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GAS PHASE REACTIONS INDUCED BY OH^- ION

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Abstract:- The site of proton abstraction by OH^- ion in some 4-substituted-3,5,6-triphenyl-Δ^1-cyclohexenes has been established from labelling studies. The further fragmentation mode of $(M-H)^-$ ion depends on its structure and stereochemistry. The exo and endo nitro isomers exhibit stereochemical differences in the elimination of HNO_2 while the amino and cyano analogues show stereochemically controlled RDA fragmentation mode.

High Pressure Mass Spectrometry[1](HPMS), Ion Cyclotron Resonance[2] (ICR), and Flowing Afterglow[3] (FA) techniques have been used to study the gas phase ion-molecule reactions involving OH^- ion. The FA technique is superior to HPMS and ICR because of spatial separation of ion production and reaction regions[4]. The well known reaction induced by OH^- ion is proton abstraction. Nucleophilic substitution[5], addition[3b,6] (cluster formation) and elimination[3b] reactions are also initiated by OH^- ion. Gas phase acidity studies have shown[4] that in many instances the behaviour in gas phase is different from the known behaviour in solution. However, in all cases the gas phase results are invariably in agreement with the data available from the application of ab-initio molecular orbital theory[7].

EXPERIMENTAL

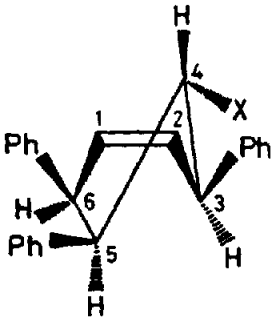
Preparation of the compounds. The 4-substituted triphenyl cyclohexenes were prepared by well described procedures[8,9]. The 4-substituted exo and endo isomers were carefully separated on silicagel by chromatographic techniques. Their structures and stereochemistry were assigned from spectral data. The NMR spectra were recorded on a Varian T-60 instrument. The labelled compounds were > 96% deuterated.

Scanning of the samples. Hydroxy ion negative chemical ionization spectra were recorded on a Finnigan 3300 GC/MS system using N_2O and CH_4 (1:1) as reagent gases. The pressure of the source was maintained at 0.4 torr and temperature at 200°C. All relative abundances are expressed as percentage of total ionization (% Σ90).

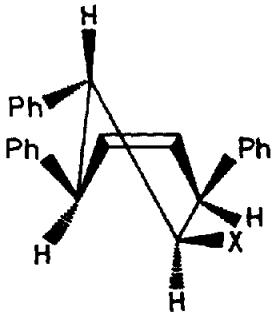
RESULTS AND DISCUSSION

The present work is on some gas phase reactions of exo and endo 4-nitro, cyano and amino substituted -3,5,6-triphenyl -Δ^1-cyclohexenes induced by OH^- ion (Scheme 1). The relative abundances of $(M-H)^-$ ions are different (Table-I). An analysis of the spectra of these compounds showed that the site of proton abstraction and the further fragmentation of $(M-H)^-$ ions depend on the nature of the C_4-substituent. The $(M-H)^-$ ions of the nitro isomers undergo HNO_2 elimination (m/z 307) and H_2O loss

(m/z 336). The $(M-H)^-$ ions of the amino and cyano isomers fragment by RDA. Considerable stereochemical effects were observed in the nitrous acid elimination and RDA fragmentation modes.



