

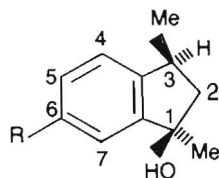
Mass Spectral Fragmentation of Substituted Indanols

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ABSTRACT. The mass spectra of substituted 1,3-dimethylindan-1-ols (R=H, NH₂, Cl) have been recorded under similar conditions, and mechanistic schemes proposed to explain their fragmentation. It has been observed that the substituents have little effect on the mode of fragmentation, other than expected. Some of the proposed cleavages have been substantiated by appropriate metastable peaks, while the mass spectra of some related compounds support the generation of some other observed ions.

Substituted indanols (I) were prepared



R = H; Cl; NH₂

(1)

in connection with our earlier studies to obtain corresponding 1,3-dimethylindanes which, in turn, were required as ligands for a continuation of our studies of the effect of metal complex formation on ligand reactivity. It was of interest to study the effect of the substituents, if any, on the mode of their mass spectral fragmentation. For this purpose mass spectra of various indanols (I) will be compared with that of *trans*-1,3-dimethyl-indan-1-ol (I; R=H).

Experimental

Melting points were determined on a Kofler microscope hot stage and were uncorrected. Mass spectra were determined on an AEI MS9 mass spectrometer with a heated inlet system and operating at a beam energy of 70 eV, ionising chamber temperature of 120° and multiplier voltage of 2.2 kV.

trans-1, 3-Dimethylindan-1-ol:

3-Methylindan-1-one, b.p. 76-86°/8-1 mm, $\eta_D^{19.5}$ 1.5568 (lit. b.p. 132-137°/15 mm, η_D^{18} 1.5589) was prepared by the method of Koelsch *et al.* (1943). The ketone was converted to *trans*-1,3-dimethylindan-1-ol, through the Grignard reaction as described by Gracey *et al.* (1969).

trans-6-Amino-1,3-dimethylindan-1-ol

6-Amino-3-methylindan-1-one, m.p. 98-100° (lit. m.p. 103.5°), was prepared from 3-methylindan-1-one following a method detailed by Braun and Heider (1916). A Grignard reaction of this aminoketone with methylmagnesium iodide yielded a viscous brown residue, which was chromatographed on deactivated alumina and afforded *trans*-6-amino-1,3-dimethylindan-1-ol, m.p. 115-116°, following details described by Ashraf and Jackson (1978).

The deuterated amino-indanol was prepared by shaking the amino-indanol with D₂O, followed by extraction with ether and thereafter removal of the solvent from the dehydrated extract.

Chloro-1,3-dimethylindan-1-ol and *Chloro*-1,3-dimethylindene

These were prepared from chloro-1,3-methylindan-1-one and methylmagnesium iodide (Ashraf *et al.* 1975).

Results and Discussion

The mass spectrum of *trans*-1,3-dimethylindan-1-ol (I; R=H) has been recorded in Table 1. To account for the formation of its important fragments, Scheme 1 has also been proposed. It shows molecular ion peak at m/z 162. Its $M + 1$ peak at m/z 163 is 12.76% of the molecular ion and approximates to the additional contribution by natural abundance of isotopes in its molecule. The molecular radical ion ($\dot{1}$) loses a $\dot{C}H_3$ from position 3 to yield $\dot{2}$ (m/z 147), which then loses H₂O to generate $\dot{3}$ (m/z 129). The metastable ion \dot{m}/z at 113.21 supports this fragmentation. Alternatively ($\dot{1}$) may initially lose a neutral molecule, H₂O, to produce an indene radical $\dot{4}$ (m/z 144), and then cleave to lose $\dot{C}H_3$ producing $\dot{3}$ again. The appearance of a peak at m/z 144 for $\dot{4}$ is in line with the general rules outlined for predicting prominent peaks in a mass spectrum

(Silverstein *et al.* 1974). Nevertheless, it is probable that both the proposed routes may be operating simultaneously to afford $\underline{3}$.

According to the general rules referred to above, the C-C bonds next to the hetero-atom are frequently cleaved leaving the charge on the fragment containing the hetero-atom.

In conformity with these rules, the peak at m/z 147 proposed for $\underline{2}$ may more likely be due to another ion $\underline{5}$ (having the same m/z). The recording of m/z 105 for the alkyl substituted benzylic ion $\underline{5}$ by elimination of a ketene molecule supports this contention (see later). The indene ion $\underline{3}$ may successively lose $\dot{\text{H}}$ to produce $\underline{8(a)}$ and/or $\underline{8(b)}$ (m/z 128), and vinylic indene $\underline{9}$ (m/z 127). The radical ions corresponding to m/z 115, 91, 78 and 77 are considered to be generated through a complex degradation process, not indicated in Scheme 1.

