A Facile Synthesis of 3*H*-Indolium Perchlorates by One-pot Hydrazone Formation/Fischer Indolization

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N-Substituted *N*-phenylhydrazines **1**, α-branched ketones **2** and perchloric acid react in boiling ethanol to give *via* the *in situ* formed hydrazones **3** 1,2,3,3-tetrasubstituted 3*H*-indolium perchlorates **4**. The scope and limitations of this facile synthesis of 3*H*-indolium derivatives which combines the hydrazone formation and the Fischer indolization to an one-pot procedure are discussed.

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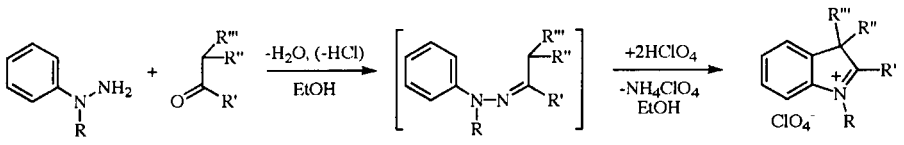
1,3,3-Trisubstituted 2-methyleneindolines (Fischer base and derivatives thereof) are known to be important starting materials for the synthesis of a wide range of polymethine dyes which are not only of academic interest but also find various practical applications ranging from spectral sensitization to laser technology and optical data storage [1]. From the same type of compounds spiroindolines with valuable photochromic properties can be obtained [2]. Since 2-methyleneindolines are usually prepared by deprotonation of the related 3*H*-indolium salts [3] a strong demand for effective syntheses for these salts exists. Until now the most important access to 3*H*-indolium salts consist in the condensation of *N*-arylhydrazines with ketones to *N*-arylhydrazones followed by a Fischer indolization [4] to 1*H*- or 3*H*-indoles. In the final step an alkylation, preferentially carried out with an iodide at high pressure [3,5] or sonochernical activation [6], is necessary. The application of such special reaction techniques can be avoided by condensing *N*-substituted *N*-arylhydrazines, easy available by alkylation of *N*-arylhydrazines under normal conditions [7,8], with ketones to the related arylhydrazones and subsequent Fischer cyclization to 3*H*-indolium salts [3]. Starting from *N,N*-diarylhydrazines 1-aryl-3*H*-indolium derivatives can be obtained in this way [3].

Recently we reported on spiro[cyclohexadiene-indolines] which represent a novel class of photochromic substances [9]. They are prepared in high yield by diastereoselective ring transformation of 2,4,6-triarylpyrylium salts with 2-methyleneindolines used as such or generated *in situ* from the related 3*H*-indolium salts [10]. Hence, a short and effective synthesis of these salts with a high variability of the substituents at the positions 1, 2, and 3 was necessary. Because of its good crystallization properties perchlorate salts were preferred. So the idea arose to react *N*-substituted *N*-phenylhydrazines with suitable ketones in the presence of perchloric acid in an appropriate solvent to the desired 3*H*-indolium perchlorates by an one-pot combination of the well-known hydrazone formation [11] with the Fischer indolization [4]. Although numerous catalysts such as zinc chloride, boron triflouride, aluminium chloride, hydrochloric acid, hydroiodic acid, sulfuric acid, polyphosphoric acid and other Lewis and protic acids have been used to effect Fischer-type cyclizations [4], perchloric acid has been applied only in a few cases for the preparation of 1*H*-indoles [12]. To the best



(·HCl) Hydrazone Formation Fischer Indolization

1 **2** **3** **4**

1	2	R	R'	R''		R'''	4
a	**a**	Me	Me	Me		Me	**a**
a	**b**	Me	Me	Me		Et	**b**
a	**c**	Me	Me	Me		CH_2Ph	**c**
a	**d**	Me	Me	Me		Ph	**d**
a	**e**	Me	Me	Et		Ph	**e**
a	**f**	Me	Me	n-Pr		Ph	**f**
a	**g**	Me	Me		$(CH_2)_5$		**g**
a	**h**	Me	Me		$CH_2C_6H_4(o)CH_2$		**h**
a	**i**	Me	Et	Me		Me	**i**
a	**j**	Me	*n*-Pr	Me		Me	**j**
a	**k**	Me	*i*-Pr	Me		Me	**k**
a	**l**	Me	Ph	Me		Me	**l**
a	**m**	Me	4-Me-C_6H_4	Me		Me	**m**
a	**n**	Me	4-Et-C_6H_4	Me		Me	**n**

