# REACTION OF N-ARYLIDENE-2-NAPHTHYLAMINES WITH ALLYLACETONE

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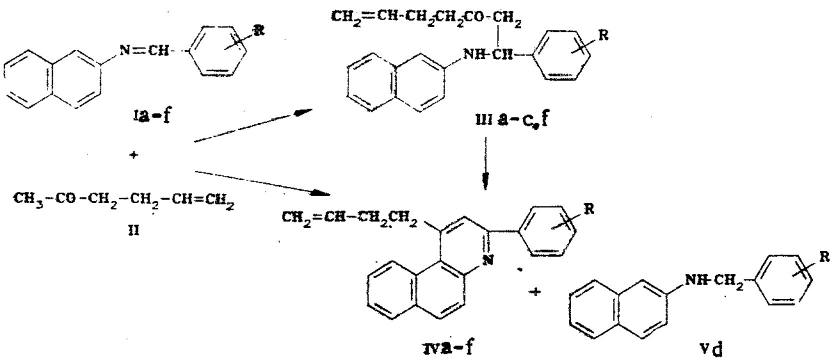
The reaction between N-arylidene-2-naphthylamines and allylacetone leads to the formation of 1,3-disubstituted benzo[f]quinolines having a butenyl radical in position 1. It is shown that the reaction proceeds via intermediate aminoketones — 1-(2-naphthylamine)-1-aryl-6-heptene-3-ones.

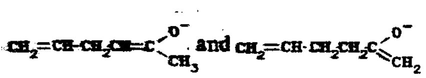
In an earlier paper [1], we reported the results of studies of the preparation and physicochemical properties of derivatives of benzo[f]quinoline; the present paper extends this to the condensation of N-arylidene-2-naphthylamines with allylacetone to form new benzo[f]quinolines having a butenyl radical in position 1 (see reaction scheme):



a R=H, b R=p-OCH$_3$, c R=p-F, d R=p-Br, e R=p-NO$_2$, f R=o-OH

The reaction was carried out be heating the starting materials in a solvent in the presence of a proton catalyst and an oxidizing agent. The characterisitcs of the compounds prepared are set out in Table 1.

It has been shown that the cyclic products are formed via intermediate aminoketones (III) (Table 1) in the formation of which a new C—C bond comes into being as a result of the reaction of an electrophilic, protonated azomethine group with a nucleophilic carbonyl compound. Here, allylacetone plays the part of the carbon nucleophile and, being an asymmetrical ketone, it contains two types of α-protons and hence can form two types of enolate-anion on deprotanation, A and B:


$$CH_2{=}CH{-}CH_2CH{=}C\begin{smallmatrix}O^-\\ CH_3\end{smallmatrix} \text{ and } CH_2{=}CH{-}CH_2CH_2C\begin{smallmatrix}O^-\\ CH_2\end{smallmatrix}$$

A, B

The proportion of the two possible anions depends on the reaction conditions [2]. It is known that separation of a proton takes place most easily on the least hindered C—H bond adjacent to the carbonyl group [3]. The enolate anion formed under the conditions of the reaction being studied was identified on the basis of the NMR spectra of the benzol[f]quinolines IV which were obtained (Table 2). The absence from the NMR spectra of signals for a methyl group leads one to conclude that detachment of a proton takes place from the methyl group in allylacetone and not from the methylene group, which evidently proves to be the more hindered on account of the steric hindrance resulting from the allyl fragment. A similar steric effect on the detachment of a proton has been reported in [4].

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TABLE 1. Characteristics of 1-(2-Naphthylamine)-1-aryl-6-heptene-3-ones (III) and 1-(Buten-3-yl)-3-arylbenzo[f]-quinolines (IV)

