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The Syntheses of 4- and 5-(α- and β-Naphthyl)tropolones[1)]

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Synopsis. 4- And 5-(α- and β-naphthyl)tropolones have been synthesized *via* naphthyl-tropilidenes, -tropones, and -aminotropones.

Only 3-(α- and β-naphthyl)tropolones in a series of naphthyl-substituted tropolones have ever been reported.[2)] This paper describes the syntheses of 4- and 5-(α- and β-naphthyl)tropolones by the successive reactions: tropenylations of naphthalene, transformation of naphthyltropilidenes to naphthyltropones and then to (naphthyl)aminotropones, and hydrolysis to naphthyltropolones.

7-Ethoxytropilidene was allowed to react with α-naphthylmagnesium bromide[3)] to produce a mixture of isomeric α-naphthyltropilidenes (Iα, 44%), which was treated with phosphorus pentachloride in carbon tetrachloride, alkali, and acid successively to yield a mixture of isomeric α-naphthyltropones (IIα and IIIα, 85%).[4)] Separation of them by chromatography or by fractional recrystallization of their picrates was unsuccessful. The mixture of IIα and IIIα was treated with 80% hydrazine in ethanol to afford three aminonaphthyltropones (IVα, Vα, and VIα; 3.4, 55, and 16%). The position of the amino group on these tropones became partially evident only after independent hydrolysis of each aminotropone with alkali.[5)] IVα and VIα were hydrolyzed respectively to yield the same α-naphthyltropolone (VIIα, 86%), while Vα afforded α-naphthyltropolone (VIIIα, 80%). From these results, it is found that VIIα is 4-(α-naphthyl)tropolone and therefore IVα or VIα is 2-amino-4- or 2-amino-6-(α-naphthyl)tropone, although which is which remains unknown, and VIIIα is 5-(α-naphthyl)tropolone and Vα is 2-amino-5-(α-naphthyl)tropone.

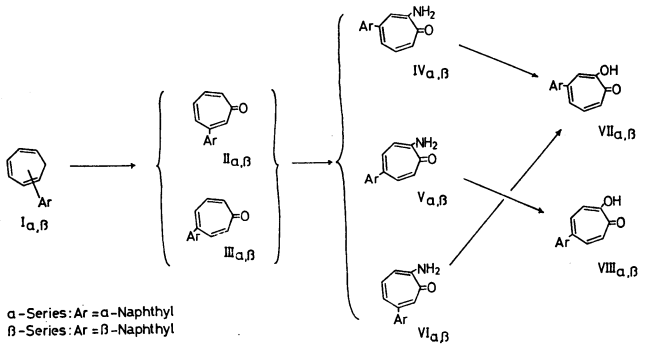
For the β-naphthyl series, a mixture of β-naphthyltropilidenes (Iβ, 30%), a mixture of isomeric β-naph-

TABLE 1. α- AND β-NAPHTHYL-SUBSTITUTED TROPILIDENES, TROPONES, AMINOTROPONES, AND TROPOLONES

Compound	Appearance, Mp or Bp (°C)	Molecular formula	Analytical data[a)]		
			C(%)	H(%)	N(%)
Iα	A pale yellow oil, 148.0—169.5/2 mmHg	$C_{17}H_{14}$	93.32	6.68	
			(93.53)	(6.47)	
Iβ	A pale yellow oil, 163.0—168.0/1.5 mmHg	$C_{17}H_{14}$	93.23	6.52	
IIα and IIIα (mixture)	Yellow oily crystals	$C_{17}H_{12}O_2$	87.95	5.11	
			(87.90)	(5.21)	
IIβ and IIIβ (mixture)	Yellow crystals, 132.5—135.0	$C_{17}H_{12}O_2$	87.77	5.19	
Picrates of IIα and IIIα	Yellow needles, 108.0—109.0	$C_{23}H_{15}O_8N_3$	60.05	3.34	9.11
			(59.87)	(3.28)	(9.11)
Picrates of IIβ and IIIβ	Brown needles, 128.5—129.5	$C_{23}H_{15}O_8N_3$	60.14	3.40	9.03
2,4-DNP of IIα and IIIα	Dark brown crystals, 162.0—164.0	$C_{23}H_{16}O_4N_4$	66.66	4.06	13.86
			(66.98)	(3.91)	(13.59)
2,4-DNP of IIβ and IIIβ	Black powder, 210.0—212.0	$C_{23}H_{16}O_4N_4$	66.68	3.85	13.26
IVα	Yellow plates, 162.0—163.0	$C_{17}H_{13}ON$	82.64	5.49	5.89
			(82.57)	(5.30)	(5.66)
IVβ	Yellow needles, 195.5—196.5	$C_{17}H_{13}ON$	82.66	5.28	5.77
Vα	Yellow plates, 201.0—202.0	$C_{17}H_{13}ON$	82.91	5.32	5.70
Vβ	Yellow leaflets, 200.5—201.5	$C_{17}H_{13}ON$	82.48	5.46	5.75
VIα	Yellow pyramids, 188.0—189.0	$C_{17}H_{13}ON$	82.70	5.25	5.53
VIβ	Yellow needles, 141.0—142.0	$C_{17}H_{13}ON$	82.40	5.30	5.51
Acetate of IVα	Pale yellow needles, 135.0—136.0	$C_{19}H_{15}O_2N$	78.80	5.24	4.73
			(78.87)	(5.23)	(4.84)
Acetate of IVβ	Yellow leaflets, 170.0—172.0	$C_{19}H_{15}O_2N$	78.71	5.26	4.93
Acetate of Vα	Yellow pyramids, 168.0—169.0	$C_{19}H_{15}O_2N$	79.02	5.37	4.75
Acetate of Vβ	Yellow leaflets, 166.5—167.5	$C_{19}H_{15}O_2N$	78.46	5.26	4.90
Acetate of VIα	Yellow plates, 189.5—190.5	$C_{19}H_{15}O_2N$	79.25	5.42	4.77
Acetate of VIβ	Yellow crystals, 174.0—176.0	$C_{19}H_{15}O_2N$	78.60	5.23	4.73
VIIα	Pale yellow needles, 117.0—118.0	$C_{17}H_{12}O_2$	82.31	4.78	
			(82.24)	(4.87)	
VIIβ	Pale yellow leaflets, 149.5—150.5	$C_{17}H_{12}O_2$	82.34	4.69	
VIIIα	Yellow pyramids, 138.5—139.0	$C_{17}H_{12}O_2$	82.13	4.84	
VIIIβ	Pale yellow needles, 201.0—202.0	$C_{17}H_{12}O_2$	82.30	4.78	