exo



endo

$X = NO_2$
$= NH_2$
$= CN$

Scheme 1

TABLE-I

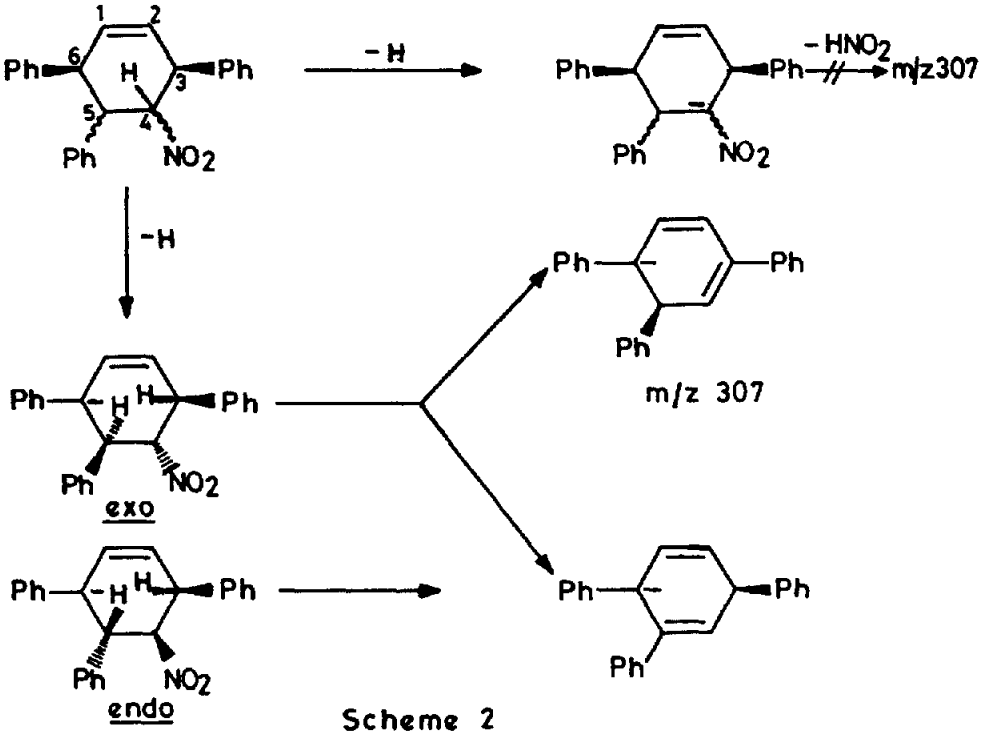
Substituent		$(M-H)^-$	m/z 307	m/z 336	(Dienophile-H)$^-$
NO_2	exo	00.66	65.17	09.31	-
	endo	15.00	15.00	20.00	-
NH_2	exo	71.61	-	-	04.65
	endo	55.48	-	-	24.09
CN	exo	51.04	-	-	29.00
	endo	44.88	-	-	32.64

A study of the OH^- ion negative chemical ionization (NCI) spectra of C_4- and C_5- deuterated nitro isomers, C_4- deuterated cyano and deuterated amino (ND_2) compounds has thrown some light on the sites of proton abstraction in these compounds. The spectra of C_5- deuterated exo and endo nitro isomers showed that the C_5- deuterium is not abstracted. However, the spectra of C_4- deuterated nitro and cyano compounds revealed that the loss of both C_4- deuterium and C_3 or C_6 proton. In the amino compound as expected the proton is abstracted from amino group only.

The further fragmentation of the $(M-H)^-$ ions in the nitro compound is a preferred HNO_2 elimination (m/z 307). It is difficult to rationalise the elimination of HNO_2 from the $(M-H)^-$ ion formed by the loss of C_4- proton unless there is a prior proton migration. However, HNO_2 elimination can operate after the primary loss of C_3 or C_6 proton. The observed stereochemical differences in the relative abundances of m/z 307 ion in the exo and endo isomers could be rationalised if C_6- proton is abstracted in the primary step. In the exo isomer two cis-eliminations are possible. In the endo isomer only one cis-elimination can operate (Scheme 2).

The loss of H_2O in nitro compounds is known under electron ionization conditions[10]. The nitro derivatives under study also showed loss of H_2O from the $(M-H)^-$ ion.

Exclusive loss of HDO was observed in the spectrum of C_4- deuterated compounds while loss of H_2O and HDO were observed in the spectrum of C_5- deuterated analogues (Table-II).



