

Homolytic Aromatic Substitution by Heterocyclic Free Radicals. Reaction of 3-Quinolyl and 8-Quinolyl Radicals with Aromatic Compounds.

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Free radicals obtained from 3- and 8-aminoquinolines were studied in various aromatic substrates. Isomer percent, reaction yields, and overall reactivities towards benzene are recorded.

Most of the heterocyclic radicals studied in the literature are monocyclic (1,2,3,4,5,6). We wish to report results dealing with bicyclic free radicals: 3-quinolyl and 8-quinolyl radicals.

EXPERIMENTAL

These radicals were obtained by decomposition of 3- and 8-aminoquinolines with isoamyl nitrite in an appropriate aromatic substrate. The general procedure of this reaction has been described in several papers (7,8,9,10,11). The reaction products were first separated by tlc and then analyzed by glc/ms. (Varian Mat III, 80 eV).

An example of general work up for quinolylation is the following: 3-aminoquinoline (0.36 g., 0.0025 mole) was dissolved in 10 ml. of substrate. Isoamyl nitrite (1 g., 0.0084 mole) was then added, and the mixture was kept for 4 hours at 70° with stirring. After the reaction, the substrate was distilled under vacuum and the residual material analyzed. In competitive experiments 0.0025 mole of benzene and 0.0025 mole of substrate were allowed to react with 0.0012 mole of amine and 0.0042 mole of nitrite. In this case the substrates were not distilled off at the end of the reaction, the crude products being separated from the reaction mixture by preparative tlc and further analyzed by glc/ms.

I Isomer Ratio and Reaction Yields

Substrates	3-Quinolylation				8-Quinolylation			
	62	21	17	35%	62	20	19	25%
Toluene	62	21	17	35%	62	20	19	25%
<i>t</i> -Butylbenzene	20	53	27	38%	25	51	23	25%
Chlorobenzene	56	25	19	35%	46	28	26	27%
Benzonitrile	53	14	23	33%	45	14	41	24%
Anisole	71	14	15	36%	70	10	20	29%

The results are given in the order *o*, *m*, *p*. The approximation is ± 1.5 of the mean value.

II Overall Reactivity Towards Benzene

Substrates	3-Quinolylation		8-Quinolylation		Phenyl (5,12)
	1.65	1.65	1.5	1.5	
Toluene	1.65	1.65	1.5	1.5	1.65
Chlorobenzene	1.15	1.15	1.0	1.0	1.65
Benzonitrile	2.8	2.8	2.7	2.7	3.5
Anisole	3	3	2.9	2.9	1.85

III Unusual Fragmentation of 8-Arylquinolines

Compounds	x	Molecular weight	M+ - x	i%	M+	i%
8- <i>o</i> -Tolyl	CH ₃	15	204	100	219	42
8- <i>o</i> -Chloro-phenyl (a)	Cl	35	204	100	239	5
8- <i>o</i> -Methoxy-phenyl	<i>o</i> -CH ₃	31	204	100	235	4
8-Phenyl	H	1	204	100	205	42

(a) Same for Cl = 37

The 3-arylquinolines showed the usual fragmentation of this heterocycle (14), but, in the case of the 8-arylquinoline substituted by x on the phenyl ring, an unusual fragmentation was observed.

IV Discussion.

The preceding results (overall reactivities) show that the quinolyl radicals are electrophilic, but less so than the monocyclic radical [eg. the pyridyl radical (13)]. The yields of the reaction were close to 30% towards the amine, and they were better than those obtained from the Gomberg reaction with the same amine and substrates (20 to 15%). This method may then be used to prepare 3- or 8-arylquinolines.

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