

## Regioselective, Mild Acylation of 2-Methylindole with Di- and Trialkoxycarbenium Tetrafluoroborates—A Simple Procedure for Deriving 3-Acyl-2-methyl-indoles and 3-Methoxycarbonyl-2-methylindole

### Reactions of Electron-rich Heterocycles with Derivatives of Carboxylic Ortho Acids, VII<sup>1</sup>.

Ulf Pindur\* and Camran Flo

Institut für Pharmazie und Lebensmittelchemie, Universität Würzburg,  
D-8700 Würzburg, Bundesrepublik Deutschland

(Received 21 March 1985. Accepted 23 April 1985)

The regioselective acylation of 2-methylindole (**2**) with acyclic di- and trialkoxycarbenium tetrafluoroborates **1** produces, by way of the stable indolyl-alkoxycarbenium ions **4**, the 3-acylated indoles **5a–5c**, and the 3-methoxycarbonylindole **5d**. The ambident electrophilic cations **1** all react as a<sup>1</sup>-electrophiles with the very nucleophilic indole **2**. In the reaction of **2** with trimethoxycarbenium tetrafluoroborate (**2d**) methylated products are formed additionally.

(Keywords: 3-Acylated 2-methylindoles; Synthesis with di- and trialkoxycarbenium tetrafluoroborates)

*Reaktionen von elektronenreichen Heterocyclen mit Orthocarbonsäure-Derivaten, VII<sup>1</sup>. Regioselective milde Acylierung von 2-Methylindol mit Di- und Trialkoxycarbenium-tetrafluoroboraten — ein einfacher Zugang zu 3-Acyl-2-methylindolen und 3-Methoxycarbonyl-2-methylindol*

Die regioselective Acylierung von 2-Methylindol (**2**) mit acyclischen Di- und Trialkoxycarbenium-tetrafluoroboraten **1** liefert über die stabilen Indolyl-alkoxycarbenium-Ionen **4** die 3-acylierten Indole **5a–5c** und das 3-Methoxycarbonylindol **5d**. Die ambidenten elektrophilen Kationen **1** reagieren gegenüber dem gut nukleophilen Indol **2** bevorzugt als a<sup>1</sup>-Elektrophil. In der Reaktion von **2** mit dem Trimethoxycarbenium-tetrafluoroborat **1d** werden zusätzlich auch methylierte Produkte gebildet.

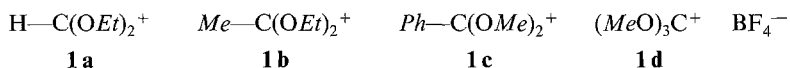
\* New Address: Fachbereich Pharmazie, Johannes-Gutenberg-Universität, Saarstrasse 21, D-6500 Mainz, BRD.

### Introduction

Regioselective acylations at the indole nucleus continue to occupy a central position in building-block chemistry concerned with constructing indole alkaloids and pharmacologically active compounds<sup>2-4</sup>. After a critical perusal of the literature it still appears to be well worth undertaking a search for new, regioselective and mild electrophilic acylation procedures. As part of our studies related to functionalizing the indole nucleus with  $S_N1$ -active ortho esters we now report on the reaction paths and on the synthetic potential of the ambident alkoxy-carbenium tetrafluoroborates **1**<sup>5</sup> in connection with the model substance 2-methylindole (**2**). So far we have studied the behaviour of these cations in reaction with indoles only under *in situ* conditions<sup>6-9</sup>. This allowed us to trace reaction paths of indoles and ortho esters, with proton catalysis. Thus an investigation of the true reactivity of the cations which are employed as tetrafluoroborates remains to be carried out and also an analysis of the acylation potential. Only in one case have alkoxy-carbenium ion reactions with the basic indole compound and 1,3-dioxolanium salts been described<sup>10</sup>.

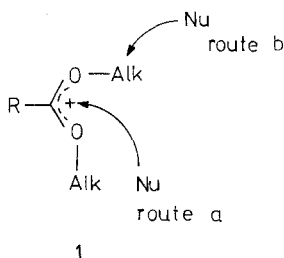
### Results and Discussion

The dialkoxy-carbenium ions **1 a**, **1 b**, **1 c** and the trimethoxy-carbenium ion **1 d** were derived as stable tetrafluoroborates from the corresponding ortho esters by means of cleavage using  $\text{HBF}_4$ -etherate. This derivation method, which originally goes back to *H. Meerwein*<sup>10</sup>, has been modified somewhat by us, giving an almost quantitative yield of the cations **1**<sup>12,13</sup>.



