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Conjugated *Schiff* Bases, XIII.[1]
Sterically Congested 1,4-Diazabutadienes as Dipolar Reagents in 1,3-Cycloaddition

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Use of sterically congested 1,4-diazabutadienes as dipols in reactions with some heterocumulenes has been investigated. A synchronous concerted mechanism has been considered. The hydantoine-type structure of products has been discussed with respect to their chemical and spectral behaviour.

(Keywords: 1,3-Cycloaddition; 1,4-Diazabutadienes; Imidazolin-2,4-diones; Imidazolin-2-ones, 4-phenylimino-; Mechanism)

Konjugierte Schiff-Basen, 13. Mitt.: Raumbeanspruchend substituierte 1,4-Diazabutadiene als dipolare Reagentien bei 1,3-Cycloadditionen

Es wird die Verwendung sterisch beanspruchter 1,4-Diazabutadiene als dipolare Agentien bei der Reaktion mit einigen Heterocumulenen untersucht. Ein synchroner, konzertierter Mechanismus wird erwogen. Die Produkte vom Hydantoin-Typ werden mittels ihres chemischen Verhaltens und ihrer spektroskopischen Daten charakterisiert.

1,3-Heterodienes containing nitrogen[2–4] are not typical dipols used for 1,3-cycloaddition[5], however, they can react with heterocumulenes such as aryl isocyanates after patterns of 1,3-cycloaddition[6,7] yielding derivatives of hydantoine, i.e., imidazolidin-2,4-dione[8,9]. This capability is involved by specific steric structure called *"pseudo-gauche"*

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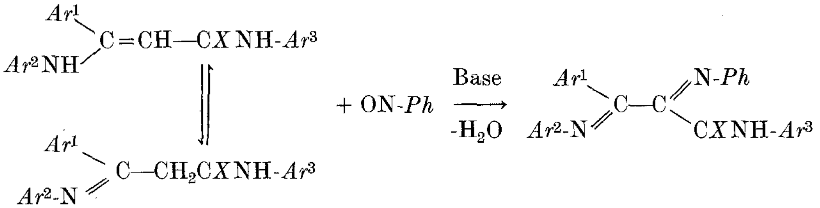
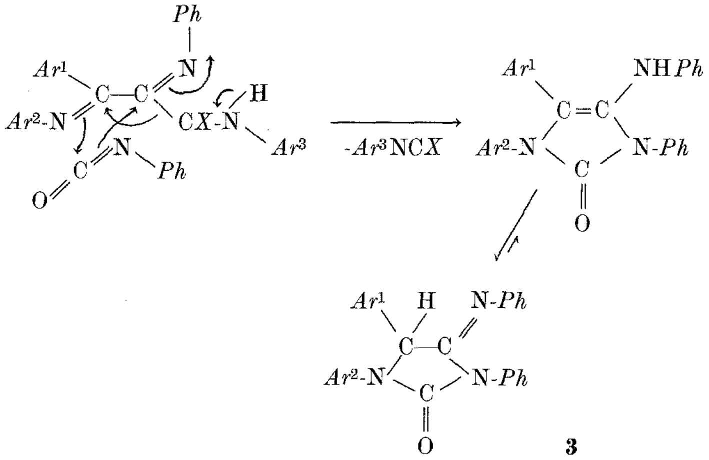
conformation[10] facilitating two-centre contacts between 1,4-diazabutadiene molecules and polar heteroene bonds[11]. The "*pseudo-gauche*" conformation is forced by an expanding effect of bulky groups linking 1,4-diazabutadiene system. On the other hand mass of great substituents may eclipse reaction centres making impossible or, at least, very difficult the course of 1,3-cycloaddition. In order to investigate the effect of steric congestion on dipolar cycloaddition of aryl isocyanates to some 1,4-diazabutadienes, these compounds were chosen because they contain great substituents in all possible positions of the 1,4-diazabutadiene skeleton. They were synthesized via condensation of β-arylaminocinnamic acid arylamides[12, 13] and thioamides[14, 15] with nitrosobenzene[16]:



