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Study of the reactivity of 1,1'-dimethylbistetrazole towards catalytic hydrogenation and chemical reduction

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Abstract

Investigating the possibility of a straightforward formation of tetrazoline or tetrazolidine structures, the reactivity of a tetrazole derivative towards reducing conditions has been studied. The catalytic hydrogenation of 1,1'-dimethylbistetrazole (DMBT) was carried out using various catalysts (Pd/C, Pt/C, Rh/C, Pd/Pt/C, Lindlar, PtO_2 and Raney Ni) over a wide range of hydrogen pressure (35–150 bar) and a temperature range from 20 to 60 °C. This exhaustive study enabled to find the optimal conditions for DMBT hydrogenation and to suggest a plausible reaction mechanism. The chemical reduction of DMBT was conducted using several hydrides (BH_3, $NaBH_4$, DIBAL and $LiAlH_4$). The reduction products were identified subsequently to conditions optimizing. The suggested reaction mechanism, featuring a retro-[3 + 2]-cycloaddition, was validated by both experimental and theoretical approaches.

Keywords 1,1'-dimethylbistetrazole · Catalytic hydrogenation · Chemical reduction · Lithium aluminum hydride · Retro-[3 + 2]-cycloaddition

Introduction

Tetrazoles are nitrogen-rich compounds that present a widely known interest as stable energetic materials, due to their high positive heats of formation combined with their high thermal stability, resulting from the aromaticity of the tetrazole ring [1–6].

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Tetrazoles had been thoroughly studied and described in the literature [1–6], however, very few examples of the reduced forms of tetrazoles had been mentioned. Indeed, few literature studies had reported tetrasubstituted tetrahydrotetrazole structures carrying aryl or bulky groups (Fig. 1a, b) [7–10], and only one recent structural evidence of such compounds had been published by Breton et al. [10]. Authors presented a crystal structure of a tetrasubstituted tetrahydrotetrazole (Fig. 1c) with the formula $C_{25}H_{30}N_4O_4$ namely, 1,2-di-tert-butyl 3-phenyl-1*H*,2*H*,3*H*,10b*H*-[1,2,3,4]tetrazolo[5,1-a]isoquinoline-1,2-dicarboxylate, that was originally reported by Bast et al. [9].

Moreover, Linke et al. [11] had reported a study investigating the synthesis of an unsubstituted tetrazolidine derivative. In this study, a thiocarbamide was reacted with hydrazine and the reaction mixture was heated up to 170 °C (Scheme 1). The authors [11] carried out a mass spectrometric investigation on the reaction products, and obviously no tetrazolidine derivative can be detected. They indicated that obviously polymeric compounds had been obtained, which decomposed above 200 °C. They also concluded that it was impossible to obtain the unsubstituted tetrazolidine derivative through the aforementioned reaction.

In this regard, we have been interested in the reduced structures of the tetrazole-based structures and we have focused on some typical tetrazoline and tetrazolidine derivatives that have showed promising results upon the calculation of their heats of formation and their energetic performances as ingredients for solid or liquid propulsion [12]. Therefore, we have carried out a study on the reactivity of tetrazoles to chemical reduction and catalytic hydrogenation to confirm or disprove the formation of such unsubtituted tetrazoline and tetrazolidine structures (Fig. 2).
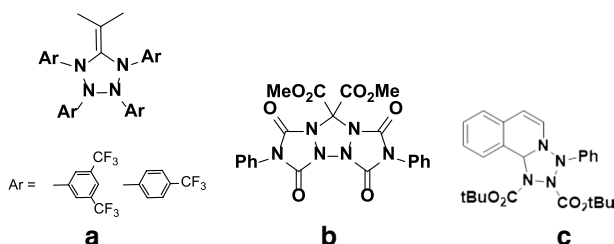

Fig. 1 Reported structures of reduced tetrazole structures

Scheme 1 Reported study [11] disproving the formation of the tetrazolidine derivative
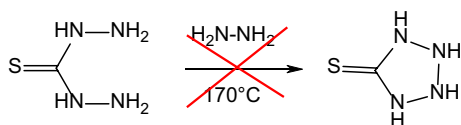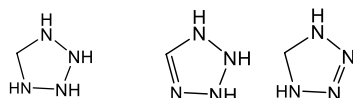

Fig. 2 Structures of 1,2,3,4-tetrazolidine (left) and 1,2,3,4-tetrazoline (right)

In order to carry out such an experimental approach, we first had to select a stable and non-sensitive (towards mechanical stimuli and electrostatic discharge) tetrazole-based derivative that can generate detectable fragments in mass spectrometry or NMR in case of cycle breaking. For our study, we have identified 1,1'-dimethylbistetrazole (DMBT, Fig. 3) as a tetrazole-based test compound for the hydrogenation/reduction essays.

