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Indolenine Oxides, VIII[1a)]

Reaction of 5,7-Di-*tert*-butyl-3,3-dimethyl-3*H*-indole 1-Oxide with Grignard Reagents. – A New Stable Aminyl Oxide[1b)] (Nitroxide)

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The title compound **1**, unsubstituted at C-2, is efficiently converted into its 2-substituted derivatives **4a, b** by Grignard addition and lead dioxide oxidation. **4a**, when subjected to the same sequence, gives high yields of the aminyl oxide **5a** which is also formed in small amounts in the conversion of **1** together with two other minor compounds. The course of the reaction is influenced by the presence of a bulky *tert*-butyl group at C-7 in **1** and by the solvent used for the Grignard reaction.

Indoleninoxide, VIII[1a)]

Umsetzung von 5,7-Di-*tert*-butyl-3,3-dimethyl-3*H*-indol-1-oxid mit Grignard-Reagenzien. – Ein neues stabiles Aminyloxid[1b)] (Nitroxid)

Die an C-2 unsubstituierte Titelverbindung **1** wird durch Addition von Grignard-Reagentien und nachgeschaltete Bleidioxid-Oxidation in guten Ausbeuten in ihre 2-substituierten Derivate **4a, b**

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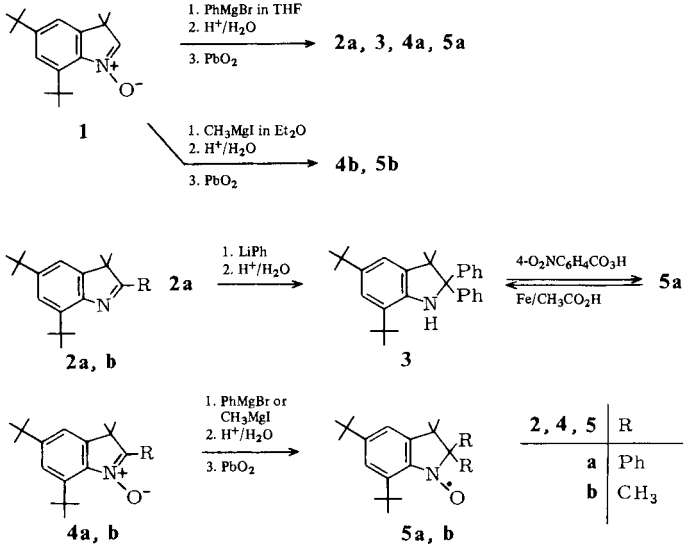
umgewandelt. Unter den gleichen Bedingungen erhält man aus **4a** in hoher Ausbeute das Aminyloxid **5a**, das auch in der Umsetzung von **1** in kleiner Menge neben zwei weiteren Nebenprodukten anfällt. Der Reaktionsverlauf wird durch die Anwesenheit einer sperrigen *tert*-Butylgruppe an C-7 von **1** und durch das für die Grignard-Reaktion benutzte Lösungsmittel beeinflußt.

Reaction of 2-substituted *N*-oxides of the indole[2] and quinoline[3] series with Grignard reagents followed by lead dioxide treatment of the adducts leads to 2,2-disubstituted stable aminyl oxide radicals. Under the same conditions, unsubstituted *N*-oxides of the quinoline[4,5] and benzoquinoline[6] series with Grignard reagents yield the corresponding 2-substituted *N*-oxides, the 2-substituted free bases, and the 2,2-disubstituted aminyl oxide radicals. Further, the spectrum of products obtained depends on the solvent used[4]. The reactions of 5,7-di-*tert*-butyl-3,3-dimethyl-3*H*-indole 1-oxide (**1**) with phenylmagnesium bromide and methylmagnesium iodide, described in the paper, match the analogous reactions of quinolines[5] and benzoquinolines[6] and, in particular, provide an access to certain indolenine 1-oxides (namely **4a, b**), which are difficult to prepare by the classical *N*-oxidation methods of the corresponding 2-substituted free bases.

Results

The nitrone **1** readily reacted with phenylmagnesium bromide in a 1:3 molar ratio in tetrahydrofuran at room temperature. By subsequent lead dioxide treatment of the mixture of adducts the products **2a**, **3**, **4a** (main product), and **5a** were obtained.

