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C-PHOSPHORYLATION OF CARBAZOLE

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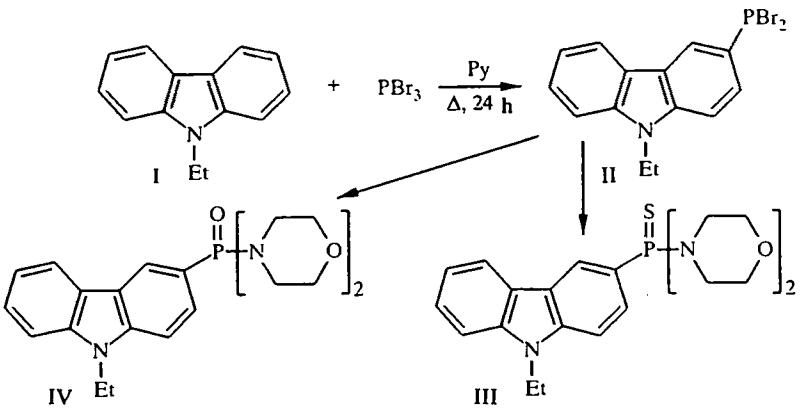
N-Ethylcarbazole is electrophilically phosphorylated by phosphorus tribromide to give 9-ethylcarbazolyl-3-dibromophosphine under more forcing conditions than for pyrrole and indole.

N-Vinylcarbazole is phosphorylated by phosphorus pentachloride at the vinyl group [1]. At the same time, the chemistry of aromatic ring phosphorylation in N-alkylcarbazoles has not currently been developed.

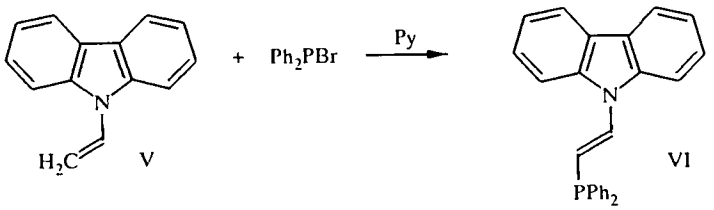
We have found that N-ethylcarbazole (I) reacts with phosphorus tribromide when refluxing in pyridine to give the dibromophosphine II.



As is the case for other electrophilic substitution reactions [3], carbazole is a less active heterocyclic system than pyrrole and indole for which the phosphorylation reaction occurs in very mild conditions [4].

The dibromophosphine II was converted by us to the amides III and IV.

Reaction of N-vinylcarbazole (V) with bromodiphenylphosphine gives the phosphine VI.



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The reaction of N-vinylcarbazole with phosphorus tribromide gives a complex mixture of compounds.

EXPERIMENTAL

^1H and ^{31}P NMR spectra were recorded on a Gemini-200 instrument (internal standard TMS, external 85% phosphoric acid). The reactions were performed in anhydrous solvents.

9-Ethylcarbazolyl-3-dibromophosphine (II). A mixture of N-ethylcarbazole (0.01 mole) and phosphorus tribromide (0.01 mole) in pyridine (25 ml) was refluxed for 12 h. The product was cooled, the precipitate separated, and the filtrate evaporated *in vacuo*. The residue was dissolved in benzene, filtered, and the filtrate evaporated. The residue was then crystallized from octane. Yield 72%. Mp 110°C. PMR spectrum ($CDCl_3$): 1.46 (3H, t, J_{HH} = 7.0 Hz, CH_3); 4.42 (2H, q, J_{HH} = 7.0 Hz, N—$\underline{CH_2}CH_3$); 7.33 (1H, m, 6-H); 7.49 (3H, m, 1-, 5-, 8-H); 8.09 (1H, t, J_{HH} = 8.1 Hz, 7-H); 8.15 (1H, d, J_{HP} = 7.5 Hz, 4-H); 8.67 ppm (1H, dd, J_{HH} = 10.8, J_{HP} = 13.2 Hz, 2-H). ^{31}P NMR spectrum (C_6H_6): 151.2 ppm. Found, %: N 3.69; P 8.01. $C_{14}H_{12}Br_2NP$. Calculated, %: N 3.64; P 8.04.

