Syntheses of Polymerizable Aromatic Mannich Bases by Means of Amine Exchange Reaction

Hiroyoshi KAMOGAWA, Kuniaki KUBOTA, and Masato NANASAWA
Department of Applied Chemistry, Yamanashi University, Takeda, Kofu 400

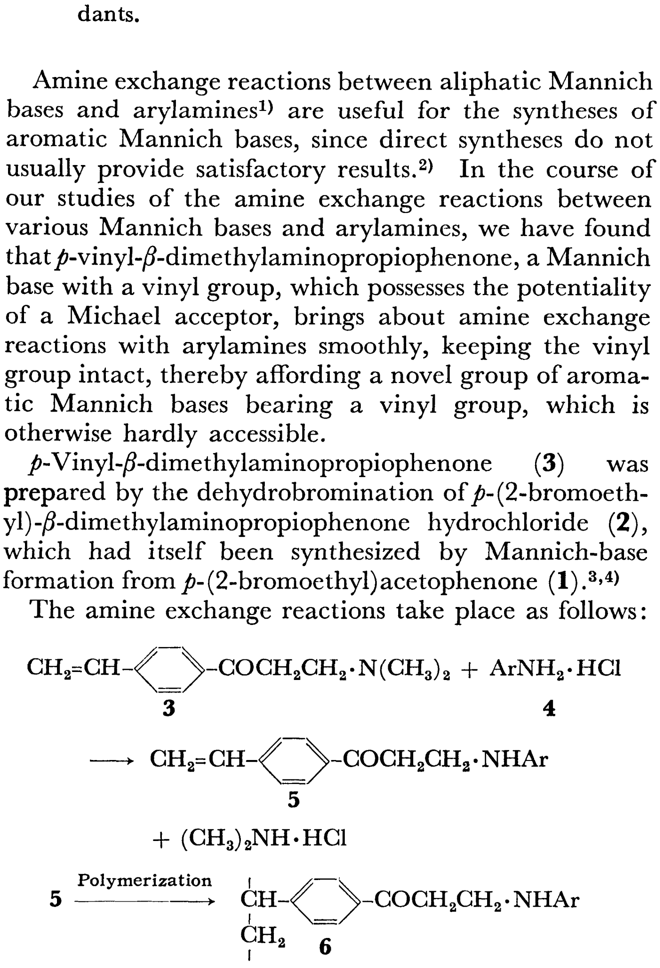
(Received July 21, 1977)

Amine exchange reactions between *p*-vinyl-*β*-dimethylaminopropiophenone and arylamine hydrochloride provided six novel aromatic Mannich bases bearing a vinyl group which were otherwise hardly accessible. Thus, by refluxing in ethanol–water (1: 1), *p*-vinyl-*β*-(*p*-anisidino)-, *p*-vinyl-*β*-(*p*-toluidino)-, *p*-vinyl-*β*-(*p*-hydroxyanilino)-, *p*-vinyl-*β*-anilino-, *p*-vinyl-*β*-(*p*-carboxyanilino)-, and *p*-vinyl-*β*-(*p*-nitroanilino)-propiophenones were obtained in 62.0, 55.2, 24.5, 32.0, 47.3, and 29.1% yields, respectively. The Mannich bases thus synthesized underwent ready radical polymerizations to afford the corresponding vinyl polymers, bearing aromatic Mannich base units as pendants.

Amine exchange reactions between aliphatic Mannich bases and arylamines[1)] are useful for the syntheses of aromatic Mannich bases, since direct syntheses do not usually provide satisfactory results.[2)] In the course of our studies of the amine exchange reactions between various Mannich bases and arylamines, we have found that *p*-vinyl-*β*-dimethylaminopropiophenone, a Mannich base with a vinyl group, which possesses the potentiality of a Michael acceptor, brings about amine exchange reactions with arylamines smoothly, keeping the vinyl group intact, thereby affording a novel group of aromatic Mannich bases bearing a vinyl group, which is otherwise hardly accessible.

p-Vinyl-*β*-dimethylaminopropiophenone (**3**) was prepared by the dehydrobromination of *p*-(2-bromoethyl)-*β*-dimethylaminopropiophenone hydrochloride (**2**), which had itself been synthesized by Mannich-base formation from *p*-(2-bromoethyl)acetophenone (**1**).[3,4)]

The amine exchange reactions take place as follows:



4a, 5a, 6a: Ar=p-$CH_3OC_6H_4$
4b, 5b, 6b: Ar=p-$CH_3C_6H_4$
4c, 5c, 6c: Ar=p-HOC_6H_4
4d, 5d, 6d: Ar=C_6H_5
4e, 5e, 6e: Ar=p-$HOOCC_6H_4$
4f, 5f, 6f: Ar=p-O_2N-C_6H_4

The novel aromatic Mannich bases synthesized (**5**) underwent radical polymerizations under conventional conditions to afford the corresponding polymers (**6**).