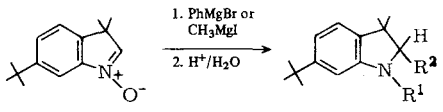


Compound **3** was identified by its analytical and spectroscopic data and, in particular, by formation of aminyl oxide radical **5a** on oxidation with *p*-nitroperbenzoic acid. On the other hand, the iron/acetic acid reduction of **5a** forming the indoline **3** in good

yield confirmed the structures of both **3** and **5a**. The indolenine structures of **2a** and **4a** were verified by the multiplets at $\delta = 8.1-8.4$ in their ^1H NMR spectra which are typical for compounds of this kind[6], and further by their mass spectra and their reactions with carbanionoids: **2a** reacted with phenyllithium to form the indoline **3**, and **4a** formed the aminyl oxide **5a** in good yield by the reaction with phenylmagnesium bromide and subsequent oxidation of the adduct by lead dioxide.

Compound **1**, when dissolved in tetrahydrofuran and treated with methylmagnesium iodide (prepared in diethyl ether) and hereafter with lead dioxide under otherwise the same conditions as used in the phenylmagnesium bromide addition, gave the *N*-oxide **4b** in good yield. Additionally, the aminyl oxide **5b** was detected by ESR spectroscopy in the reaction solution after hydrolysis and oxidation. Two repetitive runs confirmed the yields of **4b** and the formation of trace amounts of **5b**. In addition, two yellow compounds are formed in very small amounts which could so far not be identified. Methylmagnesium iodide treatment of **4b**, followed by lead dioxide treatment of the reaction solution after hydrolysis, gave also traces of **5b** and again two yellow high molecular weight compounds, one of which was identical to one of the yellow by-products from the methylmagnesium iodide addition to **1**.

When pure diethyl ether was used instead of tetrahydrofuran as solvent for the addition of phenylmagnesium bromide or methylmagnesium iodide, the 3*H*-indoles **2a** (96%) and **2b** (72%), respectively, were isolated as the sole products after hydrolytic work-up. When, for comparison, 6-*tert*-butyl-3,3-dimethyl-3*H*-indole 1-oxide (**6**) was subjected to the addition of phenylmagnesium bromide in diethyl ether at room temperature, indolines **7a** (55%) and **7b** (27%) were isolated. Likewise, treatment of **6** with methylmagnesium iodide in diethyl ether led to the formation of **7c** in 84% yield.

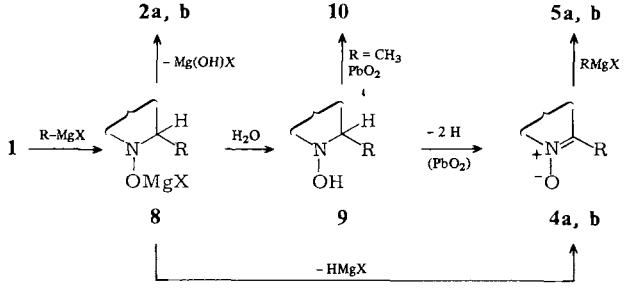


6 **7a-c**

7	R^1	R^2
a	H	Ph
b	OH	Ph
c	H	CH_3

Discussion

The above results may be explained by the steps outlined below. The intermediate **8**, formed from the sterically highly crowded nitrone **1**, may (i) eliminate Mg(OH)X to form the indolenines **2a, b**, which with excess Grignard reagent reacts to give indolines such as **3** (this step seems to be the main route in other cases[7,8]); (ii) eliminate HMgX to



form the *N*-oxides **4a, b**[9], which in turn with excess Grignard reagent and subsequent lead dioxide oxidation lead to aminyl oxides **5a** or **5b**, respectively; (iii) remain unchanged and give, after hydrolysis, the hydroxylamine **9**, which forms the *N*-oxides **4a** or **4b** upon lead dioxide oxidation. The product compositions confirm this route to be the most important one for nitrone **1**.

