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SYNTHESIS OF VINYL MONOMERS WITH ACTIVE AZAAROMATIC GROUPS. PHASE-TRANSFER CATALYTIC APPROACH.

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ABSTRACT: An efficient method based on the alkylation-elimination reactions under solid-liquid phase transfer-catalysis conditions (S/L PTC) is reported for the preparation of N-vinyl derivatives of azaheterocyclic compounds.

Several reactions that can be carried out under PTC conditions include the N-alkylation reactions of heterocyclic compounds bearing acidic hydrogen atoms attached to nitrogen, like pyrrole, pyrazole, imidazole, benzimidazole, and indole[1].

On the other hand, there is a great number of reports on elimination reactions that can be achieved in PTC systems[2]. Therefore, the combination of N-alkylation and β–elimination reactions could be excepted to be a useful method for

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the synthesis of N-vinyl derivatives of azaaromatic compounds. Such a method has been proven to be successful for the synthesis of N-vinylcarbazole and its derivatives while carbazole and 1,2-chloroethane have been employed as starting materials[3, 4]. The standard methods for the preparation of vinyl derivatives usually require drastic reaction conditions. For example, the dehydrohalogenation of aryl 2-haloethyl derivatives[5] or addition of azaaromatic compounds to acetylene[6] are effected by treatment with potassium hydroxide at high temperature. The yields are not good. Moreover, the application of these methods is limited to the preparation of azaaromatic compounds bearing non-hydrolyzable substituents in the aryl moiety. Direct N-vinylation of azaaromatic compounds with acetylene under pressure or in aprotic solvents[7], as well as synthesis through N-(2-hydoxyethyl)derivatives[8] are incovenient in laboratory use. The synthesis of those monomers by the Clemo-Perkin method e.g., reactions of azaheterocyclic compounds with 2-chlorethyl-p-toluene sulfonate requires a large excess of 2-chloroethyltosylate to be used and the reaction time has to be much prolonged[9]. Most of these reactions require isolation of intermediates, high pressure or temperature, special equipment and/or long reaction time.

Now we would like to present the general method for preparation of vinyl monomers with azaaromatic side groups under PTC conditions that can be performed at atmospheric pressure in glassware, without the need of isolation of intermediates. The monomers are expected to be good starting materials for the preparation of polymers of special application[10].

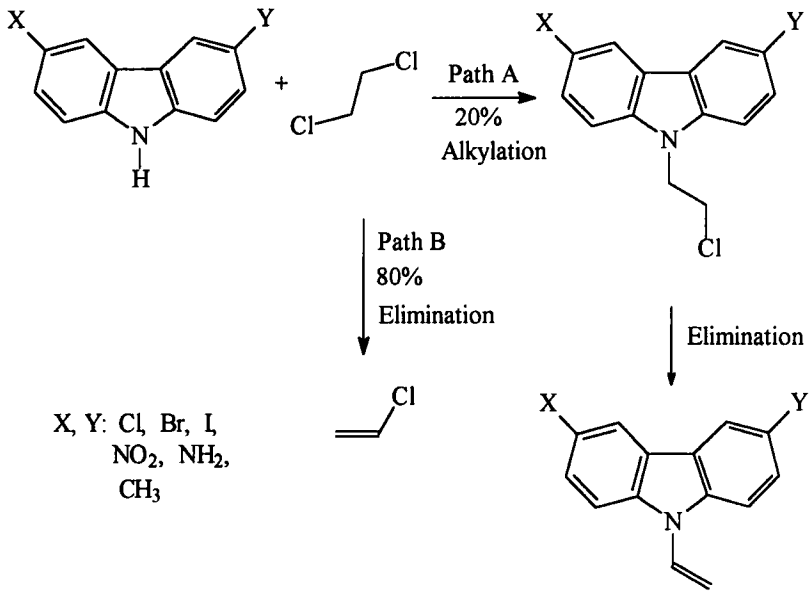


FIG.1: The synthesis of N-vinylcarbazoles by means of "alkylation-elimination" method.

