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Catalyzed reaction of triethylborane with pyrazole

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Dedicated to Professor Stanisław Pasynkiewicz on the occasion of his 70th birthday

Abstract

The reaction of triethylborane with pyrazole leading to 4,4,8,8-tetraethylpyrazabole was found to be catalyzed by carboxylic acids. 2,2′-Dimethylpropanoic (pivalic) or benzoic acids act as catalysts in this reaction. Intermediates occurring in the catalytic cycle have been isolated and characterized by NMR as well as IR spectroscopy, and in one case also by X-ray crystallography. The mechanism of the reaction is proposed. © 2000 Elsevier Science S.A. All rights reserved.

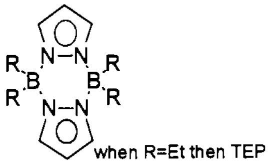
Keywords: Triethylborane; Pyrazole; Catalysis

1. Introduction

Tetraalkylpyrazaboles are usually synthesized in the reactions of pyrazole (pzH) and/or its derivatives with trialkylboranes [1] or tetraalkyldiboranes **6** [2] (Scheme 1). Due to the high stability of the boron–carbon bond these reactions require elevated temperatures (e.g. 130–150°C, Eq. (1)):

$$2Et_3B + 2pzH \xrightarrow[\text{xylene}]{130°C} TEP + 2EtH \qquad (1)$$

It is well known that carboxylic acids readily cleave B–C bonds in trialkylboranes. Brown et al. [3] and Toporcer et al. [4] explained this unusual reactivity of carboxylic acids towards BR_3 compounds by the formation of an intermediate complex possessing a six-membered ring structure. Coordination of the boron atom results in an increased charge density on the α-carbon atom, which facilitates the elimination of an alkane molecule. The product of the reaction is acyloxydialkylborane. It is unstable in the presence of water, alcohols and other –OH reagents and readily undergoes protonolysis under their influence, to afford compounds of the type R_2BOY (Y = H, R, SO_3H etc.) with recovery of carboxylic acid. A simple mechanism of this protonolysis is postulated [5]. Rothgery and Köster [6] investigated the mechanism of the reactions of Et_3B with primary amines in the presence of (2,2′-dimethyl)propanoyloxydiethylborane. They proved that in this case the mechanism is complicated by the formation of a stable addition complex of $Me_3C–COOBEt_2$ with amine, which can be isolated when the molar ratio of reactants is 1:1. Decomposition of the complex occurs only when an excess of amine is present and leads to the formation of the corresponding aminodiethylborane and ammonium salt of 2,2′-dimethylpropanoic acid. In conclusion, carboxylic acids can be used as active catalysts for protonolysis of trialkylboranes. The mechanism of catalysis depends on the type of protolytic reagent, however, the first step is always the formation of acyloxydialkylborane.



Scheme 1.

We have found that pivalic and benzoic acids catalyze also the known reaction of triethylborane with pyrazole. In a previous paper [7] we described the

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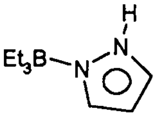


(1)

Scheme 2.

synthesis and characterization of the pyrazole complex with 2,2-dimethylpropanoyloxydiethylborane. This complex is the first relevant intermediate in the catalytic cycle leading to the formation of 4,4,8,8-tetraethylpyrazabole (TEP). In this paper we present the results of our investigations on the mechanism of this reaction.

2. Results and discussion

The addition of a catalytic amount of pivalic or benzoic acids to the Et_3B–pzH mixture in xylene decreases the reaction temperature from 130 to about 80°C. To explain the role of the acid, we have investigated this reaction step-by-step and have tried to find the stoichiometric behavior of all the reactants and intermediates in the system. This is presented in several of the following sections.

