

THE STEREOSELECTIVITY OF PHOTOBROMINATION

Werner O. Haag and El-Ahmadi I. Heiba

Socony Mobil Oil Company, Inc.

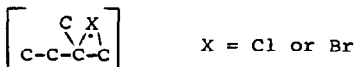
Central Research Division Laboratory

Princeton, New Jersey

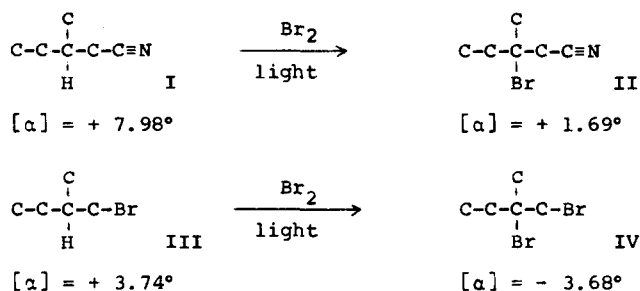
(Received 16 August 1965)

Free radicals produced by various methods at the asymmetric center in optically active compounds generally yield optically inactive products (1). The inability of simple alkyl free radicals to maintain asymmetry has been attributed to either a planar structure of the radicals or to a pyramidal structure capable of rapid inversion. Recent physical measurement indicate that the planar configuration is the most stable form of simple alkyl radicals (2).

Specifically, radical chain chlorination of optically active (+)-1-chloro-2-methylbutane produces inactive 1,2-dichloro-2-methylbutane (1a). An exception was reported recently in the photobromination of the same compound which gives optically active (-)-2-bromo-1-chloro-2-methylbutane (3). Similar stereoselectivity was observed in the bromination of (+)-1-bromo-2-methylbutane which gives (-)-1,2-dibromo-2-methylbutane. The unexpected stereoselectivity was attributed to the formation of an intermediate halogen bridge radical.



We report now the first example of stereoselective bromination in which bridged radicals cannot be intermediates. The liquid phase photobromination of (+)-1-cyano-2-methylbutane (I) with 1 molar bromine proceeds with high selectivity at the tertiary carbon to yield (+)-2-bromo-1-cyano-2-methylbutane (II). The NMR spectrum of product II confirms the assigned structure. It shows a singlet at 7τ (1.8 H); a sharp singlet at 8.1τ superimposed on a multiplet at $7.9-8.2 \tau$ (total of 5.1 H) and a triplet at 8.9τ (3.0 H) with a coupling constant of 7 c.p.s. Moreover, the NMR spectrum has a pattern identical to that of 1,2-dibromo-2-methylbutane (IV). The change in optical rotation on brominating the nitrile (I) is comparable to that observed on brominating the bromide (III).*

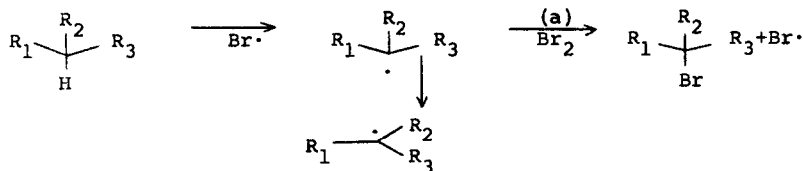


The observed stereoselective bromination of nitrile (I) rules out a free planar radical as an intermediate. Furthermore,

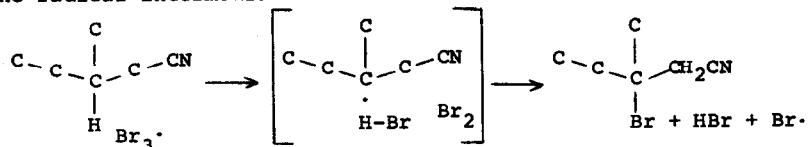
* Reference 3 reported: (III), α^{27} obsd. = + 4.89°; (IV), α^{27} obsd. = - 2.86°. All our optical rotations were determined at $\lambda = 5481 \text{ \AA}$.

neighboring group participation leading to a cyano bridged radical analogous to the proposed halogen bridged radicals (3) is most unlikely.

The following explanation is therefore offered to account for the stereoselective bromination. The initial radical formed by hydrogen abstraction has pyramidal configuration; racemization occurs either by achieving a planar configuration or by rapid inversion. However, reaction with bromine might be sufficiently fast to compete with this racemization process.



While the reactions of free radicals with bromine are generally very fast, a further rate enhancement of step (a) can be expected if the hydrogen abstracting species is $Br_3\cdot$ rather than $Br\cdot$. The bromine radical is known to complex with systems containing π - or d-orbitals. Moreover, there is precedence for the $Br_3\cdot$ concept in the explanation of certain olefin addition reactions (4). This would place a bromine molecule in immediate proximity to the radical intermediate as it is formed.



The concept of short-lived non-planar radicals has been invoked recently to explain the stereochemistry of 9-decalyl free radicals in reactions towards oxygen (5). Our observed

stereoselective bromination of compound I demonstrates that non-planar radicals are not only possible in bicyclic systems, but that even in simple open-chain compounds they can exist long enough to be intercepted in fast reactions.

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