REACTION OF QUINOBROMIDE COMPOUNDS WITH AMINES

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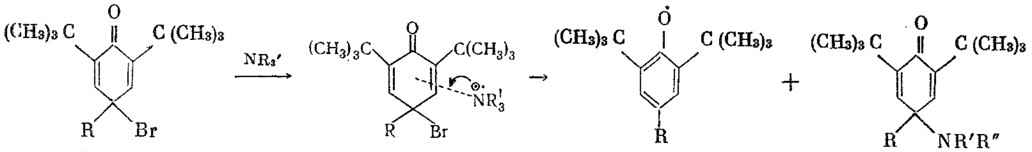
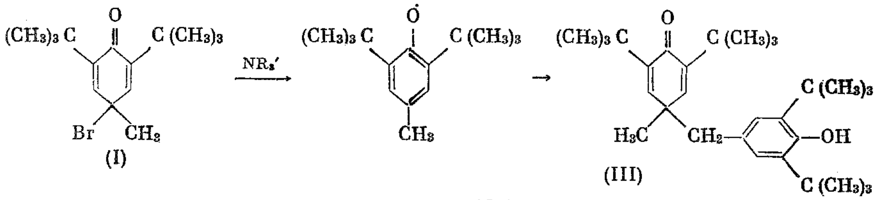
Quinobromide compounds, belonging to the class of sterically hindered cyclohexadienones, have a number of specific properties that are determined by the structure of the molecule as a whole, a high electron affinity, and a comparatively low stability of the C–Br bond [1-3]. In view of these peculiarities, quinobromide compounds are capable of reactions involving one electron, in which connection one of the criteria of the mechanism involving the transfer of one electron is the appearance of phenoxyl radicals in the reaction mixture as a result of their escape from the reaction "cage" [4].

The present paper is devoted to a study of the reaction of quinobromide compounds with amines. The formation of quinamines could be expected during this reaction process; up to now these are compounds that have received little study and most of them have not been obtained. On the example of the reaction of 4-bromo-4-methyl-2,6-di-tert-butyl-2,5-cyclohexadienone (I) and 4-bromo-2,4,6-tri-tert-butyl-2,5-cyclohexadienone (II) with a number of primary, secondary, and tertiary amines it was shown that the reaction proceeds by the mechanism of one-electron transfer, in which connection the amines are the electron donors in the given example



(I) $R=CH_3$
(II) $R=C(CH_3)_3$

The formation of phenoxyl radicals as the result of the reaction of quinobromide compounds (I) and (II) with amines was proved by the EPR method. Despite the single mechanism of all of the studied reactions, the end results are importantly dependent on the nature of the amine, while the yields of the individual reaction products change substantially with change in the solvent. Thus, the reaction of quinobromide (I) with morpholine, piperidine, pyrrolidine, and methylamine gives the corresponding quinamines in yields ranging from 15 to 85%, whereas quinamines are practically not obtained when (I) is reacted with dimethylamine, diethylamine, diisopropylamine, and propylamine, and the principal reaction product is 4-(4-hydroxy-3,5-di-tert-butylbenzyl)-4-methyl-2,6-di-tert-butyl-2,5-cyclohexadienone (III)



$NR_3'=H_2NC_3H_7$, $HN(CH_3)_2$, $HN(C_2H_5)_2$, $HN(C_3H_7)_2$

The predominant formation of cyclohexadienone (III) occurs due to the recombination of 4-methyl-2,6-di-tert-butylphenoxyl, which escapes from the reaction "cage," with its isomeric benzyl radical, the

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TABLE 1. Reaction Products of Amines with 4-Bromo-4-alkyl-2,6-di-tert-butyl-2,5-cyclohexadienones (Quinobromide compounds)

Quinobromide 4-R	Amine NR_3'	Quinamine		Phenol		Quinol (III)†	Stilbenequinone
		yield, %	retention time*	yield, %	retention time*	yield, %	
CH_3	HNC_4H_8O	85	10,0	11	3,35	2	—
CH_3	HNC_5H_{10}	64	5,33	11	3,35	5	6
CH_3	HNC_4H_8	61	—	16	3,35	6	4
CH_3	H_2NCH_3	15	6,35	12	3,35	62	6
CH_3	$HN(CH_3)_2$	—	—	10	3,35	74	8
CH_3	$HN(C_2H_5)_2$	—	—	18	3,35	68	7
CH_3	$HN(C_3H_7)_2$	—	—	12	3,35	74	4
CH_3	$H_2NC_3H_7$	—	—	16	3,35	72	6
$C(CH_3)_3$	HNC_4H_8O	72	—	25	3,20	—	—
$C(CH_3)_3$	$HN(CH_3)_2$	14	—	80	3,20	—	—
$C(CH_3)_3$	HNC_5H_{10}	—	—	88	3,20	—	—

*In the study we used a Khrom-31 chromatograph, equipped with a flame-ionization detector, while Celite C-22 [15% poly(ethylene glycol adipate)] was used as the filler.

