MASS SPECTRA OF ETHYL ARYLHYDRAZONOCYANOACETYLCARBAMATES

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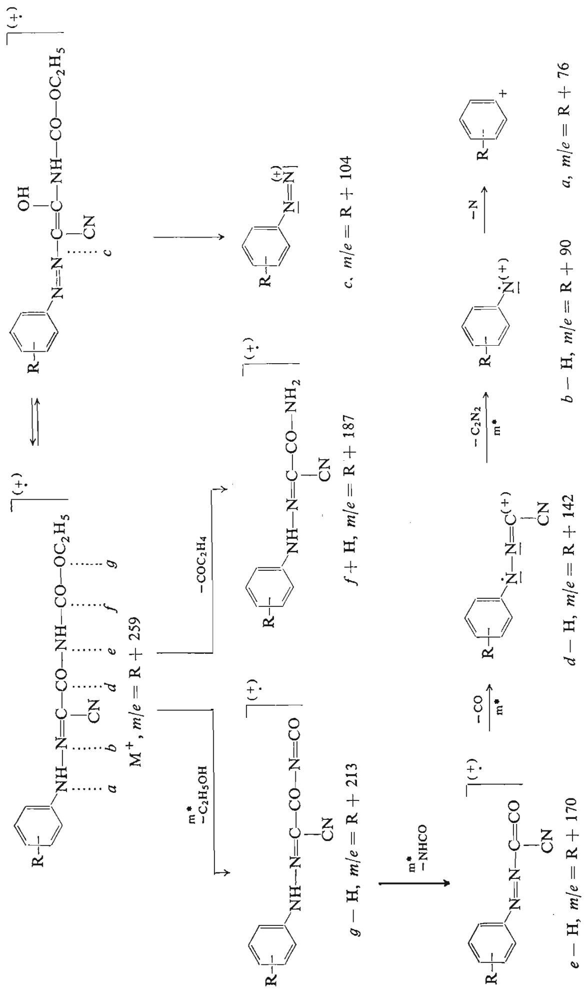
Received June 27th, 1973

Mass spectra of ethyl arylhydrazonocyanoacetylcarbamates were recorded and interpreted using the observed metastable transitions and high-resolution measurements. The mass spectra confirmed that the studied compounds exist partially as azo-tautomers.

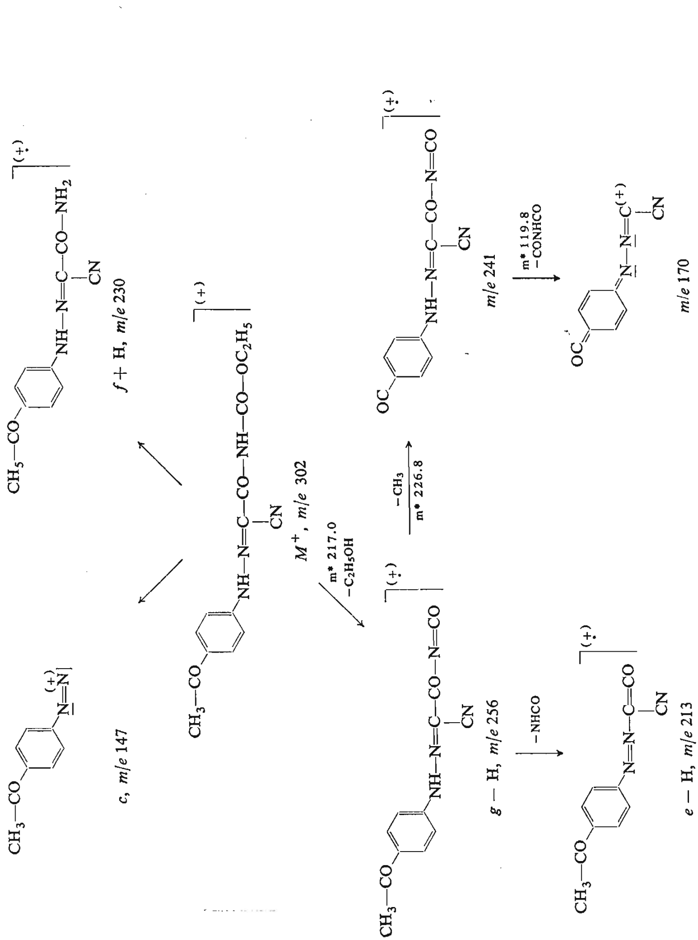
Mass spectra of ethyl arylhydrazonocyanoacetylcarbamates were measured in connection with a complex investigation of these compounds. It was found from the earlier measured infra-red[1] and NMR (ref.[2]) spectra that beside the predominant hydrazo-form, the substances occur also to a small extent as azo-tautomers (Scheme 1) in the solid state as well as in some non-polar solvents.