1 **2**

2	*Ar*^{1}	*Ar*^{2}	*Ar*^{3}	*X*
a	*Ph*	*Ph*	*Ph*	O
b	*Ph*	4-C_6H_4Cl	*Ph*	O
c	*Ph*	4-C_6H_4Br	*Ph*	O
d	*Ph*	*Ph*	4-C_6H_4Cl	O
e	*Ph*	4-$C_6H_4OCH_3$	*Ph*	O
f	*Ph*	C_6H_{11}	*Ph*	O
g	*Ph*	4-$C_6H_4NO_2$	*Ph*	O
h	*Ph*	4-$C_6H_4CO_2C_2H_5$	*Ph*	O
i	*Ph*	*Ph*	*Ph*	S
j	4-C_6H_4Cl	*Ph*	*Ph*	S
k	4-$C_6H_4CH_3$	*Ph*	*Ph*	S

The obtained 1,4-diazabutadienes **2** proved to be also prone to react with the C=N double bond of the aryl isocyanate molecule. Independence of the reaction rate on the solvent polarity suggested a synchronous concerted mechanism analogous to that reported for the model reaction of this type between β-iminobutyramide and isocyanic acid[11]:



3

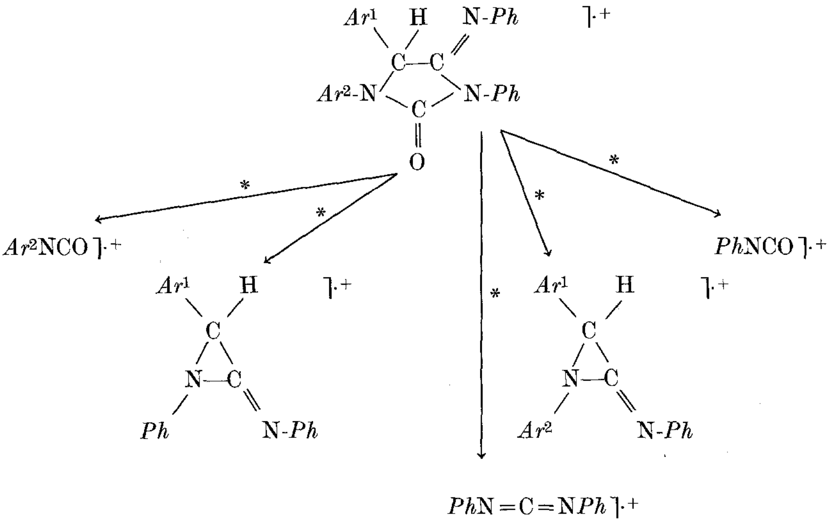
3	Ar^1	Ar^2
a	*Ph*	*Ph*
b	*Ph*	4-C_6H_4Cl
c	*Ph*	4-C_6H_4Br
d	*Ph*	4-$C_6H_4OCH_3$
e	*Ph*	C_6H_{11}
f	*Ph*	4-$C_6H_4NO_2$
g	*Ph*	4-$C_6H_4CO_2C_2H_5$
h	4-C_6H_4Cl	*Ph*
i	4-$C_6H_4CH_3$	*Ph*

Then the proper cycloaddition was combined with 1,4-sigmatropic shift of the anilide hydrogen atom to the α anilo nitrogen atom and synchronous elimination of the anilide or thioanilide fragment as the corresponding aryl iso- or isothio-cyanate; products **3** were obtained.

4-Imidazolin-2-ones forming as the proper out-come of the reaction isomerized to a high degree into more stable 4-phenylimino-imidazolidin-2-ones **3**. Structure of these products **3** was supported by their chemical and spectral properties.

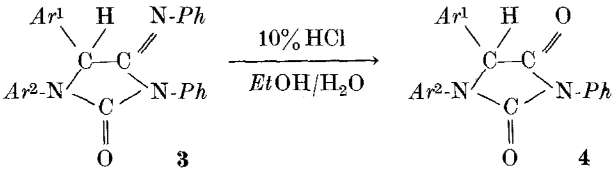
Thus the i.r. spectra revealed strong absorption typical for stretching vibrations of the carbonyl and azomethine double bonds at approximately 1 740 and 1 670 cm^{-1}, respectively. Very weak absorption in the NH stretching vibration region was sometimes observable due to the presence of traces of isomeric 4-imidazolin-2-ones. Shoulders on the longwave side of the azomethine bonds also evidenced these isomers showing absorption of the carbon, carbon double bonds of the imidazoline ring. The ^{1}H n.m.r. spectra exhibited one proton singulets at 5.90 ppm besides the aromatic proton multiplet and signals of groups containing protons such as methyl, methoxyl, etc. Signals of the isomeric 4-imidazolin-2-ones corresponding to the NH protons were not seen probably due to the overlapping with the aromatic proton multiplet[11]. On the contrary, the ^{13}C n.m.r. spectra contained signals characterizing both isomers.

