SYNTHESIS OF DIIXOCHROMENYLS AND UNUSUAL REACTION INVOLVING CLEAVAGE OF THE C – C BOND

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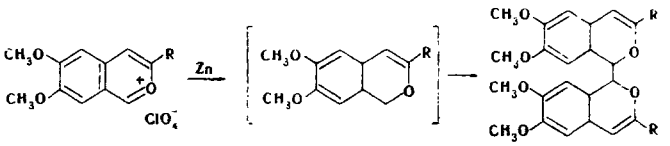
It was recently shown [1] that pyrylium radicals that are readily dimerized to give the corresponding 4,4'-dihydropyranyls are formed in the reduction of 4-unsubstituted pyrylium salts with metals. We have shown that the reduction of 1-unsubstituted 2-benzopyrylium salts (I) with zinc in a mixture of water and ether evidently also proceeds through a step involving the formation of isochromenyl radicals (II), since diisochromenyls III [IIIa, mp 155° (from ethanol), M^+ 410; IIIb, mp 156° (from ethanol)] are formed in 74 and 44% yields, respectively.

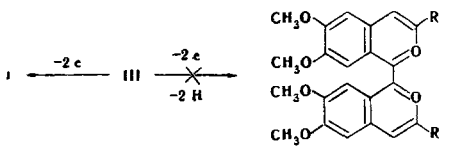


I II III

I–III a R = CH_3, b R = p-$CH_3OC_6H_4$

The results of elementary analysis of IIIa, b are in agreement with the calculated values, and the IR spectra confirm the proposed structure.

Elimination of two electrons involved in the $C_{(1)}-C_{(1)'}$ bond to give starting salts Ia, b occurs under the influence of strong electron acceptors (triphenylmethyl perchlorate or acetyl perchlorate) on IIIa, b, but the detachment of an electron and a hydrogen atom (formally a hydride ion) that usually occurs in such cases, which should lead to diisochromylium salts (IV), does not occur.



IV

This trend of the reaction is in agreement with the mass spectroscopic data, which indicate the lability of the $C_{(1)}-C_{(1)'}$ bond in diisochromenyls III, since the intensity of the M/2 peak is the maximum intensity in the spectrum, whereas the intensity of the molecular ion peak is 2.08%.

LITERATURE CITED

1. L. A. Polyakova, K. A. Bilevich, N. N. Bubnov, G. N. Dorofeenko, and O. Yu. Okhlobystin, Dokl. Akad. Nauk SSSR, 213, 370 (1973).

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