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REACTION OF CARBONYL COMPOUNDS WITH DIAZOALKANES AS A METHOD FOR EPOXIDE SYNTHESIS. A REVIEW

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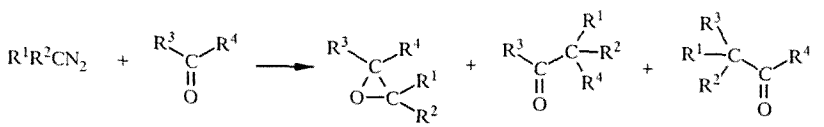
The application of the reaction of carbonyl compounds with diazoalkanes for the preparation of epoxides is reviewed. The effects of the structures of the reagent and substrate and of the solvent on the reaction course and product yield are examined. The stereochemistry of epoxide formation is discussed.

The first communication indicating that carbonyl compounds are capable of reacting with diazomethane appeared in 1885. However, the systematic study of this reaction commenced only in 1920-1939 and showed that it is very general in nature and applicable for both aldehydes and ketones. Considerable experimental data were reviewed by Gutsche in the mid-1950's [1].

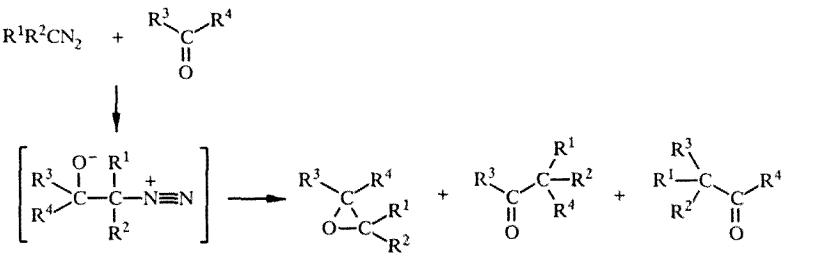
The following products may be formed in the reaction of diazoalkanes:



In the present review, we treat mainly those reactions of carbonyl compounds with diazoalkanes, which lead to significant yields of epoxides. Esters are included in the group of carbonyl compounds along with aldehydes and ketones if they react with diazoalkanes at the carbonyl group to give epoxides. On the other hand, the reactions of carbonyl compounds leading to the insertion of a methylene unit or proceeding at another part of the molecule (for example, cycloaddition at the double bond in α,β-unsaturated ketones) are examined only to the extent necessary for elucidation of the major subject of this review. The effects of the structures of the starting carbonyl compounds and diazoalkanes and nature of the solvent on the epoxide yield are analyzed. The last part of this review is devoted to the stereochemistry of this reaction.

1. REACTION MECHANISM

According to the most common viewpoint [1], the mechanism of this reaction involves initial nucleophilic addition of the diazoalkane at the carbonyl group to give a zwitter-ionic intermediate, which then undergoes either a 1,2-shift of the alkyl group or cyclization to the epoxide.



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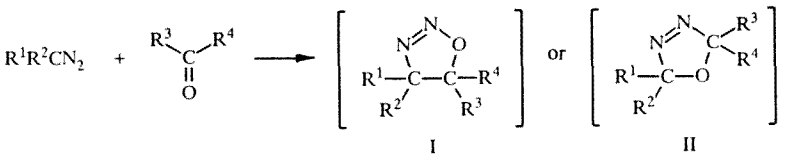
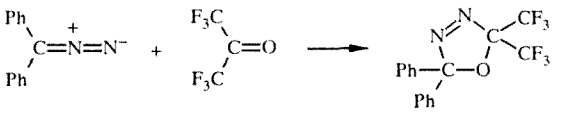
In an alternative hypothesis, the intermediate is not a dipolar ion but rather an oxadiazoline, which may have either structure I or II [2].



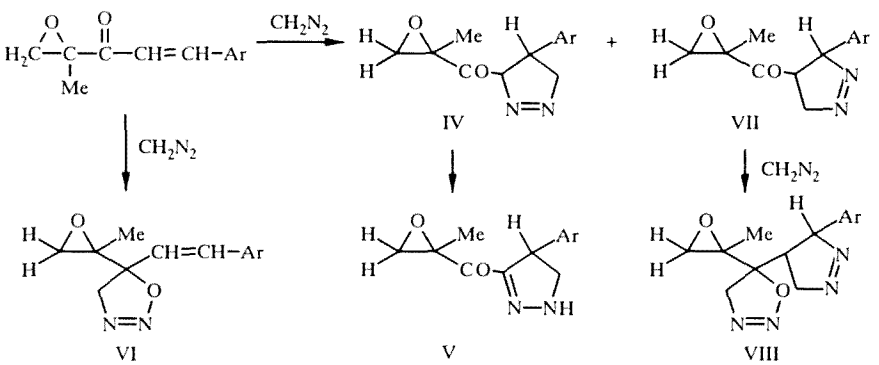
I II

In some cases, the oxadiazolines are stable compounds and may be isolated. Thus, the adduct of diphenyldiazomethane and hexafluoroacetone III was obtained in 95% yield [3].



III

Oxadiazolines stable under ordinary conditions were isolated in small amounts in the reaction of diazomethane with β-arylacryloyloxiranes [4, 5].

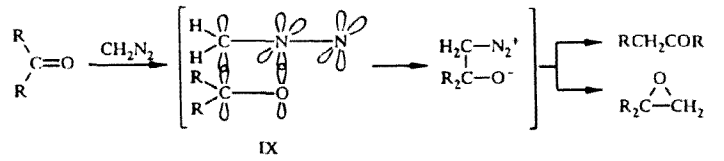


The predominant direction of the reaction in all cases is the 1,3-dipolar cycloaddition of the double bond according to the Auers' rule to give Δ^{-1}-pyrazoline IV, which spontaneously isomerizes to Δ^{2}-pyrazoline V. The addition of the reagent at the carbonyl group leading to oxadiazoline VI is observed to a significant extent only if the aromatic ring has electron-donor substituents, which diminish the reactivity of the double bond. In some cases, a small amount of adduct VII formed counter to the Auers' rule may be isolated. The carbonyl group in VII is not in conjugation, which facilitates addition of diazomethane at this group to give VIII.

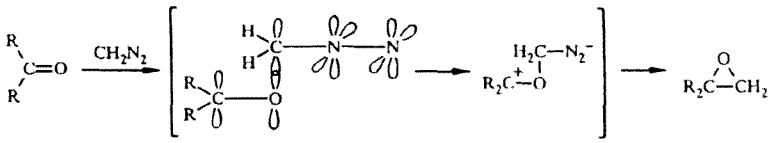
The question whether the oxadiazoline is in equilibrium with a zwitter-ion or if one of these compounds is an intermediate leading to the other remains open. In any case, the participation of a cationoid intermediate for the 1,2-shift of the alkyl substituent is necessary.

