Indian Journal of Chemistry
Vol. 45B, May 2006, pp. 1234-1241

Mass spectral fragmentation of substituted adamantane-2,4-diones

M Giasuddin Ahmed[a]* Syed M Iqbal Moeiz[a], S Asghari Ahmed[a] & Abul Hussam[b]

[a]Department of Chemistry, University of Dhaka, Dhaka 1000, Bangladesh

[b]Chemistry Department, MSN 3E2, George Mason University, Fairfax, VA 22030 USA

E-mail: mgahmed1@yahoo.com

Received 30 April 2004; accepted (revised) 8 December 2005

A number of suitably substituted adamantane derivatives are potentially biologically active. Keeping this in mind, the mass spectral fragmentation patterns of substituted adamantane-2, 4-diones **1a-6b** have been studied.

Keywords: Substituted adamantane-2,4-diones, mass spectral fragmentation

IPC: **Int.Cl.^{8} C 07 C**

Several reports[1-5] are available on the potential biological activity of a number of suitably substituted adamantane derivatives in the literature. Having this background, mass spectral fragmentation pattern of substituted adamantane-2, 4-diones (**1a-6b**) have been reported in the present paper.

Mass spectral fragmentations of adamantane derivatives have received much attention[6-21] but not much progress is made for their analysis. A few generalizations are advanced, however, primarily on the basis of the nature of the substituents and the positions they occupy at the adamantanoid compounds.

Bauer *et al.*[21] reported that the molecular ions of 1-substituted adamantanes (1-AdmX) undergo primary fragmentation following one or more of three pathways: (a) loss of substituent X as a radical, (b) loss of HX as a neutral molecule, (c) loss of the C_4H_9 hydrocarbon radical but no structure was assigned to the resulting ion. It was observed that the path as well as the degree of fragmentation varied in the sulphur-linked, oxygen-linked, carbon-linked and phosphorous-linked adamantanes.

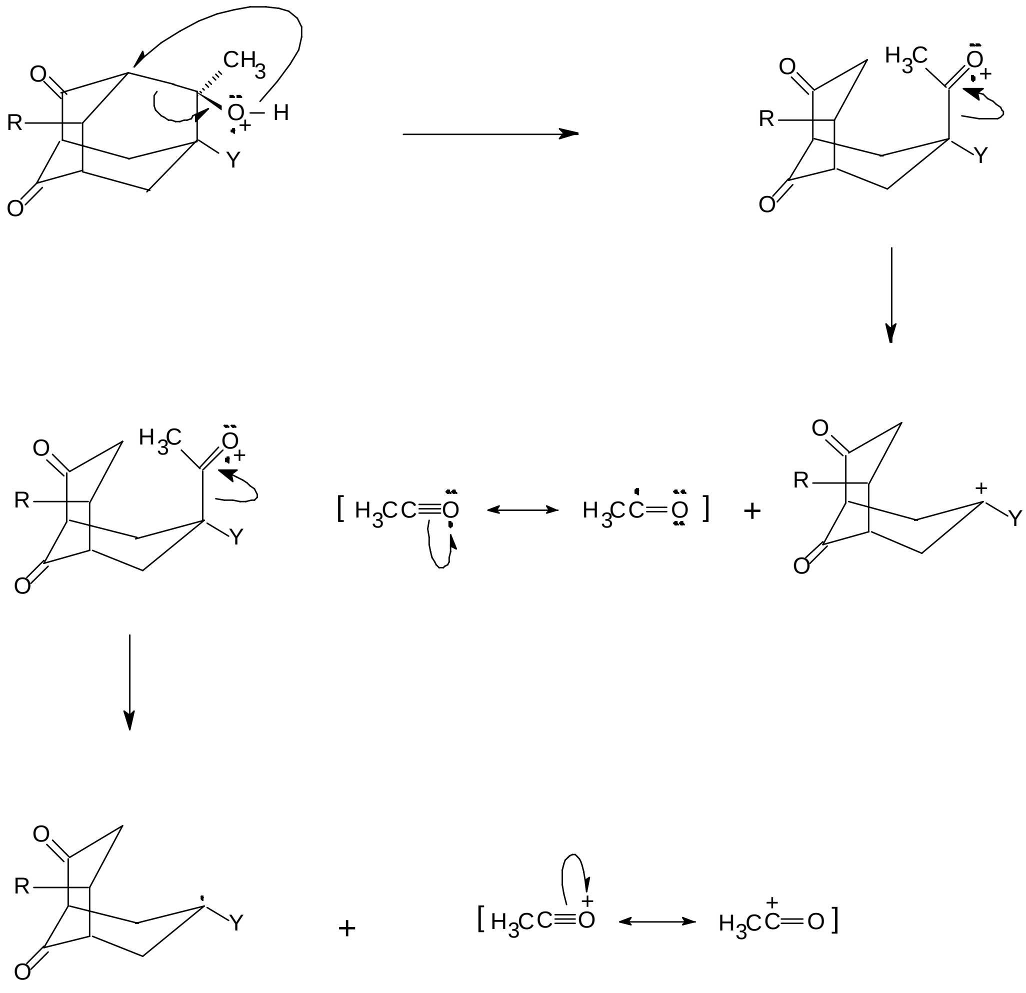
In the mass spectra of 2-substituted adamantanes (2-AdmX), in most cases $[M-HX]^+$ ion was recognized as the most prominent peak[14-23]. Such an ion was thought to possess a structure corresponding to the molecular ion of protoadamantene[22] rather than that of 2,4-dehydroadamantane as considered earlier[15]. An investigation into the fragmentation of a series of β-substituted adamantanones and adamantanediones[20] showed that in addition to the formation of $[M-HX]^+$ ions, elemination of X also takes place as neutral atoms in the cases of halogens giving the corresponding 2-adamantyl cation. β-Substituted adamantanediones having various COR- and NR_1R_2 - groups exhibit characteristic ion peaks which are formed by McLafferty rearrangement and α–cleavage with subsequent elimination of carbon monoxide and allylic bond fission. In the mass spectra of some disubstituted adamantanes, an indication of possible occurrence of the adamantene ion was noted[24].

