

A Study on the Mass Spectrum of 2,3-Dihydro-4-Phenylthieno(2,3-b)Quinoline

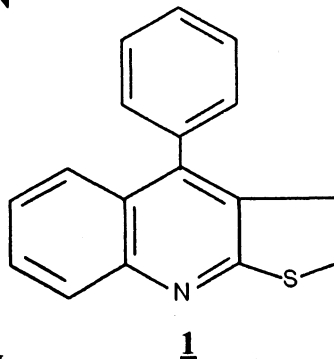
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A study has been made on the fragmentation upon electron impact of 2,3-dihydro-4-phenylthieno(2,3-b)quinoline. As a dihydrothiophene, the molecular ion expels H° , CS and CHS° species. Also, it eliminates H_2 , CH_2S and SH° radicals. The first derived ions undergo further disintegration. The presence of 4-phenyl group causes 'Proximity effect' leading to the cyclisation of the daughter ions with the elimination of the elements of hydrogen.

Key Words: Mass spectrum, 2,3-Dihydro-4-phenylthieno(2,3-b)quinoline.

INTRODUCTION

In a route to the synthesis of thieno(2,3-b)quinolines, we prepared several substituted 2,3-dihydrothieno(2,3-b)quinolines¹⁻⁴, including 2,3-dihydro-4-phenylthieno(2,3-b)quinoline (**1**). We herein report a detailed account of the fragmentations of the compound **1**. Interest in this system stems from the presence of 4-phenyl group and its possible chemical and biological points of view.



EXPERIMENTAL

The mass spectrum was obtained by the direct insertion of the sample into the ion source of a Hitachi-Perkin-Elmer RMU-6E mass spectrometer. The energy of the electron beam was 70 eV. The compound used in the study was of analytical purity and it is well known^{3,4} and it was prepared by heating 3-(2'-hydroxy ethyl)-4-phenyl-2-quinolone⁵ with P_4S_{10} .¹⁻⁴

RESULTS AND DISCUSSION

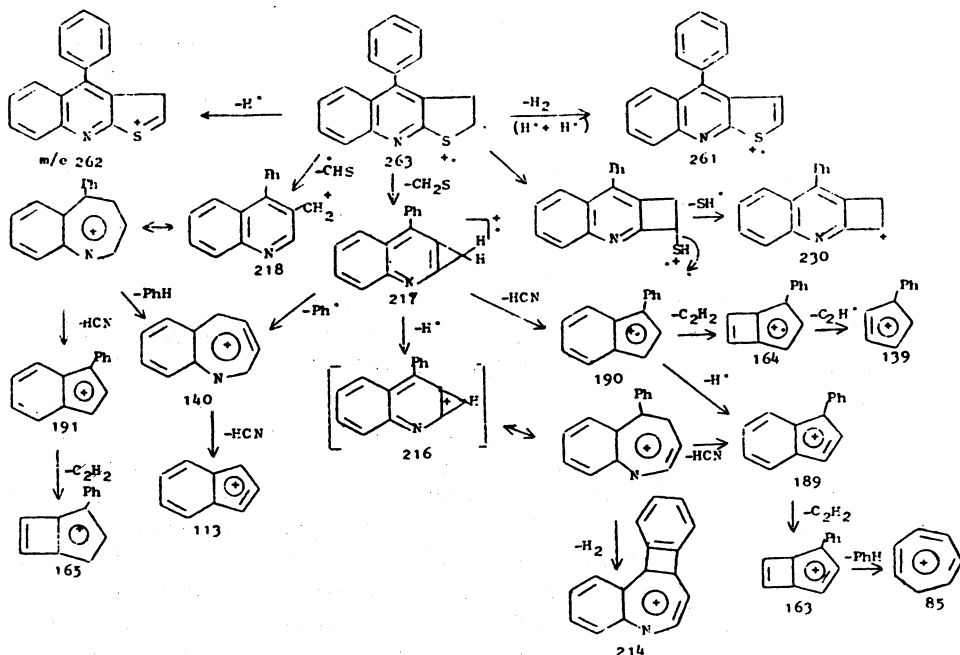
The mass spectrum of the compound **1** is reported in Table-1. Structures written for the fragment ions are only tentative and are proposed to relate the fragmentation processes to the structure of the compound.

