Competitive Photoisomerizations of 1-Substituted Cycloheptatrienes[1]

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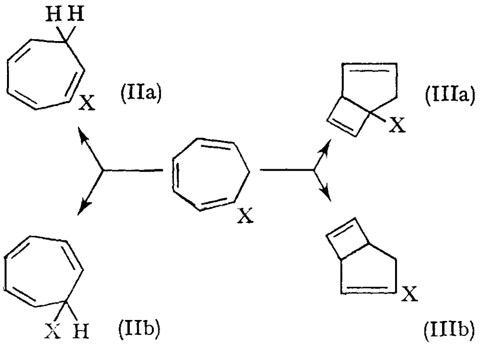
Two photoisomerizations of cycloheptatriene are known: a valence tautomerization to bicyclo[3,2,0]hepta-2,6-diene[2] and a 1—7 shift of hydrogen.[3–5] In the neat liquid the ratio of the two processes (as derived[5] from the results with 7-deuterocycloheptatriene) is 0·002. Preliminary results obtained by Chapman and Borden[6] suggested that a substituent (alkoxy-group) might change this ratio considerably, as has recently been confirmed.[7] We report here the behaviour of 1-substituted cycloheptatrienes (I) upon irradiation, which was carried out as described in reference 5.

As depicted in the scheme below, either photochemical reaction may yield two products:



As reported previously,[5] a 1-phenyl substituent shows no specific effect, isomerization by a shift of hydrogen being the only process observed and 2- (IIa) and 7-phenyl-cycloheptatriene (IIb) being formed in approximately equal amounts.

With the electron-attracting cyano-group in the 1-position, a shift of hydrogen is similarly the only process observed, but the direction of the shift is highly specific: only 2-cyanocycloheptatriene (IIa) is formed. With electron-donating groups (Me, MeS, MeO) in the 1-position the shift occurs in the opposite direction, and 7-X-cycloheptatriene (IIb) is the major product with little or no 2-isomer formed.

With increasing electron-donating capacity of the substituent, valence tautomerization to (III) (occurring to a very minor extent in the unsubstituted compound) gains in importance. In the case of the dimethylamino-compound the products resulting from a shift of hydrogen, 2- and 7-Me_2N-C_7H_7, could not be detected (< 1%).

The direction of the valence tautomerization, as already noted by Chapman *et al.*,[7] for the methoxy-compound, is very specific. 5-Methoxy- and 5-methylthio-bicyclo[3,2,0]hepta-2,6-diene (IIIa) were the only valence tautomers observed, but a few per cent of the corresponding 3-isomers (IIIb) may have escaped detection. 1-Dimethylaminocycloheptatriene yielded in addition to the major product (IIIa) *ca.* 3% of 3-dimethylaminobicyclo[3,2,0]hepta-2,6-diene (IIIb), which was isolated and identified by comparison with an independently synthesized sample.

TABLE

(*Initial*) *Products of irradiation* (in %) *of* 1-*substituted cycloheptatriene*

	Products			
Substituent	(IIa)	(IIb)	(IIIa)	(IIIb)
CN	100	—	—	—
Ph	50	50	—	—
Me	2	98	—	—
SMe	—	65	35	—
OMe	—	35	65	—
NMe_2	—	—	97	3

These results, summarized in the Table, show that substituents can change the ratio of competing photochemical pathways by several orders of magnitude. Thus, for instance, the presence of a dimethylamino-group in the 1-position of cycloheptatriene increases the ratio of valence tautomerization to the 1—7 shift of hydrogen by a factor of at least 50,000.

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