We report herein the reactivity of this tetrazole derivative towards various reducing conditions within either catalytic hydrogenation or chemical reduction. The experimental approach carried out, combined with a chemical quantum calculation study, enabled the identification of the products issued from tetrazole-reducing reactions as well as the suggestion of a reaction mechanism in each case.

Experimental part

Synthesis of 1,1'-dimethylbistetrazole (DMBT)

12 g (103 mmol, 1 eq.) of DMOX and 77 mL of acetonitrile were introduced into a 250 mL round flask. Under stirring, the solution was cooled down to 5 °C by means of an ice bath. 43.1 g (207 mmol, 2 eq.) of PCl_5 were then added by portions to the reaction mixture, so that temperature does not exceed 12 °C. The mixture turns gradually translucent and orange colored. After 30 min stirring, the reaction medium was degassed using a dry pump equipped with a NaOH trap to remove HCl formed during the reaction. The mixture was then transferred into an isobaric dropping funnel. 26.9 g (414 mmol, 4 eq.) of NaN_3 and 38 mL of acetonitrile were introduced into a 250 mL round flask and the solution was cooled down to 0 °C, using an ice bath. The orange solution, previously obtained, was added dropwise to the latter so that temperature does not exceed 12 °C. The reaction mixture was then refluxed for 1 h and let to cool down to room temperature, afterwards it was poured into 200 mL of sodium hydroxide solution (1.6 g of NaOH). As the reaction mixture was stirred, crystals were formed; they were filtered off, washed with water and dried in an oven, leading to 9.99 g of a white solid (58.2%).

^{1}H RMN (acetone-d6, 25 °C, 400 MHz): δ (ppm) = 4.54 (s, 6H, CH_3); ^{13}C {^{1}H} NMR (acetone-d_6, 25 °C, 100 MHz): δ (ppm) = 143.4 (2C, $C_{\text{tetrazole}}$), 36.4 (2C, CH_3); ^{15}N NMR (acetone-d_6, 25 °C, 500 MHz): δ (ppm) = 392.9 (2 N, N=N), 375.6 (2 N, N=C), 331.8 (2 N, NMe). IR [KBr, ν (cm^{-1})] = 1452, 1374, 1264, 1211, 1139, 1105, 1067, 1031, 995, 720, 679. MS (CI): [MH]$^+$ at m/z = 167.2. DSC (50–250 °C, 10 °C

Fig. 3 1,1'-dimethylbistetrazole (DMBT)
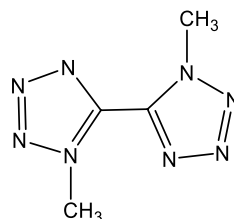
min^{-1}): T$_m$ (onset) = 206 °C (endo, 158 J g^{-1}). BAM: ISI (constant energy) > 50 J, ISF (constant force) > 353 N.

Optimized protocol for catalytic hydrogenation of DMBT

780 mg (4.7 mmol, 1 eq.) of DMBT were solubilized in 200 mL of ethanol and introduced into a hydrogenation thermostatted reactor. 156 mg of 5% loaded Pd/C were added to the solution. The autoclave was then closed and the leak test protocol was carried out. Temperature was set at 60 °C and P$_{H2}$ at 150 bar. The reaction mixture was stirred for 3 days, after which, hydrogen was evacuated and the reactor was purged with Nitrogen. The reaction mixture was filtered off on celite and the substrate was washed with ethanol. The filtrate was evaporated to dryness and the crude was solubilized in 10 mL of demineralized water, resulting in crystals precipitation, which were filtered off. The pale yellow filtrate was concentrated under vacuum, leading to 200 mg of a yellow viscous oil (50%).

^{1}H NMR (CDCl$_3$, 25 °C, 400 MHz): δ (ppm) = 8.68 (s, 1H, CH), 4.20 (s, 3H, CH_3); ^{13}C {^{1}H} NMR (CDCl$_3$, 25 °C, 100 MHz): δ (ppm) = 143.3 (1C, $C_{\text{tetrazole}}$), 34.3 (1C, CH_3). IR [golden gate, ν (cm^{-1})] = 3110, 2963, 1640, 1496, 1445, 1420, 1380, 1278, 1175, 1109, 1017, 964, 925, 877, 799, 722, 680, 657. MS (CI): [MH]$^+$ at m/z = 85.0.

