3*H*-Indolium Salts Efficiently Prepared from *N*-Substituted Anilines and α-Branched Ketones by an One-pot Synthesis

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Starting with the *N*-substituted anilines **4**/**12** and the α-branched ketones **3** the 3*H*-indolium salts **1** and their fused derivatives **13** are prepared by combining a sodium nitrite nitrosation, a zinc dust reduction, a hydrazone formation and a Fischer indolization to a reaction sequence in which the isolation and purification of intermediates is not necessary. The scope and limitations of this effective one-pot synthesis are discussed.

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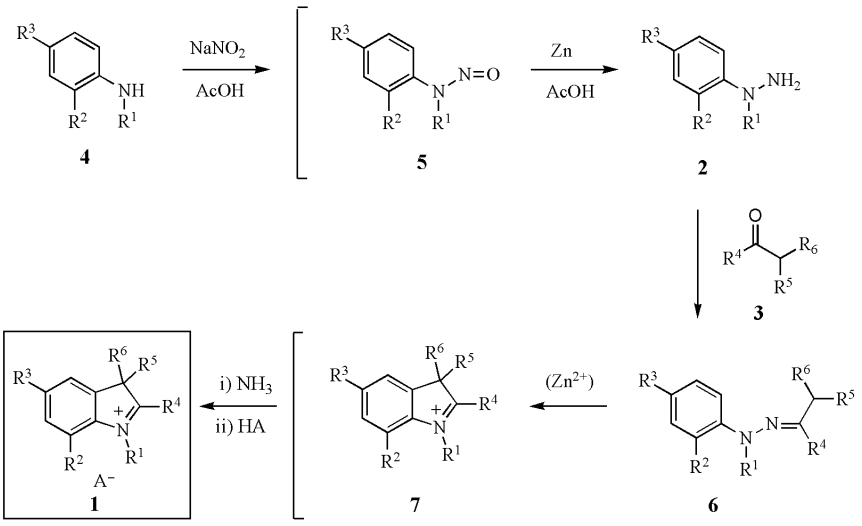
In recent years the improvement of the synthesis of 3*H*-indolium salts **1** [1] has attracted considerable attention since these salts represent important starting materials for the preparation of compounds, such as polymethine dyes [2] or photochromic spiroindolines [3], possessing valuable properties for applications in the field of spectral sensitization, laser construction, optical data storage, conversion of sun energy and other modern technologies. Until now, the most important access to 3*H*-indolium salts **1** consists in the condensation of *N*-arylhydrazines with ketones to *N*-arylhydrazones, subsequent Fischer indolization [4] to indolenines and final *N*-alkylation and in the reaction of *N*-substituted *N*-arylhydrazines with ketones to arylhydrazones followed by a Fischer type cyclization [4].



4	3	HA	R^1	R^2	R^3	R^4	R^5	R^6	A^-	1
a	**a**	$HClO_4$	Me	H	H	Me	Me	Me	ClO_4^-	**a**
a	**a**	HI	Me	H	H	Me	Me	Me	I^-	**a´**
a	**a**	HBF_4	Me	H	H	Me	Me	Me	BF_4^-	**a´´**
b	**a**	$HClO_4$	Me	Me	H	Me	Me	Me	ClO_4^-	**b**
c	**a**	$HClO_4$	Me	H	Me	Me	Me	Me	ClO_4^-	**c**
d	**a**	$HClO_4$	Me	H	Cl	Me	Me	Me	ClO_4^-	**d**
e	**a**	$HClO_4$	Et	H	H	Me	Me	Me	ClO_4^-	**e**
f	**a**	$HClO_4$	i-Pr	H	H	Me	Me	Me	ClO_4^-	**f**
g	**a**	$HClO_4$	n-Bu	H	H	Me	Me	Me	ClO_4^-	**g**
h	**a**	$HClO_4$	C_6H_{11}	H	H	Me	Me	Me	ClO_4^-	**h**
i	**a**	$HClO_4$	CH_2Ph	H	H	Me	Me	Me	ClO_4^-	**i**
j	**a**	$HClO_4$	$CH_2CH{=}CH_2$	H	H	Me	Me	Me	ClO_4^-	**j**
k	**a**	$HClO_4$	$(CH_2)_2OH$	H	H	Me	Me	Me	ClO_4^-	**k**
a	**b**	$HClO_4$	Me	H	H	Et	Me	Me	ClO_4^-	**l**
a	**c**	$HClO_4$	Me	H	H	n-Pr	Me	Me	ClO_4^-	**m**
a	**d**	$HClO_4$	Me	H	H	i-Pr	Me	Me	ClO_4^-	**n**
a	**e**	$HClO_4$	Me	H	H	Me	Me	Et	ClO_4^-	**o**
a	**f**	$HClO_4$	Me	H	H	Me	$(CH_2)_5$		ClO_4^-	**p**