Thus the spectra of the representatively chosen compounds **3 a** and **3 d** revealed signals of the carbonyl carbon atom in position 2 of the fivemembered ring at 152.4 and 154.5 ppm, and the azomethine carbon atom at 157.6 and 158.8 ppm, respectively. Double bonded carbon atoms of the 4-imidazolin-2-one ring produced closely positioned signals at 165.0 and 166.5 ppm in the case of the compound **3 a** and, 165.8 and 166.7 ppm for the compound **3 d**. Signals appearing at higher field were attributed to the carbon atoms bonded with phenyl substituents. Tertiary carbons gave signals at 59.1 and 53.1 ppm, methoxyl group carbon atom was marked by signal at 97.9 ppm. Aromatic carbons were responsible for a number of signals located in the range from 112 to 136 ppm. This assessment of signals was fully confirmed with the help of "off-resonance" measurements. Further evidences proving hydantoine-type structure of the products **3** were provided with mass spectra. These compounds fragmentated under electron impact after the following main pathways established by means of appropriate metastables and precursor measurements:



The above mentioned pathways were in good accordance with fragmentation patterns reported for the similar hydantoine derivatives[17,18].

As expected 4-phenylimino-imidazolidin-2-ones **3** hydrolized easily under influence of acids yielding imidazolidin-2,4-diones **4**.



4	*Ar*^{1}	*Ar*^{2}
a	*Ph*	*Ph*
b	*Ph*	4-C_6H_4Br
c	*Ph*	4-$C_6H_4OCH_3$
d	*Ph*	4-$C_6H_4NO_2$
e	*Ph*	4-$C_6H_4CO_2C_2H_5$

Hydrolysis products showed sharp absorption in the carbonyl region of the i.r. spectra at approximately 1780 and 1740 cm^{-1} originating from stretching vibrations of carbon-oxygen double bonds of 4-C=O and 2-C=O groups of the heterocyclic ring, respectively. The ^{13}C n.m.r. spectrum of the representative compound **4a** was reduced to two carbon atom signals occurring at 162.5 and 151.2 ppm for 4-CO and 2-CO groups. The other signals remained practically unchanged in comparison with the spectrum of the original phenylimino derivative **3a**. The mass spectra were also consistent withe fragmentation considered before[19].

It is worth noticing that the compound **4a** proved to be identical with that described before[8], obtained by thermal decomposition of 1,3,5-triphenyl-imidazolidin-2,4-dion-5-carboxylic acid anilide. This was the final argument supporting definitely the structure of the products **3** and **4**.

Experimental

3-Substituted 1,2,4-triaryl-1,4-diazabutadienes 2

To ethanolic solution (25 to 45 ml) containing a corresponding β-arylamino cinnamic acid anilide or thioanilide **1** (0.01 mol) and freshly synthesized nitrosobenzene (0.01 mol) 33% ethanolic solution of sodium hydroxide (0.1 to 0.3 ml) is added with stirring. The mixture is warmed a little on a steam bath if necessary to initiate an exothermic, sometimes violent reaction connected with change of colour from deep green to orange or pale red. Soon crystalline product begins to precipitate. It is filtered off after cooling and purified by repeated crystallization from ethanol. If the crude product does not crystallize upon cooling the solvent is removed and red oily residue is dissolved in dry benzene (30 ml), filtered and distilled again to remove benzene. The remained oil is dissolved in the smallest possible amount of the mixture containing 7 parts of dry benzene, 2 parts of *n*-hexane, and 1 part of dry chloroform and put into a column filled by silicagel MN 60. This mixture is then used as an eluent. The orange-red fraction is collected and the solvent is distilled off. The obtained oil is usually pure enough to use it for further synthesis. The physical and chemical data of the 1,4-diazabutadienes investigated are collected in Table 1.

