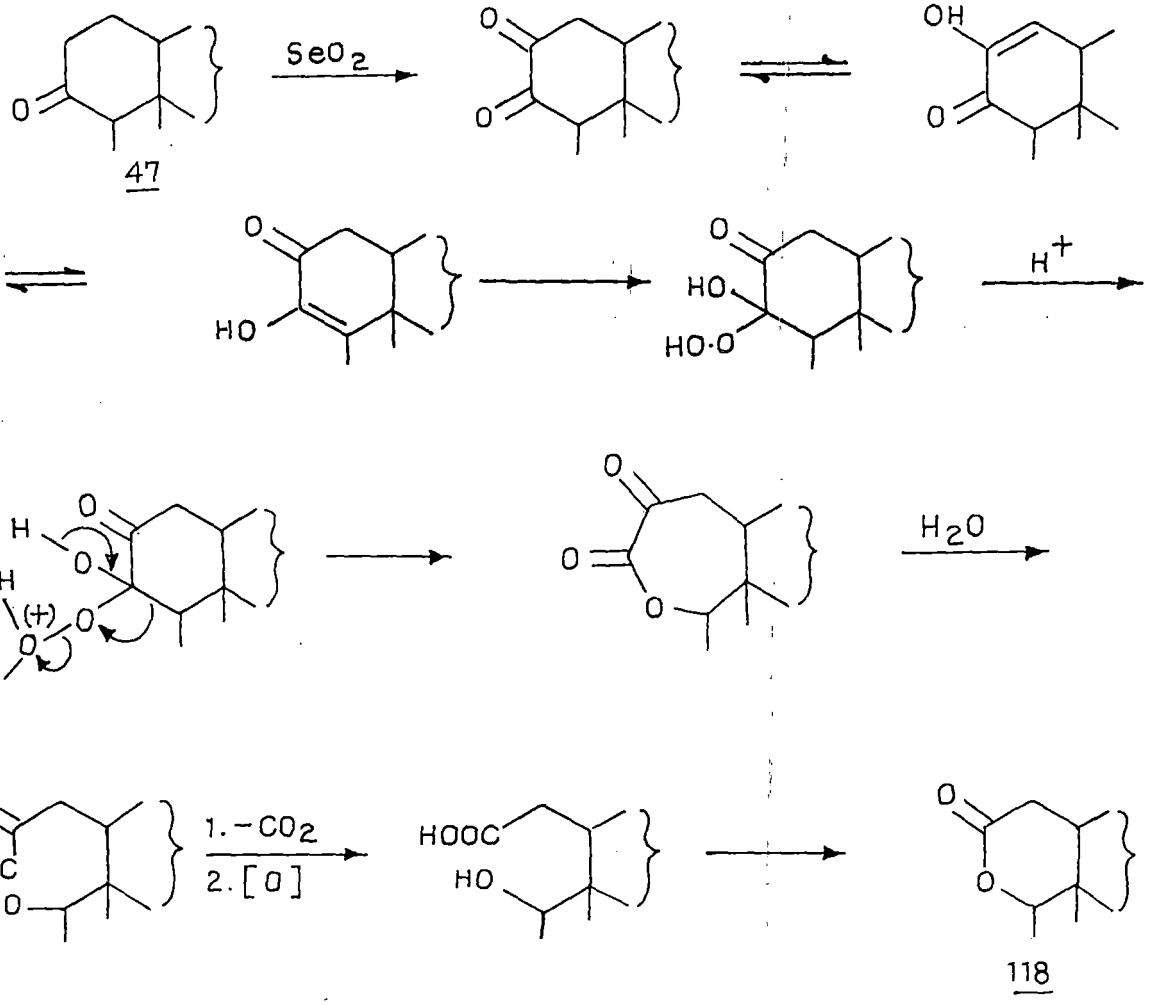


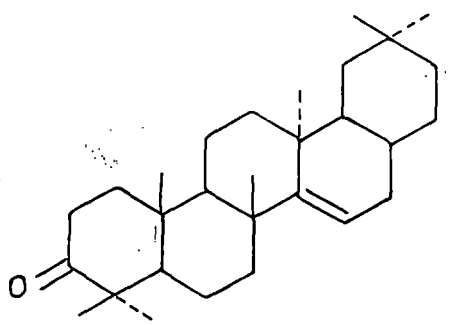
118

They[70] suggested the mechanism shown in Scheme XVI.