The ambident electrophilic reactivity of the alkoxy-carbenium ions **1** can, in principle, be derived by means of two characteristic reaction paths<sup>5</sup>. The reaction of relatively hard or very strong nucleophiles is normally kinetically controlled and involves addition on the carbenium nucleus of **1** (route a). Soft and neutral nucleophiles generally react with cations **1** in a thermodynamically controlled way, peripherally and  $S_N2$ -like and are, as a result, alkylated (route b). The predominance of these two reaction paths is also determined by the thermodynamic stability of the ambident cationic system<sup>5</sup>. The present paper clarifies the route taken by the highly nucleophilic substance **2** in the reaction with **1**. Since the electrophiles in the series **1 a**–**1 d** exhibit increasing thermodynamic stability<sup>14</sup>, important competitive reaction paths should be expected particularly in the case of the highly stabilized cation **1 d**.

Under kinetically controlled conditions the cations **1a**, **1b** and **1c** react as a<sup>1</sup>-C-synthons with **2** almost quantitatively (route a). This result corresponds, as far as the first step is concerned, with our first

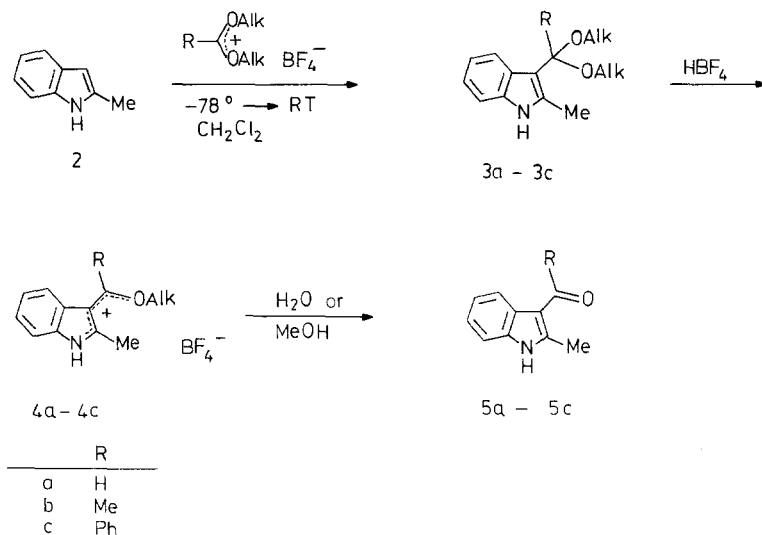


investigations, in which the corresponding ortho esters were introduced as electrophilic reaction partners for indoles with proton catalysis (*in situ* acylation). In the reaction presented here, however, the eminently controllable conditions of the reaction enable a smooth 1:1 molar conversion of **1a**, **1b** and **1c** with **2** to be achieved, which is not always possible under *in situ* conditions<sup>6</sup>. The 1:1 molar reaction sequence of the acylation can now be formulated as follows. The first step (Scheme 1) sees the formulation of the indolylacetals **3**, which, in the absence of a base to accept protons, spontaneously split, protons being liberated from the  $\sigma$ -complex, to form the resonance stabilized 3-indolylalkoxycarbenium ions **4a**, **4b** and **4c** (vinylogous alkoxy-amino-carbenium ions). The cations **4b** and **4c** are highly stable<sup>8,9</sup>. Thus they can be isolated and exhibit almost no further significant carbenium ion reactivity. The cation **4a**, on the other hand, cannot be derived in pure form in this way, because in the process of isolation it tends to split, forming the indole-3-carbaldehyde **5a**. However, the unsymmetrical polymethine cations **4a**, **4b** and **4c** can all be peripherally dealkylated under mild conditions with any good nucleophilic solvent, with almost quantitative yields. In this way a sufficient yield of the 3-acylindoles **5a–5c** can be derived (crude yield: 70–98%; pure yield 41–65%).

These results demonstrate that the ambident cations **1a–1c** can be successfully employed as powerful acylation equivalents in order to acylate reactive indoles. The thoroughly established a<sup>1</sup>-reactivity of these cations is clearly the only possible reaction path (route a), as our investigations have shown. Although the alkylation potential (route b) of these ambident electrophiles is well known<sup>13,15–18</sup>, we were unable to detect the presence of any alkylated product using the sensitive DC control during the reaction of **1a**, **1b** and **1c** with **2** under thermodynamic reaction control (room temperature, 12 hours or elevated temperature in the solvent nitromethane).

