# Mass Spectral Study of 2-Aryl-4-arylhydrazono-4,5,6,7-tetrahydro-2*H*-benzo-1,2,3-triazoles



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The mass spectra upon electron impact at 70 eV of the title compounds are examined. The fragmentation pattern of the tetrahydro-benzotriazoles with unsymmetrically substituted the aryl groups in 2-position and in hydrazone group cannot support the aspect for a mononuclear heterocyclic rearrangement.

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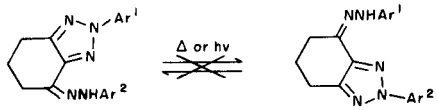
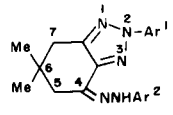
It has been shown previously [1,2] that attempts to induce a mononuclear heterocyclic rearrangement in unsymmetrically bis-aryl-substituted tetrahydrobenzotriazoles **1-2** was unsuccessful in agreement with other literature data [3].




**1** **2**

We have therefore undertaken the present study to examine whether the above heterocyclic rearrangement [4,5] of the type **1** to **2** is possible to occur under mass spectrometric conditions.

From the compounds under examination, **3a-c** have been prepared [2] by lead tetraacetate oxidation of trisarylhydrazones of 5,5-dimethyl-cyclohexane-1,2,3-trione, whereas the unsymmetrically substituted in the aryl groups **3d-f** from the reaction of the corresponding 4-oxo-derivative with the appropriate arylhydrazine.




**3**

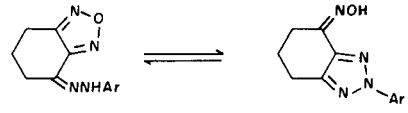
a $Ar^1 = Ar^2 = C_6H_5$
b $Ar^1 = Ar^2 = C_6H_4CH_3(p)$
c $Ar^1 = Ar^2 = C_6H_4Cl(p)$
d $Ar^1 = C_6H_5$, $Ar^2 = C_6H_4CH_3(p)$
e $Ar^1 = C_6H_5$, $Ar^2 = C_6H_4Cl(p)$
f $Ar^1 = C_6H_5$, $Ar^2 = C_6H_4NO_2(p)$

The electron impact mass spectra at 70 eV of the compounds **3** show the presence of the molecular ion $M^{+\cdot}$ as an abudant ion peak and they do not give the $[M-N_2]^{+\cdot}$ ion fragment, which is a very characteristic fragmentation mode for 1H-1,2,3-triazoles [6,7] and benzotriazin-4-ones [8]. The molecular ions give rise to the formation of $[M-15]^+$ and $[M-56]^+$ ions by a loss of a $CH_3$- group and a $(CH_3)_2C=CH_2$ molecule respectively, as evidenced by high resolution mass measurements carried out on compound **3d**. These ion peaks appear with a low intensity and the ion $[M-56]^+$ is absent in the specrum of **3f** (Table).

Very characteristic ion fragments are those corresponding to the ions $[Ar^1N]^+$, $[Ar^2NH]^+$ and $[Ar^2NHNH]^+$ or $[Ar^2NHNH_2]^{+\cdot}$, as well as those of $[M-Ar^2NH]^+$ and $[M-CH_3-Ar^2N_2H]^+$ (Figure 1). The last ion fragments could be used as a diagnostic tool to confirm the operation of a mononuclear heterocyclic rearrangement **1** to **2**, because in this case ions of the type $[Ar^1NHNH]^+$, $[Ar^1NHNH_2]^{+\cdot}$ and $[M-CH_3-Ar^1N_2H]^+$ should be also observed.

However, careful examination of the mass spectra of the unsymmetrically substituted compounds **3d-f** reveal the absence of these ions and argue against the aspect of rearrangement of the type **1** to **2**, in agreement with other similar findings [3].

It is worth mentioning that the heterocyclic rearrangement of the type **4** to **5** was also confirmed to operate under electron ionization mass spectrometric conditions [1,9] on the basis of the ions $[M-OH]^+$ and $[M-NHOH]^+$ observed in the mass spectrum of the compound **4**.