Table 1
Physical, Analytical and Spectral Data for the Salts **1**/**13**

No.	Compound	Yield (%)	Mp [a] (°C)	Molecular Formula (Molecular Weight)	Analysis (%) Calcd./Found C	H	N	^{1}H-NMR (dimethyl-d_6 sulfoxide) δ (ppm)
1a	1,2,3,3-Tetramethyl-3*H*-indolium perchlorate	60	201-202 (198 [11])	$C_{12}H_{16}ClNO_4$ (273.7)	52.66 52.70	5.89 5.95	5.12 5.20	1.46 (s, 6H, 3-CH_3), 2.69 (s, 3H, 2-CH_3), 3.92 (s, 3H, 1-CH_3), 7.52-7.85 (m, 4H, arom-H)
1a'	1,2,3,3-Tetramethyl-3*H*-indolium iodide	40	273-274 (262 [12])	$C_{12}H_{16}N$ (301.2)	47.86 47.83	5.35 5.40	4.65 4.70	1.49 (s, 6H, 3-CH_3), 2.76 (s, 3H, 2-CH_3), 3.95 (s, 3H, 1-CH_3), 7.54-7.90 (m, 4H, arom-H)
1a''	1,2,3,3-Tetramethyl-3*H*-indolium tetrafluoroborate	55	204-205 (201-203 [13])	$C_{12}H_{16}BF_4N$ (261.1)	55.21 55.30	6.18 6.21	5.37 5.42	1.46 (s, 6H, 3-CH_3), 2.69 (s, 3H, 2-CH_3), 3.90 (s, 3H, 1-CH_3), 7.54-7.85 (m, 4H, arom-H)
1b	1,2,3,3,7-Pentamethyl-3*H*-indolium perchlorate	28	246-248	$C_{13}H_{18}ClNO_4$ (287.8)	54.26 54.31	6.31 6.35	4.87 4.90	1.43 (s, 6H, 3-CH_3), 2.68 (s, 6H, 2-CH_3, 7-CH_3), 4.05 (s, 3H, 1-CH_3), 7.28-7.58 (m, 3H, arom-H)
1c	1,2,3,3,5-Pentamethyl-3*H*-indolium perchlorate	39	239-240	$C_{13}H_{18}ClNO_4$ (287.8)	54.26 54.30	6.31 6.35	4.87 4.75	1.45 (s, 6H, 3-CH_3), 2.37 (s, 3H, 5-CH_3), 2.67 (s, 3H, 2-CH_3), 3.89 (s, 3H, 1-CH_3), 7.33-7.72 (m, 3H, arom-H)
1d	5-Chloro-1,2,3,3-tetramethyl-3*H*-indolium perchlorate	38	239-240 (222-223 [14])	$C_{12}H_{15}Cl_2NO_4$ (308.2)	46.77 46.81	4.91 4.95	4.55 4.60	1.48 (s, 6H, 3-CH_3), 2.69 (s, 3H, 2-CH_3), 3.90 (s, 3H, 1-CH_3), 7.64-7.97 (m, 3H, arom-H)
