A Photochemical Synthesis of 11*H*-Benzo[*a*]carbazole

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11*H*-Benzo[*a*]carbazole was prepared from 5-acetamido-1,2,3,4-tetrahydronaphthalene in four steps. A Goldberg arylation followed by hydrolysis afforded *N*-phenyl-1,2,3,4-tetrahydro-5-naphthylamine (**3**). Photolysis of **3** produced 1,2,3,4-tetrahydro-11*H*-benzo[*a*]carbazole (**4**) which was converted to 11*H*-benzo[*a*]-carbazole by dehydrogenation with chloranil.

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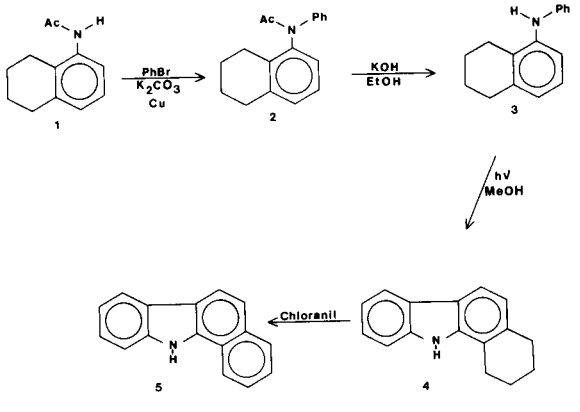
The photochemical dehydrocyclization of diarylamines to carbazole derivatives is a reaction which has been the subject of several mechanistic studies (2) and which has found occasional synthetic use. The reaction occurs to give good yields of carbazoles and can be applied to many substituted diphenylamines and heterocyclic analogs (3,4). One apparent limitation on the utility of the reaction is the observed failure of *N*-arylnaphthylamines (3,4) and some larger polycyclic derivatives (5) to undergo the photocyclization. The reasons for these differences in reactivity are not completely understood (6). We would like to report the synthesis of 11*H*-benzo[*a*]carbazole by an indirect route which circumvents this problem by carrying out the photocyclization step using a tetrahydronaphthylamine derivative. This tetrahydro compound (**3** in Scheme 1) might be expected to exhibit photochemical behavior more like that of a dialkyl diphenylamine than *N*-phenyl-1-naphthylamine. Since alkyl groups are known not to inhibit the photocyclization reaction a successful photochemical step would be anticipated. The synthesis of **3** and subsequent reactions leading to 11*H*-benzo[*a*]carbazole are outlined in Scheme 1.



1 2 3 5 4

Scheme 1

The starting point for the synthesis is 5-acetamido-1,2,3,4-tetrahydronaphthalene (**1**), a known compound which can be prepared from 1-naphthylamine by reduction using metallic sodium in amyl alcohol (7) followed by acetylation with acetic anhydride in benzene (8). Amide **1** was arylated by subjecting it to Goldberg reaction conditions. Thus, the reaction of **1** with copper foil and potassium carbonate in an excess of refluxing bromobenzene afforded *N*-Phenyl amide **2**. Compound **2** was isolated as a crystalline solid by column chromatography, however, it proved to be more convenient to hydrolyze **2** without prior purification. Hydrolysis in alcoholic potassium hydroxide produced diarylamine **3** as a colorless oil in a yield of 70% for the two steps.

As anticipated, **3** was found to photocyclize in the absence of an added oxidizing agent as was clearly indicated by the appearance in the ^{1}H nmr spectrum of a characteristic two hydrogen multiplet at 7.7-8.1 ppm. Irradiation for 5 hours of a 0.006*M* solution of **3** in nitrogen sparged methanol using a 450-W medium-pressure Hanovia lamp fitted with a Vycor sleeve ($\lambda > 230$ nm) afforded 1,2,3,4-tetrahydro-11*H*-benzo[*a*]carbazole (**4**) in a 65% yield (essentially 100% conversion). In the final step, dehydrogenation of **4** to produce 11*H*-benzo[*a*]carbazole (**5**) was effected by allowing the tetrahydro derivative to react with two equivalents of chloranil in refluxing xylene (41% yield). The structure of **5** was verified by comparison of physical and spectral properties with those described in the literature (9).