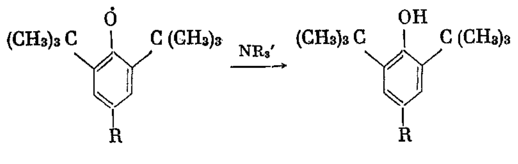
†Mp 156-157°. From [6]: mp 154-156°.

TABLE 2. 4-N,N-Dialkylamino-4-alkyl-2,6-di-tert-butyl-2,5-cyclohexadienones (Quinoamines)

R	NR_2'	mp, °C	R_f (benzene – methanol 1:1)	λ_{max}, nm	lg ε	Found, %			Empirical formula	Calc., %		
						C	H	N		C	H	N
CH_3	NC_5H_{10}	75—78	0,74	233	3,93	79,37 79,27	11,06 11,04	5,1 5,1	$C_{20}H_{33}ON$	79,25	10,96	4,6
CH_3	NC_4H_8	55—57	0,75	233	4,01	78,89 78,65	10,70 10,67	5,3 5,3	$C_{19}H_{31}ON$	78,89	10,79	4,8
CH_3	NC_4H_8O	104—106	0,72	230	4,06	74,31 74,57	10,04 10,19	4,7 4,5	$C_{19}H_{31}O_2N$	74,71	10,32	4,6
CH_3	$NH(CH_3)$	100—101	0,71	234	4,03	76,95 77,11	11,00 11,16	5,5 5,6	$C_{16}H_{27}ON$	77,05	10,88	5,6
$C(CH_3)_3$	NC_4H_8O	95—97	0,78	241	4,02	75,48 75,78	10,64 10,75	4,8 4,4	$C_{22}H_{37}O_2N$	76,03	10,73	4,2
$C(CH_3)_3$	$N(CH_3)_2$	24—26	0,79	239	4,05	78,86 78,91	11,55 11,55	5,6 5,4	$C_{20}H_{35}ON$	78,65	11,53	5,8

formation of which is apparently favored by the reaction medium. The maximum yield of the quinamines was obtained when the reaction was run in excess amine without a solvent.

One of the products from the reaction of quinobromides (I) and (II) with amines is the 4-alkyl-2,6-di-tert-butylphenol, which is formed due to the reaction of the phenoxyl radical, which escapes from the "cage," with excess amine, in which connection this reaction also proceeds with the involvement of one electron, which was shown previously [5]



In harmony with this, when quinobromide (II) is reacted with amines, due to the stability of the intermediately formed 2,4,6-tri-tert-butylphenoxyl, a substantial increase in the yield of the phenol occurs, in which connection 2,4,6-tri-tert-butylphenol is practically the sole product when (II) is reacted with piperidine.

The structure of the obtained quinamines was corroborated spectroscopically. In the IR spectra of these compounds is present a doublet at 1640-1660 cm^{-1} due to the vibrations of a conjugated carbonyl group, while the absorption maximum in the 235 nm region testifies to their p-quinolide structure.

EXPERIMENTAL METHOD

A mixture of either 0.01 mole of quinobromide (I) or (II) and 0.1 mole of the amine was kept in an argon stream for 25 min at 25°C, after which the reaction mixture was diluted with 30 ml of hexane, washed with water, the solvent was vacuum-distilled, and the residue was chromatographed (TLC) on Al_2O_3 in the system of solvents: benzene–heptane, 1 : 1. The yields, physical constants and elemental analysis data for the quinamines are given in Tables 1 and 2.

CONCLUSIONS

A study was made of the reaction of 4-bromo-4-methyl-2,6-di-tert-butyl-2,5-cyclohexadienone and 4-bromo-2,4,6-tri-tert-butyl-2,5-cyclohexadienone with amines.

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