The results of a proton-catalysed reaction of the trimethyl orthocarbonate with 3-unsubstituted indoles presented in paper<sup>6</sup> showed that the cation **1 d**, produced *in situ*, fails to enter a C—C-bond formation,

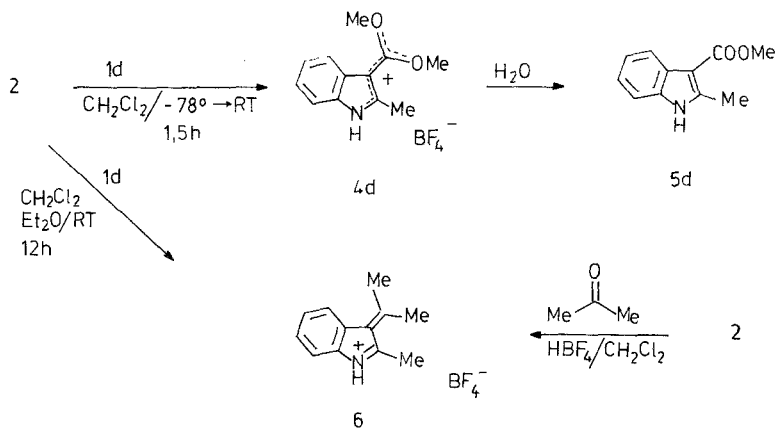
Scheme 1



even with reactive indoles. The reason is that in the proton acidic medium indole protonization and dimerization take place quicker than a reaction with the *in situ*-generated cation **1 d**. Thus, in order to enable us to find out the “true” reactivity of **1 d** and to analyse the reaction path (route a and/or route b), we now offered the tetrafluoroborate **1 d** as a salt to the indole **2** for the reaction. The result (Scheme 2), analogous to the reaction with **1 a–1 c**, was that the cation **1 d**, as an  $a^1$ -reagent in the reaction with **2** was converted into the 3-indolyl-dimethoxycarbenium tetrafluoroborate **4 d** under kinetic reaction control. This compound is extremely sensitive against nucleophiles, because dealkylation proceeds quickly to methyl-ester **5 d** by working up. However, the crude yield of **4 d** or **5 d** (30%) unequivocally suggests that the cation **1 d**, an optimally stabilized (relatively hard) “Y-aromatic” compound<sup>19</sup>, undergoes a significant loss of  $a^1$ -reactivity, compared to **1 a–1 c**, as a result of a ground state effect.

After 12 hours at room temperature the reaction of **2** with **1 d** yields another side-product, 3-indoleninium tetrafluoroborate **6** (9% yield). The constitution of this compound was proved by an independent synthesis via condensation of **2** with acetone in dichloromethane/HBF<sub>4</sub>, a variation of an already known reaction<sup>20</sup>. The mechanism of the formation of **6** is still unknown, but we think that **1 d** should play an important role as

Scheme 2



methylating reagent (route b) in the reaction with intermediate indole derivatives. Nevertheless, the reaction of **2** with **1d** gave under severe conditions of thermodynamic reaction control (5 hours,  $100^\circ\text{C}$ , nitromethane), besides **4d**, small amounts of the alkylation product 2,3-dimethylindole, which could be identified by tlc. These results reflect the ambident reactivity (route a, b) of this type of highly stabilized cation **1d**<sup>5</sup>. The course of the reaction is sensitively controlled by the reaction conditions (kinetic or thermodynamic control).

For the present it must be conceded that no great success has been achieved from the synthetic point of view, concerning the yields of **4d** and the methyl ester **5d**. Nevertheless, a study of the literature relating to indole carboxylic acid derivatives would suggest that this conversion procedure, which can also be carried out as a one pot reaction, may be of synthetic interest if refinements were successful. The advantage of this method lies undoubtedly in the fact that the reaction is simple and highly regioselective as compared to procedures familiar from the literature, which usually involve several steps<sup>21</sup>.

We are at present studying the possibility of applying the acylation method discussed here to other indole compounds and other (activated) hetarenes, using 1,3-dioxolane-type cyclic alkoxy-carbenium ions<sup>22</sup> as well.