1	2	R	R'	R''	R'''	4
a	**o**	Me	4-*tert*-Bu-C_6H_4	Me	Me	**o**
a	**p**	Me	4-Ph-C_6H_4	Me	Me	**p**
a	**q**	Me	4-MeO-C_6H_4	Me	Me	**q**
a	**r**	Me	4-F-C_6H_4	Me	Me	**r**
a	**s**	Me	4-Cl-C_6H_4	Me	Me	**s**
a	**t**	Me	4-Br-C_6H_4	Me	Me	**t**
b	**b**	Et	Me	Me	Et	**u**
b	**c**	Et	Me	Me	CH_2Ph	**v**
b	**d**	Et	Me	Me	Ph	**w**
c	**b**	*i*-Pr	Me	Me	Et	**x**
c	**c**	*i*-Pr	Me	Me	CH_2Ph	**y**
c	**d**	*i*-Pr	Me	Me	Ph	**z**
d	**a**	Ph	Me	Me	Me	**aa**
d	**l**	Ph	Ph	Me	Me	**bb**

Table I

Physical, Analytical and Spectral Data for the 3*H*-Indolium Perchlorates **4**

No.	3*H*-indolium perchlorate	Yield (%)	Mp [a] (°C)	Molecular Formula (Molecular Weight)	Analysis (%) Calcd./Found C	H	N	^{1}H-NMR (dimethyl-d_6 sulfoxide) δ (ppm)
4a	1,2,3,3-Tetramethyl-	83	201-202 (198 [24])	$C_{12}H_{16}ClNO_4$ (273.7)	52.66 52.63	5.89 5.96	5.12 5.26	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)
4b	3-Ethyl-1,2,3-trimethyl-	83	230-231	$C_{13}H_{18}ClNO_4$ (287.7)	54.26 54.18	6.31 6.39	4.87 4.95	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)
4c	3-Benzyl-1,2,3-trimethyl-	67	154-155	$C_{18}H_{20}ClNO_4$ (349.8)	61.80 61.93	5.76 5.84	4.00 4.18	1.60 (s, 3H, 3-CH_3), 2.88 (s, 3H, 2-CH_3), 3.37 (d, J = 13.5 Hz, 1H, 3-CH_2Ph), 3.46 (d, J = 13.5 Hz, 1H, 3-CH_2Ph), 3.77 (s, 3H, 1-CH_3), 6.68-7.67 (m, 9H, arom-H)
4d	1,2,3-Trimethyl-3-phenyl-	52	233-234	$C_{17}H_{18}ClNO_4$ (335.8)	60.81 60.93	5.40 5.48	4.17 4.20	1.90 (s, 3H, 3-CH_3), 2.59 (s, 3H, 2-CH_3), 4.04 (s, 3 H, 1-CH_3), 7.17-7.97 (m, 9H, arom-H)
4e	1,2-Dimethyl-3-ethyl-3-phenyl-	47	155-156	$C_{18}H_{20}ClNO_4$ (349.8)	61.80 61.89	5.76 5.84	4.00 4.10	0.45 (t, 3H, 3-CH_2CH_3), 2.49-2.80 (m, 2H, 3-CH_2CH_3), 2.65 (s, 3H, 2-CH_3), 4.10 (s, 3H, 1-CH_3), 7.17-8.01 (m, 9H, arom-H)
