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Thermal Rearrangement of *N*-(Substituted allyl)-1-naphthylamines

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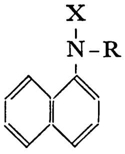
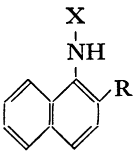
Synopsis. The title reaction was examined and the results were compared with those of the thermal reaction of the corresponding *N*-tosyl derivatives.

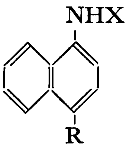
In the previous papers,1) we have reported the *amido*-Claisen rearrangement of *N*-tosyl and *N*-mesyl derivatives of aromatic *N*-allylamines which proceeds almost quantitatively in *N,N*-dialkylaniline solvent containing a small amount of triphenylphosphine. In the course of our studies, it was found that the thermal reaction of *N*-(substituted allyl)-*N*-tosyl-1-naphthylamines (**1f**—**h**) forms para-rearranged products (**3d**—**f**) as well as ortho-rearranged ones (**2g**, **2h**) respectively, when the allyl group contains substituents in γ-position.2) So we were interested to confirm whether the thermal reaction of the corresponding *N*-(substituted allyl)-1-naphthylamines was accompanied by the para-rearrangement. About *N*-allyl-1- (**1a**) and 2-naphthylamine themselves, Marcinkiewicz *et al.* reported the formation of ortho rearranged product as sole one,3) which have formed the only successful example of the aromatic *amino*-Claisen rearrangement.



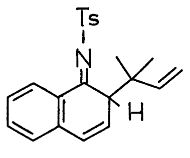
1a: X=H, R=$CH_2CH=CH_2$
1b: X=H, R=$CH_2C(CH_3)=CH_2$
1c: X=H, R=$CH_2CH=CHCH_3$
1d: X=H, R=$CH_2CH=C(CH_3)_2$
1e: X=H, R=$CH_2CH=CHC_6H_5$
1f: X=Ts, R=$CH_2CH=CHCH_3$
1g: X=Ts, R=$CH_2CH=C(CH_3)_2$
1h: X=Ts, R=$CH_2CH=CHC_6H_5$



2a: X=H, R=$CH_2CH=CH_2$
2b: X=H, R=$CH_2C(CH_3)=CH_2$
2c: X=H, R=$CH(CH_3)CH=CH_2$
2d: X=H, R=$CH(C_6H_5)CH=CH_2$
2e: X=H, R=$CH_2CH=CHC_6H_5$
2f: X=H, R=H
2g: X=Ts, R=$CH(CH_3)CH=CH_2$
2h: X=Ts, R=$CH(C_6H_5)CH=CH_2$



3a: X=H, R=$CH_2CH=CHCH_3$
3b: X=H, R=$CH_2CH=C(CH_3)_2$
3c: X=H, R=$CH_2CH=CHC_6H_5$
3d: X=Ts, R=$CH_2CH=CHCH_3$
3e: X=Ts, R=$CH_2CH=C(CH_3)_2$
3f: X=Ts, R=$CH_2CH=CHC_6H_5$



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The amines (**1a**—**1e**) neat were heated at 260±0.3 °C under nitrogen. In general, the thermal reaction of these amines gave complicated products, together with some amount of tarry matters.4) The reaction mixtures from **1a**—**1e** were converted to the ones of *N*-tosylamines by treating them with tosyl chloride in pyridine immediately after the reaction and analyzed according to the method previously described. The results are shown in Table.

The main products were the ortho rearranged ones throughout the reactions except for **1d** from which the deallylated product **2f** was formed as the only confirmable one. The formation of para-rearranged products was not observed except **3c** formed from **1e**.5) It may be reasonably considered that **3c** should be formed partially at least *via* a dissociation-recombination process, since the formation of **2e** involving a sterically retained cinnamyl group in ortho position was also observed. In general, the ortho-rearrangement apparently proceeds *via* a [3,3]-sigmatropic reaction as denoted by the examples of the amines containing an asymmetrically-substituted allyl group (**1c**, **1e**). The results accorded with what we deduced about the para-rearrangement in the corresponding *amido*-Claisen rearrangement; a steric repulsion between a tosyl group and α-substituents in an inverted allyl group which is involved in the intermediate such as **4** formed by the first [3,3]-shift promotes the second one to para rearranged products.