| Compound | mp, °C | UV spectrum, $\lambda_{max}$, nm (log ε) | Found, % |  |  | Empirical formula | Calculated, % |  |  | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | C | H | N (Br) |  | C | H | N (Br) |  |
| IIIa | 93—94 | 246 (4,69), 273 (3,85), 283 (3,97), 294 (3,94) | 83,7 | 7,0 | 4,2 | $C_{23}H_{23}NO$ | 83,8 | 7,0 | 4,2 | 55 |
| IIIb | 91—92 | 248 (4,73), 273 (4,04), 284 (4,13), 294 (4.09) | 80.1 | 7,0 | 4,0 | $C_{24}H_{25}NO_2$ | 80,2 | 7,0 | 3,9 | 44 |
| IIIc | 96—97 | 246 (4,64), 275 (3,89), 284 (3,96), 294 (3,91) | — | — | 3,8 | $C_{23}H_{22}NOF$ | — | — | 4,0 | 32 |
| IIIf | 151—152 | 245 (4,88), 275 (4,17), 284 (4,28), 294 (4,15) | 79,7 | 6,7 | 4,2 | $C_{23}H_{23}NO_2$ | 80,0 | 6,7 | 4,0 | 5 |
| IVa | 102—103 | 280 (4,59), 294 (4,37), 346 (3,67), 361 (3,67) | 89,3 | 6,2 | 4,6 | $C_{23}H_{19}N$ | 89,3 | 6,2 | 4,5 | 39 |
| IVb | 111—112 | 285 (4,64), 294 (4,58), 348 (3,95), 365 (3,98) | 85,2 | 6,2 | 4,1 | $C_{24}H_{21}NO$ | 84,9 | 6,2 | 4,1 | 35 |
| IVc | 97—98 | 279 (4,67), 294 (4,47), 345 (3,85), 362 (3,88) | — | — | 3,9 | $C_{23}H_{18}NF$ | — | — | 4,3 | 30 |
| IVd | 109—110 | 282 (4,74), 294 (4,58), 346 (3,90), 363 (3,93) | 71,2 | 5,0 | 3,5<br>(20,5) | $C_{23}H_{18}NBr$ | 71,1 | 4,7 | 3,6<br>(20,6) | 49 |
| IVe | 141—142 | 287 (4,44), 297 (4,43), 367 (4,08) | 77,6 | 5,2 | 7,6 | $C_{23}H_{18}N_2O_2$ | 77,9 | 5,1 | 7,9 | 28 |
| IVf | 97—98 | 267 (4,60), 282 (4,63), 294 (4,50), 353 (4,16), 370 (4,22) | 84,6 | 5,8 | 4,1 | $C_{23}H_{19}NO$ | 84,9 | 5,9 | 4,3 | 25 |

TABLE 2. Proton NMR Spectra of Benzo[f]quinolines IV

| Compound | Chemical shift, δ, ppm* |  |  |  |  |
|---|---|---|---|---|---|
|  | $>C{=}\underset{\vert}{C}{-}CH_2{-}$ | $>C{=}\underset{\vert}{C}{-}\overset{\vert}{\underset{\vert}{C}}{-}CH_2{-}$ | $H_2C{=}\underset{\vert}{C}{-}$ | $>C{=}CH{-}$ | C—H arom |
| IVa | 2,60 | 3,40 | 5,12 | 5,85 | 7,20—8,55 (12H) |
| IVb** | 2,47 | 3,33 | 5,07 | 5,92 | 6,72—8,41 (11H) |
| IVc | 2,52 | 3,35 | 5,05 | 5,82 | 6,87—8,50 (11H) |
| IVd | 2,45 | 3,30 | 5,05 | 5,90 | 7,27—8,35 (11H) |
| IVf | 2,47 | 3,30 | 5,12 | 5,90 | 6,57—8,32 (11 arom and OH) |

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*All protons gave chemical shifts in the form of multiplets.
**3.70 s ($OCH_3$).

On boiling in alcohol in the presence of concentrated hydrochloric acid, the aminoketones III were converted into the corresponding benzo[f]quinolines as a result of electrophilic attack by the carbonyl group of the aminoketone on the α-position of the naphthalene nucleus.

The structure of the compounds which we prepared was unequivocally established by elemental analysis, IR, UV, and NMR spectroscopy, and mass spectrometry. There are absorption bands in the IR spectra of the aminoketones III for carbonyl (1715-1700 cm$^{-1}$) and aminogroups (≈3400 cm$^{-1}$) which are absent from the spectra of compounds IV, confirming the cyclization of the aminoketones. In compound IIIf (R = OH) these peaks are found to be shifted into a lower frequency region (1630 and 3270 cm$^{-1}$, respectively) apparently on account of hydrogen bonding. In the IR spectra of the benzo[f]quinolines there are characteristic bands for stretching and bending vibrations of the heteroaromatic nucleus [5], and a band at 1620-1637 cm$^{-1}$ due to C=C exocyclic. A band at ≈840 cm$^{-1}$ is evidence of the angular connection of the rings. The position of the substituents in the benzene ring is confirmed by the presence of bands in the region of 760-755 and 705, 830-825 cm$^{-1}$ in the IR spectra of the benzo[f]quinolines; these are characteristic for mono- and 1,4-disubstituted benzene [7].