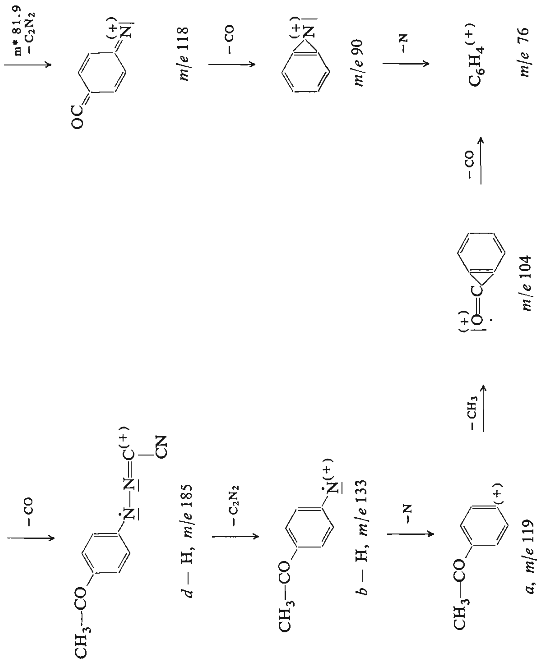
We measured the mass spectra of these compounds and analysed them with the use of metastable transitions and by precise measurements of the ion masses using the high resolution technique. The basic fragmentation scheme is shown in Scheme 2. First, the elimination of ethanol from the molecular ion takes place, followed by the elimination of neutral fragments NHCO, CO, C_2N_2, and N, until a substituted phenyl is formed. Further fragmentation is not considerable. Besides the intensive peaks formed in the above mentioned processes, minor peaks of masses $m/e = X + 187$ were observed in the mass spectra; these originated directly from the molecular ion. Ions of mass $m/e = X + 104$ are formed presumably from the molecular ion of the azo-form. The intensity of this peak is low, in agreement with the rather low abundance of the azo-form as estimated from the infra-red spectra.

Compounds with more complicated substituents (4-$COCH_3$, 4-SO_2NH_2, 4-$COOC_2.H_5$) and nitro derivatives yield main fragments by the elimination from the substituent, too. As an example, Scheme 3 shows the fragmentation of 4-$COCH_3$ derivative. In the spectra of both nitro derivatives a high-intensity peak of m/e 90 is observed which originates – as confirmed by the occurrence of the metastable peaks – by splitting off of the nitro group from the fragment $b - H$. Furthermore, it is remarkable that the abudance the ion NO^+ is several times higher in the mass spectra of the com-


M⁺, m/e = R + 259
−COC₂H₄
m* −C₂H₅OH
c, m/e = R + 104
f + H, m/e = R + 187
g − H, m/e = R + 213
m* −NHCO
−CO m*
−C₂N₂ m*
−N
e − H, m/e = R + 170
d − H, m/e = R + 142
b − H, m/e = R + 90
a, m/e = R + 76

SCHEME 2


f + H, m/e 230
c, m/e 147
M+, m/e 302
m* 217.0
−C2H5OH
−CH3
m* 226.8
m/e 241
m* 119.8
−CONHCO
m/e 170
g − H, m/e 256
−NHCO
e − H, m/e 213

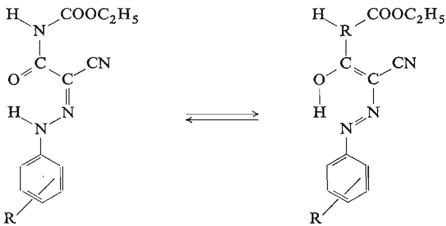


m* 81.9
− C2N2
m/e 118
− CO
m/e 90
− N
C6H4(+)
m/e 76
− CO
m/e 104
− CH3
− CO
d − H, m/e 185
− C2N2
b − H, m/e 133
− N
a, m/e 119

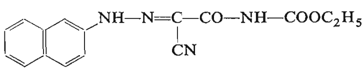
SCHEME 3

pounds containing the nitro group in the *para*-position than in those containing the nitro group in the *meta*-position. This phenomenon has not been described so far. We observed the same behaviour in the mass spectra of methylsulfoanilide nitro derivatives, too[3]. We assume that the formation of NO^+ in *p*-nitro compounds is favoured, because the eliminated neutral fragment has a stable quinonimine structure.