The effect of substitutions particularly at the bridgehead position of substituted adamantane-2, 4-diones (**1a-6b**), have been reported in this paper.

The adamantanediones produced peaks for the respective molecular ions in varying intensities (**Table I**). Loss of a mass number 43 was observed in all the compounds in varying amounts (**Table I**) and it was attributed to the removal of CH_3CO radical from the molecular ions (**Scheme I**). Loss of H_2O molecule giving rise to $[M-18]^+$ ion was insignificant in most of the compounds except in **1a** (12%), **2b** (6%), **6a** (6%) and **6b** (7%). This is in contrast to the reported mass spectral behaviour of β-hydroxy substituted adamantanes[14,20,23] and may be attributed to the production of less stable $[M-18]^+$ ions in the compounds of present study due to steric interactions. 6-Hydroxyl group was eliminated as a radical in significant amounts from the molecular ions of **1a**, **2a**, **2b**, and **2c** in 48%, 80%, 48% and 25%, respectively

Table I — Ions of Direct Fragmentation and Lower Mass numbers

Ion/ Ion radical	**1a**		**1b**		**2a**		**2b**		**2c**		**3**		**4a**		**4b**		**4c**		**5**		**6a**		**6b**	
	m/z	I	m/z	I	m/z	I	m/z	I	m/z	I	m/z	I	m/z	I	m/z	I	m/z	I	m/z	I	m/z	I	m/z	I
M^+	208	10	222	23	270	60	284	20	346	13	346	15	234	7	248	7	310	4	310	1	266	35	280	13
M^+-CH_3CO	165	37	179	19	227	3	241	4	303	10	303	10	191	7	205	9	267	4	267	1	223	11	237	12
M^+-H_2O	190	12					266	6													248	6	262	7
M^+-OH	191	48			253	80	267	48	329	25	329	25												
M^+-CH_3																					251	9	265	17
M^+-CO	180	18	194	28																	238	3	252	2
M^+-(CO,H_2O)	162	48	176	39					300	25	300	12									220	17	234	34
M^+-$COOCH_2CH_3$																					193	24	207	22
M^+-$HCOOCH_2CH_3$																					192	35	206	68
H-C=O																	29	100	29	100				
CH_3-C=O	43	65	43	100	43	15	43	17	43	6	43	44	43	100	43	100	43	6	43	2	43	100	43	100
CH_2-CH=C=O	55	50	55	57			55	7			55	1	55	54	55	42	55	4	55	1	55	67	55	62
CH_3CH-CH=C=O			69	41			69	20					69	11	69	34					69	10	69	63
C_6H_5CH-CH=C=O									131	25	131	56					131	7	131	2				



Scheme I

and to a lesser extent in **3** (5%). Instances of such a loss of OH radical from the β-hydroxy substituted adamantanes do not appear to be reported in the literature. However, 1-adamantanol is reported[21] to produce a minor peak at m/z 135 (5%) due to the loss of OH radical from the molecular ion.

In compounds **1a** and **2a-c** -OH group is axial to the ring and in **3** it is equatorial. Compounds **2a-c** and **3** have a common substituent phenyl at the 7-position and **1a** has a methyl substituent at this position. Loss of OH radical from the molecular ions of these compounds produced a carbocation at the 6-position which is probably stabilized by electron releasing groups like phenyl and methyl. The stabilization of the carbocation produced may be attributed to the resonance effect due to the phenyl group and hyperconjugation arising from methyl group.

The $[M\text{-}17]^+$ ions formed from the molecular ions of **1a** and **2a-c** due to loss of OH radical underwent a further loss of a CO molecule whereby a keto carbonyl group was lost producing $[M\text{-}17\text{-}28]^+$ ions having 23%, 7%, 5% and 10% relative abundance, respectively.

