

# Enones derived from 4-dimethylaminobenzaldehyde

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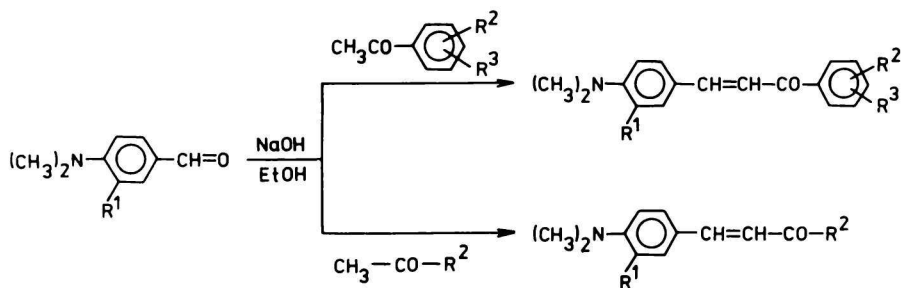
Fifteen new enones were prepared by basically catalyzed condensation of 4-dimethylaminobenzaldehyde or 4-dimethylamino-3-nitrobenzaldehyde with corresponding acetophenones or with other methyl ketones. Their characterization by means of elemental analysis, infrared spectroscopy, and mass spectrometry is presented. Quaternization of 4-dimethylamino group of one chalcone is also given.

Основанием катализированной конденсацией 4-диметиламинобензальдегида и 4-диметиламино-3-нитробензальдегида со соответствующими ацетофенонами и другими метилкетонами было приготовлено 15 новых энонов. Показана их характеристика с помощью элементного анализа, ИК-спектроскопии и масс-спектрометрии. Также показано метилирование 4-диметиламино группы одного халкона на четвертичную соль.

Aromatic or aromatic-aliphatic enones represent an interesting group of compounds from the point of view of their synthesis as well as relating to their application in the preparation of other more complicated compounds (e.g. pyrazolines, pyrazoles, isoxazoles, isoxazolines, benzofuranones, etc.) necessary in the organic synthesis. Furthermore, some enones of the chalcone type showed antibacterial effects [1—4].

In our work we focused our attention on the preparation of some enones by condensation of 4-dimethylaminobenzaldehyde as well as 4-dimethylamino-3-nitrobenzaldehyde with substituted acetophenones or with other methyl ketones (Scheme 1), because only few derivatives were described in the literature from this group of compounds [5—7]. We applied the most frequently used method for synthesis of chalcones — basically catalyzed condensation of aldehyde with an appropriate acetophenone [8—10]. The mentioned reactions occurred smoothly and the products in most cases crystallized spontaneously from the reaction mixture and one crystallization from ethanol was sufficient for their purification.

All the prepared compounds were identified and characterized on the basis of data of mass and i.r. spectra, and elemental analysis. The results of elemental



Scheme 1

analysis as well as melting points and yields are presented in Table 1. Spectral data are summarized in Table 2.

The i.r. spectra of the prepared enones showed strong absorption bands in the region of  $\tilde{\nu} = 1633\text{--}1664\text{ cm}^{-1}$  belonging to stretching vibrations of  $\text{C}=\text{O}$  bond of carbonyl group, conjugated with double  $\text{C}=\text{C}$  bond. The absorption bands in the region of  $\tilde{\nu} = 1585\text{--}1620\text{ cm}^{-1}$  were attributed to stretching vibrations of conjugated  $\text{C}=\text{C}$  bond. The stretching vibrations of aromatic  $\text{C}=\text{C}$  bonds showed strong absorption bands in the region of  $\tilde{\nu} = 1510\text{--}1602\text{ cm}^{-1}$ .

In the mass spectra of all compounds, peaks of molecular ions were observed and, in most cases, these presented base peaks of the spectrum. Further fragmentation depended on benzene ring substitution. Enones having  $\text{R}^1 = \text{H}$  showed significant peak at  $m/z = 174$ , corresponding to the ion  $(\text{CH}_3)_2\text{N}-\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{CO}^+$  and peak at  $m/z = 121$ , corresponding to the ion  $[(\text{CH}_3)_2\text{NH}-\text{C}_6\text{H}_4]^{++}$ . On the other hand, fragmentation of this type was in most cases negligible for enones having  $\text{R}^1 = \text{NO}_2$ . Significant peaks for these derivatives corresponded to ions  $[M-\text{NO}]^+$ ,  $[M-\text{N}(\text{CH}_3)_2]^{++}$ ,  $[M-\text{NO}_2]^+$ , and to the ion  $\text{R}^2\text{R}^3\text{C}_6\text{H}_3\text{CO}^+$ . Enones in which  $\text{R}^2$  and  $\text{R}^3$  were no halogen (with the exception of compounds X and XI, having however, unlike the others OH group) showed quasimolecular ions  $[M+\text{H}]^+$ . In several cases, the peaks corresponding to ions  $[M+\text{H}-\text{O}]^{++}$  and  $[M-\text{O}]^+$  were observed.