Scheme XVI



Pradhan et al[71] extended the reaction to taraxerone 119, a 3-keto triterpenoid having a trisubstituted double bond. They[71] reported that taraxerone 119 on oxidation with hydrogen peroxide in presence of selenium dioxide in tertiary butanol afforded 1α, 2α-epoxide 120, 4,23,24-tri-nor-taraxerene - 3 ⟶ 5 olide, a δ -lactone 121 and taraxerene - ϵ - lactone 122 from neutral part and 2α-carboxy-A-nor-taraxerene 123 together with taraxerene-3, 4-seco- dicarboxylic acid 124 from acid part. The formation of the products 120, 121, 122, 123, 124 showed that in the selenium dioxide oxidation of taraxerone 119 no migration of 14-15 double bond took place. They[71] concluded from previous studies and present observations that the δ -lactones were formed irrespective of the presence of methyl groups at C-4 position. The isolation of ϵ -lactone 122 supported the mechanism of formation of δ -lactone via the ϵ -lactone . They[71] also suggested that the epoxide 120 was most probably formed via the unsaturated ketone.



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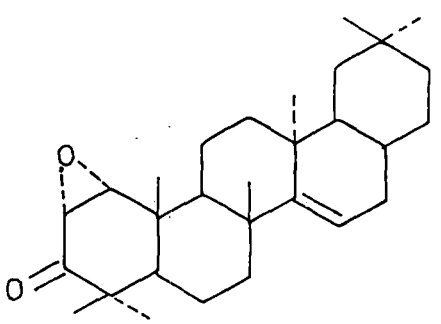
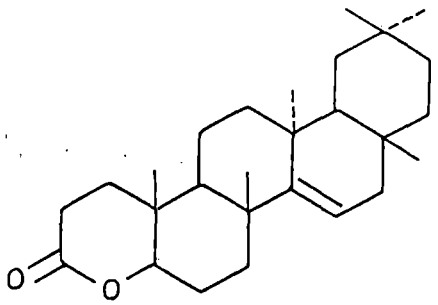


120



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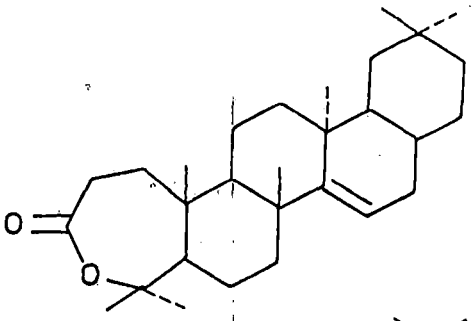

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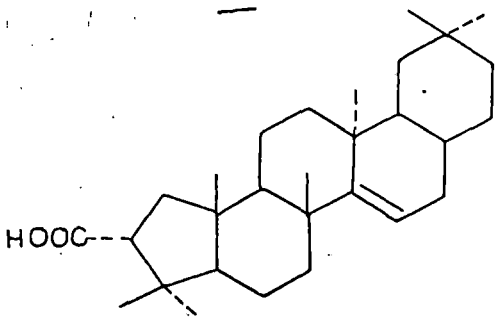

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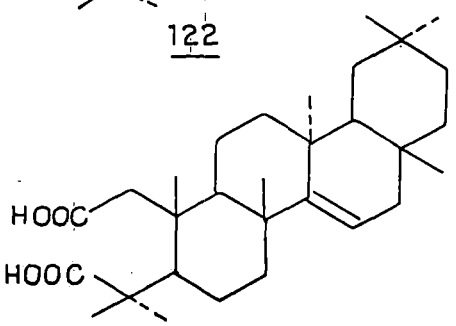
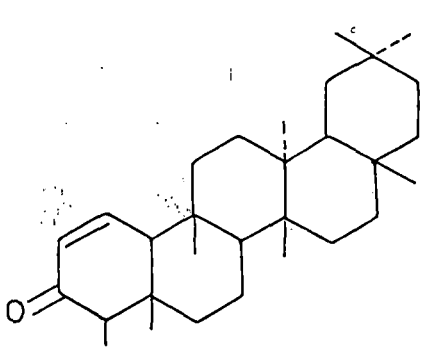


124

It is obvious from the work of Pradhan et al[71] that the 3 keto triterpenoid can be transformed to tris-nor-triterpenoid lactone in a single pot reaction along with other products.

