# SYNTHESIS AND ULTRAVIOLET SPECTRA
# OF SUBSTITUTED AMINOMETHYLENEQUINONES

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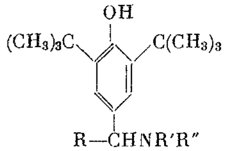
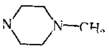
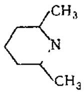
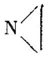
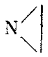
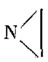
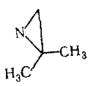
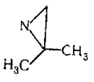
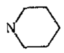
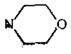
UDC 542.91+543.422.6+547.567

In an earlier report [1] we showed the theoretical feasibility of obtaining substituted methylenequinones containing an amino group at the double bond of the methylene group. Continuing this work, we have synthesized a number of α-alkyl(phenyl)-α-dialkylamino-2,6-di-tert-butylmethylenequinones (I)-(XIII) and studied the effect of electron reaction of the amino group with the conjugated bonds of methylenequinone; this study was based on the UV spectra of these compounds. The latter were synthesized from the corresponding alkyl-substituted methylenequinones by addition of secondary amines, followed by oxidation of α-alkyl-4-hydroxy-3,5-di-tert-butylbenzylamines with potassium ferrocyanide in alkali (see scheme on p. 1533).

TABLE 1. 4-[(α-Alkyl-α-dialkylamino)-methyl]-2,6-di-tert-butylphenols



| Cpd. No. | R | NR'R" | mp, °C | Yield, % | Empirical formula | Found, % |  | Calculated,% |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | C | H | C | H |
| XIV | H |  | 91—93 | 88 | $C_{20}H_{34}ON_2$ | 75,56<br>75,64 | 10,84<br>10,81 | 75,41 | 10,72 |
| XV | H |  | 100—102 | 82 | $C_{22}H_{37}ON$ | 79,81<br>79,73 | 11,26<br>11,08 | 79,68 | 11,25 |
| XVI | H |  | 148—150* | 77 | $C_{17}H_{27}ON$ | 78,22<br>78,12 | 10,54<br>10,42 | 78,11 | 10,41 |
| XVII | $CH_3$ |  | 89—91 | 85 | $C_{18}H_{29}ON$ | 78,64<br>78,59 | 10,72<br>10,78 | 78,52 | 10,61 |
| XVIII | $C_6H_5$ |  | 95—98 | 88 | $C_{23}H_{31}ON$ | 82,03<br>81,96 | 9,33<br>9,30 | 81,83 | 9,26 |
| XIX | $CH_3$ |  | 19—21 | 66 | $C_{20}H_{33}ON$ | 79,36<br>79,20 | 10,87<br>10,95 | 79,18 | 10,91 |
| XX | $C_6H_5$ |  | 83—84 | 71 | $C_{25}H_{35}ON$ | 82,24<br>82,17 | 9,81<br>9,76 | 82,12 | 9,70 |
| XXI | $C_6H_5$ |  | 150—151 | 88 | $C_{26}H_{37}ON$ | 82,31<br>82,41 | 9,84<br>9,97 | 82,26 | 9,82 |
| XXII | $C_6H_5$ |  | 131—132 | 93 | $C_{25}H_{35}O_2N$ | 78,94<br>78,81 | 9,37<br>9,41 | 78,72 | 9,28 |

* Literature data [5]: mp 148-150°.

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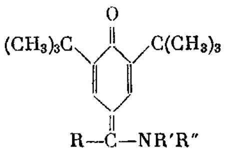
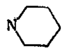
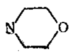
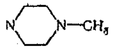
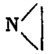
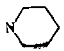
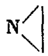
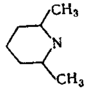
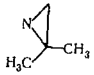
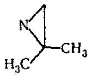
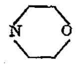
Institute of Chemical Physics, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1592-1596, July, 1967. Original article submitted January 4, 1967.

