

ACID CATALYZED REARRANGEMENT OF 3,5,3',5'-TETRA-TERT-BUTYLSTILBENE-4,4'-QUINONE

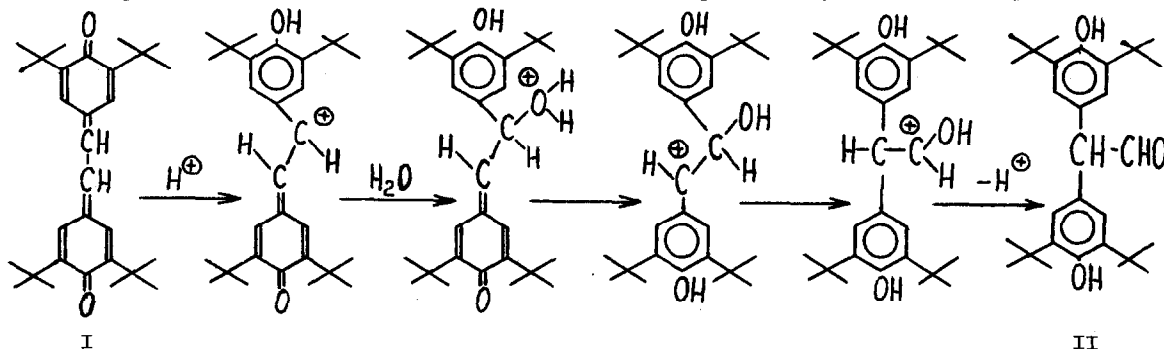
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It has been found that chloroform solutions of some derivatives of stilbenequinone (I) are unstable, unless the traces of hydrogen chloride had been removed from the solvent used. A mixture of 1% of the chloroform solution of I (100 ml) and p-toluenesulphonic acid hydrate (0.5 g) gave after 2 hours of stirring at room temperature in an inert atmosphere and after the usual treatment a compound which was identified as 2,2-bis(3,5-ditert-butyl-4-hydroxyphenyl)acetaldehyde (II) in a yield 62% (m.p. 178-9°C, heptane). Found 79.45% C, 9.92% H; calculated for $C_{30}H_{44}O_3$ (452.7) 79.60% C, 9.80% H.

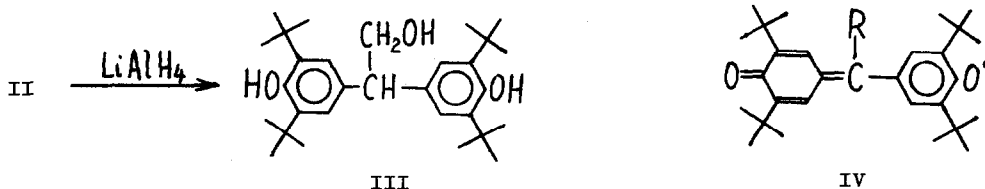
The probable mechanism of formation of II is expressed by the following scheme:



Reduction of II with lithiumaluminium hydride in ether gives rise to III in a yield 50% (crystallizing in two modifications, m.p. 146-7, and 155-6°C, hexane). Found 79.13% C, 10.49% H; calculated for $C_{30}H_{46}O_3$ (454.7) 79.25% C, 10.20 % H.

Compound	Mass spectrum		IR spectrum		CO group ^b
	mol. peak	main peak	region ^a	3100-4000 cm ⁻¹	
II	452	423 ^c	3642(s)	-	1715(s)
III	454	423 ^c	3645(s)	3597(m)	-

^a0.04% solution in CCl₄, 10 mm cell. ^bKBr pellet. ^cDue to splitting off of the -CHO or -CH₂OH group resp.



Chemical Shifts τ^a of compounds II and III in the NMR spectra^b

Compound	tert-Bu	alcohol.OH	H at the central C ^c	phenol.OH	H arom.	CHO
II	8.59 (36)	-	5.285 (1) 5.25	4.77 (2) ^d	2.91 (4)	0.10 (1) 0.065
III	8.60 (36)	8.26 (1) ^d	6.01 (3)	4.91 (2) ^d	2.94 (4)	-

^aIntensities are given in brackets. ^bCDCl₃ was used as solvent. ^cIn the case of compound III combined into a single peak with the absorption of H at the neighbouring C. ^dIntensity is reduced after shaking with D₂O.

Oxidation of II or III resp. with lead tetroxide (2) or potassium ferricyanide (3) leads either to galvinoxyl (IV, R=H) or some other relatively stable radicals, probably derivatives of the latter (IV, R=CH₂OH, CHO, COOH), depending on the conditions of the reaction.

REFERENCES

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