Optimized protocol for LAH reduction of DMBT

750 mg (4.52 mmol, 1 eq.) of DMBT were introduced into a 100 mL three-neck round flask equipped with a cooling tube and a temperature sensor. An overpressure of nitrogen was maintained in the set-up and 80 mL of anhydrous THF were then added. The reaction mixture was then cooled at 0 °C and 650 mg (17.2 mmol, 3.8 eq.) of LiAlH$_4$ were gradually added, under stirring, to the solution.

Work-up A: the reaction mixture was maintained at 0 °C for 7 h.

Work-up B: the reaction mixture was maintained at room temperature (23 °C) for 24 h.

Work-up C: the reaction mixture was heated up to 40 °C for 7 h.

At the end of each pathway, the excess LAH was hydrolyzed by adding 10 mL of ethanol, followed by 10 mL of water at 0 °C (the hydrolysis is exothermic and produces dihydrogen). The solution was filtered off to remove Aluminum hydroxide that was formed, and the filtrate was evaporated to dryness leading to a solid crude more or less greasy, depending on the work-up step (for details, see SI).

Work-up C led to 230 mg of a translucent viscous oil (58%): ^{1}H NMR (acetone-d$_6$, 25 °C, 400 MHz): δ (ppm) = 2.72 (s, 2H, CH_2), 2.22 (s, 3H, CH_3); ^{13}C {^{1}H} NMR (acetone-d$_6$, 25 °C, 100 MHz): δ (ppm) = 50.4 (2C, CH_2), 34.9 (2C, CH_3). IR [golden gate, ν (cm^{-1})] = 2952, 2868, 2812, 1497, 1339, 1105, 714. MS (CI): [MH]$^+$ at m/z = 89.1.
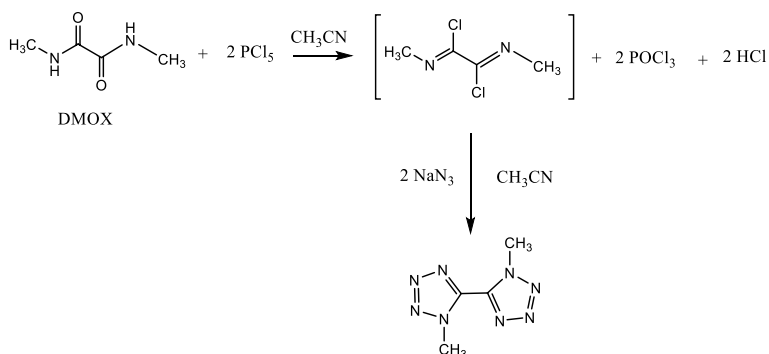
Scheme 2 Synthesis scheme of DMBT starting from DMOX

Results and discussion

Synthesis of DMBT

DMBT was synthesized in two steps, using *N*,*N'*-dimethyloxamide (DMOX) as starting material, according to the procedure described in the literature [13] (Scheme 2). The intermediate compound of the first step was not isolated (see experimental part).

DMBT is a white solid, stable at room temperature and not sensitive to oxidation. This synthesis does not involve major difficulties; however, phosphorus pentachloride (PCl_5) reacts rapidly to release hydrochloric acid and phosphorus oxides (Scheme 2).

As in the second step, the reaction mixture was added to a sodium azide solution, it was essential to neutralize HCl before addition to avoid the formation of large amounts of highly explosive hydrogen azide (HN_3). Hence, the reaction mixture was degassed and gaseous HCl was trapped in a sodium hydroxide solution, and the reaction mixture pH was measured to check if traces of HCl are still inside. During synthesis, DMBT crystallizes as a pure solid and there was no need for further purification.

Sensitivity tests to impact and friction carried out showed that the compound is not sensitive to impact (ISI = 50 J) or friction (ISF = 353 N), and that it can be handled without specific precaution and synthesized with no amount limitations.

