A New Ring Expansion of a Benzofurobenzopyran into Benzofurobenzoxepinone Derivatives

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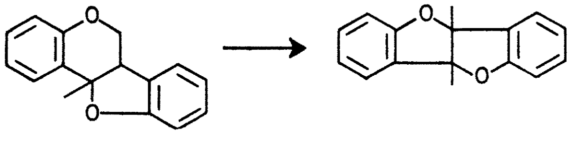
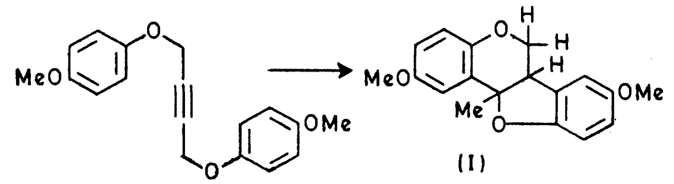
Summary Bromination of the benzopyranobenzofuran (I) with *N*-bromosuccinimide in carbon tetrachloride affords a novel ring expansion to give 2,8-dimethoxy-6*H*-benzofuro[3,2-*c*]-[1]-benzoxepinone and its 12-bromo-derivative.

SOME years ago we reported the unusual ring contraction of a benzofurobenzopyran into the isomeric benzofurobenzofuran.[1]



We now report a novel ring enlargement of the same system into a benzofurobenzoxepinone derivative under a different set of conditions. Thermal rearrangement of 1,4-bis-(*p*-methoxyphenoxy)but-2-yne in accordance with our published procedures[2] gave the benzofurobenzopyran (I).

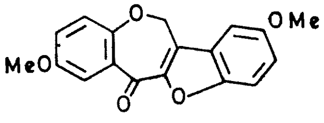


(I)

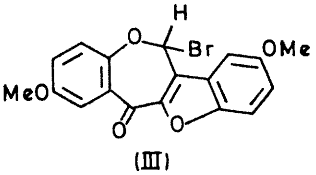
Compound (I) shows characteristic peaks in the n.m.r. at δ 1·65 for the quaternary methyl group, the ABC pattern for the $-OCH_2$ protons and the benzylic proton being between δ 3·25 and 4·35 p.p.m. With the intention of placing a bromine atom on the benzylic carbon, a mixture of (I) (3 g), benzoyl peroxide (5 mg), and an excess of *N*-bromosuccinimide (NBS) (2·5 g) in carbon tetrachloride (450 ml) was heated under reflux for 4 h. Within 10 min, the reaction mixture turned brown. Considerable evolution of hydrogen bromide and a rapid precipitation of succinimide followed after 30 min. After 4 h, the dark-green mixture was freed of succinimide, stripped of the solvent, and the residue chromatographed over neutral alumina. Chloroform eluted a golden-yellow solid in 23—25% yields. Preparative t.l.c. resolved this into two very closely moving compounds (II) and (III) melting at 205° and 220°, respectively. Compound (II) analysed correctly for $C_{18}H_{14}O_5$, showed a molecular weight of 310 by mass spectrometry, a carbonyl band at 1710 cm^{-1}, and maxima in the u.v. at 252, 285, 312, 322, and 398 nm. The appearance of the carbonyl band, the intense yellow colour of the compound, and the long-wavelength absorptions in the u.v. indicated a conjugated carbonyl function interposed between the aromatic rings. This was further corroborated by the n.m.r. spectrum of (II) with signals at δ 3·90 for 6 protons of the methoxy-group, at 5·20 for 2 protons of the $O-CH_2-C=C$ function, at 6·90—7·30 for 5 of the aromatic protons, and at 8·20 for the other aromatic proton, this last signal arising from a benzene ring proton adjoining the carbonyl function. Particularly revealing was the absence of the quaternary methyl signal in the n.m.r. spectrum of (II).

Compound (III) which moves closely with (II) on the t.l.c., analysed correctly for $C_{18}H_{13}BrO_5$, showed molecular ion peaks at 388 and 390 in the mass spectrum, and a carbonyl band at 1701 cm^{-1}. The u.v. absorption spectrum with maxima at 252, 285, 322, and 398 nm was virtually identical with that of (II). In the n.m.r. spectrum, it showed signals at δ 3·85—3·95 for the 6 protons of the methoxy-groups, at 5·25 for *one* proton of the $O-CH(Br)-C=C-$ function, at 6·9—7·30 for 5 of the aromatic protons, and at 8·30 for one more aromatic proton flanked by the carbonyl group. There were no signals for the quaternary methyl function nor were any signals found in either (II) or (III) for aldehydic protons.

Based on the above data, the following two formulations are suggested for the products (II) and (III).



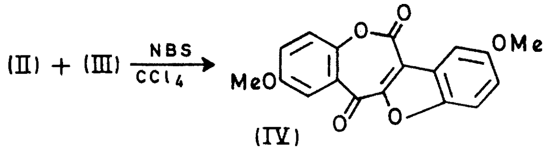
(II)



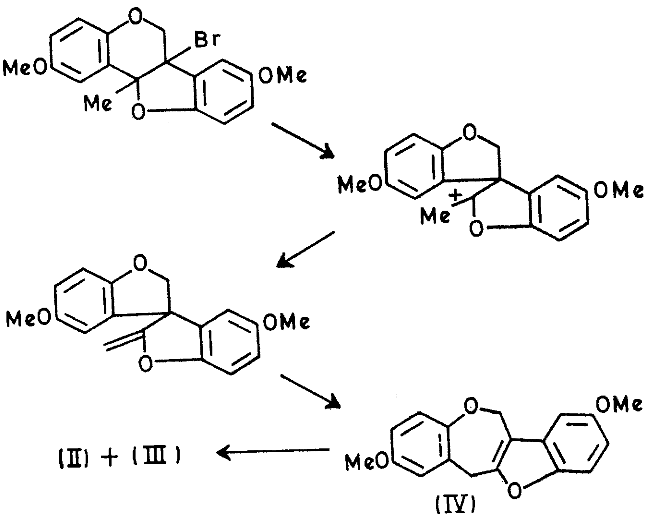
(III)

Bearing in mind the *cis*-stereochemistry of the ring junction in (I), the reaction could proceed by the following pathway. A ready entry of bromine on the benzylic carbon, followed by its intramolecular displacement by the benzylic bond results in a stable cation. The latter could lose a proton, undergo an allylic migration, and give the ring expanded product. Oxidation of the benzylic-allylic methylene by *N*-bromosuccinimide affords (II), while further bromination on C-12 gives the bromo-derivative (III) (see Scheme).

In further support of such a postulate, we have oxidized both (II) and (III) with more *N*-bromosuccinimide, to the lactone (IV), m.p. 304°. This lactone analyses for $C_{18}H_{12}O_6$, shows carbonyl peaks at 1693 and 1720 cm^{-1} (KBr), and shows maxima in the u.v. at 240, 293, 346, and 443 nm. A molecular ion peak at 324 confirms the molecular weight and the removal of the bromine by oxidation.



(IV)



SCHEME

The oxidation of benzyl-methylene functions to benzoyl derivatives by *N*-bromosuccinimide has been amply demonstrated in a variety of other molecules.[3]

We thank Prof. C. D. Hurd, Professor Emeritus, Northwestern University, for useful discussions and for help in naming the system. We thank the Graduate School of the University of Idaho for grants.

(*Received, August* 10*th*, 1970; *Com.* 1325.)

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