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CONVERSION OF CARBONYL FUNCTIONAL GROUP INTO METHYLENE GROUP BY TWO CHEMICAL STALWARTS: CLEMMENSEN REDUCTION & WOLFF– KISHNER REDUCTION

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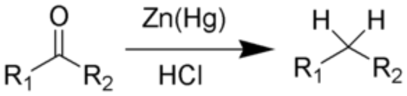
ABSTRACT

Clemmensen reduction is a chemical reaction described as a reduction of ketones (or aldehydes) to alkanes using zinc amalgam and concentrated hydrochloric acid. This reaction is named after Erik Christian Clemmensen, a Danish chemist. The original Clemmensen reduction conditions are particularly effective at reducing aryl–alkyl ketones, such as those formed in a Friedel–Crafts acylation. The two–step sequence of Friedel–Crafts acylation followed by Clemmensen reduction constitutes a classical strategy for the primary alkylation of arenes. With aliphatic or cyclic ketones, modified Clemmensen conditions using activated zinc dust in an anhydrous solution of hydrogen chloride in diethyl ether or acetic anhydride is much more effective. The Wolff–Kishner reduction is a reaction used in organic chemistry to convert carbonyl functionalities into methylene groups. In the context of complex molecule synthesis, it is most frequently employed to remove a carbonyl group after it has served its synthetic purpose of activating an intermediate in a preceding step. As such, there is no obvious retron for this reaction. Originally reported by Nikolai Kischner in 1911 and Ludwig Wolff in 1912, it has been applied to the total synthesis of scopadulcic acid B, aspidospermidine and dysidiolide. The Wolff-Kishner reduction reaction usually proceeds under strongly basic conditions in the presence of a large

amount of heat. This reaction is known to require a polar protic solvent. On the other hand, the Clemmensen reduction reaction is known to be performed under highly acidic conditions.

KEYWORDS: Zinc amalgam, HCl, aldehyde/ketone, hydrazine, electrolysis.

INTRODUCTION



Figure–1: General Reaction of Clemmensen Reaction.

This reaction is particularly effective in aryl–alkyl ketones reduction formed in Friedel–Crafts acylation. The reaction is more effective in reduction of cyclic ketones or aliphatic and zinc metal. The substrate must be tolerant of the strongly acidic conditions of the Clemmensen reduction (37% HCl). Several alternatives are available. Acid–sensitive substrates that are stable to strong base can be reduced using the Wolff–Kishner reduction; a further, milder method for substrates stable to hydrogenolysis in the presence of Raney nickel is the two–step Mozingo reduction.

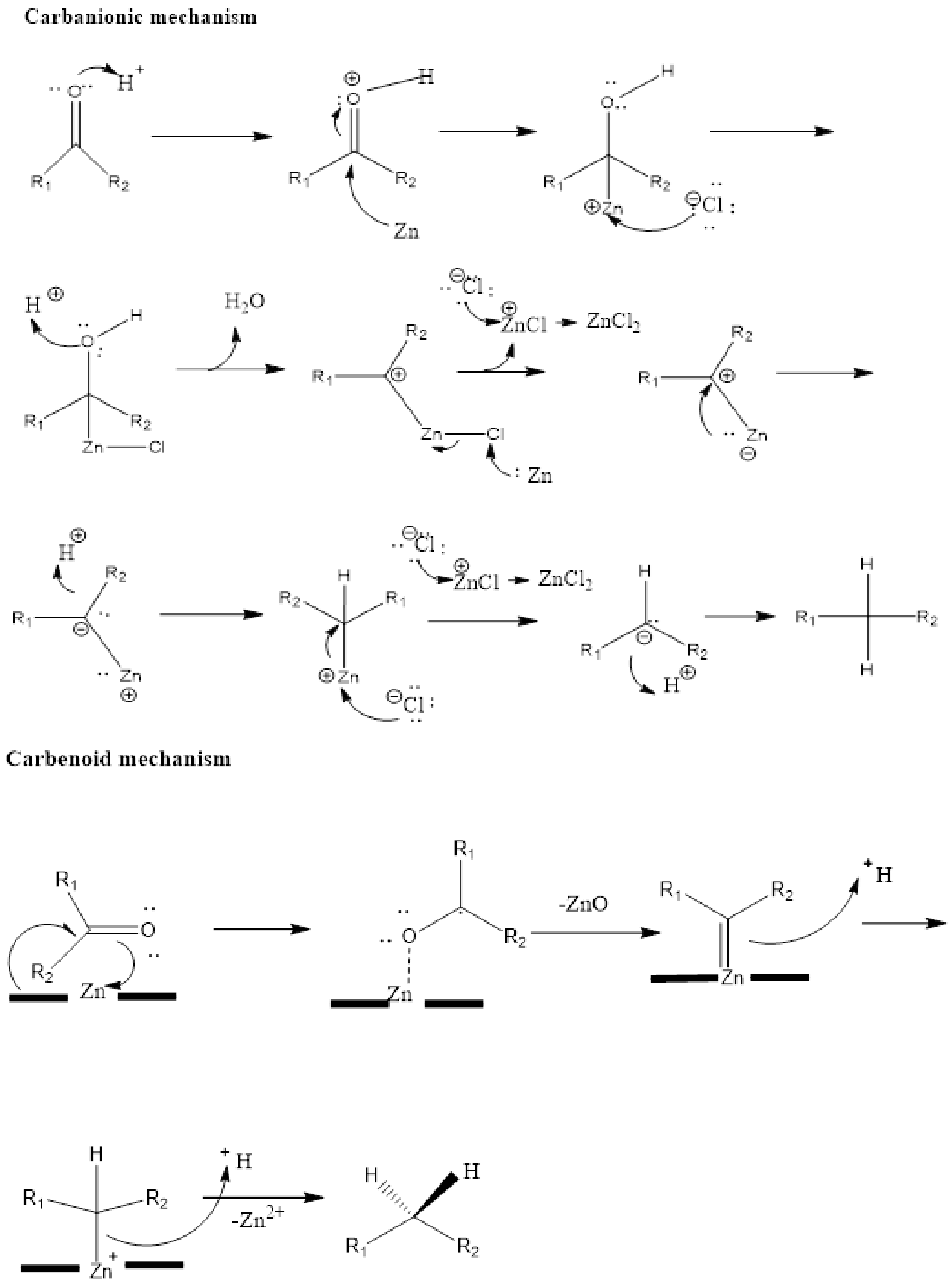
In spite of the antiquity of this reaction, the mechanism of the Clemmensen reduction remains obscure. Due to the heterogeneous nature of the reaction, mechanistic studies are difficult, and only a handful of studies have been disclosed. Mechanistic proposals generally invoke organozinc intermediates, sometimes including zinc carbenoids, either as discrete species or as organic fragments bound to the zinc metal surface. However, the corresponding alcohol is believed not to be an intermediate, since subjection of the alcohol to Clemmensen conditions generally does not afford the alkane product.[1]

