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SELECTIVE PREPARATION. 32. PHOSPHORIC ACID CATALYZED CYCLIZATION AND DE-TERT-BUTYLATION OF 2,2'-DIAMINO-4,4'-DI-TERT-BUTYLBIPHENYL AFFORDING CARBAZOLE[1]

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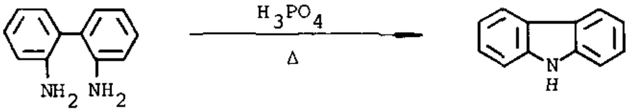
Abstract —— *Heating of 2,2'-diamino-4,4'-di-tert-butyldiphenyl (5) in 85% H_3PO_4 afforded carbazole (2). However, use of diethylene glycol as a solvent did not give 2 but 2,7-di-tert-butylcarbazole (7) was formed in 64% yield.*

It has been previously reported that[2] treatment of 4,4'-di-tert-butyl-2-nitrobiphenyl with triethylphosphite afforded 2,7-di-tert-butylcarbazole which was easily trans-tert-butylated with $AlCl_3$ catalyst in benzene to give carbazole (2). Compound (2) was also prepared by acid-catalyzed cyclization[3] of 2,2'-diaminobiphenyl (1).



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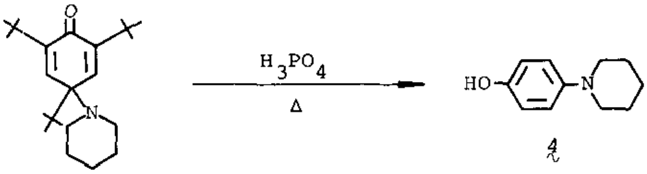
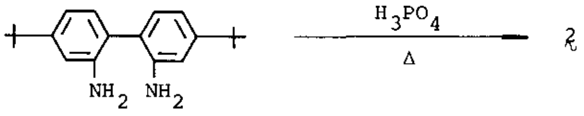


3 4

*On the other hand, phosphoric acid-catalyzed de-tert-butylation of 4-piperidino-*2,4,6-tri-tert-butyl-2,5-cyclohexa-dien-1-one (3) afforded 4-piperidinophenol (4).[4]

The above results suggest that compound 2 might be prepared by acid-catalyzed cyclization as well as de-tert-butylation of 2,2'-diamino-4,4'-di-tert-butylbiphenyl (5)[5] in one step.



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Treatment of 5 with phosphoric acid was carried out under various conditions, and the results are summarized in Table 1. As is shown in Table 1, the yield of the expected 2 increased with increasing of reaction time and with elevation of reaction temperature. However, at 250°C, the yield is lower than that of temperature of 220°C and it decreased with increasing of reaction time. This means that the product 2 may be unstable at such higher temperature. When polyphosphoric acid was used instead of phosphoric acid, the yield of 2 was lower than that of the latter case. It was also found in all above cases that a small amount of 2-tert-butylcarbazole (6) was detected by GC analysis. Authentic sample of 6 was previously prepared by the reported method.[2]

It should be noted that 2,7-di-tert-butylcarbazole (7)[2] was obtained in considerable yield as a sole product but not compound 2, when diethylene glycol was used as a solvent.

Unfortunately, why such different results were arisen from the different conditions used is not clear by the available data.

From the above results, it might be assumed that the compounds 7 and 6 would be intermediates for the formation of 2 from 5 under the conditions used. However, heating of the both compounds 7 and 6 under similar conditions did not give any product but the starting compounds were recovered in almost quantitative yields, respectively.

$$6 \xrightarrow[\Delta]{H_3PO_4 \quad /\!/} 2 \xleftarrow[\Delta]{/\!/ \quad H_3PO_4} 7$$

Based on the above results, it might be concluded that initially de-tert-butylation occurred to give 2,2'-diaminobiphenyl (1) via 4-tert-butyl-2,2'-diamino derivate 8 and then cyclization of 1 happened to afford compound 2. However, formation of a small amount of 6 indicates somewhat occurrence of cyclization of 8.