1e	1-Ethyl-2,3,3-trimethyl-3*H*-indolium perchlorate	43	209-210	$C_{13}H_{18}ClNO_4$ (287.8)	54.26 54.31	6.31 6.40	4.87 4.93	1.40 (t, 3H, 1-CH_2CH_3), 1.48 (s, 6H, 3-CH_3), 2,77 (s, 3H, 2-CH_3), 4.44 (q, 2H, 1-CH_2CH_3), 7.54-7.93 (m, 4H, arom-H)
1f	1-Isopropyl-2,3,3-trimethyl-3*H*-indolium perchlorate	33	248-249	$C_{14}H_{20}ClNO_4$ (301.8)	55.72 55.81	6.68 6.75	4.64 4.70	1.48 (s, 6H, 3-CH_3), 1.66 (d, 6H, 1-$CH(CH_3)_2$), 2.80 (s, 3H, 2-CH_3), 5.08 (m, 1H, 1-$CH(CH_3)_2$), 7.52-8.07 (m, 4H, arom-H)
1g	1-Butyl-2,3,3-trimethyl-3*H*-indolium perchlorate	54	123-124	$C_{15}H_{22}ClNO_4$ (315.8)	57.05 57.10	7.02 7.11	4.44 4.38	0.89 (t, 3H, 1-$CH_2CH_2CH_2CH_3$), 1.40 (m, 2H, 1- $CH_2CH_2CH_2CH_3$), 1.49 (s, 6H, 3-CH_3), 1.78 (m, 2H, 1-$CH_2CH_2CH_2CH_3$), 2.78 (s, 3H, 2-CH_3), 4.40 (t, 2H, 1-$CH_2CH_2CH_2CH_3$), 7.55-7.94 (m, 4H, arom-H)
1h	1-Cyclohexyl-2,3,3-trimethyl-3*H*-indolium perchlorate	21	247-248	$C_{17}H_{24}ClNO_4$ (341.8)	59.73 59.70	7.08 7.15	4.10 4.08	1.42-2.29 (m, 10H, 1-$CH(CH_2)_5$), 1.48 (s, 6H, 3-CH_3), 2.85 (s, 3H, 2-CH_3), 4,66 (m, 1H, 1-$CH(CH_2)_5$), 7.51-8.15 (m, 4H, arom-H)
1i	1-Benzyl-2,3,3-trimethyl-3*H*-indolium perchlorate	49	169-170	$C_{18}H_{20}ClNO_4$ (349.8)	61.80 61.83	5.76 5.85	4.00 4.10	1.56 (s, 6H, 3-CH_3), 2.94 (s, 3H, 2-CH_3), 5.79 (s, 2H, 1-CH_2Ph), 7.32-7.82 (m, 9H, arom-H)
1j	1-Allyl-2,3,3-trimethyl-3*H*-indolium perchlorate	33	168-169	$C_{14}H_{18}ClNO_4$ (299.8)	56.10 56.18	6.05 6.11	4.67 4.73	1.51 (s, 6H, 3-CH_3), 2.79 (s, 3H, 2-CH_3), 5.12 (m, 2H, 1-$CH_2CH=CH_2$), 5.37 (m, 2H, 1-$CH_2CH=CH_2$), 6.03 (m, 1H, 1-$CH_2CH=CH_2$), 7.55-7.86 (m, 4H, arom-H)
1k	1-(2-Hydroxyethyl)-2,3,3-trimethyl-3*H*-indolium perchlorate	50	152-153	$C_{13}H_{18}ClNO_5$ (303.7)	51.41 51.42	5.97 5.98	4.61 4.72	1.50 (s, 6H, 3-CH_3), 2.76 (s, 3H, 2-CH_3), 3.84 (t, 2H, 1-CH_2CH_2OH), 4.45 (s, 1H, 1-CH_2CH_2OH), 4.54 (t, 2H, 1-CH_2CH_2OH), 7.55-7.90 (m, 4H, arom-H)
