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INVESTIGATION ON 2,3'-BIQUINOLYL SERIES.

21.* REACTIONS OF 1'-ALKYL-4'-ARYL-1',4'-DIHYDRO-2,3'-BIQUINOLYLS AND 1'-ALKYL-2'-ARYL-1',2'-DIHYDRO-2,3'-BIQUINOLYLS WITH SULFUR

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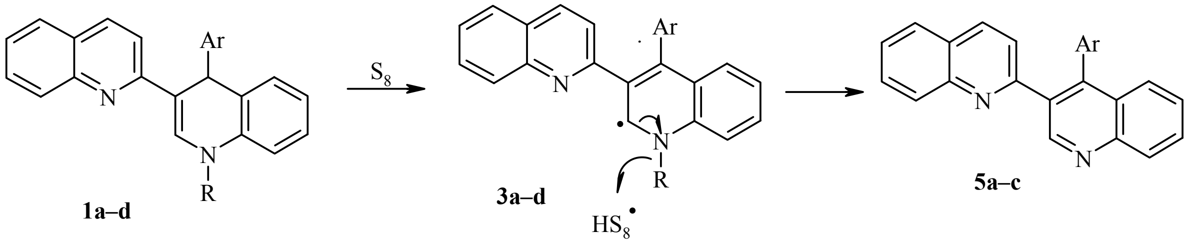
A method has been developed for the synthesis of 2'- and 4'-aryl-2,3'-biquinolyls based on the reaction of 1'-alkyl-2'-aryl-1',2'-dihydro-2,3'-biquinolyls and 1'-alkyl-4'-aryl-1',4'-dihydro-2,3'-biquinolyls with sulfur in DMF.

Keywords: 2,3'-biquinolyls, 1',2'-dihydro-2,3'-biquinolyls, 1',4'-dihydro-2,3'-biquinolyls, sulfur, desalkylation, oxidation.

In a continuation of our study of the reactions of 2,3'-biquinolyls with sulfur [2-6] we have examine the reactions of 1'-alkyl-4'-aryl-1',4'-dihydro-2,3'-biquinolyls **1** and 1'-alkyl-2'-aryl-1',2'-dihydro-2,3'-biquinolyls **2** with this reagent.

It is known that sulfur forms a donor-acceptor complex with amines [7], full transfer of an electron in which leads to an $R_3N^{+\cdot}S_8^{-\cdot}$ ion radical pair [8]. Cation radicals generally undergo fission of a proton [9] and this is observed, in particular, in the oxidation of dihydropyridines (quinolines). The reaction of the radicals formed is governed by the electronic and steric effects of the R substituent. Hence we have shown before that in the thiolation of 1'-alkyl-1',4'-dihydro-2,3'-biquinolyls both complex formation [5, 6] and steric factors [5] are significant.



1 a-c R = Me, **d** R = CH_2CHCH_2; **1**, **5 a** Ar = Ph, **b** Ar = 1-$C_{10}H_7$, **c**, **d** Ar = 3-indolyl

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* For Communication 20 see [1].

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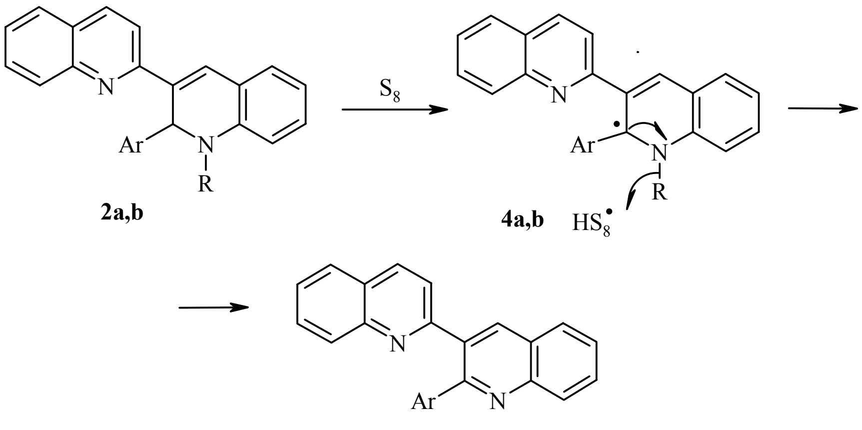

2a,b **4a,b** **6a,b**

2 a, **b** R = Me; **2**, **6 a** Ar = Ph, **b** Ar = 1-C$_{10}$H$_7$

We have proposed that the reactions of compounds **1** and **2** with sulfur also lead to the corresponding radicals **3** and **4**. However, because of steric hindrance due to 2'-aryl, 4'-aryl, and 3-quinolyl the process is completed by the transition of the 1'-alkyl to the S-radical [10]. Thus the final reaction products are the 2'- and 4'-aryl-2,3'-biquinolyls **5** and **6**.

In fact, the reaction of the dihydro derivatives **1a-d** and **2a,b** with sulfur gives the corresponding arylbiquinolyls **5a-c** and **6a,b** in 21-57% yields.