Catalytic hydrogenation

Preliminary essays

There are many papers on the catalytic hydrogenation of aromatic rings and in particular the conversion of benzene into cyclohexane [14–22]. In general, it is necessary to use extreme conditions (T > 100 °C, P_{H2} > 100 bar) to reduce

Table 1 Reaction conditions for DMBT catalytic hydrogenation (cat.: Pd/C, $P_{H2} \leq 60$ bar)

DMBT amount m (g)	Pd/C amount X (mg)	Pressure P_{H2} (bar)	Temperature T (°C)	Reaction time H (h)
0.1	5	50	20	16
0.1	5	50	60	16
0.2	5	45	60	16
0.2	10	45	60	16
0.2	20	45	60	16
0.2	10	45	60	16
0.2	10	45	60	72

Table 2 Reaction conditions for DMBT catalytic hydrogenation with different catalysts

Catalyst	m (g)	X (mg)	P_{H2} (bar)	T (°C)	H (h)
$Pd_{Lindlar}$	0.2	10	45	60	16
Ni_{Raney}	0.5	25	50	60	19
Pt/C	0.5	100	50	60	19
Pd/Pt/C	0.5	100	50	60	19
PtO_2	0.5	100	50	60	19
Rh/C	0.5	100	50	60	60

aromatic rings, however, the use of catalysts such as Rh/C or Ru/C enables working under milder experimental conditions (T ≈ 50 °C, P_{H2} ≈ 20 bar).

Hydrogenation experiments have been first carried out under a moderate H_2 pressure, with Pd/C as a catalyst (Table 1). A standard experimental protocol was set up as follows: m (g) of DMBT were solubilized in 200 mL of ethanol and introduced into a thermostatted reactor. X (mg) of 5% loaded Pd/C were then added to the solution. The autoclave was then closed and the leak test protocol was carried out. Hydrogen pressure P_{H2} was set up under T (°C) for a reaction time of H (h). At the end of the reaction, the reactor was drained and then purged with Nitrogen. The reaction mixture was filtered off on celite to remove the catalyst and the filtrate was evaporated under vacuum.

The temperature effect has been studied in the first two experiments. Also, the effect of the catalyst amount has been studied in a second step and finally the influence of the reaction time. The crude obtained (white solid) from each of these experiments has been analysed by NMR (^{1}H, ^{13}C) and IR. Analysis confirmed that it is pure DMBT that was recovered, regardless of the parameters studied. Hence, catalytic hydrogenation of DMBT was ineffective in these conditions and we considered testing other catalysts (Table 2) before increasing the hydrogen pressure.

Analyses revealed that, in all these experiments, the product obtained at the end of the reaction is pure DMBT, and the use of powerful catalysts did not enable to hydrogenate, even partially, DMBT.

Table 3 Reaction conditions for DMBT catalytic hydrogenation (catalyst: Pd/C, $P_{H2} > 60$ bar)

Entry	m (g)	X (mg)	P_{H2} (bar)	T (°C)	H (h)
1	0.50	100	90	60	48
2	0.78	39	99	60	28
3	0.78	78	99	60	16
4	0.78	156	99	60	16
5	0.78	156	150	60	16
6	0.78	156	150	60	72
7	0.78	156	150	60	60
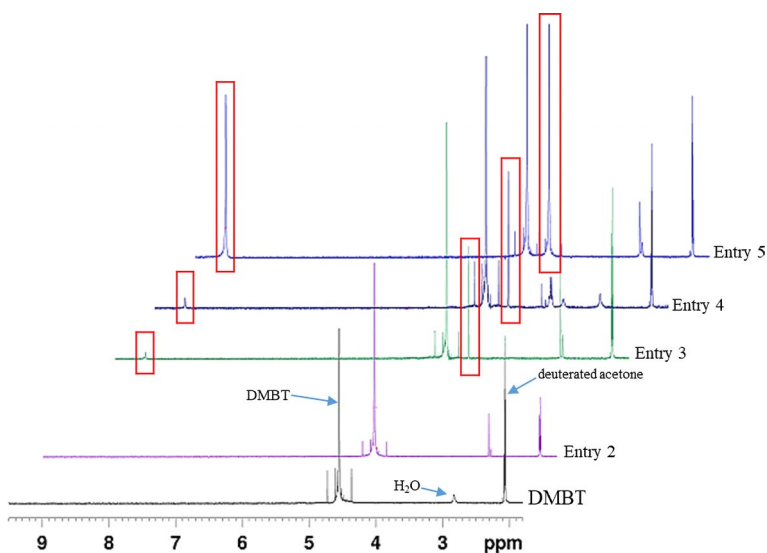
Fig. 4 Superposition of ^{1}H NMR spectra (400 MHz), in deuterated acetone, for DMBT and reaction crude

High hydrogen pressure experiments

In light of these results, we have considered increasing the hydrogen pressure inside the autoclave, to study its effect on tetrazole rings reduction. Experiments conditions are summarized in Table 3.