4f	1,2-Dimethyl-3-phenyl-3-propyl-	38	145-146	$C_{19}H_{22}ClNO_4$ (363.8)	62.72 62.80	6.09 6.14	3.85 3.92	0.52-0.91 (m, 2H, 3-$CH_2CH_2CH_3$), 0.78 (t, 3H, 3-$CH_2CH_2CH_3$), 2.39-2.72 (m, 2H, 3-$CH_2CH_2CH_3$), 2.65 (s, 3H, 2-CH_3), 4.08 (s, 3H, 1-CH_3), 7.16-8.00 (m, 9H, arom-H)
4g	1',2'-Dimethyl-spiro-[cyclohexane-1,3'-]	83	248-249	$C_{15}H_{20}ClNO_4$ (313.8)	57.42 57.38	6.42 6.50	4.46 4.53	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)
4h	1',2'-Dimethyl-spiro-[indan-2,3'-]	88	220-221	$C_{18}H_{18}ClNO_4$ (347.8)	62.16 62.26	5.22 5.29	4.03 3.99	2.54 (s, 3H, 2'-CH_3), 3.35 (d, J = 16.5 Hz, 2H, 3',3'-$(CH_2)_2C_6H_4$), 3.56 (d, J = 16.5 Hz, 2H, 3',3'-$(CH_2)_2C_6H_4$), 3.93 (s, 3H, 1'-CH_3), 7.24-7.89 (m, 8H, arom-H)
4i	2-Ethyl-1,3,3-trimethyl-	44	177-178	$C_{13}H_{18}ClNO_4$ (287.7)	54.26 54.30	6.31 6.38	4.87 4.91	1.25 (t, 3H, 2-CH_2CH_3), 1.51 (s, 3H, 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)
4j	1,3,3-Trimethyl-2-propyl-	57	139-140	$C_{14}H_{20}ClNO_4$ (301.8)	55.72 55.80	6.68 6.73	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)
4k	2-Isopropyl-1,3,3-trimethyl-	19	196-197	$C_{14}H_{20}ClNO_4$ (301.8)	55.72 55.80	6.68 6.72	4.64 4.71	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)
4l	1,3,3-Trimethyl-2-phenyl-	54	199-200	$C_{17}H_{18}ClNO_4$ (335.8)	60.81 60.91	5.40 5.46	4.17 4.20	1.52 (s, 6H, 3-CH_3), 3.83 (s, 3H, 1-CH_3), 7.63-8.04 (m, 9H, arom-H)
4m	1,3,3-Trimethyl-2-(4-methylphenyl)-	48	200-201	$C_{18}H_{20}ClNO_4$ (349.8)	61.80 61.91	5.76 5.83	4.00 3.95	1.52 (s, 6H, 3-CH_3), 2.40 (s, 3H, 2-$C_6H_4CH_3$), 3.85 (s, 3H, 1-CH_3), 7.49-8.01 (m, 8H, arom-H)
4n	2-(4-Ethylphenyl)-1,3,3-trimethyl-	40	178-179	$C_{19}H_{22}ClNO_4$ (363.8)	62.72 62.79	6.09 6.19	3.85 3.92	1.20 (t, 3H, 2-$C_6H_4CH_2CH_3$), 1.53 (s, 6H, 3-CH_3), 2.71 (q, 2H, 2-$C_6H_4CH_2CH_3$), 3.85 (s, 3H, 1-CH_3), 7.53-8.01 (m, 8H, arom-H)