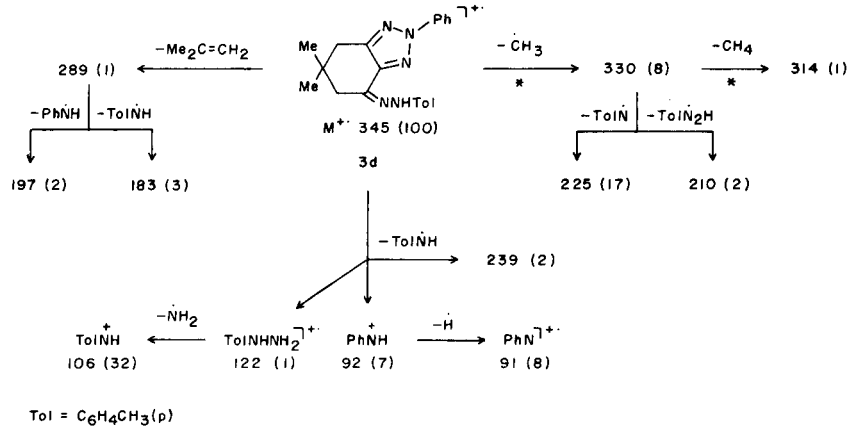

**4** **5**

Table

Principal Fragment Ions in the Mass Spectra of Compounds **3**, m/z (% Relative Intensities)

| | |
|---|---|
| **3a** | 331 (83) $M^{+\cdot}$, 316 (10), 300 (3), 275 (3), 239 (3), 225 (13), 224 (19), 210 (4), 183 (12), 108 (5), 92 (63), 91 (49), 77 (100) |
| **3b** | 359 (100) $M^{+\cdot}$, 344 (8), 330 (2), 303 (3), 254 (2), 239 (4), 198 (5), 106 (28), 105 (8), 91 (13), 77 (13) |
| **3c** | 403/401/399 (100) $M^{+\cdot}$, 388/386/384 (4), 374/372/370 (1), 347/345/343 (1), 276/274 (3), 275/273 (2), 261/259 (4), 246/244 (1), 220/218 (9), 219/217 (3), 144/142 (1), 129/127 (100), 128/126 (13), 113/111 (16) |
| **3d** | 345 (100) $M^{+\cdot}$, 330 (8), 314 (1), 239 (2), 225 (17), 210 (2), 197 (2), 183 (3), 122 (1), 106 (32), 92 (7), 91 (26), 77 (100) |
| **3e** | 367/365 (62) $M^{+\cdot}$, 352/350 (7), 338/336 (1), 311/309 (1), 239 (4), 209 (4), 183 (9), 144/142 (1), 128/126 (100), 92 (20), 91 (19), 77 (20) |
| **3f** | 376 (100) $M^{+\cdot}$, 361 (15), 347 (2), 240 (8), 239 (3), 224 (18), 210 (7), 184 (20), 183 (12), 138 (75), 108 (20), 92 (27), 91 (47), 77 (28) |

Scheme




Tol = $C_6H_4CH_3$(p)

A general fragmentation patern upon electron impact for the compound **3d** is given in Scheme, where the proposed composition for all ions was confirmed by high resolution mass measurements.

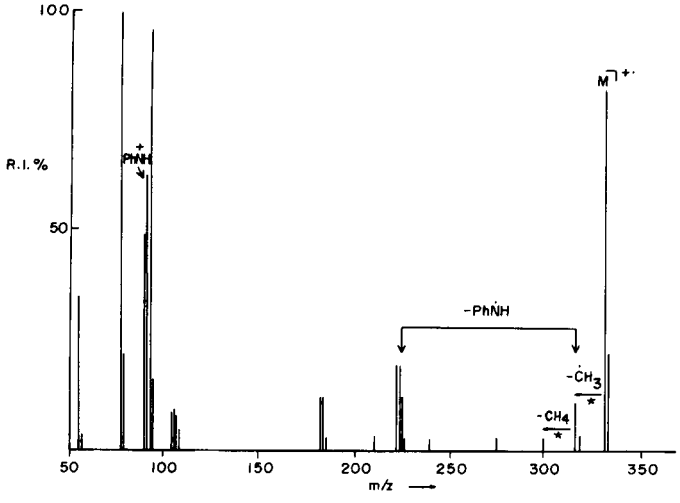



Figure 1. Mass spectrum of compound 3a.

## EXPERIMENTAL

All melting points are uncorrected and they are obtained with a Kofler hot stage apparatus. Ir spectra were obtained with a Perkin-Elmer Model 297 spectrophotometer, whereas nmr spectra reported in $\delta$ units with a Varian Associates A-60A spectrometer with TMS as internal reference. The mass spectra were measured with a Hitachi-Perkin-Elmer RMU-6L single focusing spectrometer, whereas the high resolution mass measurements were obtained with a VG U-Mass 7070-H spectrometer with ionization energy both at 70 eV. Analyses were performed with a Perkin-Elmer Model 240B CHN Analyzer.

