Tetrahedron Letters No. 14, pp 1205–1208, 1978. Pergamon Press. Printed in Great Britain.

ELECTROREDUCTIVE SYNTHESES OF CYCLOPROPANES FROM α,β-UNSATURATED CARBONYL COMPOUNDS[1]

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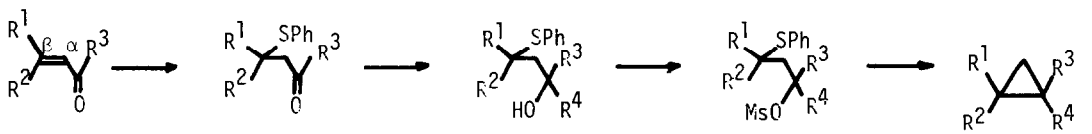
(Received in Japan 23 January 1978; received in UK for publication 14 February 1978)

General methods[2] of syntheses of cyclopropanes from α,β-unsaturated carbonyl compounds by the formation of a bond between the carbonyl carbon and the β-carbon (**1**→**5** in the Scheme I) had not been developed until a reductive method[3] by lithium metal in liquid ammonia was recently reported, though it is low yield and not selective.

The publication[3] of the metallic reduction method prompted us to report herein one of our continuing studies on the electroreductive elimination which gives a more selective and highly efficient route to syntheses of cyclopropanes from α,β-unsaturated carbonyl compounds according to the pathway depicted in the Scheme I.

Scheme I

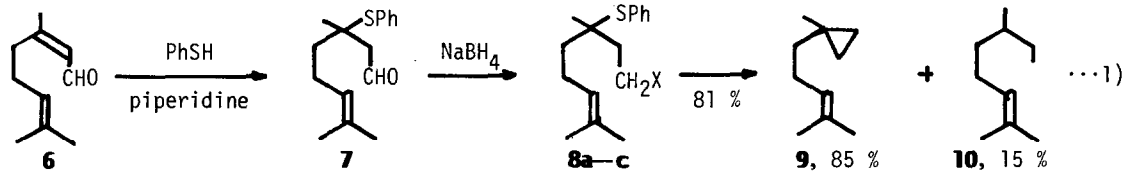


1 **2** **3** **4** **5**

R^1, R^2, R^3, and R^4 = H or alkyl Ms = CH_3SO_2—

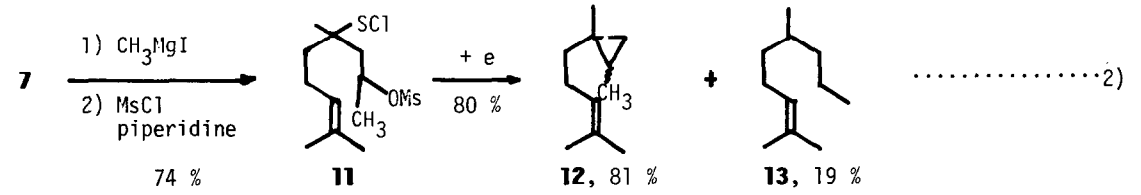
The Michael addition of thiophenol (1.0 mol) to citral (**6**, 1.0 mol) in benzene (50 ml) catalyzed with piperidine gave the β-(phenylthio)aldehyde (**7**), which was reduced with methanolic sodium borohydride to the (phenylthio)alcohol (**8a**). The yield of **8a** from **6** was 86 %. The electrochemical reduction of **8a** or its benzoate (**8a**) failed to give any cyclopropane product. The methanesulfonate (**8c**), however, yielded a mixture of the cyclopropane (**9**) and the acyclic hydrocarbon (**10**) in a 81 % yield. The distribution of **9** and **10** was 85 % and 15 %, respectively.[4] The general procedure of the electrochemical reduction is as follows.

A solution of a substrate (10 mmol) in dry DMF (40 ml) containing tetraethylammonium *p*-toluenesulfonate (4.0 g) as a supporting electrolyte was reduced in a divided cell equipped with platinum anodes and lead cathodes. The cathode potential was -1.65—-1.80 V *vs.* SCE. The yield was obtained after 4 *F*/mol of electricity was passed.

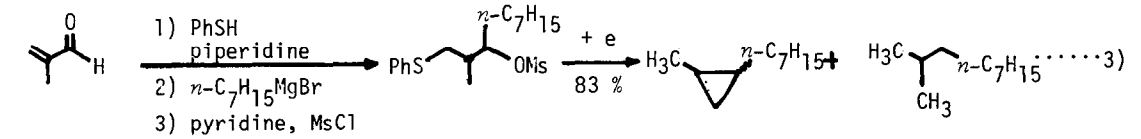


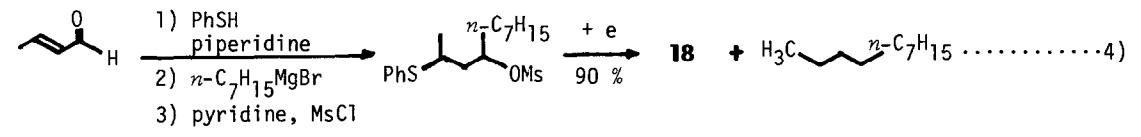
a: X = OH, b: X = OBz, c: X = OMs

The electroreduction of the secondary methanesulfonate (**11**), which was synthesized by the reaction of **7** with methylmagnesium iodide followed by the mesylation of a hydroxy group, gave an isomeric mixture of the trialkyl substituted cyclopropanes (**12**) along with **13**. The yield and distribution are shown in equation 2.[5]