The paper is related to our previous work where it has been shown that under PTC conditions ethylene chloride could be used as a reagent for alkylation of carbazole and its derivatives to give N-(β–chloroethyl)-carbazole derivatives. In the next step, the elimination of hydrogen chloride from N-(β–chloroethyl) derivatives led straight to N-vinylcarbazole (Fig.1; path A). Although the method has been useful for the preparation of series of vinyl-carbazoles, it has turned out not to have a general application for aromatic and azaaromatic compounds. A number of attempts to use the alkylation-elimination sequence for the synthesis of other vinyl monomers has failed. Moreover, in the first stage, the alkylation of carbazole, N-(β–chloroethyl)carbazole has been obtained with only 20% selectivity towards ethylene chloride. The remaining 80% of ethylene chloride has undergone competitive elimination reaction to vinyl chloride (Fig.1; path B). Furthermore, it

Table 1. Results of β–chloroethylation of various azaheterocyclic compounds

Entry	Product	Time [h]	bp [°C/Torr]	Lit. bp [°C/Torr]	Yield [%]	Ref.
1a	N-(2-chloroethyl)pyrrole	4.5	77-83/20	84/20	39	[11]
2a	N-(2-chloroethyl)imidazole	3.5	160-2[a]	-	87	-
3a	N-(2-chloroethyl)pyrazole	3.5	170-6/40	178/40	91	[12]
4a	N-(2-chloroethyl)indole	4.5	oil	-	85	-
5a	N-(2-chloroethyl)benzimidazole[b], N-vinylbenzimidazole	3.5	-	-	-	-
6a	N-(2-chloroethyl)carbazole	5.5	130-2[a]	130-1	90	[13]

a) - melting point; b) - in that case the mixture of **5b** and **5c** was obtain and was take directly to the next stage.

has been found that, for instance, phenol and other compounds, which are less nucleophilic than carbazole, did not react with ethylene chloride under similar conditions. The entire quantity of ethylene chloride was consumed in the elimination to vinyl chloride. Finally, after studying different PTC systems and trying to modify them, we has found that the best method for alkylation of various compounds with ethylene chloride is not a liquid-liquid (L/L) but a solid-liquid S/L) PTC system. Under S/L PTC conditions, ethylene chloride is prevented from the elimination reaction of hydrogen chloride to form vinyl chloride, and the nucleophilic substitution of one of the chloride atoms can be accomplished much faster than under „standard" conditions. The method turned out to have a general application, and we have been able to obtained N-(β–chloroethyl) derivatives of a number of azaheterocyclic compounds under mild conditions (Fig.2).

Moreover, in some cases (e.g. benzimidazole) it was possible to obtain an N-vinyl derivative directly by the reaction of ethylene chloride with an azahetero-

Table 2. Results of elimination reactions of (β–chloroethyl) derivatives.

Entry	Product	Time [h]	bp [°C/Torr]	Lit. bp [°C/Torr]	Yield [%]	Ref.
1c	N-vinylpyrrole	1[A]	120-4	122	41	[15]
2c	N-vinylimidazole	2[B]	190-4	80/10	95	[16]
3c	N-vinylpyrazole	3[A]	135-40	139-40	52	[17]
4c	N-vinylindole	1.5[B]	29-32[C]	29-30[C]	97	[18]
5c	N-vinylbenzimidazole	0.5[B]	145-9/12	145-7/12	85	[19, 20]
6c	N-vinylcarbazole	1[B]	63-5[C]	62-3[C]	87	[3]

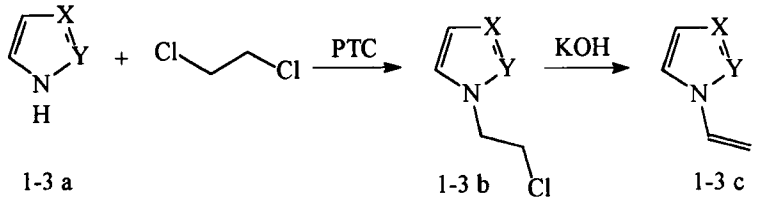
[A] - EtOH, [B] - i-PrOH, [C] - melting point

cycle, since the elimination reaction of an (β–chloroethyl) derivative could follow immediately the N-alkylation of heterocyclic compound. The results of β–chloro-ethylation reaction of azaheterocyclic compounds are summarised in Table 1.

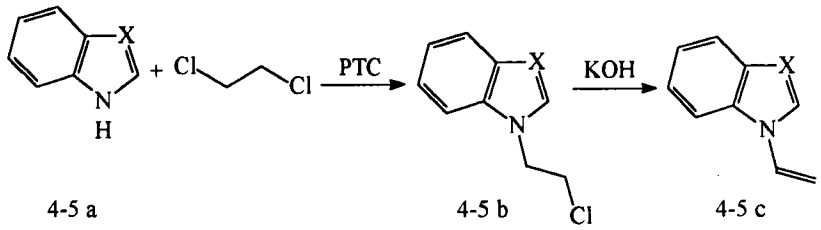
Only one limitation of the method has been found: in order to undergo an alkylation reaction with ethylene chloride under S/L PTC conditions, an organic compounds has to possess relatively acidic hydrogen atom ($pK_a < 25$).