2.1. *An equilibrium in the system triethylborane–pyrazole*

The reaction of triethylborane with pyrazole at ambient temperature gives a stable addition complex Et_3B·pzH (**1**), which shows no tendency to decompose into the substrates or TEP under these conditions [7] (Scheme 2). Nevertheless, we proved a significant dynamic character of this compound. The ^{11}B-NMR spectrum of the pure complex shows a signal at 0 ppm, in the range typical for many other R_3B-nitrogen donor complexes [8]. However, when an excess of Et_3B was added, we did not observe the two signals of Et_3B and Et_3B·pzH at 86 and 0 ppm, respectively. Instead, only one broadened signal in the range 86 and 0 ppm is present in the spectrum, and its chemical shift depends on the Et_3B:pzH molar ratio. The ^{1}H-NMR spectrum confirms the dynamic character of the complex because two protons in the α-positions to nitrogen atoms of the pyrazole ring are equivalent and give one signal. This is possible only when the fast (in the NMR time scale) exchange of the azole proton and Et_3B between molecules of the complex is assumed. The fact of the dynamic character of the complex is very important because the rate of the catalyzed reaction depends mainly on the concentration of free Et_3B in the system. The faster the exchange process in the complex solution, the higher the 'concentration' of 'free' Et_3B and its ability to react with the catalyst molecule.

2.2. *System triethylborane–pyrazole–pivalic acid*

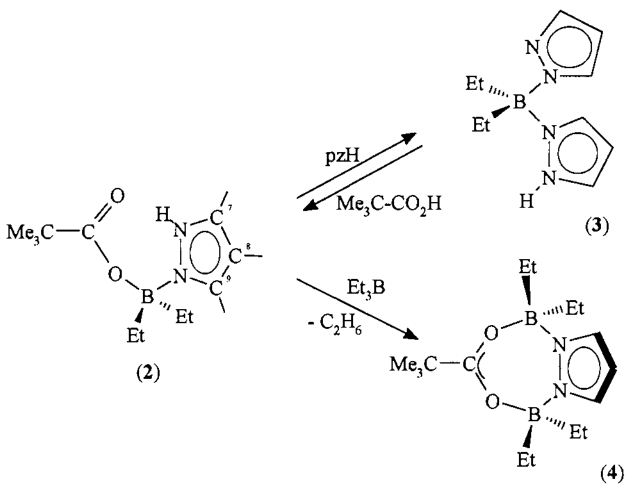
In the next step we investigated an interaction between the triethylborane–pyrazole complex and pivalic acid. The reaction in the molar ratio 1:1 afforded the addition complex of Me_3C–$COOBEt_2$ with pyrazole (**2**) [7] (Scheme 3).

Complex **2** has a dynamic character but it is stable and can be stored at room temperature for several weeks without decomposition. It is also stable for several hours at 60°C in $CDCl_3$ and decomposes rapidly only above 100°C to yield tetraethylpyrazabole and pivalic acid. This unexpected stability is probably mostly due to the seven-membered ring structure. This explanation can be supported by the fact that our attempts to obtain the corresponding complex of type **2** with imidazole were unsuccessful. Considering the great thermal stability of **2**, it became clear to us that the direct decomposition of the complex to TEP is not important in view of the catalysis.

2.3. *Reaction of **2** with pyrazole*

Complex **2** reacts quite rapidly at room temperature with an excess of pyrazole, to afford a colorless crystalline solid, only sparsely soluble in hexane. NMR and IR data allowed one to propose the structure of the (1-pyrazolyl)diethylborane-pyrazole adduct (**3**) for this product. The reaction is reversible (Scheme 3). Compounds of this type were reported by Yalpani et al. [2] although it should be mentioned here that they obtained complexes with a 1,5-cyclooctanediyl substituent on the boron atom.

As can be expected, the rapid proton exchange in solution makes pyrazole rings of **3** equivalent. Compound **3** is air stable but it slowly decomposes even at room temperature and rapidly when melted (100°C), to produce TEP and pzH. The decomposition of **3** is very



Scheme 3.

