The proton-decoupled ^{13}C nmr spectrum of I shows peaks at δ 105.7, 97.9, 67.6, and 66.6, i.e., four of the five peaks expected with a symmetry plane perpendicular to the ring. The first two of these peaks are due to carbons 2, 4, 5, and 7, and the last (triplet in off-resonance spectrum and smaller than the other three) to carbon 9. The missing peak is probably obscured by the THF peak at δ 66.1.

Our failure to observe pmr peaks for the monoanion IV during the metalation of III to I contrasts with the metalation behavior of related acyclic alkenes[13] and is probably due partly to the instability of intermediate monoanion IV (angle strain in form with maximum π overlap) and partly to the stabilizing effect of developing homoaromaticity on the transition state between IV and I.

Since electron exchange between I and the anion-radical with one fewer electron is sufficiently rapid to cause broadening of the ESR lines of the latter species, it has been proposed that these species possess similar geometry.[14] To the extent that this is true, the evidence described herein for the shape of I applies to the anion-radical as well.

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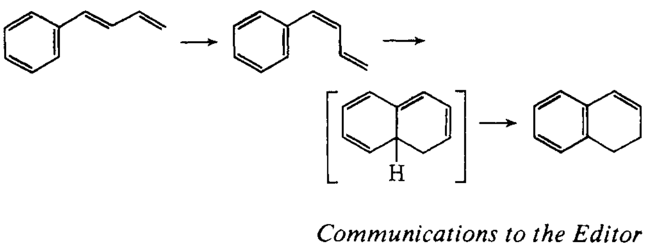
Pyrolysis of 1-Phenyl-1,3-butadienes. A New Synthesis of 1,2-Dihydronaphthalenes

Sir:

The synthesis of specifically substituted dihydronapthalenes remains a challenge since there is no general simple procedure. Reduction of naphthalene by lithium or sodium in liquid ammonia yields a 1,4-dihydronaphthalene,[1-3] which can be isomerized by strong base to the thermodynamically more stable 1,2-dihydro isomer.[4,5] While this simple sequence is applicable to substituted naphthalenes, the choice of which ring undergoes reduction is determined by the position and type of substituent.[2] Substituents in the 1-position direct reduction to the adjacent ring if electron releasing and to the same ring if electron withdrawing. Thus 1-methylnaphthalene is reduced to the corresponding 1-methyl-5,8-dihydronaphthalene.[2] Clearly, other 1-methyldihydronaphthalene isomers are not accessible by this route. Several less direct but more specific synthetic routes exist. Addition of an appropriate Grignard or organolithium reagent to 1-tetralone followed by dehydration of the alcohol constitutes a general route to 1-substituted 3,4-dihydronaphthalenes,[6,7] while cyclization of 4-substituted 4-phenylbutyric acids by treatment with polyphosphoric acid yields 4-substituted 1-tetralones which can be reduced to the alcohol and dehydrated to 1-substituted 1,2-dihydronaphthalenes.[8-10] However, synthesis of 4-substituted 4-phenylbutyric acids needed for this procedure often involves several steps.

We should like to report a new synthetic route to substituted 1,2-dihydronaphthalenes based on gas phase pyrolysis under controlled conditions of the appropriate 1-phenyl-1,3-butadiene. Thus pyrolysis of *trans*-1-phenyl-1,3-butadiene[11] at 450° yields 1,2-dihydronaphthalene[12] in 81% yield. The other products isolated are *cis*-1-phenyl-1,3-butadiene (11%)[13,14] and naphthalene (6%). Yields reported are based on recovered starting material, 30%. The pyrolysis conditions are quite critical since pyrolysis of *trans*-1-phenyl-1,3-butadiene under more vigorous conditions (550°) yields naphthalene,[15,16] while pyrolysis of *trans,trans*-1,4-diphenyl-1,3-butadiene[17] under similar vigorous conditions yields 1-phenylnaphthalene as the major product.[18]

The formation of 1,2-dihydronaphthalene from *trans*-1-phenyl-1,3-butadiene can be rationalized by a three-step reaction sequence. The first step is an isomerization of *trans*-1-phenyl-1,3-butadiene to *cis*-1-phenyl-1,3-butadiene.[13,14] The second is an electrocyclic reaction converting a conjugated triene into a 1,3-cyclohexadiene in a thermally allowed disrotatory fashion.[19-22] The triene undergoing this reaction is composed of the two double bonds of the 1,3-butadiene and one double bond of the benzene ring. Clearly, this electrocyclic reaction involves disruption of the 6π electron system of the benzene ring. The high energy of activation required for the reaction probably reflects the loss of resonance energy in the transition state. A comparison between *trans,cis,trans*-octa-2,4,6-triene which is converted to *cis*-5,6-dimethylcyclohexa-1,3-diene at 130° [22] and *trans*-1-phenyl-1,3-butadiene which does not yield 1,2-dihydronapthalene till 400° may reflect this loss of aromatic stabilization. A related example of participation of a double bond of a benzene ring in an electrocyclic reaction is the pyrolysis of 1,2-dipropenyl benzene to yield 2,3-dimethyl-1,2-dihydronaphthalene.[23] The photochemical conversion of stilbenes to phenanthrenes under oxidizing conditions similarly involves participation of double bonds from two benzene rings in an electrocyclic reaction.[24-26] The final step in our reaction sequence would be a symmetry allowed 1,5-suprafacial sigmatropic hydrogen migration leading to restoration of the aromatic nucleus.[27]



