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FVP OF BIS- AND TRIS-(PYRAZOL-1-YL)METHANE. A RADICAL REACTION

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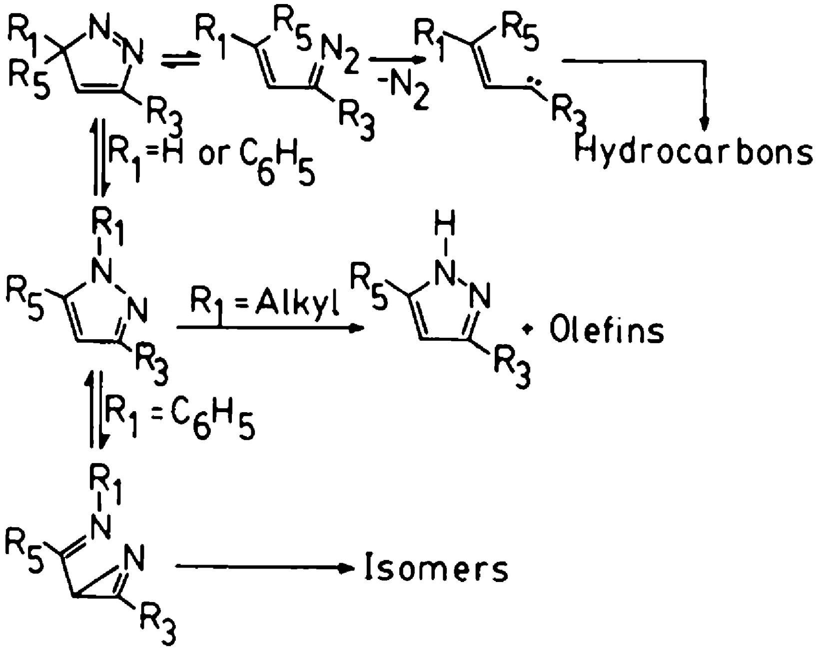
Abstract.- Flash vacuum pyrolysis of bis- and tris-(pyrazol-1-yl) methane was carried out. Alpha, gamma and radical eliminations were considered. The products actually formed correspond to a radical reaction. In the case of bis-(pyrazol-1-yl)methane, working at higher temperatures, pyrimidine was obtained. This compound is formed by rearrangement of a $PzCH_2^{\cdot}$ radical.

Introduction.-During previous studies on the FVP of pyrazoles, we (J.D.P. & G.I.Y.) found that N-sustituents have larger influence than C-substituents on the reaction course. Thus, in the case of NH-pyrazoles, nitrogen extrusion and formation of hydrocarbons were observed (1). Changing the H- by C_6H_5-leads to pyrazole isomers, imidazole and nitrile, depending on ring substitution (2). Finally, when the N-substituent is an alkyl group with α and β hydrogens, the reaction products are pyrazole and alkenes, formed by a concerted elimination (3). In scheme 1 are summarized the different possibilities described above.



Scheme 1

Searching for new reactions in the pyrazole series, tris-(pyrazol-1-yl)methane **1a** and bis(pyrazol-1-yl)methane **1b** were selected. Taking into account the results of Scheme 1 and other literature reports (4,5) on FVP of pyrazoles different behaviors are possible for **1a** and **1b** : α-elimination of a pyrazole molecule to form a carbene; γ-elimination involving an aromatic C-H bond, and homolytic cleavage to form different radicals.

Results and discussion.-Reactions of **1a** and **1b** were carried out in a FVP system previously described (6) at 450-500°C for **1a** and 600-750°C for **1b**. The reaction products were trapped at liquid air temperature and then submitted to the usual analytical techniques (GLC, ^{1}H NMR, MS). In both cases pressures were about 10^{-2} mm, giving contact times between 10^{-1} and 10^{-2} sec.

Pyrolysis of tris(pyrazol-1-yl)methane (1a). Starting material (1a), 1H-pyrazole (2) as well as bis(pyrazol-1-yl)methane (1b) were found in all reactions. The presence of these compounds was checked by comparison with authentic samples by TLC and GLC. Besides the MS of the reaction crudes showed other signals, one of these peaks, m/z=134, was assigned to a bipyrazolyl derivative (3) (Table 1).

Pyrolysis of bis(pyrazol-1-yl)methane (1b). In this case (Table 2), besides starting material (1b), pyrazole (2), tris(pyrazol-1-yl)methane (1a) and 1-methylpyrazole (4) were identified by mass spectrometry. The NMR analysis of the reaction crude does not show the pyrazole signals, since this pyrolysis was carried out at temperatures high enough to decompose 2 into nitrogen and propyne (1). At higher temperatures (750-850°C) pyrimidine (5) was formed and identified (MS and NMR) by comparison with an authentic sample.