Mechanism of Clemmensen Reduction Reaction

The mechanism of this reaction is not completely understood, but there are two proposals:– **Carbanionic mechanism & Carbenoid mechanism.**

Carbanionic mechanism

The carbanionic mechanism of reaction shows that the zinc attacks directly to the protonated carbon.



Carbanionic mechanism

Carbenoid mechanism

Figure-2: Difference between Carbanionic mechanism & Carbenoid mechanism.

Carbenoid mechanism: The carbenoid mechanism is a radical process and reduces the happenings on zinc metal surface. The reduction takes place at the surface of the zinc catalyst. In this reaction, alcohols are not postulated as intermediates, because subjection of the corresponding alcohols to these same reaction conditions does not lead to alkanes. The following proposal employs the intermediacy of zinc carbenoids to rationalize the mechanism of the Clemmensen Reduction:

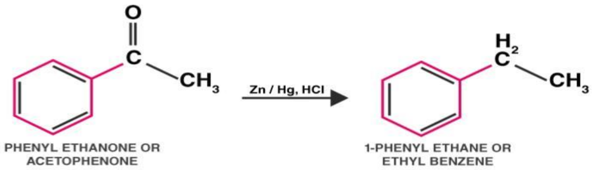
The underlying substance must not react to the acidic conditions. The acid sensitive base substance reacts in the Wolff–Kishner reduction that has a strong base if it is milder than it is Mozingo reduction. The reaction is not for the substances that are sensitive to acids. The heterogeneous nature makes the mechanism remains obscure, in spite of its antiquity and the studies on mechanism are difficult. There are only a few studies on the particular reaction proposed like possibly zinc carbenoids and organozinc intermediates.[2]

Clemmensen reduction & Wolff Kishner reduction.

Clemmensen Reduction

The Clemmensen reduction is a reaction that is used to reduce aldehydes or ketones to alkanes using hydrochloric acid and zinc amalgam. The Clemmensen reduction is named after a Danish chemist, Erik Christian Clemmensen.

Example



Figure–3: Examples.

Uses:– The Clemmensen reduction is a reaction that is used to reduce aldehydes or ketones to alkanes using hydrochloric acid and zinc amalgam.

Example: Clemmensen reduction.

Wolff–Kishner reduction	
Named after	Ludwig Wolff Nikolai Kischner
Reaction type	Organic redox reaction
Identifiers	
Organic Chemistry Portal	wolff–kishner–reduction
RSC ontology ID	RXNO:0000226

The **Wolff–Kishner reduction** is a reaction used in organic chemistry to convert carbonyl functionalities into methylene groups. In the context of complex molecule synthesis, it is most frequently employed to remove a carbonyl group after it has served its synthetic purpose of activating an intermediate in a preceding step. As such, there is no obvious retron for this reaction. Originally reported by Nikolai Kischner in 1911 and Ludwig Wolff in 1912, it has been applied to the total synthesis of scopadulcic acid B, aspidospermidine and dysidiolide.

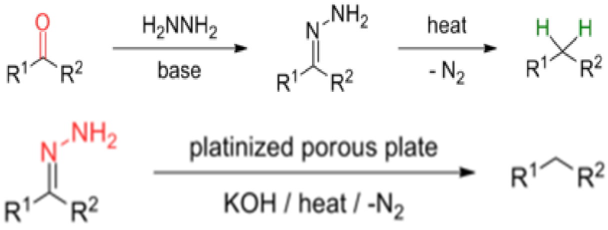


Figure-4: Wolff–Kishner reduction.

In general, the reaction mechanism first involves the *in–situ* generation of a hydrazone by condensation of hydrazine with the ketone or aldehyde substrate. Sometimes it is however advantageous to use a pre–formed hydrazone as substrate. The rate determining step of the reaction is de–protonation of the hydrazone by an alkoxide base to form a diimide anion by a concerted, solvent mediated protonation/de–protonation step. Collapse of this alkyldiimide with loss of N_2 leads to formation of an alkylanion which can be protonated by solvent to give the desired product.[3]

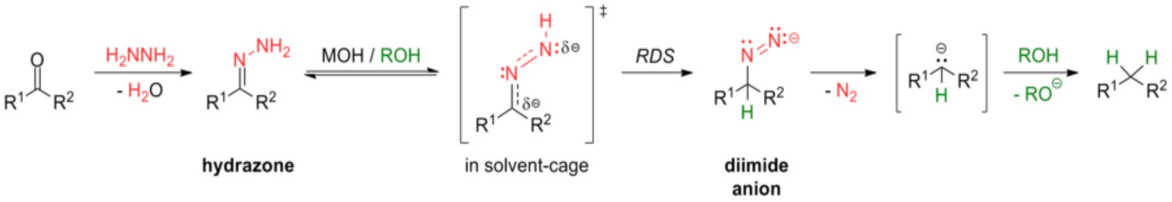


Figure-5: Mechanism of Wolff–Kishner reduction.

Because the Wolff–Kishner reduction requires highly basic conditions, it is unsuitable for base–sensitive substrates. In some cases, formation of the required hydrazone will not occur at sterically hindered carbonyl groups, preventing the reaction. However, this method can be superior to the related Clemmensen reduction for compounds containing acid–sensitive functional groups such as pyrroles and for high–molecular weight compounds.