In each of the compounds **2a,b** and **3** the molecular ion lost a mass of 126 to produce the corresponding base peak. This may be explained by the loss of $C_6H_5O_2$ from the $[M\text{-}17]^+$ ions probably resulting from the cleavage of the ring containing both the keto groups.

On the other hand, the compound **2c** which is an epimer of **3** at the 6-position lost a mass of 95 from its molecular ion to give the base peak. This may be explained by the simultaneous loss of a H_2O molecule and removal of the $-C_6H_5$ group at 9-position as a radical whereby the steric strain is relieved in the resulting dehydrated structure[22]. All the fragmentation patterns discussed above are shown in **Scheme II**.

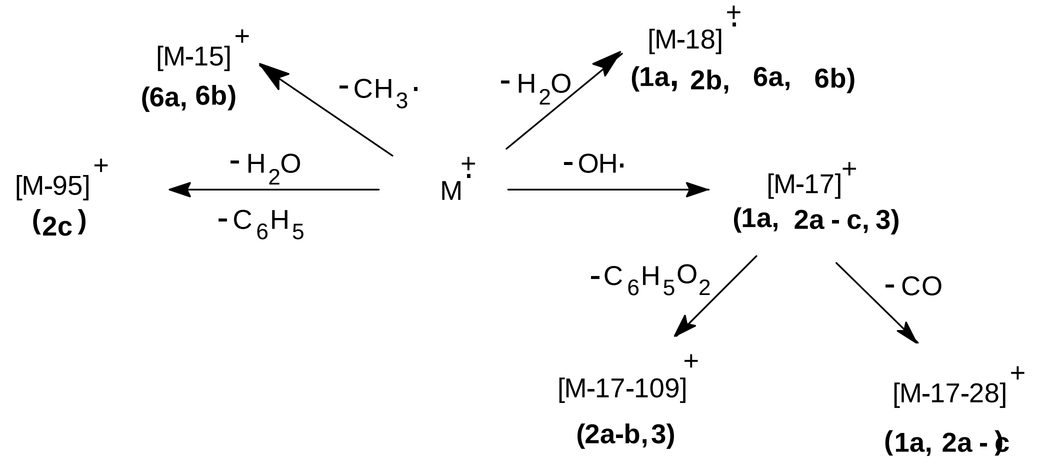
Loss of $-CH_3$ group as a radical from 2-position (**Scheme III**) was observed in the cases of **6a** and **6b** probably because of the stabilization received in the corresponding carbocation produced through a weak hydrogen bonding formed between the -OH group at the 2-position and $-COOC_2H_5$ group at 1-position. None of these compounds showed peaks due to the loss of CH_4 molecule from the molecular ion.

An indication of decarbonylation of one keto carbonyl group was noted as a loss of mass 28 from the molecular ions of **1a** (18%) and **1b** (28%) and to a smaller extent in **6a** (3%) and **6b** (2%). A secondary fragmentation of these ions took place due to a loss of mass 18 as H_2O molecule producing fragment ions, $[M\text{-}28\text{-}18]^+$ in **1a** (48%), **1b** (39%), **6a** (17%) and **6b** (34%).

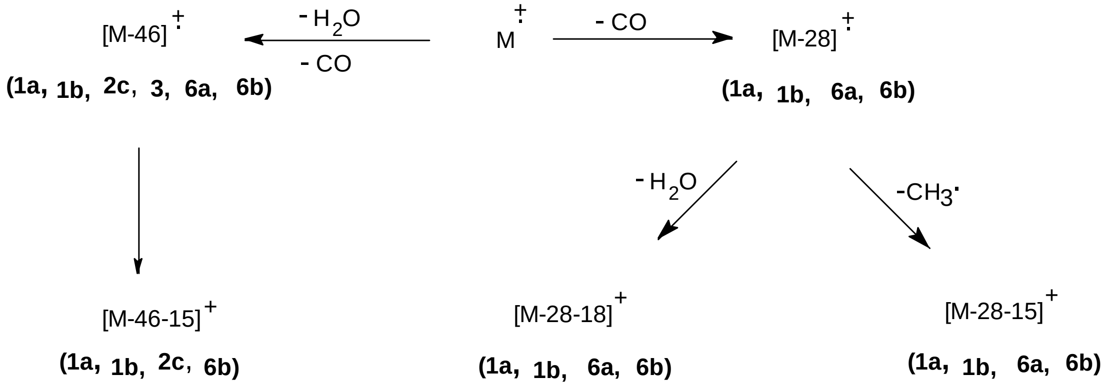
Another mode of secondary fragmentation due to loss of CH_3 radical giving fragment ions, $[M\text{-}28\text{-}15]^+$ occurred in **1a** (37%), **1b** (19%), **6a** (11%) and **6b** (12%).

Peaks due to the loss of a mass number 46 were produced from the molecular ions of **2c** (25%) and **3** (12%) whereby H_2O and CO were lost simultaneously. In addition to the stepwise losses simultaneous loss of H_2O and CO molecule might have taken place also in **1a, 1b, 6a** and **6b** since the relative intensities of $[M\text{-}46]^+$ ions in these compounds were reasonably high. A further loss of mass 15 due to CH_3 radical giving $[M\text{-}46\text{-}15]^+$ ions were recognizable in the cases of **1a** (20%), **1b** (28%), **2c** (14%) and **6b** (28%).