Table 1 summarizes the results obtained in the amine exchange reactions. It can be seen from this table that electron-donating para substituents, such as methoxyl and methyl groups in the starting arylamine hydrochlorides (**4**), provide higher yields than the electron-withdrawing ones, such as the nitro group, in spite of the prolonged reaction times assigned to the latter.

TABLE 1. EFFECT OF THE *p*-SUBSTITUENTS ON THE YIELDS OF THE AROMATIC MANNICH BASES PRODUCED IN THE AMINE EXCHANGE REACTIONS

Product	*p*-Substituent	Reaction time h	Yield %
5a	CH_3O	2	62.0
5b	CH_3	2	55.2
5c	OH	2	24.5 (50.8)[a)]
5d	H	2	32.0
5e	COOH	10	47.3
5f	NO_2	25	29.1

a) Under nitrogen.

The fact that the yield for the electron-donating hydroxyl group (**5c**) was low indicates that the starting arylamine (*p*-aminophenol) was very susceptible to air oxidation, thereby affording considerable amounts of oxidation products.

Craig and Moyle[1)] proposed three mechanisms for the amine exchange reactions of *β*-diethylaminopropiophenones: S_N1, S_N2, and the Michael addition to the vinyl ketone produced. The step common to all three mechanisms is the nucleophilic attack of the arylamines produced from **4** by the hydrogen chloride exchange with **3**. Accordingly, it appears reasonable that more nucleophilic arylamines bearing more electron-donating para substituents promote the reaction.

Table 2 indicates the polymerization behavior of the **5** monomers. As expected, the **5a** and **5b** monomers, with electron-donating para substituents, provide lower values of $[\eta]$ than do **5e** and **5f**, with electron-withdrawing ones, presumably because of the enhanced radical

TABLE 2. POLYMERIZATION BEHAVIOR OF THE **5a—f** MONOMERS

Monomer	Conversion %	Appearance of polymer	$[\eta]$dl[a)]/g
5a	77	Light yellow powder	0.25
5b	80	Light yellow powder	0.30
5c	84	Light brown powder[b)]	0.33
5d	83	Light yellow powder	0.33
5e	93	Light brown powder	0.65
5f	84	Yellow powder	0.41

a) Intrinsic viscosity at 25°C in a *N,N*-dimethylformamide solution. b) Insolubilized by air oxidation.

trapping actions of the ArNH– portions in the former.

The synthetic procedure described here leads readily to vinyl polymers with pendant aromatic Mannich base units which are novel and which may be used for various purposes, including the preparation of functional polymers.

Experimental

The IR, ^{1}H-NMR, and mass spectra were obtained with Hitachi EPI-G spectrophotometer, a JNM-PMX 60 spectrometer, and a Hitachi RMU-6 MG spectrometer, respectively, under standard measurement conditions. The elemental analyses were carried out using a Perkin-Elmer 240 instrument.

p-*Vinyl-β-dimethylaminopropiophenone (3).* A 5.5-g (17 mmol) portion of **2** in 60 ml of methanol containing 2.4 g (43 mmol) of potassium hydroxide was stirred at room temperature for 24 h in the presence of a small amount of hydroquinone. To the resulting dark solution we then added 2.4 g (43 mmol) of potassium hydroxide, after which stirring was continued for 3 more h. The reaction mixture was then poured into iced water and extracted with ether. The organic layer was washed with water, dried over anhydrous sodium sulfate, and evaporated *in vacuo* at 40 °C to leave a crude product, which was recrystallized from petroleum ether to afford colorless needles of mp 52—55 °C (lit,3) 54.5—58.5 °C) in a 46.4% yield. The IR, NMR, and mass spectra as well as the CHN analyses identified it as **3**.

General Procedure for Amine Exchange Reactions. A mixture of 8 mmol of **3**, 9 mmol of an arylamine hydrochloride (**4**), a small amount of hydroquinone, and 7 ml of water–ethanol (1: 1) was refluxed for 2—25 h in an oil bath. The reaction mixture, sometimes with the crystalline precipitates thus produced, was cooled in a refrigerator overnight with or without the addition of water to provide the crude product, which was then purified by repeated recrystallizations.

p-*Vinyl-β-(*p-*anisidino)propiophenone (5a).* Recrystallizations of the crude product from ethanol provided lustrous, pale yellow needles with a mp of 140—141 °C. Found: C, 76.72; H, 6.84; N, 5.01%. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98%. IR(KBr): 1660 (C=O), 990, 930 (vinyl) cm^{-1}. NMR ($CDCl_3$): δ 3.2 (d, 2H, CH_2), 3.5 (d, 2H, CH_2), 3.8 (s, 3H, OCH_3), 5.4 (d, 1H, vinyl), 5.8 (d, 1H, vinyl), 6.5—8.0 (m, 9H, vinyl+ArH) ppm. Mass (*m/e*): 281 (M^+, 100).