History: The Wolff–Kishner reduction was discovered independently by N. Kishner in 1911 and Ludwig Wolff in 1912. Kishner found that addition of pre–formed hydrazone to hot potassium hydroxide containing crushed platinized porous plate led to formation of the corresponding hydrocarbon. A review titled “Disability, Despotism, Deoxygenation—From Exile to Academy Member: Nikolai Matveevich Kizhner” describing the life and work of Kishner was published in 2013. Wolff later accomplished the same result by heating an ethanol solution of semicarbazones or hydrazones in a sealed tube to 180°C in the presence of sodium ethoxide.

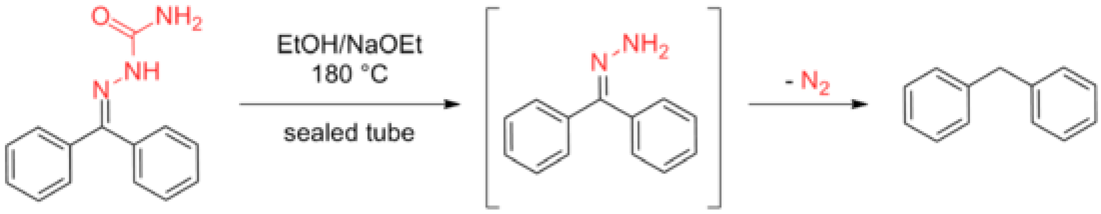


Figure-6: Release of nitrogen from hydrazone during Wolff–Kishner reduction.

The method developed by Kishner has the advantage of avoiding the requirement of a sealed tube, but both methodologies suffered from unreliability when applied to many hindered substrates. These disadvantages promoted the development of Wolff's procedure, wherein the use of high–boiling solvents such as ethylene glycol and triethylene glycol were implemented to allow for the high temperatures required for the reaction while avoiding the need of a sealed tube. These initial modifications were followed by many other improvements as described below.[4]

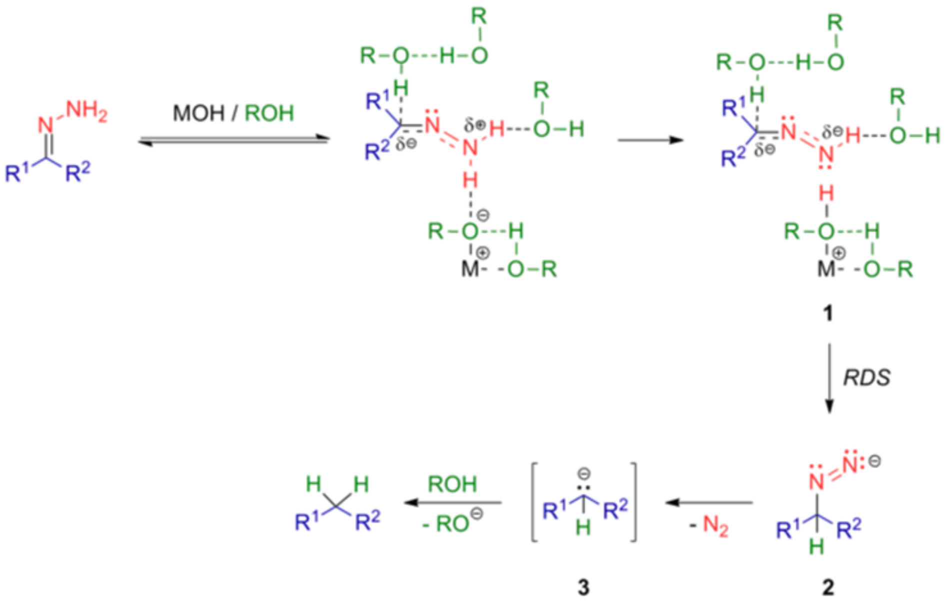


Figure-7: Mechanism of Wolff-Kishner reduction.

Mechanism: The mechanism of the Wolff–Kishner reduction has been studied by Szmant and coworkers. According to Szmant's research, the first step in this reaction is the formation of a hydrazone anion **1** by deprotonation of the terminal nitrogen by MOH. If semicarbazones are used as substrates, initial conversion into the corresponding hydrazone is followed by deprotonation. A range of mechanistic data suggests that the rate–determining step involves formation of a new carbon–hydrogen bond at the carbon terminal in the delocalized hydrazone anion. This proton capture takes place in a concerted fashion with a solvent–induced abstraction of the second proton at the nitrogen terminal. Szmant's finding that this reaction is first order in both hydroxide ion and ketone hydrazone supports this mechanistic proposal. Several molecules of solvent have to be involved in this process in order to allow for a concerted process. A detailed Hammett analysis of aryl aldehydes, methyl aryl ketones and diaryl ketones showed a non–linear relationship which the authors attribute to the complexity of the rate–determining step. Mildly electron–withdrawing substituents favor carbon–hydrogen bond formation, but highly electron–withdrawing substituents will decrease the negative charge at the terminal nitrogen and in turn favor a bigger and harder solvation shell that will render breaking of the N–H bond more difficult. The exceptionally high negative entropy of activation values observed can be explained by the high degree of organization in the proposed transition state. It was furthermore found that the rate of the reaction depends on the concentration of the hydroxylic solvent and on the cation in the alkoxide catalyst. The presence of crown ether in the reaction medium can increase the reactivity of the hydrazone anion **1** by dissociating the ion pair and therefore enhance the reaction rate. The final step of the Wolff–Kishner reduction is the collapse of the diimide anion **2** in the presence of a proton source to give the hydrocarbon via loss of dinitrogen to afford an alkyl anion **3**, which undergoes rapid and irreversible acid–base reaction with solvent to give the alkane. Evidence for this high–energy intermediate was obtained by Taber via intramolecular trapping. The stereochemical outcome of this experiment was more consistent with an alkyl anion intermediate than the alternative possibility of an alkyl radical. The overall driving force of the reaction is the evolution of nitrogen gas from the reaction mixture.