In the cases of **6a** and **6b** $-COOCH_2CH_3$ group was lost from the bridgehead 1-position as a radical to give $[M\text{-}73]^+$ ions in 24% and 22% relative abundance, respectively. Loss of similar structural moiety has been reported[21]. The $-COOCH_2CH_3$ group was also lost



Scheme II



Scheme III

along with a hydrogen atom from **6a** and **6b** producing $[M-74]^+$ ions in 35% and 68% relative abundance, respectively. A further loss of mass 15 due to CH_3 radical occurred from $[M-74]^+$ ions producing peaks having 50% and 46% relative abundance, respectively in **6a** and **6b**. $[M-74-15]^+$ ions thus produced further lost a keto group as CO molecule giving rise to $[M-74-15-28]^+$ ions from **6a** and **6b** in 11% and 21% relative intensities respectively. All these fragmentation pathways are shown in **Scheme IV**.

In the lower mass number area the most intense peak (base peak) for the compounds **4c** and **5** was produced at m/z 29 and this may be attributed to the formation of a formyl cation (**Scheme V**). A peak at m/z 43 was common to all the compounds in varying amounts and this was the base peak in **1b**, **4a**, **4b**, **6a** and **6b**. This has been probably due to the production of an acetyl cation (**Scheme I**). In the case of **1a** the most intense peak was observed at m/z 109, $[M+1]^+$ ion. This is probably due to some impurities present. The second most intense peak in **1a** was at m/z 43.

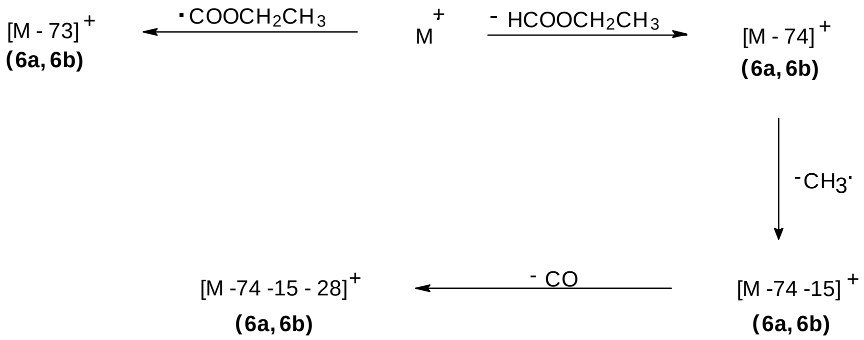
Another very prominent peak was found at m/z 55 except in the compounds with a phenyl substituent at either or both 7- and 9-positions where the peak was either absent or less prominent. This was most likely formed by a three-carbon fragment containing a keto carbonyl group giving rise to $[CH_2\text{-}CH{=}C{=}O]^+$. In a similar way compounds having a methyl substituent at position 9 (10 in **6b**) produced an intense peak at m/z 69 probably due to $[CH_3\text{-}CH\text{-}CH{=}C{=}O]^+$ ion. A minor contribution to the peak at m/z 69 was observed in the cases of **4a** (11%) and **6a** (10%) without a methyl substituent at 9-position (10 in **6a**). In these cases, however, four ring carbons might have participated to produce this fragment ion. Compounds **2c**, **3**, **4c**, **5**, having a phenyl substituent at the 9-position underwent similar type of fragmentation and gave a peak at m/z 131 due to $[C_6H_5CH\text{-}CH{=}C{=}O]^+$ ion. All these ions having relatively lower m/z value are shown in **Table I**. Characterization data for the compounds are given in **Table II-IV**.