9-Ethylcarbazolyl-3-dimorpholinothiophosphonate (III). Morpholine (0.02 mole) and triethylamine (0.03 mole) in benzene (15 ml) were added with stirring to a solution of dibromophosphine II (0.01 mole) in benzene (25 ml) and held for 1 h at room temperature. The product was filtered, sulfur (0.01 mole) added, and it was refluxed for 2 h. After evaporation *in vacuo* the residue was crystallized from alcohol. Yield 81%. Mp 85°C. PMR spectrum ($CDCl_3$): 1.47 (3H, t, J_{HH} = 7.0 Hz, CH_3); 3.14 (8H, m, N—CH_2); 3.68 (8H, m, O—CH_2); 4.42 (2H, q, J_{HH} = 7.0 Hz, N—$\underline{CH_2}CH_3$); 7.32 (2H, m, 1-, 8-H); 7.49 (2H, m, 6-, 7-H); 7.96 (1H, dd, J_{HH} = 8.1, J_{HP} = 13.2 Hz, 2-H); 8.17 (1H, d, J_{HH} = 8.1 Hz, 5-H); 8.71 ppm (1-H, d, J_{HP} = 13.2 Hz, 4-H). ^{31}P NMR spectrum (C_6H_6): 62.4 ppm. Found, %: N 9.80; P 7.17. $C_{22}H_{28}N_3O_2PS$. Calculated, %: N 9.78; P 7.21.

9-Ethylcarbazolyl-3-dimorpholinophosphonate (IV). Morpholine (0.02 mole) and triethylamine (0.03 mole) in benzene (15 ml) were added with stirring to a solution of the dibromophosphine II (0.01 mole) in benzene (25 ml) and held for 1 h at room temperature. After filtration, hexachloroethane (0.01 mole) in benzene (20 ml) was added to the filtrate. After 30 min, the solvent was decanted off and the precipitate dissolved in chloroform and treated with a 5% solution of aqueous alkali (30 ml). The organic layer was separated, dried, and evaporated *in vacuo*. The residue was dissolved in benzene, filtered, and the filtrate evaporated. The residue was crystallized from octane. Yield 78%. Mp 79-80°C. PMR spectrum ($CDCl_3$): 1.33 (3H, t, J_{HH} = 7.0 Hz, CH_3); 3.01 (8H, m, N—CH_2); 3.55 (8H, m, O—CH_2); 4.47 (2H, q, J_{HH} = 7.0 Hz, N—$\underline{CH_2}CH_3$); 7.50 (5H, m, 1-, 2-, 6-, 7-, 8-H); 8.30 (1H, d, J_{HH} = 7.5 Hz, 5-H); 8.53 ppm (1H, d, J_{HP} = 12.0 Hz, 4-H). ^{31}P NMR spectrum (C_6H_6): 15.3 ppm. Found, %: N 10.20; P 7.41. $C_{22}H_{28}N_3O_3P$. Calculated, %: N 10.16; P 7.49.

2-(9-Carbazolyl)vinyldiphenylphosphine (VI). Bromodiphenylphosphine (0.01 mole) was added with stirring to a mixture of N-vinylcarbazole (0.01 mole) and pyridine (0.01 mole). After 12 h, the pyridine was evaporated *in vacuo*. The residue was extracted with benzene (3 × 20 ml), the benzene solution was evaporated, and the residue crystallized from benzene. Yield 80%. Mp 160-162°C. PMR spectrum (C_6D_6): 6.67 (1H, d, J_{HH} = 10.4 Hz, CH); 7.14 (11H, m, Ph + CH); 7.38 (2H, d, J_{HH} = 5.0 Hz, 1-, 8-H); 7.56 (4H, m, 2-, 3-, 6-, 7-H); 7.82 ppm (2H, d, J_{HH} = 5.0 Hz, 4-, 5-H). ^{31}P NMR spectrum (C_6H_6): –12.2 ppm. Found, %: N 3.69; P 8.18. $C_{20}H_{20}NP$. Calculated, %: N 3.71; P 8.21.

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