Table 1. Mass spectral fragments of *trans*-1,3-dimethylindan-1-ol

m/z	% of base peak	m/z	% of base peak	m/z	% of base peak	m/z	% of base peak
163	6	144	73	129	82	105	17
162	47	143	17	128	55	103	15
148	12	132	7	127	23	102	10
147	100	131	20	119	6	91	25
145	9	130	25	115	20	78	17
						77	10

The mass spectrum of 6-amino-*trans*-1,3-dimethylindan-1-ol (I; R=NH₂) is shown in Table 2. Scheme 2 outlines the mode of fragmentation. A comparison of the fragmentation pattern of this aminoindanol (Scheme 2) with unsubstituted indanol (I; R=H; Scheme 1) reveals a great similarity. Thus, the fragments $\underline{1}$ to $\underline{8}$ are similar in both cases. Moreover, the proposed conversion of the molecular ion- $\underline{1}$ (m/z 177) to $\underline{5}$ (m/z 162) and that of the latter to fragment $\underline{6}$ (m/z 120) in Scheme 2 is substantiated by \dot{m}/z at 148.27 and 88.99 for these cleavages respectively. However, since the fragments $\underline{2}$ and $\underline{5}$ have identical masses (m/z 162), the \dot{m}/z at 148.27 may also be attributed to cleavage of $\underline{1} \rightarrow \underline{2}$.

In analogy with the compounds containing an amino group, both the fragments corresponding to m/z 120 (C₈H₁₀N⁺) and m/z 106 (C₇H₈N⁺) are considered to initially lose HCN to generate fragments C₇H₉⁺ and C₆H₇⁺ respectively, which are not recorded (William and Fleming 1973). These fragments lose H₂ and yield C₇H₇⁺ (benzylic or tropylium cation) and C₆H₅⁺ (phenyl cation)

respectively. It may be pertinent to note the percentages abundance of fragments corresponding to m/z 120 and 106 (I; R= NH_2) are 35 and 30 respectively; whereas the corresponding cations in Scheme 1, when R=H, have their respective percentages abundance of 17 and 25 (Table 1). The higher percentages in case of former (I; R= NH_2) are obviously due to extra stability conferred on them by the electron donating amino group.