1l	2-Ethyl-1,3,3-trimethyl-3*H*-indolium perchlorate	44	177-178 (177-178 [7])	$C_{13}H_{18}ClNO_4$ (287.7)	54.26 54.31	6.31 6.28	4.87 4.92	1.25 (t, 3H, 2-CH_2CH_3), 1.51 (s, 6H, 3-CH_3), 3.09 (q, 2H, 2-CH_2CH_3), 3.97 (s, 3H, 1-CH_3), 7.54-7.87 (m, 4H, arom-H)
1m	1,3,3-Trimethyl-2-propyl-3*H*-indolium perchlorate	34	137-138 (139-140 [7])	$C_{14}H_{20}ClNO_4$ (301.8)	55.72 55.80	6.68 6.75	4.64 4.71	1.07 (t, 3H, 2-$CH_2CH_2CH_3$), 1.51 (s, 6H, 3-CH_3), 1.66 (m, 2H, 2-$CH_2CH_2CH_3$), 3.03 (m, 2H, 2-$CH_2CH_2CH_3$), 3.98 (s, 3H, 1-CH_3), 7.54-7.86 (m, 4H, arom-H)
1n	2-Isopropyl-1,3,3-trimethyl-3*H*-indolium perchlorate	9	197-198 (196-197 [7])	$C_{14}H_{20}ClNO_4$ (301.8)	55.72 55.77	6.68 6.70	4.64 4.69	1.41 (d, 6H, 2-$CH(CH_3)_2$), 1.55 (s, 6H, 3-CH_3), 3.65 (m, 1H, 2-$CH(CH_3)_2$), 4.03 (s, 3H, 1-CH_3), 7.55-7.89 (m, 4H, arom-H)
1o	3-Ethyl-1,2,3-trimethyl-3*H*-indolium perchlorate	55	229-230 (230-231 [7])	$C_{13}H_{18}ClNO_4$ (287.7)	54.26 54.38	6.31 6.50	4.87 4.93	0.35 (t, 3H, 3-CH_2CH_3), 1.48 (s, 3H, 3-CH_3), 2.10 (m, 2H, 3-CH_2CH_3), 2.73 (s, 3H, 2-CH_3), 3.98 (s, 3H, 1-CH_3), 7.56-7.89 (m, 4H, arom-H)
1p	1',2'-Dimethylspiro[cyclohexane-1,3'-3*H*-indolium] perchlorate	60	246-247 (248-249 [7])	$C_{15}H_{20}ClNO_4$ (313.8)	57.42 57.50	6.42 6.50	4.46 4.51	1.32-2.03 (m, 10H, 3',3'-$(CH_2)_5$), 2.73 (s, 3H, 2'-CH_3), 3.92 (s, 3H, 1'-CH_3), 7.49-8.06 (m, 4H, arom-H)
13a	4,4,5-Trimethyl-2,5-dihydro-1*H*-pyrrolo[3,2,1-*hi*]indolium perchlorate	24	245-246	$C_{13}H_{16}ClNO_4$ (285.7)	54.65 54.61	5.64 5.70	4.90 4.91	1.50 (s, 6H, 5-CH_3), 2.56 (s, 3H, 4-CH_3), 3.75 (t, 2H, 2-CH_2), 4.65 (t, 2H, 1-CH_2), 7.42-7.48 (m, 3H, arom-H)