In order to explain the regioselectivity of this reaction, in particular, the tendency of sterically-hindered ketones to convert predominantly to the corresponding epoxides, Gutsche and Bowers [6] proposed that diazomethane, which has partial negative charge on the terminal nitrogen atom and the carbon atom, may react with carbonyl compounds through two pathways.

According to this hypothesis, complex IX is capable of converting to both carbonyl compounds and epoxides, while complex X may undergo only cyclization to give an epoxide through the corresponding intermediate.

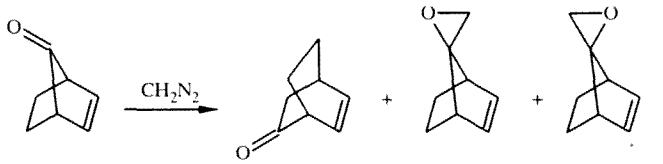


IX



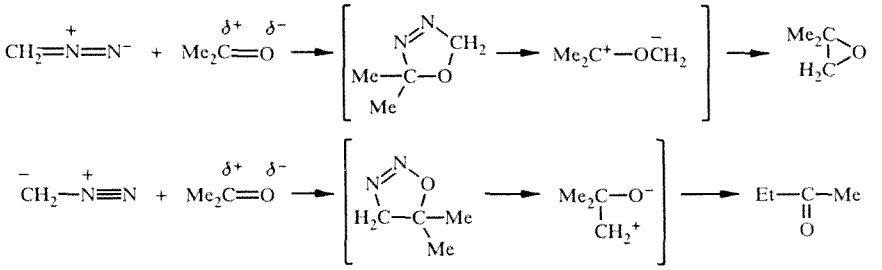
X

Bly [7] noted that this scheme does not account for the experimental results. Thus, the reason that only epoxide XIII is formed from ketone XI along with ketone XII and not XIV is unclear.

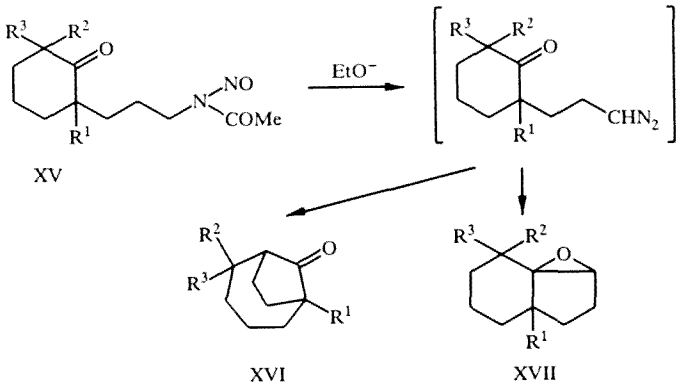


XI XII (44%) XIII (34%) XIV (0%)

At the same time, Ledwith [8, 9] proposed a mechanism involving formation of two regioisomeric oxadiazolines on the basis of a kinetic study of the reaction of diazomethane with acetone in the presence of butanol as the catalyst.



The addition of the diazoalkane may occur not through nucleophilic attack but rather through a concerted [3+2] cycloaddition. The data of Gutsche [6, 10] support this hypothesis.



XV XVI XVII

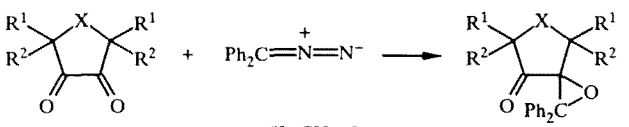
Bicyclic ketone XVI is the predominant product when $R^1 = R^2 = R^3 = H$, while almost exclusive formation of epoxide XVII is observed when $R^1 = R^2 = R^3 = CH_3$. Such sensitivity of the reaction to the steric factor suggests a concerted mechanism.

Thus, a common viewpoint on the mechanism of the reaction of diazoalkanes with carbonyl compounds is lacking though it has been established, at least in a few cases, that the reaction proceeds through a concerted mechanism and involves formation of an oxadiazoline.

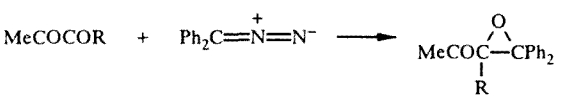
2. EFFECT OF VARIOUS FACTORS ON THE PRODUCT RATIO

2.1. STRUCTURE OF THE DIAZO COMPOUND

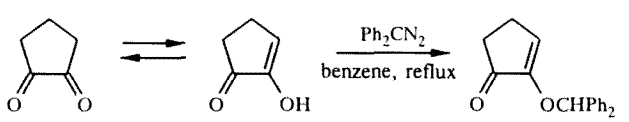
Various workers in the period from 1930 to 1949 established that presence of electron-donating groups in the diazoalkane facilitates the reaction, while the presence of electron-withdrawing groups hinders the reaction [11-15]. According to this rule, diazomethane is somewhat less reactive than its higher homologs and is much more reactive than compounds such as diphenyldiazomethane or ethyl diazoacetate. Thus, diphenyldiazomethane adds only at the carbonyl group of heterocyclic [16], acyclic, and alicyclic α-diketones [17].



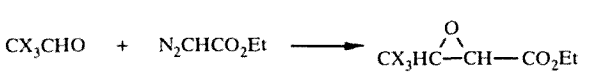
X=CH_2, O



On the other hand, diphenyldiazomethane does not react with tetrahydrofuran monoketones either in protic solvents such as methanol or aprotic solvents such as benzene and ether even in the presence of boron trifluoride etherate as the catalyst. If on the other hand, a strongly enolized ketone is used, the formation of a benzhydryl ether of the enol is most likely.

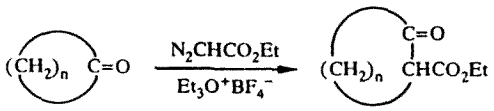


Ethyl diazoacetate, which contains an electron-withdrawing ester group, is even less capable of addition at a carbonyl group. However, this compound gives epoxides in rather high yield with reactive aldehydes such as chloral or bromal [1].

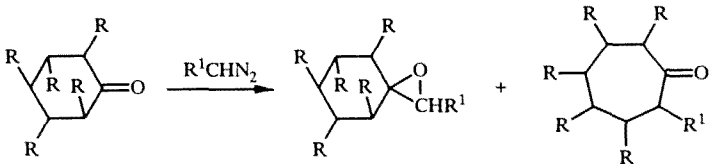


X=Cl (72%), Br (54%)

Ethyl diazoacetate reacts with ketones only in the presence of catalysts, the most efficient of which is triethyloxonium tetrafluoroborate [18]. In this case, epoxides are not obtained. However, this reaction is a good method for introducing a carboethoxymethylene unit.