Experimental

IR spectra were determined on a Shimadzu IR-27G spectrometer and NMR spectra on a Hitachi R-24 spectrometer; chemical shifts are given in δ with TMS as an internal standard. *N*-(Substituted allyl)-1-naphthylamines were obtained in excellent yields by the corresponding *N*-allylations of *N*-trifluoroacetyl-1-naphthylamine and the subsequent hydrolysis.

*N-(Substituted allyl)-*N*-trifluoroacetyl-1-naphthylamines.* To a stirred mixture of *N*-trifluoroacetyl-1-naphthylamine6) (80 g, 0.33 mol) and K_2CO_3 (46.2 g, 0.33 mol) in DMF (100 ml) was added the corresponding allyl bromide (0.40 mol) at room temperature. Then the mixture was stirred for 2 h at 60 °C. The usual work up gave the following *N*-(substituted allyl) derivatives in 88—99% yields.

TABLE 1. THERMAL REARRANGEMENT OF *N*-(SUBSTITUTED ALLYL)-1-NAPHTHYLAMINES (260 °C, neat)

Starting material	React. time/h	Recovered (%)	Products (%)			
1a	1.1	58.0	**2a**: 30.4	**2f**: 3.2		
	2	40.8	40.9	3.3		
	3	30.0	54.5	5.1		
1b	1.1	65.4	**2b**: 21.8	**2f**: 2.2		
	2	47.0	31.9	4.4		
	3	32.7	43.5	6.4		
1c	1.1	63.8	**2c**: 17.7	**3a**: —[a]	**2f**: 5.1	
	2	48.1	28.7	—	6.9	
	3	35.4	36.4	—	6.3	
1d	1	61.9	**3b**: —[a]	**2f**: 7.8		
	2	55.7	—	9.3		
	3	46.9	—	11.5		
1e	1	47.9	**2d**: 30.8	**2e**: 8.7	**3c**: 1.6	**2f**: 4.7
	2	28.4	37.7	14.0	2.1	7.5
	3	14.9	34.1	15.5	2.2	9.5

a) The formation was not observed. See Ref. 5.

N-Allyl Derivative: Mp 45.5—46 °C. IR (KBr): 1690, 1210, 1180, 1150 cm^{-1}. Found: C, 64.70; H, 4.41; N, 4.91%. Calcd for $C_{15}H_{12}F_3NO$: C, 64.51; H, 4.33; N, 5.02%.

N-(β-Methylallyl) Derivative: Mp 61.5—62 °C. IR (KBr): 1690, 1210, 1190, 1145 cm^{-1}. Found: C, 65.38; H, 4.77; N, 4.54%. Calcd for $C_{16}H_{14}F_3NO$: C, 65.52; H, 4.81; N, 4.78%.

N-(γ-Methylallyl) Derivative: Mp 54.5—55.5 °C. IR (KBr): 1690, 1210, 1190, 1145, 965 cm^{-1}. Found: C, 65.49; H, 4.63; N, 4.66%. Calcd for $C_{16}H_{14}F_3NO$: C, 65.52; H, 4.81; N, 4.78%

N-(γ,γ-Dimethylallyl) Derivative: Bp 119.5—121 °C (1 mmHg). IR (neat): 1690, 1210, 1170, 1150 cm^{-1}. Found: C, 66.71; H, 5.03; N, 4.65%. Calcd for $C_{17}H_{16}F_3NO$: C, 66.44; H, 5.25; N, 4.56%.

N-(γ-Phenylallyl) Derivative: Mp 88.5—89.5 °C. IR (KBr): 1690, 1210, 1185, 1155, 975 cm^{-1}. Found: C, 71.14; H, 4.78; N, 4.07%. Calcd for $C_{21}H_{16}F_3NO$: C, 70.98; H, 4.54; N, 3.94%.