Scheme 1

Proposed mass spectral fragmentation of *trans*-1,3-dimethylindan-1-ol

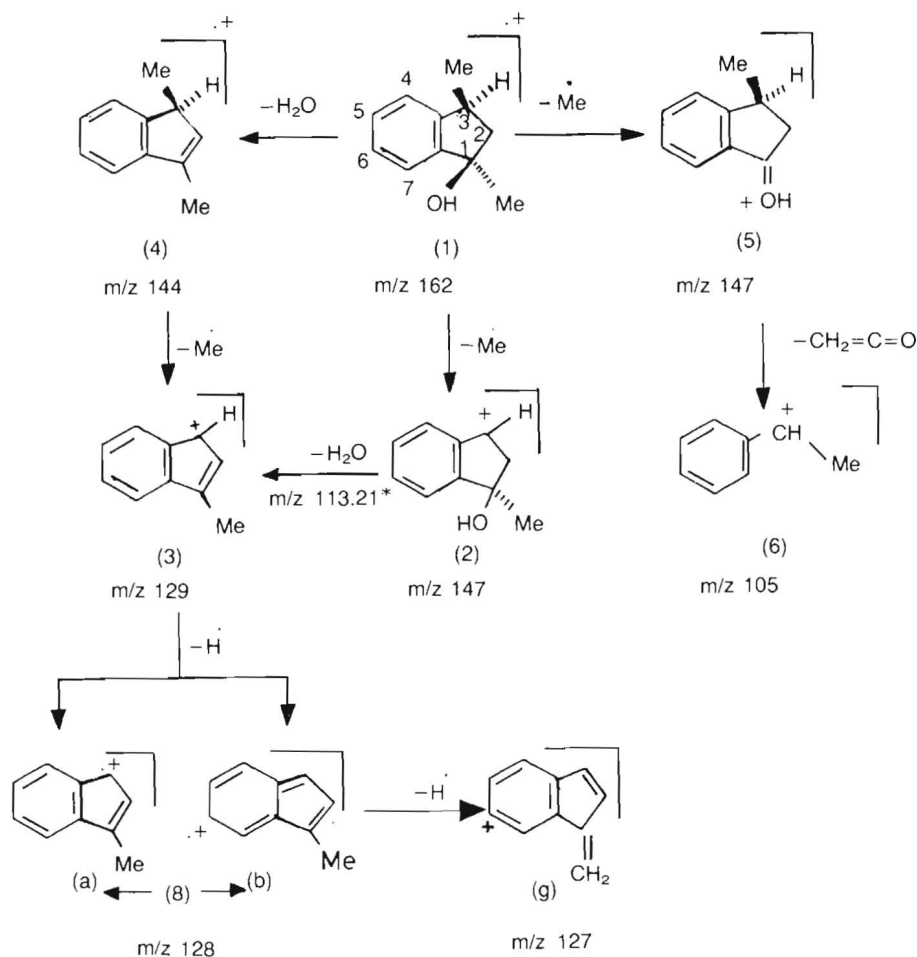
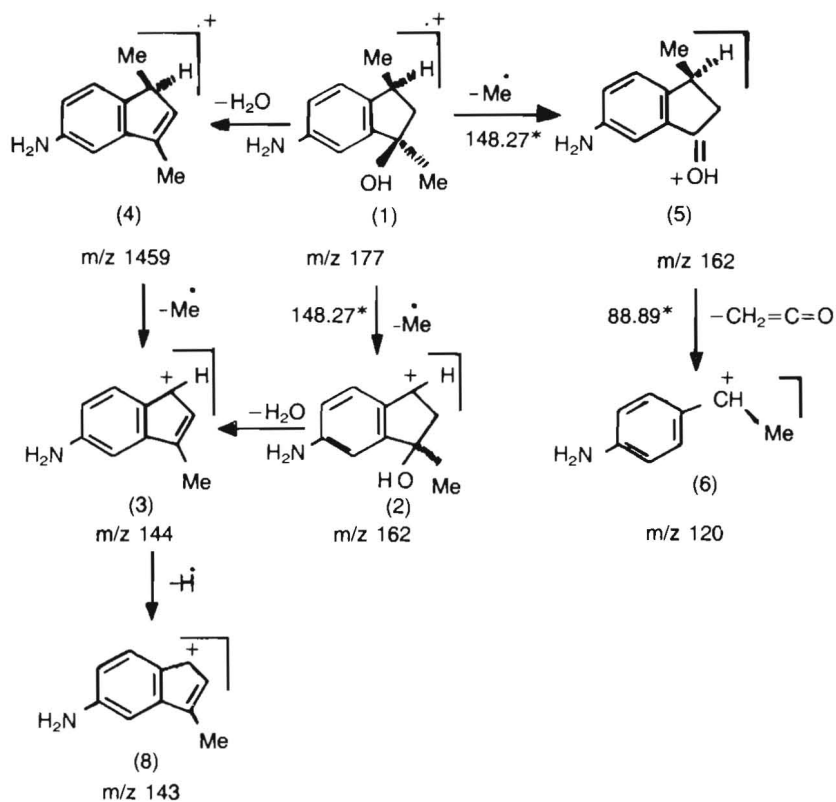
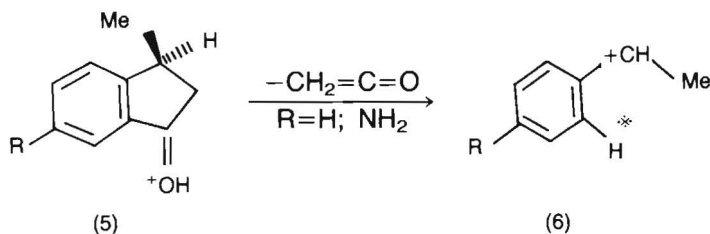


Table 2. Mass spectral fragments of 6-amino- *trans*-1,3-dimethylindan-1-ol

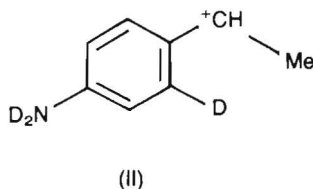
<i>m/z</i>	% of base peak	<i>m/z</i>	% of base peak	<i>m/z</i>	% of base peak	<i>m/z</i>	% of base peak
178	9	161	2	134	3	81	7
177	70	159	12	121	4	77	4
176	4	158	2	120	35	43	17
163	10	144	19	106	30	39	4
162	100	143	8	91	7		

Scheme 2Proposed mass spectral fragmentation of 6-amino-*trans*-1,3-dimethylindan-1-ol

In case of both the indanols discussed so far, the proposed rupture of fragment $\underline{5}$ to $\underline{6}$ is shown as follows:



During this cleavage, $\overset{*}{\text{H}}$ from ($\underline{5}$) is transferred to the benzene nucleus in ($\underline{6}$). To support this contention deuterated amino-indanol (I; R=NH₂) was investigated. This revealed peak at m/z 123 corresponding to $\underline{11}$, which is 3 units higher than the corresponding peak for the undeuterated amino-indanol (I; R=NH₂). This observation demonstrates the validity of this contention.



