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Synthesis of *N*-Vinylcarbazole Derivatives with Acceptor Groups

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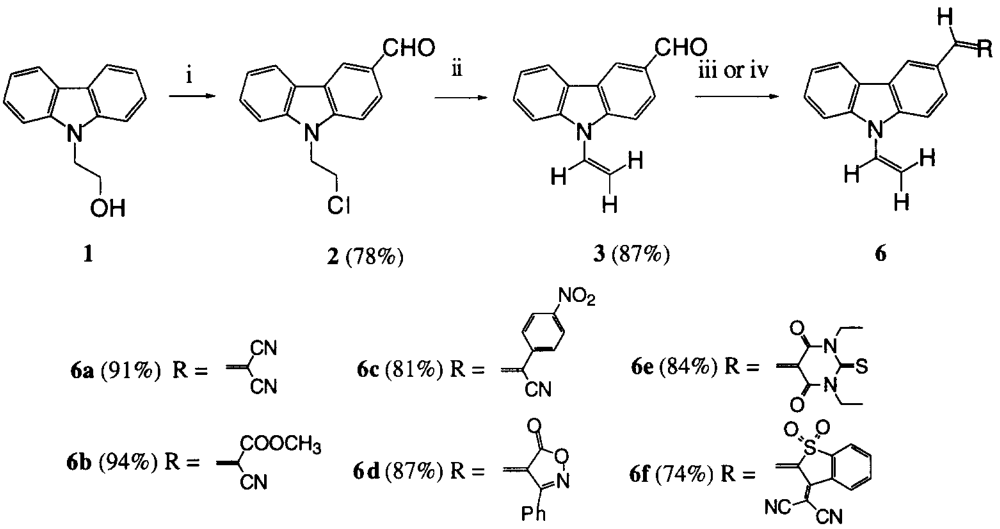
ABSTRACT: A new series of *N*-vinylcarbazole with various acceptor groups has been synthesized starting from 3-formyl-*N*-vinylcarbazole by the Knoevenagel condensation. The key starting compound, 3-formyl-*N*-vinylcarbazole, was prepared from 3-formyl-*N*-(2-chloroethyl)carbazole by 1,2-elimination reaction. © 1997 Elsevier Science Ltd.

Polymers containing a carbazole moiety, such as poly(*N*-vinylcarbazole) yielded from *N*-vinylcarbazole, can be used as many functional materials, such as photoconductive,[1] nonlinear optical,[2] photorefractive,[3] and electroluminescent materials.[4] It has been found that the acceptor groups in such polymers play an important role in generating many new functions, including spectral sensitizing,[5] second-order nonlinear optical response,[6] electron transporting and emission,[7] etc. However, the types of *N*-vinylcarbazoles as the key monomers for poly(*N*-vinylcarbazole)s are very limited. In this paper, we report an efficient approach to the synthesis of *N*-vinylcarbazoles substituted with acceptor groups.

The general process for the synthesis of *N*-vinylcarbazoles **6a-f** is shown in Scheme 1. 3-Formyl-*N*-(2-chloroethyl)carbazole **2** was prepared from **1** in one-pot. In this reaction, a formyl group could be introduced and at same time the hydroxy group could be replaced by a chloride atom via a nucleophilic substitution under the formylation condition. 3-Formyl-*N*-vinylcarbazole **3** could be synthesized from **2** via a 1,2-elimination reaction in DMF in the presence of a base. It was found that the rate of the elimination reaction was very slow when an inorganic base, K_2CO_3, was used. This might be due to the poor solubility of K_2CO_3 in DMF. In order to increase the rate of elimination reaction, phenol as a potential organic base was added. The organic base, a phenoxy anion with good solubility, could be obtained after an active hydrogen atom was abstracted by K_2CO_3. It was found that only elimination product **3** was obtained in the presence of a phenoxy anion as a base. It is well known that the phenoxy anion is a good nucleophile. However, no nucleophilic substituted products could be obtained in this reaction condition.

Various acceptor groups could be introduced based on a formyl group by the Knoevenagel condensation. Compounds **6a-c** were obtained from the condensation of **3** with malononitrile **4a**, methyl cyanoacetate **4b** or *p*-nitrobenzyl cyanide **4c** in the presence of 4-dimethylaminopyridine (DMAP) as a base. Compound **3** could be reacted with 3-phenyl-5-isoxazolone **5a**, diethylthiobarbituric acid **5b** or 3-dicyanomethylidene-2,3-dihydrobenzothiophene-1,1-dioxide **5c** to give compounds **6d-f** without a basic catalyst. 3-Substituted *N*-

vinylcarbazoles were purified by column chromatography or recrystallization and characterized by ^{1}H NMR, IR, MS and elemental analysis.



Scheme 1 Reagents and conditions: i, $POCl_3$/DMF, 90°C, 4 h; ii, phenol/K_2CO_3/DMF, 60°C, 6 h; iii, malononitrile **4a**, methyl cyanoacetate **4b** or *p*-nitrobenzyl cyanide **4c**/DMAP/THF, rt, 1-12 h; iv, 3-phenyl-5-isoxazolone **5a**, diethylthiobarbituric acid **5b** or 3-dicyanomethylidene-2,3-dihydrobenzothiophene-1,1-dioxide **5c**/EtOH, 70°C, 0.5-1 h.

In conclusion, we have synthesized, for the first time to our knowledge, a series of *N*-vinylcarbazoles with various acceptor groups on the 3-position. These acceptor-substituted *N*-vinylcarbazoles are expected to be used as co-monomers for generating new high T_g poly(*N*-vinylcarbazole)s exhibiting multifunctional properties for nonlinear optical and photorefractive applications.

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