AZO-COUPLING OF 2,6-DI-tert-BUTYL-p-BENZOQUINONE DIAZIDE WITH β-DICARBONYL COMPOUNDS

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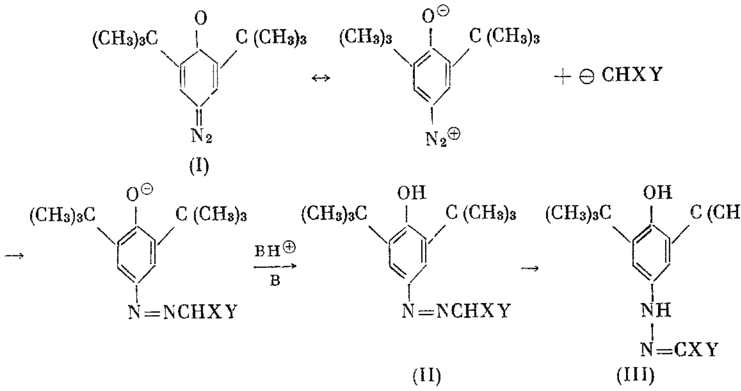
Previously we had shown [1-3] that 2,6-di-tert-butyl-p-benzoquinone diazide (I) easily enters into the azo-coupling reaction with strong nucleophilic agents, like alkylaminomagnesium halides, alkylmagnesium halides, and amines. At the same time, it is known [4] that quinone diazide (I) does not couple in alkaline medium with phenols and naphthols. This is evidently explained by the lower nucleophilicity of the phenolate ion, which is associated with the substantial delocalization of the negative charge along the system of the aromatic ring. In view of this it was interesting to study such objects where the dispersal of the negative charge would occur to a lesser degree.

The present paper is devoted to a study of the azo-coupling of quinone diazide (I) with β-dicarbonyl compounds. As our studies disclosed, (I) couples readily with these compounds in the presence of bases to form azo derivatives (II), which spontaneously isomerize to hydrazones (III)

$$YCH_2X + B \rightarrow \ominus CHXY + BH^{\oplus}$$



An exception is the coupling product of (I) with methylacetylacetone, where the possibility of azo-hydrazo tautomerism is absent, and the process stops at the step of forming the azo compound (II).

Since the process for the condensation of quinone diazides with β-dicarbonyl compounds can be regarded as being an attack of the carbanion ⊖CHXY by the positively charged diazo group of quinone diazides, then it is natural that the presence of bases in the reaction medium should facilitate the reaction to a considerable degree. However, the use of such a strong base as sodium methylate, even despite its very low concentration and a low temperature of the reaction medium (down to −25°), gave a low yield of the azo-coupling products (20%). This low yield is explained by the side process of decomposition of the quinone diazides under the influence of strong bases to the corresponding phenols [5]. Actually, when the reaction was run in the presence of sodium methylate, depending on the temperature conditions, we isolated 2,6-di-tert-butylphenol in 30-60% yield. The best conditions for coupling quinone diazide (I) with β-dicarbonyl compounds is to run the reaction in absolute pyridine solution. In the case of the azo-coupling of (I) with acetoacetic and cyanoacetic esters, in order to obtain the highest yield of the hydrazones (III),

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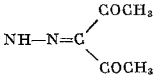
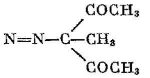
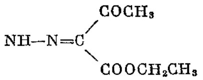
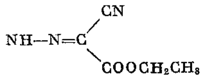
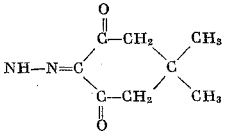
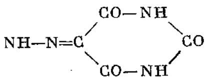
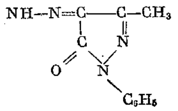
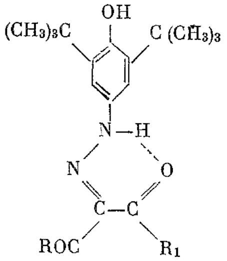
TABLE 1. Azo-Coupling Products of 2,6-Di-tert-butyl-p-benzoquinone Diazide (I) with β-Dicarbonyl Compounds and Their Analogs

