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Synthesis of 1-Alkyl-2-methylnaphthalenes from 3-Phenyl-2-alkanones

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1,2-Dialkylnaphthalenes are found in crude oil obtained from various oil fields [1]. Authentic samples of such hydrocarbons are often needed in research related to the petrochemical industry. Recently, amino-nitrile derivatives of these hydrocarbons were employed as starting compounds for the preparation of certain dyes [2].

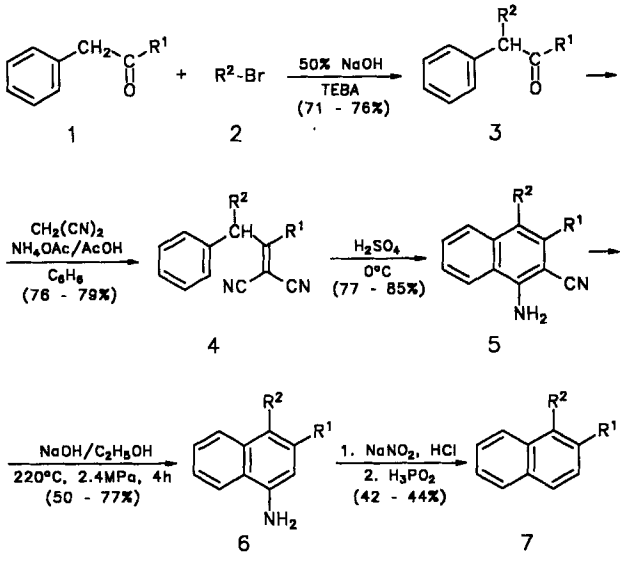
In this report we describe a simple, four-step synthesis of 1-alkyl-2-methylnaphthalenes from 3-phenyl-2-alkanones. Our synthetic approach is based on the annulation of alkylated 1-phenyl-2-alkanones, with the aid of a malonodinitrile building block. The annulation technique reported herein is still rather seldom used in organic synthesis [3, 4].

Cyclization of alkylidenemalonodinitriles to alkyl-substituted naphthalene amino-nitriles is not a new transformation. This reaction was investigated three decades ago by Campaigne et al. [5, 6]. However, the difficulties in further elaboration of relatively easily synthesized aromatic amino-nitriles rendered the discussed reaction of a very limited use in organic chemistry.

Several synthetic routes leading to 1,2-dialkylnaphthalenes have been reported in the literature. A major approach involves the use of 2-alkyl-1,2,3,4-tetrahydronaphthalene-1-one, which is then elaborated into 1,2-dialkylnaphthalene via the reaction with an alkyl Grignard reagent. Starting 2-alkyl-1-tetralones are synthesized from the corresponding α-alkyl-γ-phenylbutyric acids [7, 8]. In an alternative and frequently used method, 1-tetralone is treated with dimethyl or diethyl oxalate to afford a ketoester which is subsequently alkylated and then converted into 2-alkyl-1-tetralone [9–16]. 1,2-Dialkylnaphthalenes are also prepared from 2-alkyl-1-bromonaphthalenes and alkyllithiums or employing Grignard reagents [17, 18]. Other reported methods involve a rearrangement of dialkyltetralins [11, 19] or are specific for a particular dialkylnaphthalene such as 1,2-diethyl- [19, 20], 1,2-di(n-propyl)- [21], or 1,2-di(n-butyl)naphthalene [22].

Results and Discussion

We limited our investigations to 1-phenyl-2-propanone (**1a**). Ketone **1a** was alkylated under phase-transfer conditions with ethyl or n-propyl bromide to afford ketones **3a** or **3b**, respectively. Other 1-phenyl-2-alkanones (**1**) are relatively easy to synthesize [23] or are presently commercially available. Hence ketones **3** having a variety of alkyl groups R^1 and R^2 [24, 25] might be obtained in a simple manner and then used for the preparation of hydrocarbons **7**.



a: R^1= CH_3, R^2= C_2H_5

b: R^1= CH_3, R^2= n-C_3H_7

Condensation of ketones **3a** or **3b** with malonodinitrile gave the oily dinitriles **4a** or **4b**, respectively. These dinitriles were cyclized to amino-nitriles **5** by dissolving in cold, concentrated sulfuric acid. Ring closure of the second carbocyclic ring in **4** and aromatization of the naphthalene framework of **5** were thus carried out in a simple and convenient manner which is characteristic of the ylidenemalonodinitrile approach. This is in contrast to a variety of earlier synthetic routes reported in the literature and briefly discussed above.