4o	2-(4-*tert*-Butylphenyl)-1,3,3-trimethyl-	37	201-202	$C_{21}H_{26}ClNO_4$ (391.9)	76.92 77.01	7.99 8.00	4.27 4.32	1.31 (s, 9H, 2-$C_6H_4C(CH_3)_3$), 1.53 (s, 6H, 3-CH_3), 3.85 (s, 3H, 1-CH_3), 7.63-8.02 (m, 8H, arom-H)
4p	2-(Biphenyl-4-yl)-1,3,3-trimethyl-	61	234-235	$C_{23}H_{22}ClNO_4$ (411.9)	67.07 67.15	5.38 5.26	3.40 3.34	1.58 (s, 6H, 3-CH_3), 3.91 (s, 3H, 1-CH_3), 7.38-8.06 (m, 13H, arom-H)
4q	2-(4-Methoxyphenyl)-1,3,3-trimethyl-	49	207-208	$C_{18}H_{20}ClNO_5$ (365.8)	59.10 59.16	5.51 5.60	3.83 3.90	1.54 (s, 6H, 3-CH_3), 3.86 (s, 3H, 2-$C_6H_4OCH_3$), 3.89 (s, 3H, 1-CH_3), 7.23-7.98 (m, 8H, arom-H)
4r	2-(4-Fluorophenyl)-1,3,3-trimethyl-	37	144-145 170-171 [b]	$C_{17}H_{17}ClFNO_4$ (353.8)	57.72 57.80	4.84 4.91	4.52 4.60	1.53 (s, 6H, 3-CH_3), 3.85 (s, 3H, 1-CH_3), 7.53-8.04 (m, 8H, arom-H)
4s	2-(4-Chlorophenyl)-1,3,3-trimethyl-	48	218-219	$C_{17}H_{17}Cl_2NO_4$ (370.2)	55.15 55.20	4.63 4.70	3.78 3.82	1.52 (s, 6H, 3-CH_3), 3.84 (s, 3H, 1-CH_3), 7.65-8.05 (m, 8H, arom-H)
4t	2-(4-Bromophenyl)-1,3,3-trimethyl-	42	223-224	$C_{17}H_7BrClNO_4$ (414.7)	49.24 49.10	4.13 4.20	3.38 3.47	1.52 (s, 6H, 3-CH_3), 3.85 (s, 3H, 1-CH_3), 7.64-8.04 (m, 8H, arom-H)
4u	1,3-Diethyl-2,3-dimethyl-	65	172-173 (123-125 [25])	$C_{14}H_{20}ClNO_4$ (301.8)	55.72 55.80	6.68 6.73	4.64 4.70	0.29 (t, 3H, 3-CH_2CH_3), 1.40 (t, 3H, 1-CH_2CH_3), 1.50 (s, 3H, 3-CH_3), 1.95-2.28 (m, 2H, 3-CH_2CH_3), 2.81 (s, 3H, 2-CH_3), 4.49 (q, 3H, 1-CH_2CH_3), 7.58-7.97 (m, 4H, arom-H)
4v	3-Benzyl-1-ethyl-2,3-dimethyl-	66	158-159	$C_{19}H_{22}ClNO_4$ (363.8)	62.72 62.80	6.09 6.00	3.85 3.79	0.82 (t, 3H, 1-CH_2CH_3), 1.64 (s, 3H, 3-CH_3), 2.90 (s, 3H, 2-CH_3), 3.51 (s, 2H, 3-CH_2Ph), 4.22 (q, 2H, 1-CH_2CH_3), 6.56-7.92 (m, 9H, arom-H)