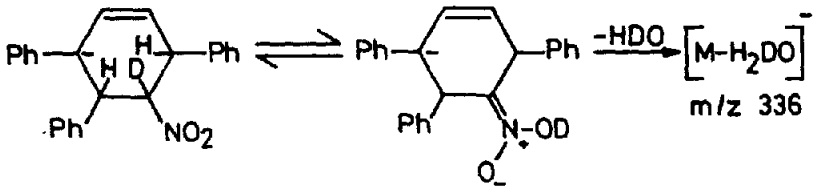
Scheme 2

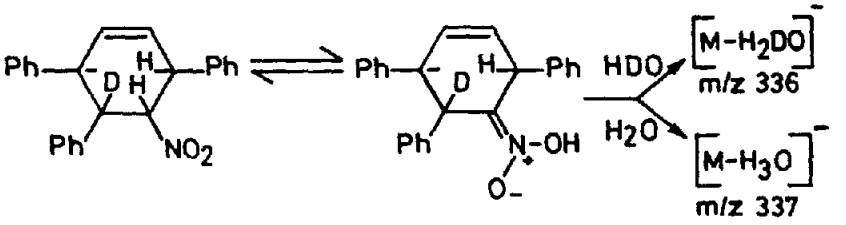
TABLE-II

Position of deuterium		$(M-H)^-$	$(M-D)^-$	m/z 307	m/z 308	m/z 336	m/z 337
C_4	exo	0.22	-	3.96	66.88	6.16	0.20
	endo	3.62	5.92	1.60	12.80	18.56	0.50
C_5	exo	0.92	-	28.52	34.04	1.84	9.24
	endo	8.00	0.64	6.08	16.30	6.40	11.84

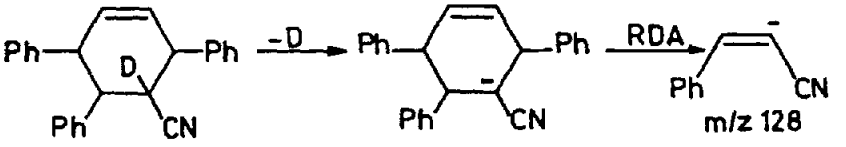
A possible mechanism involving tautomerization to aciform and abstraction of any one of the neighbouring protons has been proposed on the basis of the available data (Scheme 3).

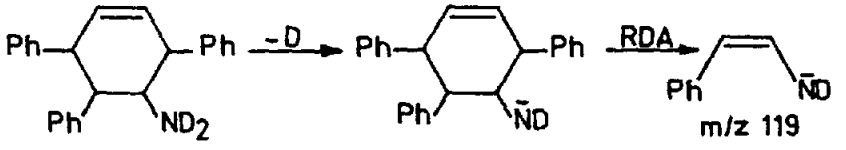
Mandelbaum and co-workers[11] have reported stereochemical effects on RDA induced by chemical ionization in carbenium ions. RDA reaction in carbanions were observed by Bowie and coworkers[12]. The $(M-H)^-$ ions of the exo and endo isomers of the 4-cyano and amino derivatives undergo RDA fragmentations to give the $(dienophile-H)^-$ ions (Scheme 4). The deuterium atom is totally absent in the RDA product ion from both exo and endo C_4- deuterated cyano derivatives even though both $(M-H)^-$ and $(M-D)^-$ ions were observed (Table III). Hence, the RDA reaction takes place only after deuterium abstraction or alternatively after C_3- proton loss followed by a deuterium transfer.





Scheme 3





Scheme 4

TABLE-III

Substituent		$(M-H)^-$	$(M-D)^-$	$(Dienophile-D)^-$
CN (C_4-D)	exo	45.56	29.24	10.88
	endo	42.00	39.60	10.00
ND_2	exo	-	69.50	4.50
	endo	-	50.00	28.50

The spectra of deuterated exo and endo amino (ND_2) isomers showed only $(M-D)^-$ ion and (dienophile-D)$^-$ion containing only one deuterium. The relative intensities of the RDA product of exo and endo isomers are shown in Table III. This is the first example of the $(M-H)^-$ ions undergoing RDA fragmentation mode which is stereochemically controlled. The formation of $(M-H)^-$ ion itself depends on many factors. In the cyano compounds the abstraction of C_4- proton results in the loss of stereochemical difference at that position. In the amino compound the $(M-H)^-$ ion retains the original stereochemical configuration.

The electron capture behaviour of these compounds showed that the $M^{\cdot-}$ ion loses a H-atom preferably from the C_6 and to a minor extent from C_5-positions. No evidence was obtained for any loss of H-atom from C_4-position. The loss of H_2O was not a significant process from $(M-H)^-$ ion. The loss of HNO_2 and RDA fragmentation modes operate from the $(M-H)^-$ ion and similar stereochemical effects were observed as described under OH^- ion NCI behaviour of these compounds.

The present studies demonstrate that the site of proton abstraction depends on many factors which are not well understood. Factors other than acidity appear to play a significant role. The further fragmentation mode of $(M-H)^-$ ion depends on its structure and stereochemistry.

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