In the case of the sterically non-crowded nitrone **6**, reductive N – O bond cleavage by the Grignard reagent obviously takes place either prior or subsequent to addition at C-2. The occurrence of biphenyl in the reaction mixture after addition of phenylmagnesium bromide to **6** supports this view, since the formation of biphenyl very likely originates from an electron transfer process.

The formation of **9**, which is the precursor of *N*-oxides **4a, b** and which is analogous to the isolable 1-hydroxyindoline **7b**, was also indirectly verified in the reaction of nitrone **1** with methylmagnesium iodide, when a 2 ml portion of the reaction solution was taken away, hydrolyzed, and oxidized with lead dioxide in the ESR cavity, to give the signal characteristical of the aminyl oxide **10** (see table and figure). The hfcc value (15.3 Gauss) of the C-2 hydrogen of **10** is in agreement with the values observed for α-hydrogens in aminyl oxides of indoline structure[10,11]. The hfcc values for radicals **5a** and **5b** are in agreement with those observed for similar structures[12] (see table).

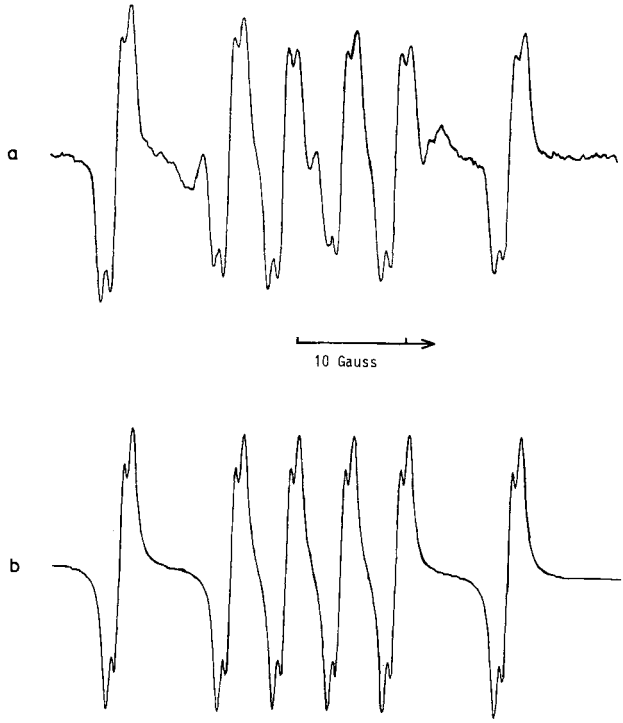
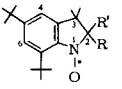


Figure: Experimental (a) and computer simulated (b) signals of aminyl oxide **10**

The radical **5a** is perfectly stable and, by comparison with 4-hydroxy-2,2,6,6-tetramethylpiperidinyl 1-oxide[13] or with 3-oxo-2,2-diphenylindolinyl 1-oxide[2], is demonstrated to have one unpaired electron per molecule.

Table: Hyperfine coupling constants (in Gauss) of radicals **5a, b**, and **10** (in chloroform)



	R	R'	a^N	$a^{4\text{-H}} = a^{6\text{-H}}$	a^R
5a	Ph	Ph	10.57	0.83 (2H)	–
5b	Me	Me	10.68	0.92 (2H)	–
10	H	Me	10.25	0.75 (2H)	15.30 (1H)

The *N*-oxide **4a** is a stable compound both in solid state and in solution, while the corresponding 2-methyl substituted *N*-oxide **4b** undergoes autoxidation in solution to form a mixture of yellow compounds similar to those resulting from the reaction of nitrone **1** with methylmagnesium iodide. Even if these compounds have not yet been identified, we assume that their formation originates from the high reactivity of the C-2 methyl group in agreement with the reactivity of α-methyl groups in aromatic *N*-oxides[14]. The masses of their molecular ions suggest that they may originate from an oxidative bimolecular coupling of **4b**.

Summarizing, the reaction of nitrone **1** with Grignard reagents in tetrahydrofuran followed by lead dioxide oxidation is a facile and convenient method to prepare *N*-oxides such as **4a, b**. Furthermore, the aminyl oxide **5a** can be prepared in good yield by the reaction of **4a** with phenylmagnesium bromide in tetrahydrofuran. A different product pattern results when pure diethyl ether is used as solvent. Also, the presence of the bulky *tert*-butyl group at C-7 in **1** is of influence on the product distribution, as is demonstrated by the different product pattern obtained from the addition of Grignard reagents to nitrone **6**.