To test the proposed mechanism the pyrolysis of 1-phenyl-*2′,4′,6′*-d_3-1,3-butadiene[28] was carried out at 490°. 1,2-Dihydronaphthalene-*2′,5,7*-d_3, the predicted product, was obtained in 78% yield as well as naphthalene-*1,3,6*-d_3 (5%). The formation of naphthalene as a minor product under our reaction conditions and as the major product under more vigorous conditions can be explained by the observation that 1,2-dihydronaphthalene undergoes dehydrogenation under slightly more vigorous pyrolysis conditions (550°) to yield naphthalene.

This reaction is also useful for the synthesis of substituted 1,2-dihydronaphthalenes. Thus pyrolysis of 1-phenyl-1,3-pentadiene[30] at 450° in the gas phase yields 1-methyl-1,2-dihydronaphthalene (60%)[7] and 1-methylnaphthalene (6%). On the other hand, pyrolysis at 475° of a mixture of *cis*- and *trans*-1-methyl-1-phenyl-1,3-butadiene[31] yields the thermodynamically more stable isomer 1-methyl-3,4-dihydronaphthalene[32] in 86% yield. Pyrolysis of *trans,trans*-1,4-diphenyl-1,3-butadiene under similar conditions yields 1-phenyl-1,2-dihydronaphthalene[33] (45%) and 1-phenylnaphthalene.[7] *trans*-1-Mesityl-1,3-butadiene[34] was pyrolyzed at 470° to give the predicted product 2,5,7-trimethyl-1,2-dihydronaphthalene in 25% yield. The third step of the reaction may involve a suprafacial 1,5-sigmatropic rearrangement of a methyl group rather than a hydrogen. This might be expected to be less facile.[35] The scope of this reaction is under active investigation.[36]

Procedure for the pyrolysis of substituted 1-phenyl-1,3-butadienes is as follows. The pyrolysis was performed using a vertical tube oven. The pyrolysis tube consisted of a 30 cm long Pyrex glass tube (o.d. 12.5 mm, i.d. 9 mm) packed with 1 cm long pieces of 3-mm Pyrex tubing. The exit of the column was connected to one neck of a two-necked flask which was immersed in a Dry Ice-acetone bath. The second neck of the flask was connected to a gas flow meter. The nitrogen flow rate was adjusted to 30 cm³/min. The entire apparatus was flame dried while allowing the column to come to temperature. The substituted 1-phenyl-1,3-butadiene was added at the rate of one drop every 10–15 sec. The material from the trap was collected and subjected to analysis by GLPC on a 0.25 in. × 24 ft 20% polyphenyl ether on chromosorb P column maintained at 170°.

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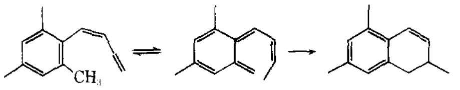

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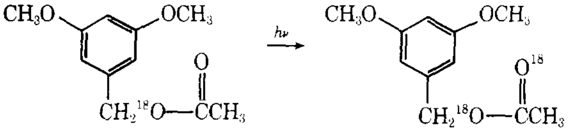
Photochemistry of Aromatic Compounds. Internal Return in the Photosolvolysis of 3,5-Dimethoxybenzyl Acetate

Sir:

Photochemical solvolyses of substituted and unsubstituted benzyl systems including acetates,[1] ethers,[2] halides,[1,3] and ammonium[4] and sulfonium[5] salts have been studied. In general, carbenium ion intermediates have been proposed but conclusively demonstrated only with 2-bromohomotriptycene[3a] and with α-phenylethyltrimethylammonium iodide.[4b] Equilibration of carboxyl oxygen atoms in esters undergoing ground state solvolysis without rearrangement has been employed[6] in detection of internal return of ion pairs, and the same principle can be applied to photosolvolysis. Mechanistic interest in photosolvolysis and in photochemistry of esters led us to investigate the possibility of carboxyl oxygen equilibration (eq 1) accompanying photosolvolysis of 3,5-dimethoxybenzyl acetate-*ether*-^{18}O (**1a**).[7,8]



1a **1b** (1)