Attempts to quaternize the nitrogen atom in 4-dimethylamino-4'-bromochalcone by methyl iodide were unsuccessful. Quaternized product — 4-trimethylammonium-4'-bromochalcone sulfate — was prepared by the reaction of corresponding chalcone with dimethyl sulfate at  $100^\circ\text{C}$  without solvent.

### Experimental

4-Dimethylaminobenzaldehyde used in this work was commercial (Lachema, Brno), 4-dimethylamino-3-nitrobenzaldehyde was prepared by nitration of 4-dimethylaminobenz-

Table 1  
Characterization of the prepared enones

Compound	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Formula	M <sub>r</sub>	w <sub>i</sub> (calc.)/w <sub>i</sub> (found)			Yield	M.p.
						% C	% H	% N	%	°C
I	H	4-Br	H	C <sub>17</sub> H <sub>16</sub> BrNO	330.08	61.85	4.85	4.24	88	109—110
						61.79	4.92	4.17		
II	NO <sub>2</sub>	4-Cl	H	C <sub>17</sub> H <sub>15</sub> ClN <sub>2</sub> O <sub>3</sub>	330.62	61.75	4.54	8.47	86	160—161
						61.70	4.63	8.49		
III	NO <sub>2</sub>	4-Br	H	C <sub>17</sub> H <sub>15</sub> BrN <sub>2</sub> O <sub>3</sub>	375.08	54.43	4.00	7.46	88	154—155
						54.39	4.11	7.41		
IV	H	3-Cl	4-Cl	C <sub>17</sub> H <sub>15</sub> Cl <sub>2</sub> NO	320.07	63.79	4.69	4.37	93	98—99
						63.83	4.74	4.28		
V	NO <sub>2</sub>	3-Cl	4-Cl	C <sub>17</sub> H <sub>14</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>3</sub>	365.07	55.93	3.83	7.67	91	216—217
						55.86	3.91	7.59		
VI	H	3-NO <sub>2</sub>	4-CH <sub>3</sub>	C <sub>18</sub> H <sub>18</sub> N <sub>2</sub> O <sub>3</sub>	310.18	69.69	5.80	9.03	74	151—152
						69.73	5.86	9.00		
VII	NO <sub>2</sub>	3-NO <sub>2</sub>	H	C <sub>17</sub> H <sub>15</sub> N <sub>3</sub> O <sub>5</sub>	341.17	59.84	4.39	12.31	81	204—205
						59.75	4.47	12.37		
VIII	H	4-CH(CH <sub>3</sub> ) <sub>2</sub>	H	C <sub>20</sub> H <sub>23</sub> NO	293.20	81.92	7.84	4.77	72	58—59
						81.89	7.91	4.79		
IX	NO <sub>2</sub>	3-NO <sub>2</sub>	4-CH <sub>3</sub>	C <sub>18</sub> H <sub>17</sub> N <sub>3</sub> O <sub>5</sub>	355.18	60.86	4.79	11.82	70	104—105
						60.92	4.86	11.76		
X	H	2-OH	5-Cl	C <sub>17</sub> H <sub>16</sub> ClNO <sub>2</sub>	301.62	67.69	5.30	4.64	69	134—135
						67.65	5.38	4.60		
XI	NO <sub>2</sub>	2-OH	5-Cl	C <sub>17</sub> H <sub>15</sub> ClN <sub>2</sub> O <sub>4</sub>	346.62	58.90	4.33	8.08	66	119—120
						58.82	4.41	8.11		
XII	H	(CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	—	C <sub>17</sub> H <sub>25</sub> NO	259.17	78.78	9.65	5.40	82	53—54

Table 1 (Continued)