Anjaneyulu et al[72] reinvestigated the oxidation of friedelin 47 with H_2O_2 in presence of selenium dioxide in tertiary butanol and reported the formation of friedel-1-ene-3-one 125 and friedelolactone 126 along with 116 and 117 already reported by Pradhan et al[70].



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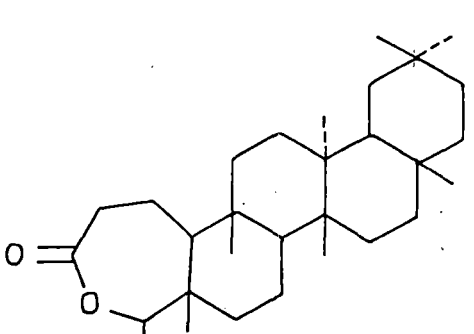
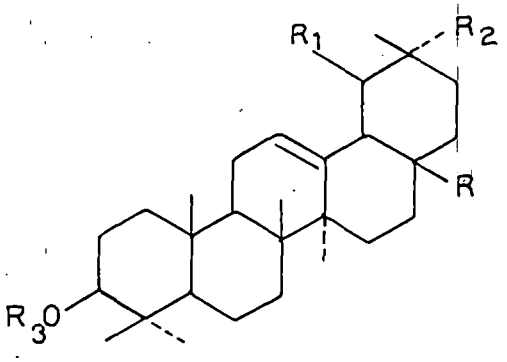
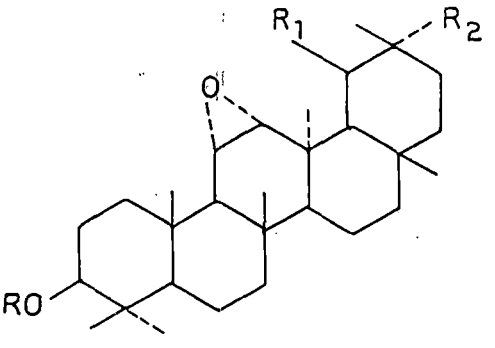


126

Pradhan et al[73] provided an interesting transformation of oleanane and ursane skeletons to 11α, 12α-oxidotriterpenoids with hydrogen peroxide and selenium dioxide in tertiary butanol. They reported the formation of 128a and 128b from β-amyrin acetate 127a and 129a and 129b from β-amyrin acetate 127b respectively. The structure of these compounds were established on the basis of analytical and spectral data.





127a, $R_1=R_3=H$; $R=R_2=Me$

127b, $R=R_1=Me$; $R_2=R_3=H$

127c, $R_1=R_3=H$; $R_2=Me$, $R=CO_2H$

127d, $R_1=R_3=H$; $R=CH_2OH$
$R_2=Me$

127e, $R_2=R_3=H$; $R_1=Me$; $R=CH_2OH$

128f, $R_3=Ac$; $R_1=H$, $R_2=Me$
$R=CO_2Me$

128g, $R_3=Ac$; $R_2=H$; $R_1=Me$;
$R = CO_2Me$

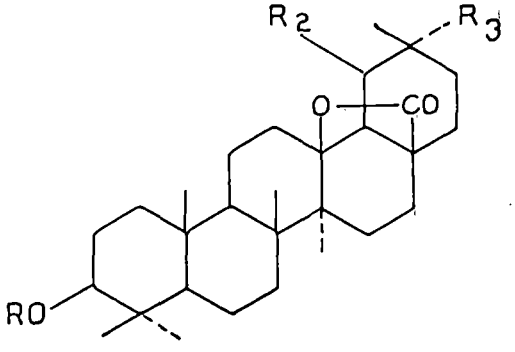
128a, $R=Ac$; $R_1=H$; $R_2=Me$

128b, $R=R_1=H$; $R_2=Me$

129a, $R=R_2=H$; $R_1=Me$

129b, $R=Ac$; $R_1=Me$; $R_2=H$

They also[73] carried out the same reaction on acetyl oleanolic acid 127e which also gave a mixture of two compounds. The less polar one was isolated as 11α, 12α-epoxy-oleanan-28 ⟶ 13-olide-3β-yl acetate 130a and the more polar compound was identified as 130b.



