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Experiments Towards the Preparation of Some Binaphthalene Derivatives

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Oxidative dimerizations of some naphthalene derivatives were studied. With vanadium oxytrichloride either a new C—C bond formation occured or the reagent caused chlorination of the ring. Attempts to induce photochemically a new C—C bond failed.

(Keywords: Cyclization; C—C bond formation; Substituted naphthalenes)

Versuche zur Herstellung einiger Binaphthalin-Derivate

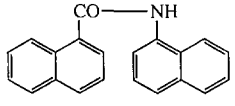
Die oxidative Dimerisierung einiger Naphthalinderivate wurde untersucht. Mit Vanadiumoxytrichlorid wird eine neue C—C-Bindung gebildet, es wurde jedoch auch Chlorierung des Naphthalinringes beobachtet. Versuche zur photochemischen Bildung einer C—C-Bindung scheiterten.

Introduction

There are several general and many individual synthetic approaches for binaphthalenes [1]. For the most part symmetrically linked binaphthalenes, i.e. with either 1,1′- or 2,2′-bonds, have been obtained by chemical transformations of naphthols and related compounds. We have recently reported on the formation of binaphthalenes by arylation of ambident naphtholate ions [2]. We now present some results on the dimerization of molecules containing two naphthalene rings linked together with various functional groups. Since only a few naphthalenes have been dimerized by oxidative coupling in the presence of vanadium oxytrichloride or vanadium tetrachloride [2, 3], it was of interest to investigate in more detail the utility of the first mentioned reagent for the preparation of binaphthalenes.

Results and Discussion

It is well known that oxidative coupling of phenols is not a regioselective reaction, although one of the possible regioisomers is usually isolated or is the predominant one. For example, oxidative coupling of the naphthols can yield a mixture of 1,1′-, 2,2′- or 1,2′-isomers. This reaction was established when 1-naphthol was treated with ferric chloride [4–7]. In order to minimize the formation of the several possible isomeric products, it was of interest to establish if a preoriented molecule can undergo an unambiguous and regioselective dimerization. Therefore, we have prepared some model compounds in which two naphthalene rings are linked with various functional groups, such as —NHCO—, —$NHSO_2$—, —O—, etc. In such molecules there is less freedom of motion of both rings. Therefore, it was anticipated that new C—C bond formation would only take place between certain positions, thus forcing the molecule to undergo a regioselective new bond formation. Moreover, such functional groups should also promote photoinduced coupling since several cases of benzanilides or heterocyclic amide derivatives were shown to undergo photochemical ring closure [8–11].



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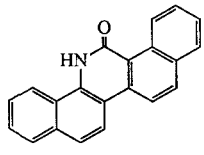

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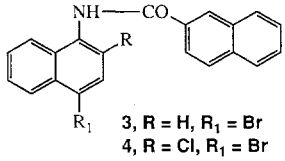
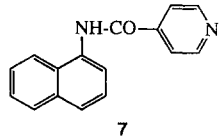


3, R = H, R_1 = Br
4, R = Cl, R_1 = Br
5, R = R_1 = H
6, R = R_1 = Cl



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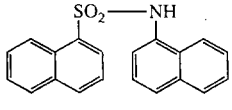

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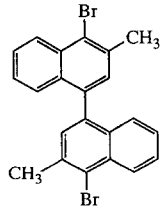

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We have prepared the necessary starting amides or sulfonamides from the corresponding aminonaphthalenes and acid chlorides. N-(1-Naphthyl)-1-naphthalene carboxamide (**1**) when treated with vanadium oxytrichloride in a solution of methylene chloride afforded in moderate yield the pentacyclic dibenzo[c,i]phenanthridin-14(13*H*)-one (**2**). A similar experiment with N-(4-bromo-1-naphthyl)-2-naphthalene-carboxamide (**3**) gave, however, not the cyclic product but instead a compound where a chlorine atom was introduced into the molecule. Preliminary results of an X-ray structure determination revealed that substitution occured at position 2 of the naphthylamine part. As shown in Fig. 1 the mean plain of both naphthalene rings are twisted to each other

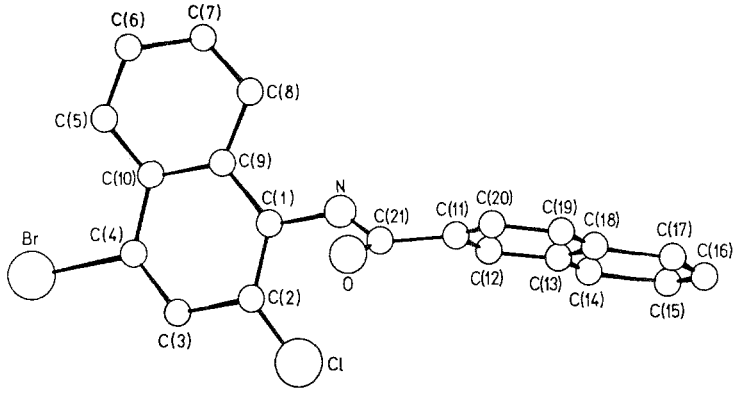

Fig. 1.