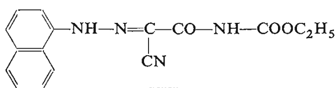
A somewhat different fragmentation takes place in the 4-$NHCOCH_3$ derivative (Scheme 4). The elimination of ethyl alcohol is followed by the elimination of ketene from the substituent; thereafter, the neutral fragment NHCO is split off as in the case of the main fragmentation process described in Scheme 2. Further decomposition of the ion of $m/e = 158$ was not observed in the spectrum. Besides it, the ion $g - H$ ($m/e = 271$) affords the ion $b - H$ ($m/e = 148$) which further dissociates according to the main fragmentation pattern. High-resolution measurements showed that the composition of the ion of $m/e = 106$ is $C_6H_6N_2$. This ion is presumably formed from the molecular ion. Mass $m/e = 79$ consists of three ions $C_4H_3N_2$: : C_5H_5N : C_6H_7 with the relative intensities ratio 4·8 : 4·2 : 1, respectively. The former two ions may be formed through the fragmentation of the ion of mass $m/e = 106$.



In formula *I*–*XIX*: R = H; 4-CH_3; 4-CHO; 4-COOH; 3-NO_2; 4-NO_2; 3-Br; 4-Br; 4-F; 4-I; 4-Cl; 2,5-di-Cl; 3-OCH_3; 4-OCH_3; 4-OC_2H_5; 4-$COCH_3$; 4-$COOC_2H_5$; 4-SO_2NH_2; 4-$NHCOCH_3$

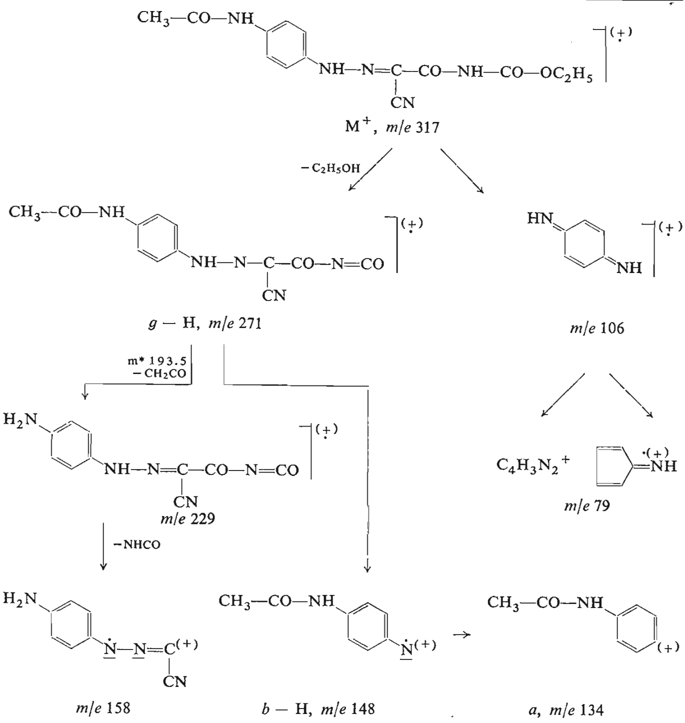


XX



XXI

SCHEME 1



SCHEME 4

The mass spectra of the compounds discussed are shown in a shortened tabular form in the Experimental.

The influence of substituents on the fragmentation rates of various ions cannot be formulated in a quantitative way by means of a simple linear equation. Qualitatively, it can be said that electronegative substituents speed up the molecular ion fragmentation to $g - H, f + H$, and c, as well as the fragmentation process $g - H \rightarrow e - H$. The rate of the fragmentation processes $e - H \rightarrow d - H$, and $d - H \rightarrow b - H$ is increased by electropositive substituents. No influence of polar properties of substituents was observed on the rate of the fragmentation process $b - H \rightarrow a$. The higher ratio of the intensities of ions c and M^+ in the case of electronegative substituents might be caused by a higher content of the azo-form in these derivatives.

