The reaction of o-phenylenediamine with phenacyldimethylsulfonium iodide gave 2-phenylquinoxaline. The same reaction by use of 3,4-diaminotoluene and 1,2-diamino-4-chlorobenzene instead of o-phenylenediamine afforded a mixture of the corresponding 6- and 7-substituted 2-phenylquinoxalines. In the case of 1,2-diamino-4-nitrobenzene, 6-nitro-2-phenylquinoxaline was obtained. On the other hand, the reaction of 1,2-diamino-4-methoxybenzene and phenacyldimethylsulfonium iodide gave 7-methoxy-2-phenylquinoxaline. Furthermore, condensation of maleonitrile with phenacyldimethylsulfonium iodide gave 2,3-dicyANO-6-phenylpyrazine.

Sulfonium salts are widely used as one of significant and versatile intermediates in organic synthesis. The reaction of phenacyldimethylsulfonium bromide with primary aromatic amines provides the useful method for the synthesis of 2-phenylindoles (Scheme 1). We examined the similar reaction by use of o-phenylenediamine.

\[
\begin{array}{c}
\text{C}_6\text{H}_5\text{C}-\text{CH}_2\text{S}\text{CH}_3\text{Br}^- + \begin{array}{c} \text{R}_1 \\
\text{NH}_2
\end{array}
\text{C}_6\text{H}_5\text{N(C}_2\text{H}_5)_2
\end{array}
\xrightarrow{\Delta}
\begin{array}{c}
\text{R}_1 = \text{H}, \text{CH}_3, \text{F}; \text{R}_2 = \text{H}, \text{CH}_3
\end{array}
\]

Scheme 1
diamine (R2-NH2 in Scheme 1) and phenacyldimethylsulfonium iodide in the expect-
ation that 2-phenylquinoxaline would be formed instead of 7'-aminoindole. We wish
to report these results in this paper.

α-Phenylenediamine (1a) was heated in ethanol under reflux in the presence of
one equiv. of phenacyldimethylsulfonium iodide (2) for 2 hr to afford 2-phenyl-
quinoxaline (3a) in 27% yield, mp 75-77 °C (lit. mp 77 °C) as expected, though
in low yield. It is of interest to examine whether 6-substituted 2-phenylquinoxa-
line or the corresponding 7-isomer would be obtained on treatment of 4-substi-
tuted 1,2-diaminobenzene with 2. Treatment of 3,4-diaminotoluene (1b) with 2 in
ethanol as above yielded a mixture of 6-methyl-2-phenylquinoxaline (3b; 14 %),
mp 77-79 °C (lit. 79 °C) and 7-methyl-2-phenylquinoxaline (3c; 14 %), mp 133-
136 °C (lit. 136 °C) without positional selectivity. The structures of these
products were confirmed by conversion to the corresponding N4-oxides (4a) and
(4b), respectively by oxidation with m-chloroperbenzoic acid (m-CPBA) as Mannore
and Kano reported. These position isomers were easily distinguished by the
observation of the aromatic proton signals in their 1HNMR spectra. The reac-
tion of 1,2-diamino-4-chlorobenzene (1c) with 2 under the similar conditions gave
a mixture of 6-chloro-2-phenylquinoxaline (3d) and 7-chloro-2-phenylquinoxala-
line (3e) in 27 % yield; this has led to a mixture of the corresponding N4-oxides (4c)
and (4d) by oxidation with m-CPBA to determine the structures and the
ratio of 3d and 3e, since it was difficult to distinguish the isomers of these
parent bases from their 1HNMR spectra. The ratio of 3d and 3e was easily confirm-
ed as 1:2 by the observation of the aromatic proton signals in the 1HNMR spectra
of 4c and 4d as above. In the case of 1,2-diamino-4-nitrobenzene (1d) and 1,2-
diamino-4-methoxybenzene (1e), the reaction proceeded with the positional select-
ivity. Condensation of 1d with 2 as above gave 6-nitro-2-phenylquinoxaline (3f)
in 30 % yield without formation of the corresponding 7-isomer, mp 208-210 °C
(lit. mp 209-210 °C). On the other hand, the reaction between 1e and 2 afforded
7-methoxy-2-phenylquinoxaline (3g), mp 86-88 °C (lit. mp 86-88 °C). These
products were easily distinguished from alternative possible isomers by oxidation
to N4-oxides (4e) and (4f) with m-CPBA, respectively. The positionally selective
synthesis of disubstituted quinoxaline derivatives (3f) and (3g) most probably
proceeds by preferential reaction of the α-methylene carbon of the sulfonium salt
with more basic amino group in 1d and 1e (Scheme 2).
Successively we examined the condensation of diaminomaleonitrile (5) with 2. Diaminomaleonitrile was heated with 2 in ethanol for 2 hr to yield 2,3-dicyano-6-phenylpyrazine (6) in 72% yield, mp 168-169 °C (lit.9 170 °C) (Scheme 3).
References and Notes

3 Prepared by methylation of α-methylthioacetophenone with methyl iodide in methanol under mild reflux for 2 hr, mp 207-209 °C.
5 E. Leilmann and A. Donner, Ber., 23, 166 (1890).

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