Experimental Section

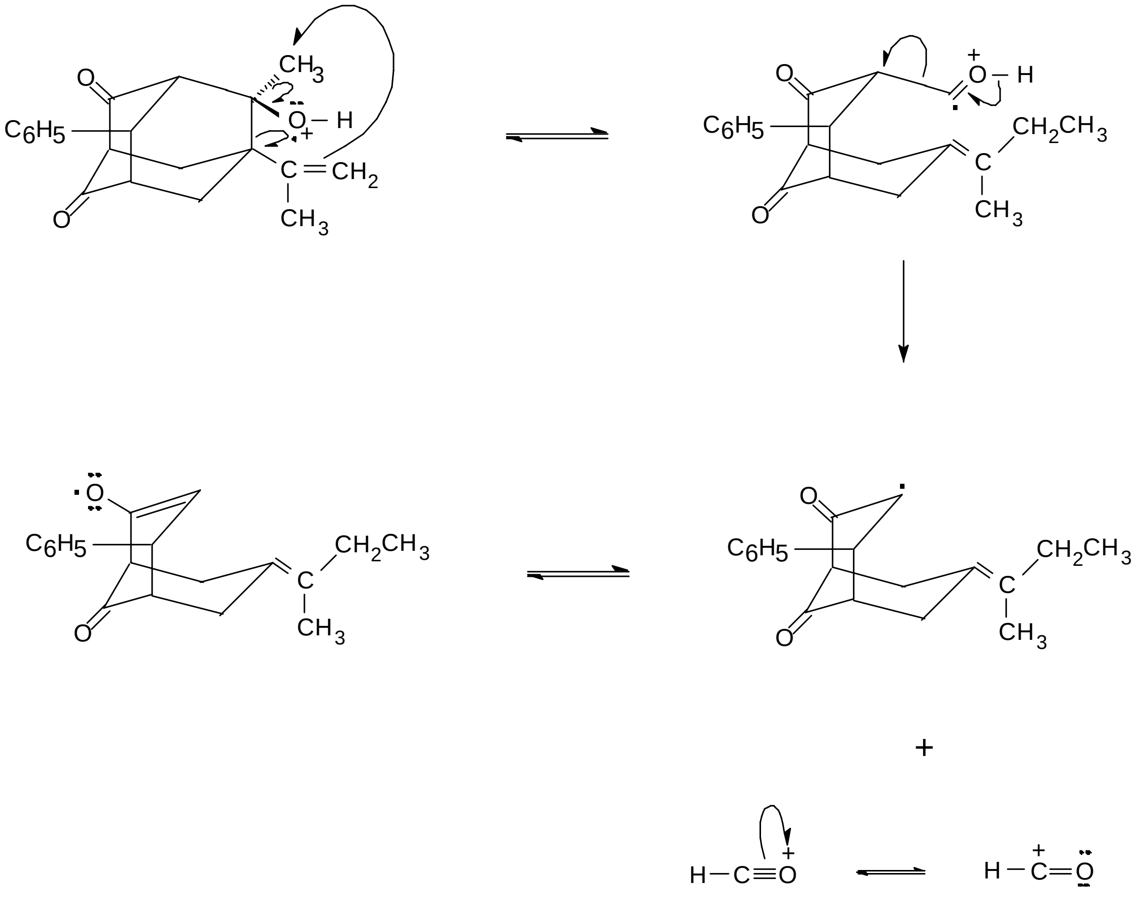
In the GC-MS studies Hewlett Packard 5890 gas chromatograph and Finnigan MAT mass spectrometer having an ion trap detector (ITD) were used. The mass spectrometer was operated at 70 eV. A single peak was shown in the chromatograph by each of the compounds **1a-6b**. The effluent vapour of each of these compounds was introduced from the gas chromatograph into the mass spectrometer. The peak (m/z) values in the mass spectrometer were thus confirmed to be due to the fragments produced from each of the pure compounds.

Compounds **1a-6b** were prepared as reported elsewhere[25-27]. The general method of formation of these compounds is given below.

General Method — The α,β-unsaturated acid chloride (20.55-21.02 mmol) in dry benzene (40-45 mL) was added dropwise to a boiling solution of enamine (20.55 mmol) in dry benzene (130-160 mL) during 2h. During the addition a solid was precipitated from the reaction mixture. The mixture was then heated under reflux with stirring for 20h, cooled and the precipitated iminium salt was then filtered off, washed with dry benzene and hydrolyzed by stirring with ice cold water (50 mL) for 10 h. The crude adamantane derivatives were isolated by extraction with ether (5×25 mL) and purified either by fractional recrystallization from chloroform and light petroleum (60-80°C) or with the help of column chromatography (silica gel column) eluted initially with light petroleum (60-80°C), followed by gradual addition of chloroform.



Scheme IV



Scheme V

(6*R*)-6-Hydroxy-6, 7-dimethyladamantane-2, 4-dione 1a[25]:

Yield 34%, purified with the help of column chromatography where silica gel 100 and light petroleum - chloroform with the gradual increase of polarity upto 10:1 were used, m.p. 247-48°C, R_f 0.32 (chloroform-ethyl acetate, 5:1). HRMS: Calcd for $C_{12}H_{16}O_3$ (M^+) 208.1099; Found 208.1099.

(6*R*,9*R*)-6-Hydroxy-6, 7, 9-trimethyladamantane-2,4-dione 1b[26]: Yield 22.8%, purified by recrystallization from chloroform and light petroleum

Table II — ^{1}H NMR spectral data of the adamantanedions **1a, 1b, 2a, 2b, 2c, 3, 4c, 5, 6a and 6b** (Chemical shifts in δ) Solvent $CDCl_3$/TMS