These results can be explained in the following way. It is known that steric factors can affect a competitive SET and polar mechanism. In compounds **2a,b** there is steric hindrance to the approach of the S-radical to the 1'-methyl on the 2' substituent side. This decreases the likelihood of a one electron transfer and favors a radical process. The reactions of **2a,b** with sulfur give complex mixtures of substances from which compounds **6a,b** are separated with difficulty and in low yields.

The increase in yield upon desalkylation of 4'-(3-indolyl) derivatives **1c,d** when compared with the 4'-phenyl derivative **1a** can be explained by the π-donor effect of the indolyl substituent. As a result this eases both the formation of the π -complexes and the subsequent electron transfer.

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Bruker WP-200 (200 MHz) instrument using CD$_3$CN solvent and TMS internal standard. Mass spectra were taken on an MAT-311A instrument. IR spectra were recorded on a Hitachi 215 instrument. Monitoring of the reaction course and the purity of the synthesized compounds was carried out on Silufol UV-254 plates using ethyl acetate–petroleum ether (1:1).

Compounds **1** and **2** were prepared by methods in [11, 12].

Dehydrogenation of the Dihydrobiquinolyls 1 and 2 by Sulfur (General Method). A mixture of 1'-R-2'-aryl-1',2'-dihydro- or 1'-R-4'-aryl-1',4'-dihydro-2,3'-biquinolyl (2 mmol) and elemental sulfur (0.1 g, 3 mmol) was refluxed in DMF (10 ml) for 3 h. The reaction mixture was cooled and poured into water (100 ml). The precipitate was filtered off, washed with water, and dried.

4'-Phenyl-2,3'-biquinolyl (5a, C$_{24}$H$_{16}$N$_2$) was prepared from 1'-methyl-4'-phenyl-1',4'-dihydro-2,3'-biquinolyl. Yield 35%; mp 133-134°C (benzene) (mp 133-134°C [13]). The ^{1}H NMR spectrum agreed with that given in [13].

4'-(1-Naphthyl)-2,3'-biquinolyl (5b, $C_{28}H_{18}N_2$) was prepared from 1'-methyl-4'-(1-naphthyl)-1',4'-dihydro-2,3'-biquinolyl. Yield 42%; mp 158-159°C (benzene–hexane) (mp 158-159°C [13]). The ^{1}H NMR spectrum agreed with that given in [13].

4'-(3-Indolyl)-2,3'-biquinolyl (5c) was prepared from 4'-(3-indolyl)-1'-methyl-1',4'-dihydro-2,3'-biquinolyl (53% yield) and from 1'-allyl-4'-(3-indolyl)-1',4'-dihydro-2,3'-biquinolyl (46% yield); mp 173-175°C (benzene–hexane). IR spectrum (KBr tablet), ν, cm^{-1}: 3210 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.88 (1H, dd, $J_{4'',5''}$ = 7.95, $J_{5'',6''}$ = 7.77, H-5'); 7.06 (1H, d, $J_{3,4}$ = 8.97, H-3); 7.08 (1H, d, $J_{4'',5''}$ = 7.95, H-4"); 7.13 (1H, dd, $J_{5'',6''}$ = 7.7, $J_{6'',7''}$ = 7.56, H-6"); 7.24 (1H, d, $J_{2''\text{-NH}}$ = 2.56, 2"-H); 7.48 (1H, d, $J_{6'',7''}$ = 7.56, H-7"); 7.55 (1H, dd, $J_{5,6}$ = 8.06, $J_{6,7}$ = 7.11, H-6); 7.56 (1H, d, $J_{5',6'}$ = 8.29, H-5'); 7.80 (4H, m, H-4,6',7,7'); 7.96 (1H, d, $J_{5,6}$ = 8.06, H-5); 8.11 (1H, d, $J_{7',8'}$ = 8.45, H-8'); 8.20 (1H, d, $J_{7,8}$ = 8.24, H-8); 9.31 (1H, s, H-4'); 9.64 (1H, br. d, $J_{2''\text{-NH}}$ = 2.56, NH). Mass spectrum (70 eV), *m/z* (I_rel, %): 371 $[M]^+$ (82), 370 [M-1] (100). Found, %: C 84.14; H 4.57; N 11.29. $C_{26}H_{17}N_3$. Calculated, %: C 84.07; H 4.61; N 11.31.

2'-Phenyl-2,3'-biquinolyl (6a, $C_{24}H_{16}N_2$) was prepared from 1'-methyl-2'-phenyl-1',2'-dihydro-2,3'-biquinolyl. Yield 24%; mp 76-77°C (benzene–hexane) (mp 76-77°C [14]). The ^{1}H NMR spectrum agreed with that given in [14].

2'-(1-Naphthyl)-2,3'-biquinolyl (6b, $C_{28}H_{18}N_2$) was prepared from 1'-methyl-2'-(1-naphthyl)-1',2'-dihydro-2,3'-biquinolyl. Yield 21%; mp 77-78°C (benzene–hexane) (mp 77-78°C [14]). The ^{1}H NMR spectrum agreed with that given in [14].

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