The (β–chloroethyl) derivatives of various compounds can then be converted into vinyl monomers by one of the common methods including reactions under PTC conditions[14] or reactions with KOH in an alcoholic solution. The results of elimination reactions in alcoholic solutions are shown in Table 2.

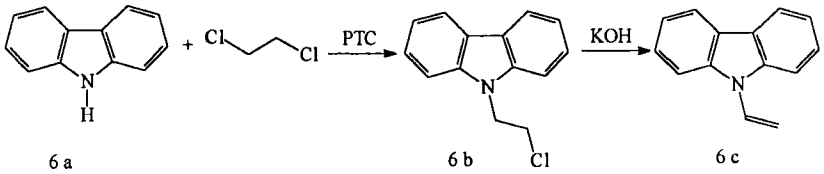
In conclusion, phase transfer catalysis has been proven to be an attractive method for the synthesis of various monomers with active azaaromatic side groups.



1: X, Y = CH - pyrrole, 2: X = N, Y = CH, - imidazole 3: X = CH, Y = N - pyrazole



4: X = CH – indole, 5: X = N - benzimidazole



6: carbazole

FIG. 2: Synthesis of various N-vinyl derivatives of azaheterocyclic compounds.

The implementation of the method (alkylation- elimination sequence) is a subject of ongoing work with another group of compounds. A consequence of our work is the study of a farther application of our „alkylation-elimination method" to active molecules bonded to polymeric matrix.

Experimental

Melting points, measured on a Boetius-PHMK 05 microscope plates, are uncorrected. ^{1}H NMR spectra were recorded with a TESLA 487 C spectrometer, TMS being used as a internal standard; the chemical shifts are expressed in δ values downfield from TMS. MS spectra were recorded on a Hewllet-Packard 5985 spectrometer. IR spectra were performed on a Bio-Rad FTS–165 spectrophotometer, and the wave numbers were given with a precision of 2 cm^{-1}.

General procedure for the β–chloroethylation of azaheterocyclic compounds: An azaheterocyclic compound (75 mmol) was added to an intensity stirred mixture of ethylene chloride (200 mL), tetrabutylammonium bromide (0.52 g, 1.6 mmol), KOH (28g, 500mmol), K_2CO_3 (22.1 g, 160 mmol). The stirring was continued at 45-50° for 3.5-5.5h. After cooling, the inorganic material was filtered off, and the organic solution washed with water (2 x 25 ml). The solution was then dried over anhydrous $MgSO_4$, filtered, and the solvent was evaporated to dryness. Then all the liquid compounds were purified by Kugelrohr distillation, while compound **6b** was purified by crystallization from ethanol.

N-(2-chloroethyl)pyrrole **(1b): MS** m/z = 129 (M^+, 46), 80 (100), 67 (13). **IR** (film) ν = 3120(w), 3112(w), 2965(s), 2854(s), 1507(s), 1469(m), 1456(m), 1289(s), 1109(s), 1080(s), 728(s) cm^{-1}. **^{1}H NMR** (80 MHz, $CDCl_3$) δ(ppm) = 3.65 (t, J = 6.1 Hz, 2H, -CH_2-), 4.12 (t, J = 6.1 Hz, 2H, -CH_2-), 6.15 (t, J = 2.0 Hz, 2H) and 6.64 (t, J = 2.1 Hz, 2H) aromatic protons.

N-(2-chloroethyl)imidazole **(2b): MS** m/z = 130 (M^+, 56), 81 (100), 68 (10). **IR** (film) ν = 3650-2800(b, s), 3110(s), 2953(m), 2941(m), 1506(s), 1455(m), 1426(s), 1361(w), 1285(m), 1234(s), 1127(m), 1107(m), 1081(m), 943(m), 915(m), 823(m), 746(s), 663(s), 645(m) cm^{-1}. **^{1}H NMR** (80 MHz, $CDCl_3$) δ(ppm) = 3.75 (t, J = 6.4 Hz, 2H, $-CH_2$), 4.29 (t, J = 6.1 Hz, 2H, $-CH_2$-), 6.87-7.27 (q, 2H) and 7.56 (s, 1H) aromatic protons.