The relative percentages of Tables 1 and 2 were determined by GLC, using authentic samples of **1a**, **1b**, **2** and **4** as standards. This prevented the quantitative determination of the relative amount of compound 3.

Table 1

MS of FVP of compound 1a

m/z	Compound	%
68 (M)	2	11.8
134 (M)	3	n.d.
148 (M)	1b	21.1
149 (M+1)	1b	
214 (M)	1a	67.1

Table 2

MS of FVP of compound 1b

m/z	Compound	%
68 (M)	2	25.2
82 (M)	4	10.0
134 (M)	3	n.d.
148 (M)	1b	34.0
149 (M+1)	1b	
214 (M)	1a	30.8
80 (M)[a]	5	

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[a] Formed at ~800°C

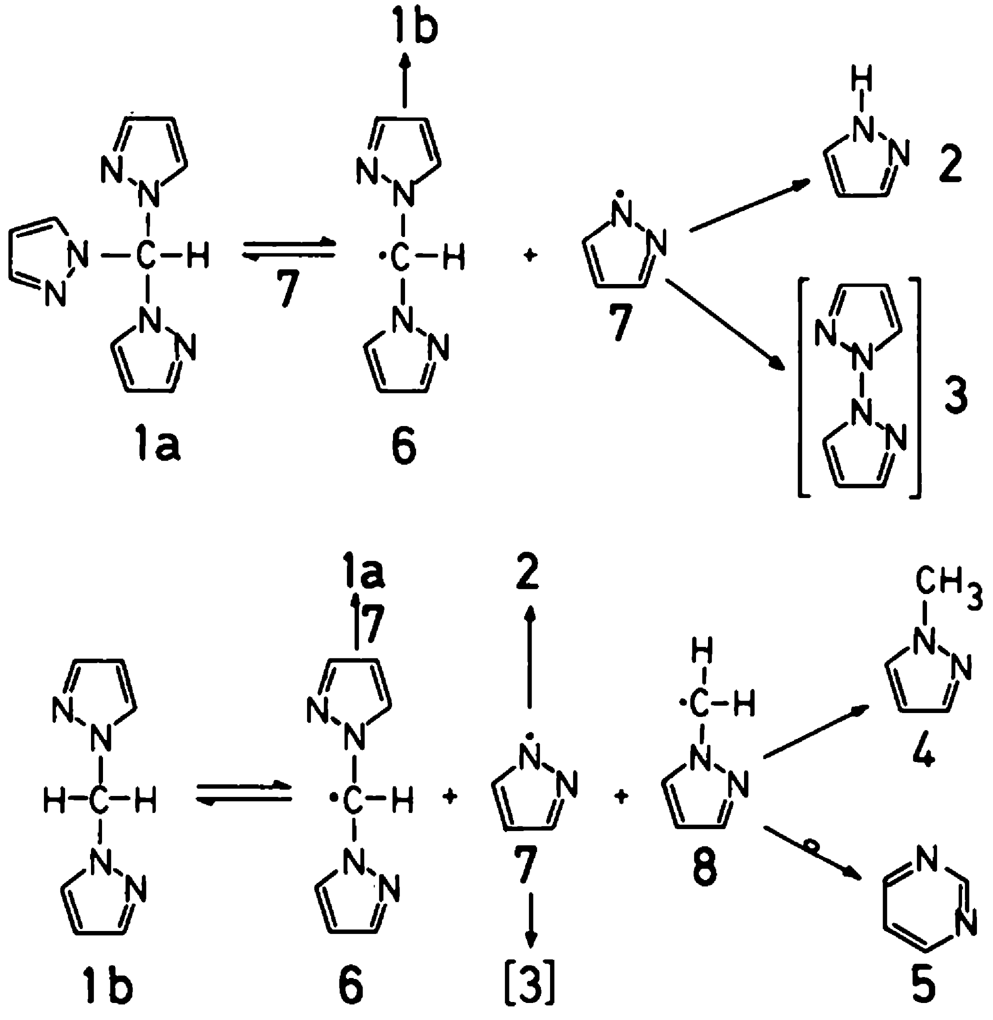
In order to obtain additional information, tris-(pyrazol-1-yl)methane-d_1(1a d) and bis -(pyrazol-1-yl)methane-d_2 (1b d_2) were synthesized and their FVP reactions were studied. In the reactions of 1a d only pyrazole (2) (m/z=68) was detected and no pyrazole-d_1 (2 d) (m/z=69); besides only monodeuterated bis(pyrazol-1-yl)methane (1b d) was detected (m/z=149). On the other hand, in reactions of 1b d_2 both 2 and 2 d and 4 d_3 (m/z=85) were found.