The electronic absorption spectra of compounds IV are typical of benzo[f]quinolines [8]. They include β-, p-, and α-bands, the latter having vibrational character (Table 1). The introduction of substituents has little or no effect on the position and intensity of the absorption bands. The nitro group is an exception, its introduction leading to the disappearance of the vibrational structure of the α-band. The UV spectra of the aminoketones differ considerably from those of the benzo[f]quinolines and are similar to the spectra of 2-naphthylamine which points to the absence of conjugation in these compounds.

From an examination of the mass spectra of the benzo[f]quinolines one can evaluate the resistance of these compounds to electron bombardment, their spectra being characterized by a small number of intense diagnostic peaks. All the benzo[f]quinolines which we prepared showed typical allyl breakdown with the formation of the ion peak $[M-CH_2-CH=CH_2]^+$. Peaks for the ions $[M-R]^+$ and $[M-Ar]^+$ are also present, formed as a result of elimination of the R substituent and the whole of the aryl substituent from position 3. The appearance of ion peaks $[M-CH_3O]^+$, $[M-CH_2O]^+$, and $[M-CHO]^+$ in the spectrum of compound IVb is evidence of the presence of the $OCH_3$ group. The presence of nitro and hydroxy groups in compounds IVe and f is confirmed by the formation of ion peaks $[M-H-NO_2]^+$, $[M-NO]^+$, and $[M-OH]^+$, respectively. The presence of an isotopic peak for ions $[M+2]^+$ and $[M-Br]^+$ confirms the presence of bromine in compound IVd.

## EXPERIMENTAL

Infrared spectra were run on a UR-20 instrument using KBr disks, and UV spectra on a Specord UV-Vis spectrophotometer in ethanol. A Varian MAT-311 mass spectrometer was used to obtain the mass spectra, the samples being directly introduced into the ion source with an ionization energy of 70 eV. The volatilization temperature was 100°C. NMR spectra were obtained on a Bruker WM-360 (360 MHz) instrument using 10% deuterochloroform solutions and TMS as internal standard.

1-(2-Naphthylamine)-1-aryl-6-heptene-3-one (IIIa-c, f). A mixture of 0.01 mole compound I, 0.04 mole compound II, 40-60 ml ethanol (in the case of IIIf, 5 ml DMF), and 1 drop conc. HCl was heated to 60-70°C and kept for 24 h at room temperature (in the case of IIIb, heated 1 h on a boiling-water bath). The reaction mixture was cooled, and the precipitated solid removed by filtration and neutralized with 25% aqueous ammonia to yield compounds IIIa-c.

For the ketone IIIf, the reaction mixture was evaporated somewhat and the benzo[f]quinoline IVf separated out. The mother liquor was evaporated and compound IIIf filtered off. The aminoketones IIIa-c and f were recrystallized from isopropanol.

1-(Buten-3-yl)-3-arylbenzo[f]quinolines (IVa-f). A mixture of 0.01 mole compound I, 0.04 mole compound II, 60 ml ethanol, 8 drops conc. HCl, and 20 drops nitrobenzene (for IVf, 5 ml DMF, 8 drops conc. HCl) was heated for 2 h on a boiling-water bath (IVf, 5 h) and cooled; the precipitate was removed by filtration, neutralized with 25% aqueous ammonia, and recrystallized from isopropanol.

In the case of IVd, 2-naphthyl(p-bromobenzyl)amine Vd separated from the mother liquor. This had mp 110-111°C (from isopropanol); literature [9], mp 110-111°C.

Cyclization of the Aminoketones IIIa-c. An alcoholic solution of 0.01 mole aminoketone III, and 4 drops conc. HCl was heated 30 min on a boiling-water bath. The reaction mixture was cooled, the precipitate filtered off and neutralized with 25% aqueous ammonia to yield compounds IVa-c.

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