

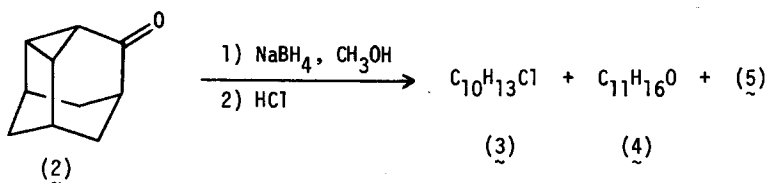
METHANOLIC SODIUM BOROHYDRIDE REDUCTION WITH HYDROCHLORIC ACID WORK-UP OF
8,9-DEHYDRO-2-ADAMANTANONE: A CORRECTION

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In an attempted preparation of 8,9-dehydro-2-adamantanol (1), Baldwin and Foglesong have reported that treatment of 8,9-dehydro-2-adamantanone (2) with excess sodium borohydride in methanol, followed by hydrochloric acid work-up, gave two major products of molecular formula $C_{10}H_{13}Cl$ (3) and $C_{11}H_{16}O$ (4), and an uncharacterized minor product (5).¹ Owing to the great



similarity in the mass spectral fragmentation patterns of (3) and (4) in comparison to (1), the major products of the reaction were presumed to be 2-chloro-8,9-dehydroadamantane (6) and 2-methoxy-8,9-dehydroadamantane (7).¹ However, the proclivity of cyclopropylcarbonyl systems to solvolyze to unpredictable mixtures of cyclopropylcarbonyl, cyclobutyl, and allylcarbonyl products² suggested to us that these structure assignments might not be secure and, consequently, we have reinvestigated this reaction in detail.

Reaction of (1)¹ with the 1:1 complex of methyl sulfide and *N*-chlorosuccinimide in methylene chloride³ provided chloride (6)⁴ in ca. 65% yield.⁵ Hydrogenolysis of (6) with lithium aluminum hydride in ether gave the known hydrocarbon,⁶ 2,4-dehydroadamantane (8). Chloride (6) was

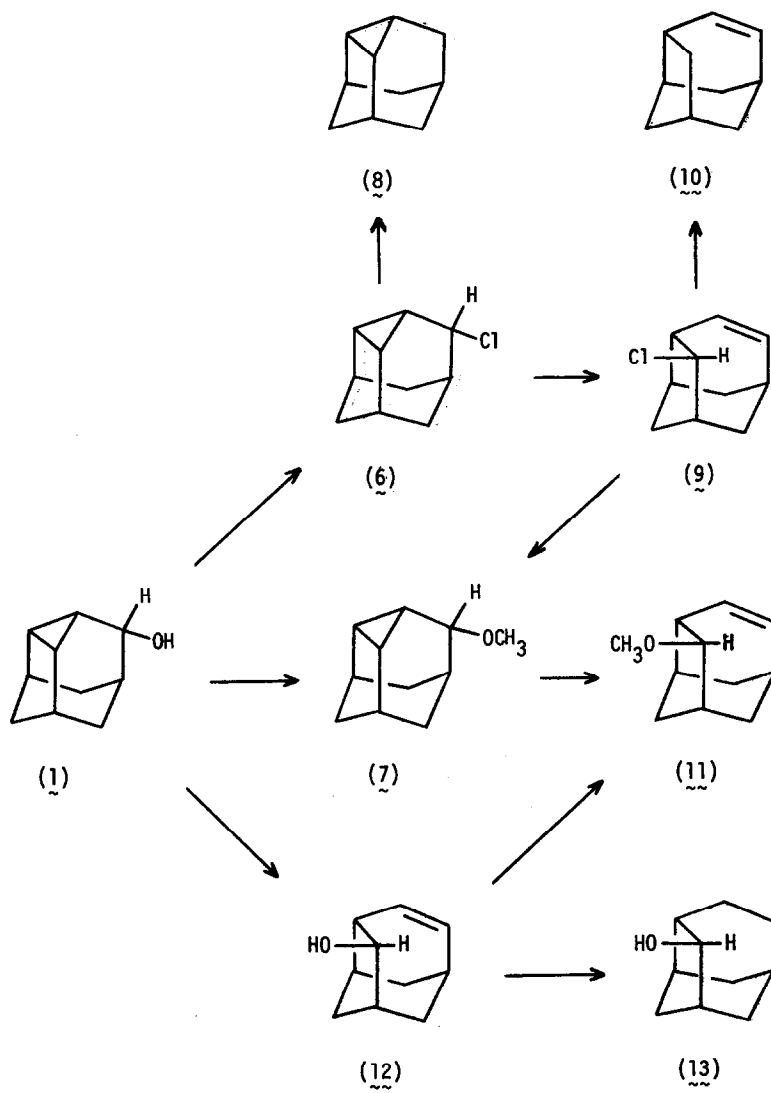
quantitatively isomerized at 110⁰ in the injection port of a gas chromatograph to 2-exo-chloro-protoadamantene (9), mp 57-58⁰. Lithium-tetrahydrofuran-t-butyl alcohol dechlorination⁷ of (9) afforded the known hydrocarbon,^{6b,8} protoadamantene (10). Since Baldwin and Foglesong purified (3) and (4) by glpc at 155⁰,¹ it is apparent that the C₁₀H₁₃Cl compound isolated by them was (9) and not (6).

Alkylation of (1) with methyl iodide and sodium hydride in dimethylformamide (DMF) gave (7), which was identical with (4), and thus the earlier reported¹ structure assignment was confirmed. Treatment of chloride (9) with silver perchlorate in methanol at 25⁰ for two min also afforded (7) in ca. 80% yield.⁹ This reaction provides the first example of the synthesis of a dehydroadamantyl derivative by the solvolytic π -route.

Ether (7) was cleanly converted with 3 mol % of silver perchlorate in anhydrous benzene¹⁰ at 25⁰ to 2-exo-methoxyprotoadamantene (11). Moreover, (11) was found to be identical with (5). The skeletal framework of (11) and the skeletal position and stereochemistry of the methoxy substituent in (11) were established by the chemical correlation of (11) with the known alcohol,¹¹ 2-exo-protoadamantanol (13), by means of the following reaction sequence. Isomerization of (1) with 0.05 M perchloric acid in refluxing 80% aqueous acetone gave 2-exo-protoadamantanol (12), mp 188-189⁰. Alkylation of (12) with methyl iodide and sodium hydride in DMF afforded (11), and hydrogenation of (12) with 5% palladium on charcoal gave (13).

As expected,² the distribution of products resulting from the methanolic sodium borohydride reduction with hydrochloric acid work-up of (2) depends strikingly on the exact reaction conditions. However, repetition of the reaction under conditions identical to those employed in the earlier report¹ gave (9), (7), and (11) in a relative ratio of 4.5 : 1.5 : 1.

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Footnotes and References

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