Comparison of the Stereochemistry of the Bromination of an Enol and of its Methyl Ether

By M. BETTAHAR and M. CHARPENTIER*

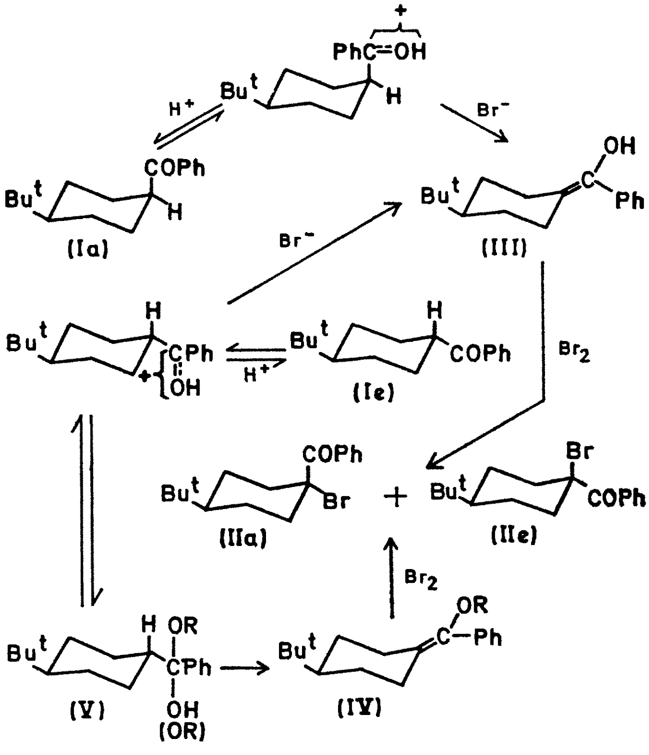
(*Groupe de Recherches nº 12-C.N.R.S., 2 à 8 rue Henry Dunant, 94-Thiais, France*)

Summary The stereochemical result of an enol ether bromination may differ from that of the corresponding enol.

BROMINATION by molecular bromine dissolved in CCl_4 (or HOAc) of the ketones (Ie) and (Ia) ([ketone] = $[Br_2]$ = $0{\cdot}04$ M) gives† the two brominated ketones (IIe) and (IIa) (see Scheme) in the same ratio 1 : 1 (g.l.c. analysis). The bromination of the same ketones, at the same concentrations but either in $CHCl_3$ stabilised by $0{\cdot}5\%$-EtOH or in CCl_4 containing $0{\cdot}5\%$-EtOH leads to different results: (Ia) gives a mixture of ketones (II) in the ratio (IIe) : (IIa) = 1 : 1, while (Ie) forms (IIe) preferentially (in each solvent 80% and 65% of the mixture, respectively).

In the absence of ethanol, each ketone (I) forms the brominated ketones in the same ratio (IIe) : (IIa) = 1 : 1, thus implying a common intermediate, which, according to the classical mechanism of halogenation of ketones[1] must be the enol (III).

In the presence of ethanol, the ketones (I) do not form the brominated ketones (II) in the same relative ratio, thus ruling out the existence of a common intermediate. Under these conditions, (Ia) still forms the products in the ratio (IIe) : (IIa) = 1 : 1, with the enol (III) as the possible intermediate. The preferential formation of (IIe) during the bromination of (Ie) can be explained if the intermediate is the enol ether (IV) formed from the hemiacetal or acetal (V).[2] This implies that the stereochemical result of the bromination of an enol ether differs from that of an enol.



SCHEME

---

† We have verified that the less stable brominated ketone (IIa) is not isomerized into (IIe) in the reaction medium.

We therefore brominated the acetal (V; R = Me)‡ and the enol ether (IV; R = Me) and established that under these conditions these two compounds lead, after hydrolysis of the reaction mixture, principally to (IIe) (95% of the mixture of brominated ketones).

The fact that (Ia) does not give (V) under the same bromination conditions may be explained by the slower reactivity towards nucleophiles of an axial compared to an equatorial keto-group.[3]

Our results show that the stereochemical result of an enol ether bromination may differ from that of the corresponding enol.

(*Received, March 20th*, 1970; *Com.* 397.)

---

‡ R was chosen Me for easier n.m.r. spectral analysis.

[1] R. P. Bell, "The Proton in Chemistry," Cornell University Press, New York, 1959, p. 143.

[2] A. Marquet, M. Dvolaitzky, H. B. Kagan, L. Mamlok, C. Ouannes, and J. Jacques, *Bull. Soc. chim. France*, 1961, 1822.

[3] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York, 1966, p. 72.