Modifications: Many of the efforts devoted to improve the Wolff–Kishner reduction have focused on more efficient formation of the hydrazone intermediate by removal of water and a faster rate of hydrazone decomposition by increasing the reaction temperature. Some of the newer modifications provide more significant advances and allow for reactions under considerably milder conditions. The table shows a summary of some of the modifications that have been developed since the initial discovery.[5]

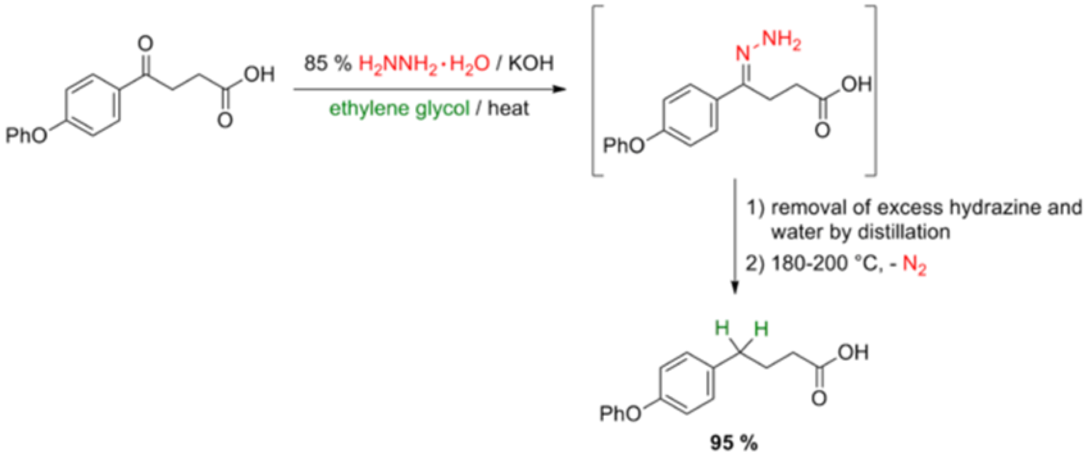


Figure-8: Huang Minlon modification.

Huang Minlon modification: In 1946, Huang Minlon reported a modified procedure for the Wolff–Kishner reduction of ketones in which excess hydrazine and water were removed by distillation after hydrazone formation. The temperature–lowering effect of water that was produced in hydrazone formation usually resulted in long reaction times and harsh reaction conditions even if anhydrous hydrazine was used in the formation of the hydrazone. The modified procedure consists of refluxing the carbonyl compound in 85% hydrazine hydrate with three equivalents of sodium hydroxide followed by distillation of water and excess hydrazine and elevation of the temperature to 200°C. Significantly reduced reaction times and improved yields can be obtained using this modification. Huang Minlon's original report described the reduction of *β*–(*p*–phenoxybenzoyl)propionic acid to *γ*–(*p*–phenoxyphenyl) butyric acid in 95% yield compared to 48% yield obtained by the traditional procedure.

	Original procedure	**Huang Minlon**	**Barton**	**Cram**	**Henbest**	**Caglioti**	**Myers**
Reagents	carbonyl compound, 100% H_2NNH_2, Na or NaOEt	carbonyl compound, 85% H_2NNH_2, KOH	carbonyl compound, anhydrous H_2NNH_2, Na	preformed hydrazone, KO*t*Bu	preformed hydrazone, KO*t*Bu	tosylhydrazone, hydride donor	carbonyl compound, 1,2–bis(*tert*–butyldimethylsilyl)–hydrazine, $Sc(OTf)_3$, KO*t*Bu
Solvent	high–boiling solvent, e.g. ethylene glycol	high–boiling solvent, e.g. ethylene glycol	high–boiling solvent, e.g. diethylene glycol	anh. DMSO	toluene	THF	DMSO
Temperature	200°C	180–200°C (after removal of water and excess hydrazine)	210°C	25°C	111°C	66°C	25°C
Advantages	single step procedure	reduced reaction times, higher temperatures can be reached, no need to use anh. hydrazine	allows decarbonylation of sterically hindered substrates	proceeds at room temperature	no slow addition of hydrazone necessary	mild reaction conditions, possible with a variety of reducing agents	very mild reaction conditions
Disadvantages	long reaction times (50–100 h)	distillation necessary	harsh reaction conditions	isolation of hydrazone and slow addition necessary	isolation of hydrazone necessary	isolation of tosylhydrazone necessary. hydride donor may act as base	synthesis of 1,2–bis(*tert*–butyldimethylsilyl)–hydrazine necessary

Functional group tolerance	does not tolerate esters, amides, halogens, cyano–, and nitro–groups	similar to original procedure	similar to original procedure	tolerates amides	higher tolerance of *α*–substituents that would undergo elimination and *α,β*–unsaturated enones that would undergo migration under original conditions	tolerates esters, amides, cyano–, nitro– and chloro–substituents with $NaBH_3CN$ as hydride source, does not tolerate primary bromo– and iodo–substituents	not reported

Barton modification: Nine years after Huang Minlon's first modification, Barton developed a method for the reduction of sterically hindered carbonyl groups. This method features vigorous exclusion of water, higher temperatures, and longer reaction times as well as sodium in diethylene glycol instead of alkoxide base. Under these conditions, some of the problems that normally arise with hindered ketones can be alleviated—for example, the C_{11}–carbonyl group in the steroidal compound shown below was successfully reduced under Barton's conditions while Huang–Minlon conditions failed to effect this transformation.

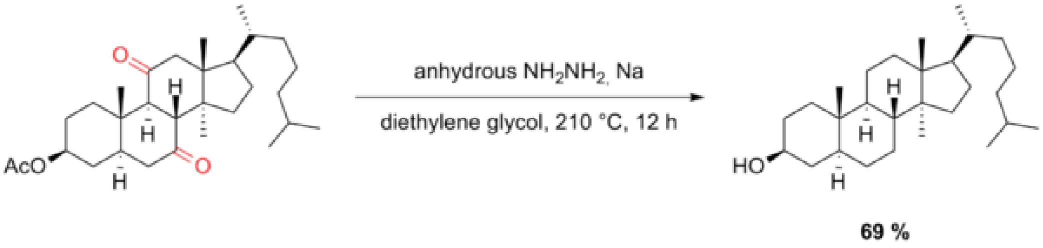


Figure-9: Barton modification.