As already noted, the differences in the reactivity of diazomethane and its homologs are not as significant as in the case of ethyl diazoacetate and diazomethane but are nevertheless sometimes manifest [19].



XVIII XIX

R=MeCOO; R^1=H, Me, Et

When R^1 = H, only XVIII is formed, while diazoethane and diazopropane give a mixture of epoxide XVIII and ketone XIX.

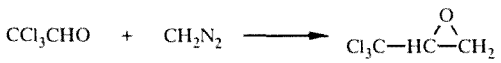
Thus, the high reactivity of diazoalkanes facilitates competing side-reactions more than epoxide formation. On the other hand, diazo compounds with low reactivity do not tend to give insertion products but are converted to epoxides only with most reactive carbonyl compounds such as aldehydes or nonenolizable α-diketones.

2.2. STRUCTURE OF THE CARBONYL COMPOUND

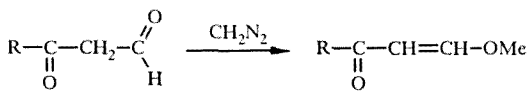
2.2.1. ALDEHYDES

Simple aliphatic aldehydes react with diazomethane to give ketones and, in most cases, epoxides. The ketone yield, as a rule, increases with increasing length of the aliphatic side-chain of the aldehyde [1]. Arylacetaldehydes give mixtures containing arylacetones and epoxides in ratios determined by the electron-donor or electron-withdrawing properties of the substituent in the aromatic ring and nature of the solvent. The effect of the solvent is discussed in section 2.3.

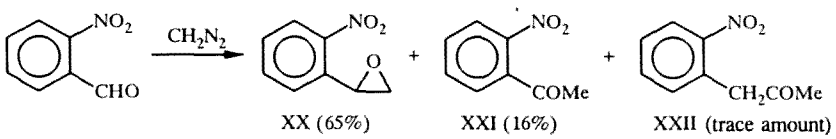
Aliphatic aldehydes with electron-withdrawing substituents at the α-carbon atom, as a rule, form epoxides. Thus, chloral gives trichloromethyloxirane almost exclusively [1].



An enol ether is formed in the case of readily enolizable aldehydes such as β-ketoaldehydes [20].



Aromatic aldehydes give epoxides or methyl aryl ketones. The product ratio depends on the nature of the substituents in the aromatic ring. Electron-donor substituents facilitate ketone formation, while electron-withdrawing substituents lead to epoxide formation. For example, acetophenone is obtained in 97% yield from benzaldehyde, while a mixture of XX—XXII is formed from *o*-nitrobenzaldehyde [1].



XX (65%) XXI (16%) XXII (trace amount)

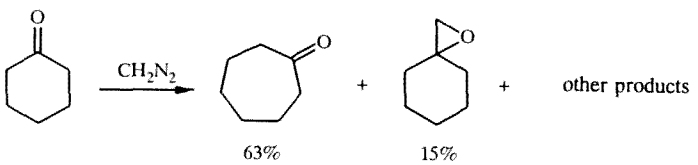
Higher diazoalkanes convert aldehydes mainly into ketones. The corresponding arylaliphatic ketones were obtained from benzaldehyde in 89-100% yield [12].

We should note that the homologous aldehyde has never been obtained as the result of an aldehyde with a diazoalkane. In other words, hydrogen undergoes 1,2-migration rather than the alkyl or aryl group.

2.2.2 KETONES

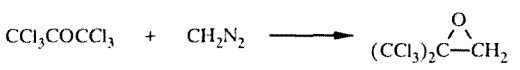
Acyclic ketones react much more slowly than the corresponding aldehydes and are more likely to form epoxides. As a rule, the yield of the homologous ketone falls with increasing chain length. 2-Undecanone forms only epoxide [1]. Alcohols (usually methanol or ethanol) are sometimes added to promote the reaction.

Carbocyclic ketones react predominantly with ring expansion although oxiranes are formed in significant amounts. The reactivity of cycloalkanones drops, as in the case of many other nucleophilic reactions, in the following order $C_6 > C_7 > C_5 > C_8$. For this reason, cyclopentanone does not form cyclohexanone upon reaction with diazomethane but rather mostly cycloheptanone. Cyclohexanone reacts with one mole of diazomethane to give the following product mixture.



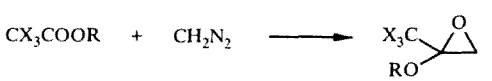
If, on the other hand, this reaction is carried out with two moles diazomethane, cyclooctanone is obtained in about 60% yield.

The presence of electron-withdrawing substituents in the α position relative to the carbonyl facilitates epoxide formation. Thus, epoxide XXIII is obtained from hexachloroacetone in virtually quantitative yield upon treatment with diazomethane [21].



XXIII

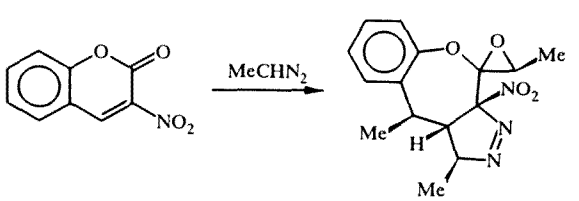
Even the ester oxo group may be converted into an epoxide group by the action of diazomethane if an electron-withdrawing group is found in the α position. Thus, esters of trichloroacetic and trifluoroacetic acids form the corresponding epoxides XXIV in 40-88% yield [22, 23].



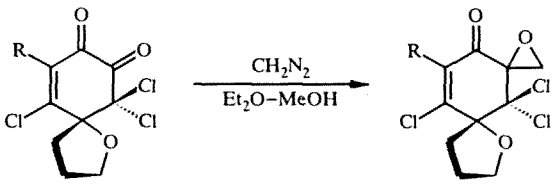
XXIV

X=Cl, F

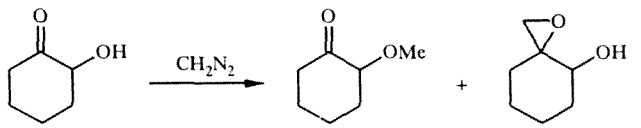
The α-nitro group has a similar effect. Dean and Park [24] observed the addition of three moles of diazoethane to 3-nitrocoumarin.



α-Diketones react with diazomethane often to give α-ketoepoxides due to the electron-withdrawing effect of the adjacent carbonyl group. An example of such a conversion has been described by McKague [25].



