Tetrahedron Letters No.42, pp. 3727-3728, 1970. Pergamon Press. Printed in Great Britain.

PHOTOINDUCED REACTIONS. XLVII. PHOTOCHEMICAL TRANSPOSITION OF 2,6-DI-t-BUTYLPHENOLS[1]

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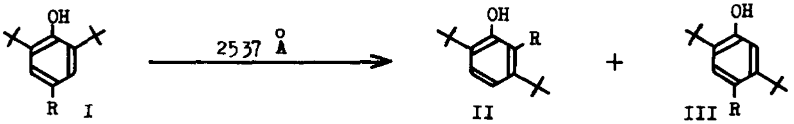
(Received in Japan 17 July 1970; received in UK for publication 11 August 1970)

The photochemical transposition of alkylbenzenes through their valence tautomers has recently received much attention.[2] We wish to report a new type of photochemical transposition of hindered 2,6-di-t-butylphenols.

Irradiation[3] of 2,6-di-t-butylphenols (Ia, Ib and Ic) in n-hexane or in methanol gave rearranged products which were isolated by silica gel chromatography. The results (Table) indicate that two types of transposition reactions as represented by a general equation took place, although they are indistinguishable in the case of Ia. It should be noted that the product ratio was dependent on solvent polarity in the cases of Ib and Ic. Irradiation of Id in n-hexane resulted in the simultaneous de-t-butylation to give IIa.

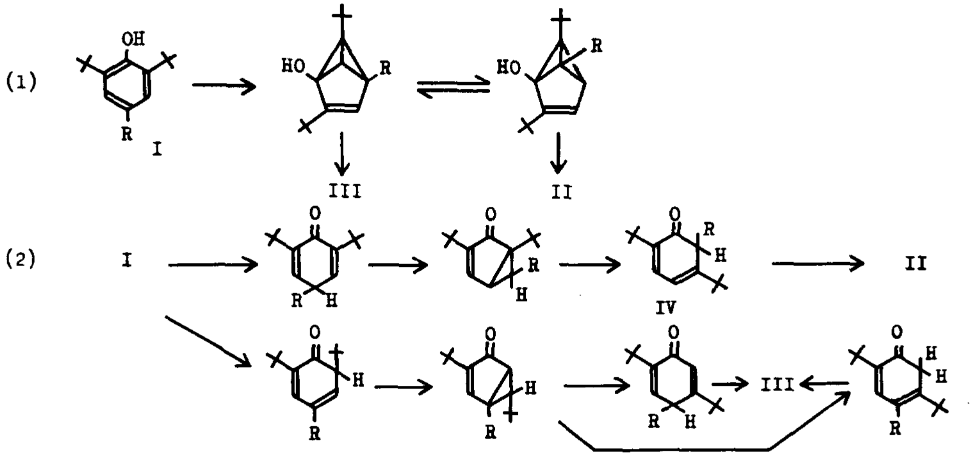


Ia (R=H)	n-hexane	41% (IIa or IIIa)	
	MeOH	16% (IIa or IIIa)	
Ib (R=Me)	n-hexane	28% (IIb)	0% (IIIb)
	MeOH	0% (IIb)	10% (IIIb)
Ic (R=OMe)	n-hexane	10% (IIc)	7% (IIIc)
	MeOH	1.5% (IIc)	6.5% (IIIc)
Id (R=t-Bu)	n-hexane	10% (IIa)	

Two possible mechanisms were considered. One (eq. 1) involves benzvalene type intermediates as formulated for the photochemical transposition of alkylbenzenes,[2] and the other (eq. 2) involves ketone tautomer intermediates as formulated for the photochemical reaction of 3,5-di-t-butyl-4-hydroxyphenyl ketones.[4] Such ketone tautomers can rearrange to II and III by known photochemical processes.[5,6] The former mechanism was ruled out from the following experimental results. Irradiation of the methyl ether of Ib did not give products ıg to II and III, but largely gave the recovered starting substance. Irradiation OD gave about 1:1 mixture of ortho- and para-deuterated IIa (or IIIa) with 84%

D-content, as confirmed by nmr and mass spectra. The formation of 2,5-di-t-butylphenol (IIa) from Id can also be rationalized by the latter mechanism in which pyrolytic de-t-butylation of an intermediate IV may occurs.[4,7,8]

Identification of products:[9] 2,5-Di-t-butylphenol (IIa) was prepared by the photochemical hydroxylation of 1,4-di-t-butylbenzene in acetonitrile.[10] The structures of IIb and IIIb were established from the following results. The nmr spectra of IIb and IIIb showed an AB quartet (τ 2.92 and 3.13, J=9cps) and two singlets (τ 3.18 and 3.52), respectively. On treatment with aluminum chloride IIb gave o-cresol and IIIb gave p-cresol. The methyl ether of IIb was converted to 2,5-di-t-butylanisole (the methyl ether of IIa) by permanganate oxidation followed by decarboxylation of the resulting carboxylic acid. IIc[7] and IIIc[11] are known compounds.



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