N-(2-chloroethyl)pyrazole **(3b): MS** m/z = 130 (M^+, 38), 95 (28), 81 (100), 68 (71). **IR** (film) ν = 3590-3310(b, m), 3116(m), 3017(w), 2964(m), 2940(s), 2874(w), 2851(w), 1634(w), 1516(s), 1452(s), 1433(s), 1397(s), 1370(m), 1351(m), 1278(s), 1143(w), 1090(s), 1052(s), 1030(m), 969(m), 946(m), 901(m), 837(w), 754(s), 701(m), 677(m), 647(m), 616(m) cm^{-1}. **^{1}H NMR** (80 MHz, $CDCl_3$) δ(ppm) = 3.87(t, J = 6.1 Hz, 2H, $-CH_2$-), 4.22 (t, J = 6.0 Hz, 2H, $-CH_2$-), 6.42 (t, 1H, J = 2.9 Hz) and 7.50 (dd, 2H, J_{AB} = 4.2 Hz, J_{AC} = 18.4 Hz) aromatic protons).

N-(2-chloroethyl)indole **(4b): MS** m/z = 179 (M^+, 26), 130 (100), 117 (10). **IR** (KBr) ν = 3087(w), 3054(m), 2958(w), 2870(w), 1612(w), 1556(w), 1512(s), 1484(m), 1463(s), 1399(m), 1316(s), 1247(m), 1192(m), 830(s), 762(m), 739(s) cm^{-1}. **^{1}H NMR** (80 MHz, $CDCl_3$) δ(ppm) = 3.74 (t, J = 6.6 Hz, 2H, $-CH_2$-), 4.38 (t, J = 6.1 Hz, 2H, $-CH_2$-), 6.50 (d, 1H, J = 3.2 Hz) and 7.07-7.27 (m, 4H) and 7.57-7.68 (m, 1H) aromatic protons.

N-(2-chloroethyl)carbazole **(6b): MS** m/z = 229 (M^+, 29%), 231 (M^{+2}, 10%), 180 (100%), 152 (12%). **IR** (KBr) ν = 3050(w), 2960(w), 2923(w), 1594(m),

1487(s), 1458(s), 1381(w), 1355(m), 1328(s), 1296(w), 1220(m), 1180(w), 1159(w), 1124(w), 1017(w), 927(w), 899(w), 846(m), 748(s), 723(s) cm^{-1}. **^{1}H NMR** (80 MHz, $CDCl_3$) δ(ppm) = 3.83 (t, 2H, J = 7.0 Hz $-CH_2-$), 4.61 (t, 2H, J = 7.1 Hz, $-CH_2-$), 6.74-7.48 (m, 6H), 7.94-8.04 (d, 2H) aromatic protons.

General procedure for the elimination of β–chloroethyl derivatives of azaheterocyclic compounds: A mixture of β–chloroethyl derivative of azaheterocyclic compound (5.0 mmol), KOH (1.12g 120 mmol), and hydroquinone (ca. 25-30 mg 0.22-0.27 mmol) was placed in an appropriate alcohol (30 mL) (i.e., 2-propanol or ethanol) and refluxed for 30 min. to 3 hours (see Table 2). Next the alcohol was evaporated under reduced pressure, and the organic material was extracted from the reaction mixture by means of methylene chloride (3 x 20 ml). The extract was then dried over anhydrous $MgSO_4$, filtered, and the solvent was evaporated to dryness. All the liquid N-vinyl derivatives **1c-5c** were purified by Kugelrohr distillation, while compound **6c** was purified by crystallization from methanol.

N-vinylpyrrole **(1c): MS** m/z = 93 (M^+, 100), 67 (19), 66 (34). **IR** (film) ν = 3108(w), 1638(s), 1638(s), 1507(s), 1456(m), 1289(m), 1109(s), 1080(m), 957(m), 917(m), 851(s), 728(s) cm^{-1}. **^{1}H NMR** (80 MHz, $CDCl_3$) δ(ppm) = 4.76 (dd, 1H, $-CH_A$), 5.21 (dd, 1H, $-CH_B$), 6.41 (dd, 1H, $-CH_C-$), (J_{AB} = 1.0 Hz, J_{AC} = 9.7 Hz, J_{BC} = 15.6 Hz), 6.18 (t, J = 2.2 Hz, 2H) and 6.66 (t, J = 2.2 Hz, 2H) aromatic protons.