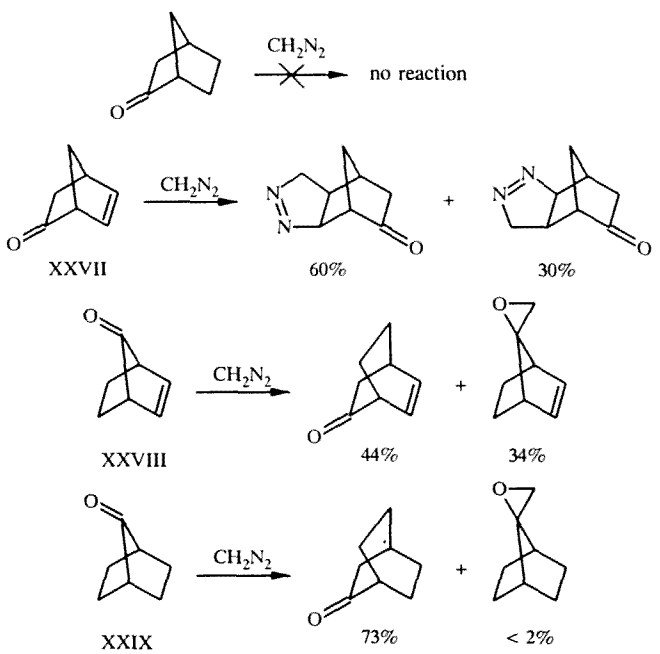
The presence of even one α-hydroxyl group may significantly alter the product ratio toward epoxide formation. Thus, 2-hydroxycyclohexanone reacts with diazomethane to give a mixture of XXV and XXVI [26]. It is interesting that cycloheptane derivatives are not formed at all in this case.



XXV (10%) XXVI (90%)

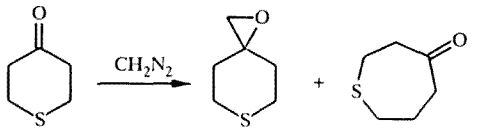
The steric factor is no less important. The presence of bulky substituents at the α position relative to the carbonyl group almost always lowers the product yield [1]. Substituents distant from the carbonyl group usually have only a weak effect on the reaction course.

Interesting effects may be observed in the case of strained bridge structures, in particular, norbornane derivatives [7]. Slight differences in the substrate structure in this case may lead to significant change in the direction of the reaction.



We should note that the observed 1,3-dipolar cycloaddition of diazomethane to ketone XXVII at the nonactivated double bond is a rather rare case. Comparison of the result of the reaction of XXVIII and XXIX with diazomethane shows that change in the molecular geometry upon the introduction of a double bond (ketone XXVIII) markedly enhances the epoxide yield in comparison with saturated ketone XXIX.

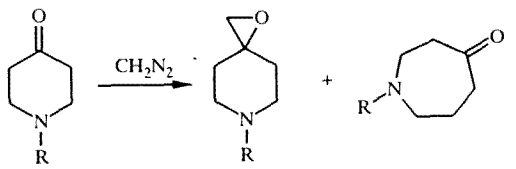
The reaction of heterocyclic ketones with diazoalkanes has not been studied extensively until recently. In 1956, Overberger and Katchman [27] showed that 4-tetrahydrothiopyranone reacts with diazomethane to give a mixture of epoxide XXX and ring expansion product XXXI [27].



XXX (40%) XXXI (42%)

However, the sulfone obtained from 4-tetrahydrothiopyranone gives only epoxide under these conditions [27].

The chemiselectivity of the reaction of various heterocycloalkanones with diazomethane has been studied in the case of piperidine compounds [28-33].



The greatest epoxide yield was achieved when R = $PhSO_2$ (82%) and R = NO (the yield was not reported but the only product was found to be an epoxide) [33].

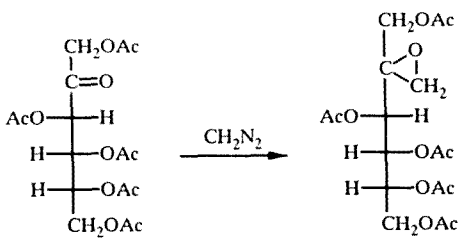
These effects of substrate structure on the epoxide yield indicate that the presence of electron-withdrawing substituents in the α position relative to the carbonyl group and steric accessibility of this group facilitate epoxide formation.

2.3. EFFECT OF THE SOLVENT

The reaction of carbonyl compounds with diazoalkanes is usually carried out in an inert aprotic solvent. As a rule, an ester is used but many ketones and even some aldehydes in dry alcohol-free ether are inert relative to diazomethane [1]. Catalysis by protic solvents is required in these cases. Water and alcohol, especially, methanol, are most often employed as such catalysts.

The catalytic action of alcohols is usually presumed to be related to their coordination at the carbonyl group oxygen due to hydrogen bond formation, which leads to an increase in the effective charge β^+ on the carbonyl carbon atom and increase in its reactivity. There is a dual effect of protic catalysis on the reaction course. On one hand, the reaction rate increases with increasing alcohol content in the reaction mixture. On the other hand, an increased alcohol content facilitates more rapid formation of carbonyl compounds in comparison with epoxide. Thus, the reaction of norcamphor and dehydronorcamphor with diazomethane in methanol leads to a mixture of insertion products, while the epoxide is not formed at all [34, 35]. Bicyclo[3.3.1]nonan-2-one reacts with diazomethane in ether—methanol to give only traces of epoxide, while the major products result from ring expansion [36].

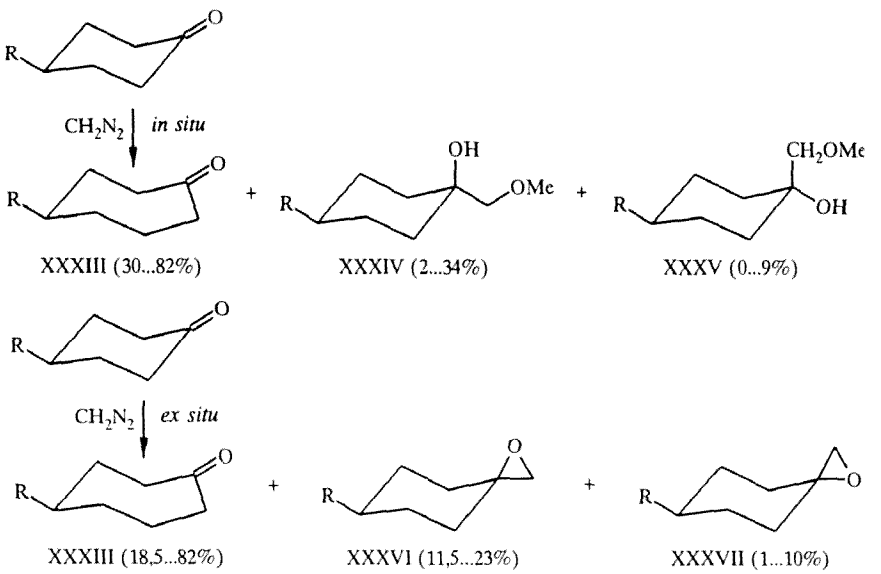
On the other hand, if trace amounts of methanol are used, a high epoxide yield and suitable reaction rate may both be achieved. Thus, *D*-fructose pentaacetate in chloroform containing traces of methanol reacts with diazomethane and forms epoxide XXXII in 75% yield [37, 38].



