

Rearrangement-*cum*-cleavage would in both cases lead to a more stable radical than would simple fission of the α C-C bond. Rearrangement in 3 would lead to loss of *tert*-butyl radicals, which are about 5 kcal/mol more stable than isobutyl radicals.⁸ For 4, 1,2-hydrogen migration concurrent with cleavage would lead to $C_6H_5CHCH_3$ rather than $C_6H_5CH_2CH_2$, where the difference in heats of formation is estimated to be *ca.* 13 kcal/mol, based on the bond dissociation energies (BDE) for primary alkyl C-H (Ref. 8) and secondary benzylic C-H (Ref. 9). A slightly higher value (17 kcal/mol) is obtained if the estimate is based on the stabilization energy for benzylic radicals together with the difference between the BDEs for primary and secondary aliphatic C-H. The [M-57]/[M-58] ratio observed for 3 is 1.10; the [M-105]/[M-107] ratio for 4 is 1.16 (1.08 per D). These ratios are very close to the values expected for β -secondary deuterium isotope effects,⁶ which establishes the absence of primary kinetic isotope effects on these reactions and in turn leads to the conclusion that the incipient radicals retain their structural identity during simple cleavage reactions.

Experimental. The isotope effects were determined as the ratio of the peak heights for the competing α -cleavage reactions in metastable ion spectra (MIKE spectra) recorded on double-focusing mass spectrometers of reversed geometry (magnetic analyzer preceding electric analyzer), using a wide collector slit. The α -cleavage ions carry more than 90 % of the fragmenting ion current for all compounds examined. The energy of the ionizing electrons was 70 eV. Measurements for 2 and 3 were performed on the unusually large double-focusing mass spectrometer (MMM) at the University of New South Wales (Sydney).¹⁰ The results for 4 were obtained on a VG ZAB-2F instrument at the University of Bielefeld.

Compound 2 was prepared from diisopentylamine by exchange with D_2O in the mass spectrometer inlet system. 3 was synthesized by reaction of the Grignard reagent derived from isobutylbromide-2-*d* with *N*-methoxymethyl-*N*-methylisopentylamine.¹¹ Compound 4 was prepared by $LiAlH_4$ reduction of the *N*-(3-phenylpropyl)-*N*-methylamide of 3-phenylpropionic acid-3,3-*d*₂.

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