Cram modification: Slow addition of preformed hydrazones to potassium *tert*–butoxide in DMSO as reaction medium instead of glycols allows hydrocarbon formation to be conducted successfully at temperatures as low as 23°C. Cram attributed the higher reactivity in DMSO as solvent to higher base strength of potassium *tert*–butoxide in this medium.

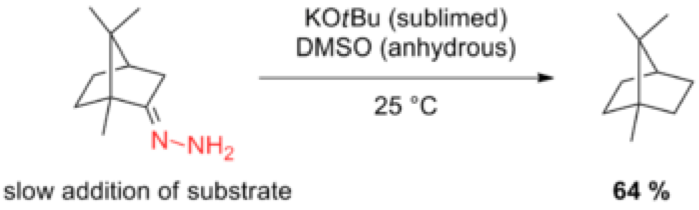


Figure-10: Cram modification.

This modification has not been exploited to great extent in organic synthesis due to the necessity to isolate preformed hydrazone substrates and to add the hydrazone over several hours to the reaction mixture.

Henbest modification: Henbest extended Cram's procedure by refluxing carbonyl hydrazones and potassium *tert*–butoxide in dry toluene. Slow addition of the hydrazone is not necessary and it was found that this procedure is better suited for carbonyl compounds prone to base–induced side reactions than Cram's modification. It has for example been found that double bond migration in *α,β*–unsaturated enones and functional group elimination of certain *α*–substituted ketones are less likely to occur under Henbest's conditions.

Caglioti reaction: Treatment of tosylhydrazones with hydride–donor reagents to obtain the corresponding alkanes is known as the Caglioti reaction. The initially reported reaction conditions have been modified and hydride donors such as sodium cyanoborohydride, sodium triacetoxyborohydride, or catecholborane can reduce tosylhydrazones to hydrocarbons. The reaction proceeds under relatively mild conditions and can therefore tolerate a wider array of functional groups than the original procedure. Reductions with sodium cyanoborohydride as reducing agent can be conducted in the presence of esters, amides, cyano–, nitro– and chloro–substituents. Primary bromo– and iodo–substituents are displaced by nucleophilic hydride under these conditions.[6]

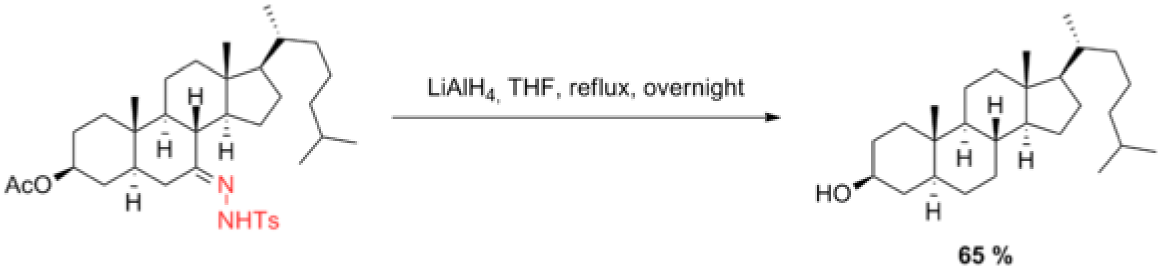


Figure-11: Caglioti reaction.

Several papers have studied the mechanism of this reduction and multiple reaction pathways are possible, depending on the pH of the reaction, the reducing agent used and the electronic properties of the substrate. One possibility, occurring under acidic conditions, includes direct hydride attack of iminium ion **1** following prior protonation of the tosylhydrazone. The resulting tosylhydrazine derivative **2** subsequently undergoes elimination of *p*–toluenesulfinic acid and decomposes via a diimine intermediate **3** to the corresponding hydrocarbon.

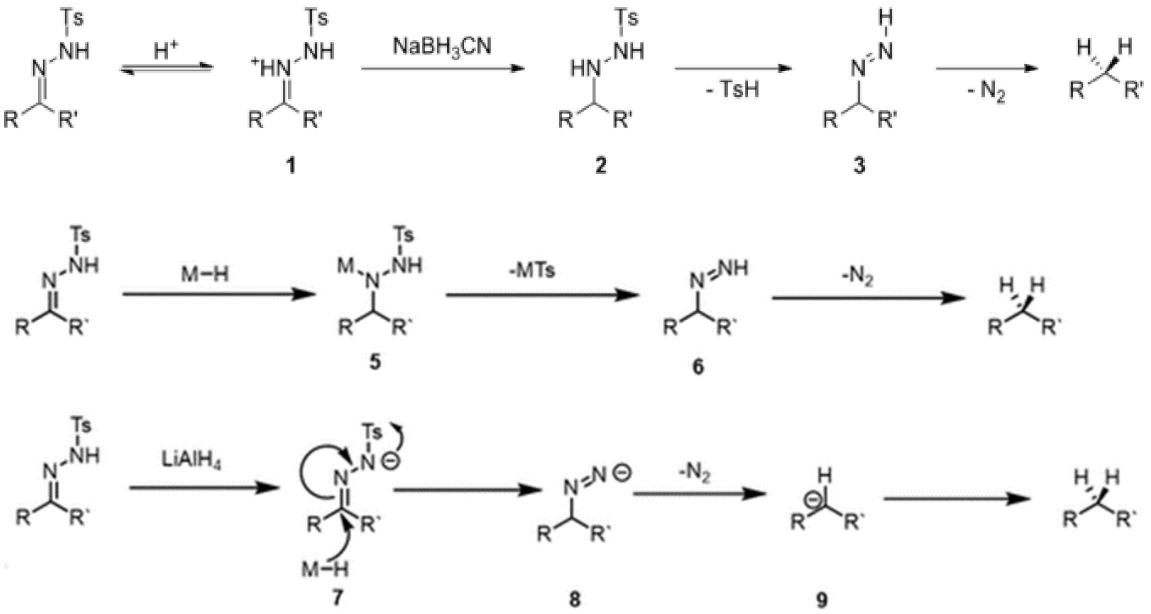
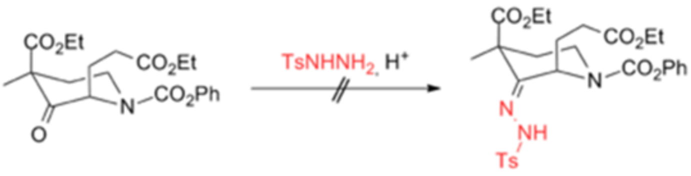


Figure-12: Mechanism of Caglioti reaction.