XXXII

One method for carrying out the reaction of diazoalkanes with carbonyl compounds is generation of the diazoalkane *in situ* using alkali or an alkali metal carbonate from an N-nitrosoalkylurea or N-nitrosoalkylurethane. This operation is usually carried out in ethanol—water or ethanol—water—ether. Literature data showed that epoxide preparation under such conditions is difficult. The reaction mixture usually contains ketone obtained due to the insertion of a methylene unit and, in some cases, other products. For example, 4-*tert*-butylcyclohexanone gives 49% 4-*tert*-butylcycloheptanone upon the action of N-nitrosomethylurethane in KOH/H_2O—EtOH [39].

Favre et al. [29] compared the reactions of substituted cyclohexanes with diazomethane *ex situ* (CH_2N_2 in ether—methanol) or *in situ* (N-nitrosomethylurethane in KOH/H_2O—MeOH).

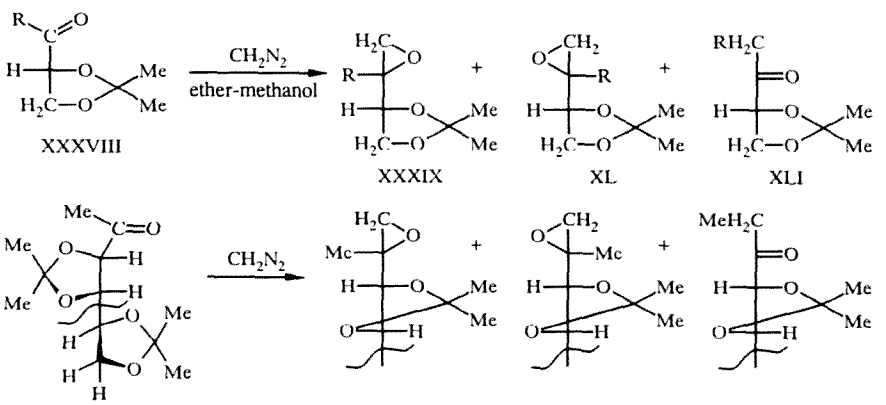


The formation of methoxyalcohols XXXIV and XXXV in the *ex situ* case proceeds through the same intermediate as the formation of epoxides XXXVI and XXXVII in the *in situ* case since the direct opening of the epoxide ring under the *in situ* conditions proceeds much more slowly.

In most of the examples described in the literature, it is difficult to evaluate the solvent effect as such apart from other factors, primarily, the structure of the starting reagents. However, a tendency is observed for an increased reaction rate but decrease in epoxide yield with increasing content of protic solvent in the reaction mixture.

3. STEREOCHEMISTRY OF EPOXIDE FORMATION

The three-dimensional structure of the epoxides formed is one of the most important problems in the methylenation of carbon compounds by the action of diazoalkanes but most of the studies on this subject are devoted to sugars and their analogs.

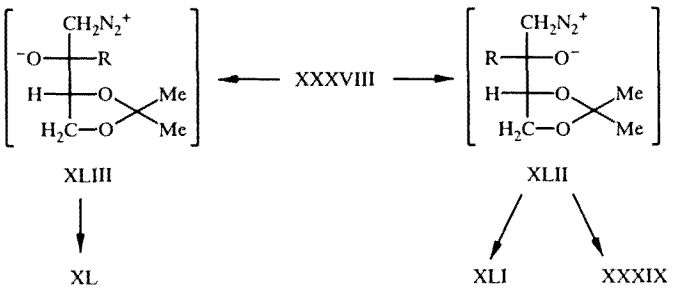


Thus, Scandinavian workers have published a series of studies on the reaction of carbohydrates and related compounds with diazomethane [40-43].

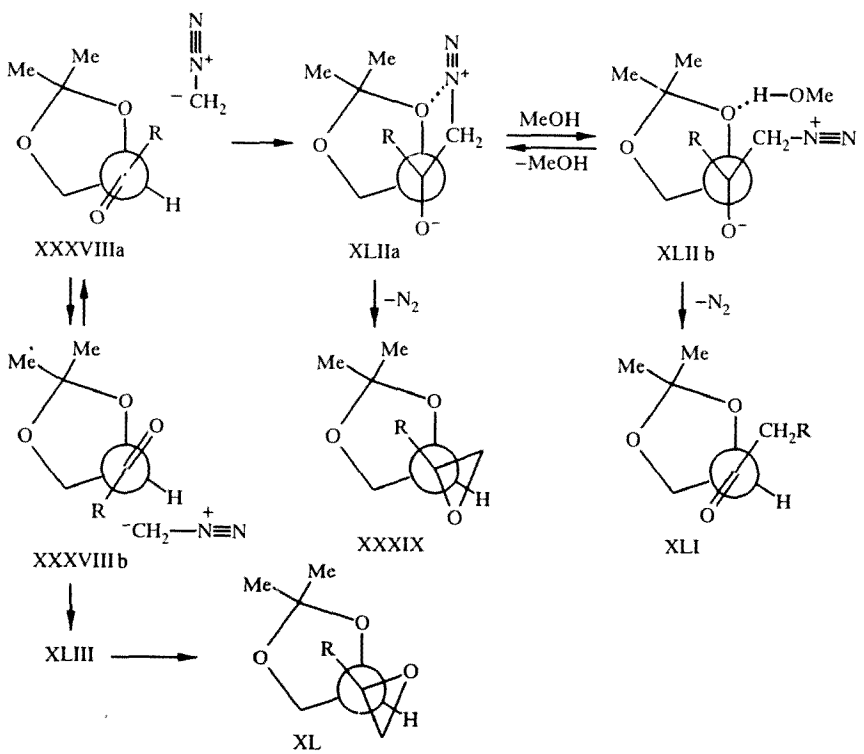
The yield of XXXIX, XL, and XLI is a function of the structure of the starting compound and content of methanol in the reaction mixture. While the amount of *erythro* epoxide XXIX formed decreases somewhat with increasing methanol concentration, the amount of ketone XLI, on the other hand, increases. The yield of *threo* epoxide XL, as a rule, hardly depends on the alcohol concentration and only a slight increase in the yield of this product is noted with increasing alcohol concentration.