Compound	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Formula	M <sub>r</sub>	w <sub>i</sub> (calc.)/w <sub>i</sub> (found)			Yield	M.p.
						% C	% H	% N	%	°C
XIII	NO <sub>2</sub>	(CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	—	C <sub>17</sub> H <sub>24</sub> N <sub>2</sub> O <sub>3</sub>	304.17	78.72	9.73	5.37	79	59—60
						67.12	7.89	9.20		
						67.03	7.96	9.13		
XIV	H	2-Furyl	—	C <sub>15</sub> H <sub>15</sub> NO <sub>2</sub>	241.15	74.70	6.22	5.80	68	94—95
						74.66	6.31	5.77		
XV	NO <sub>2</sub>	2-Furyl	—	C <sub>15</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub>	286.15	62.96	4.89	9.78	67	92—93
						62.90	4.96	9.71		

**Table 2**  
Infrared and mass spectral data of the prepared enones

Compound	$\tilde{\nu}/\text{cm}^{-1}$		$m/z$ ( $I_r/\%$ ) — Significant peaks
	C=O	C=C	
<i>I</i>	1650	1610	331, 329 ( $M^{++}$ ; 100), 250 (5.8), 174 (8.3), 121 (9.2)
<i>II</i>	1661	1618	332, 330 ( $M^{++}$ ; 14.8, 48.2), 317, 315 (14.8, 48.2), 288 (11), 286 (42.6), 284 (28), 141, 139 (33.3, 100), 113, 111 (23, 74)
<i>III</i>	1658	1620	376, 374 ( $M^{++}$ ; 60.5), 361, 359 (60.5), 332 (50), 330 (76.3), 328 (36.5), 185, 183 (100), 157, 155 (76.3)
<i>IV</i>	1652	1615	323, 321, 319 ( $M^{++}$ ; 13, 65, 100), 175 (5), 174 (12.7), 173 (7), 121 (13.7)
<i>V</i>	1662	1618	368, 366, 364 ( $M^{++}$ ; 12, 69, 100), 352, 350, 348 (8, 41, 63), 324, 322, 320 (5.5, 25.3, 49.3), 318 (19.3), 177, 175, 173 (5.5, 15, 23.3)
<i>VI</i>	1656	1612	311 (20), 310 ( $M^{++}$ ; 100), 280 (6), 174 (3.3), 121 (3.3)
<i>VII</i>	1664	1615	342 (18), 341 ( $M^{++}$ ; 100), 325 (76.8), 297 (75), 295 (57), 150 (85.7)
<i>VIII</i>	1646	1601	294 (20), 293 ( $M^{++}$ ; 100), 292 (12), 250 (26), 174 (14.8), 121 (11)
<i>IX</i>	1661	1611	356 (15), 355 ( $M^{++}$ ; 100), 338 (42.5), 311 (40), 309 (23.4), 164 (45.3), 146 (32.5)
<i>X</i>	1633	1612	304, 302 (5.3, 14.8), 303, 301 ( $M^{++}$ ; 33.7, 100), 146 (84.2), 134 (19.7)
<i>XI</i>	1640	1618	349, 347 (6.8, 22), 348, 346 ( $M^{++}$ ; 31.7, 100), 332, 330 (23.6, 68.5), 304 (14), 302 (48), 300 (27), 191 (5.3), 155 (9.4)
<i>XII</i>	1643	1585	260 (7.2), 259 ( $M^{++}$ ; 39), 189 (18.3), 188 (10), 175 (11), 174 (100), 134 (16)
<i>XIII</i>	1649	1591	305 (13), 304 ( $M^{++}$ ; 91), 288 (96), 260 (58.4), 258 (29.3), 234 (34.8), 219 (100), 113 (14.5)
<i>XIV</i>	1643	1615	242 (17.5), 241 ( $M^{++}$ ; 100), 240 (12.3), 213 (4.2), 197 (3.5), 174 (3.2), 121 (3.2)
<i>XV</i>	1650	1618	287 (17), 286 ( $M^{++}$ ; 100), 271 (10.3), 270 (46.4), 242 (35.4), 240 (21.3), 95 (15.4)

aldehyde with concentrated  $\text{HNO}_3$  in concentrated  $\text{H}_2\text{SO}_4$  according to known procedure [11]. The acetophenones used were commercial or they were prepared according to known procedures by Friedel—Crafts reaction of benzene derivatives with acetyl chloride or acetic anhydride and  $\text{AlCl}_3$  in  $\text{CS}_2$ .

All the prepared chalcones were recrystallized from 96 % ethanol. Melting points were determined on a Kofler hot-stage.

Infrared spectra (in KBr pellets; 2.0—3.0 mg of compound per 400 mg KBr) were measured on a Perkin—Elmer 457 instrument. Mass spectra (12 eV) were obtained on a JMS 100-D mass spectrometer at an emission of 300  $\mu\text{A}$ , applying direct sample-introduction technique.