All these experiments are only consistent with a radical mechanism. In addition, it is necessary to assume that the hydrogen abstraction by radical 7 involves an heterocyclic C-H bond and not the central methine hydrogen, in reactions of 1a, and both possibilities in reactions of 1b. An additional evidence for the radical mechanism was obtained when the pyrolysis of 1b was carried out using toluene as carrier. Fragments m/z 91 and 182 were found in the MS, a strong evidence of the presence of bibenzyl. Scheme 2 summarizes the origin of the different products formed in the FVP experiments.

The 1,1'-bipyrazolyl structure (3) is only tentatively assigned. As this compound is unknown and by no means easy to synthesize (7), alternative structures, N,C– or C,C– bonded, cannot be excluded. The presence of 2 d could be evidence for the α-elimination (scheme 3). Pyrimidine (5) formation may be explained by this pathway, since in all probability carbene 9 will insert into the N-N bond and not into the C-N bond (formation of pyridazine 10); insertion of nitrenes into the pyrazolic N-N bond is well documented (8). However, since Wentrup et al. (5) have found a pyrimidine in a reaction where a carbene (similar to 9 but with 3,5-dimethyl substituents on the pyrazole ring) is highly improbable, we prefer to consider that 5 is formed by rearrangement of 8, but the α-elimination cannot be rejected since 2 d was formed in the reactions of 1b d_2.

Concerning the reason why the hydrogen abstraction involves an aromatic C-H instead of the C(sp^3)-H bond in 1a and in certain extent in 1b, some considerations could be of interest. The radical 6 is not stabilized by conjugation; the C-N bond prevents the typical delocalization of polyarylmethane radicals, and the C-H proton is well protected by the three rings (in 1a) against an attack by radicals 6 and 7. The pyrolysis of triphenylmethane (9, 10) has been reported; the authors found benzene and diphenylmethane, indicating that the C-C bond is broken as well as the

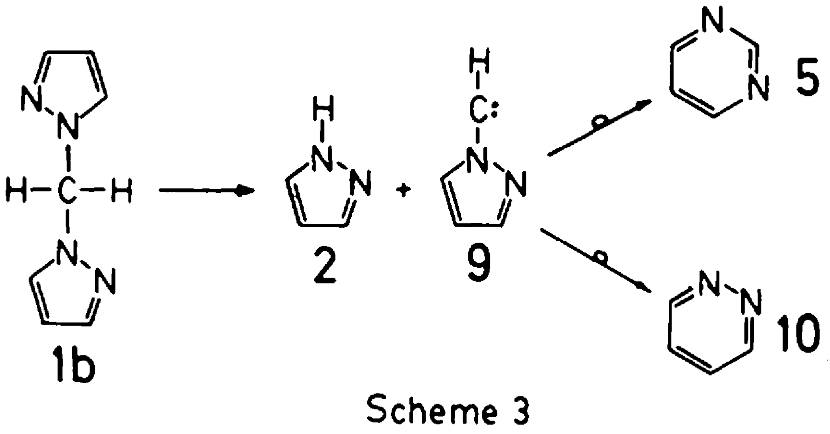
C-H bond, perhaps due to the bulky substituents. In the reactions of 1b $\underline{d}_2$, the presence of 2, 2 $\underline{d}$ and 4 $\underline{d}_3$ could be evidence of hydrogen abstraction by the central carbon from radicals 7 and 8. In the case of 7, the hydrogen abstraction only takes place from the heterocyclic rings.



Scheme 2

The results depicted in Scheme 2 correspond to a different behaviour for compounds 1a and 1b. In the case of tris(pyrazol-1-yl)methane only the C-N bond cleavage was necessary to explain the products formed. On the other hand, the products obtained in the FVP of 1b, correspond to cleavages of both the C-N (formation of 6 and 7) and the C-H bonds (formation of $H^{\bullet}$and 8).

Since the radical 7 is a σ and not a π radical (11, 12) the lower C-N dissociation energy in 1a can be attributed to a higher steric hindrance which is relieved when the C-N cleavage occurs.



Scheme 3

EXPERIMENTAL

^1H NMR spectra were recorded in Cl_4C using a Varian T-60 NMR Spectrometer (δ values). Mass spectra were recorded on a Finnigan 3300 equiped with a 1500 Incos data system. Silica gel was used for TLC and column chromatography. Analytical GLC conditions were: column, 1.3 m SE_{54} 4% chromosorb B; linear temperature programming: 2°/min between 90 and 150°C; nitrogen flow rate: 0.7 ml/sec.

Tris(pyrazol-1-yl)methane 1a and bis(pyrazol-1-yl)methane 1b were synthesized as previously described (13, 14).

Tris(pyrazol-1-yl)methane-d (1a d) and bis(pyrazol-1-yl)methaned-d_2 (1b d_2)were prepared according to the literature (13, 14) changing $CHCl_3$ to $CDCl_3$ and $CHCl_2$ to $CDCl_2$; purification was achieved by column chromatography. These compounds were identified by their ^1H NMR and MS (m/z 215 and 150 M^+).

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