The injected volumn was typically 2 $\mu$L and did not significantly change the total volume of the solution. The reaction times were between 10 and 40 min. Excess tributylstannane in the cooled mixture was quenched by the addition of methyl iodide. The samples were then analyzed by GC.

**Acknowledgment.** We are indebted to the Australian Research Council, Deakin University, and the Ramsay Memorial Fellowship Trust for financial support. Thanks also to the University of London Computer Centre for time on the CRAY-1S/2200 supercomputer and the Computer Centres of Flinders and Deakin Universities for access to the various processors used in this study.

---

# Electrochemistry of Anilines. 6.[1] Reactions of Electrogenerated Biphenylylnitrenium Ions

Anton Rieker* and Bernd Speiser

*Universität Tübingen, Institut für Organische Chemie, Auf der Morgenstelle 18, D-7400 Tübingen 1, FRG*

*Received February 11, 1991 (Revised Manuscript Received April 16, 1991)*

3,5-Di-*tert*-butyl-substituted biphenyl-4-ylnitrenium ions are generated by anodic oxidation of the corresponding biphenylylamines in acetonitrile in the presence of a base. The reactions of these species with several nucleophiles are studied. The principal reaction sites are identified as the positions ortho and para to the =NH moiety. No reactions at the iminium nitrogen and in the second ring of the biphenyl system are observed. Products are characterized by spectroscopic techniques. Some common spectroscopic features of the iminoquinolide reaction products are discussed.

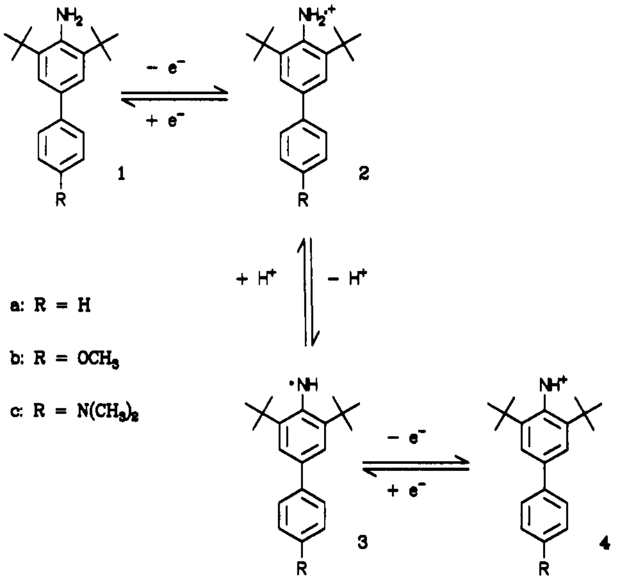
## Introduction

Investigations into the anodic oxidation of anilines 1 have shown[2] that *nitrenium ions* 4 are among the key intermediates of this reaction. Genies and Lapkowski have found spectroelectrochemical evidence for the involvement of a nitrenium ion in the electropolymerization of unsubstituted aniline.[3] A persistent ion **4c** has been characterized by spectroscopic and electrochemical methods.[4] The hypothesis has been formulated that the ions[5] are formed by an overall two-electron transfer via radical cations 2[6] and most likely the nitryl radicals 3 (Scheme I).

The proton-transfer equilibrium lies far to the radical cation side in acetonitrile,[6] but may be shifted to the neutral radical side in the presence of a base. The pathway from 1 to 4 corresponds to the ECE mechanism or one of its nuances.[7,8] Voltammetric evidence for this mechanism has recently been presented[9] in the case of 1-naphthylamine oxidation in DMSO.

Although the intermediate occurrence of secondary[10-14] and primary[3,15-17] nitrenium ions in the anodic oxidation of several anilines has been formulated, no systematic study of the reactions undergone by electrogenerated electrophiles of this type with nucleophiles has appeared to our knowledge.

Scheme I



In this paper, we report on chemical reactions of three electrogenerated biphenylylnitrenium ions **4a–c** with various nucleophiles.

