Crown Ether Complexes of Molecular Bromine as Stereoselective Brominating Agents

By KEITH H. PANNELL and ARMIN MAYR
(*Department of Chemistry, University of Texas at El Paso, El Paso, Texas* 79968)

Summary Isolable crown ether complexes of molecular bromine have been shown to effect highly stereoselective brominations of *cis*- and *trans*-β-methylstyrene.

THE dioxan–bromine complex has long been known and utilized as a brominating reagent.[1] Since dioxan is the first member of a series of cyclic polyethers it is not surprising that the larger macrocyclic polyethers (crown ethers) also form isolable complexes with molecular bromine. We have measured the formation constants of the bromine complexes of several polyethers of different sizes and find essentially no selectivity of complex formation, *i.e.*, K is 1·2 l mol^{-1} for dioxan, 2·2 for 12-crown-4, 0·8 for 15-crown-5, 1·0 for 18-crown-6, and 1·2 for dicyclohexyl-18-crown-6.[2] Such results imply that the binding of the bromine to the polyethers does not involve the cavity of the crowns but rather that the bonding is essentially the same as for the dioxan complex involving a single oxygen–bromine interaction.[3]

We have utilized dibenzo-18-crown-6·Br_2 (DBC·Br_2), pyridine·Br_2 (py·Br_2), and Br_2 alone as brominating agents with *cis*- and *trans*-β-methylstyrene and the stereochemical results of these bromine additions are recorded in the Table.

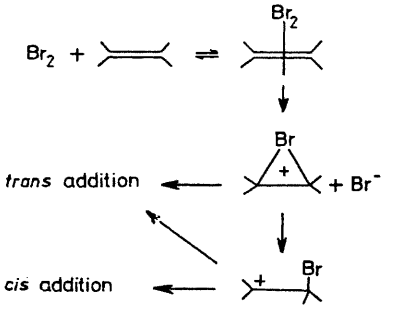
TABLE. % *trans* Addition to *cis*- or *trans*- PhCH=CHMe.[a]

Solvent	Brominating reagent					
	Br_2		Py·Br_2		DBC·Br_2	
	cis	*trans*	*cis*	*trans*	*cis*	*trans*
C_6H_{12}	85	92	—	—	100	100
$C_4H_8O_2$	25	79	46	89	25	100
CH_2Cl_2	72	90	84	97	100	100
$MeNO_2$	46	81	62	86	96	100
MeCN	69	89	59	90	98	100

[a] Products for *trans* addition to *cis*- and *trans*-isomers are *threo*- and *erythro*-1-phenyl-1,2-dibromopropane respectively, as analysed by ^{1}H n.m.r. spectroscopy.

The DBC·Br_2 complex exhibits the greatest stereoselectivity of the brominating reagents utilized; indeed for the bromination of the *trans*-β-methylstyrene a stereospecific *trans*-addition is obtained regardless of the polarity of the solvent.

The mechanism of the bromination of olefins, *e.g.*, the β-methylstyrenes, is thought to involve the initial formation of a bromine–olefin charge-transfer π complex followed by a rate-determining transformation to a bridged bromonium ion[4,5] which may either react directly with the Br^- counter ion in a stereospecific formation of a *trans*-dibromide, or open up to a solvent stabilized carbonium ion which will be brominated in a non-stereospecific fashion (see Scheme).



SCHEME

The implication of the present results is that the bromonium ion is stabilized by the crown ethers relative to the open carbonium ion in all solvents, this stabilization being greater for the *trans* isomer. The favoured process in dioxan is ring opening of the bromonium ion even in the presence of the crown ether. This observation has been noted before in bromination reactions,[5] and also for the acid catalysed hydrolysis of epoxides.[6]

We have performed a kinetic study on the bromination of *cis*-β-methylstyrene in methanol using a stopped flow technique under pseudo first order conditions with respect to Br_2. The study was performed in the presence of dioxan, 12-crown-4, and 18-crown-6, and in the absence of all polyethers for comparison. The results indicate that very little rate enhancement is produced by the polyethers, *i.e.*, k is 1260 l mol^{-1} s^{-1} for dioxan, 1540 for 12-crown-4, 1330 for 18-crown-6, and 1070 for Br_2 alone.[7] Since the mechanism of bromination according to the Scheme involves a pre-equilibrium between the olefin and Br_2, complexation of the Br_2 by the crown ethers will tend to reduce the overall rate of the reaction; however, the complexation of the bromonium ion by the crown ethers will tend to counter this effect, and a modest overall rate enhancement is found. The major effect of the presence of the crown ethers is, however, the very significant increase in stereoselectivity.

Preliminary results from the bromination studies using phenyl acetylene and hex-1-yne as substrates indicate that similar increases in stereoselectivity occur when using the DBC·Br_2 complex.

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[6] H. A. Weiner and R. A. Sneen, *J. Amer. Chem. Soc.*, 1962, **84**, 3599; *Tetrahedron Letters*, 1963, 1309.
[7] This result parallels that obtained in the bromination of stilbene in the presence of dicyclohexyl-18-crown-6: E. Schori and J. Jagur-Grodzinski, *Israel J. Chem.*, 1972, **10**, 959.