a) Numerals in parentheses indicate calculated values.

thyltropones (IIβ and IIIβ, 61%), three isomeric amino-β-naphthyltropones (IVβ, Vβ, and VIβ; 31, 41, and 18%), of which IVβ or VIβ is 2-amino-4- or 2-amino-6-(β-naphthyl)tropone, and two β-naphthyltropolones (VIIβ and VIIIβ, 41%) were obtained successively in a similar manner.



Experimental

α-Naphthyltropilidenes (Iα). 7-Ethoxytropilidene (55 g) was added to the Grignard reagent, prepared from α-bromonaphthalene (84.1 g) and magnesium (10.8 g) in dry ether (240 ml), and the ether was evaporated. The reaction mixture was heated for 3 hr at about 130 °C to yield naphthalene (5.6 g) and Iα (37.4 g); δ (CCl_4): 2.15 (t, J=6.8 Hz), 2.19 (t, J=6.8 Hz), 2.69 (d, J=6.8 Hz) and the peak areas of these methylene protons of the tropenyl groups suggest that the ratio between 3-, 2-, and 1-(α-naphthyl)tropilidenes is 3 to 10 to 13; 5.17 (1.65 H, m, tropyl), 6.07 (1.65 H, m, tropyl), 6.42 (1.65 H, m, tropyl), 6.88—8.12 (7H, m, naphthyl).

3- And 4-(α-naphthyl)tropones (IIα and IIIα, mixture). A mixture of phosphorus pentachloride (12.5 g), dry carbon tetrachloride (120 ml), and Iα (6.54 g) was stirred at room temperature overnight. The extraction of the mixture with cold water, neutralization of the water layer and extraction of it with ether afforded a yellow oil (4.55 g). This was hydrolyzed with concentrated hydrochloric acid to give recovered Iα (2.7 g) and a mixture of IIα and IIIα (2.27 g); ν (neat); 1630, 1575 cm^{-1}.

Amino-α-naphthyltropones (IVα, Vα, and VIα). A mixture of IIα and IIIα (590 mg), 80% hydrazine (0.5 ml), and ethanol (10 ml) was refluxed for 6 hr. The reaction mixture was separated through a silica-gel column with benzene–ether to afford three products: VIα (21 mg), IVα (345 mg), and Vα (98 mg), successively.

Acetate of VIα; λ_{max}^{MeOH}, nm (log ε): 220.5 (4.83), 261 (4.33), 290 (3.98 sh), 326 (4.14 sh), 370 (3.97 sh). ν(Nujol): 3230, 1693, 1616, 1220, 837, 808, 783, 730 cm^{-1}.

Acetate of IVα; λ_{max}^{MeOH}, nm (log ε): 221 (4.84), 250—255 (4.34), 324 (4.17), 368 (3.97), 3.88 (3.81 sh). ν(Nujol): 3235, 1692, 1617, 1225, 918, 793, 780, 726 cm^{-1}.

Acetate of Vα; λ_{max}^{MeOH}, nm (log ε): 219 (4.80), 253 (4.31), 280 (4.00 sh), 344 (4.20), 390 (4.01 sh). ν (KBr): 3240, 1693, 1618, 1248, 1220, 1203, 875, 869, 861, 808, 783, 743 cm^{-1}.

4-(α-Naphthyl)tropolone (VIIα). A mixture of IVα (600 mg), potassium hydroxide (660 mg), water (1.5 ml), and ethanol (4 ml) was refluxed for 12 hr and the solvent was evaporated off. The residue was acidified with 3 M sulfuric acid and extracted with chloroform (50 ml) to afford a brown solid of VIIα (518 mg, which was purified from cyclohexane); λ_{max}^{MeOH}, nm (log ε): 220.5 (4.79), 248 (4.42), 319 (4.16), 386 (3.83). ν (KBr): 3200, 1610, 1550, 915, 830, 800, 795, 775 cm^{-1}.

5-(α-Naphthyl)tropolone (VIIIα). This was prepared from Vα (purified from methanol) in a similar manner. λ_{max}^{MeOH}, nm (log ε): 219 (4.80), 346 (4.24). ν (KBr): 3400, 1615, 1550, 862, 805, 785 cm^{-1}.

The compounds of β-naphthyl series were prepared by practically the same treatment as in the α-naphthyl series described above.

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