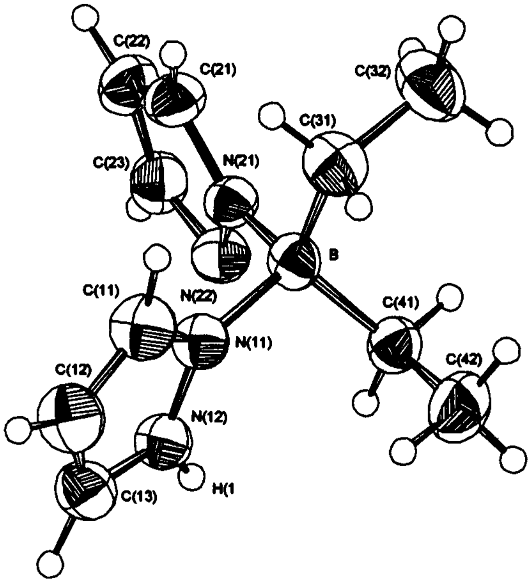


Fig. 1. ORTEP plot of a single molecule of **3**.

Table 1
Selected bond lengths (Å) and angles (°) for **3**

Bond lengths			
B–N(11)	1.615(2)	B–N(21)	1.561(2)
B–C(31)	1.612(3)	B–C(41)	1.609(3)
N(11)–N(12)	1.346(2)	N(21)–N(22)	1.354(2)
N(11)–C(11)	1.336(2)	N(21)–C(21)	1.349(2)
N(12)–C(13)	1.334(2)	N(22)–C(23)	1.338(2)
C(11)–C(12)	1.374(3)	C(21)–C(22)	1.363(3)
C(12)–C(13)	1.361(3)	C(22)–C(23)	1.367(3)
N(12)–H(1)	0.89(2)		
Bond angles			
N(21)–B–N(11)	105.66(13)	C(41)–B–C(31)	114.5(2)
C(31)–B–N(11)	107.2(2)	N(21)–B–C(31)	110.5(2)
C(41)–B–N(11)	107.8(2)	N(21)–B–C(41)	110.81(14)
C(11)–N(11)–B	131.5(2)	C(21)–N(21)–B	129.4(2)
N(12)–N(11)–B	122.92(14)	N(22)–N(21)–B	122.06(13)
C(11)–N(11)–N(12)	105.6(2)	C(21)–N(21)–N(22)	108.5(2)
N(11)–C(11)–C(12)	110.4(2)	N(21)–C(21)–C(22)	109.6(2)
C(13)–C(12)–C(11)	105.4(2)	C(21)–C(22)–C(23)	104.3(2)
N(12)–C(13)–C(12)	107.9(2)	N(22)–C(23)–C(22)	111.4(2)
C(13)–N(12)–N(11)	110.6(2)	C(23)–N(22)–N(21)	106.2(2)

rapid in the presence of Et_3B due to the stronger Lewis acidity of the boron atom in the Et_3B molecule compared with Et_2Bpz. In effect, the formation of **1** in this system is preferred.

2.4. Molecular structure of 3

The molecular structure and atom-numbering scheme of **3** are shown in Fig. 1 [9]. Selected bond lengths and angles are presented in Table 1. The tetragonal boron atom is surrounded by two ethyl groups and two pyrazolyl ligands. The important structural detail to be noted is the difference between B–N bonds (0.054 Å). This is a consequence of the non-equivalency of pyrazolyl ligands — the B–N bond is longer for contact with the acidic pyrazole ring, pzH, and shorter with anionic pz. These bond lengths seem to be standard when compared with average distances obtained from the Cambridge Crystallographic Data Base [10]: for B–N(pzH) it is 1.614(20) Å and for B–N(pz) 1.560(2) Å.