A slight variation of this mechanism occurs when tautomerization to the azohydrazone is facilitated by inductive effects. The transient azohydrazine **4** can then be reduced to the tosylhydrazine derivative **2** and furnish the decarbonylated product analogously to the first possibility. This mechanism operates when relatively weak hydride donors are used, such as sodium cyanoborohydride. It is known that these sodium cyanoborohydride is not strong enough to reduce imines, but can reduce iminium ions. When stronger hydride donors are used, a different mechanism is operational, which avoids the use of acidic conditions. Hydride delivery occurs to give intermediate **5,** followed by elimination of the metal sulfinate to give azo intermediate **6**. This intermediate then decomposes, with loss of nitrogen gas, to give the reduced compound. When strongly basic hydride donors are used such as lithium aluminium hydride, then deprotonation of the tosyl hydrazone can occur before hydride delivery. Intermediate anion **7** can undergo hydride attack, eliminating a metal sulfinate to give azo anion **8**. This readily decomposes to carbanion **9**, which is protonated to give the reduced product. As with the parent Wolff–Kishner reduction, the decarbonylation reaction can often fail due to unsuccessful formation of the corresponding tosylhydrazone. This is common for sterically hindered ketones, as was the case for the cyclic amino ketone shown below.



Alternative methods of reduction can be employed when formation of the hydrazone fail, including thioketal reduction with Raney nickel or reaction with sodium triethylborohydride.[7]

Deoxygenation of *α,β*–unsaturated carbonyl compounds: *α,β*–Unsaturated carbonyl tosylhydrazones can be converted into the corresponding alkenes with migration of the double bond. The reduction proceeds stereo selectively to furnish the *E* geometric isomer.

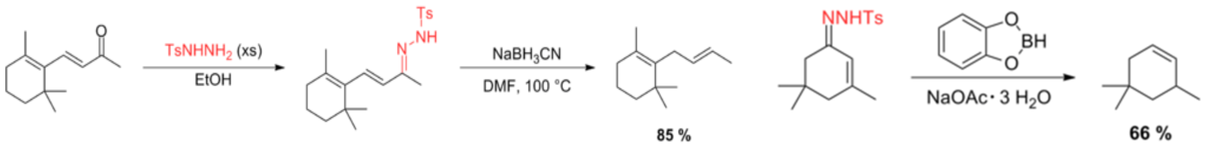


Figure-13: Deoxygenation of α,β–unsaturated carbonyl compounds.

A very mild method was developed by Kabalka *et al.* who used one equivalent of catecholborane to reduce *α,β*–unsaturated tosylhydrazones. Djerassi *et al.* studied the mechanism of $NaBH_3CN$ reduction of *α,β*–unsaturated tosylhydrazones. Based on deuterium–labeling experiments, they concluded that alkene formation is initiated by hydride reduction of the iminium ion followed by double bond migration and nitrogen extrusion which occur in a concerted manner. Allylic diazene rearrangement as the final step in the reductive 1,3–transposition of *α,β*–unsaturated tosylhydrazones to the reduced alkenes can also be used to establish sp^3–stereocenters from allylic diazenes containing prochiral stereocenters. The influence of the alkoxy stereocenter results in diastereoselective reduction of the *α,β*–unsaturated tosylhydrazone. The authors predicted that diastereoselective transfer of the diazene hydrogen to one face of the prochiral alkene could be enforced during the suprafacial rearrangement.

Myers modification: In 2004, Myers and coworkers developed a method for the preparation of *N*–*tert*–butyldimethylsilylhydrazones from carbonyl–containing compounds. These products can be used as a superior alternative to hydrazones in the transformation of ketones into alkanes. The advantages of this procedure are considerably milder reaction conditions and higher efficiency as well as operational convenience. The condensation of 1,2–bis(*tert*–

butyldimethylsilyl)–hydrazine with aldehydes and ketones with $Sc(OTf)_3$ as catalyst is rapid and efficient at ambient temperature. Formation and reduction of *N–tert–*butyldimethylsilylhydrazones can be conducted in a one pot procedure in high yield.

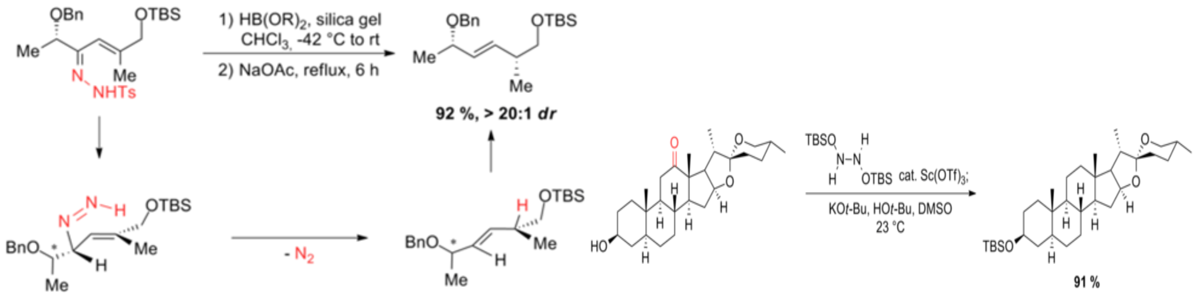


Figure-14: Myers modification.