4-Phenylimino-1,3,5-triaryl-imidazolidin-2-ones 3

An appropriate 3-substituted 1,2,4-triaryl-1,4-diazabutadiene **2** (0.01 mol) is dissolved in dry benzene (20 to 30 ml) containing phenyl isocyanate (0.01 ml) and the mixture is refluxed for 3 to 5 h. Then petroleum ether (5 to 10 ml) is added. Colourless crystals precipitate after cooling. The crude product is filtered off, washed with cold mixture of benzene and petroleum ether (1 : 1) and purified by repeated crystallization from ethanol. Yields, melting points, and spectral data are listed in Table 2.

Table 1. *1,4-Diazabutadienes* **2**

2	Yield %	M.p. °C	Formula[b]	i.r.[c,d] ν_{max} cm^{-1}	^{1}H n.m.r.[d], ppm	m.s.[e], *m/Z* (Int)
a	73	116-118	$C_{27}H_{21}N_3O$ m.w. 403	C=N 1 638 broad, C=O 1 685, NH 3 330	6.37-8.32 (m, 20 H_{ar}), 9.24 (s, 1 H, NH)	403 (28.0), 180 (100), 181 (17.2), 77 (43.2)
b	82	140-142	$C_{27}H_{20}N_3OCl$ m.w. 437	C=N 1 648 broad, C=O 1 695, NH 3 318	6.32-8.03 (m, 19 Har), 9.18 (s, 1 H, NH)	439 (24.5), 437 (9.8), 216 (32.4), 214 (100), 113 (6.6), 111 (20.3)
c	68	168-169	$C_{27}H_{20}N_3OBr$ m.w. 481	C=N 1 647 broad, C=O 1 685, NH 3 400	6.25-7.83 (m, 19 H_{ar}), 9.21 (s, 1 H, NH)	483 (26.2), 481 (26.4), 258 (100), 256 (99.6), 119 (9.3), 104 (13.9)
d	69	145-146	$C_{27}H_{20}N_3OCl$ m.w. 437	C=N 1 645 broad, C=O 1 685, NH 3 365	6.35-7.78 (m, 19 H_{ar}), 9.30 (s, 1 H, NH)	439 (5.8), 437 (13.6), 181 (15.4), 180 (100), 77 (44.7)
e	73	142-144	$C_{28}H_{23}N_3O_2$ m.w. 433	C=N 1 662 broad, C=O 1 683, OCH_3 2 837, NH 3 295	3.75 (s, 3 H, OCH_3), 6.39-7.88 (m, 19 H_{ar})	403 (27.9), 210 (100), 195 (36.2), 180 (11.2), 119 (6.5), 104 (17.2)
f	65	75-76	$C_{33}H_{31}N_3O$ m.w. 485	C=N 1 648 broad, C=O 1 687, CH_{al} 2 905, 2 930, NH 3 295	1.03-1.52 (m, 11 H_{al}), 6.30-8.02 (m, 15 H_{ar}), 9.08 (s, 1 H, NH)	409 (27.4), 366 (12.5), 186 (20.3), 104 (100)
g	71	172-173	$C_{27}H_{20}N_4O_3$ m.w. 448	C=N 1 648 broad, C=O 1 692, NH 3 402, NO_2 1 515, 1 327	6.37-8.08 (m, 19 H_{ar}), 9.26 (s, 1 H, NH)	448 (39.3), 225 (100), 195 (12.5), 180 (12.7), 179 (38.0), 104 (16.1)
h	70	184-185	$C_{30}H_{25}N_3O_3$ m.w. 475	C=N 1 649 broad, C=O 1 681, CO_e 1 732, OCH_2 2 852, NH 3 320	1.40 (t, 3 H, CH_3), 4.38 (q, 2 H, CH_2), 6.48-8.02 (m, 19 H_{ar}), 9.31 (s, 1 H, NH)	475 (29.7), 252 (100), 224 (26.2), 104 (23.5)
i	61	oil[a]	$C_{27}H_{21}N_3S$ m.w. 419	C=N 1 680 broad, C=S 1 155, NH 3 220	6.68-8.30 (m, 19 H_{ar}), 11.10 (s, 1 H, NH)	419 (14.6), 284 (7.2), 195 (11.2), 181 (16.4), 180 (90.1), 104 (16.5)

