Stereospecific Cyclopropane Formation *via* Internal Methylene Transfer

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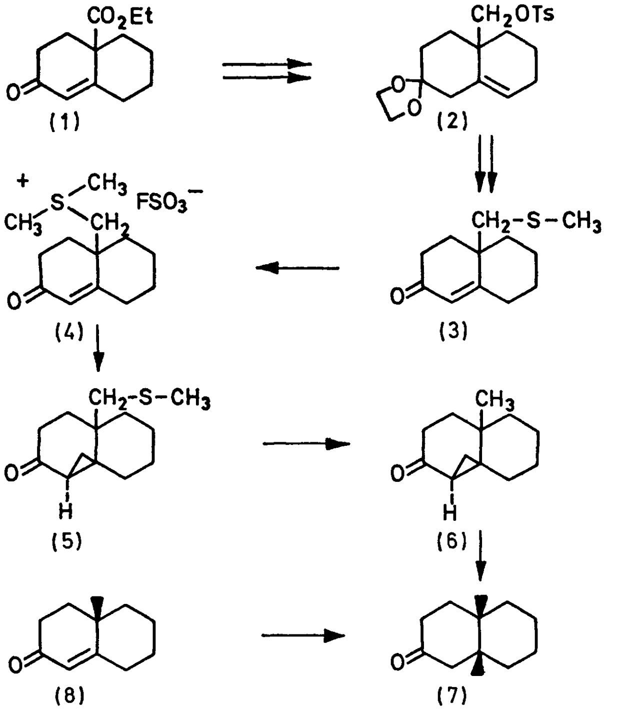
Summary Treatment of the sulphonium salt (4) with potassium t-butoxide in 1,2-dimethoxyethane results in the addition of a methylene group across the double bond to give the cyclopropyl compound (5) in high yield.

WE recently described[1] the synthesis of epoxides whose stereochemistry was defined and controlled completely by pre-existing chiral centres in the molecule.

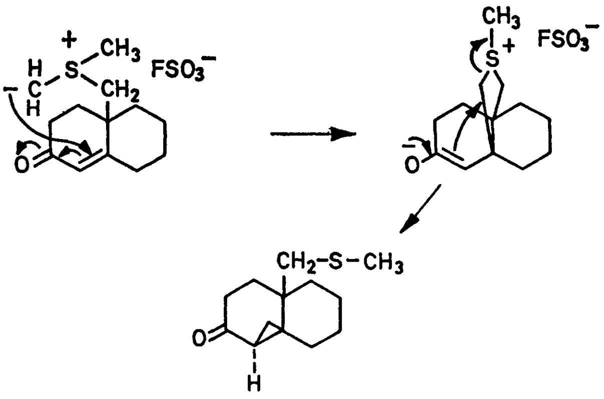
We now report a reaction leading to cyclopropyl ketones whose stereochemical course is similarly dictated. The reaction sequence leading to these results is shown in Scheme 1.



SCHEME 1

The ester[2] (1) could be transformed in 90% yield into the acetal (2) by acetalization, reduction with LiAlH$_4$, and treatment with toluene-*p*-sulphonyl chloride in pyridine.† The acetal (2) with LiSMe in refluxing 2-methoxyethanol gave an acetal sulphide which on exposure to concentrated aqueous HCl in tetrahydrofuran for 3 days gave the keto-sulphide (3) [i.r. (neat) λ_{max} 6·00, 6·25, 6·95, and 7·6 μm and n.m.r. δ (CDCl$_3$) 5·7, s (1 H); 2·84, m (2 H), 2·15 s (3 H)].

Reaction of (3) with 1 equiv. of methyl fluorosulphonate[4] in methylene chloride gave, after washing with hexane, the pure sulphonium salt (4) [i.r. (KBr) λ_{max} 6·1, 6·24, 6·95, 7·7, and 8·25 μm] in 90% yield. We were gratified to observe that smooth methylene transfer occurred in >95% yield on exposure of the sulphonium salt to potassium t-butoxide in anhydrous 1,2-dimethoxyethane for 0·5 h at 0°, followed by 3·5 h at 25° and 0·5 h at 40° to give (5) [i.r. (neat) λ_{max} 3·34, 6·0, 6·95, and 7·65 μm; n.m.r. (CDCl$_3$) δ 2·84 m (2 H), 2·14, S (3 H), and 0·85, m (3 H)]. Compound (5) could be desulphurized quantitatively with Raney nickel in acetone to give the cyclopropyl ketone (6). The stereochemistry of this product was verified by reduction of the cyclopropyl ketone with sodium in liquid ammonia[4] to the dimethyl ketone (7) which was identical



SCHEME 2

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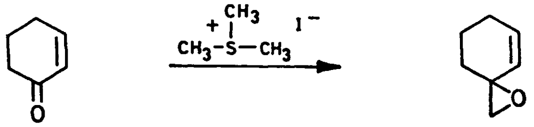
† All new compounds have satisfactory analytical and spectral data.

in all respects with the authentic compound prepared by conjugate addition of methylmagnesium iodide in the presence of cupric acetate to (8) in the manner described by Marshall.[5] The mechanism of this reaction, by analogy with other sulphur ylide reactions,[6,7] is probably that shown in Scheme 2.

With the exception of the above mentioned reaction, no cases of the conjugate addition of unstabilized sulphonium salts to αβ-unsaturated ketones have previously been described. In fact, in such a situation (*e.g.*, that shown in Scheme 3) only 1,2-addition is observed.[6]

This difference is assumed to be a consequence of the intramolecular character of the reaction, since addition to the carbonyl group would require a rather unfavourable seven-membered transition state. The high overall yield and simple prerequisites may make this reaction sequence attractive for the stereospecific construction of more complex molecules.



SCHEME 3

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