The use of a $P_{H2} = 90$ bar was not sufficient to achieve the reduction of the tetrazole ring, however new proton signals (framed in Fig. 4) appeared in ^{1}H NMR spectrum, when P_{H2} reached 99 bar.

As shown in Fig. 4, raising the catalyst amount in the reaction medium increases, to some extent, the proportion of the product formed (spectra entries 3 and 4). However, it appears that the formation of the hydrogenated product depends mainly on the hydrogen pressure used (entry 5), and that a hydrogen pressure of 99 bar is sufficient to cross the activation barrier for DMBT hydrogenation. Experiments

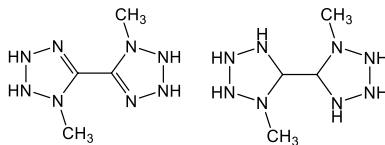**Fig. 5** Structures of 1,1'-dimethylbistetrazoline (M = 170 g mol⁻¹) and 1,1'-dimethylbistetrazolidine (M = 172 g mol⁻¹)

Table 4 Average values of bond dissociation energies [25] for DMBT bonds type

Structure of DMBT	Bond type	Bond energy (kJ mol⁻¹)
	C–C	340
	C–N	460
	C=N	615
	N–N	350
	N=N	418

conducted with a reaction time over 24 h, at a hydrogen pressure higher than 150 bar, also showed an increase in the proportion of hydrogenated product compared to DMBT.

Thus, it was possible to define an optimized protocol for the hydrogenation of DMBT (see experimental part). The yellow oil obtained after purification was characterized by ^{1}H and ^{13}C NMR, IR and MS. IR analyses showed an absorption band at 3110 cm⁻¹ characteristic of the C-H bond elongation, while mass spectrometry (CI) showed a majority peak at m/z = 85.

As a result, these analyses do not support the formation of the expected hydrogenated forms of DMBT involving tetrazolines or tetrazolidines (Fig. 5).

The collected characterization results enabled to identify the hydrogenation product as being 1-methyltetrazole, which was confirmed by the literature data [23, 24] as well as the molecular weight of this compound. Moreover, 1-methyltetrazole has a low melting point of 39 °C, which is consistent with the viscous oil aspect of the hydrogenation product (see discussion below). Consequently, this study revealed that it is possible to reduce DMBT leading to 1-methyltetrazole, however its hydrogenation did not lead to the expected tetrazoline or tetrazolidine derivatives.

Validation of the hydrogenation compound and suggestion of a reaction mechanism

In order to support the formation of 1-methyltetrazole from catalytic hydrogenation of DMBT, the C–C bond energy has been compared to the ones of other bonds connecting atoms in DMBT (Table 4).

The energy of the C–C bond is high but remains lower than that of the other bonds of the molecule. Additionally, this bond is not part of the aromatic ring, unlike the other bonds mentioned in Table 4. Thus, it is possible to figure out that DMBT
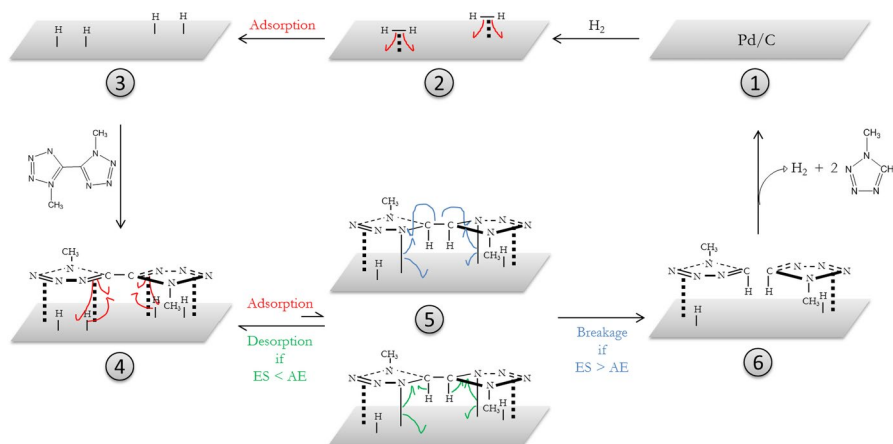
Scheme 3 Suggested reaction mechanism for the Pd/C hydrogenation of DMBT leading to 1-methyltetrazole ($P_{H2} > 90$ bar)

adsorbs to the catalyst, and that the C–C bond breaks as soon as the energy supplied (ES) to the reaction becomes sufficient to cross the activation barrier (AE). Moreover, the reaction is favored by the entropy increase, as one equivalent of DMBT generates two eq. of methyltetrazole. According to this hypothesis, one can presume that the hydrogenation of DMBT could follow a reactional pathway composed of 6 steps (Scheme 3): the first three steps consist of the adsorption of H_2 on the catalyst, followed by the DMBT adsorption, and the addition of adsorbed hydrogen onto the C–C bond (steps 4 to 5), the final step would be the breakage of the C–C bond.