j	63	oil[a]	$C_{27}H_{20}N_3SCl$ m.w. 453	C=N 1 662 broad, C=S 1 157, NH 3 290	6.60-8.25 (m, 19 H_{ar}), 11.13 (s, 1H, NH)	455 (6.3), 453 (13.6), 331 (11.3), 216 (19.6), 214 (52.6), 104 (19.7), 77 (100)
k	61	oil[a]	$C_{28}H_{23}N_3S$ m.w. 433	C=N 1 675 broad, C=S 1 152, CH_3 2 915, NH 3 282	2.38 (s, 3H, CH_3), 6.62-8.15 (m, 19 H_{ar}), 11.15 (s, 1H, NH)	433 (24.8), 396 (10.5), 358 (13.1), 194 (100), 119 (31.5), 104 (36.3)

[a] Products purified by column chromatography.

[b] Combustion analyses were performed on a Perkin-Elmer Analyser Type 240. The results of elemental analyses (C, H, N, Cl, Br, S) were in full agreement with the proposed structures.

[c] The i.r. spectra were recorded on an IR-75 Zeiss spectrophotometer using nujol and hexachlorbutadiene mulls.

[d] The n.m.r. spectra were determined on a JEOL-100 spectrometer in $CDCl_3$ using *TMS* as internal standard. Index "ar" designates "aromatic", "al" aliphatic, "e" ester, "s" singulet, "t" triplet, "q" quartet, and "m" multiplet, respectively.

[e] The m.s. spectra were recorded on an LKB 9000 S spectrometer by D.I. system at 70 eV and a.V. 3.5 kV. Temperature of probe 60-80 °C, I.C.T. 250 °C.

Table 2. *1,3,5-Tiaryl-4-phenylimino-imidazolidin-2-ones* **3**

3	Yield %	M.p. °C	Formula	i.r. ν_{max} cm^{-1}	^{1}H n.m.r., ppm	m.s., *m/Z* (Int)
a	57	186-187	$C_{27}H_{21}N_3O$ m.w. 403	2-C=O 1742, 4-C=N 1678	5.90 (s, 1H, CH), 6.40-7.42 (m, 20 H_{ar})	403 (100), 283 (24.9), 194 (13.5), 181 (53.3), 180 (69.3)
b	60	204-205	$C_{27}H_{20}N_3OCl$ m.w. 437	2-C=O 1748, 4-C=N 1680	5.84 (s, 1H, CH), 6.50-7.75 (m, 19 H_{ar})	439 (39.4), 437 (100), 283 (18.7), 216 (21.8), 214 (45.2), 181 (11.2), 180 (21.2), 113 (5.1), 111 (15.4)
c	63	205-206	$C_{27}H_{20}N_3OBr$ m.w. 481	2-C=O 1755, 4-C=N 1686	5.77 (s, 1H, CH), 6.35-7.58 (m, 19 H_{ar})	482 (100), 480 (100), 283 (27.1), 260 (35.6), 258 (32.7), 195 (13.6), 194 (22.3), 181 (15.4), 180 (31.6), 157 (10.1)
d	51	173-174	$C_{28}H_{23}N_3O_2$ m.w. 433	2-C=O 1752, 4-C=N 1689	5.80 (s, 1H, CH), 3.70 (s, 3H, OCH_3), 6.40-7.52 (m, 19 H_{ar})	433 (100), 283 (13.3), 211 (44.3), 210 (18.0), 196 (32.8), 181 (9.1), 180 (14.5)
e	48	139-140	$C_{27}H_{27}N_3O$ m.w. 409	2-C=O 1742, 4-C=N 1693	0.93-1.12 (m, 5 H_{al}), 1.38-1.76 (m, 6 H_{al}), 5.28 (s, 1H, CH), 6.19-7.55 (m, 15 H_{ar})	409 (100), 283 (11.9), 195 (16.3), 194 (27.8), 181 (12.8), 180 (33.5)
f	69	188-189	$C_{27}H_{20}N_4O_3$ m.w. 448	2-C=O 1770, 4-C=N 1698	5.97 (s, 1H, CH), 6.21-7.82 (m, 19 H_{ar})	448 (100), 283 (14.8), 253 (28.3), 208 (27.2), 195 (10.5), 194 (20.2), 181 (12.2), 180 (33.5)