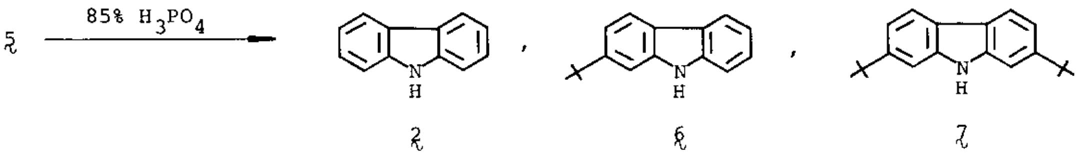


Table 1. Treatment of 2,2'-diamino-4,4'-di-tert-butylbiphenyl (5) with phosphoric acid.[a]

Run	Temp (°C)[b]	Time (h)	Product (%)[c]	
1	160	24	no reaction[d]	
2[e]	180	24	2 (5) ,	6 (+)[f]
3	220	3	2 (23) ,	6 (+)
4	220	10	2 (25) ,	6 (+)
5	220	48	2 (43) ,	6 (+)
6	220	120	2 (37) ,	6 (+)
7	250	65	2 (29) ,	6 (+)
8	250	24	2 (24) ,	6 (+)
9[g]	220	24	2 (20) ,	6 (+)
10[h]	200	24	7 (45)[i],	
11[j]	220	24	7 (64)[i],	

a) A mixture of 100 mg of 5 and 6 ml of phosphoric acid was heated under an atomosphere of dry nitrogen, unless indicated otherwise.

b) The temperature of oil bath are shown.

c) The yields were determined by G.C..

d) The starting compound 5 was recovered in almost quantitative yield.

e) Compound 5 was recovered in 40% yield.

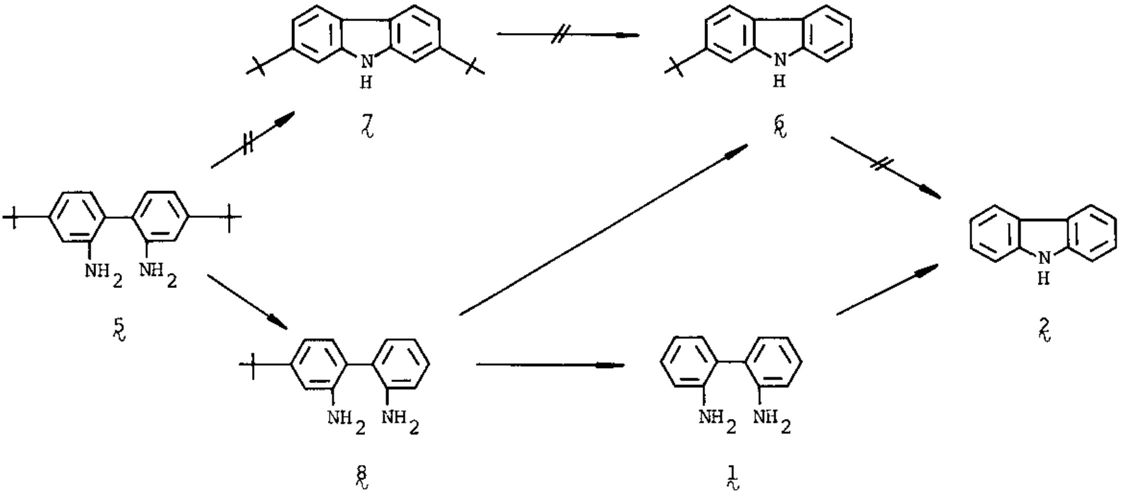
f) The plus sign means less than 1% yield.

g) Polyphosphoric acid (commercially available) was used instead of phosphoric acid.

h) A mixture of 100 mg of 5, 0.1 ml of phosphoric acid, and 8 ml of ethylene glycol was heated.

i) The isolated yields are shown.

j) A mixture of 5 g of 5, 1.25 ml of 85% H_3PO_4 and 50 ml of diethylene glycol was heated.



Scheme 1

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