The following trends are seen. Firstly, the tendency for predominant formation of epoxide rather than ketone increases with increasing chain length in going from R = H to CH_3 and C_2H_5. Secondly, the *erythro-threo* selectivity drops concurrently due to an increase in the amount of the *threo* isomer.

In order to explain this behavior, Anthonsen et al. [40-43] proposed a scheme, in which XXXIX and XLI are formed from the same intermediate XLII, while *threo* epoxide XL is formed from intermediate XLIII.



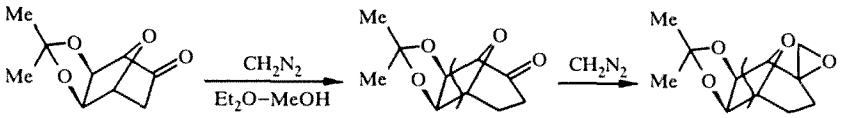
The most favorable conformation of starting XXXVIII is XXXVIIIa, in which the oxygen atoms of the carbonyl group and isopropylidenoxy groups are anti-periplanar. Attack of the reagent occurs from the less sterically hindered side. Several conformations are also possible for intermediate XLII, the most favored of which, at least in ether solution, is conformation XLIIa, in which the positively charged atom of the diazo group is coordinated at oxygen. Conformation XLIIa is most favorable for cyclization to give epoxide XXXIX.



The addition of methanol diminishes the attraction of the oxygen and diazo group due to formation of a hydrogen bond with the oxygen bond such that the probability of conformation XLIIb with anti-periplanar arrangement of R and N_2^+ increases. Correspondingly, the yield of the ketone formed due to 1,2-migration of R requiring conformation XLIIb also increases.

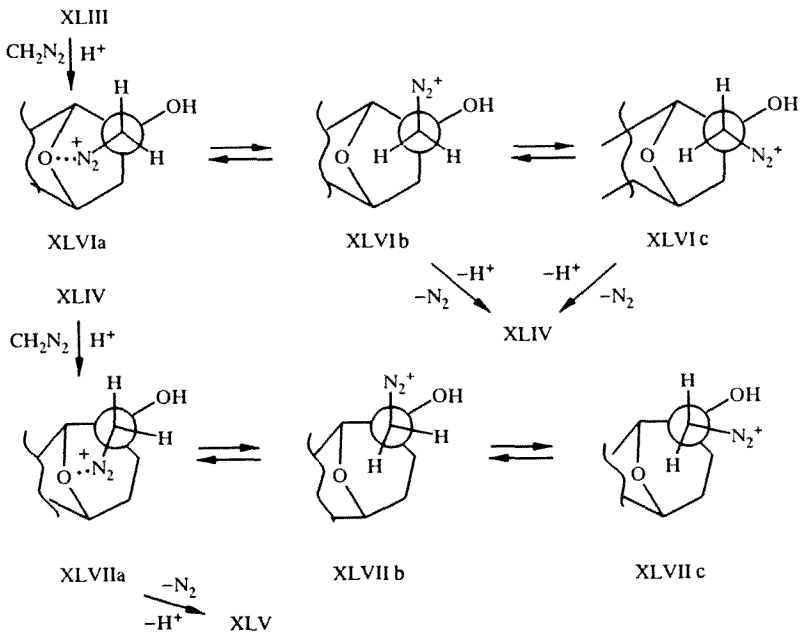
This model accounts for the decrease in *erythro—threo* selectivity with increasing bulk of the R group since such an increase enhances the steric hindrance in conformation XXXVIIIa, which diminishes its stability relative to XXXVIIIb, and the formation of *threo* isomer becomes more likely.

Studies of the stereochemistry of the reaction of diazomethane with carbonyl compounds have also been carried out on conformationally rigid structures. Thus, Vogel et al. [44] studied the reaction of derivatives of 7-oxabicyclo[2.2.1]heptan-2-one with diazomethane.



XLIII XLIV XLV

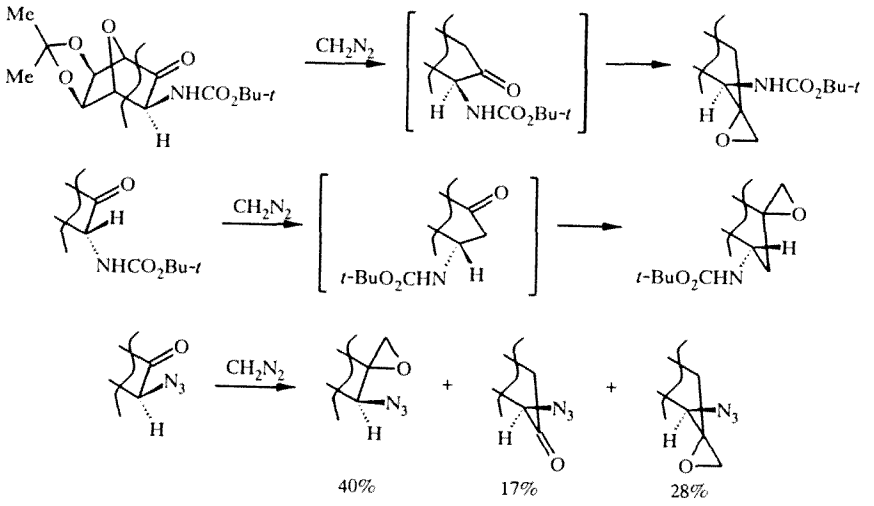
The reaction of ketone XLIII with diazomethane to epoxide XLV as the only product in the case of excess diazomethane, while a mixture of XLIV and XLV is obtained when the approximately equimolar amounts of the reagents are taken.



These authors examined possible conformations of the intermediates formed upon the addition of diazomethane to ketones XLIII and XLIV.

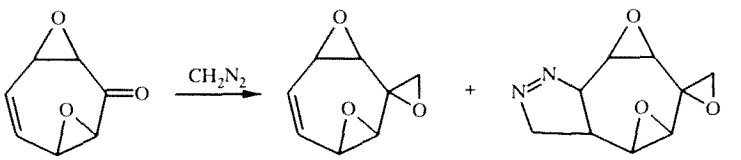
Conformation XLVIa is unfavorable for intermediate XLVI due to excessive frontal strain. As a consequence, ketone XLIV formed from XLVIb and XLVIc is the reaction product in the first step. The addition of a second diazomethane molecule at the bridging oxygen makes conformer XLVIIa most stable and formation of epoxide XLV becomes the predominant process. It is readily seen that the possibility of such stabilization of the intermediate would be excluded upon attack of diazomethane from the opposite side of the carbonyl group. This discrepancy accounts for the stereoselectivity of the reaction.