TABLE 2. α-Alkyl(phenyl)-α-dialkylamino-2,6-di-tert-butylmethylenequinones



| Cpd. No. | R | NR′R″ | mp, °C | $\lambda_{max}$, mμ | log ε | Yield, % | Empirical formula | Found, % |  | Calculated, % |  |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  |  | C | H | C | H |
| I | H | $N(CH_3)_2$ | 173—175 | 380 | 4,49 | 83 | $C_{17}H_{27}ON$ | 78,13; 78,23 | 10,83; 10,66 | 78,11 | 10,45 |
| II | H |  | 170—171* | 380 | 4,53 | 80 | — | — | — | — | — |
| III | H |  | 165—168 | 375 | 4,39 | 87 | $C_{19}H_{29}O_2N$ | 75,34; 75,43 | 9,82; 9,75 | 75,25 | 9,63 |
| IV | H |  | 167—169 | 380 | 4,58 | 74 | $C_{20}H_{32}ON_2$ | 76,12; 76,14 | 10,34; 10,21 | 75,91 | 10,20 |
| V | H |  | 99—100 | 352 | 4,41 | 64 | $C_{17}H_{25}ON$ | 78,91; 78,94 | 9,83; 9,72 | 78,66 | 9,71 |
| VI | $CH_3$ |  | 104—106 | 365 | 4,43 | 59 | $C_{18}H_{27}ON$ | 79,15; 79,25 | 9,83; 9,81 | 79,09 | 9,94 |
| VII | $C_6H_5$ |  | 190—191 | 425 | 4,49 | 81 | $C_{26}H_{35}ON$ | 83,03; 82,84 | 9,51; 9,44 | 82,73 | 9,34 |
| VIII | $C_6H_5$ |  | 109—110 | 370 | 4,47 | 66 | $C_{23}H_{29}ON$ | 82,46; 82,34 | 8,93; 8,87 | 82,35 | 8,76 |
| IX | H | $N(C_2H_5)_2$ | 133—134 | 325 | 4,35 | 71 | $C_{19}H_{31}ON$ | 79,13; 79,01 | 10,93; 10,92 | 78,84 | 10,80 |
| X | H |  | 122—125 | 325 | 4,34 | 72 | $C_{22}H_{35}ON$ | 79,98; 80,11 | 10,57; 10,62 | 80,17 | 10,71 |
| XI | $CH_3$ |  | 102—106 | 378 | 4,40 | 77 | $C_{20}H_{31}ON$ | 79,53; 79,81 | 10,13; 9,99 | 79,69 | 10,36 |
| XII | $C_6H_5$ |  | 150—152 | 383 | 4,48 | 81 | $C_{25}H_{33}ON$ | 83,05; 83,01 | 9,21; 9,23 | 82,58 | 9,14 |
| XIII | $C_6H_5$ |  | 188—190 | 424 | 4,46 | 87 | $C_{25}H_{33}O_2N$ | 78,97; 79,21 | 9,12; 8,98 | 79,07 | 8,79 |

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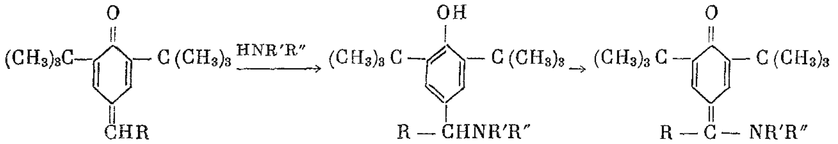
* Literature data [1]: mp 170-171°.



The addition of amines to α-substituted 2,6-di-tert-butylmethylenequinones gives good yields (Table 1) when the methylene is treated with the secondary amine in benzene. Under these conditions aminomethylenequinones (I)-(XIII) are formed with equal readiness, giving yields up to 90% (Table 2). The structure of these aminomethylenequinones has been confirmed by the IR spectra, which contain conjugated carbonyl bands in the range 1620-1650 $cm^{-1}$ but no bands of sterically hindered phenolic hydroxyl (3640 $cm^{-1}$). The spectra of methylenequinones (V), (VI), (VIII), (XI), and (XII) also contain a 3060 $cm^{-1}$ band, characteristic of the ethylene-imine ring.