### Experimental

All melting points are uncorrected. Spectra were recorded on the following instruments: Jeol JNMC 60 HL ( $^1\text{H}$ -NMR); Bruker WM 400 (400 MHz,  $^1\text{H}$ -NMR); Beckman IR 4240 [IR (KBr)-spectra]; LKB Producter 2091 (mass spectra by 70 eV). Elemental analyses were performed on a Carlo-Erba 1106 C,H,N-analyzer.

*Dialkoxycarbenium tetrafluoroborates (1a–1c) and trimethoxycarbenium tetrafluoroborate (1d) (general method, modified from Lit.<sup>11,12</sup>)*

In a special oxonium frit (s. Fig. 1)<sup>12</sup>, 25 mmol ortho ester were placed in anhydrous diethyl ether, cooled to  $-78^{\circ}\text{C}$  in a nitrogen atmosphere. Then, 70 mmol  $\text{HBF}_4$ -etherate (54% solution of  $\text{HBF}_4$  in diethylether) was added with stirring. After the  $\text{HBF}_4$ -etherate addition was completed, a white precipitate was formed. The cooling bath was removed and the stirring continued about 5 min. The precipitate was filtered, washed several times with anhydrous diethyl ether and dried in vacuum. All operations were done in a nitrogen atmosphere.

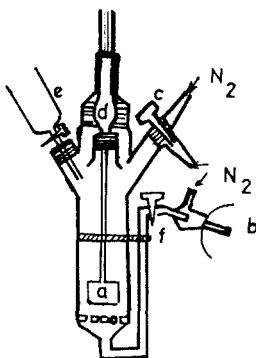


Fig. 1. Special oxonium frit for synthesis of di- and trialkoxycarbenium ions; a: stirring whisk; b: flask; c: T-valve; d:  $\text{CaCl}_2$ -flask; e: dropping-tube; f: clip

*Diethoxycarbenium tetrafluoroborate (1a)*

Yield: 87%; salt decomposes and is very hygroscopic; m.p.:  $20^{\circ}\text{11}$ .

*Diethoxymethylcarbenium tetrafluoroborate (1b)*

Yield: 94%; hygroscopic; m.p.:  $55^{\circ}$ .  $^1\text{H-NMR}$  ( $\text{CD}_3\text{NO}_2$ ):  $\delta = 1.25\text{--}1.80$  (t, 6 H,  $J = 7.3$  Hz,  $\text{CH}_3\text{--CH}_2\text{O}$ ), 2.76 (s, 3 H,  $\text{C}^+\text{--CH}_3$ ), 4.65–5.25 (q, 4 H,  $J = 7.3$  Hz,  $\text{CH}_3\text{--CH}_2\text{--O}$ ).

*Diethoxyphenylcarbenium tetrafluoroborate (1c)*

Yield: 86%; salt decomposes and is very hygroscopic; m.p.:  $88\text{--}90^{\circ}\text{11}$ .

*Trimethoxycarbenium tetrafluoroborate (1d)*

Yield: 93%; less hygroscopic; m.p.:  $138^{\circ}\text{11}$ .  $^1\text{H-NMR}$  ( $\text{CD}_3\text{NO}_2$ ):  $\delta = 4.45$  (s, 9 H,  $\text{CH}_3$ ).

*Acylation of 2-methylindole (2) with 1a–1c and methoxycarbonylation with 1d (general method)*

25 mmol alkoxycarbenium tetrafluoroborate **1a–1d** were added to 10 ml dichloromethane and cooled to  $-78^{\circ}$  in a nitrogen atmosphere. Then 2.62 g

(20 mmol) 2-methylindole (**2**), in 20 ml dichloromethane were added slowly under stirring. The mixture was stirred 1/2 h by  $-78^{\circ}$  and then 1 h by room temperature. In the reaction with **1b** and **1c** the alkoxy-(2-methylindol-3-yl)-carbenium tetrafluoroborates **4b** and **4c** precipitated immediately. In the case of the reaction with **1a** and **1d**, dealkylation of the corresponding cations **4a** and **4d** proceeded very fast in the mixture and by working up.