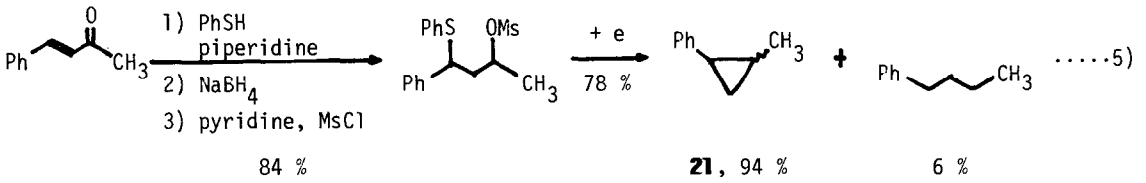


Interestingly, the same 1,2-dialkyl substituted cyclopropanes can be prepared from both α-alkyl and β-alkyl α,β-unsaturated carbonyl compounds as it is exemplified in equations 3 and 4.[7]

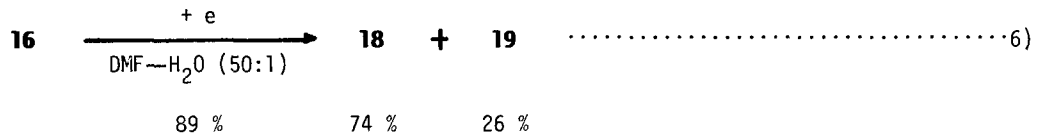




Aryl substituted cyclopropanes were also synthesized through this electroreductive method.[8]



The selectivity of the formation of the cyclopropane ring may depend on the concentration of proton donors in the reaction system. The increase in the amount of proton donors will result in the increase in the formation of the undesired acyclic compounds. This concept is supported by the fact that the formation of the acyclic compound (**19**) increased considerably in the reduction of **16** in DMF containing 2 % water.



Thus, solvents of proton donating nature such as liquid ammonia[3] are essentially unfavorable to this reductive cyclopropane formation.

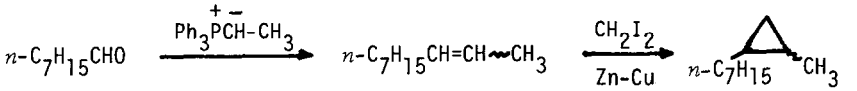
The considerably lower reduction potential of **16** (Ep,[9] -1.60 V *vs.* SCE) than those of thioanisol (Ep,[9] <-2.20 V *vs.* SCE) and *n*-butyl methanesulfonate (Ep,[9] <-2.20 V *vs.* SCE) strongly suggests the interaction between phenylthio group and methanesulfonate group at the step of the electron transfer.

Because of the ready availability of the starting compounds and the high yield and selectivity, this new electrochemical 1,3-elimination would be highly potential in syntheses of cyclopropanes. Further development and electrochemical studies are in progress.

References and Notes

1. Electroorganic Chemistry 35.
2. Some paticular reactions of formation of cyclopropanes from α,β-unsaturated compounds. (a) $LiAlH_4$ reduction of cinnamate esters, R. J. Quellette, R. D. Robins, and A. South, Jr., *J. Am. Chem. Soc.*, **90**, 1619 (1968); (b) Wolf - Kishner reduction of benzalacetone, D. Darcidson and J. Feldman, *J. Am. Chem. Soc.*, **66**, 488 (1944).

3. Y. H. Chang, D. E. Champbell, and H. W. Pinnik, *Tetrahedron Lett.*, **1977**, 3337. The yields of cyclopropanes by this method are 11 - 48 % and this method is applicable to only primary methanesulfonates.
4. The mixture of **9** and **10** was distilled at 85 - 90 °C/80 mm. This mixture showed the spectroscopic data characteristic to a cyclopropane ring, though the separation of **9** and **10** could not be accomplished: IR (neat); 3070 and 1020 cm^{-1}: NMR; δ 9.80. The ratio of **9** and **10** was calculated from the ratio of the olefinic protons and cyclopropyl protons.
5. These products could not be separated (bp 62 - 64 °C/15 mm) each other. The spectra of the mixture strongly suggested the exsistence of a cyclopropane ring: IR (neat); 3050 and 1020 cm^{-1}: NMR (in CCl_4); δ 10.05 (m, 1H), 9.1 - 9.7 (m, 2H). Since the chemical shifts of protons of trialkyl substituted cyclopropanes are known[6] to be δ 10.05 (1H) and 9.13 - 9.67 (2H), the ratio of **12** and **13** was calculated from the relative strength of the peaks at δ 10.05 (a cyclopropyl proton) and δ 5.3 (an olefinic proton).
6. "The Sadtler Standard Spectra," Sadtler Research Laboratories, Philadelphia, 8183M, 1975.
7. The boiling point of the mixture of **18** and **19** was 71 - 72 °C/12 mm. Each stereoisomer of **18** and **19** was separable by preparative gas chromatography, and the stereoisomers of **18** were identified by the comparison of their spectra and glc behavior with those of the authentic samples prepared as follows.



cis and *trans* **18**

The separation and identification of **18** and **20** were feasible in a similar way.
8. The identification of **21** was carried out by the spectroscopic comparison with the authentic sample.[2(b)] The ratio of **21** and *n*-butylbenzene was obtained by gas chromatographic analysis.
9. Reduction potentials were measured under the following conditions. Substrate, 0.1 M; Solvent, DMF; Supporting Electrolyte, 0.05 M Et_4NCl; Cathode, Pt; Anode, Pt; Scanning rate, 100 mV/sec.