The nitrile group was removed from amino-nitriles **5** by heating these compounds in an autoclave at 220 °C with ethanolic sodium hydroxide solution. Under these severe reaction conditions the nitrile function of **5** was hydrolyzed and the resulting aminocarboxylic anions underwent decarboxylation. Aromatic amines **6a** and **6b** were obtained as colorless, low melting solids, which were relatively stable during storage. These new amines are potentially useful starting compounds for further synthetic transformations. An obvious possibility connected with the present investigations is the synthesis of 1,2,4-trialkylnaphthalenes.

In a final step the amines **6a** and **6b** were converted into hydrochlorides and then diazotized. The diazonium compounds were treated with a solution of hypophosphorous acid to afford hydrocarbons **7a** and **7b** in moderate yield.

Experimental

Melting points were determined on a Boëtius hot-stage microscope and are corrected. The IR spectra were recorded on a Specord M81 (C. Zeiss Jena) instrument. The ^{1}H-NMR spectra were obtained on a Tesla BS 587A (100 MHz) spectrometer with Me_4Si as an internal standard. Elemental analyses were performed using a Perkin Elmer Analyzer Type 240.

3-Phenyl-2-pentanone (**3a**)

In a 250 ml flask fitted with an efficient mechanical stirrer tipped with a teflon blade, a dropping funnel, and a thermometer, was placed 50 % sodium hydroxide solution (50 ml), phenylacetone (14.0 g, 0.10 mol), and triethylbenzylammonium chloride (0.8 g, 4 mmol). Ethyl bromide (12.0 g, 0.11 mol) was slowly added during 45 min. to the vigorously stirred mixture while the temperature rose to 28–32 °C. After addition of ethyl bromide had been complete, stirring of the mixture was continued for 50 min. Water (50 ml) and benzene (60 ml) were then added, the organic phase was separated, thoroughly washed with water, and dried over anhydrous magnesium sulfate. Benzene was removed on a rotary evaporator and the remaining oil was distilled under reduced pressure to afford 12.8 g (76 %) of **3a** as colorless liquid; b.p. 72–74 °C/3 hPa; (Lit. [24] b.p. 82–84 °C/5 hPa).

IR (neat) [cm^{-1}]: 3047, 3013, 2955, 2917, 2863, 2698, (CO), 1587, 1480, 1440, 1344, 1147, 747, 724, 693. ^{1}**H-NMR** ($CDCl_3$) δ[ppm]: 0.82 (t, 3H, CH_2**C**H_3, J=7.1 Hz), 1.76 (quintet, 2H, CH-C**H**$_2$-CH_3, J=7.1 Hz), 2.02 (s, 3H, CO-C**H**$_3$), 3.51 (t, 1H, C**H**-CH_2, J=7.1 Hz), 7.12–7.54 (m, 5H, Ar-**H**).

3-Phenyl-2-hexanone (**3b**)

Phenylacetone (14.0 g, 0.10 mol) was alkylated with n-propyl bromide (13.0 g, 0.10 mol) under the same conditions as described for **3a**. Distillation of the crude product under reduced pressure gave 12.59 (71 %) of **3b** as colorless oil; b.p. 75–77 °C/2 hPa, (Lit. [24] b.p. 83–84 °C/3 hPa).