#### 2-Methylindole-3-carbaldehyde (**5a**)

To the reaction mixture of **2** with **1a** methanol was added under stirring. After 10 min the organic layer was extracted two times with a diluted (watery) solution of sodium hydroxide and then washed with water. The organic layer was separated and concentrated under reduced pressure. To the resulting solution *n*-hexane was added and a white precipitate of **5a** was formed. Crude yield: 98%; pure yield: 49%; m.p.:  $192^{\circ}$  (*n*-hexane/ethanol).  $^1\text{H-NMR}$  (acetone- $d_6$ ):  $\delta$  = 2.72 (s, 3 H,  $\text{CH}_3$ ), 7.25–8.20 (m, 4 H, H-aromat.), 9.95 (s, 1 H, CHO), 10.65 (s, 1 H, NH). IR (KBr): 3 230 (NH), 1 630 (C=O)  $\text{cm}^{-1}$ . MS ( $m/e$ ): 159 ( $M^+$ , 18), 158 (21), 130 (41), 39 (100).

$\text{C}_{10}\text{H}_9\text{NO}$  (159.19).      Calc. C 75.45 H 5.69 N 8.80.  
Found. C 75.47 H 5.66 N 8.67.

#### Ethoxy-methyl-(2-methylindole-3-yl)-carbenium tetrafluoroborate (**4b**) and 3-Acetyl-2-methylindole (**5b**)

In the reaction of **2** with **1b** the cation **4b** precipitated in the mixture. The crystals were collected and washed three times with 20 ml dichloromethane and dried in vacuum.

**4b**: Yield 95%; m.p.:  $138\text{--}140^{\circ}$ .  $^1\text{H-NMR}$  ( $\text{CD}_3\text{NO}_2$ ):  $\delta$  = 1.67 a. 1.73 (2 t, 3 H,  $J$  = 7.3 Hz,  $\text{CH}_3\text{—CH}_2\text{—O}$ ), 2.81 a. 3.03 (2 s, 3 H,  $\text{C}^+\text{—CH}_3$ ), 2.92 a. 2.93 (2 s, 3 H, indole- $\text{CH}_3$ ), 4.85 a. 4.88 (2 q, 2 H,  $J$  = 7.3 Hz,  $\text{CH}_3\text{—CH}_2\text{—O}$ ), 7.27–8.11 (m, 4 H, H-aromat.), 11.2 (s, 1 H, NH); 2 stable conformations. IR (KBr): 3 260–2 500 (NH-assoc.), 1 150–950 ( $\text{BF}_4^-$ )  $\text{cm}^{-1}$ . MS ( $m/e$ ): 201 ( $M^+\text{—HBF}_4$ , 89), 173 (33), 172 (45), 158 (100), 157 (100), 130 (33).

$\text{C}_{13}\text{H}_{16}\text{NO} \cdot \text{BF}_4$  (289.08).      Calc. C 54.01 H 5.58 N 4.85.  
Found. C 53.90 H 5.45 N 4.60.

**5b**: To the resulting compound **4b** a mixture of chloroform/water (1 : 1) was added and the mixture was stirred for 20 min. Then, a diluted (watery) solution of sodium hydroxide was added, the organic layer separated and washed with water. The residue was crystallized from *n*-hexane/acetone. Crude yield 95%; pure yield 65%; m.p.:  $200^{\circ}$  (*n*-hexane, acetone).  $^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ ):  $\delta$  = 2.50 (s, 3 H,  $\text{CH}_3$ ), 2.70 (s, 3 H,  $\text{COCH}_3$ ), 6.90–8.20 (m, 4 H, H-aromat.), 11.90 (s, 1 H, NH). IR (KBr): 3 180 (NH), 1 615 (C=O)  $\text{cm}^{-1}$ . MS ( $m/e$ ): 173 ( $M^+$ , 28), 159 (18), 158 (100), 130 (69).

$\text{C}_{11}\text{H}_{11}\text{NO}$  (173.21).      Calc. C 76.30 H 6.36 N 8.09.  
Found. C 76.00 H 6.59 N 8.09.

*Ethoxy-(2-methyl-indole-3-yl)-phenylcarbenium tetrafluoroborate (4c)*  
*and 3-Benzoyl-2-methylindole (5c)*

In the reaction of **2** with **1c** the cation **4c** precipitated in the mixture. The precipitate was collected and washed three times with 20 ml dichloromethane and dried in vacuum.