p-*Vinyl-β-(*p-*toluidino)propiophenone (5c).* Lustrous, pale yellow plates (mp 142—143 °C) were isolated from ethanol. Found: C, 81.33; H, 7.33; N, 5.27%. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.22: N, 5.28%. IR(KBr): 1670 (C=O), 990, 910 (vinyl) cm^{-1}. NMR ($CDCl_3$): δ 2.3 (s, 3H, CH_3), 3.2 (t, 2H, CH_2), 3.6 (t, 2H, CH_2), 5.35 (d, 1H, vinyl), 5.7 (d, 1H, vinyl), 6.5—8.0 (m, 9H, vinyl+ArH) ppm. Mass (*m/e*): 265 (M^+, 80), 120 (100).

p-*Vinyl-β-(*p-*hydroxyanilino)propiophenone (5c).* A yellow, crystalline powder (mp 136—137 °C) was obtained by recrystallization from ethanol. Found: C, 76.72; H, 6.58; N, 4.73%. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24%. IR(KBr): 3370 (OH), 1660 (C=O), 990, 920 (vinyl) cm^{-1}. NMR (DMSO-d_6+CCl_4): δ 3.1—3.9 (m, 4H, 2CH_2), 5.4 (d, 1H, vinyl), 5.8 (d, 1H, vinyl), 6.3—8.2 (m, 10H, vinyl+OH+ArH) ppm. Mass (*m/e*): 267 (M^+, 63), 131 (100).

p-*Vinyl-β-anilinopropiophenone (5d).* Recrystallizations from ethanol afforded a lustrous, yellow, crystalline powder (mp 111—113 °C). Found: C, 81.24; H, 6.76; N, 5.62%. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57%. IR(KBr): 1660 (C=O), 990, 910 (vinyl) cm^{-1}. NMR ($CDCl_3$): δ 3.4—3.9 (m, 4H, 2CH_2), 5.6 (d, 1H, vinyl), 6.0 (d, 1H, vinyl), 6.8—8.1 (m, 10H, vinyl+ArH) ppm. Mass (*m/e*): 251 (M^+, 9), 18 (100).

p-*Vinyl-β-(*p-*carboxyanilino)propiophenone (5e).* Recrystallizations from *N,N*-dimethylformamide–water afforded a colorless, crystalline powder with a mp of 205—206 °C. Found: C, 73.19; H, 5.95; N, 4.62%. Calcd for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N, 4.72%. IR(KBr): 1660 (C=O), 985, 915 (vinyl) cm^{-1}. NMR (DMSO-d_6+CCl_4): δ 3.0—3.8 (m, 4H, 2CH_2), 5.4 (d, 1H, vinyl), 5.9 (d, 1H, vinyl), 6.5—8.0 (m, 9H, vinyl+ArH) ppm. Mass (*m/e*): 295 (M^+, 20), 131 (100).

p-*Vinyl-β-(*p-*nitroanilino)propiophenone (5f).* A yellow crystalline powder (mp 136—137 °C) was isolated from ethanol–water. Found: C, 68.99; H, 5.42; N, 9.32%. Calcd for $C_{18}H_{16}NO_3$: C, 68.91; H, 5.44; N, 9.45%. IR(KBr): 1660 (C=O), 1300 (NO_2), 990, 935 (vinyl) cm^{-1}. NMR (DMSO-d_6+$CDCl_3$): δ 3.4 (d, 2H, CH_2), 3.6 (d, 2H, CH_2), 5.5 (d, 1H, vinyl), 5.9 (d, 1H, vinyl), 6.9—8.2 (m, 9H, vinyl+ArH) ppm. Mass (*m/e*): 296 (M^+, 100).

Polymerization of the ***5a—f*** *Monomers.* A solution of 0.3 g of a monomer, 0.003 g of α,α′-azobisisobutyronitrile, and 2 ml of *N,N*-dimethylformamide in a deaerated Pyrex glass ampoule was kept at 70 °C for 48 h. The resulting viscous solution was poured into ethanol to precipitate the polymer. The IR spectra of all the polymers thus synthesized indicated no vinyl absorptions in the 900—930 cm^{-1} region, only strong CH_2 absorptions attributable to the polymer backbone at 1930 and 1860 cm^{-1}, together with characteristic absorptions of the aromatic Mannich bases.

References

1) J. C. Craig and M. Moyle, *J. Org. Chem.*, **29**, 410 (1964).

2) S. R. Sandler and M. Karo, "Organic Functional Group Preparations I," Academic Press, New York (1968), p. 335.

3) S. Tanimoto, J. Horikawa, M. Okano, and R. Oda, *J. Synthetic Org. Chem., Jpn.*, **26**, No. 8, 43 (1968).

4) S. R. Sandler and M. Karo, Ref. 2, p. 178.

5) E. C. Horning, *Org. Synthe.*, Coll. Vol. III, 305 (1955).