The synthesis just described should provide a general route to benzo[*a*]carbazole derivatives in yields which are comparable to most previously described procedures. Our route offers the additional advantage of affording the hitherto unknown 1,2,3,4-tetrahydro derivative **4** as a key intermediate. Work is currently in progress to extend the synthesis to other polycyclic carbazole derivatives.

EXPERIMENTAL

General.

Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are corrected. ^{1}H Nmr spectra were recorded on a Varian T-60 spectrometer. Chemical shifts are reported on the δ scale, parts per million downfield from a tetramethylsilane internal standard. Infrared spectra were recorded on either a Perkin-Elmer 457 or

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Beckman IR-8 spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

N-Phenyl-1,2,3,4-tetrahydro-5-naphthylamine (**3**).

A mixture of 1.0 g. (5.3 mmoles) of 5-acetamido-1,2,3,4-tetrahydronaphthalene (**1**), 0.6 g. of anhydrous potassium carbonate, a 1 × 1 cm. piece of freshly cleaned copper foil (10) and 5.0 ml. of bromobenzene was stirred magnetically for 44 hours at 155°. The mixture was then cooled and extracted with chloroform. The chloroform was evaporated and the excess bromobenzene was removed by steam distillation with 10 ml. of water. The crude amide was dried by azeotropic distillation with benzene and ethanol and hydrolyzed by heating at the reflux temperature for 16 hours with 1.0 g. of potassium hydroxide in 25 ml. of absolute ethanol. The ethanol was removed *in vacuo* and the resulting mixture was partitioned between water and chloroform. The aqueous phase was extracted with chloroform and the combined chloroform extracts were dried over anhydrous magnesium sulfate and evaporated. The product was purified by chromatography on a silica gel column (benzene eluent) to afford 0.83 g. (70%) of **3**; ^{1}H nmr (carbon tetrachloride): δ 1.6-2.0 (m, 4H), 2.3-2.9 (m, 4H), 4.9 (bs, 1H) and 6.5-7.3 (m, 8H); ir (neat): 3430, 700 and 755 cm^{-1}.

In one of the runs, the crude *N*-phenyl amide was subjected to chromatography on a silica gel column (chloroform eluent) followed by crystallization from petroleum ether to afford an analytical sample of **2**, m.p. 128-129°; ^{1}H nmr (carbon tetrachloride): δ 1.5-2.1 (multiplet with a singlet at 1.82, 7H), 2.3-3.0 (m, 4H) and 6.9-7.5 (m, 8H); ir (potassium bromide): 1670, 700, 730, 765 and 785 cm^{-1}.

Anal. Calcd. for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.71; H, 7.14; N, 5.28.

1,2,3,4-Tetrahydro-11*H*-benzo[*a*]carbazole (**4**).

A solution of 0.686 g. (3.08 mmoles) of **3** in 500 ml. of methanol was sparged with nitrogen for 20 minutes and irradiated for 5 hours with a 450-W medium-pressure Hanovia lamp fitted with a Vycor sleeve. The methanol was removed *in vacuo* and the product was purified by chromatography on an alumina column (benzene eluent) to afford 0.440 g. (65%) of **4**. The chromatographed product was recrystallized from benzene/petroleum ether, m.p. 164-165°; ^{1}H nmr (deuteriochloroform): δ 1.7-2.2 (m, 4H), 2.6-3.1 (m, 4H), 6.8-7.5 (m, 4H) and 7.7-8.1 (m, 2H); ir (Nujol): 3470, 740, 760, 775 and 825 cm^{-1}.

Anal. Calcd. for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33. Found: C, 87.02; H, 6.97; N, 6.28.

11*H*-Benzo[*a*]carbazole (**5**).

A solution of 0.190 g. (0.860 mmoles) of **4** and 0.430 g. (1.75 mmoles) of chloranil in 10 ml. of xylene was heated at the reflux temperature for 18 hours. After cooling, the mixture was diluted with ether and washed with 2M sodium hydroxide and water. The ether solution was dried over anhydrous magnesium sulfate and the solvents were evaporated. The product was purified by chromatography on an alumina column (benzene eluent) to afford 0.077 g. (41%) of **5**. The chromatographed product was recrystallized from benzene/petroleum ether, m.p. 226-227°, lit. (9) m.p. 227-228°; ^{1}H nmr (deuteriochloroform): δ 7.1-8.3 (m, 10H) and 8.8 (bs, 1H); ir (Nujol): 3450, 735 and 825 cm^{-1}.

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