EXPERIMENTAL

Ethyl arylhydrazonocyanoacetylcarbamates were prepared as intermediate products in the synthesis of 1-aryl-6-azauracyls by diazotisation of the corresponding substituted anilines and coupling of the thus-obtained diazonium salts with ethyl cyanoacetylcarbamate[4–7].

Mass spectra of all the compounds were recorded on an A.E.I. MS 902 mass spectrometer using a direct inlet. The energy of ionizing electrons was 70 eV, the temperature of the ion source varied for various studied compounds between 140 and 228°C.

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Translated by Z. Herman.

Mass Spectra of Ethyl Arylhydrazonocyanoacetylcarbamates

m/e (% relative intensity)

I, R = H (M.w. 260): 29 (35), 31 (23), 39 (16), 45 (15), 77 (100), 91 (71), 92 (20), 105 (24), 118 (10), 143 (62), 144 (10), 171 (13), 172 (7), 188 (3), 189 (1), 214 (77), 215 (11), 260 (4)

II, R = 4-CH_3 (M.w. 274): 29 (40), 31 (48), 45 (25), 77 (38), 78 (20), 79 (18), 91 (84), 104–106 (21, 100, 27), 119 (11), 157 (60), 158 (7), 185 (4), 186 (3), 202 (1), 228 (51), 229 (7), 274 (8)

III, R = 4-CHO (M.w. 288): 29 (32), 31 (100), 45 (47), 77 (29), 90–92 (18, 45, 14), 105 (44), 119 (73), 120 (10), 133 (8), 171 (57), 172 (7), 199 (6), 200 (2), 216 (3), 242 (75), 243 (11), 288 (7)

IV, R = 4-COOH (M.w. 304): 29 (17), 31 (90), 45 (41), 89–93 (11, 21, 8, 14, 11), 107 (17), 117 (13), 121 (45), 135 (100), 136 (9), 149 (8), 187(78), 188 (10), 215 (4), 216 (1), 232 (10), 233 (2), 258 (78), 259 (11), 304 (1·4)

V, R = 3-NO_2 (M.w. 305): 29 (20), 30 (9), 31 (74), 45 (39), 63 (55), 64 (25), 75 (18), 76 (17), 90 (100), 91 (15), 122 (29), 136 (46), 137 (4), 150 (9), 188 (78), 189 (9), 216 (18), 217 (3), 233 (5), 259 (61), 260 (8), 305 (3·8)

VI, R = 4-NO_2 (M.w. 305): 29 (28), 30 (51), 31 (100), 45 (51), 63 (58), 64 (31), 75 (22), 76 (19), 90 (51), 91 (10), 122 (32), 136 (58), 137 (5), 150 (7), 188 (76), 189 (9), 216 (14), 217 (3), 233 (6), 259 (60), 260 (8), 305 (3·5)

VII, 3-Br (M.w. 338): 29 (74), 31 (56), 45 (43), 63 (46), 64 (29), 75 (21), 76 (24), 90 (76), 91 (49), 143 (8), 145 (8), 155 (65), 157 (65), 169–186 (56, 10, 61, 10, 9, 17, 3, 17, 4), 196 (11), 198 (11), 221–224 (72, 10, 71, 10), 249–252 (15, 10, 15, 6), 266 (4), 268 (4), 292 (100), 294 (99), 338 (28)

VIII, 4-Br (M.w. 338): 29 (54), 31 (52), 45 (42), 63 (45), 64 (24), 75 (19), 76 (19), 90 (53), 91 (36), 143 (8), 145 (8), 155 (46), 157 (45), 164—185 (70, 15, 74, 15, 7, 12, 1, 12, 3), 196 (6), 198(6) 221—224 (70, 8, 69, 8), 249—252 (11, 4, 11, 3), 266 (2), 268 (2), 292 (100), 294 (99), 338 (17)

IX, 4-F, (M.w. 278): 29 (64), 31 (21), 45 (12), 75 (15), 82 (17), 83 (46), 94 (16), 95 (79), 109 (100), 110 (31), 123 (22), 161 (59), 162 (7), 189 (5), 190 (4), 206 (4), 207 (1), 232 (54), 233 (8), 278 (17)

X, 4-I (M.w. 386): 29 (16), 31 (77), 45 (42), 63 (57), 64 (33), 76 (40), 90 (69), 91 (28), 203 (28), 204 (2), 217 (61), 218 (11), 231 (5), 269 (61), 270 (6), 297 (6), 298 (2), 340 (100), 341 (13), 386 (12)