Table 1 (continued)

No.	Compound	Yield (%)	Mp [a] (°C)	Molecular Formula (Molecular Weight)	Analysis (%) Calcd./Found C	H	N	^{1}H-NMR (dimethyl-d_6 sulfoxide) δ (ppm)
13b	1,1,2-Trimethyl-1,4,5,6-tetrahydropyrrolo[3,2,1-*ij*]quinolinium perchlorate	49	270-271	$C_{14}H_{18}ClNO_4$ (299.8)	56.10 56.20	6.05 6.01	4.67 4.61	1.46 (s, 6H, 1-CH_3), 2.13 (m, 2H, 5-CH_2), 2.63 (s, 3H, 2-CH_3), 2.87 (t, 2H, 6-CH_2), 4.30 (t, 2H, 4-CH_2), 7.30-7.54 (m, 3H, arom-H)
13c	1,1,2,8-Tetramethyl-1,4,5,6-tetrahydropyrrolo[3,2,1-*ij*]quinolinium perchlorate	15	243-244	$C_{15}H_{20}ClNO_4$ (313.8)	57.42 57.38	6.42 6.30	4.46 4.50	1.44 (s, 6H, 1-CH_3), 2.14 (m, 2H, 5-CH_2), 2.34 (s, 3H, 8-CH_3), 2.60 (s, 3H, 2-CH_3), 2.82 (t, 2H, 6-CH_2), 4.27 (t, 2H, 4-CH_2), 7.14, 7,35 (2s, 2H, arom-H)
13d	2-Ethyl-1,1-dimethyl-1,4,5,6-tetrahydropyrrolo-[3,2,1-*ij*]quinolinium perchlorate	42	213-214	$C_{15}H_{20}ClNO_4$ (313.8)	57.42 57.31	6.42 6.50	4.46 4.51	1.24 (t, 3H, 2-CH_2CH_3), 1.50 (s, 6H, 1-CH_3), 2.17 (m, 2H, 5-CH_2), 2.88 (t, 2H, 6-CH_2), 3.05 (q, 2H, 2-CH_2CH_3), 4.37 (t, 2H, 4-CH_2), 7.31-7.56 (m, 3H, arom-H)
13e	1,1-Dimethyl-2-propyl-1,4,5,6-tetrahydropyrrolo-[3,2,1-*ij*]quinolinium perchlorate	41	201-202	$C_{16}H_{22}ClNO_4$ (327.8)	58.62 58.54	6.76 6.83	4.27 4.33	1.04 (t, 3H, 2-$CH_2CH_2CH_3$), 1.50 (s, 6H, 1-CH_3), 1.67 (m, 2H, 2-$CH_2CH_2CH_3$), 2.17 (t, 2H, 5-CH_2), 2.88 (t, 2H, 6-CH_2), 2.99 (t, 2H, 2-$CH_2CH_2CH_3$), 4.39 (t, 2H, 4-CH_2), 7.36-7.56 (m, 3H, arom-H)
13f	1-Ethyl-1,2-dimethyl-1,4,5,6-tetrahydropyrrolo-[3,2,1-*ij*]quinolinium perchlorate	43	239-240	$C_{15}H_{20}ClNO_4$ (313.8)	57.42 57.50	6.42 6.50	4.46 4.50	0.43 (t, 3H, 1-CH_2CH_3), 1.46 (s, 3H, 1-CH_3), 1.92-2.19 (m, 4H, 1-CH_2CH_3, 5-CH_2), 2.67 (s, 3H, 2-CH_3), 2.90 (m, 2H, 6-CH_2), 4.31 (m, 1H, 4-CH_2), 4.41 (m, 1H, 4-CH_2), 7.34-7.52 (m, 3H, arom-H)
13g	2'-Methyl-1',4',5',6'-tetra-hydrospiro[cyclohexane-1,2'-pyrrolo[3,2,1-*ij*]quino-linium] perchlorate	44	258-259	$C_{17}H_{22}ClNO_4$ (339.8)	60.09 60.15	6.53 6.58	4.12 4.10	1.33-1.97 (m, 10H, 1',1'-$(CH_2)_5$), 2.15 (m, 2H, 5'- CH_2), 2,66 (s, 3H, 2'-CH_3), 2.88 (t, 2H, 6'-CH_2), 4.29 (t, 2H, 4'-CH_2), 7.36-7.82 (m, 3H, arom-H)
13h	1,1,2-Trimethyl-4,5,6,7-tetrahydro-1*H*-azepino-[3,2,1-*hi*]indolium perchlo-rate	52	247-248	$C_{15}H_{20}ClNO_4$ (313.8)	57.42 57.31	6.42 6.34	4.46 4.41	1.44 (s, 6H, 1-CH_3), 1.89-2.16 (m, 4H, 5-CH_2, 6-CH_2), 2.67 (s, 3H, 2-CH_3), 3.06 (t, 2H, 7-CH_2), 4.48 (t, 2H, 4-CH_2), 7.27-7.57 (m, 3H, arom-H)