g	71	198-199	$C_{30}H_{25}N_3O_3$ m.w. 475	2-C=O 1 762, 4-C=N 1 688, C=O$_e$ 1 738, OCH$_2$ 2 845	1.27 (t, 3H, CH$_3$), 4.25 (q, 2H, CH$_2$), 5.93 (s, 1H, CH), 6.32-7.91 (m, 19H$_{ar}$)	475 (100), 282 (20.2), 253 (28.3), 208 (27.2), 195 (15.0), 194 (23.0), 181 (8.8), 180 (20.9)
h	55	135-136	$C_{27}H_{20}N_3OCl$ m.w. 437	2-C=O 1 759, 4-C=N 1 685	5.93 (s, 1H, CH), 6.43-7.62 (m, 19H$_{ar}$)	439 (34.9), 437 (100), 317 (18.5), 216 (27.6), 216 (27.6), 214 (59.3), 195 (10.3), 194 (28.5)
i	59	168-169	$C_{28}H_{23}N_3O$ m.w. 417	2-C=O 1 761, 4-C=N 1 684	2.27 (s, 3H, CH$_3$), 5.82 (s, 1H, CH), 6.37-7.56 (m, 19H$_{ar}$)	417 (100), 296 (22.2), 195 (63.5), 194 (81.9)

See: notes added to Table 1.

Table 3. *1,3,5-Triaryl-imidazolidin-2,4-diones* **4**

4	Yield %	M.p. °C	Formula	i.r., cm^{-1}	^{1}H n.m.r., ppm	m.s. *m/Z* (Int)
a	82	118-119				
b	84	169-170	$C_{21}H_{15}N_2O_2Br$ m.w. 406	2-CO 1 794 4-CO 1 729	5.53 (s, 1H, CH), 6.59-7.63 (m, 14H)	408 (98.3), 406 (100), 261 (97.5), 259 (98.3), 181 (22.4), 180 (30.8), 157 (20.7), 155 (22.4)
c	80	128-129	$C_{22}H_{18}N_2O_3$ m.w. 358	2-CO 1 790 4-CO 1 725 OCH_3 2 862	5.50 (s, 1H, CH), 3.74 (s, 3H, OCH_3) 6.68-7.89 (m, 14H)	358 (100), 211 (56.0), 196 (45.0) 181 (7.2), 180 (8.1)
d	82	177-178	$C_{21}H_{15}N_3O_4$ m.w. 373	2-CO 1 798 4-CO 1 739 NO_2 1 503, 1293	5.54 (s, 1H, CH), 6.70-7.63 (m, 14H)	373 (83.2), 226 (100), 196 (18.7) 181 (15.9), 180 (22.6), 152 (13.0)
e	78	170-171	$C_{24}H_{20}N_2O_4$ m.w. 400	2-CO 1 795 4-CO 1 735 CO_e 1 730 OCH_2 2 835	1.31 (t, 3H, CH_3) 4.25 (q, 2H, CH_2) 5.55 (s, 1H, CH) 6.79-7.98 (m, 14H)	400 (100), 253 (84.8), 208 (39.4) 181 (14.5), 180 (22.1), 152 (13.1) 119 (11.7)

See: notes added to Table 1.

Table 4. *New β-arylaminocinnamic acid anilides* **1**

1	Yield%	M.p. °C	Formula	i.r. cm^{-1}	^{1}H n.m.r., ppm	m.s. *m/Z* (Int)
a	68	223-224	$C_{21}H_{17}N_2OBr$ m.w. 392	C=O 1638, NH 3362	5.08 (s, 1H, CH) 6.32 (s, 1H, NH) 6.46-7.23 (m, 14H) 11.16 (s, 1H, NH)	394 (29.3), 392 (29.6), 302 (99.6), 300 (100), 274 (38.0), 272 (37.8), 260 (26.9), 258 (26.5), 119 (11.6)
b	60	129-130	$C_{21}H_{24}N_2O$ m.w. 320	C=O 1642, NH 3388 CH_{al} 2985, 2930	1.09-1.55 (m, 11H) 5.03 (s, 1H, CH) 6.18 (s, 1H, NH) 6.32-7.55 (m, 10H) 11.09 (s, 1H, NH)	320 (31.6), 228 (100), 200 (44.6) 186 (26.2), 119 (8.3)
c	69	175-176	$C_{24}H_{22}N_2O_3$ m.w. 386	C=O 1640, NH 3375 $C=O_e$ 1702	1.32 (t, 3H, CH_3) 4.32 (q, 2H, CH_2) 5.12 (s, 1H, CH) 6.12 (s, 1H, NH) 6.57-7.30 (m, 14H) 11.30 (s, 1H, NH)	386 (32.6), 294 (100), 267 (35.3), 266 (34.9), 253 (22.3), 193 (20.0) 119 (13.0)

See: notes added to Table 1.

