Free-radical Bromination of Ketones

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Summary The bromination of some unsymmetrical ketones in the presence of an epoxide as HBr scavenger is reported; the reaction products indicate a free-radical process.

IT is established[1–3] that the acid-catalysed bromination of ketones, with halogen concentrations $> 10^{-4}$M, proceeds by a rate-determining enolization, and in the bromination of unsymmetrical ketones the ratio of the two brominated products has been taken as a measure of the relative content of the possible enols.[4] We were interested to see whether the orientation in the bromination of unsymmetric ketones was influenced by the HBr produced during the reaction, as found in the bromination of phenols.[5] We have therefore used an epoxide as HBr scavenger because it cannot influence the keto–enol equilibrium. Bromination in the dark of some benzyl ketones in CCl_4 with bromine and cyclohexene oxide as hydracid scavenger stopped after a rapid, small initial uptake of halogen. Upon irradiation with a 40 W tungsten lamp, however, the ketones react rapidly to give bromoketones whose orientation differs from that obtained by brominating the ketones without the epoxide and in the dark. The orientation in the bromination of ketones in the usual manner depends upon whether the reaction is carried out in the dark or exposed to light (Table).

TABLE

Bromination of ketones[a] with and without added epoxide in dry CCl_4 at 20°.

Ketone		% Substitution products[b] Benzylic	Alkylic
Benzyl methyl ..	(A)	100	0
	(B)	95	5
Benzyl ethyl ..	(A)	100	0
	(B)	60	40
Benzyl ethyl[c] ..		80	20
Benzyl isopropyl ..	(A)	66	33
	(B)	23	77

[a] Br_2 and the ketone (each 0·06M) in CCl_4: (A) with cyclohexene oxide (0·1M) and irradiation from a 40 W tungsten lamp; (B) without cyclohexene and in the dark. [b] Total yield of the monobrominated ketones was *ca.* 90% with small amounts (*ca.* 5%) of $\alpha\alpha'$-dibrominated products and cyclohexane bromohydrin byproduct. [c] Without cyclohexene oxide, as in (B), but with irradiation, as in (A).

It is clear that the epoxide hinders the acid auto-catalysed enolization of the ketones and therefore the reaction occurs almost completely on the unenolized ketones. Moreover the preponderance of benzyl-substituted products and the light catalysis suggest a free-radical mechanism; *cf.* brominations with *N*-bromosuccinimmide.[3,6]

Apart from the synthetic utility of our results, we suggest that during the usual brominations of ketones both ionic and radical mechanisms can operate so that the ratio of the brominated products may not be a correct measure of the relative content of the enols.

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