In connection with our investigations on spiro[cyclohexadiene-azaheterocycles] [5], a novel class of compounds with photochromic properties [6], which are easily obtained by ring transformation of 2,4,6-triarylpyrylium salts with methyleneindolines derived from the 3*H*-indolium salts **1**, we have shown that the synthesis of the salts **1** can considerably be improved by combining the hydrazone formation and the Fischer indolization to an one-pot procedure [7]. In this way, from *N*-arylhydrazines **2**, α-branched ketones **3** and perchloric acid in ethanol the 3*H*-indolium perchlorates **1** (A^-= ClO_4^-) with a wide range of substituents in the 1-, 2- and 3-position were prepared in good yield and high purity. Although this procedure is very simple, in contrast to the ketones **3** the hydrazines **2** used are in some cases expensive materials, unstable compounds or have to be prepared in one or more additional reaction steps. To avoid these disadvantages, the idea arose to start with the usually more inexpensive and better available *N*-substituted anilines **4** and to combine their transformation to the hydrazines **2** with the hydrazone formation and the Fischer indolization to a reaction sequence in which the isolation and purification of intermediates is not necessary. In this paper we wish to report on the results of these investigations.

The nitrosation of *N*-substituted anilines to *N*-nitrosoanilines and their reduction to hydrazines are well established procedures in organic chemistry for which various nitrosation agents, reduction systems and solvents have been used [8]. To avoid the isolation of the carcinogenic nitroso compounds they are advantageously reduced *in situ* to the corresponding hydrazines [8]. With subsequent transformation to the 3*H*-indolium salts **1** in mind, which should proceed in the same solvent and without any negative interference of the by-products of the nitrosation and reduction step, the *N*-substituted anilines **4** were nitrosated with an aqueous solution of sodium nitrite in glacial acetic acid at room temperature to the *N*-nitroso derivatives **5**. The subsequent reduction with zinc dust was performed in the presence of the α-branched ketones **3**. In this way, the hydrazines **2** formed were immediately trapped by the ketones **3** to give the hydrazones **6** avoiding competition reactions of the sensitive hydrazine species. Then the reaction mixture was refluxed to effect the thermal cyclization of the hydrazones **6** to the 3*H*-indolium derivatives **7**, which is additionally accelerated by the zinc ions formed in the reduction step that are known to be efficient catalysts in Fischer type indolizations [4]. Finally, the introduction of the desired anion A^- of **1** was achieved by a special work up procedure (*cf.* Experimental part).

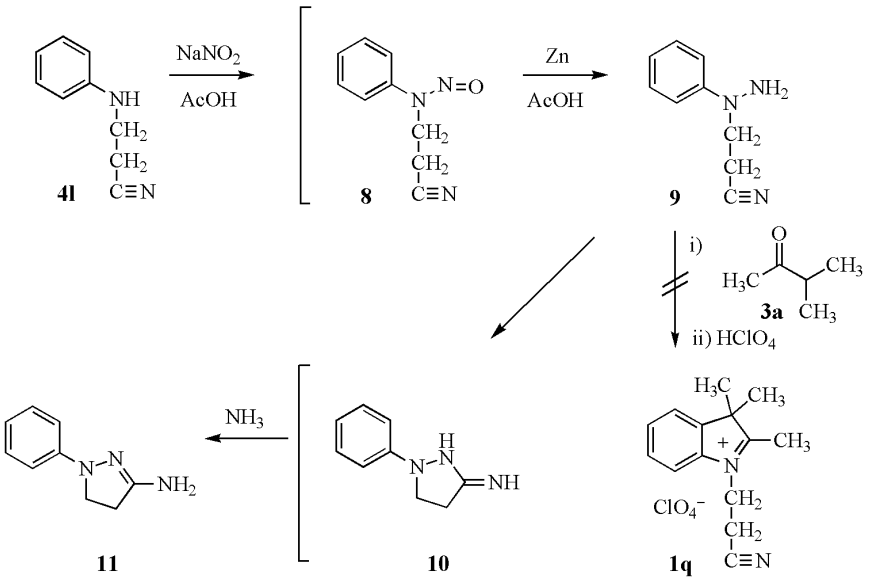
To determine the scope and limitations of this synthesis of 3*H*-indolium salts anilines **4** and ketones **3** with various substituents were tested as starting materials. On reacting