about 78 (1)°. Further refinement of the X-ray structure in still in progress and results will be published elsewhere. Substitution at position 2 is consistent with the greater activation of the naphthalene ring with an attached amino group rather than the other naphthalene, where a deactivating carbonyl group is present. The same type of reaction was observed with N-(1-naphthyl)-2-naphthalenecarboxamide (**5**). In this case, a dichloro compound (**6**) was obtained. The attempted cyclization of N-(1-naphthyl)-2-naphthalenecarboxamide (**7**) or N-(1-naphthyl)-1-naphthalenesulfonamide (**8**) gave no new products, only the starting material was recovered. Among simple substituted naphthalenes, oxidative dimerization with vanadium oxytrichloride was only successful for 1-bromo-2-methylnaphthalene, although 4,4′-dibromo-3,3′-dimethyl-1,1′-binaphthalene (**9**) was obtained in a low yield.

From these results, it appears that aromatic compounds with an acylamino group are less reactive in oxidative dimerization than those containing a phenolic hydroxyl group. This may be in part due to the observation that the hydroxyl group is involved in a complex formation with vanadium oxytrichloride or vanadium tetrachloride. After this first stage, the oxidative coupling occurs by a rearrangement of electrons in this complex [3]. However, it is not known whether oxidations occur by a two-electron or one-electron transfer from phenol to the metal center.

Attempts to induce photochemically new C—C bond formation failed. Photochemical experiments were performed on compounds **5** and **7** as well as with (3-chloropyridazinyl-6)-1-(or 2-)naphthyl ether. The last two compounds were recovered unchanged after 22 h of irradiation, whereas compounds **2** and **4** suffered extensive degradation. A GC separation of 6 product of the two reactions was attempted but no structure assignments could be made.

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Experimental

Melting points were determined in capillaries or on a *Kofler* hot plate m.p. apparatus. Mass spectra were recorded on a Hitachi-Perkin-Elmer RMU-6L spectrometer. Elemental analyses (C, H, N) were obtained on Perkin-Elmer CHN analyzer 240 C. For irradiation a Hanovia 679 A high pressure mercury lamp was used and gas chromatographic separations were made on a Varian 3400 instrument using a column with Chromosorb G mesh 100/120 impregnated with 10% silicon GE SE-30 (Applied Laboratories).

N-(1-Naphthyl)-2-naphthalenecarboxamide (**5**)

To a solution of 1.43 g of 1-naphthylamine in 20 ml of benzene and 1.0 g of triethylamine, a warm solution of 1.9 g of 2-naphthoyl chloride in 15 ml of benzene was added and the mixture was heated under reflux for 1 h. Upon cooling the product separated and was crystallized from benzene with addition of charcoal to give 1.8 g (61%) of colourless, crystals, m.p. 155–157 °C. MS (*m*/e): 297 (M^+).

$C_{21}H_{15}NO$ (297.34). Calcd. C 84.82 H 5.09 N 4.71.
Found C 84.49 H 5.51 N 4.96.

N-(1-Naphthyl)-1-naphthalenecarboxamide (**1**)

It was prepared in a similar manner as the above 2-naphthoyl analogue in 92% yield. The product was crystallized from a large quantity of benzene, m.p. 230–233 °C. MS (*m*/e): 297 (M^+).

$C_{21}H_{15}NO$ (297.34). Calcd. C 84.82 H 5.09 N 4.71.
Found C 84.72 H 5.44 N 4.77.

N-(4-Bromo-1-naphthyl)-2-naphthalenecarboxamide (**3**)

A solution of 4.44 g of 4-bromo-1-naphthylamine in 40 ml of benzene was treated with 2.0 g of triethylamine and a solution of 3.8 g of 2-naphthoyl chloride in 30 ml of benzene. The mixture was heated under reflux for 15 min and left aside for 1 h. Upon filtration the product was suspended in water, filtered and crystallized from ethanol with addition of some water. The pure compound (7.2 g, 95%) had m.p. 206–208 °C. MS (*m/e*): 376 (M^+). NMR (*DMSO-d*$_6$): δ 7.10 (m, 13 H), 8.32 (m, NH).

$C_{21}H_{14}BrNO$ (376.25). Calcd. C 67.03 H 3.75 N 3.72.
Found C 67.14 H 3.85 N 3.67.