## Results and Discussion

**Cyclic Voltammetry.** Cyclic voltammograms of the anilines **1a–c** in acetonitrile in the presence of 2,6-lutidine (lu) were obtained (Figure 1). The anodic peaks increase to approximately twice their height in neutral solvent,

---

(1) For part 5 of this series, see ref 4.

(2) Speiser, B.; Rieker, A.; Pons, S. *J. Electroanal. Chem.* **1983**, *159*, 63.

(3) Genies, E. M.; Lapkowski, M. *J. Electroanal. Chem.* **1987**, *236*, 189.

(4) Rieker, A.; Speiser, B. *Tetrahedron Lett.* **1990**, *30*, 5013.

(5) The positive charge is distributed over the entire aromatic system in these cations.[4] From the possible mesomeric structures only that having the charge at the NH group is shown here.

(6) Speiser, B.; Rieker, A.; Pons, S. *J. Electroanal. Chem.* **1983**, *147*, 205.

(7) Amatore, C.; Savéant, J. M. *J. Electroanal. Chem.* **1977**, *85*, 27.

(8) Amatore, C.; Savéant, J. M. *J. Electroanal. Chem.* **1978**, *86*, 227.

(9) Daniele, S.; Ugo, P.; Mazzochin, G. A.; Bontempelli, G. *J. Electroanal. Chem.* **1989**, *267*, 129.

(10) Leedy, D. W.; Adams, R. N. *J. Am. Chem. Soc.* **1970**, *92*, 1646.

(11) Cauquis, G.; Delhomme, H.; Serve, D. *Electrochim. Acta* **1976**, *21*, 557.

(12) Serve, D. *Bull. Soc. Chim. Fr.* **1976**, 1993.

(13) Svanholm, U.; Parker, V. D. *J. Am. Chem. Soc.* **1974**, *96*, 1234.

(14) Serve, D. *J. Am. Chem. Soc.* **1975**, *97*, 432.

(15) Cauquis, G.; Fauvelot, G.; Rigaudy, J. *C. R. Acad. Sci. Paris C* **1967**, 1958.

(16) Cauquis, G.; Fauvelot, G.; Rigaudy, J. *Bull. Soc. Chim. Fr.* **1968**, 4928.

(17) Cauquis, G.; Cros, J.-L. *Bull. Soc. Chim. Fr.* **1971**, 3760–3772.

**Table I. Preparative-Scale Anodic Oxidation[a] Products of 1a and 1b**

| aniline | base | nucleophile | product | charge passed, F/mol | isolated yield, % |
|---|---|---|---|---|---|
| **1a** | lu | $H_2O$ | **5a** | 2 | 18–55[b] |
| **1a** | lu | $CH_3OH$ | **5b** | 2 | 76 |
| **1a** | lu | $C_2H_5OH$ | **5c** | 2 | 58 |
| **1a** | lu | $Cl^-$ | **6** | 4 | 32 |
| **1a** | $Na_2CO_3$ | $Cl^-$[c] | **7a** | 3.7 | 21 |
| **1a** | $Na_2CO_3$ | $Cl^-$ | **7a** | >4 | 47 |
| **1b** | lu | $H_2O$ | **5d** | 2 | 32–73[b] |
| **1b** | lu | $CH_3OH$ | **5e** | 2 | 73 |
| **1b** | lu | $C_2H_5OH$ | **5f** | 2 | 77 |
| **1b** | lu | $CN^-$[c] | **8b** | 2 | 36 |
| **1b** | $Na_2CO_3$ | $Cl^-$ | **7b** | >4 | 56 |

[a] Electrode potential: +1.0 V vs SCE, except where noted otherwise. [b] Dependent on the aniline concentration, $c^0$. [c] Electrode potential: +0.85 V vs SCE.

where a reversible one-electron transfer was found.[6,18] Thus, a second electron-transfer reaction occurs after the primary redox reaction $1 \rightleftharpoons 2$. The peak moves to less positive potentials with increasing electron-donating power of the substituent R, as in the case of the one-electron oxidation to the radical cation.[6,18] In all cases, the voltammetric features depend on the scan rate $\nu$ and the concentration of both the aniline and lu. The reverse peak (observed without base and corresponding to the reduction of **2** to **1**) has disappeared in the voltammogram of **1a**. It is found only for fast scan rates ($\nu = 10$ V $s^{-1}$). In the current–potential curves recorded for **1b** and **1c** this peak has decreased considerably in height compared to the experiments without base. Obviously, the radical cations **2** react with the base.