The wavelength of the absorption maximum of methylenequinones (I)-(XIII) in the UV range depends on the character of the α-substituent and its degree of conjugation with the π-electrons of the methylenequinone system; the phenomena observed in the present work are consistent with the general laws of the effect of the molecule's degree of conjugation on the character and value of the displacement of the maximum in the UV range [2]. If the substituent is a dimethylamino, piperidino, morpholino or N-methylpiperazino group, the corresponding methylenequinones have maxima in the narrow range 375-380 mμ, which corresponds to maximum conjugation of the free pair of nitrogen electrons in the α-substituent forms part of, say, the ethylene-imine ring, the electron reaction with the π-electrons of the methylenequinone will be somewhat less and the maxima of such methylenequinones (V) and (VI) displaced towards the shortwaves (see Table 2). Addition of the phenyl group as the second α-substituent is accompanied by bathochromic displacement of the absorption maximum [cf., for example, (I) and (VII), and (V) and (VIII)].

It is known [3] that the degree of conjugation of the free electron pair of nitrogen with the π-electrons of a conjugated system is largely determined by steric factors. Owing to this, an increase in the alkyl substituents in the dialkylamino group is accompanied by a reduction in the conjugation of the free pair of electrons of the amino group's nitrogen atom with the π-electrons of methylenequinone. In fact, in the case of (IX) and (X) the maximum is displaced towards the shortwaves and is 325 mμ. The opposite effect was observed when we compared the spectra of α-(2,2-dimethylethylene-imino)2,6-di-tert-butylmethylenequinones (XI) and (XII) with those of (VI) and (VIII). The steric effect of the two methyl groups should have reduced still further the degree of conjugation of the free electron pair of the ethylene-imine ring's nitrogen atom with the methylenequinone system; however, in this case the maximum is displaced somewhat towards the longwaves, which indicates an increase in the system's conjugation. This is probably due to the ethylene-imine ring's capacity to propagate conjugation, i.e., in the given compound we evidently observe the "hyperconjugation effect" of the methylene groups and the methylenequinone system via the ethylene-imine ring. A similar effect has already been noted [4] in a number of cyclopropane compounds.

## EXPERIMENTAL

α-Alkyl(phenyl)-α-dialkylamino-2,6-di-tert-butylmethylenequinones (I)-(XIII). To a mixture of 2 g of potassium ferrocyanide and 2.5 g of KOH in 25 ml of water was added (in a current of argon) a solution of 0.005 M of the corresponding phenol in 25 ml of benzene. The mixture was stirred for 30 min at 40°, the organic layer separated, washed with water, dried with $CaCl_2$, the solvent distilled in vacuum and the residue crystallized from hexane. Table 2 gives the yields, physical constants and ultimate analyses of the compounds.

4-(N,N-Dialkylaminomethyl)-2,6-di-tert-butylphenols (XIV)-(XVI). To a solution of 0.01 M of 4-hydroxy-3,5-di-tert-butylbenzyl bromide in 50 ml of ether was added 0.02 M of the secondary amine and 0.02 M of triethyl amine in 2 ml of ether. After 30 min the solution was treated with water, the organic layer dried with $MgSO_4$, the solvent distilled and the residue crystallized from hexane. Table 1 gives the yields, physical constants and ultimate analyses of the compounds.

4-[α-Alkyl-α-dialkyamino)-methy]-2,6-di-tert-butylphenols (XVII)-(XXII). To a solution of α-methyl(phenyl)-2,6-di-tert-butylmethylenequinone in 50 ml of hexane was added 0.02 M of the secondary amine. After 2 h the solvent was distilled in vacuum and the residue crystallized from hexane. Table 1 gives the yields, melting points and ultimate analyses of the compounds.

We would like to thank N. M. Emanuel' for his interest in this work.

## CONCLUSIONS

1. The authors have synthesized 4-{[α-alkyl(phenyl)-α-dialkylamino]methyl}-2,6-di-tert-butylphenols by reacting α-methyl(phenyl)-2,6-di-tert-butylmethylenequinones with secondary amines.

2. A number of α-alkyl(phenyl)-α-dialkylamino-2,6-di-tert-butylmethylenequinones have been obtained by oxidizing the corresponding phenols with potassium ferrocyanide.

3. The absorption maxima of α-alkyl(phenyl)-α-dialkylamino-2,6-di-tert-butylmethylenequinones in the UV region depends on the character of the dialkylamino group and is related to the capacity of the free electron pair of the nitrogen atoms to participate in conjugation with the π-electrons of the methylenequinone system.

## LITERATURE CITED

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5. Yu. A. Bruk and R. Yu. Rachinskii, Zh. obshch. khimii, 34, 2983 (1964).