The reaction of diazomethane with analogs of ketone XLIII containing a substituent at $C_{(3)}$ was also studied [44].



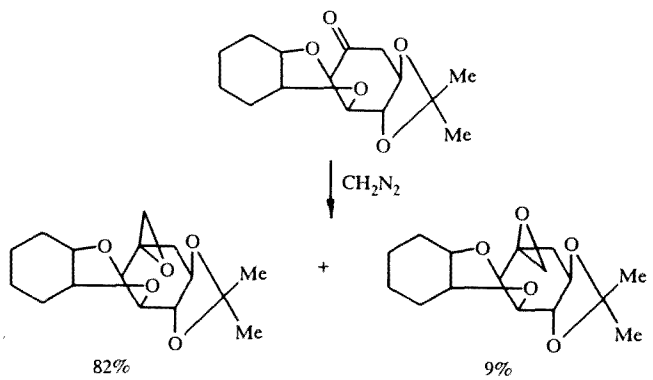
The above schemes show that the configuration of the epoxide formed in all cases is such that the methylene group of the epoxide ring is *cisoid* to the nearest heteroatom possessing an unshared electron pair (oxygen or nitrogen). The authors also relate this result to stabilization of the intermediate due to coordination of the positively charged diazo group at the heteroatom.

Prinzbach et al. [45] studied the reaction of the (1,4-*syn*)diepoxide of tropone XLVIII with diazomethane.

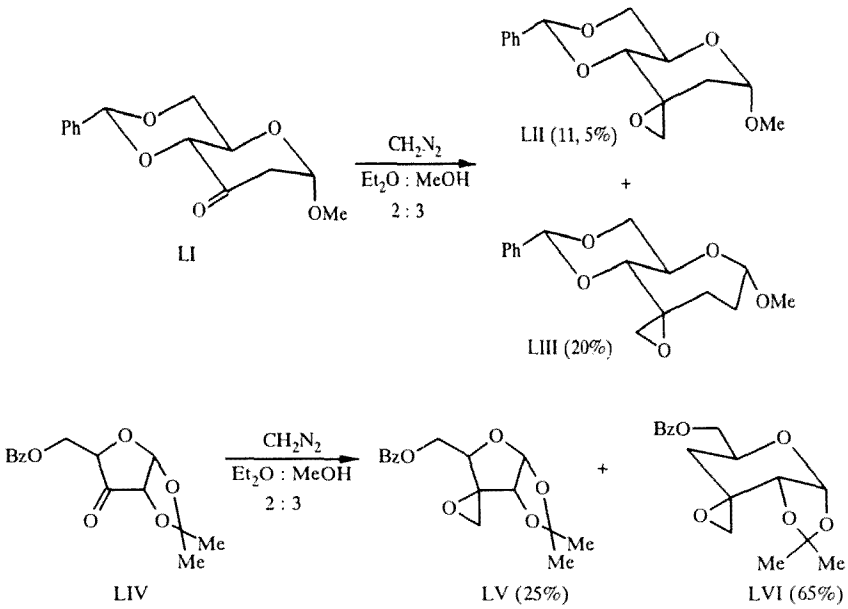


It is readily seen that the stereochemistry of this reaction corresponds to the behavior discussed above. The attack of the reagent takes place from the side of the α-heteroatom or α-heteroatoms bearing an unshared electron pair. We should note that diazomethane also adds at the double bond furthest from the carbonyl group. This addition occurs to give an epoxide since XLIX is not converted to L under the reaction conditions. The double bond is probably activated by conjugation with the carbonyl group through the epoxide ring.

The possibility of the stereoselective introduction of a new carbon unit by means of the reaction of ketoses and their analogs with diazoalkanes has been used repeatedly for the stereoselective preparation of carbohydrates with an elaborated chain. Thus, Suami et al. [46] used this method in one of the steps in the synthesis of pseudo-β-*DL*-galactopyranose.

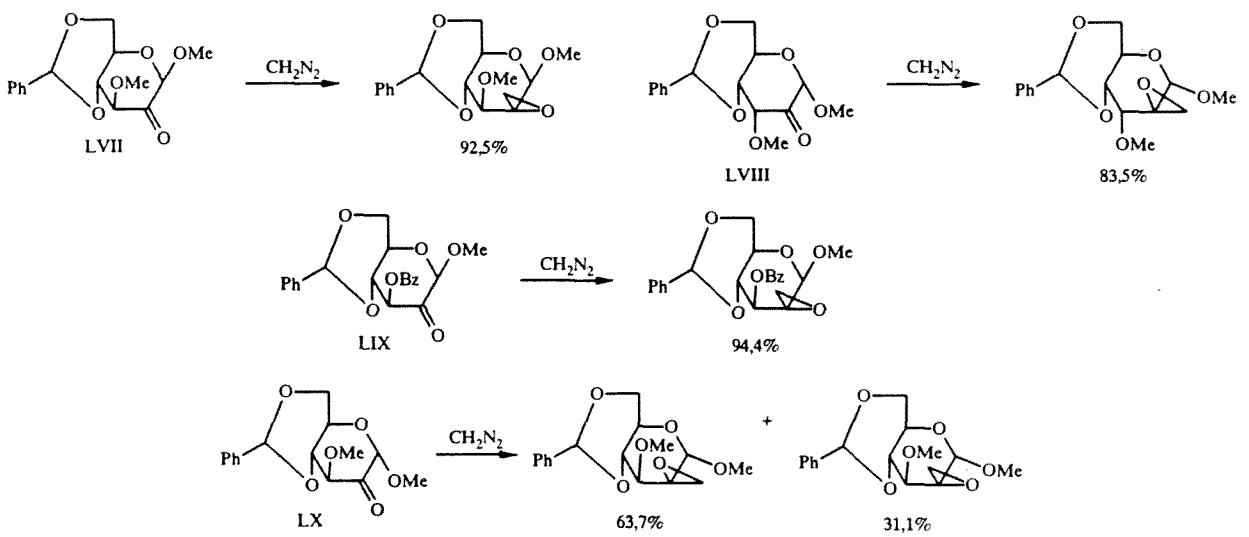


Flaherty et al. [47] observed ring expansion of both ketopyranoses and ketofuranoses along with epoxide formation upon the action of diazomethane. However, the expanded-ring ketone formed in both cases reacts further with diazomethane to give the corresponding epoxide.