IR (neat) [cm^{-1}]: 3050, 3015, 2948, 2921, 2862, 1705 (CO), 1590, 1442, 1342, 1153, 740, 720, 690. ^{1}**H-NMR** ($CDCl_3$) δ[ppm]: 0.88 (t, 3H, CH_2-C**H**$_3$, J=6.1 Hz), 1.21 (sextet, 2H, CH_2-C**H**$_2$-CH_3, J=6.6 Hz), 1.57–1.98 (m, 2H, CH-C**H**$_2$-CH_2), 2.03 (s, 3H, CO-C**H**$_3$), 3.61 (t, 1H, C**H**-CH_2 J=7.0 Hz), 7.00–7.49 (m, 5H, Ar-**H**).

3-Phenyl-2-pentylidenemalonodinitrile (**4a**)

In a 50 ml flask equipped with a Dean-Stark water trap and a reflux condenser were placed acetic acid (2.1 g, 0.04 mol), ammonium acetate (1.0 g, 0.01 mol), malonodinitrile (3.4 g, 0.05 mol), benzene (20 ml), and freshly distilled ketone **3a** (8.0 g, 0.05 mol). The mixture was heated under reflux until separation of water was complete (4h). The solution was washed with water, saturated sodium hydrogen carbonate solution, and finally again with water. After drying over anhydrous magnesium sulfate benzene was removed on a rotary evaporator and remaining liquid was distilled under vacuum to give 8.2 g (79 %) of the dinitrile **4a** as yellowish oil; b.p. 150–151 °C/5 hPa, n_D^{20}=1.5440.

IR (neat) [cm^{-1}]: 3080, 3053, 3017, 2953, 2923, 2867, 2220, (CN), 1580, 1483, 1440, 1027, 693. ^{1}**H-NMR** ($CDCl_3$) δ[ppm]: 0.98 (t, 3H, CH_2-C**H**$_3$), J=7.1 Hz), 1.97 (quintet, 2H, CH-C**H**$_2$-CH_3, J=7.0 Hz), 2.07 (s, 3H, =C-C**H**$_3$), 4.21 (t, 1H, C**H**-CH_2, J=7.0 Hz), 7.05–7.77 (m, 5H, Ar-**H**).

$C_{14}H_{14}N_2$	Calcd: C 79.97	H 6.71	N 13.32
(210.28)	Found: C 80.32	H 6.85	N 13.58

3-Phenyl-2-hexylidenemalonodinitrile (**4b**)

3-Phenyl-2-hexanone **3b** (8.8 g, 0.05 mol) was condensed with malonodinitrile (3.4 g, 0.05 mol) in the same manner as described for the dinitrile **4a**. Distillation of the condensation product gave 8.5 g (76 %) of **4b** as slightly yellow oil; b.p. 142–145 °C/3 hPa, n_D^{20}=1.5358.

IR (neat) [cm^{-1}]: 3075, 3049, 3020, 2953, 2864, 2225 (CN), 1581, 1491, 1439, 739, 696. ^{1}**H-NMR** ($CDCl_3$) δ[ppm]: 0.99 (t, 3H, CH_2-C**H**$_3$, J=6.1 Hz), 1.17–1.51 (m, 2H, CH_2-C**H**$_2$-CH_3), 1.81–2.10 (m, 2H, CH-C**H**$_2$-CH_2), 2.06 (s, 3H, =C-C**H**$_3$), 4.32 (t, 1H, C**H**-CH_2, J=7.5 Hz), 7.03–7.83 (m, 5H, Ar-**H**).

$C_{15}H_{16}N_2$	Calcd: C 80.32	H 7.19	N 12.49
(224.31)	Found: C 80.18	H 7.34	N 12.33

1-Amino-4-ethyl-3-methylnaphthalene-2-carbonitrile (**5a**)

Ylidenemalonodinitrile **4a** (2.0 g, 9.5 mmol) was slowly dropped into concentrated sulfuric acid (10 ml) which was cooled in an ice-bath. The solution turned yellow, orange, and finally deep green. The flask was kept in the ice-bath for one hour and then at room temperature for 2h. The solution was poured onto ice. The precipitate slowly solidified and after one hour was filtered off and washed several times with water. Recrystallization from ethanol furnished 1.55 g (77 %) of pale yellow crystals, m.p. 113–114 °C.