anilines bearing at the nitrogen an alkyl (**4a**-**g**), cycloalkyl (**4h**), aralkyl (**4i**), alkenyl (**4j**) or hydroxyalkyl (**4k**) substituent without (**4a**, **4e**-**k**) or with (**4b**-**d**) an additional group at the benzene ring and 3-methylbutan-2-one (**3a**), the related 3*H*-indolium salts **1a**-**k** were obtained in yields up to 60%. Besides **3a** other α-branched ketones with longer alkyl chains (**3b**-**e**) as well as cycloalkyl derivatives (**3f**) can be used which are performed with *N*-methylaniline (**4a**) to the 3*H*-indolium salts **1l**-**p**. As shown for the example **4a** + **3a** → **1a**/**1a'**/**1a''**, the anion of the salts **1** (**1a**: ClO_4^-, **1a'**: I^-, **1a''**: BF_4^-) can be varied by changing the acid used for the precipitation in the work-up of the reaction mixture.

Surprisingly, then the *N*-cyanoethylaniline (**4l**) was nitrosated and reduced in the presence of 3-methylbutan-2-one (**3a**) 3-amino-1-phenyl-4,5-dihydro-1*H*-pyrazole (**11**) was obtained as the sole product (yield 45%) instead of the expected 3*H*-indolium salt **1q**. In this case the amino group of the hydrazine derivative **9**, intermediately formed *via* **8** by nitrosation/reduction, obviously does not react with the ketone **3a** but attacks the cyano carbon giving rise to the imino derivative **10**, which is stabilized by a proton shift to the aminodihydropyrazole **11**.

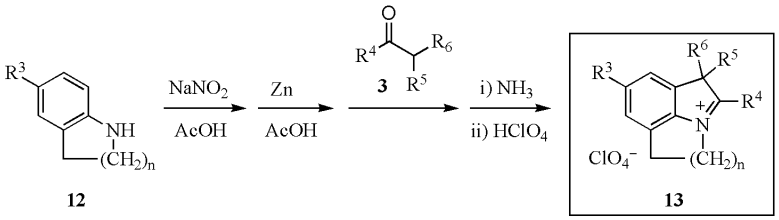
The desired synthesis of indolium salts could be successfully extended to *N*-substituted anilines with a saturated carbon chain connecting the nitrogen with the adjacent carbon atom of the benzene ring. In this way, 4,5,5-trimethyl-2,5-dihydro-1*H*-pyrrolo[3,2,1-*hi*]indolium perchlorate (**13a**), the 1,4,5,6-tetrahydropyrrolo[3,2,1-*ij*]quinolinium perchlorates **13b**-**g** and the 1,1,2-trimethyl-4,5,6,7-tetrahydro-1*H*-azepino[3,2,1-*hi*]indolium perchlorate (**13h**) were obtained from 2,3-dihydroindole (**12a**), the tetrahydroquinolines **12b**,**c** and 2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine (**12d**), respectively, and α-branched ketones bearing alkyl (**3a**-**c**, **3e**) or cycloalkyl (**3f**) substituents in up to 52% yield.

In comparison to our previous reported [7] and to other known methods for the preparation of 3*H*-indolium salts **1** and their fused derivatives **13** the one-pot synthesis described here is more facile and effective. It starts from inexpensive and well accessible materials, it combines four reaction steps (nitrosation, reduction, hydrazone formation, Fischer indolization) to a sequence in which the isolation of intermediates is not necessary and it provides well crystallized and easily separable salts with any desired anion.



Attempts to use *N*,*N*-diphenylamine as aniline component and react it with sodium nitrite, zinc dust and 3-methylbutan-2-one (**3a**) was unsuccessful. Although from the related *N*,*N*-diphenylhydrazine, **3a** and perchloric acid in ethanol the desired 2,3,3-trimethyl-1-phenyl-3*H*-indolium perchlorate was prepared in good yield [7], here no appropriate product was obtained which can be explained by a retarded nitrosation of the electron deficient *N*,*N*-diphenylamine.

The structure and purity of the indolium salts **1**/**13** was proved by elemental analyses, by nmr spectroscopy and in the case of known compounds by comparison of their physical data with those reported in the literature. In the ^1H nmr spectra the signals of the protons of the *N*-bonded carbons appear at relatively low field caused by the positive charged nitrogen. Thus, the singlet of the *N*-CH_3 protons in **1a**-**d** and **1l**-**p** is located at 3.89-4.05 ppm and the triplet of the NCH_2-moiety in **13a**-**h** can be found at 4.27-4.65 ppm.