Chemical reduction

Preliminary essays

Many studies reported in the literature referred to the reduction of lactames or oxazolidine derivatives by hydrides, in particular lithium aluminum hydride (LAH) [26–28], which results in reducing molecules with ring breakage. As for tetrazole derivatives, a study, published by Laforge et al. [29] reported the reduction of 1,5-disubstituted tetrazoles by LAH, resulting on ring opening, without any valuable proof confirming it. Recently, Duchamp et al. [30] have proposed a mechanism for the reductive cleavage of tetrazoles using LAH, which highlighted the extrusion of an azide anion. In this regard, we decided to conduct our own study on the chemical reduction of DMBT by testing several hydride donors.

For our study, four, more or less powerful, reducing agents have been selected, namely: borane (BH_3), sodium borohydride ($NaBH_4$), diisobutylaluminum hydride (DIBAL) and lithium aluminum hydride ($LiAlH_4$ or LAH).

All the reduction tests performed on DMBT are summarized in Table 5. Reactions were conducted using circa 5 mmol of DMBT (1 eq.) in anhydrous THF, under nitrogen to avoid the reaction of hydrides with H_2O traces present in the air. ^{1}H NMR

Table 5 Summary of the chemical reduction essays on DMBT

Reducing agent	Molar ratio reducing agent/ DMBT	T (°C)	H (h)	^{1}H NMR results
BH$_3$	2.0	30	24	Pure DMBT was recovered at the end of the reaction
NaBH$_4$	2.0	30	8	
DIBAL	1.0	30	7	
DIBAL	1.0	30	24	
DIBAL	2.0	30	48	
LiAlH$_4$	1.0	0	4	DMBT as a main product, several new peaks also detected
LiAlH$_4$	2.0	50	16	No peaks corresponding to DMBT, two major peaks detected

analyses in D$_2$O have been performed to identify the compounds obtained at the end of the reaction.

From these results, one can conclude that the first three reagents are ineffective in reducing DMBT tetrazole rings, while it reacts with LAH. Indeed, only a hydride donor strong enough as LAH is able to reduce the tetrazole rings. This can be explained by the high aromaticity of the substrate due to its two bridged tetrazole rings, enabling the free circulation of electrons over the entire structure.

Study of the DMBT/LAH reaction

In order to identify the reduction products, a thorough study of the DMBT/LAH reaction has been carried out and an optimized protocol has been defined, followed by a work-up step according to three different pathways A, B or C (see experimental part).

Crudes A, B and C were characterized by ^{1}H and ^{13}C NMR, IR and MS (CI). The combination of the results of these various analyses enabled to postulate the structures of the reduction products as being: 1-methyl-5-(*N*-methyl-methanamino)-tetrazole (MMMAT, Fig. 6) and *N,N'*-dimethylethylenediamine (DMEDA) as well as remaining DMBT. The proportions of these products and DMBT vary according to the work-up conditions (see SI: Figs. S1 and S2 for details and NMR spectra of crudes A, B and C).

Based on the integration of the NMR signals (see SI: Fig. S2), it was possible to estimate the proportion of the reduction products as follows: 80% MMMAT, 5% DMBT and 15% DMEDA in A; 89% DMEDA, 5% DMBT and 6% MMMAT in B; 0% MMMAT, 0% DMBT and 100% DMEDA in C (see SI).

Accordingly, MS analyses (CI) of crude A showed a main molecular peak of m/z = 128.1 attributable to MMMAT (M$_{MMMAT}$ = 127 g mol^{-1}) and a minor

Fig. 6 Structure of 1-methyl-5-(*N*-methyl-methanamino)-tetrazole (MMMAT)
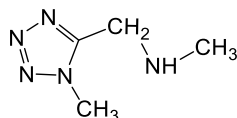
molecular peak of m/z $= 167.2$ corresponding to DMBT ($M_{DMBT} = 166$ g mol^{-1}); however, no peak corresponding to DMEDA was observed ($M_{DMEDA} = 88$ g mol^{-1}). This latter was observed, as a main peak (m/z $= 89.1$) in the mass spectrum of crude B; the peak corresponding to MMMAT was also observed and a minor peak attributable to DMBT. The mass spectrum of crude C gave the molecular peak corresponding to DMEDA.