*N-(Substituted allyl)-1-naphthylamines (**1a**—**1e**).* A solution of the trifluoroacetamide (0.125 mol) in water–ethanol (1:3, 400 ml) containing NaOH (8.0 g) was refluxed for 10 min. The usual work up gave the hydrolyzed products in 80—99% yields. The melting points and IR spectra of the *N*-tosylated amines corresponded to those of the authentic samples.

1a: Bp 120—120.5 °C (2 mmHg). Mp of HCl salt, 229.5—231 °C (lit,[3] mp 229—230 °C).

1b: Bp 104.2—104.8 °C (2 mmHg). IR (neat): 3475, 1655, 890 cm^{-1}. NMR (CCl_4): 1.69 (s, 3H, β-CH_3), 3.58 (broad s, 2H, α-H), 4.89 (broad d, J=7 Hz, 2H, γ-H). Found: C, 85.10; H, 7.48; N, 6.97%. Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66; N, 7.10%.

1c: Bp 131—131.5 °C (0.8 mmHg). IR (neat): 3450, 1675, 965 cm^{-1}. NMR (CCl_4): 1.60 (broad d, J=4 Hz, 3H, γ-CH_3), 3.53—3.65 (m, 2H, α-H), 5.48—5.65 (m, 2H, β- and γ-H). Found: C, 85.44; H, 7.79; N, 7.10%. Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66; N, 7.10%.

1d: Bp 147—148 °C (2 mmHg). IR (neat): 3450, 1665 cm^{-1}. NMR (CCl_4): 1.63 and 1.69 (s, 3H, γ-CH_3, resp.), 3.67 (broad d, J=6 Hz, 2H, α-H), 5.35 (broad t, J=7 Hz, 1H, β-H). Found: C, 85.41; H, 8.36; N, 6.75%. Calcd for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63%.

1e: Mp 83—83.5 °C. IR (KBr): 3475, 1660, 970 cm^{-1}. NMR ($CDCl_3$): 3.76 (broad d, J=5 Hz, 2H, α-H), 5.89—6.46 (m, 2H, β- and γ-H). Found: C, 88.22; H, 6.89; N, 5.51%. Calcd for $C_{19}H_{17}N$: C, 87.99; H, 6.61; N, 5.40%.

*Thermal Rearrangement of **1a**—**1e**.* A test-tube containing *N*-(substituted allyl)-1-naphthylamines (2—3 g) under nitrogen was immersed for an appropriate period of time in an oil bath, the temperature of which was maintained at 260.0±0.3 °C. The chilled reaction mixture was dissolved in pyridine (25 ml) and tosyl chloride (1.2 equivalents to **1**) was added. The whole solution was stirred at 60—70 °C for 6 h and poured into diluted hydrochloric acid (1:3). The resulting precipitate was filtered, washed with diluted hydrochloric acid and water, and dried. The samples thus obtained were analyzed by the method described previously.[2]

References

1) S. Inada, S. Hirabayashi, K. Taguchi, and M. Okazaki, *Nippon Kagaku Kaishi*, **1978**, 86 and other articles cited therein.

2) For example, when a solution of **1f** (1.00 g) in *N,N*-dibutylaniline (15 ml) containing a small amount of PPh_3 (0.1 g) was heated under nitrogen at 245 °C for 1.2 h, the ortho-rearranged product **2g** and the para-rearranged product **3d** were obtained in 63.0 and 26.8% yields, respectively. S. Inada, R. Kurata, T. Ishida, T. Uda, and M. Okazaki, *Nippon Kagaku Kaishi*, **1978**, 723.

3) S. Marcinkiewicz, J. Green, and P. Mamalis, *Tetrahedron*, **14**, 208 (1961).

4) For example, 6 spots were at least observed on TLC as the reaction products from **1a**.

5) The authentic samples of **3a**, **3b**, and **3c** which might be expected to form had been prepared in the form of their *N*-tosyl derivatives from the *amido*-Claisen rearrangement mentioned above and the possibility of their existence in the reaction mixture was examined on TLC and HLC.

6) M. Pailer and W. J. Hübsch, *Monat. Chem.*, **97**, 1553 (1966).