

Homo- S'_H Reactions on Allylmethyl Iodide leading to Substituted Cyclopropanes

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OUR recent observations that $I[CH_2]_3I^{1a}$ and CH_2I_2 -olefin^{1b} produce the cyclopropane ring system when treated with peroxides prompted us, in our search for new types of free-radical reactions, to attempt to incorporate closure of a γ -iodopropyl

radical to a cyclopropane into a sequence of free-radical processes. Consequently, we have performed experiments designed to determine whether such a step can occur, sequentially or concertedly, along with radical addition to a double bond. We

TABLE. Peroxide-induced reaction of RI with $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\text{I}^a$

RI			% Yield ^b of $\Delta\text{-CH}_2\text{R}$			
			79° (PhCO ₂) ₂ ^c	114° (PhCO ₂) ₂ ^c	134° (^t -BuO) ₂ ^c	168° (^t -BuO) ₂ ^c
MeCH ₂ I ^d	38	35	38	34
CH ₂ :CH·CH ₂ ·CH ₂ I ^d	1.3	2.6	1	2
Me ₂ CHI ^d	47	39		
ICH ₂ ·CO ₂ H ^d	53	73	< 0.5	< 0.5
Me ₃ CI	< 0.1	< 0.1	< 1	< 1
CH ₂ :CH·CH ₂ I	< 0.1	< 0.1	< 0.1	< 0.5

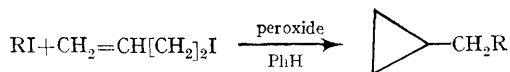
^a Less than 0.1% of cyclopropane-containing products was produced in the absence of $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\text{I}$. ^b Based on RI and determined by use of n.m.r. spectroscopy and g.l.c. ^c No reaction occurred in the absence of peroxide.

^d In all these reactions, with both peroxides where applicable, less than 0.1% of RR, RCH₂·CH₂·CH:CH₂, (CH₂:CH·CH₂·CH₂)₂, 5-cyclopropylpent-1-ene, and 1,2-dicyclopropylethane was formed with the following exceptions: we did not determine (MeCH₂)₂ in the MeCH₂I-(PhCO₂)₂ runs or 1,2-dicyclopropylethane in the CH₂:CHCH₂CH₂I/(Bu^tO)₂ runs; less than 1% of (CH₂:CHCH₂CH₂)₂ and 5-cyclopropylpent-1-ene was formed in the MeCH₂I-(Bu^tO)₂ runs.

report some reactions which may be visualized as being of the homo-S'_H type,



We have found that reaction of an organic iodide and $\text{CH}_2\text{:CH}[\text{CH}_2]_2\text{I}^\dagger$ with benzoyl or di-*t*-butyl peroxide results in the formation of a side-chain substituted methyl-cyclopropane:



Results are summarized in the Table.

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[†] Prepared by reaction of $\text{CH}_2\text{:CH}[\text{CH}_2]_2\text{Br}$ with NaI in acetone; this material is unusually light-sensitive for a primary iodide. Its n.m.r. spectrum (CCl₄) consists of the usual $\text{CH}_2=\text{CH}-$ absorption between τ 3.8 and 5.2 (3.0 H) and multiplets at about τ 6.9 (2.0 H) and 7.4 (2.0 H). (Found: C, 26.6; H, 4.0; I, 69.6; Calc. for C₄H₇I: C, 26.4; H, 4.0; I, 69.7.)

¹ (a) L. Kaplan, *J. Amer. Chem. Soc.*, 1967, **89**, 1753; (b) L. Kaplan, *ibid.*, p. 4566.

² J. D. Roberts and R. H. Mazur, *J. Amer. Chem. Soc.*, 1951, **73**, 2509; H. C. Brown and M. Borkowski, *ibid.*, 1952, **74**, 1894; E. Renk, P. R. Shafer, W. H. Graham, R. H. Mazur, and J. D. Roberts, *ibid.*, 1961, **83**, 1987; C. Walling and P. S. Fredricks, *ibid.*, 1962, **84**, 3326; E. S. Huyser and L. R. Munson, *J. Org. Chem.*, 1965, **30**, 1436; E. S. Huyser and J. D. Taliaferro, *ibid.*, 1963, **28**, 3442; M. L. Poutsma, *J. Amer. Chem. Soc.*, 1965, **87**, 2172; D. J. Patel, C. L. Hamilton, and J. D. Roberts, *ibid.*, p. 5144; L. K. Montgomery, J. W. Matt, and J. R. Webster, *ibid.*, 1967, **89**, 923; L. K. Montgomery and J. W. Matt, *ibid.*, p. 934, 6556; T. A. Halgren, M. E. H. Howden, M. E. Medof, and J. D. Roberts, *ibid.*, p. 3051.