Protons	**1a**	**1b**	**2a**	**2b**	**2c**	**3**	**4a**	**4b**	**4c**	**5**	**6a**	**6b**
1-H	2.67	2.52	2.80	2.66	3.23	3.34	2.71	2.58	3.09	3.20	2.78	2.61
3-H	2.65	3.26	3.50	3.43	3.52	3.47	3.39	3.31	3.39	3.38	3.40	3.33
5-H	3.32	2.52	2.80	2.66	3.19	3.17	2.71	2.58	3.09	3.07	2.78	2.61
8-H^e	2.52	2.62	3.28	3.30	3.50	3.04	2.91	2.93	3.12	2.64	2.89	2.90
8-H^a	1.67	1.71	1.95	1.99	2.14	2.53	1.85	1.84	2.00	2.37	2.06	2.10
9-H^e	2.55	2.76	2.73	2.94	4.24	3.63	2.64	2.83	4.12	3.52	2.70	2.90
9-H^a	1.54	…	1.64	---	---	---	1.54	…	---	---	1.56	0.79
10-H^e	2.07	2.02	2.86	2.84	2.90	3.53	2.48	2.46	2.51	3.17	2.35	2.36
10-H^a	2.02	2.02	2.38	2.35	2.43	2.20	2.21	2.17	2.28	2.05	2.64	2.56
6-OH	1.78	1.71	1.75	1.61	1.75	1.90	1.79	1.97	1.56	1.58	4.16	4.20
6-CH_3	1.31	1.30	1.07	1.06	1.13	1.29	1.28	1.28	1.34	1.54	1.32	1.32
9-CH_3	---	0.79	----	0.85	---	---	….	0.79	---	---		
$7\text{-C}_6\text{H}_5$	---		7.30-7.41	7.30-7.42	7.16-7.44	7.15-7.17	….	….	---	---		
$9\text{-C}_6\text{H}_5$	---		---	---	7.16-7.44	7.17-7.45	….	….	7.11-7.27	7.12-7.28		
7-H^c	---		---	---	---	---	4.89	4.89	4.92	4.89		
7-H^t	---		---	---	---	---	5.15	5.15	5.18	5.14		
7-CH_3	1.00	1.00	---	---	---	---	1.88	1.88	1.90	1.92		
7-O-CCH_3											1.30	1.30
7-OCH_2											4.24	4.24

Table−III — Coupling constants (J in Hz) of the adamantanediones **1a, 1b, 2a, 2b, 2c, 3, 4c, 5, 6a** and **6b**

Protons	**1a**	**1b**	**2a**	**2b**	**2c**	**3**	**4a**	**4b**	**4c**	**5**	**6a**	**6b**
$8^a,8^e$	13.29		13.08	13.20	13.08	13.67	12.8	12.8	14.00	13.75		
$1,8^e$	3.20		3.64	3.60	3.33	3.42			3.30	3.80		
$1,8^a$	2.29		3.11	3.30	3.10	3.41			4.00	3.30		
$8^e,10^e$	3.67	3.9	4.20	4.20	3.63	4.40	3.8	3.8	3.91	4.00	12.2	12.9
$10^a,10^e$	13.75		13.83	13.50	13.30	12.70	13.5	13.6	13.55	13.10	13.3	
$3,10^e$	3.66	2.8	3.70	3.90	3.71	3.90	3.8	3.8	3.95	4.12	3.4	3.5
$3,10^a$	2.75		2.50	2.80	2.04	2.44	3.0	2.8	2.80	2.72	2.9	2.9
$9^a,9^e$	13.75	7.3					13.0	7.3				
$1,9^a$	3.21											
$1,9^e$	2.75											
$5,9^a$	2.29											
$5,9^e$	2.75											
$7\text{-CH}_3,\text{H}^c$							1.3	1.3				
$7\text{-CH}_3,\text{H}^t$							0.6	….				
$7\text{- H}^t, \text{H}^c$							1.3	1.1				
7-Et											7.2	7.2

Table IV — ^{13}C NMR spectral data of the adamantanedions **1a, 1b, 2a, 2b, 2c, 3, 4c, 5, 6a and 6b** (Chemical shifts in δ)
Solvent $CDCl_3$/TMS