XI, 4-Cl (M.w. 294): 29 (75), 31 (76), 36 (10), 45 (43), 90 (40), 111 (55), 113 (17), 125 (100), 127 (33), 139 (11), 141 (3), 177 (58), 179 (18), 205 (6), 206 (2), 222 (2), 223 (1), 248 (40), 250 (13), 294 (6)

XII, 2,5 di-Cl (M.w. 328): 29 (17), 31 (56), 36 (30), 45 (35), 133 (40), 135 (26), 145—150 (67, 6, 42, 6, 8, 3), 159—164 (69, 14, 56, 10, 15, 3), 173—177 (28, 3, 18, 3, 5) 186—190 (14, 6, 10, 4, 3), 211—215 (69, 9, 45, 6, 8), 239—243 (8, 6, 6, 5, 3), 247—250 (100, 13, 32, 4), 256—258 (8, 3, 4) 282—286 (64, 9, 42, 6, 8), 328 (31)

XIII, 3-OCH_3 (M.w. 290): 29 (41), 31 (49), 45 (29), 77 (34), 106 (42), 107 (62), 121 (60), 122 (10), 135 (5), 173 (74), 174 (18), 201 (4), 202 (6), 218 (2), 219 (3), 244 (100), 245 (14), 290 (23)

XIV, 4-OCH_3 (M.w.2 90): 29 (31), 31 (45), 45 (24), 77 (29, 106 (16), 107 (35), 121 (91), 122 (63), 135 (10), 173 (63), 174 (7), 201 (4), 202 (4), 218 (1), 219 (1), 244 (100), 245 (14), 290 (19)

XV, 4-OC_2H_5 (M.w. 304): 29 (10), 31(4), 45 (11), 107 (76), 108 (61), 121 (24), 122 (3), 135 (70), 136 (24), 159 (41), 187 (40), 188 (5), 215 (2), 216 (3), 230 (18), 231 (3), 258 (100), 259 (16), 304 (18)

XVI, 4-$COCH_3$ (M.w. 302): 29 (21), 31 (37), 43 (75), 45 (23), 76 (6), 90—92 (26, 20, 48), 104 (4), 118 (16), 119 (19), 133 (14), 147 (3), 170 (48), 171 (5), 185 (10), 213—215 (1, 2, 7), 230 (1), 241 (100), 242 (13), 256 (44), 257 (7), 302 (12)

XVII, 4-$COOC_2H_5$ (M.w. 332): 29 (100), 31 (48), 45 (28), 90 (41), 91 (21), 118 (18), 120 (14), 135 (20), 149 (43), 150 (5), 163 (54), 164 (9), 170 (36), 177 (3), 187 (24), 215 (37), 216 (6), 241—244 (68, 12, 3, 3), 258 (34), 259 (5), 286 (61), 287 (15), 332 (17)

XVIII, 4-SO_2NH_2 (M.w. 339): 29 (16), 31 (49), 44 (43), 45 (27), 62—65 (24, 100, 56, 24), 90 (79), 91 (32), 106 (70), 139 (15), 156 (42), 157 (7), 170 (55), 171 (5), 182 (13), 184 (8), 196 (16), 213 (12), 222—225 (98, 12, 6, 10), 229 (7), 248—251 (15, 6, 5, 3), 267 (23), 268 (4), 277 (9), 293 (74), 294 (10), 319 (10), 320 (2), 339 (absent)

XIX, R = 4-$NHCOCH_3$ (M.w. 317): 29 (90), 31 (100), 43 (31), 45 (37), 79 (6), 106 (13), 134 (7), 135 (1), 148—150 (1, 1, 1), 158 (4), 229 (6), 271 (4), 317 (0·2)

XX, (M.w. 310): 29 (17), 31 (41), 45 (18), 101 (4), 113—116 (10, 22, 36. 4), 127 (46), 128 (7), 140—143 (30, 100, 16, 5), 155 (2), 169 (6), 193 (36), 194 (7), 221 (1), 222 (1), 238 (1), 264 (68), 265 (12), 310 (10)

XXI, (M.w. 310): 29 (4), 31 (32), 45 (14), 101 (5), 113—116 (10, 21, 75, 10), 127 (79), 128 (12), 140—143 (32, 100, 33, 10), 155 (3), 169 (8), 193 (54), 194 (12), 221 (2), 223 (3), 238 (1), 264 (66), 265 (12), 310 (21)