Moreover, IR spectrum of A has different bands from those of DMBT, for which there are no signals beyond 1600 cm^{-1} (see IR spectra in SI: Figs. S3 and S4). However, it is not possible to specifically assign those corresponding to DMBT, MMMAT or DMEDA. Nevertheless, a band at 2053 cm^{-1} characteristic of an azido group was also observed. This latter was observed in the IR spectrum of B as well as C–H elongation bands of DMEDA at 2916 and 2848 cm^{-1}. The IR analysis of C corresponds to the one performed with commercially supplied DMEDA, exempt from the band relating to the azido function.

Consequently, the NMR, IR and MS analyses are consistent with the proposed structures. Additionally, analyses of commercially provided DMEDA confirmed that it is present in the reaction crudes A, B and C. Hence, the postulated hypothesis, regarding the identity of the DMBT reduction products, has been validated but still this cannot explain the IR characteristic band of azido group detected in most samples. Thus, a reaction mechanism has been suggested to validate all these experimental observations.
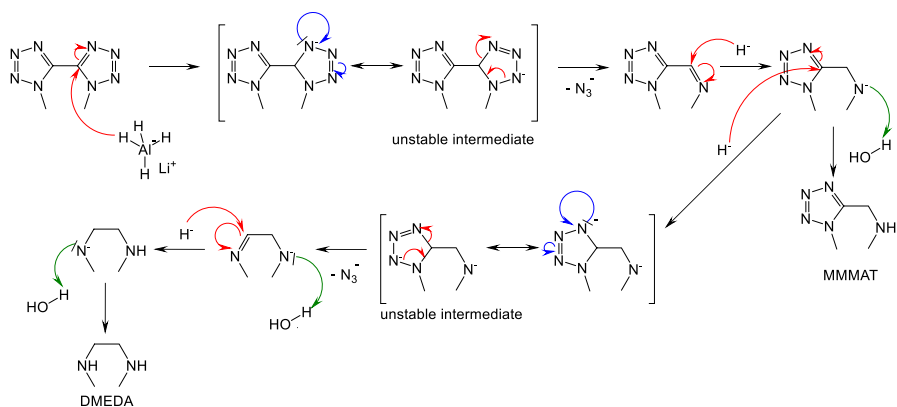
Suggestion of a reaction mechanism

LAH being a hard nucleophile, it will preferentially attack the carbon of DMBT, which is the most electrophilic atom of this molecule. Several mesomeric structures can then be imagined following the addition of hydride to carbon, one of which is significantly more unstable than the others. This instability results in the ring breakage and the extrusion of one azide anion, as supported by Duchamp et al. [30]. The mechanism is a kind of retro-[3 + 2]-cycloaddition.

This phenomenon is the leading clue for the DMBT reduction mechanism (Scheme 4). Thereafter, a second hydride eq. reduces the imine function formed by the extrusion of another azide anion, followed by a hydrolysis of the intermediate formed, leading to MMMAT. This intermediate is likely to react with a third hydride eq. to form another imine, which would be readily reduced by a fourth hydride eq. leading after hydrolysis to DMEDA. For the last two steps, a similar pathway can be imagined from MMMAT leading to DMEDA.

Theoretical validation of the retro-[3 + 2]-cycloaddition

In order to confirm the retro-[3 + 2]-cycloaddition mechanism, theoretical calculations on DMBT bonds lengths were performed-using B3LYP/6-311+G(2d,p) quantum method- before and after hydride addition on the tetrazole carbon (Fig. 7).

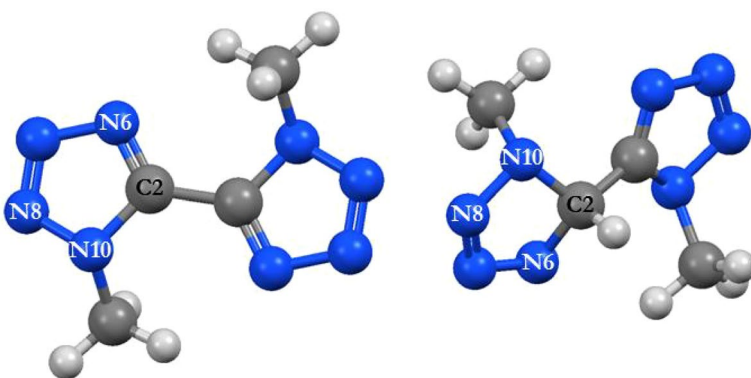**Scheme 4** Suggested reaction mechanism for DMBT reduction with LAH