IR (nujol) [cm^{-1}]: 3456, 3364, 3240 (NH_2), 2187 (CN), 1627, 1421, 752, 647. ^{1}**H-NMR** ($CDCl_3$) δ[ppm]: 1.20 (t, 3H, CH_2-C**H**$_3$, J=7.1 Hz), 2.56 (s, 3H, Ar-C**H**$_3$), 2.98 (q, 2H, C**H**$_2$-CH_3, J=7.5 Hz), 4.99 (bs, 2H, NH_2), 7.26–8.04 (m, 4H, Ar-**H**).

$C_{14}H_{14}N_2$	Calcd: C 79.97	H 6.71	N 13.32
(210.28)	Found: C 79.88	H 6.66	N 13.18

1-Amino-3-methyl-4-(n-propyl)naphthalene-2-carbonitrile (**5b**)

Ylidenemalonodinitrile **4b** (2.0 g, 9 mmol) was cyclized in cold, concentrated sulfuric acid in the same manner as described for amino-nitrile **5a**. Crude product was recrystallized from ethanol to give 1.7 g (85 %) of yellowish crystals; m.p. 109 °C.

IR (nujol) [cm^{-1}]: 3454, 3366, 3236 (NH_2), 2188 (CN), 1628, 1426, 748, 643. ^{1}**H-NMR** ($CDCl_3$) δ[ppm]: 1.12 (t, 3H, CH_2-C**H**$_3$, J=6.5 Hz), 1.42–1.77 (m, 2H, CH_2-C**H**$_2$-CH_3), 2.52 (s, 3H, Ar-C**H**$_3$), 2.85 (t, 2H, Ar-C**H**$_2$-CH_2, J=6.6 Hz), 4.90 (bs, 2H, N**H**$_2$), 7.33–8.07 (m, 4H, Ar-**H**).

$C_{15}H_{16}N_2$	Calcd: C 80.32	H 7.19	N 12.49
(224.31)	Found: C 80.23	H 7.27	N 12.41

1-Amino-4-ethyl-3-methylnaphthalene (**6a**)

Amino-nitrile **5a** (505 mg, 2.4 mmol) and sodium hydroxide (2.0 g, 50 mmol) were dissolved in ethanol (100 ml). The solution was heated in a 250 ml autoclave at ~220 °C for 4h. Ethanol was removed on a rotary evaporator and the remaining mixture was diluted with water (50 ml). Dark oil which separated from the solution, slowly solidified on standing overnight at room temperature. The solid was filtered off and washed with water. Sublimation under reduced pressure

and recrystallization from n-hexane gave 340 mg (77 %) of the amine **6a** as colorless crystals; m.p. 76.5–77.5 °C.

IR (nujol) [cm^{-1}]: 3392, 3302, 3190 (NH_2), 1621, 1576, 848, 736, 615. **^{1}H-NMR** ($CDCl_3$) δ[ppm]: 1.22 (t, 3H, CH_2-**CH_3**, J=7.5 Hz), 2.41 (s, 3H, Ar-**CH_3**), 3.00 (q, 2H, **CH_2**-CH_3, J=7.5 Hz), 3.60 (bs, 2H, NH_2), 6.65 (s, 1H, C2-**H**), 7.25–7.56 (m, 2H, C6-**H**, C7-**H**), 7.80 (dd, 1H, C5-**H**, J=7.5 Hz, J=2.5 Hz), 7.99 (dd, 1H, C8-**8**, J=7.5 Hz, J=2.5 Hz).

$C_{13}H_{15}N$	Calcd: C 85.21	H 7.15	N 7.64
(185.27)	Found: C 85.19	H 7.23	N 7.70

1-Amino-4-(n-propyl)-3-methylnaphthalene (**6b**)

The nitrile group was removed from the amino-nitrile **5b** (503 mg, 2.2 mmol) under the same conditions as reported for **6a**. Sublimation of crude **6b** under reduced pressure and recrystallization from n-hexane afforded 225 mg (50 %) of colorless needles; m.p. 57–58 °C.