N-vinylimidazole **(2c): MS** m/z = 94 (M^+, 100), 67 (20), 41 (24). **IR** (film) ν = 3600-2800(b, s), 3111(s), 3004(m), 1649(s), 1506(s), 1495(s), 1421(w), 1371(w), 1325(m), 1282(s), 1229(s), 1106(m), 1058(m), 1006(m), 962(m), 905(m), 884(m), 819(m), 735(s), 657(s), 597(m) cm^{-1}. **^{1}H NMR** (80 MHz, $CDCl_3$) δ(ppm) = 4.89 (dd, 1H, $-CH_A$), 5.28 (dd, 1H, $-CH_B$), 6.81 (d, 1H, $-CH_C-$), (J_{AB} = 1.7 Hz, J_{AC} = 8.8 Hz, J_{BC} = 15.7 Hz), 6.95-7.27 (q, 2H) and 7.95 (s, 1H) aromatic protons.

N-vinylpyrazole **(3c): MS** m/z = 94 (M^+, 100), 67 (98), 41 (29). **IR** (film) ν = 3550-3350(b, m), 3114(m), 3064(m), 3015(w), 1650(s), 1517(s), 1448(w), 1435(w), 1395(s), 1335(w), 1295(s), 1280(s), 1210(w), 1089(s), 1048(s), 986(s), 915(m), 882(s), 755(s), 701(m), 672(m), 643(m), 620(m) cm^{-1}. **^{1}H NMR** (80 MHz, $CDCl_3$) δ(ppm) = 4.72 (dd, 1H, $-CH_A$), 5.45 (dd, 1H, $-CH_B$), 6.98 (d, 1H, $-CH_C-$), (J_{AB} = 1.0 Hz, J_{AC} = 8.1 Hz, J_{BC} = 15.7 Hz), 6.25 (t, 1H, J = 2.9 Hz) and 7.51 (dd, 2H, J_{AB} = 4.2 Hz, J_{AC} = 18.5 Hz) aromatic protons.

N-vinylindole **(4c): MS** m/z = 143 (M^+, 100), 117 (18), 115 (43), 89 (30). **IR** (KBr) ν = 3432 (b, w), 3135(w), 3110(w), 3086(w), 3034(w), 1641(s), 1612(w), 1575(m), 15107(w), 1461(s), 1395(m), 1327(s), 1316(s), 1230(s), 1195(w), 1156(w), 1027(w), 957(m), 851(s), 764(m), 739(s) cm^{-1}. **^{1}H NMR** (80 MHz, $CDCl_3$) δ(ppm) = 4.74 (dd, 1H, $-CH_A$), 5.16 (dd, 1H, $-CH_B$), 6.61 (dd, 1H, $-CH_C$), (J_{AB} = 1.2 Hz, J_{AC} = 9.0 Hz, J_{BC} = 15.6 Hz), 6.42-7.67 (m, 6H, aromatic protons).

N-vinylbenzimidazole **(5c): MS** m/z = 144 (M^+, 100), 131 (10), 117 (17), 91 (10). **IR** (film) ν = 3550-2750(b, m), 3115(m), 3089(w), 3088(m), 3055(m), 1646(s), 1610(m), 1585(w), 1500(s), 1458(s), 1371(m), 1313(m), 1285(s), 1232(s),

1204(m), 1009(m), 958(m), 886(m), 781(m), 764(m), 742(s) cm^{-1}. **^{1}H NMR** (80 MHz, $CDCl_3$) δ(ppm) = 5.09 (dd, 1H, $-CH_A$), 5.52 (dd, 1H, $-CH_B$), 7.14 (dd, 1H, $-CH_C$-), (J_{AB} = 1.4 Hz, J_{AC} = 9.1 Hz, J_{BC} = 15.9 Hz), 7.27-7.81 (m, 4H) and 8.14 (s, 1H) aromatic protons.

N-vinylcarbazole **(6c): MS** m/z = 193 (M^+, 100%), 192 (53%), 166 (9%). **IR** (KBr) ν = 3045(w), 1638(m), 1621(m), 1595(m), 1480(m), 1453(s), 1370(m), 1336(m), 1315(m), 1224(m), 1159(m), 1122(w), 961(m), 926(m), 855(m), 749(s), 722(s) cm^{-1}. **^{1}H NMR** (80 MHz, $CDCl_3$) δ(ppm) = 4.94 (dd, 1H, $=CH_A$), 5.36 (dd, 1H, $=CH_B$), 7.06 (dd, 1H, $-CH_C$-), (J_{AB} = 0.6 Hz, J_{AC} = 9.4 Hz, J_{BC} = 15.9 Hz), 6.84–7.48 (m, 6H), 7.92–8.02 (d, 2H) aromatic protons.

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