Fig. 7 DMBT structure before hydride addition (left) and after addition (right)

DMBT	Bond	Bond length (Å)
Before addition	C2–N6	1.326
	N8–N10	1.348
After addition	C2–N6	1.486
	N8–N10	1.479

Table 6 C2-N6 and N8-N10 bonds lengths before and after hydride addition on DMBT

In particular, attention was payed to C2–N6 and N8–N10 bonds lengths, as carbon C2 is the one that is attacked by a hydride. Calculations results are summarized in Table 6.

The addition of a hydride to carbon C2 induces an average increase in C2–N6 and N8–N10 bonds of 0.1455 Å. Thus, the increase of these two bonds compared

$$FeCl_3 \ + \ 3\ LiN_3 \ \longrightarrow \ Fe(N_3)_3 + \ 3\ LiCl$$
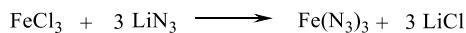
Scheme 5 Formation of $Fe(N_3)_3$ highlighting the presence of azide anion as a result of DMBT reduction by LAH

to the others explains the instability of the mesomeric form of this intermediate, resulting in the azido group leaving as a N_3^-.

Experimental validation of the retro-[3 + 2]-cycloaddition

The suggested mechanism and the performed calculations showed that the reaction releases N_3^- ions, which were detected by IR analyses of the DMBT reduction crudes (band at 2050 cm^{-1}). As the structures of the proposed reduction products do not contain this function, the band observed at 2050 cm^{-1} could therefore come from a stable species involving the azido anion. Thus, due to the presence of the lithium cation in the reaction medium, LiN_3 species could be formed during the reaction. As the latter is commercially available as a white solid, this may explain the "wetty solid" aspect of the reduction crude obtained.

In order to confirm the formation of N_3^- ions during the reaction, a colorimetric detection method described in the literature [31] was applied. It is based on the formation of brown solid iron (III) azide from the reaction between iron (III) sulfate and sodium azide (see SI: Scheme S1).

In order to highlight the presence of the azide anion in the reaction medium of C, the following protocol was used: a solution of iron (III) chloride in methanol was added to a solution of crude C in methanol, the mixture quickly turned bright red, and a brown solid precipitated (see SI: Figs. S5 and S6), indicating the formation of the $Fe(N_3)_3$ species, according to the following reaction (Scheme 5):

Consequently, the suggested mechanism for the DMBT-LAH reaction has been validated, on the one hand, by theoretical calculations that indicate an elongation of the bonds allowing the release of the N_3^- ion, and on the other hand, thanks to its characteristic IR signal and to a colorimetric detection method.

Conclusion

In order to investigate the formation of tetrazoline and tetrazolidine structures from tetrazole-reducing reactions, an exhaustive study was carried out on 1,1'-dimethylbistetrazole (DMBT) following two different reduction pathways:

– DMBT was subjected to catalytic hydrogenation using various catalysts over a wide range of hydrogen pressure (35 to 150 bar) and a temperature range from 20 to 60 °C. This study enabled to find the optimal hydrogenation conditions for DMBT: T = 60 °C, P_{H2} = 150 bar, Pd/C as catalyst, with reaction time = 72 h. The reaction product obtained was identified as being 1-methyltetrazole and a

reaction mechanism, highlighting the breakage of the C–C bond connecting the tetrazole rings of DMBT, was suggested.

– The action of $LiAlH_4$, a powerful hydride donor, on DMBT was studied under various conditions and led to tetrazole ring openning. A reaction mechanism was suggested on the light of the reduction products that were obtained: the first step corresponds to the tetrazole carbon attack by a hydride, followed by a retro-[3 + 2]-cycloaddition resulting in azido anion release. The imine compound that is obtained is reduced by a second hydride. These two steps are occurring repeatedly for the reduction of the second tetrazole ring. Depending on the operating conditions, it is possible to control the number of hydride equivalents and hence, the reaction product. The suggested mechanism was supported by both theoretical chemical calculations and colorimetric detection method that were carried out.

In conclusion, the results of the reducing study undertaken on DMBT tetrazole rings by catalytic hydrogenation and chemical reduction have given clear answers as to the impossibility of tetrazoline and tetrazolidine structures formation by this route.

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