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A CONVENIENT SYNTHESIS OF SPIRO[3.4]OCTA-5,7-DIENE

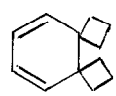
Ihsan Erden* and Edmund M. Sorenson

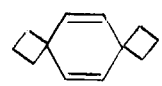
San Francisco State University, Chemistry Department, San Francisco, CA 94132

Summary: A facile synthesis of spiro[3.4]octa-5,7-diene by way of dichloroketene addition to methylene cyclobutane is described.

The ability of the cyclopropyl group to interact with an adjacent vinyl group or sp^2-hybridized center has extensively been studied in recent years[1,2]. Theoretical studies predict similar conjugative interactions for the cyclobutane ring with neighboring π-electron systems[3]. Preliminary studies[4] indicate significant overlap of cyclobutane quasi-Walsh orbitals[3] with adjacent sp^2-hybridized centers, however, systematic studies have been hampered by the poor accessibility of suitable model systems like 1, 2 and 3.

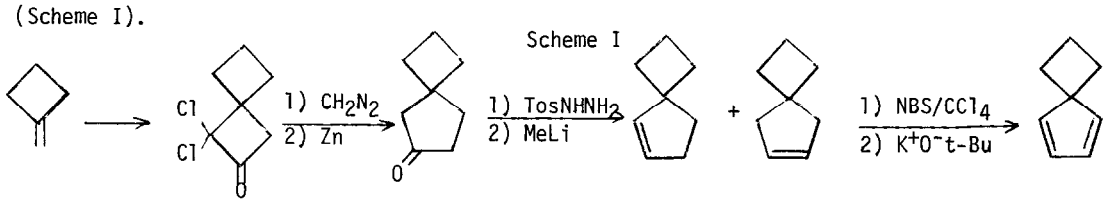

1


2


3

Numerous research groups have therefore attempted to prepare 1[5,6] but only two have succeeded[7,8], and the spirocyclobutyl substituted cyclohexadienes 2 and 3 are still unknown. Herein we describe an alternative synthesis of 1 which is suitable for the preparation of material in sufficient quantities to permit extensive physical and chemical studies (Scheme I).

Scheme I



4 6 8 9 1

Methylene cyclobutane, available in practically unlimited quantities from pentaerythrytol in two steps[9], has previously been reported to undergo a [2+2]-cycloaddition with

dichloroketene to give 4 in 33% yield[10]. When dichloroketene was generated by the zinc dehalogenation method[11] in the presence of methylene cyclobutane a 60% yield of 4 was obtained. Ring expansion[12] of 4 with diazomethane followed by reductive dechlorination with zinc in acetic acid at 70°C furnished the novel spiro[3.4]octan-6-one (6) in 84% overall yield (from 4)[13]. Conversion of 6 to its tosylhydrazone 7 in ethanol at room temperature followed by the Shapiro-Heath reaction[14] afforded a 1:1 mixture of the known spiro[3.4]octenes 8 and 9[15]. Allylic bromination with N-bromosuccinimide in CCl_4 and subsequent treatment of the crude bromides with potassium tert-butoxide gave 1 in 45% yield (from 6).

Investigation of the chemistry of 1 (e.g. photooxidation) and the applicability of our approach to the synthesis of 5,5 -disubstituted cyclopentadienes is proceeding.

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