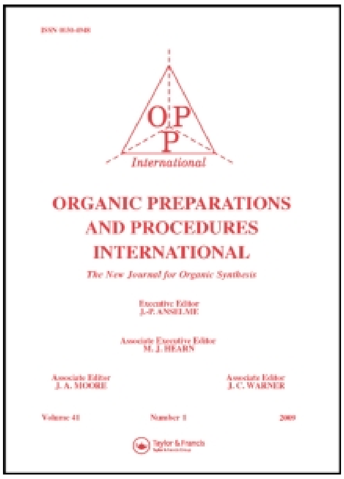

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A CONVENIENT SYNTHESIS OF 1,1'- and 1,2'-DINAPHTHYLMETHANONES

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A CONVENIENT SYNTHESIS OF 1,1'- and 1,2'-DINAPHTHYLMETHANONES

Submitted by (11/15/02)

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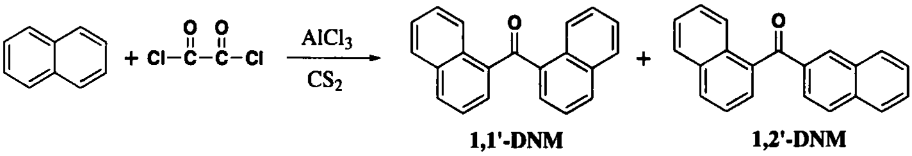
Because of their increased ability to absorb UV radiation (4 times that of benzophenone), dinaphthylmethanones (DNMs) are considered a new generation of UV-absorbing agents.[1] In addition, because of their high electron density, favorable symmetry and stability, they are used to synthesize polyaryl ethers and ketones. They also serve as intermediates for the preparation of dyestuffs, electronic devices, coatings and other commercial products. Therefore, an effective synthesis for DNMs is needed and is a goal of our current research.

Larock *et al.*[2] investigated the synthesis of symmetrical divinyl and diaryl ketones *via* rhodium-catalyzed carbonylation of vinyl- and arylmercurials. Although they obtained diaryl methanones in excellent yields (up to 95%), relatively vigorous conditions including high carbon monoxide pressure (1000-1525 psi), expensive and toxic catalyst $[Rh(CO)_2Cl]_2$ and long reaction time (24 h) make their process inconvenient and economically unattractive. Cho *et al.*[3] synthesized diaryl methanones using the tetrakis(triphenylphosphine)palladium(0)-catalyzed reaction of an arylboronic acid with carbon monoxide, 1,1'-dinaphthylmethanone (1,1'-DNM) was obtained only in 27% yield. We now report that the reaction of naphthalene with oxalyl chloride in the presence of anhydrous aluminium chloride at room temperature provides an effective approach to the synthesis of 1,1'- and 1,2'-DNMs in *ca.* 60% and 29% yields, respectively. It should be noted that under these conditions small amounts of 2,2'-DNM (< 5%), 1- and 2-naphthoic acids (< 8%) and dinaphthylethanedione (< 3%) could be detected by GC/MS analysis.[4] The high yield and selective synthesis of 1,1'- and 1,2'-DNMs from inexpensive and commercially available naphthalene and oxalyl chloride makes this procedure the better choice for the preparation of 1,1'- and 1,2'-DNMs.



EXPERIMENTAL SECTION

Naphthalene, oxalyl chloride, aluminium chloride, carbon disulfide, diethyl ether, anhydrous methanol and hydrochloric acid were analytically pure and commercially available. Prior to use, naphthalene was recrystallized from acetone and carbon disulfide was dried over anhydrous $MgSO_4$, followed by distillation under nitrogen. Aluminum chloride was sublimed under nitrogen. Melting points were determined in capillaries and are uncorrected. ^1H NMR spectra were recorded on a JEOL Lambda 400 spectrometer (400 MHz) with TMS as the internal standard in $CDCl_3$. Chemical shifts are expressed in parts per million (δ, ppm). FTIR spectra were obtained on a Nicolet Magna IR-560 spectrometer as neat films. GC/MS analysis was performed on a HP 6890 gas chromatograph equipped with a HP 5973 mass spectrometer and *m/z* values are given with relative intensities in parentheses. UV spectra were recorded on a Shimadzu UV-240 spectrometer in methanol. Microanalyses were carried out on a Leco CHN-2000 elemental analyzer.

Typical Procedure.- The reaction was conducted in a dry box at room temperature under nitrogen. To a stirred suspension of aluminum chloride (26.4 g, 0.20 mol) in 130 mL of carbon disulfide in a 500 mL three-necked flask, were added dropwise and simultaneously solutions of 25.6 g (0.20 mol) of naphthalene and 25.4 g (0.2 mol) of oxalyl chloride each dissolved in 130 mL of carbon disulfide. The mixture was stirred for an additional 2 h, then was poured into 10% aqueous hydrochloric acid. After separation of the organic phase, the aqueous phase was extracted three times with 200 mL of ether. The combined organic phase was washed with 10% aqueous $NaHCO_3$ and distilled water to pH 6-7, followed by drying over anhydrous $MgSO_4$ and rotary evaporation to remove CS_2 and ether. The resulting brown yellow solid was recrystallized from anhydrous methanol to give 16.9 g (60%) of 1,1'-DNM as white needle crystals, mp 100-101°C, *lit.*[3] 99-100°C. IR (KBr): 3050, 1680, 1570, 1500, 1460, 1340, 1280, 1230, 1190, 1100, 1060, 1010, 910, 790 cm^{-1}. ^1H NMR: δ 7.41-7.45 (m, 2H), 7.55-7.61 (m, 6H), 7.93-8.03 (m, 4H), 8.54-8.56 (m, 2H). MS (*m/z*): 282 (M^+, 100), 253 ($M-C_2H_5$, 27), 155 ($M-C_{10}H_7$, 86), 127 (155-CO, 90). λ_{max} (CH_3OH): 316.5 nm.

Anal. Calcd for $C_{21}H_{14}O$: C, 89.34; H, 5.00. Found: C, 89.41; H, 4.93

The solvent of the filtrate from the isolation of 1,1'-DNM was evaporated to afford a pale brown solid which was recrystallized from anhydrous methanol to yield 8.2 g (29%) of 1,2'-DNM as pale brown crystals, mp 139-140°C, *lit.*[5] 135-136°C. IR (KBr): 3050, 1690, 1620, 1500, 1470, 1350, 1280, 1230, 1190, 1160, 1110, 910, 870, 790 cm^{-1}. ^{1}H NMR: δ 7.48-7.66 (m, 5H), 7.83-7.85 (d, 1H), 7.90-7.97 (dm, 5H), 8.04-8.12 (m, 2H), 8.25 (s, 1H). MS (*m/z*): 282 (M$^+$, 100), 253 (M-C_2H_5, 24), 155 (M-$C_{10}H_8$, 78), 127 (155-CO, 90). λ_{max} (CH_3OH): 285.5 nm.
Anal. Calcd for $C_{21}H_{14}O$: C, 89.34; H, 5.00. Found: C, 89.43; H, 4.93

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SYNTHESIS OF 2,5- AND 2,6-DINITROFLUOROBENZENES AND RELATED HYDROQUINONES

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Two dinitrofluorobenzenes (**1** and **2**) and the commercially available 2,4-isomer were required in connection with a mechanistic study on the Elbs oxidation.[1] Although the 2,6-isomer (**1**) had been prepared previously using four different procedures,[2] all involving reaction of 2,6-dinitrochlorobenzene with a solid fluoride salt, the yields were difficult to reproduce. The difficulty seems to lie in the physical state of the fluoride salts as was nicely discussed by Smyth *et*