**4c**: Yield 57%; yellow crystals; m.p.: 122–124°. <sup>1</sup>H-NMR (CD<sub>3</sub>NO<sub>2</sub>): δ = 2.35 (s, 3 H, CH<sub>3</sub>), 4.26 (s, 3 H, CH<sub>3</sub>O), 7.20–8.00 (m, 9 H, H-aromat.), 11.50 (s, 1 H, NH). IR (KBr): 3 250–2 500 (NH-assoc.), 1 150–950 (BF<sub>4</sub><sup>−</sup>) cm<sup>−1</sup>. MS (*m/e*): 250 (*M*<sup>+</sup>·BF<sub>4</sub>, 22), 249 (*M*<sup>+</sup>·HBF<sub>4</sub>, 100), 234 (59), 158 (41), 130 (16).

C<sub>17</sub>H<sub>16</sub>NO·BF<sub>4</sub> (337.12). Calc. C 60.57 H 4.78 N 4.16.  
 Found. C 60.00 H 4.69 N 4.10.

**5c**: To the resulting compound **4c** a mixture of dichloromethane/water (25 ml/15 ml) was added and the mixture was stirred for 30 min. Then, a diluted (watery) solution of sodium hydroxide was added, the organic layer separated and dried over calcium chloride. After filtration, the solution was mixed with 15 ml diethyl ether. Within 12 h the crystals of **5c** were precipitating from the clear solution. Crude yield 80%; pure yield 41%; m.p.: 189° (dichloromethane/ether). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 2.52 (s, 3 H, CH<sub>3</sub>), 7.05–7.95 (m, 9 H, H-aromat.), 8.93 (s, 1 H, NH). IR (KBr): 3 180 (NH), 1 595 (C=O) cm<sup>−1</sup>. MS (*m/e*): 235 (*M*<sup>+</sup>, 77), 234 (100), 158 (76), 130 (25).

C<sub>16</sub>H<sub>13</sub>NO (235.28). Calc. C 81.70 H 5.57 N 5.96.  
 Found. C 81.77 H 5.77 N 5.68.

*2-Methyl-3-methoxycarbonylindole (5d) and 2-Methyl-3-isopropylideneindolenine tetrafluoroborate (6)*

To the reaction mixture of **2** with **1d** 50 ml diethyl ether were added dropwise under stirring. The crystals precipitating from the solution are a mixture of **4d** and protonized **2** (2-methylindolenine tetrafluoroborate). The precipitate was collected and after addition of chloroform and water, the organic layer was separated and shaken with diluted (watery) solution of sodium hydroxide. Then, the chloroform layer was washed with water and fractionated by sc (silica gel, dichloromethane/*n*-hexane, 2: 1). The eluate was concentrated and after addition of petrol ether compound **5d** crystallized within 12 h. For deriving compound **6**, the mother liquid (CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O) was allowed to stand for 12 h, whereby **6** crystallized gradually.

**5d**: Crude yield 30%; pure yield 11%; m.p.: 169° (dichloromethane/petrol ether). 400-MHz-<sup>1</sup>H-NMR(CD<sub>3</sub>NO<sub>2</sub>): δ = 2.73 (s, 3 H, indole-CH<sub>3</sub>), 3.90 (s, 3 H, COOCH<sub>3</sub>), 7.15–7.25 (m, 2 H, H-aromat.), 7.35–7.45 (m, 1 H, H-aromat.), 8.00–8.06 (m, 1 H, H-aromat.), 9.35–9.50 (s, 1 H, NH). IR (KBr): 3 280 (NH), 1 670 (C=O), 1 290 (C—O) cm<sup>−1</sup>. MS (*m/e*): 189 (*M*<sup>+</sup>, 50), 174 (19), 158 (100), 130 (44).

C<sub>11</sub>H<sub>11</sub>NO<sub>2</sub> (189.21). Calc. C 69.84 H 5.82 N 7.40.  
 Found. C 70.13 H 6.26 N 7.30.

**6**: Pure yield 9%; m.p.: 155–157° (acetic acid). 400-MHz-<sup>1</sup>H-NMR (CD<sub>3</sub>NO<sub>2</sub>): δ = 3.08 (s, 3 H, indole-CH<sub>3</sub>), 2.90 a. 2.98 [2s, 6 H, =C(CH<sub>3</sub>)<sub>2</sub>], 7.52–7.63 (m, 2 H, H-aromat.), 7.65–7.71 (m, 1 H, H-aromat.), 8.20–8.80 (m, 1 H, H-



aromat.). IR (KBr): 3 250–2 500 (NH-assoz.), 1 595 (C=C), 1 150–950 (BF<sub>4</sub>) cm<sup>-1</sup>. MS (*m/e*): 171 (*M*<sup>+</sup>·HBF<sub>4</sub>, 100), 156 (95), 141 (7), 130 (21), 129 (33), 42 (7).

