# Preparation of 2,5-Bis(alkylamino)-3,6-dimethoxy-*p*-benzoquinones

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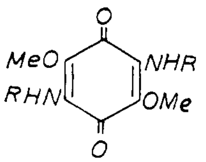
**The properties and method of preparation of several 2,5-bis(alkylamino)-3,6-dimethoxy-*p*-benzoquinones are described.**

REACTION of tetramethoxyquinone with primary amines yielded 2,5-bis(alkylamino)-3,6-dimethoxy-*p*-benzoquinones of general formula I. The scope of the reaction has



I

been previously discussed (*2*). Table I summarizes the preparation and properties of several other members of this series. The reactions proceeded smoothly in methanol at reflux temperature. Approximately 30 ml. of methanol per gram of tetramethoxyquinone was used. Usually a ratio of 4 moles of amine to 1 mole of tetramethoxyquinone was sufficient to produce complete reaction. Purity of the compounds was established by thin-layer chromatography and by elemental analysis. The compounds moved as a single spot on silica, and their analysis was within the acceptable range.

Table I. Characterization of 2,5-Bis(alkylamino)-3,6-dimethoxy-*p*-benzoquinones

| Amine | M.P., ° C. | Formula | Calcd., % C | Calcd., % H | Found, % C | Found, % H | Color | Reflux, Hr. | Crystal. Solvent | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|
| Furfuryl | 147 | $C_{18}H_{18}N_2O_6$ | 60.3 | 5.1 | 60.2 | 5.2 | Black | 10 | EtOH | 78 |
| Cyclohexyl | 165–190[a] | $C_{20}H_{30}N_2O_4$ | 66.3 | 8.3 | 66.2 | 8.4 | Green | 1 | EtOH | 90 |
| Benzyl | 213 | $C_{22}H_{22}N_2O_4$ | 69.8 | 5.9 | 69.5 | 6.0 | Black | 0.1 | $CHCl_3$ | 90 |
| α-Phenylethyl | 183 | $C_{24}H_{26}N_2O_4$ | 70.9 | 6.4 | 70.9 | 6.5 | Black | 21 | Acetone | 88 |
| β-Phenylethyl | 192 | $C_{24}H_{26}N_2O_4$ | 70.9 | 6.4 | 70.7 | 6.4 | Violet | 0.3 | $C_6H_6$ | 92 |
| *o*-Toluidine | 235 | $C_{22}H_{22}N_2O_4$ | 69.8 | 5.9 | 69.8 | 5.9 | Green | 144 | EtOH | 14 |
| *m*-Toluidine | 250 | $C_{22}H_{22}N_2O_4$ | 69.8 | 5.9 | 69.7 | 5.7 | Black | 20 | $CH_2Cl_2$ | 85 |
| *o*-Ethylaniline | 196 | $C_{24}H_{26}N_2O_4$ | 70.9 | 6.4 | 70.8 | 6.6 | Green | 117 | EtOH | 11 |
| *p*-Ethylaniline | 203 | $C_{24}H_{26}N_2O_4$ | 70.9 | 6.4 | 71.0 | 6.6 | Green | 21 | EtOH | 86 |
| *o*-Phenetidine | 183 | $C_{24}H_{26}N_2O_6$ | 65.7 | 6.0 | 65.9 | 6.0 | Black | 53 | EtOH | 50 |
| *p*-Phenetidine | 263 | $C_{24}H_{26}N_2O_6$ | 65.7 | 6.0 | 65.5 | 5.8 | Black | 15 | Dioxane | 93 |
| 2,3-Dimethylaniline | 254 | $C_{24}H_{26}N_2O_4$ | 70.9 | 6.4 | 71.1 | 6.5 | Green | 87 | $C_6H_6$ | 18 |

[a] Decomposes.

The auxochromic effect of amino groups, which deepens the color of these quinones, has been commented on in detail elsewhere (*1*, *3*). Ultraviolet absorption maxima of quinones derived from aromatic amines occur at longer wavelength than the maxima of quinones derived from aliphatic amines. The spectra of the aliphatic aminoquinones show absorptions at 220 mμ($\epsilon$ = 25,000) and 369 mμ($\epsilon$ = 20,000), while the spectra of the aromatic aminoquinones show absorptions at 260 mμ($\epsilon$ = 25,000) and 400 mμ($\epsilon$ = 17,000). The infrared spectra of these and related compounds (*1*, *2*) show absorption at 3.0 microns (N—H) and at 6.1 and 6.4 microns (quinone). Infrared spectra were obtained on a Perkin-Elmer Infracord, Model 137; ultraviolet spectra were obtained on a Bausch and Lomb Spectronic 505.

## LITERATURE CITED

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# Tetrachloroethyl and Trichlorovinyl Thiolsulfonate Esters

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**Trichlorovinyl and tetrachloroethyl thiolsulfonates have been prepared by treating sodium and zinc sulfinates with tetrachloroethanesulfenyl chloride. The resulting compounds are generally mixtures of the trichlorovinyl and tetrachloroethyl forms and are purified with difficulty by thin-layer chromatography. Infrared and NMR spectra are given.**

TRICHLOROMETHYL thiolsulfonates (*1*, *2*) are the only thiolsulfonate esters that have been reported with halogen substitution in the *S*-alkyl grouping. Tetrachloroethanesulfenyl chloride was shown to react with various nucleophiles—e.g., sodium phthalimide and sodium cyanide (*3*)—and has been employed here to produce new halogen-substituted *S*-alkyl thiolsulfonates.

In the above report (*3*) of the reaction of tetrachloroethanesulfenyl chloride with salts of phthalimide or tetrahydrophthalimide, it was noted that *N*-trichlorovinylthio-