In consideration of the larger negative charge on pz and the presence of a free electron pair on N(22) a short C(21)–C(22) bond and elongation of other bonds in the pz ring — particularly the N(21)–C(21) bond are observed. This is an effect of the free electron pair on N(22) and also the preference of the resonance form with a free electron pair on N(21), which is confirmed by its slight pyramidalization; the pz ring and B show a deviation from planarity of 0.053(2) Å, on the contrary the pzH ring is coplanar with B (deviation at 0.001(2) Å). However the free electron pair on N(22) is engaged in very strong hydrogen bonding so the differences in bond lengths and angles between pyrazole rings are not very large. As is shown in Fig. 2, two molecules are bound forming a dimer with a central 12-membered ring. This is in accord with the result previously obtained [2] for a similar species.

The N(12)···N(22′) distance of 2.773(2) Å and the N(12)–H(1)–N(22′) angle value of 156(2)° are evidence of the strong interactions (characteristic N···N hydrogen bonding distance is placed between 2.92 and 3.15 Å) [11]. The distance N(12)–H(1) is 0.89(2) Å, so the bond is asymmetric but its strength indicates a H-bond with proton transfer as was found in the liquid.

2.4.1. Reaction of 2 with triethylborane

Complex **2** reacts rapidly with triethylborane at room temperature with evolution of ethane [7]. Product **4** was obtained as an oily liquid after evaporation of the solvent. Complex **4** was also formed when **2** was treated

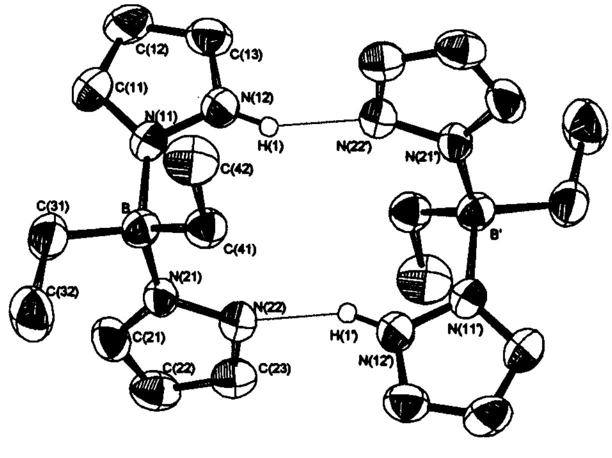
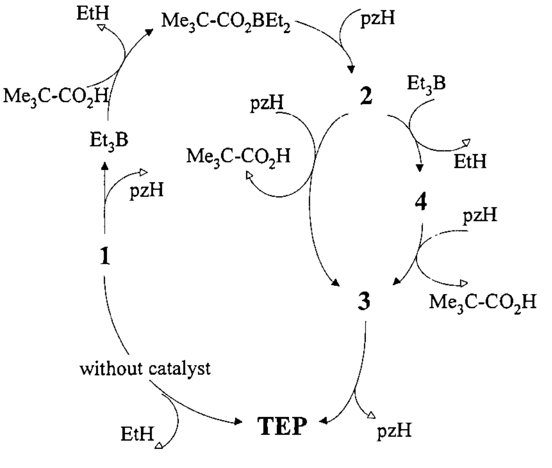


Fig. 2. ORTEP plot of **3**-dimeric structure. The hydrogen atoms are omitted for clarity (except NH).



Scheme 4. The simplified pathway of the catalyzed reaction of triethylborane with pyrazole. The reversibility of certain stages is omitted for clarity.

with $Me_3C–COOBEt_2$. Complex **4** is stable and decomposes rapidly only above 100°C to give TEP and $Me_3C–COOBEt_2$. It also decomposes readily when treated with pzH, to give **3** and pivalic acid complexed with pyrazole.