D. D. is indebted to *Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen* and *Fonds der Chemischen Industrie* for financial support, A. M. N. to *Deutscher Akademischer Austauschdienst* for a scholarship.

Experimental Part

Melting points are uncorrected. – IR spectra: Perkin-Elmer 257 (nujol mulls) and Beckman IR 20 A (KBr). – ^{1}H NMR spectra: Varian XL 100 (100 MHz) and EM 390 (90 MHz), all in $CDCl_3$ with tetramethylsilane as internal standard. – ESR spectra: Varian E 4 spectrometer. – MS (EI-mode, 70 eV): MAT 311 and 311 A. – Starting materials: 5,7-Di-*tert*-butyl-3,3-dimethyl-3*H*-indole 1-oxide (**1**)[15], 6-*tert*-butyl-3,3-dimethyl-3*H*-indole 1-oxide (**6**)[16], and lead dioxide[17] were prepared as described in the literature. – The solutions of the Grignard reagents were prepared

by conventional methods in a current of dry nitrogen using as solvents either tetrahydrofuran (THF) or diethyl ether (DEE) for phenylmagnesium bromide and DEE for methylmagnesium iodide. – Preparative layer chromatography (PLC) was carried out using 1 mm layers of silica gel Merck PF_{254} on 48 cm × 20 cm plates unless stated otherwise.

Reactions of nitrone **1** *with Grignard reagents*

Run A: A solution of phenylmagnesium bromide, prepared from 216 mg (8.9 mg atoms) of magnesium and 1.57 g (10.0 mmol) of bromobenzene in 20 ml of THF, was added with stirring to a solution of 744 mg (2.7 mmol) of **1** in 20 ml of THF at room temperature under N_2. After 3 h the mixture was poured into 50 ml of a 5% aqueous solution of NH_4Cl and extracted with chloroform. The chloroform layer was dried over Na_2SO_4 and treated with 2 g of PbO_2 for 1 h. The filtrate was concentrated, the residue taken up in benzene and chromatographed on a column (2.5 cm × 80 cm) over silica gel (10 – 40 µ). The eluate was collected in three fractions, the first (50 ml) and second (75 ml) using benzene, the third (150 ml) using benzene/acetone (3 : 2).

5,7-Di-tert-butyl-2,3-dihydro-3,3-dimethyl-2,2-diphenyl-1H-indole (**3**): The residue of the first fraction was further separated by PLC (20 cm × 20 cm plates, 1 mm of silica gel) using benzene/cyclohexane (1 : 4). From the first zone (R_F = 0.28) 37 mg (3%) were obtained, m.p. 182 °C (from hexane). – IR (nujol): 3395 (NH), 1605 (Ph – N – C) cm^{-1}. – ^1H NMR: δ = 1.17 (s, 6H), 1.26 (s, 9H), 1.35 (s, 9H), 4.03 (broad, 1H, NH), 6.9 – 7.5 (m, 12H, arom.). – MS: *m/e* = 411 (60%, M^+), 396 (26%, M – 15), 334 (100%, M – 77), 304 (18).

$C_{30}H_{37}N$ (411.6) Calcd. C 87.53 H 9.06 N 3.40 Found C 87.60 H 9.10 N 3.95

5,7-Di-tert-butyl-3,3-dimethyl-2-phenyl-3H-indole (**2a**): Elution of the second zone (R_F = 0.14) gave 45 mg (4%) of colourless crystals, m.p. 146 °C (from hexane). – IR (nujol or KBr): 1530 cm^{-1} ($C_6H_5N{=}C\langle$). – ^1H NMR: δ = 1.37 (s, 9H), 1.53 (s, 6H), 1.60 (s, 9H), 7.18 (mc, 1H, arom.), 7.41 (mc, 4H, arom.), 8.18 (mc, 2H, arom.). – MS: *m/e* = 333 (40%, M^+), 332 (20), 318 (M – 15, 90), 303 (11), 302 (11), 291 (100, M – 42), 289 (15), 287 (27), 277 (27), 276 (52), 262 (35), 247 (22).