C<sub>12</sub>H<sub>14</sub>N·BF<sub>4</sub> (259.05). Calc. C 55.59 H 5.40 N 5.40.

Found. C 55.20 H 5.00 N 5.30.

Sulphate of cation **6** s. Ref.<sup>20</sup>.

## References

- <sup>1</sup> Part VI: Pfeuffer L., Müller J., Pindur U., *Chimia* **39**, 143 (1985).
- <sup>2</sup> Kutney J. P., Total Synthesis of Natural Products (*ApSimon J.*, ed.), Vol. 3. New York: Wiley-Interscience. 1977.
- <sup>3</sup> Saxton J. E. (ed.), Indoles, Part Four. New York: Wiley-Interscience. 1983.
- <sup>4</sup> Livingstone R., Rodd's Chemistry of Carbon Compounds, Vol. IV, Suppl. A (*Ansell M. F.*, ed.), p. 428. Amsterdam-Oxford-New York-Tokyo: Elsevier. 1984.
- <sup>5</sup> Hünig S., *Angew. Chem.* **76**, 400 (1967); Gompper R., Regioselectivity in Reactions of Ambident Anions and Cations, in *Chem. Future*, Proc. IUPAC Congr., 29th 1983 (*Grünwald H.*, ed.), p. 193–198. Oxford: Pergamon. 1984.
- <sup>6</sup> Akgün E., Pindur U., Müller J., *J. Heterocyclic Chemistry* **20**, 1303 (1983).
- <sup>7</sup> Müller J., Pindur U., *Arch. Pharm. (Weinheim)* **317**, 555 (1984).
- <sup>8</sup> Pindur U., Müller J., *Chem. Ztg.* **108**, 150 (1984).
- <sup>9</sup> Pindur U., Müller J., *Chimia* **39**, 141 (1985).
- <sup>10</sup> Dorofeenko G. N., Mezheritskaya L. V., Vasserman A. L., *Zh. Obshch. Khim.* **41**, 731 (1971); *Chem. Abstr.* **75**, 35591u (1971).
- <sup>11</sup> Meerwein H., Bodenbrenner K., Borner P., Kunert F., Wunderlich K., *Justus Liebigs Ann. Chem.* **632**, 38 (1960).
- <sup>12</sup> Gerlach A., Dissertation, Universität Marburg, 1969.
- <sup>13</sup> For an excellent review about di- and trialkoxycarbenium ions: Perst H., *Oxonium Ions in Organic Chemistry*. Weinheim-New York: Verlag Chemie, Academic Press. 1971.
- <sup>14</sup> Taft R. W., Martin R. H., Lampe F. W., *J. Amer. Chem. Soc.* **87**, 2490 (1965); Holmes J. L., Lossing F. P., *Can. J. Chem.* **60**, 2365 (1982); Burt R. A., Chambers C. A., Chiang Y., Hillock C. S., Kresge A. J., Larsen J. W., *J. Org. Chem.* **49**, 2622 (1984).
- <sup>15</sup> Richter A. M., Fanghänel E., *Tetrahedron Lett.* **24**, 3577 (1983).
- <sup>16</sup> Borch R. F., *J. Chem. Soc. Chem. Commun.* **1968**, 442; Borch R. F., *J. Org. Chem.* **34**, 627 (1969).
- <sup>17</sup> Kabuß S., *Angew. Chem.* **78**, 714 (1966).
- <sup>18</sup> Dimroth K., Heinrich P., *Angew. Chem.* **78**, 714 (1966).
- <sup>19</sup> Gund P., *J. Chem. Educ.* **49**, 100 (1972); West R., Nin J., *Nonbenzoid Aromatics* (*Snyder J. P.*, ed.). New York: Academic Press. 1969.
- <sup>20</sup> Noland W. E., Venkiteswaran M. R., Richards C. G., *J. Org. Chem.* **26**, 4241 (1961); Cook A. H., Majer J. R., *J. Chem. Soc.* **1944**, 486.
- <sup>21</sup> Remers W. A., Indoles Part One (*Houlihan W. J.*, ed.). New York-London: Wiley-Interscience. 1972; and references cited therein.
- <sup>22</sup> Akgün E., Pindur U., *Monatsh. Chem.* **115**, 587 (1984).