Carbons	**1a**	**1b**	**2a**	**2b**	**2c**	**3**	**4a**	**4b**	**4c**	**5**	**6a**	**6b**
1-C	44.39	51.05	43.74	50.56	49.49	49.64	44.07	50.58	49.39	49.42	43.31	49.53
2-C	208.15	208.71	207.57	208.19	208.89	208.58	207.95	208.54	209.23	208.99	205.86	206.50
3-C	67.05	67.37	66.60	66.79	66.94	67.57	66.58	66.78	66.82	67.31	66.15	60.16
4-C	205.65	406.00	204.85	205.26	205.24	205.87	205.10	205.48	205.48	206.09	203.86	204.30
5-C	57.99	64.90	57.52	64.05	63.42	63.02	57.91	64.59	63.59	63.16	56.07	62.58
6-C	75.09	75.65	74.64	75.26	76.00	79.31	74.92	75.56	76.10	79.08	73.56	74.20
7-C	37.17	36.81	44.11	43.37	43.71	43.77	44.48	44.08	44.30	44.30	47.94	47.39
8-C	40.33	40.90	38.60	39.00	40.39	40.95	38.14	38.67	40.01	40.63	36.70	36.93
9-C	25.22	30.23	25.14	29.97	40.50	43.03	25.11	29.83	40.20	42.60	24.62	29.18
10-C	43.38	43.37	40.71	40.59	41.77	44.31	40.79	40.67	41.74	43.61	37.81	37.53
6-CH_3	23.81	23.92	24.94	25.09	24.82	24.81	25.11	25.23	25.00	24.71	25.00	24.93
9-CH_3							...	17.51			...	17.24
7-CH_3	20.17	19.85	---	---	---	---	...	...	---	---	14.09	13.96
7-C_6H_5 and/or 9-C_6H_5	---		140.54(C_1) 128.27(C_2) 127.54(C_2) 127.25(C_1)	140.31(C_1) 127.43(C_2) 128.35(C_2) 127.31(C_1)	140.07(C_1) 139.49(C_1) 128.73(C_2) 128.34(C_2) 127.43(C_2) 127.34(C_1) 126.99(C_2) 126.93(C_1)	140.17(C_1) 138.67(C_1) 129.94(C_2) 128.46(C_2) 127.41(C_1) 127.38(C_1) 127.35(C_2) 126.92(C_2)			139.50(C_1) 128.65(C_2) 127.16(C_1) 126.88(C_2)	138.53(C_1) 128.73(C_2) 127.17(C_1) 126.74(C_2)		
7-C-$\underline{C}H_3$	---		---	---	---	---	23.16	23.22	23.25	23.04		
7-$\underline{C}{=}CH_2$	---		---	---	---	---	146.33	146.16	145.75	145.63		
7-$C{=}\underline{C}H_2$	---		---	---	---	---	115.26	115.34	115.61	115.20		
7-CH_2											61.92	61.80
7-CO											174.39	174.29

(40-60°C), m.p. 120-21°C, R_f 0.46 (chloroform-ethyl acetate, 5:1) Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.3; H, 8.1%. Found: C, 69.8; H, 7.996%.

(6*R*)-6-Hydroxy-6-methyl-7-phenyladamantane-2,4-dione 2a^{25}: Yield 35%, purified by recrystallization from chloroform and light petroleum (40-60°C), m.p. 180-81°C, R_f 0.50 (chloroform-ethyl acetate, 6:1).

(6*R*,9*R*)-6-Hydroxy-6,9-dimethyl-7-phenyladamantane-2,4-dione 2b^{25}: Yield 28%, purified by recrystallization from chloroform and light petroleum (40-60° C), m.p. 178-79°C, R_f 0.74 (chloroform-ethyl acetate, 4:1).

(6*R*,9*R*)-6-Hydroxy-6-methyl-7,9-diphenyladamantane-2,4-dione 2c^{25}**:** Yield 27%, purified with the help of column chromatography where silica gel 100 and light petroleum - chloroform with the gradual increase of polarity upto 10:1 were used, m.p. 222-23°C, R_f 0.80 (chloroform-ethyl acetate, 4:1).

(6*S*,9*R*)-6-Hydroxy-6-methyl-7,9-diphenyladamantane-2,4-dione 3^{25}**:** Yield 14%, purified with the help of column chromatography where silica gel 100 and light petroleum - chloroform with the gradual increase of polarity upto 10 1 were used, m.p. 252-53° C, R_f 0.78 (chloroform-ethyl acetate, 4:1).

(6*R*)-6-Hydroxy-7-isopropenyl-6-methyladamantane-2,4-dione 4a^{27}**:** Yield 29.8%, purified by recrystallization from chloroform and light petroleum (40-60° C), m.p. 126-27°C, R_f 0.54 (chloroform-ethyl acetate, 4:1).

(6*R*,9*R*)-6-Hydroxy-7-isopropenyl-6,9-dimethyladamantane-2,4-dione 4b^{27}**:** Yield 27%, purified by preparative TLC on silica gel (eluting with chloroform - ethyl acetate, 3:1) and then further purified by recrystallization from chloroform and light petroleum (40-60° C), m.p. 157-58°C, R_f 0.68 (chloroform-ethyl acetate, 3:1). Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.6; H, 8.1. Found: C, 72.3; H, 8.2%.

(6*R*,9*R*)-6-Hydroxy-7-isopropenyl-6-methyl-9-phenyladamantane-2,4-dione 4c[27]: Yield 25%, purified with the help of column chromatography where silica gel 100 and light petroleum – chloroform were used, m.p. 160-61°C, R_f 0.48 (chloroform).

(6*S*,9*R*)-6-Hydroxy-7-isopropenyl-6-methyl-9-phenyladamantane-2,4-dione 5[27]: Yield 18%, purified with the help of column chromatography where silica gel 100 and light petroleum - chloroform were used, m.p. 180-81°C, R_f 0.20 (chloroform).

(2*R*)-2-Hydroxy-2-methyl-4,6-dioxoadamantane-1-carboxylate 6a[26]: Yield 9%, purified by preparative TLC on silica gel (eluting with chloroform - ethyl acetate, 3:1) and then further purified by recrystallization from chloroform and light petroleum (40-60° C), m.p. 105-07° C, R_f 0.44 (chloroform-ethyl acetate, 3:1). Anal. Calcd for $C_{14}H_{18}O_5$: C 63.1; H 6.7. Found: C 63.1; H 6.8%.