N-(4-Bromo-2-chloro-1-naphthyl)-2-naphthalenecarboxamide (**4**)

A three necked flask, equipped with a magnetic stirrer and a condenser was flushed with nitrogen. A mixture of 3.76 g of **3** in 150 ml CH_2Cl_2 and 2 ml of trifluoroacetic acid was added to the flask. Using a syringe 1.73 ml of $VOCl_3$ was added through a septum to the stirring mixture. The resulting mixture was stirred at room temperature for 4 h. It was transferred into a separatory funnel and treated with a concentrated aqueous solution of $NaHCO_3$. The aqueous layer was separated and a suspension of the product was filtered from the remaining solvent. The product was suspended in water, left overnight and filtered. The obtained crystals (2.29 g, 56%) were crystallized from a large quantity of ethanol, m.p. 229–230 °C. MS (*m/e*): 411 (M^+).

$C_{12}H_{13}BrClNO$ (410.70). Calcd. C 61.40 H 3.19 N 3.41.
Found C 61.80 H 3.25 N 3.41.

Dibenzo[c,i]phenanthridin-14(13H)-one (**2**)

Compound **1** (0.891 g) was reacted as in the preceding example with $VOCl_3$. After 4 h under reflux, the workup and evaporation of the solvent, 0.65 g of crude material were obtained. The product was crystallized from xylene to give the pure product, m.p. 180 °C (dec.). MS (*m/e*): 295 (M^+).

$C_{21}H_{13}NO$ (295.32). Calcd. C 85.40 H 4.44 N 4.74.
Found C 85.22 H 3.90 N 4.22.

N-(2,4-Dichloronaphthyl)-2-naphthalenecarboxamide (**6**)

The same reaction procedure as described for the preparation of **4** from **3** was applied. The reaction mixture, consisting of 4 g of **5**, 160 ml of methylene chloride, 5 ml of trifluoroacetic acid and 4 ml of $VOCl_3$ was stirred and heated under reflux for 2.5 h and thereafter at room temperature for another 2.5 h. Upon the workup and evaporation of the solvent the residue was crystallized from xylene (8% yield), m.p. 260 °C. MS (*m/e*): 366 (M^+).

$C_{21}H_{13}Cl_2NO$ (366.24). Calcd. C 68.86 H 3.58 N 3.82.
Found C 68.48 H 3.22 N 3.98.

N-(1-Naphthyl)-4-pyridinecarboxamide (**7**)

A solution of 1.43 g of 1-naphthylamine in 30 ml of benzene and 2.02 g of triethylamine was stirred with 1.78 g of 3-picolyl chloride hydrochloride. The mixture was heated under reflux for 4.5 h and the hot reaction mixture was filtered.

Most of the product crystallized and was filtered and the filtrate was evaporated in vacuo to give some more material. The product was crystallized from benzene to give the pure compound (0.8 g, 32%), m.p. 157–159 °C. MS (*m*/e: 248 (M^+).

$C_{16}H_{12}N_2O$ (248.27). Calcd. C 77.40 H 4.87 N 11.28.
Found C 77.62 H 5.20 N 11.07.

N-(1-Naphthyl)-1-naphthalenesulfonamide (**8**)

To a solution of 5.72 g 1-naphthylamine in 50 ml of acetone and 4 ml of triethylamine, a solution of 9.12 g of 1-naphthalenesulfonyl chloride in 50 ml of acetone was added. The reaction mixture was heated under reflux for 3 h and left aside overnight at room temperature. The reaction mixture was treated with water to dissolve most of the solid material. Methylene chloride was added to extract the separated oily product which solidified. Upon filtration the product was crystallized from water (1.9 g, 14%), m.p. 220–225 °C (dec.). MS (*m*/e): 333 (M^+).

$C_{20}H_{15}NO_2S$ (333.39). Calcd. C 72.06 H 4.54 N 4.20.
Found C 71.81 H 4.88 N 4.10.

4,4'-Dibromo-3,3'-dimethyl-1,1'-binaphthalene (**9**)

A solution of 2.21 g of 1-bromo-2-methylnaphthalene in 50 ml of methylene chloride was treated with 1.73 ml of $VOCl_3$ under stirring in an atmosphere of nitrogen. After addition was complete the reaction mixture was heated under reflux for 4 h and left aside at room temperature overnight. After the usual workup and evaporation of the solvent, a brown residue was obtained which was crystallized several times from *n*-heptane to give a small quantity of the pure product (6 mg), m.p. 190–192 °C, identical with an authentic specimen (Ref. [12] gives m.p. 193–195 °C). MS (*m*/e): 440 (M^+).

$C_{22}H_{16}Br_2$ (440.16). Calcd. C 60.03 H 3.66.
Found C 60.28 H 3.99.

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