130a, R=Ac; R_2=H; R_3=Me

130b, R=R_2=R_3=H

130c, R=R_2=H; R_3=Me

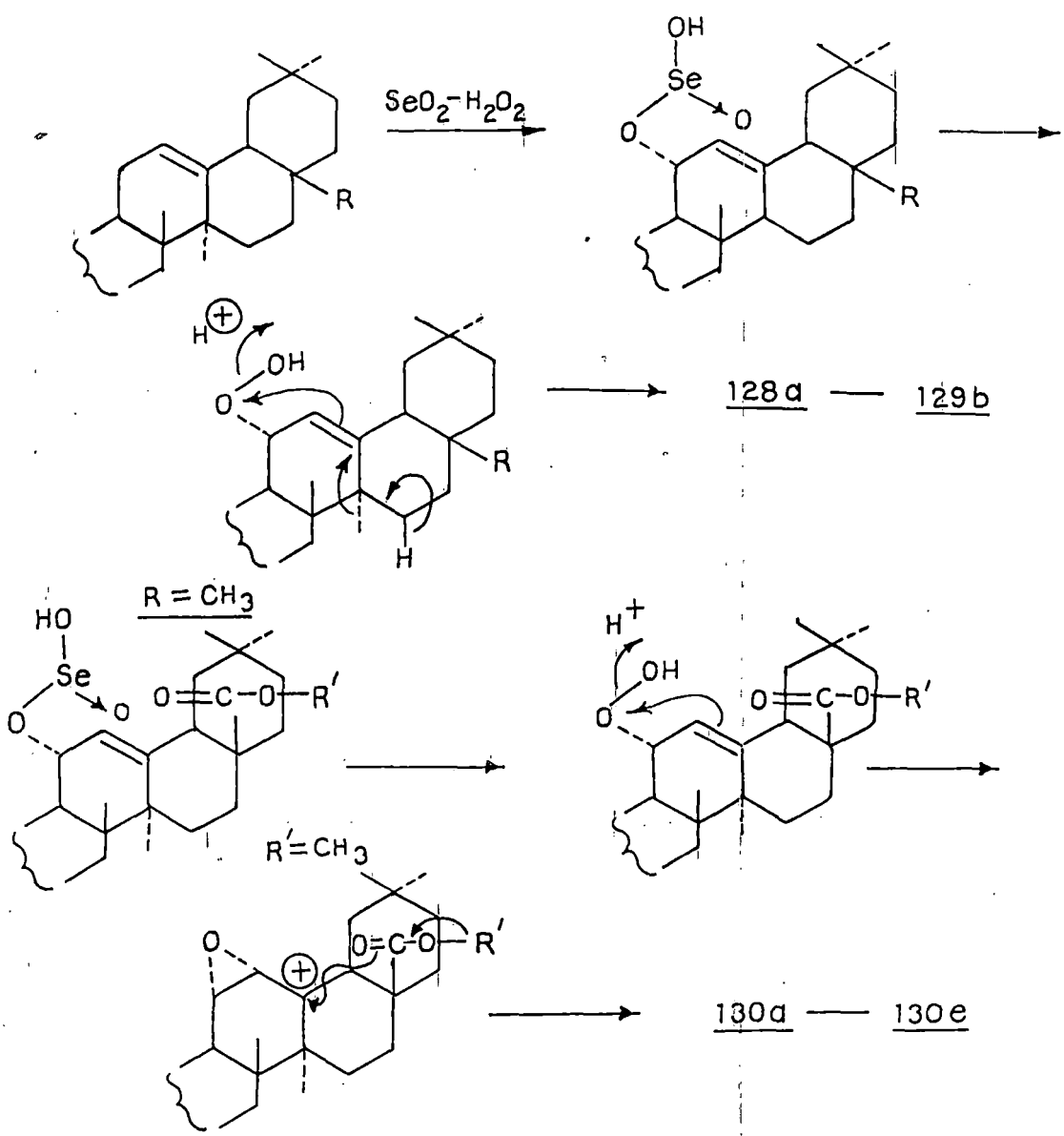
130d, R=R_3=H; R_2=Me

130e, R=Ac; R_2=Me; R_3=H

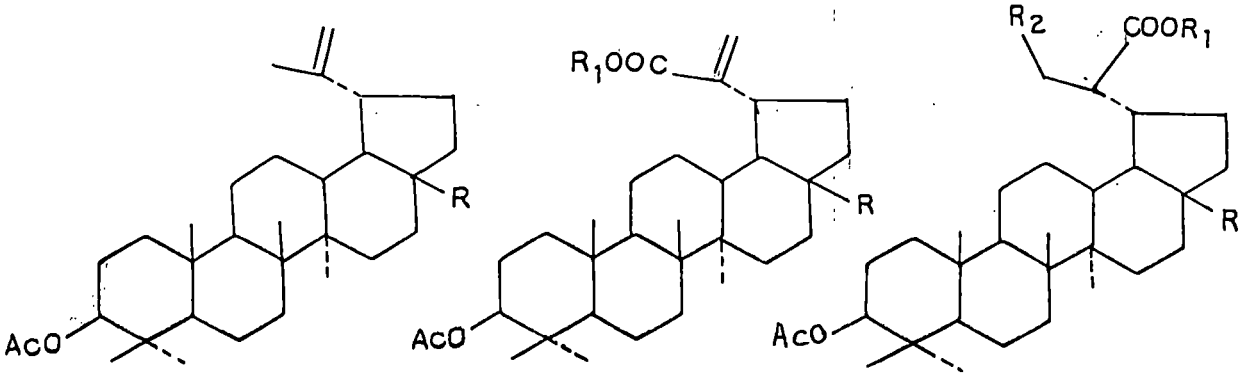
However the same oxidation on the oleanane and ursane containing CH_2OH or -COOMe group at the C-17 position afforded the corresponding epoxy lactone[73] e.g. the formation of 130c and 130d from 127d and 127e respectively; 130c and 130a from 127f and 140e and 130d from 127g respectively. From the above findings they concluded that (i) the reaction is analogous to photochemical

oxidation[74] in the formation of 11, 12-epoxide of oleanene and ursene skeletons, (ii) the C-17 methyl esters also generate lactone rings as well as the $-CH_2OH$ group. (iii) the primary acetate at C-28 position remains intact whereas the secondary acetate at C-3 undergoes hydrolysis during the reaction and (iv) the acetate group allows smooth isomerization of the double bond from C-12(13) position. Probable mechanism for the oxidation reaction suggested by Pradhan et al[73] are depicted in scheme XVII.

Scheme XVII



The present author desires to report herein the oxidative reaction of selenium dioxide containing hydrogen peroxide in t-butanol on triterpenoids containing isopropenyl side chain e.g. lupenyl acete 131a and methyl acetyl betulinate 131b. The products obtained after work up were separated after esterification and acetylation. Three different oxidation products identified as 30-carbomethoxy-lupenyl acetate 132a, 30-carbomethoxy-lupan-3β, 29-diyl acetate 132b and 29-carbomethoxy-lupan-3β-yl acetate 132e were obtained from lupenyl acetate 131a and two from compound 131b, designated as 28,30-dicarbomethoxylupenyl acetate 133a and 28,29- di carbomethoxy-lupan-3β-yl acetate 133b.



131a, R = Me

131b, R = COOMe

132a, R=R$_1$=Me

133a, R=COOMe
R$_1$ = Me

142b, R=R$_1$=Me
R$_2$=OAc

142c, R=R$_1$=Me
R$_2$ = H.