IR (nujol) [cm^{-1}]: 3378, 3313, 3209 (NH_2), 1624, 1579, 844, 749, 612. **^{1}H-NMR** ($CDCl_3$) δ[ppm]: 1.05 (t, 3H, CH_2-**CH_3**, J=7.0 Hz), 1.62 (sextet, 2H, CH_2-**CH_2**-CH_3, J=7.0 Hz), 2.39 (s, 3H, Ar-**CH_3**), 2.94 (t, 2H, Ar-**CH_2**-CH_2, J=8.0 Hz), 3.69 (bs, 2H, NH_2), 6.63 (s, 1H, C2-**H**), 7.29–7.52 (m, 2H, C6-**H**, C7-**H**), 7.79 (dd, 1H, C5-**H**, J=7.5 Hz, J=2.0 Hz), 7.98 (dd, 1H, C8-**H**).

$C_{14}H_{17}N$	Calcd: C 84.37	H 8.60	N 7.03
(199.30)	Found: C 84.42	H 8.54	N 7.03

1-Ethyl-2-methylnaphthalene (**7a**)

The amine **6a** (93 mg, 0.5 mmol) was dissolved in benzene (3 ml) and the solution was saturated with dry hydrogen chloride. The precipitated amine hydrochloride was filtered off, washed with benzene, dried and suspended in dilute (20 %) hydrochloric acid (0.6 ml). The suspension was cooled to 0 °C, diazotized with a solution of sodium nitrite (38 mg, 0.53 mmol), mixed with cold 30 % hypophosphorous acid (1.1 ml) and kept overnight in a refrigerator. The brown oily product was extracted with ether, the combined extracts were washed successively with water, dilute sodium hydroxide solution, and with water, and then dried over anhydrous magnesium sulfate. The solvent was evaporated and the remaining dark-red oil was distilled in vacuo to afford 36 mg (42 %) of 1-ethyl-2-methylnaphthalene (**7a**) as nearly colorless oil; n_D^{18}=1.5959, (Lit. [8] n_D^{20}=1.5945); picrate: yellow needles from ethanol m.p. 111–112 °C, (Lit. [8] m.p. 110–111 °C).

^{1}H-NMR ($CDCl_3$) δ[ppm] **7a:** 1.25 (t, 3H, **CH_3**-CH_2, J=7.5 Hz), 2.48 (s, 3H, Ar-**CH_3**), 3.09 (q, 2H, Ar-**CH_2**-CH_3, J=7.5 Hz), 7.21–8.19 (m, 6H, Ar-**H**)

2-Methyl-1-propylnaphthalene (**7b**)

The amine **6b** (199 mg, 1 mmol) was converted into a hydrochloride, diazotized at 0 °C with a solution of sodium nitrite (75 mg, 1.1 mmol) and then reacted with 30 % hypophosphorous acid (2.3 ml). The hydrocarbon **7b** was separated and purified in the same manner as described above for **7a**. Distillation gave 81 mg (44 %) of 2-methyl-1-propylnaphthalene (**7b**) as colorless oil; n_D^{18}=1.5968 (Lit. [11] n_D^{20}=1.5961); picrate: yellow needles from ethanol, m.p. 117–118 °C (Lit. [11] m.p. 118–119 °C).

^{1}H-NMR ($CDCl_3$) δ[ppm] **7b**: 1.08 (t, 3H, **CH_3**-CH_2, J=7.5 Hz), 1.66 (sextet, 2H, CH_3-**CH_2**-CH_2, J=7.5 Hz), 2.48 (s, 3H, Ar-**CH_3**), 3.03 (t, 2H, Ar-**CH_2**-CH_2, J=8.0 Hz), 7.15–8.13 (m, 6H, Ar-**H**).

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