12	3	n	R^3	R^4	R^5		R^6	13
a	**a**	1	H	Me	Me		Me	**a**
b	**a**	2	H	Me	Me		Me	**b**
c	**a**	2	Me	Me	Me		Me	**c**
b	**b**	2	H	Et	Me		Me	**d**
b	**c**	2	H	n-Pr	Me		Me	**e**
b	**e**	2	H	Me	Me		Et	**f**
b	**f**	2	H	Me		$(CH_2)_5$		**g**
d	**a**	3	H	Me	Me		Me	**h**

By the same reason, the protons of the methyl group connected with the iminium carbon in **1a-k**, **1o**,**p**, **13a-c** and **13f-h** resonate as a singlet at 2.56-2.94 ppm. Because of an asymmetric carbon centre in **1o** and **13f** their methylene hydrogens are diastereotopic by nature and can cause, as may be observed, resonances at different chemical shifts. All other protons present in the salts **1**/**13** show in accordance with the structure signals with the expected chemical shifts and splitting patterns.

EXPERIMENTAL

The melting points were measured on a Boëtius hot stage apparatus. The ^{1}H nmr spectra were recorded on a Varian Gemini 200 spectrometer at 199.975 MHz and on a Varian Gemini 2000 spectrometer at 200.041 MHz in dimethyl-d_6 sulfoxide at 25° with hexamethyl disiloxane as internal standard. The 2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine (**12d**) was prepared according to a literature procedure [9]. The other chemicals were purchased from commercial suppliers (Aldrich: sodium nitrite, glacial acetic acid, **3a**-**e**, **4a**-**e**, **4g**, **4j**-**l**, **12a**; Lancaster: **4f**, **12b**,**c**; Fluka: **3f**, **4h**; Acros: zinc dust, **4i**).

Synthesis of the 3*H*-Indolium Salts **1** and their Fused Analogues **13** from *N*-substituted Anilines **4** and Fused Anilines **12**, respectively, and α-Branched Ketones **3**. General Procedure (*c.f.* Table 1).

To 60 mmoles of the aniline **4**/**12**, dissolved in glacial acetic acid (30 ml), was added dropwise a solution of 4.62 g (66 mmoles) of sodium nitrite in water (10 ml) under magnetic stirring at room temperature in a period of 0.25 hours (slightly exothermic). After stirring for additional 0.5 hours and addition of the ketone **3**/**12** at once, 9.80 g (180 mmoles) zinc dust was added in small portions to avoid a too vigorous reaction. The resulting mixture was refluxed for 0.5 hours, cooled to room temperature and poured into a concentrated solution of ammonia in water (70 ml) under external cooling. The oil formed (anhydrobase of **1**/**13**) was extracted with ether (50 ml), the organic layer was washed with water (30 ml) and added dropwise without being dried to a magnetically stirred solution of 60 mmoles of the acid HA, corresponding to the desired anion A^- (can be used as aqueous solution, *e.g.* 70% $HClO_4$, 57% HI, 50% HBF_4), in 50 ml of ethanol. After addition of ether (50 ml) and cooling, the precipitated salts **1**/**13** were filtered by suction and washed with ether. In many cases the products obtained were pure enough for further manipulations. If necessary, they can be purified by recrystallization from ethanol/acetonitrile.

Isolation of the 3-Amino-1-phenyl-4,5-dihydro-1*H*-pyrazole (**11**).

According to the General procedure given above 9.13 g (60 mmol) *N*-cyanoethylaniline (**4l**) was nitrosated and reduced in the presence of 5.17 g (60 mmole) 3-methylbutan-2-one (**3a**). After pouring the resulting reaction mixture into ammonia/water, a precipitate was formed that was filtered by suction, washed with ethanol, recrystallized from ethanol and identified to be 3-amino-1-phenyl-4,5-dihydro-1*H*-pyrazole (**11**), yield 4.35 g (45%), mp 166-167° (lit. 168-169° [10]). The substance obtained was identical in all respects with an authentic sample [10].

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