TABLE-1
 MASS SPECTRUM OF 2,3-DIHYDRO-4-PHENYL(2,3-b)QUINOLINE

Principal Fragments (relative intensity %)
265(7), 264(24), 263(100), 262(54), 261(48), 260(24), 259(7), 248(2), 230(6), 229(3), 228(6), 227(5), 226(2), 218(2), 217(5), 216(8), 215(3), 214(5), 204(2.5), 203(3), 202(6), 201(4), 200(2), 190(5), 189(7), 188(2.5), 187(3), 186(8), 185(4), 177(2), 176(2.5), 175(2), 165(3), 164(2.5), 163(3), 152(2), 151(2), 150(2), 149(2), 141(2), 140(3), 139(2), 130(3), 127(3), 115(4), 114(4), 113(3), 111(2.5), 89(4), 88(4), 87(4), 86(3), 85(19), 83(10), 77(11), 75(11), 71(38), 69(18), 63(8), 57(60), 55(23), 51(8), 43(27), 41(12), 39(3).

As expected, the base peak in the spectrum of **1** is due to the molecular ion. Consistent with the aromaticity^{6, 7a} in the thienoquinolines are the formation of M^{2+} ions for M^+ , $M-1$ and $M-2$ ions.

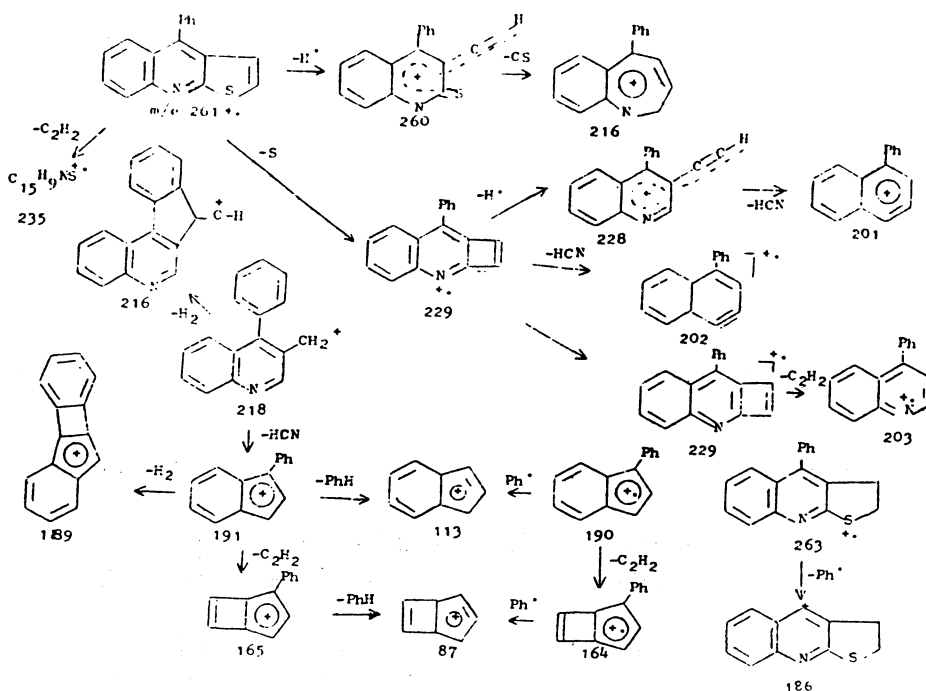
Similar to benzodihydrothiophenes^{8a} and tetradihydrothiophenes^{7b, 9}, the molecular ion of **1** expels H^{\bullet} , CS and CHS^{\bullet} . It also forms $(M-H_2)$, $(M-CH_2S)$, $(M-SH)$ ions and further fragmentations (Scheme-1). Once the loss of sulphur has occurred, the quinolinc part expels the HCN and C_2H_2 successively to form daughter ions, e.g., the formation of ions at m/e 145, 164, 165, 163.



Scheme-I

The presence of 4-phenyl group has a marked effect on the mode of fragmentation^{7c, 8b-8d, 10-13}. As in the case of phthalazines^{8b}, 4-phenyl pyrimidines^{8c}, naphthothiophens^{8d} and other phenyl compounds^{10, 11} the 4-phenyl group in this compound is also expected to induce the 'proximity effect'. It is well observed, for example, in the elimination of H₂ in the transitions m/e 216 ion to m/e 214 ion and m/e 191 ion to m/e 189 ion. Loss of phenyl radical and elements of benzene from the M⁺ ion as well as from the other fragment ions are also noted^{7c, 12, 13}

Thieno(2,3-b)quinoline ions of m/e 261 behave similar to benzothiophenes¹⁴ and decomposed by the expulsion of H⁺, CS or S or C₂H₂ (Scheme-II). After the loss of thieno part, the quinoline characteristic HCN loss is noted^{8c}. It is interesting to observe the (M-H₂S) ion to show a fragmentation behaviour similar to (M-C₂H₂) ion of acridine¹⁵. Apart from the loss of H⁺ or H₂, the ion of m/e 229 might eject HCN as well as C₂H₂ in the first step to form ions at m/e 202 and m/e 203.



Scheme-II

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