$C_{24}H_{31}N$ (333.5) Calcd. C 86.43 H 9.37 N 4.20 Found C 86.50 H 9.30 N 4.22

5,7-Di-tert-butyl-2,3-dihydro-3,3-dimethyl-2,2-diphenyl-1H-indol-1-yl 1-oxide (**5a**): From the second column eluate, 70 mg (6%) of orange crystals, m.p. 185 °C (from ethanol), were obtained. – IR (nujol mull): 1600 ($C_6H_5 - N - C$) cm^{-1}. – MS: *m/e* = 426 (25%, M^+), 411 (57), 410 (11), 409 (9), 396 (25), 394 (9), 334 (100), 333 (9), 332 (10), 304 (15), 57 (43).

$C_{30}H_{36}NO$ (426.6) Calcd. C 84.46 H 8.50 N 3.28 Found C 84.50 H 8.35 N 3.35

5,7-Di-tert-butyl-3,3-dimethyl-2-phenyl-3H-indole 1-oxide (**4a**): From the third column eluate, 780 mg (82%) of colourless crystals, m.p. 170 °C (from cyclohexane), were collected. – IR (nujol mull): 1619, 1595, 1575 cm^{-1}. – ^1H NMR: δ = 1.38 (s, 9H), 1.60 (s, 6H), 1.70 (s, 9H), 7.2 – 7.6 (m, 5H, arom.), 8.16 – 8.42 (m, 2H, arom.). – MS: *m/e* = 349 (90%, M^+), 334 (75, M – 15), 332 (100, M – 17), 307 (30), 302 (17), 292 (18), 276 (25), 244 (30), 105 (78), 77 (30), 57 (30).

$C_{24}H_{31}NO$ (349.5) Calcd. C 82.47 H 8.94 N 4.00 Found C 82.50 H 8.97 N 3.95

Run B: To 273 mg (1.0 mmol) of **1** a twofold excess of phenylmagnesium bromide in 25 ml of diethyl ether was pipetted under N_2 and the mixture left standing for 10 min at room temp., washed with 5% aqueous NH_4Cl solution and the upper layer dried over magnesium sulfate. The residue was separated into two zones by PLC with benzene/ethyl acetate (10 : 1), the second of which (R_F = 0.38) contained too little material and was discarded. The first zone (R_F = 0.53) gave 320 mg (96%) of **2a**, m.p. 147 °C.

Run C: A solution of methylmagnesium iodide was prepared from 216 mg (8.9 mmol) of magnesium turnings and 1.3 g (9.15 mmol) of methyl iodide in 20 ml of DEE under N_2. This was added to a solution of 744 mg (2.72 mmol) of **1** in 20 ml of dry THF. The reaction mixture was worked up as given under run A. A sample of the chloroform solution was transferred to the ESR cavity after lead dioxide oxidation, and the signal assigned to *5,7-di-tert-butyl-2,3-dihydro-2,2,3,3-tetramethyl-1H-indol-1-yl 1-oxide* (**5b**) was observed (see table). Column chromatography (as under run A) gave, by elution with benzene, two yellow compounds in minor amounts which could not be identified.

5,7-Di-tert-butyl-2,3,3-trimethyl-3H-indole 1-oxide (**4b**): Elution with benzene/acetone (3:2) gave 547 mg (70%) of colourless crystals, m.p. 153 °C (from heptane). – IR (nujol mull): 1613, 1598, 1540 cm^{-1}. – ^1H NMR: δ = 1.36 (15H, 2 CH_3 and *tert*-butyl), 1.67 (s, 9H), 2.26 (s, 3H, 2-CH_3), 7.38 (d, *J* = 1.8 Hz, 1H, arom.), 7.52 (d, *J* = 1.8 Hz, 1H, arom.). – MS: *m/e* = 287 (83%, M^+), 272 (90, M – 15), 270 (M – 17, 100), 256 (20), 245 (30), 244 (30), 240 (21), 230 (50), 214 (43), 57 (40).

