METHYL MIGRATION AND DEMETHYLATION IN THE 4,5-DIMETHYL-CARBAZOLE SYNTHESIS BY TAUBER METHOD.

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Applicating Täuber method to synthesis of 4,5-dimethylcarbazole 2, we obtained the considerable amounts of 3 - 5. The cyclization took place insufficiently at 180°C and the formation of the isomer 3 increased with an increase in concentration or H_0 of the acids. Considering these results, we could obtain 2 in good yields (over 90%) by heating 1 with more dilute H_2SO_4 (0.5 - 1 N) at 200°C for 24 hours.

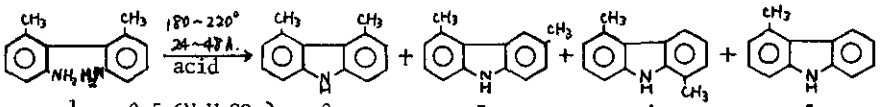


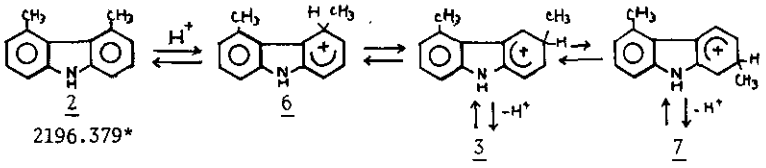
Table 1

1		2	3	4	5
	0.5-6N.H_2SO_4	0.9-95%	0.4-94%	0-1.9%	0-3.7%
	6N. HCl				
	85% H_3PO_4				

Heating of 2 with acids gave 3 and 5 (Table 2), therefore, formation of the isomers is mainly attributed to the 1,2-methyl shift, and this can be understood as a result of instability of 2, due to a steric hindrance of two methyl groups. MINDO/2 calculations indicate that 2 is less stable than 3 by 1.46 eV. The M.O. results also show that the 4-position of 2 is easily protonated, and it suggests a process from 2 to 3 via protonated species 6.

On the otherhand, 7 was not detected, although its stability was expected by MINDO and CNDO/2 calculations. It is logical to assume the existence of the highest potential barrier between two protonated species of 3 and 7. The formation of 4 in the reaction of 1 cannot be interpreted by the successive 1,2-shifts, because we could not find 7, as an intermediate expected for the reaction mechanism. The reaction giving 4 may be illustrated by a route B in Scheme 2, as demonstrated by Allen et al.(J. Chem. Soc.(C), 1968, 2406)

Scheme 1



Scheme 2

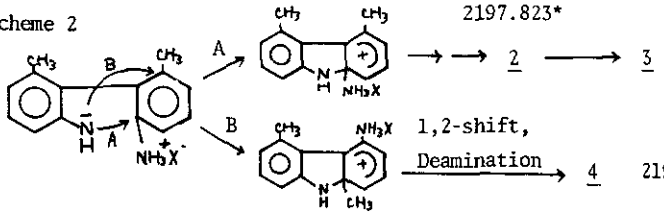


Table 2

2 —200°, 24 h.→ 3 + 5

	Yield %	
6N.H_2SO_4	9.4	0.1
6N. HCl	35.6	9.9
85% H_3PO_4	54.7	9.7

* Total energy(-eV)