The newly developed method was compared directly to the standard Huang–Minlon Wolff–Kishner reduction conditions (hydrazine hydrate, potassium hydroxide, diethylene glycol, 195°C) for the steroidal ketone shown above. The product was obtained in 79% yield compared to 91% obtained from the reduction via an intermediate *N–tert–*butyldimethylsilylhydrazone.[8]

Side reactions: The Wolff–Kishner reduction is not suitable for base–sensitive substrates and can under certain conditions be hampered by steric hindrance surrounding the carbonyl group. Some of the more common side–reactions are listed below.

Azine formation: A commonly encountered side–reaction in Wolff–Kishner reductions involves azine formation by reaction of hydrazone with the carbonyl compound. Formation of the ketone can be suppressed by vigorous exclusion of water during the reaction. Several of the presented procedures require isolation of the hydrazone compound prior to reduction. This can be complicated by further transformation of the product hydrazone to the corresponding hydrazine during product purification. Cram found that azine formation is favored by rapid addition of preformed hydrazones to potassium *tert*–butoxide in anhydrous dimethyl sulfoxide.

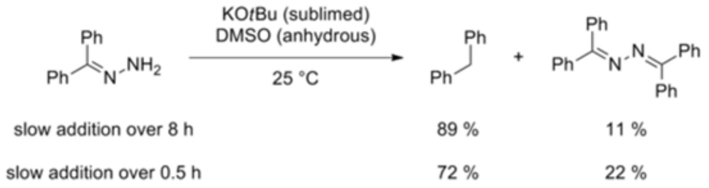


Figure-15: Azine formation.

Reduction of ketones to alcohols by sodium ethoxide: The second principal side reaction is the reduction of the ketone or aldehyde to the corresponding alcohol. After initial hydrolysis of the hydrazone, the free carbonyl derivative is reduced by alkoxide to the carbinol. In 1924, Eisenlohr reported that substantial amounts of hydroxydecalin were observed during the attempted Wolff–Kishner reduction of *trans*–*β*–decalone. In general, alcohol formation may be repressed by exclusion of water or by addition of excess hydrazine.

Kishner–Leonard elimination: Kishner noted during his initial investigations that in some instances, *α*–substitution of a carbonyl group can lead to elimination affording unsaturated hydrocarbons under typical reaction conditions. Leonard later further developed this reaction and investigated the influence of different *α*–substituents on the reaction outcome. He found that the amount of elimination increases with increasing steric bulk of the leaving group. Furthermore, *α*–dialkylamino–substituted ketones generally gave a mixture of reduction and elimination product whereas less basic leaving groups resulted in exclusive formation of the alkene product.

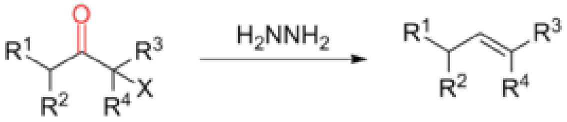


Figure-16: Kishner–Leonard elimination.

The fragmentation of *α,β*–epoxy ketones to allylic alcohols has been extended to a synthetically useful process and is known as the Wharton reaction.[9]

Cleavage or rearrangement of strained rings adjacent to the carbonyl group: Grob rearrangement of strained rings adjacent to the carbonyl group has been observed by Erman and coworkers. During an attempted Wolff–Kishner reduction of *trans*–*π*–bromocamphor under Cram's conditions, limonene was isolated as the only product.[9]

Similarly, cleavage of strained rings adjacent to the carbonyl group can occur. When 9*β*,19–cyclo–5*α*–pregnane–3,11,20–trione 3,20–diethylene ketal was subjected to Huang–Minlon conditions, ring–enlargement was observed instead of formation of the 11–deoxo–compound.

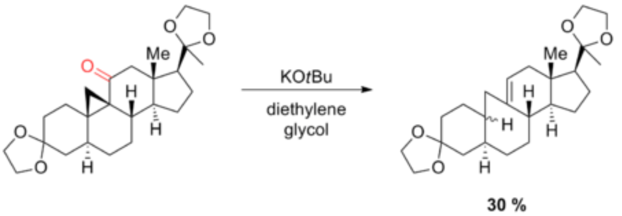


Figure-17: Grob rearrangement.

Applications: The Wolff–Kishner reduction is an effective tool in organic synthesis. For example, Ishibashi and coworkers employed the Huang Minlon modification of the Wolff–Kishner reduction as one of the final steps in their synthesis of (±)–aspidospermidine. Distillable material was removed after hydrazone formation at 160°C and then heated to 210°C overnight. The carbonyl group that was reduced in the Wolff–Kishner reduction was essential for preceding steps in the synthesis. The tertiary amide was stable to the reaction conditions and reduced subsequently by lithium aluminum hydride.

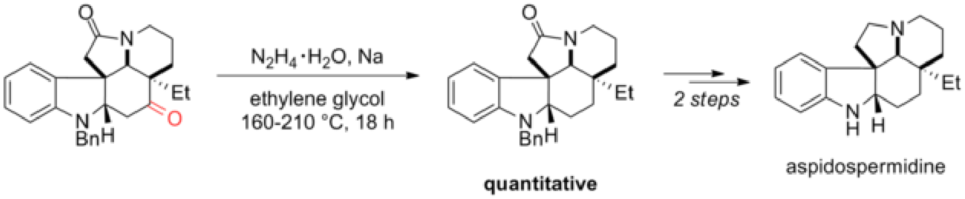


Figure-18: Huang Minlon modification.

Amides are usually not suitable substrates for the Wolff–Kishner reduction as demonstrated by the example above. Coe and coworkers found however that a twisted amide can be efficiently reduced under Wolff–Kishner conditions. The authors explain this observation with the stereoelectronic bias of the substrate which prevents “anti–Bredt” iminium ion formation and therefore favors ejection of alcohol and hydrazone formation. The amide functionality in this strained substrate can be considered as isolated amine and ketone functionalities as resonance stabilization is prevented due to torsional restrictions. The product was obtained in 68% overall yield in a two–step procedure.[10]

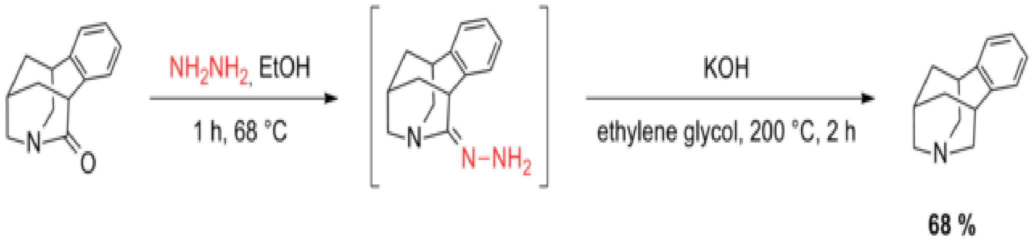


Figure-19: Wolf Kishner reduction modification.