$C_{19}H_{29}NO$ (287.4) Calcd. C 79.34 H 10.17 N 4.87 Found C 79.55 H 10.25 N 4.75

Run D: To a solution of 217 mg (0.80 mmol) of **1** in 2 ml of dry DEE was pipetted under N_2 a twofold excess of methylmagnesium iodide in 10 ml of DEE.

5,7-Di-tert-butyl-2,3,3-trimethyl-3H-indole (**2b**): Work-up as given under run B and crystallization of the residue from methanol/water gave 155 mg (72%) of colourless crystals, m.p. 65–67 °C. – IR (KBr): 1690 (C=N), 1456, 1361 cm^{-1}. – ^1H NMR: δ = 1.25 (s, 6H), 1.33 (s, 9H), 1.50 (s, 9H), 2.22 (s, 3H, 2-CH_3), 7.10 (d, *J* = 1.8 Hz, 1H, arom.), 7.25 (d, *J* = 1.8 Hz, 1H, arom.). – MS: *m/e* = 271 (44%, M^+), 270 (18), 256 (100), 241 (14), 240 (11), 229 (69, M – 42), 228 (13), 226 (34), 215 (23), 214 (38), 200 (51), 185 (21), 184 (13), 57 (18), 41 (13).

$C_{19}H_{29}N$ (271.4) Calcd. C 84.07 H 10.77 N 5.16 Found C 84.15 H 10.66 N 5.1

Reactions of nitrone **6** *with Grignard reagents*

Run E: As described under run B, 217 mg (1.00 mmol) of **6** were treated with a twofold excess of phenylmagnesium bromide for 30 min at room temp. Work-up as before and PLC (three plates, benzene/ethyl acetate 10:1) gave, in the order of decreasing R_F-values, the following compounds: 70 mg of biphenyl, m.p. 70–71 °C; 82 mg (55%) of **7a**, m.p. 114–115 °C (from hexane); 58 mg (27%) of **7b**, m.p. 140–142 °C (from hexane); 60 mg of recovered starting material **6** (yields given thus refer to converted **6**).

6-tert-Butyl-2,3-dihydro-3,3-dimethyl-2-phenyl-1H-indole (**7a**): IR (KBr): 3370 (NH), 1620, 1495, 1435, 1355, 1275 cm^{-1}. – ^1H-NMR: δ = 0.70 (s, 3H, CH_3), 1.30 (s, 9H), 140 (s, 3H, CH_3), 3.84 (broad, 1H, NH), 4.58 (s, 1H, 2-H), 6.85 (mc, 3H, arom.), 7.35 (mc, 5H, arom.). – MS: *m/e* = 279 (38%, M^+), 277 (40), 264 (27), 262 (96), 247 (17), 246 (9), 234 (6), 232 (7), 221 (8), 220 (12), 208 (100), 206 (10), 193 (17), 57 (53).

$C_{20}H_{25}N$ (279.4) Calcd. C 85.97 H 9.02 N 5.01 Found C 86.0 H 8.98 N 4.9

6-tert-Butyl-2,3-dihydro-3,3-dimethyl-2-phenyl-1H-indol-1-ol (**7b**): IR (KBr): 3538, 3499 and 3440 cm^{-1} (OH). – ^1H NMR: δ = 0.73 (s, 3H, CH_3), 1.33 (s, 9H), 1.39 (s, 3H, CH_3), 4.29 (s, 1H, 2-H), 5.45 (s, 1H, OH), 7.00–7.60 (m, 8H, arom.). – MS: *m/e* = 295 (6%, M^+), 279 (24), 278 (19), 277 (39), 264 (17), 262 (100), 247 (19), 246 (10), 208 (61), 57 (56).

$C_{20}H_{25}NO$ (295.4) Calcd. C 81.31 H 8.53 N 4.74 Found C 81.4 H 8.54 N 4.7

Run F: As described under run B, a solution of 225 mg (1.04 mmol) of **6** in 2 ml of DEE was treated with a twofold excess of methylmagnesium iodide in 10 ml of DEE for 1 h at room temp. Work-up as before and PLC (two plates, benzene) gave only one major zone ($R_F \approx 0.32$).