The mass spectrum of chloroindanol (I; R=Cl) is recorded in Table 3; and Scheme 3 indicates its proposed fragmentation. It is obvious from this scheme that even the chloroindanol (I; R=Cl) follows almost identical pattern of fragmentation to generate $\underline{1}$ - $\underline{6}$ ions similar to both the indanols (I; R=H, NH₂) discussed before. However, the chloroindene radical ion-4 (Scheme 3) is considered to lose $\overset{\cdot}{\text{Cl}}$ to generate the unsubstituted indene $\underline{10}$, which provides fragments similar to $\underline{8}$ and $\underline{9}$ obtained from the foregoing indanols. The appearance of the metastable peaks at 114.6 and 100.5 supports the one step cleavage of fragments $\underline{10}$ and $\underline{3}$ in both the cases, generating $\underline{8}$ from either route (Scheme 3). $\underline{10}$ successively loses $\overset{\cdot}{\text{H}}$ to generate fragments $\underline{11}$ and $\underline{12}$. Fragment $\underline{12}$ loses $\overset{\cdot}{\text{C}}\text{H}_3$ to give fragment $\underline{13}$ (m/z 126) which, in turn, loses $\overset{\cdot}{\text{H}}$ to generate $\underline{14}$ (m/z 125). The formation of fragments for m/z 115, aromatic clusters at m/z 78, 77 and cations like C_5H_5^+ (m/z 65), C_4H_3^+ (m/z 51), C_4H_2^+ (m/z 50) etc. have not been shown in Scheme 3, which apparently follows a complex route.

Table 3. Mass spectral fragments of chloro-1,3-dimethylindan-1-ol

<i>m/z</i>	% of base peak	<i>m/z</i>	% of base peak	<i>m/z</i>	% of base peak	<i>m/z</i>	% of base peak	<i>m/z</i>	% of base peak
198	5	142	3	117	3	78	66	62	4
196	25	141	4	116	5	77	10	51	12
183	35	139	5	115	15	75	9	50	6
181	100	129	5	103	4	74	5	47	31
178	?	128	24	102	7	73	4	38	9
165	10	127	18	101	7	65	5		
163	12	126	3	91	10	64	3		
143	15	125	12	89	6	63	9		

In all these cases, one of the proposed fragment is a molecular ion of indene. This was not recorded when chloroindanol (I; R=Cl) was subjected to mass spectral analysis. It is just possible that in view of its transitory existence, it could not be monitored, but further decomposed into species δ - $\underline{4}$. When chloro-1,3-dimethylind-1-ene was subjected to mass spectral analysis under similar conditions, it yielded fragments almost analogous to the postulated chloro-indene radical ion $\underline{4}$ (compare Scheme 3 and 4). Thus, the proposed formation of chloro-indene from chloro-indanol is substantiated.

Table 4. Mass spectral fragments of chloro-1,3-dimethylind-1-ene

<i>m/z</i>	% of base peak	<i>m/z</i>	% of base peak	<i>m/z</i>	% of base peak	<i>m/z</i>	% of base peak	<i>m/z</i>	% of base peak
180	25	155	4	141	13	126	7	89	5
179	9	153	2	140	3	125	3	77	4
178	69	152	12	139	7	117	6	75	4
177	3	145	3	137	5	116	1	70	7
165	17	144	19	129	10	115	15	63	8
163	22	143	100	128	70	102	5	51	6
162	5	142	10	127	36	101	4	44	3

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التشظية الطيفية الكتلية للاندنولات المعوضة

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مجلس البحوث العلمية والصناعية الباكستاني - قسم الكيمياء التطبيقية - مختبرات لاهور
لاهور ١٦ - باكستان

تم تسجيل طيف الكتلة ل ١, ٣ - داي ميشايلند ن - ١ أولس ($R = H, NH_2, Cl$) تحت ظروف متشابهة، وأن مخططاً ميكانيكياً افترض لشرح تشظيتهم، وقد لوحظ أن تأثير المعوضات قليل على نمط التشظية عكس ما هو متوقع. وبعض الانقسامات أو الشقوق المفترضة جُسدت عن طريق قمم شبه مستقرة ومخصصة، بينما طيف الكتلة لبعض المركبات ذات العلاقة تدعم إنتاج بعض الأيونات الملاحظة الأخرى.