### Enones

A condensing agent was added dropwise (in the case of compounds *XII* and *XIII* in one portion) and with stirring at 25 °C to a mixture of equimolar amounts of aldehyde and methyl ketone in a solvent (for quantitative data see Table 3). In the case of compounds *I*,

Table 3  
Quantitative data for the preparation of enones

Compound	Amounts of reagents	Condensing agent		Solvent
		<i>m/g</i>	<i>w</i> (NaOH)/%	
<i>I</i> , <i>IV</i> , <i>VI</i> , <i>VIII</i>	0.05 mol	1	10	30 cm <sup>3</sup> EtOH
<i>II</i> , <i>III</i> , <i>V</i>	0.035 mol	1	10	150 cm <sup>3</sup> EtOH
<i>VII</i>	0.035 mol	15	10	200 cm <sup>3</sup> MeOH
<i>IX</i>	0.035 mol	1	10	200 cm <sup>3</sup> EtOH
<i>X</i>	0.015 mol	10	50	25 cm <sup>3</sup> EtOH
<i>XI</i>	0.015 mol	15	50	50 cm <sup>3</sup> EtOH
<i>XII</i> , <i>XIII</i>	0.1 mol	40	10	350 cm <sup>3</sup> EtOH 400 cm <sup>3</sup> H <sub>2</sub> O
<i>XIV</i> , <i>XV</i>	0.05 mol	11	10	50 cm <sup>3</sup> EtOH

*IV*, *VI*, and *VIII* the mixture was heated to 50 °C, with compounds *II*, *III*, *V*, and *IX* to 80 °C; the other compounds were prepared without heating. Then the mixture was left to stand. The preparation of compounds *XII* and *XIII* required stirring until formation of a homogeneous clear solution. The compounds *VII* and *IX* began to separate from solution already during condensing agent addition, *I*—*VI* and *VIII* crystallized spontaneously after 5—10 min, *XII*—*XV* after 24—30 h. In the case of *X*, it was necessary to neutralize the mixture after 24 h by diluted acetic acid. For preparing *XI*, the mixture has been neutralized already after 5 h. The separated products of all compounds were filtered by suction, washed with cooled ethanol, and recrystallized from ethanol.

### Quaternization of 4-dimethylamino-4'-bromochalcone (I)

The mixture composed of *I* (0.92 g; 2.8 mmol) and dimethyl sulfate (3.3 g; 25 mmol) was heated at 100 °C for 10 min. Dry ether (20 cm<sup>3</sup>) was then added after cooling. The separated brown oil solidified after short stirring to a light yellow substance. This solid was isolated by suction. After washing with dry ether and acetone, the yield of 4-trimethylammonium-4'-bromochalcone sulfate was 0.95 g (86 %). M.p. = 218–219 °C.

For C<sub>36</sub>H<sub>38</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>6</sub>S (*M<sub>r</sub>* = 786.24) *w<sub>i</sub>*(calculated): 54.99 % C, 4.83 % H, 3.56 % N, 4.08 % S; *w<sub>i</sub>*(found): 54.86 % C, 4.92 % H, 3.48 % N, 4.16 % S.

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### References

1. Gabor, M., Sallai, J., and Szell, T., *Acta Pharm. Hung.* 40, 233 (1970).
2. Gabor, M., Sallai, J., and Szell, T., *Arch. Pharm. (Weinheim)* 303, 593 (1970).
3. Gabor, M., Sallai, J., and Szell, T., *Acta Physiol. (Budapest)* 34, 227 (1968).
4. Samula, K. and Cichy, B., *Acta Pol. Pharm.* 36, 427 (1979).
5. Pfeiffer, P. and Klen, H., *Ber.* 66, 1704 (1933).
6. Davey, W. and Gwilt, J. R., *J. Chem. Soc.* 1957, 1008.
7. Treibs, A. and Bader, H., *Chem. Ber.* 90, 789 (1957).
8. Barnes, R. P. and Dodson, L. B., *J. Amer. Chem. Soc.* 65, 1585 (1943).
9. Walker, E. A. and Young, J. R., *J. Chem. Soc.* 1957, 2041.
10. Lavrushin, V. F., Tsukerman, S. V., and Artemenko, A. I., *Zh. Obshch. Khim.* 31, 3037 (1961).
11. Rupe, H. and Schwarz, E., *Z. Farben- Textilindustrie* 3, 400 (1904).

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