X	mp, °C	Yield, %	Ultraviolet spectrum		Empirical formula	Found, %			Calc., %			Infrared spectrum ν, cm⁻¹			NMR spectrum δ, ppm							
			λmax, nm	lg ε		C	H	N	C	H	N	CO	C=N	NH	$C(CH_3)_3$	$COCH_3$	$COCH_2$	NH	CH_2	CH_3	OH	H_m
 $NH{-}N{=}C(COCH_3)_2$	178—179	92	258 395	4,14 4,32	$C_{19}H_{28}N_2O_3$	68,68	8,51	8,51	68,63	8,50	8,42	1672 1625	1536	3250	1,44	2,36 2,50	—	14,93	—	—	5,10	7,16
 $N{=}N{-}C(CH_3)(COCH_3)_2$	108—109	84	237 324	4,14 4,18	$C_{20}H_{30}N_2O_3$	69,32	8,68	—	69,32	8,75		1735 1712	—	—	1,45	2,15	—	—	—	2,15	4,57	7,55
 $NH{-}N{=}C(COCH_3)(COOCH_2CH_3)$	127—128	80	250 375	4,14 4,31	$C_{20}H_{30}N_2O_4$	66,46	8,40	7,97	66,27	8,34	7,73	1665	1530	3250	1,43	2,35	—	12,75	4,28	1,36	5,05	7,09
 $NH{-}N{=}C(CN)(COOCH_2CH_3)$	151—152	90	258 370	4,00 4,25	$C_{19}H_{27}N_3O_3$	66,20	7,90	12,24	66,06	7,87	12,16	1732	1560	3240	1,45	—	—	—	4,38	1,38	5,08	7,08
	188—189	90	269 294 362	4,05 4,07 4,30	$C_{22}H_{32}N_2O_3$	70,95	8,67	7,40	70,94	8,66	7,52	1673 1615	1505	3250	1,45	—	2,38 2,53	—	—	1,10	5,17	7,26
	270—271	96	268 368 422	4,05 4,06 4,22	$C_{18}H_{24}N_4O_4$	59,75	6,90	15,36	59,99	6,72	15,54	1730 1680 1650	1530	3240 3120	—	—	—	—	—	—	—	—
	154—155	90	252 420	4,34 4,39	$C_{24}H_{30}N_4O_2$	71,07	7,37	13,70	70,91	7,44	13,78	1646	1550	3250	1,45	—	—	13,75	—	2,26	5,08	7,16

triethylamine was added to the pyridine solution. This fact is in good agreement with the order of activity of methylene compounds, which was determined for them when reacted with diazonium salts [6].

The spectral analysis (UV, IR, and NMR spectroscopy) data obtained for samples of the synthesized compounds make it possible to arrive at some unequivocal conclusions regarding their structure. As is known, the absorption of arylazo compounds and arylhydrazones differs substantially in the UV region. Thus, absorption in the 300-325 nm region is characteristic for azo compounds [1, 7], whereas arylhydrazones exhibit maximum absorption in the 360-400 nm region [8]. The azo-coupling products obtained by us have the typical UV spectra of arylhydrazones (λ_{max} 362-420 nm), and only in the case of the methylacetylacetone derivative is a UV spectrum observed that is characteristic for azo compounds (λ_{max} 324 nm). The second maximum (240-270 nm), appearing in the UV spectra of all of the obtained compounds, is caused by the absorption of the β-dicarbonyl portion of their molecule. In the IR spectra of the azo-coupling products of (I) with acetylacetone, acetoacetic and cyanoacetic esters, dimedon, barbituric acid, and pyrazolone are observed two bands in the 1620-1630 and 1650-1680 cm^{-1} regions, the first of which belongs to the absorption of the carbonyl group that takes part in the formation of the hydrogen bond, while the second corresponds to the absorption of the unassociated carbonyl group. The absorption of the conjugated $C=N$ bond is manifested as a intense band at 1510-1560 cm^{-1}. The width and position (3250 cm^{-1}) of the absorption band of the NH bond indicate the existence of an intramolecular hydrogen bond. The IR spectrum of the methylacetylacetone derivative is sharply different from those discussed above: the absorption bands of the carbonyl groups are strongly shifted toward shorter wavelengths (1712 and 1735 cm^{-1}), and the absorption of the $C=N$ group is absent, but a band appears that is characteristic for the absorption of the azo group (1585 cm^{-1}). Finally, in the NMR spectra of not one of the obtained compounds was a signal detected in the 3.2-3.5 ppm region, which could be assigned to the proton of the methine group of an azo structure, but a signal was present from the proton of the NH group (Table 1). The exceedingly high value of the chemical shift of this signal (13-15 ppm) indicates the formation of a stable hydrogen bond. In addition, in the NMR spectra of the azo-coupling products of (I) with acetylacetone and dimedon are observed two signals from the protons of either methyl or methylene groups, which indicates the nonequivalence of the carbonyl groups, one of which forms an intramolecular hydrogen bond with the NH group of the nitrogen bridge [cf. structure (IV)]. In the NMR spectrum of the azo-coupling product of (I) with methylacetylacetone, due to the equivalence of the carbonyl groups, the signals from the protons of the methyl groups appear as a narrow singlet at 2.15 ppm.

As a result, the spectral data make it possible to conclude that the azo-coupling products have a hydrazone structure (IV) with an intramolecular hydrogen bond. In this connection, the formation of an intramolecular hydrogen bond between one of the carbonyl groups and the NH group of the nitrogen bridge is evidently the decisive factor that assures an ease of azo-hydrazo isomerization in the synthesized series of compounds



(IV)

EXPERIMENTAL METHOD

A solution of equimolar amounts of the β-dicarbonyl compound and quinone diazide (I) in dry pyridine (a catalytic amount of triethylamine was added to the reaction mixture when the reaction was run with acetoacetic and cyanoacetic esters, while dimethylformamide was added in the reactions with barbituric acid and dimedon in order to obtain better solubility) was kept for a day at room temperature, after which it was diluted with water and extracted with a 1 : 1 ether–hexane mixture. The organic extracts were washed with dilute HCl solution (1 : 50) and water, the solvent was removed in vacuo, and the residue was recrystallized from a benzene–hexane mixture. The yields and constants of the obtained compounds are given in Table 1.

CONCLUSIONS

The reaction of 2,4-di-tert-butyl-p-benzoquinone diazide with β-dicarbonyl compounds proceeds with the formation of azo derivatives, which spontaneously isomerize to hydrazones.

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