HETEROCYCLES, Vol 20, No 4, 1983

REACTION OF 2,2'-DIAMINO-4,4'-DI-TERT-BUTYLDIPHENYL WITH EXCESS SO_2Cl_2 AFFORDING 1,3,4,6,8-PENTACHLORO-2,7-DI-TERT-BUTYLCARBAZOLE

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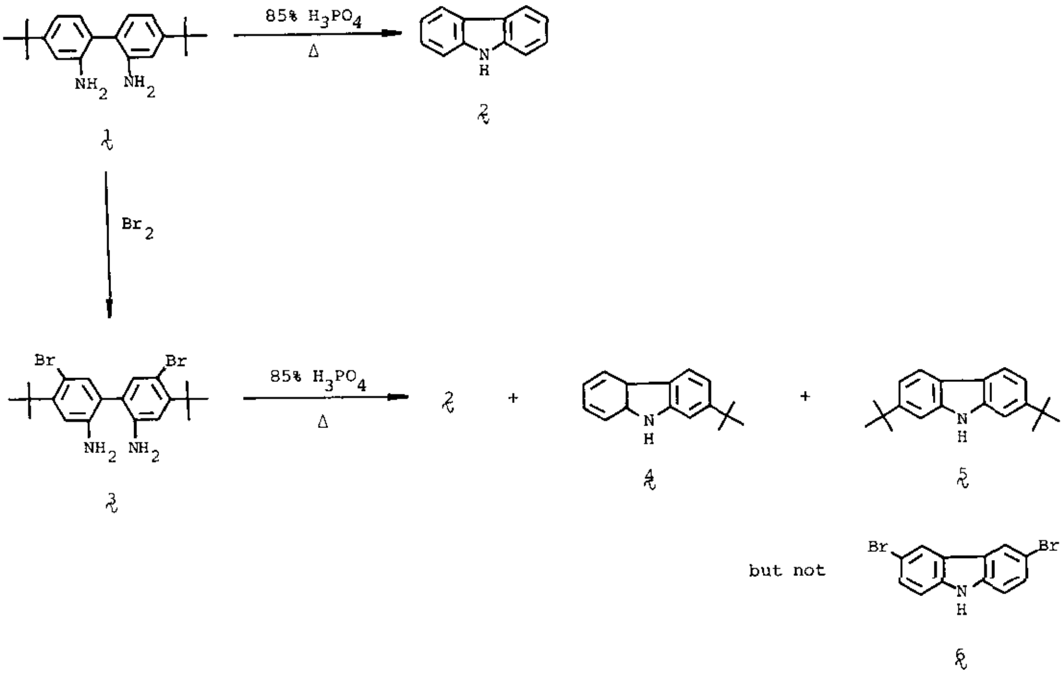
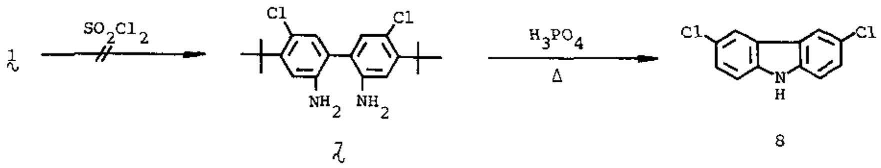
Abstract —— Treatment of 2,2'-diamino-4,4'-di-tert-butyldiphenyl with excess SO_2Cl_2 in a boiling CCl_4 solution afforded 1,3,4,6,8-pentachloro-2,7-di-tert-butylcarbazole in 80% yield. The pathway of the above reaction is also described.

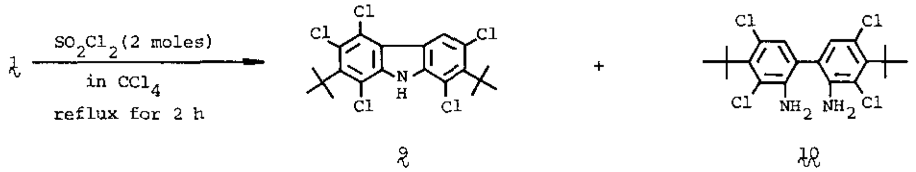
Although heating of 2,2'-diamino-4,4'-di-tert-butyldiphenyl in boiling 85% H_3PO_4 solution afforded carbazole (2), a similar treatment of its 5,5'-dibromide (3) gave 2-tert-butyl-(4) and 2,7-di-tert-butylcarbazole (5), debromination as well as trans-tert-butylation having occurred, but not 3,6-dibromocarbazole (6).[1,2]



We undertook the reaction of the title compound 1 with SO_2Cl_2 attempting to prepare the corresponding chlorinated diaminodiphenyl (7) which seems to afford the chlorinated carbazole (8) by heating in 85% H_3PO_4 solution.



However, when one eq.mole of 1 was treated with two eq.moles of SO_2Cl_2 in boiling CCl_4, the expected 7 was not obtained, but the unexpected 1,3,4,6,8-pentachloro-2,7-di-tert-butylcarbazole (9) and 2,2'-diamino-3,3',5,5'-tetrachloro-4,4'-di-tert-butyldiphenyl (10) were formed in 4% and 7% yields, respectively, and 1 was recovered in 38% yield.



Compound 9 was also obtained from 10 by treatment with SO_2Cl_2 under similar conditions.