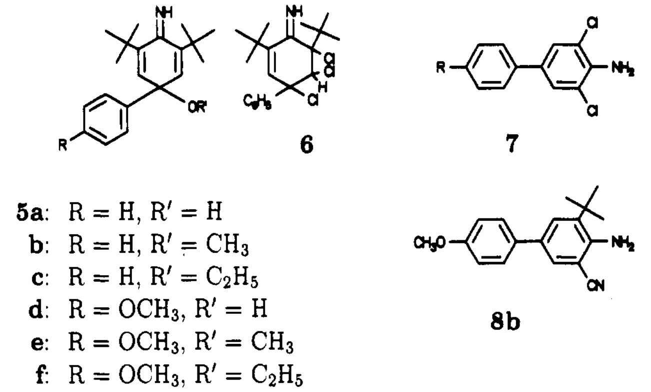
No additional peaks appear in the case of **1a** and **1b**. On the other hand, the voltammogram of **1c** in the presence of lu shows a second reduction peak at a potential approximately 250 mV more negative than the primary oxidation peak. This peak is the one observed[4] during the reduction of nitrenium ion **4c**. Thus, the two-electron oxidation product seems to be persistent here and is stabilized by the electron-donating dimethylamino substituent. In the case of **4a** and **4b**, fast follow-up reactions occur.

We do not attempt to discriminate between the ECE mechanism and its DISP nuances from these qualitative voltammetric experiments.

**Preparative Electrolyses.** *Anodic oxidations of **1a–c** on the preparative scale in the presence of a base with no deliberately added nucleophile* show that the corresponding radical cations are not persistent under these conditions: the characteristic colors of these species in neutral solution (**2a**, blue; **2b**, green; **2c**, orange)[6] can no longer be observed. Solutions of **1a** remain colorless during the electrolysis, while those of **1b** turn purple for several minutes and then yellow. In the case of **1c**, a deep purple solution results from the electrolysis. No ESR spectra can be observed during the experiments. Constant potential coulometry in all three cases shows that 2 electrons per molecule are transferred. Spectroscopic and electrochemical evidence for the generation of **4c** from **1c** under the conditions applied is given elsewhere.[4]

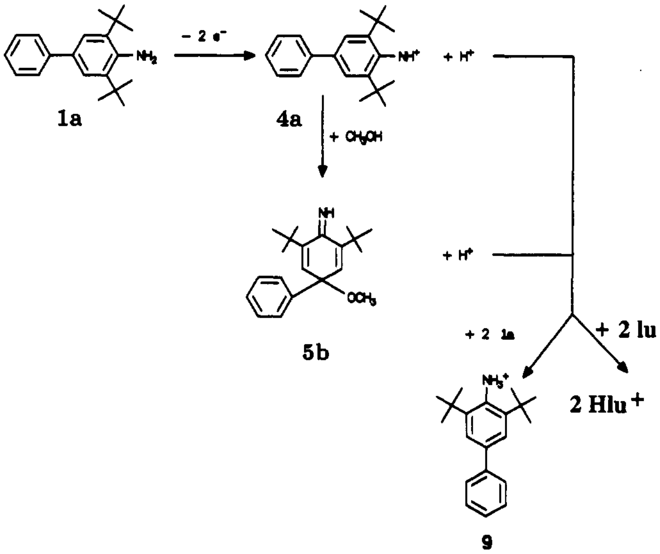
The different behavior of the three anilines may be explained by the increasing stability of the primary two-electron oxidation products **4a–c**: while **4a** immediately reacts with traces of water or other nucleophiles in the solvent, this reaction is slower in the case of **4b**. Finally, **4c** is persistent in the preparative experiments, in accordance with the voltammetric results reported previously.