In 2011, Pettus and Green reduced a tricyclic carbonyl compound using the Huang Minlon modification of the Wolff–Kishner reduction. Several attempts towards decarbonylation of tricyclic allylic acetate containing ketone failed and the acetate functionality had to be removed to allow successful Wolff–Kishner reduction. Finally, the allylic alcohol was installed via oxyplumbation.

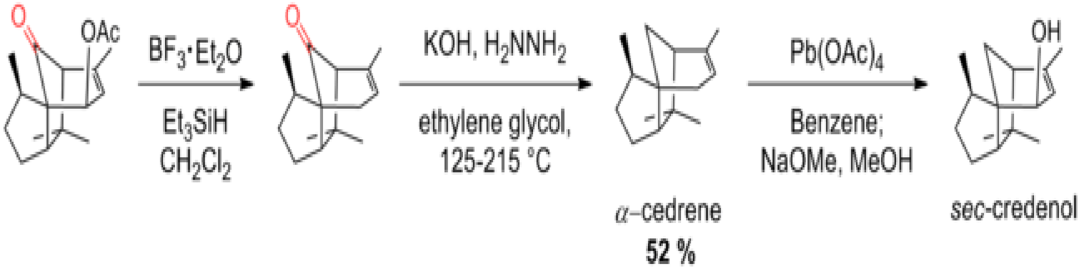


Figure-20: Huang Minlon modification for Wolff Kishner reduction.

The Wolff–Kishner reduction has also been used on kilogram scale for the synthesis of a functionalized imidazole substrate. Several alternative reduction methods were investigated, but all of the tested conditions remained unsuccessful. Safety concerns for a large–scale Wolff–Kishner reduction were addressed and a highly optimized procedure afforded to product in good yield.

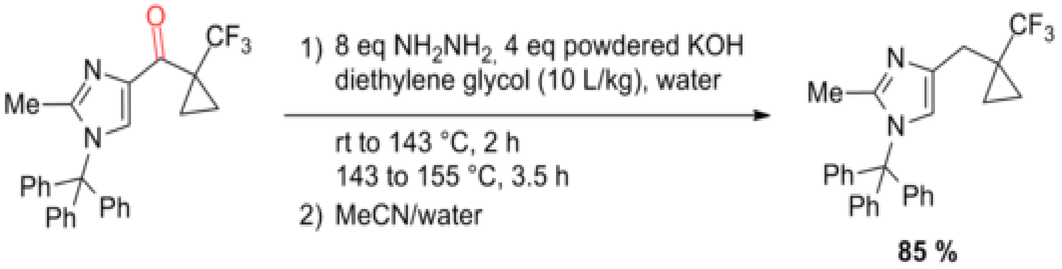


Figure-21: Green chemistry approach in Wolff Kishner reduction.

McIntosh *et al.* used an allylic diazene rearrangement in their synthesis of the C_{21}–C_{34} fragment of antascomicin B. The hydrazone was reduced selectively with catecholborane and excess reducing agent decomposed with sodium thiosulfate. The crude reaction product was then treated with sodium acetate and heated under reflux in chloroform to give the 1,4–*syn* isomer.

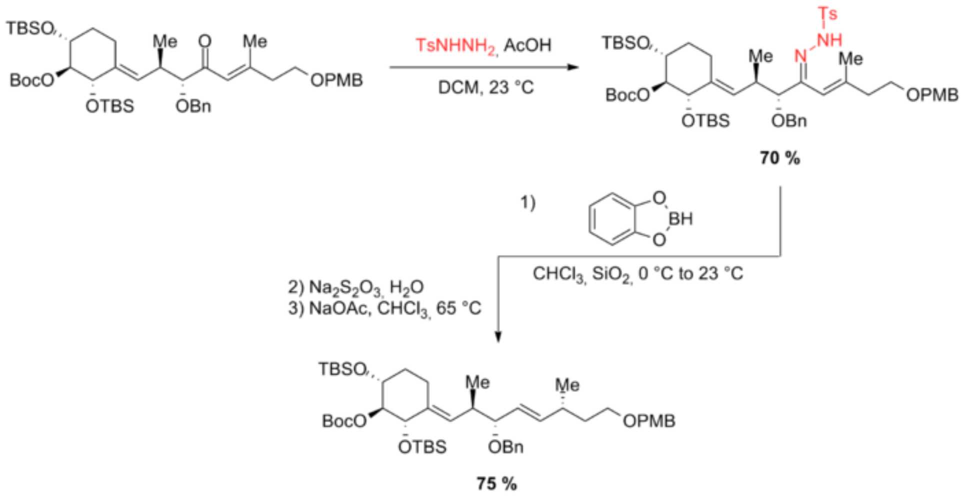


Figure-22: Allylic diazene rearrangement in Wolff Kishner reduction.

CONCLUSION

Carbonyl functional group [>C=O, –CH=O] having electronegative atom oxygen [–:O:–] which has two loan pair of electrons which undergoes reduction into alkane chain by formation of methylene [>CH_2–] group by Clemmensen reduction as well as Wolff Kishner reduction. Clemmensen reduction takes place by the reaction between zinc amalgam/HCl to convert ketone/aldehyde group into methylene linkage by incorporation of hydrogen into C=O linkage by elimination of water molecule; similarly, Wolf Kishner reduction takes place on the same group by reaction between hydrazine to form corresponding hydrazone and that is converted into methylene [alkane] chain by electrolytic cleavage by elimination of nitrogen gas.

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