2.5. Mechanism of catalysis

The collected results indicate a much more complex mechanism of catalysis than is postulated in the case of other reactions of protolysis of trialkylboranes. The simplified pathway of the catalyzed reaction is presented in Scheme 4. The rate of reaction is most probably limited mainly by the equilibrium between complex **1** and uncomplexed Et_3B and pyrazole, which are active reagents in the cycle. In fact, uncomplexed triethyborane reacts with carboxylic acids rapidly below 0°C, whereas, when it is complexed with pyrazole, imidazole as well as quinuclidine, ethane evolution occurs only above 15–20°C. In the next step, the $Me_3C–COOBEt_2$ is immediately complexed with pyrazole, to give **2**. An analogy with the previously proposed [6] mechanism of aminolysis appears. This intermediate is a key compound in the system: it can interact either with pzH or with Et_3B, to yield **3** or **4**, respectively. Complex **4** is unstable in the presence of pzH and decomposes to **3**. Complex **3** is the most kinetically unstable intermediate in the system so it readily undergoes dismutation, particularly in the presence of Et_3B, to yield pzH and the final product TEP (Scheme 4).

3. Experimental

^{1}H-, ^{13}C-, ^{11}B-NMR as well as IR spectra were recorded at room temperature (r.t.) (unless otherwise noted). Chemical shifts are given in ppm relative to TMS in ^{1}H- and ^{13}C-NMR spectra and relative to $Et_2O·BF_3$ in ^{11}B-NMR spectra. $CDCl_3$ was the solvent (NMR spectra). Molecular-weight determination was performed cryoscopically in benzene. Triethylborane, 98%, was provided by MPI für Kohlenforschung, Mülheim–Ruhr. Pyrazole (98%) and 2,2′-dimethylpropanoic acid (99%) were provided by Aldrich; benzoic acid (pure) was purchased from POCh–Gliwice, Poland. (2,2′-Dimethyl)propanoyloxydiethylborane was synthesized as described in the literature [5].

All reactions were carried out in an argon atmosphere using standard Schlenk techniques. Pyrazole and benzoic acid were dried in vacuo prior to use. Solvents were dried with (Na,K)-benzophenone ketyl, distilled under argon and stored over 4 Å molecular sieves. Other reagents were used without purification.

3.1. Reaction of $Et_3B·pzH$ (**1**) with $Me_3C–COOH$

A solution of Me_3CCOOH (4.15 g, 40.7 mmol) in heptane (15 ml) was quickly added to precooled (0°C) $Et_3B·pzH$ (6.76 g, 40.7 mmol). After warming to 15°C ethane evolution started. The solution was stirred at r.t. for 1.5 h. During the next 1.5 h the temperature was gradually raised to 50°C, to complete the reaction. The total volume of ethane evolved was 0.82 NL (36.5 mmol, 90%). After evaporation of the solvent 9.50 g (39.9 mmol, yield 98%) of a colorless, oily liquid was obtained. ^{11}B-NMR (96.24 MHz): δ 7.1 [12].

3.2. Preparation of 1-pyrazolyldiethylborane–pyrazole adduct **3** in the reaction of **2** with pzH

Compound **2** (2.49 g, 10.5 mmol) was added to a suspension of pzH (1.35 g, 19.8 mmol) in hexane (15 ml) over 2 min. The mixture was stirred for 30 min at r.t. The precipitated white solid was filtered, washed with hexane (4 × 5 ml), and dried in vacuo, yielding 0.72 g (3.5 mmol, 33%) **3**. M.p. 95–102°C (dec.). Anal. Calc. for $C_{10}H_{17}BN_4$: C, 58.85; H, 8.40; N, 27.45. Found: C, 57.66; H, 8.33; N, 27.53. ^{1}H-NMR (300 MHz): δ 13.8 (br, ~1H, NH), 7.67 (br, 2H, CH), 7.62 (br, 2H, CH), 6.34 (t, 2H, CH), 0.79 (q, 4H, CH_2), 0.64 (t, 6H, CH_3). ^{11}B-NMR (96.24 MHz, recrystallized from hexane): δ 2.6. IR (KBr, recrystallized from hexane): 3300–2200 cm^{-1} (N–H···N).