Table I (continued)

No.	3*H*-indolium perchlorate	Yield (%)	Mp [a] (°C)	Molecular Formula (Molecular Weight)	Analysis (%) Calcd./Found C	H	N	^{1}H-NMR (dimethyl-d$_6$ sulfoxide) δ (ppm)
4w	1-Ethyl-2,3-dimethyl-3-phenyl-	31	164-165	$C_{18}H_{20}ClNO_4$ (349.8)	61.80 61.83	5.76 5.82	4.00 4.03	1.49 (t, 3H, 1-CH_2CH_3), 1.92 (s, 3H, 3-CH_3), 2.66 (s, 3H, 2-CH_3), 4.57 (q, 2H, 1-CH_2CH_3), 7.13-8.05 (m, 9H, arom-H)
4x	3-Ethyl-1-isopropyl-2,3-dimethyl-	49	173-174	$C_{15}H_{22}ClNO_4$ (315.8)	57.05 57.11	7.02 7.08	4.44 4.51	0.26 (t, 3H, 3-CH_2CH_3), 1.51 (s, 3H, 3-CH_3), 1.65 (d, 3H, 1-$CH(CH_3)_2$), 1.68 (d, 3H, 1-$CH(CH_3)_2$), 2.14 (m, 2H, 3-CH_2CH_3), 2.85 (s, 3H, 2-CH_3), 5.13 (m, 1H, 1-$CH(CH_3)_2$), 7.55-8.11 (m, 4H, arom-H)
4y	3-Benzyl-1-isopropyl-2,3-dimethyl-	68	220-221	$C_{20}H_{24}ClNO_4$ (377.9)	63.57 63.48	6.40 6.34	3.71 3.69	1.04 (d, 3H, 1-$CH(CH_3)_2$), 1.47 (d, 3H, 1-$CH(CH_3)_2$), 1.69 (s, 3H, 3-CH_3), 2.96 (s, 3H, 2-CH_3), 3.52 (s, 2H, 3-CH_2Ph), 4.87 (m, 1H, 1-$CH(CH_3)_2$), 6.51-7.97 (m, 9H, arom-H)
4z	1-Isopropyl-2,3-dimethyl-3-phenyl-	43	152-153	$C_{19}H_{22}ClNO_4$ (363.8)	62.72 62.80	6.09 6.11	3.85 3.89	1.74 (d, 3H, 1-$CH(CH_3)_2$), 1.75 (d, 3H, 1-$CH(CH_3)_2$), 1.94 (s, 3H, 3-CH_3), 2.70 (s, 3H, 2-CH_3), 5.16 (m, 1H, 1-$CH(CH_3)_2$), 7.10-8.20 (m, 9H, arom-H)
4aa	2,3,3-Trimethyl-1-phenyl-	39	200-201 (194-196) [26])	$C_{17}H_{18}ClNO_4$ (335.8)	60.81 60.89	5.40 5.49	4.17 4.23	1.68 (s, 6H, 3-CH_3), 2.62 (s, 3H, 2-CH_3), 7.06-7.90 (m, 9H, arom-H)
4bb	3,3-Dimethyl- 1,2-diphenyl-	31	201-202 (209 [27])	$C_{22}H_{20}ClNO_4$ (397.9)	66.42 66.49	5.07 5.15	3.52 3.58	1.75 (s, 6H, 3-CH_3), 7.25-8.03 (m, 14H, arom-H)

[a] The melting points reported in the literature are given in parentheses. [b] Double melting point.

of our knowledge the envisaged one-pot synthesis of 3*H*-indoliurn perchlorates from *N*-substituted *N*-phenylhydrazines, α-branched ketones and perchloric acid, on the scope and limitations of which we want to report in this paper, has never been described.

The investigations were started with the *N*-methyl substituted *N*-phenylhydrazine **1a**. When **1a** was refluxed with the methyl ketones **2a-f** (R' = Me) bearing two alkyl groups (**2a,b**), an alkyl and an aralkyl substituent (**2c**) or an alkyl and an aryl residue (**2d-f**) at the α-carbon in ethanol in the presence of two equivalents of perchloric acid (70% in water) the 3*H*-indolium perchlorates **4a-f** were formed in good yields via *in situ* formed *N*-methyl-*N*-phenylhydrazones of the type **3**.

On using the cyclohexyl methyl ketone **2g** or the indan-2-yl methyl ketone **2h** the 3*H*-indolium salts **4g,h** possessing a spiro condensed carbocycle at C-3 were obtained. The related cyclizations with cyclopropyl methyl ketone or cyclobutyl methyl ketone failed. Obviously, the small ring ketones are not stable enough under the reaction conditions applied or the hydrazone-enehydrazine interconversion usually occurring in the course of the Fischer indolization [4] is sterically hindered in small ring ketone hydrazones.

With the alkyl isopropyl ketones **2i-k** the related 3*H*-indolium perchlorates **4i-k** were smoothly formed. The same is true for the aryl isopropyl ketones **2l-t** which give rise to the salts **4l-t** with an aryl substituent at C-2 and two methyl groups at C-3.

