Nucleophilic Substitution Reactions of Allylic Halides Carrying Electron-withdrawing Substituents in the γ-Position. Formation of Cyclopropanes from Dimethyl 2-Bromo-2-methylpropylidenemalonate

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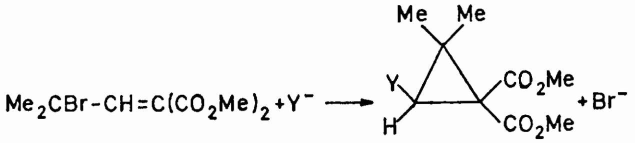
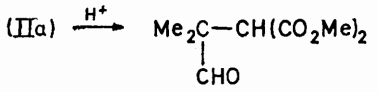
Summary Reaction of dimethyl 2-bromo-2-methylpropylidenemalonate with sodium methoxide or potassium cyanide in methanol produces cyclopropane derivatives in high yields, thus indicating an overall substitution with nucleophilic attack occurring at the β-position of the allylic halide.

Nucleophilic substitution reactions of allylic halides are normally found to take place at the α- or γ-position following S_N1, S_N2 and S_N1', S_N2' mechanisms, respectively.[1] We report reactions between an allylic halide and selected nucleophiles where the formation of the reaction products can only be explained by invoking nucleophilic attack on the β-carbon of the halide followed by cyclisation. A reaction bearing some similarities to the one investigated, the base induced conversion of *trans*-γ-bromodypnone into 1,2-dibenzoylethane,[2] was proposed to proceed through a cyclopropane intermediate which, however, could not be isolated.



(I) (II) a; Y=OMe
b; Y=CN



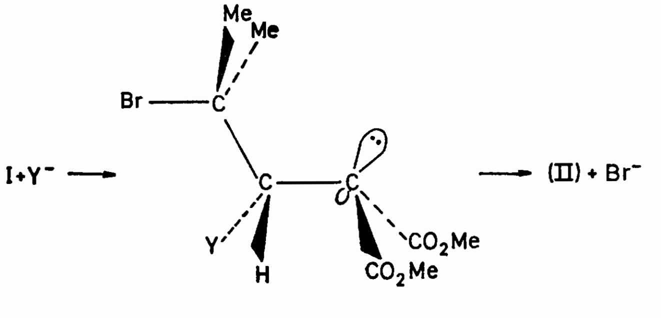
$$\text{(IIa)} \xrightarrow{H^+} \underset{\displaystyle \text{CHO}}{\text{Me}_2\text{C}}\text{—CH(CO}_2\text{Me)}_2$$

(III)

The malonate (I), readily prepared by bromination of dimethyl isobutylidenemalonate with *N*-bromosuccinimide, reacts rapidly with sodium methoxide or potassium cyanide in methanol to give the cyclopropanes (II) in nearly quantitative yields [(IIa) = b.p. 111—114° at 12 mmHg; ν_{max} 1715 cm^{-1} (C=O); M^+, m/e 216; (IIb): b.p. 139—140° at 10 mmHg; ν_{max} 1730 (C=O) and 2240 (C≡N) cm^{-1}; M^+, m/e 211].

Elemental analyses of the products indicated overall substitution. The structural assignments were based spectroscopically on n.m.r. and i.r. analyses and chemically on the ready acid-catalysed conversion of (IIa) into (III).

The kinetics of the reaction were investigated by n.m.r. spectroscopy by measuring the rate of disappearance of the geminal dimethyl signal in (I) [δ 1·97 p.p.m. (6H, s)] and the rate of appearance of the corresponding signals in (IIb) [δ 1·32 (3H, s), 1·48 p.p.m. (3H, s)]. The reaction was of second order, first order in (I) and in potassium cyanide, having a rate constant $k = 1{\cdot}40 \pm 0{\cdot}04 \times 10^{-3}$ l mol^{-1} s^{-1} at $-5 \pm 0{\cdot}5$ °C.



(IV)

The reaction mechanism may be formulated as a rate-determining nucleophilic attack on the β-carbon in (I) forming a carbanion (IV) which subsequently attacks in a nucleophilic manner at the α-position, expelling Br$^-$ with formation of a cyclopropane. A concerted mechanism may well operate.

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[2] R. E. Lutz, L. T. Slade, and P. A. Zoretic, *J. Org. Chem.* 1963, **28**, 1358.