6-tert-Butyl-2,3-dihydro-2,3,3-trimethyl-1H-indole (**7c**): Crystallization from methanol/water gave 188 mg (84%) of colourless crystals, m.p. 65–66°C. – IR (KBr): 3365 and 3280 cm^{-1} (NH). – ^1H NMR: δ = 1.00 (s, 3H, 3-CH_3), 1.15 (d, *J* = 6.6 Hz, 3H, 2-CH_3), 1.25 (12H, 3-CH_3 and *t*Bu), 3.21 (broad, 1H, NH), 3.52 (q, *J* = 6.6 Hz, 1H, 2-H), 6.83 (mc, 3H, arom.). – MS: *m/e* = 217 (25%, M^+), 215 (5), 202 (18), 200 (18), 146 (100).

$C_{15}H_{23}N$ (217.3) Calcd. C 82.89 H 10.67 N 6.45 Found C 82.8 H 10.63 N 6.3

Other conversions

3 *from* **2a**: A solution of 1 mmol of phenyllithium in 3 ml of THF was added to a solution of 100 mg (0.30 mmol) of **2a** in 10 ml of THF with stirring at room temp. After 1 h, the reaction mixture was hydrolyzed and extracted with chloroform as described under run A. The chloroform layer was dried over Na_2SO_4 and concentrated to dryness. The residue was chromatographed with petroleum ether/ethyl acetate (9:1) over a silica gel column (2.5 cm × 80 cm, 10–40 µ), and 105 mg (85%), m.p. 182°C (from hexane), were collected.

3 *from* **5a**: A solution of 852 mg (2.0 mmol) of **5a** in 20 ml of glacial acetic acid was refluxed with 1 g of iron powder for 10 min, cooled to room temp., filtered, and the filtrate diluted with 50 ml of water, neutralized with $NaHCO_3$, and extracted with benzene. The benzene layer was dried over Na_2SO_4 and the residue chromatographed on a silica gel column as described before with benzene to give 740 mg (90%) of material, m.p. 182°C.

5a *from* **4a**: A solution of 6 mmol of phenylmagnesium bromide in THF was added to a solution of 700 mg (2.0 mmol) of **4a** in 20 ml of THF. Work-up, lead dioxide oxidation and column chromatography as under run A gave 639 mg (75%) of **5a**, m.p. 185°C (from ethanol).

5a *from* **3**: A 1.5 ml sample of a solution of *p*-nitroperbenzoic acid (10^{-3} M) in $CHCl_3$ and 1.5 ml of a 10^{-4} M solution of **3** were mixed inside the ESR-cavity. Within 3 min the signal corresponding to **5a** was recorded. A thin layer chromatogram of the mixture and **5a** as reference also confirmed the formation of **5a**.

5b *from* **4b**: To a solution of 144 mg (0.5 mmol) of **4b** in 10 ml of THF a solution of 1.5 mmol of methylmagnesium iodide in 10 ml of DEE was added and the mixture left standing for 0.5 h at room temp. Work-up and lead dioxide oxidation corresponded to run A. A sample of the chloroform solution after oxidation was transferred to the ESR-cavity and showed the presence of **5b**. Work-up by concentrating and column chromatography (elution with benzene) gave 18 mg of a mixture of two yellow compounds. One of these was identical to one isolated from the reaction of **1** with methylmagnesium iodide, MS: *m/e* = 554 (53%, M^+), 539 (17, M – 15), 526 (100), 511 (17). An impurity gave an additional molecular ion peak at *m/e* = 570.

Percentage of unpaired electron in **5a**: The ESR signals of benzene solutions (10^{-4} M) of **5a**, *4-hydroxy-2,2,6,6-tetramethylpiperidinyl 1-oxide* and *2,3-dihydro-3-oxo-2,2-diphenyl-1H-indol-1-yl 1-oxide* were recorded under identical conditions. Comparison of the corresponding areas by the method described by *Wyard*[18] demonstrated **5a** to be 100% radical.

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1) [1a] Part. VII: *D. Döpp* and *H. Weiler,* Chem. Ber. **112**, 3950 (1979). – [1b] Nomenclature according to IUPAC-Rule C 81.2.
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