When the *N*-alkyl substituted *N*-phenylhydrazines **1b,c** (R = Et, i-Pr) were treated with the same type of ketones as in the case of **1a** and two equivalents of perchloric acid in ethanol the 3*H*-indolium perchlorates **4u-z** with these substituents at the nitrogen were obtained.

Finally, the *N,N*-diphenylhydrazine **1d**, used as hydrochloride, reacted with isopropyl methyl ketone (**2a**) or isopropyl phenyl ketone (**2l**) and one equivalent of perchloric acid to give the 1-phenyl-3*H*-indolium perchlorates **4aa,bb.**

Although in some cases the yields of 3*H*-indolium salts **4** were only moderate, the one-pot synthesis from *N*-substituted *N*-phenylhydrazines **1**, α-branched ketones **2** and perchloric acid described is of high practical significance, since it is facile, *i.e.* it works without high pressure or sonochemical activation, and the products precipitate from the reaction mixtures as crystalls and hence are well separable solids which contain practically no impurities.

The structure of the 3*H*-indolium perchlorates **4** 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 ^{1}H nmr spectra the nitrogen bonded methyl group of **4a-t** give the expected singlet at 3.77-4.11 ppm. The same type of signal observed in the spectra of **4a-h** and **4u-aa** at 2.54-2.96 ppm can be attributed to the 2-positoned CH_3-group, whereas the methyl group at C-3 of **4a-d** and **4i-bb** resonates at 1.46-1.94 ppm as a singlet. The protons of the benzene ring of the 3*H*-indolium cation and those of the aryl substituent present in **4c-f, 4h, 4l-t, 4v,w** and **4y-bb** are responsible for the multiplett at 6.51-8.20 ppm.

Symmetry considerations show that the 3*H*-indolium perchlorates **4b-f and 4u-z** are chiral compounds with an asymmetric carbon atom at C-3. Hence, the methylene protons of

the ethyl, *n*-propyl, and benzyl groups of **4b,c, 4e,f, 4u,v,** and **4x,y** and the methyl protons of the isopropyl group of **4x-z** are diastereotopic by nature [13] and can resonate, as observed, at different chemical shifts. Although the spiro-condensed 3*H*-indolium perchlorate **4h** is achiral, *i.e.* no asymmetric carbon atom is present, the CH_2-protons of the indan-2-yl moiety are also diastereotopic and give two signals splitt into doublets by coupling since an imagined mirror plane between the methylene protons is not the mirror plane of the entire molecule [13].

EXPERIMENTAL

The melting points were measured on a Boëtius hot stage apparatus. The ^1H 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 hydrazines **1b,c** [8] and the ketones **2c** [14], **2d** [15], **2e,f** [16], **2h** [17], **2m,q** [18], **2n** [19], **2o,s** [20], **2p** [21], **2r** [22], **2t** [23] were prepared according to literature procedures. All other ketones with exception of **2g** (Fluka), the hydrazine **1a** and the hydrazine hydrochloride **1d**·HCl were purchased from Aldrich.

Synthesis of 3*H*-Indolium Perchlorates **4** from *N*-Substituted *N*-Phenylhydrazines **1**, α-Branched Ketones **2** and Perchloric Acid. General Procedure (*cf.* Table 1).

To ethanol (20 ml) 20 mmoles of the hydrazine **1** (in the case of **1d** the appropriate hydrochloride), 20 mmoles of the ketone 2 and perchloric acid (70% in water, 5.74 g = 40 mmoles for the free hydrazine or 2.37 g = 20 mmoles for the hydrazine hydrochloride) were added under magnetic stirring at room temperature. The resulting reaction mixture was then refluxed with continous stirring for 2 hours. The 3*H*-indolium perchlorates **4** that formed, crystallized from hot solutions in some cases whereas crystallization was initiated by cooling in other cases. They were filtered by suction, washed with ethanol, water (to remove the ammonium perchlorate obtained as by-product), again with ethanol and finally with ether. A nmr analysis showed that the crude products are nearly pure. A purification can be achieved, if necessary, by dissolving the product in a minimal amount of hot acetonitrile and subsequent precipitation with ether.

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