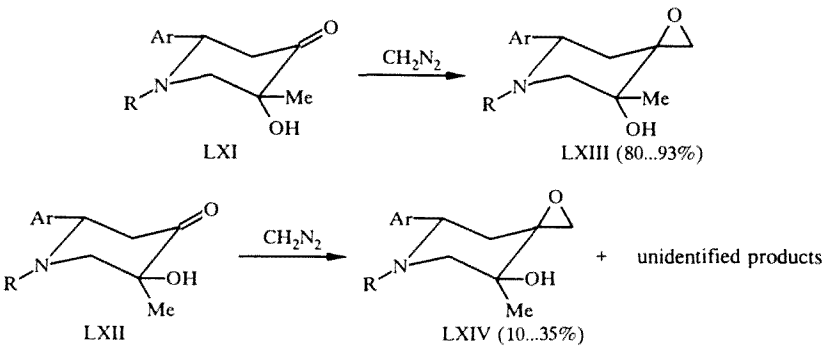
The reaction stereochemistry was not discussed by the authors. However, we should note that the configurations of the epoxide ring of products LII and LIII formed from ketone LI are opposite. Stabilization of the intermediate probably occurs through coordination of the diazo group at the oxygen atom of the methoxy group in the case of epoxide LII but at one of the oxygen atoms of the 1,3-dioxane ring in the case of epoxide LIII. The same configuration of the epoxide ring is found for LV and LVI since the intermediate may be stabilized only due to the oxygen atom of the 1,3-dioxolane ring. The predominance of ring expansion products in both cases is likely a consequence of the high methanol content in the reaction mixture. Evidence for this hypothesis is found in the preparation of only epoxide LV when the reaction of diazomethane with LIV is carried out in pure ether.

If the carbonyl carbon atom is surrounded by two functional groups with heteroatoms bearing unshared electron pairs, each of these groups may make its own contribution to stabilization of intermediate and, as a consequence, to control of the reaction stereochemistry. Of course, both "concerted" and "nonconcerted" orientation is possible, which is well illustrated in the work of Sato and Yoshimura [48].



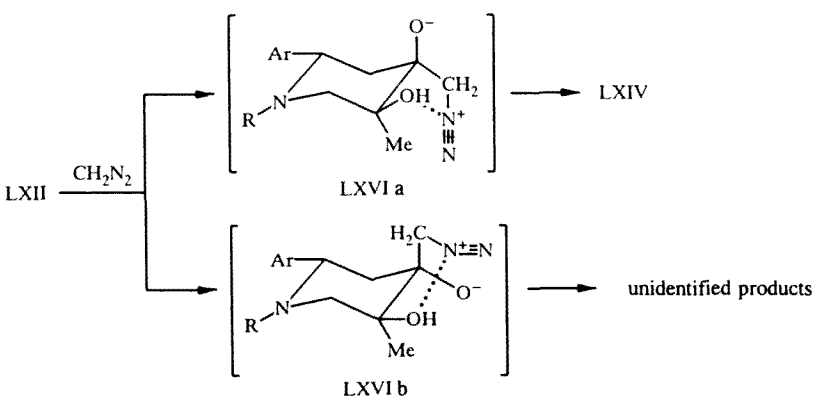
If the methoxy group (or, in the case of LIX, the methoxy and benzoyloxy groups) at $C_{(2)}$ and $C_{(4)}$ of the substrate have *cis* orientation, the reaction proceeds with high stereoselectivity (LVII—LIX). In the opposite case of LX, the intermediates formed upon reagent attack from different diastereotopic sides of the carbonyl group are stabilized to approximately the same extent and the corresponding products are obtained in comparable amounts.

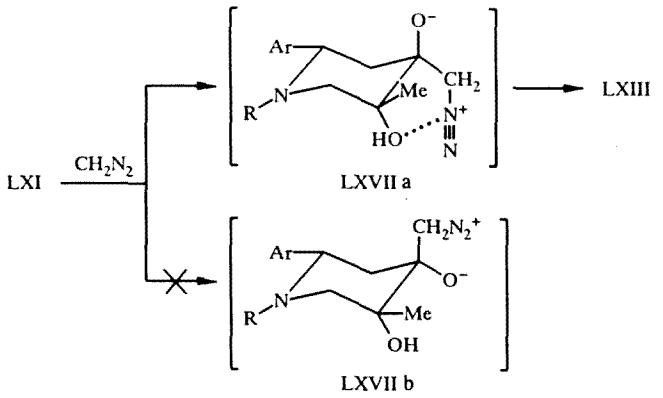
Diastereomeric 3-hydroxy-4-piperidinones react with diazomethane differently depending on the configuration of the carbonyl site of the heterocycle and nature of the substituent at the nitrogen atom [49, 50].



The configuration of the epoxide ring introduced is the same in all cases. The oxygen atom has axial orientation. 3α-Hydroxy-4-piperidinones LXI react much more rapidly than their isomers LXII with equatorial orientation of the hydroxyl group and give higher epoxide yields. 1-Benzyl-3*e*-hydroxy-3-methyl-6-phenyl-4-piperidinone also reacts smoothly with diazomethane to give the corresponding epoxide in 78% yield although this reaction proceeds more slowly and requires the addition of methanol as a catalyst. On the other hand, the methylenation of 1-methyl-3*e*-hydroxy-4-piperidinones LXII by diazomethane leads to epoxides in yield not exceeding 35%. In this case, unidentified, apparently polymeric products predominate in the reaction mixture. The stereochemistry of the reaction with diazomethane is the same as for ethers of 3-hydroxy-4-piperidinones epimeric at $C_{(3)}$.

A possible interpretation of these results rests on the difference in the stability of the intermediates formed from isomeric 3-hydroxy-4-piperidinones. In the case of LXII, both intermediates LXVIa and LXVIb are stabilized by coordination of a nitrogen atom of the diazo group at the hydroxyl oxygen but only the conformation of LXVIa with anti-periplanar arrangement of the nucleophile and leaving group facilitates cyclization to epoxide LXII. The polymeric products, in all likelihood, are formed from zwitter-ion LXVIb. In the case of LXI, only intermediate LXVIIa may be stabilized, which leads to a simpler reaction.





Thus, this review indicates the suitability of the reaction of carbonyl compounds with diazoalkanes for the stereoselective synthesis of epoxides. The possible side-reactions may often be minimized, especially if the substrate contains an activated carbonyl group. The presence of a heteroatom with an unshared electron pair in the α-position to the carbonyl group facilitates stereochemical control.

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