2-Aryl-4-arylhydrazono-6,6-dimethyl-4,5,6,7-tetrahydro-2*H*-benzo-1,2,3-triazoles (**3a-c**).

The preparation of tetrahydrobenzotriazoles **3a-c** was previously described [2]. The melting points of the samples used were as follows: **3a** 203-205°; **3b** 175-176°; **3c** 205-207°.

6,6-Dimethyl-2-phenyl-4-(*p*-tolylhydrazono)-4,5,6,7-tetrahydro-2*H*-benzo-1,2,3-triazole (**3d**).

A solution of 1 mmole of 6,6-dimethyl-4-oxo-2-phenyl-4,5,6,7-tetrahydro-2*H*-benzo-1,2,3-triazole [9] and 1.2 mmole of *p*-tolylhydrazine in 10 ml of ethanol containing a few drops of acetic acid was refluxed for 3 hours. Upon cooling the tetrahydrobenzotriazole **3d** was precipitated as yellow solid in 83% yield and recrystallized from ethanol, mp 150-151°; ir (nujol): 3290, 1610 $cm^{-1}$; nmr (deuteriochloroform): $\delta$ 1.11 (s, 6H, $CMe_2$), 2.29 (s, 3H, *p*-Me), 2.60 (s, 2H, $CH_2$), 2.75 (s, 2H, $CH_2$), 7.06 (s, 4H, *p*-tolyl), 7.18-7.62 (m, 3H, 2-phenyl), 7.94-8.16 (m, 2H, 2-phenyl) and 9.10 (br s, 1H, NH). The assignment was made in comparison with nmr spectra of the corresponding 4-oxo-derivatives; hrms: 345.1904 ($M^+$, $C_{21}H_{23}N_5$, calcd. 345.1949), 330.1723 [$(M-CH_3)^+$, $C_{20}H_{20}N_5$, calcd. 330.1715], 289.1344 [$(M-Me_2C=CH_2)^+$, $C_{17}H_{15}N_5$, calcd. 289.1325], 225.1162 [$(M-CH_3-MeC_6H_4N)^+$, $C_{13}H_{13}N_4$, calcd. 225.1138], 210.1014 [$(M-CH_3-MeC_6H_4N_2H)^+$, $C_{13}H_{12}N_3$, calcd. 210.1029].

*Anal.* Calcd. for $C_{21}H_{23}N_5$ (345.2): C, 73.01; H, 6.71; N, 20.28. Found: C, 73.29; H, 6.60; N, 20.27.

4-(*p*-Chlorophenylhydrazono)-6,6-dimethyl-2-phenyl-4,5,6,7-tetrahydro-2*H*-benzo-1,2,3-triazole (**3e**).

The procedure described above was followed and the tetrahydrobenzotriazole **3e** was isolated in 65% yield as yellow crystals, mp 177-179°; ir (nujol): 3280, 1600 $cm^{-1}$, nmr (deuteriochloroform): $\delta$ 1.10 (s, 6H, $CMe_2$), 2.58 (s, 2H, $CH_2$), 2.75 (s, 2H, $CH_2$), 7.17 (s, 4H, *p*-chlorophenyl), 7.05-7.63 (m, 3H, 2-phenyl), 7.95-8.20 (m, 2H, 2-phenyl) and 8.82 (br s, 1H, NH).

*Anal.* Calcd. for $C_{20}H_{20}ClN_5$ (365.9): C, 65.65; H, 5.51; N, 19.14. Found: C, 65.67; H, 5.71; N, 19.20.

6,6-Dimethyl-4-(*p*-nitrophenylhydrazono)-2-phenyl-4,5,6,7-tetrahydro-2*H*-benzo-1,2,3-triazole (**3f**).

The procedure described above was followed and the tetrahydrobenzotriazole **3f** was isolated in 68% yield. Yellow crystals, mp 245-246°; ir (nujol): 3280, 1590 $cm^{-1}$; nmr (deuteriochloroform): $\delta$ 1.13 (s, 6H, $CMe_2$), 2.63 (s, 2H, $CH_2$), 2.79 (s, 2H, $CH_2$), 7.00-7.65 (m, 5H, 2-phenyl), 7.85-8.25 (m, 4H, *p*-nitrophenyl) and 10.86 (br s, 1H, NH).

*Anal.* Calcd. for $C_{20}H_{20}N_6O_2$ (376.4): C, 63.82; H, 5.36; N, 22.33. Found: C, 63.78; H, 5.49; N, 22.31.

Acknowledgement.

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## REFERENCES AND NOTES

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