(2*R*,10*R*)-2-Hydroxy-2,10-dimethyl-4,6-dioxoadamantane-1-carboxylate 6b[26]: Yield 22.2%, purified by preparative TLC on silica gel (eluting with chloroform - ethyl acetate, 3:1) and obtained as a viscous liquid, R_f 0.51 (chloroform-ethyl acetate, 3:1). Anal. Calcd for $C_{14}H_{18}O_5$: C, 64.1; H, 7.1. Found: C, 64.1; H, 7.1%.

Acknowledgement

A fellowship to one of the authors (S.M.I.M.) by the University Grants Commission of Bangladesh is acknowledged. A research grant to another author (S.A.A) by the ISESCO (Islamic Scientific Educational and Cultural Organization) is gratefully acknowledged.

References

1 Davies W L, *Science*, 144, **1964**, 862.
2 Bartlett P D, Condon F E & Schneider A, *J Chem Soc*, 66, **1944**, 1531.
3 Webber W & Harthoorn P, *British Patent*, 1959819240; *Chem Abstr*, 54, **1960**, 15272.
4 Klimochklin Yu N, *Khim Farm Zh*, 26 (7-8), **1992**, 58 (Russ); *Chem Abstr*, 119, **1993**,135411f.
5 Fridman A L, Zabesov V S, Dolbilkin K V, Kon'shina L O, Sivkova M P & Moiseev I K, (Perm Farm Inst, Perm, USSR) *Khim Farm Zh*, 1978, **12** (2), 88-2 (Russ), *Chem Abstr*, 88, **1978**, 182874k.
6 Dolejsek Z, Halan S, Hanus V & Landa S, *Coll Czech Chem Comm*, 31, **1966**, 435.
7 Warren R W, Schneider A & Janoski E J, *Appl Spect*, 22, **1968**, 115 *Chem Abstr*, 69, **1968**, 66661x.
8 Sasaki S, Eguchi S & Torce T, *Tetrahedron*, 25, **1969**, 2909.
9 Lengyel I, Weiss D B, Naffisi I M M & J C Sheehan, *Org Mass Spect*, 2, **1969**, 1239.
10 Lengyel I, Solomone R A, Biewann K, *Org Mass Spect*, 3, **1970**, 789.
11 Karpenko N F, Chizov O S, Novikov S S, Yurchenko A G & Danilenko G I, *Zh Org Khim*, 7, **1971**, 416.
12 Karpenko N F, Chizov O S, Novikov S S, Yurchenko A G, Sukhoverkhov V D & Smirnova N A, *Izv Akad Nauk SSSR Ser Khim*, **1971**, 439.
13 Storesud H J, *Tetrahedron Lett*, **1971**, 3911.
14 Greidanus J W, *Canad J Chem*, 49, **1971**, 3210.
15 Greene R L, Keleschick W A & Wahl G H Jr, *Tetrahedron Lett*, **1971**, 4577.
16 Chizov O S, Novikov S S, Karpenko N F, Yurchenko A G, Sukhoverkhov V D & Stepanov F N, *Izv Akad Nauk SSSR Ser Khim*, **1972**, 1028.
17 Chizov O S, Novikov S S, Karpenko N F & Yurchenko A G, *Izv Akad Nauk SSSR Ser Khim*, **1972**, 1510.
18 Polykova A A, Khramova E V, Bagrii E I, Tsitsugina N N, Lukashenko I M, T Yu Frid & Sanin A P I, *Neftekhimiya*, 13, **1973**, 9; *Chem Abstr*, 1973, **78**, 135131z.
19 Greidanus J W, *Int J Sulfur Chem* 3, **1973**, 243; *Chem Abstr*, 79, **1973**, 125438m.
20 Eckhardt G & Fehlhaber H W, *Org Mass Spect*, 7, **1973**, 485.
21 Khullar K K, Bell C L & Bauer L, *J Org Chem*, 38, **1973**, 1042.
22 Engler E M & Schleyer P V R, *Alicyclic Compounds* edited by W Parker, (Butterworths, London) **1973**, Vol.5, p.244.
23 Majerski, Karlovie G, Digas S & Stefanovic D, *Org Mass Spect*, 12, **1977**, 37.
24 Alberts A H, Wymberg H & Strating J, *Tetrahedron Lett*, **1973**, 543.
25 Ahmed M G, Moeiz S M I, Ahmed S A, Kiuchi F, Tsuda Y & Sampson P, *J Chem Res*, 316(M), **1999(S)**, 1439.
26 Ahmed M G, Huque A K M F, Ahmed S A, Mosihuzzaman M & Andersson R, *J Chem Res*, 362(M), **1988(S)**, 2815.
27 Huque A K M F, Mosihuzzaman M, Ahmed S A, Ahmed M G & Andersson R, *J Chem Res*, 214(M), **1987(S)**, 1701.