1,3,5-Triaryl-imidazolidin-2,4-diones **4**

A corresponding 4-phenylimino-1,3,5-triaryl-imidazolidin-2-one **3** (0.01 mol) is suspended in 15% aqueous hydrochloric acid (40 ml) containing ethanol (15 ml) and refluxed for 0.5 h. The crude product which precipitates after cooling is isolated by suction, washed with ice water, and repeatedly crystallized from ethanol. Physical and chemical properties are shown in Table 3.

β-*Arylaminocinnamic acid anilides and thioanilides* **1**

For preparation the azeotropic method described earlier[13–15] was used. Their chemical and physical behaviour was reported previously[20–25] except β-*p*-bromphenylaminocinnamic acid anilide **1a**, β-cyclohexylaminocinnamic acid anilide **1b**, and β-*p*-carboethoxyphenylaminocinnamic acid anilide **1c**. Their properties are listed in Table 4.

References

[1] Part XII: *Moskal J.*, *Milart P.*, J. Chem. Res., in press.
[2] *Moskal J.*, Roczniki Chem. **48**, 2169 (1974).
[3] *Moskal J.*, Synthesis **1975**, 380.
[4] *Moskal J.*, *Moskal A.*, *Pietrzycki W.*, J. Chem. Soc. Perkin 2 **1977**, 1893.
[5] *Decimoni G.*, *Tacconi G.*, Chem. Rev. **75**, 652 (1975).
[6] *Houk K. N.*, *Sims J.*, J. Amer. Chem. Soc. **95**, 7287 (1973).
[7] *Huisgen R.*, J. Org. Chem. **33**, 2291 (1968).
[8] *Moskal J.*, *Moskal A.*, Synthesis **1979**, 794.
[9] *Moskal J.*, *Nagraba K.*, *Moskal A.*, Org. Mass Spectrom. **15**, 466 (1980).
[10] *Moskal J.*, Roczniki Chem. **49**, 1811 (1975).
[11] *Moskal J.*, *Moskal A.*, *Pietrzycki W.*, Tetrahedron **35**, 1883 (1979).
[12] *Moszew J.*, *Inasiński A.*, Roczniki Chem. **34**, 1173 (1960).
[13] *Moszew J.*, *Inasiński A.*, Bull. Pol. Acad. Sci. **9**, 303 (1961).
[14] *Moszew J.*, *Inasiński A.*, *Kubiczek K.*, *Zawrzykraj J.*, Ibid. **8**, 405 (1960).
[15] *Moszew J.*, *Jamrozik M.*, Z. Nauk. UJ **15**, 106 (1970).
[16] *Mirek J.*, *Moskal A.*, *Moskal J.*, Roczniki Chem. **46**, 2233 (1972).
[17] *Locock R. A.*, *Coutts R. T.*, Org. Mass Spectrom. **3**, 735 (1970).
[18] *Elliot T. H.*, *Natarajan P. N.*, J. Pharm. Pharmacol. **19**, 209 (1967).
[19] *Moskal J.*, *Nagraba K.*, *Moskal A.*, J. Org. Mass Spectrom. **15**, 257 (1980).
[20] *Ehrlich P.*, *Sachs F.*, Ber. **32**, 2341 (1899).
[21] *Moszew J.*, *Jamrozik M.*, *Kubicka K.*, Z. Nauk. UJ **11**, 71 (1966).
[22] *Moszew J.*, *Inasiński A.*, Ibid. **7**, 133 (1962).
[23] *Moszew J.*, *Boksa A.*, Ibid. **11**, 97 (1966).
[24] *Moszew J.*, *Inasiński A.*, *Zawrzykraj J.*, Ibid. **7**, 133 (1962).
[25] *Moszew J.*, *Podgórska-Łabuś E.*, *Wójtowicz U.*, Ibid. **11**, 94 (1966).