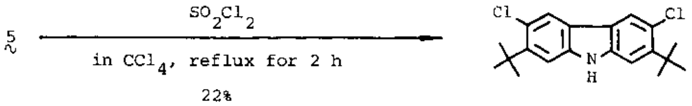
$$10 \xrightarrow{SO_2Cl_2} 9$$

It was also found that when 1 was treated with excess SO_2Cl_2 (ca. 6 molar ratio to 1 mole of 1) in refluxing CCl_4 solution for 2 h, 9 was obtained in 80% yield.

$$1 \xrightarrow[\text{in } CCl_4 \text{ reflux for 2 h}]{SO_2Cl_2\text{(6 moles)}} 9 \xleftarrow[\text{in } CCl_4]{Cl_2} 1$$

However, treatment of 1 with chlorine gas under similar conditions afforded only 18% yield of 9. The reaction of 5 with excess SO_2Cl_2 in refluxing CCl_4 solution gave 3,6-dichloro-2,7-di-tert-butylcarbazole (11) in 22% yield.

Structures of 9, 10 and 11 were assumed by their elemental analyses and spectral data.



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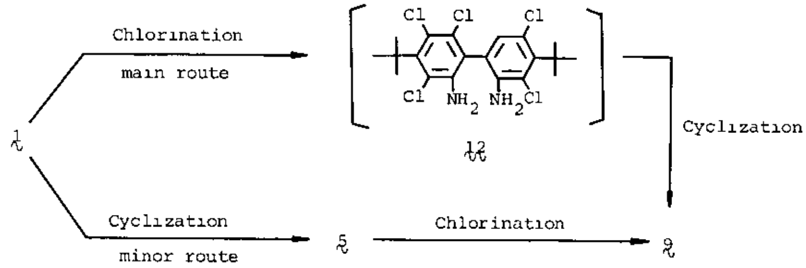
Based on the above results, it is concluded that the chlorination of 1 forms the aminopentachlorodiphenyl 12 which is transformed into 9 by a cyclization in the main route, but the route forming 9 from 1 by cyclization followed by chlorination seems to be minor.



Usually, cyclization of 2,2'-diaminodiphenyls to the corresponding carbazoles occurred only under drastic conditions.

The method described above might be useful for preparation of chlorocarbazole derivatives. The investigation about the limitation and scope of this method is progressing in our laboratory.

EXPERIMENTAL SECTION

All melting points are uncorrected. ^1H-NMR spectra were determined at 100 MHz with a Nippon Denshi, JEOL FT-100 NMR spectrometer with Me_4Si as an internal reference. IR spectra were measured in KBr pellets with a Nippon Bunko IRA-102 spectrophotometer. Mass spectra were obtained with a Nippon Denshi, JMS-01SA-2 spectrometer at 75 eV, using a direct-inlet system.

Reaction of 1 with SO_2Cl_2 (2 eq.moles).

To a solution of 300 mg (1 mmol) of 1 in 5 ml of CCl_4 was added gradually a solution of 0.18 ml (2.2 mmol) of SO_2Cl_2 in 1 ml of CCl_4 at room temperature. After the mixture was refluxed for 2 h, it was evaporated in vacuo to leave the residue containing oily material and crystals from which 18 mg (4%) of 9 was obtained by filtration. The benzene solution of the oily filtrate was washed with 10% aq. NaOH. The benzene solution was evaporated in vacuo to leave a residue which was washed with a small amount of hexane to give 110 mg (38%) of unaltered **1**. The hexane solution was chromatographed on silica gel to give 15 mg (7%) of **10** (eluent: $CHCl_3$).

9: Colorless needles (hexane); mp 251~252.5°C; IR (KBr) 3360, 2950, 1445, 1440, 1260, 870, 770, 705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.80 (s, 9H), 1.81 (s, 9H), 8.34 (s, 1H), 8.52 (broad s, 1H); Mass m/e 455 $(M+6)^+$, 453 $(M+4)^+$. Anal. Calcd for $C_{20}H_{20}Cl_4N$: C, 53.18; H, 4.46; N, 3.10. Found: C, 52.95; H, 4.42; N, 3.21.

10: Orange prisms (hexane); mp 195~197.5°C; IR (KBr) 3470, 3370, 2950, 1590, 1420, 1370, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.70 (s, 18H), 4.20 (broad s, 4H), 7.00 (s, 2H). Anal. Calcd for $C_{20}H_{24}Cl_4N$: C, 55.32; H, 5.56; N, 6.45. Found: C, 55.60; H, 5.54; N, 6.42.

Reaction with excess SO_2Cl_2.

After a solution of 200 mg (0.7 mmol) of **1** and 0.35 ml (4.3 mmol) of SO_2Cl_2 in 5 ml of CCl_4 was treated as described above, it was poured into a large amount of ice-water and the mixture was extracted with CH_2Cl_2. The extract was washed with 10% aq. NaOH and water, dried with Na_2SO_4, and evaporated *in vacuo* to leave a residue, which was washed with a small amount of ethanol to give 245 mg (80%) of **9**.

Reaction with Cl_2 gas.

After Cl_2 gas passed through a solution of 200 mg (67 mmol) of **1** in 5 ml of CCl_4 for 10 min at room temperature, the reaction mixture was worked up as described above to give 79 mg (12%) of **9** and a large amount of tarry materials.

Reaction of **5** with SO_2Cl_2.

After a solution of **5** and SO_2Cl_2 in CCl_4 was treated and worked up as described above, **11** was obtained in 22% yield.

11: Pale yellow prisms (hexane); mp 199~201°C; ^1H NMR ($CDCl_3$) δ 1.56 (s, 18H), 7.45 (s, 2H), 7.91 (s, 3H). Anal. Calcd for $C_{20}H_{23}Cl_2N$: C, 68.97; H, 6.66; N, 4.02. Found: C, 68.87; H, 6.62; N, 4.07.

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Received, 1st November, 1982