3.3. Reaction of **2** with Et_3B

Et_3B (1.45 g, 2.2 ml, 14.8 mmol) was quickly added to the solution of **2** (3.15 g, 14.7 mmol) in heptane (5 ml) at about −70°C. Ethane evolution began when the temperature increased to ca. 10°C. After the next 10 min the temperature increased to 50°C. 0.30 NL (85%) of ethane was evolved in the reaction. A yellowish solution was obtained. ^{11}B-NMR (96.24 MHz) analysis: $\delta = 10.5$ [12].

3.4. Reaction of **4** with pzH

Complex **4** (2.08 g, 6.8 mmol) was added to a suspension of pzH (1.92 g, 28.2 mmol) in heptane (10 ml). After a few minutes a fine precipitate formed. The mixture was stirred for 18 h at r.t. Then the slurry was diluted with heptane (10 ml) and stirred for an additional 4 h. A white crystalline solid was filtered, washed with hexane (3 × 15 ml), and dried in vacuo, to afford 2.00 g (9.8 mmol, yield 72%) of crude **3**. M.p. 98–105°C (dec.). Recrystallization from hexane (50 ml) afforded 0.93 g (yield 33%) of the pure product. M.p. 99–102°C (dec.). ^{11}B-NMR: (64.16 MHz): δ 2.6.

3.5. Crystal structure determination of **3**

A sample of **3** (about 0.3 g) was dissolved in hexane (20 ml) at 60°C. The solution was placed in a water bath at 45°C. Slow cooling (8 h) gave crystals suitable for X-ray analysis. Crystal data, data collection and refinement parameters for **3** are summarized in Table 2. A single crystal was measured on a Siemens P3 diffractometer at r.t. The unit cell was determined by indexing of 31 well-centered reflections. Intensity data were collected using graphite monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Two checked reflections were measured every 70 reflections and they indicated 27% crystal decomposition during data collection. After correction for the Lorentz-polarization effect and crystal decomposition, the equivalent reflections were averaged. The structure was solved by direct methods using SHELXS-86 [13] program. Full-matrix least-squares refinement method on F^2 values was carried out using the SHELXL-93 [14] program. Positional and thermal parameters were followed by subsequent conversion to anisotropic thermal coefficients for all non-hydrogen atoms. The hydrogen atom positions were located in the difference Fourier maps and were refined isotropically.

Table 2
Crystal data and structure refinement for **3**

Empirical formula	$C_{10}H_{17}BN_4$
Formula weight	204.09
Crystal class	Monoclinic
Space group	$P2_1/c$
Unit cell parameters	
a (Å)	9.4450(14)
b (Å)	7.7210(11)
c (Å)	17.132(2)
β (°)	105.570(11)
V (Å^3)	1203.5(3)
Z	4
D_{calc} (Mg m^{-3})	1.126
$F(000)$	440
Absorption coefficient (mm^{-1})	0.070
Radiation	Mo–K$_\alpha$ ($\lambda = 0.71073$ Å), graphite-monochromated
Temperature (K)	293(2)
2θ Range for data collection	4.48–50.10
Index ranges	$0<h<10$, $0<k<9$, $-20<l<19$
Reflections collected	2563
Independent reflections	1823 ($R_{int} = 2.21\%$)
Reflections observed	1495 [$I > 2\sigma(I)$]
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	$w = [\sigma^2(F_o^2) + (0.0221P)^2 + 0.4563P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$
Data/restraints/parameters	1822/0/205
Final R indices (obs. data)	$R_1 = 0.0382$, $wR_2 = 0.0825$
R indices (all data)	$R_1 = 0.0524$, $wR_2 = 0.0970$
Goodness-of-fit on F^2	1.114
Extinction coefficient	0.026(2)
Largest diff. peak and hole (e Å^{-3})	+0.142 and −0.134

4. Supplementary material

Full tables of bond distances and angles, data collection, as well as solution and refinement, tables of atomic coordinates and equivalent isotropic displacement parameters, as well as anisotropic displacement parameters for compound **3** are available (4 pages) from the Cambridge Crystallographic Data Centre, CCDC no. 138590. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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