**Chart I**



5a: R = H, R' = H
b: R = H, R' = $CH_3$
c: R = H, R' = $C_2H_5$
d: R = $OCH_3$, R' = H
e: R = $OCH_3$, R' = $CH_3$
f: R = $OCH_3$, R' = $C_2H_5$

**Scheme II**



*Preparative electrolyses of **1a** and **1b** in the presence of a base and a nucleophile* result in products from the reaction of **4a** or **4b** with the nucleophile (Table I).

The oxygen nucleophiles $H_2O$, $CH_3OH$, and $C_2H_5OH$ react in the position para to the NH group. The corresponding iminoquinols and iminoquinol ethers **5a–f** are formed (Chart I). Two electrons per molecule are transferred as shown by integration of the current over the electrolysis time. In the case of **1a** and water as nucleophile, the influence of the aniline concentration $c^0$ was studied. The yield of **5a** strongly depends on $c^0$. For a relatively high concentration of the aniline (0.04 mol $L^{-1}$) the yield of **5a** is only 18%, and highly colored products are formed that are only sparingly soluble in petroleum ether and were not identified. If the concentration of **1a** is decreased to 0.004 mol $L^{-1}$, the yield increases to 55% and only a minor amount of the side products is found. Thus, presumably, the side reaction is an oligomerization with higher order reaction steps. A similar dependence of the yield of **5d** on the aniline concentration is found for **1b**.

In the case of methanol as nucleophile, the yield of **5b** in the presence of lu is about three times larger than in a solvent without a proton acceptor.[19] This fact is in

---

(18) Hertl, P.; Rieker, A.; Speiser, B. *J. Electroanal. Chem.* **1986**, *200*, 147.

(19) Bracht, J. Dissertation, Universität Tübingen, 1977.

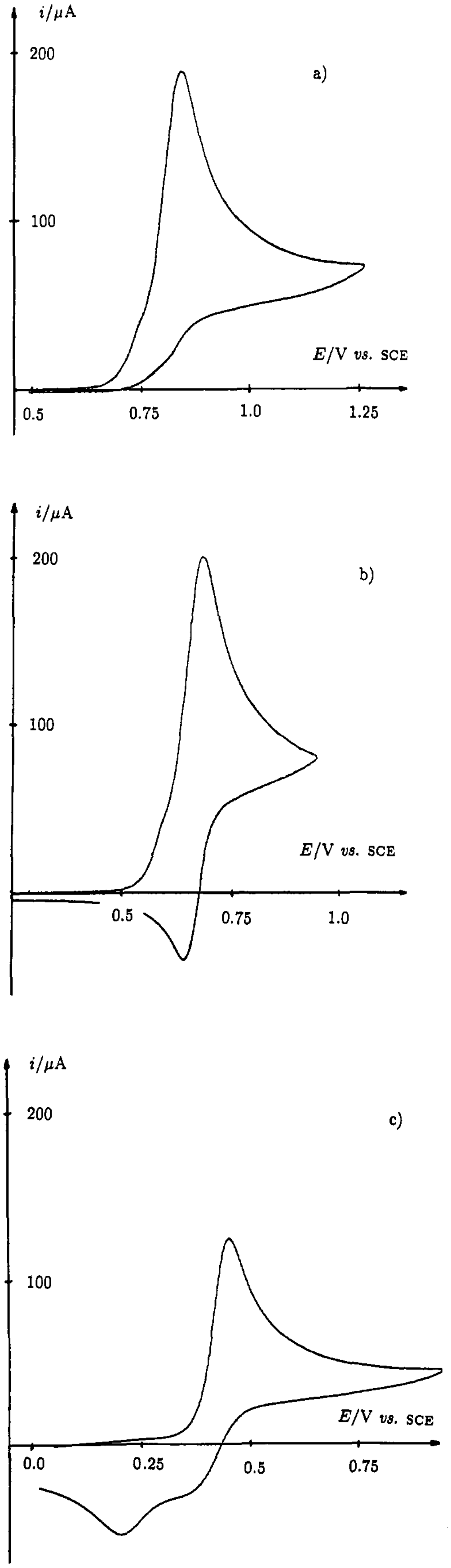
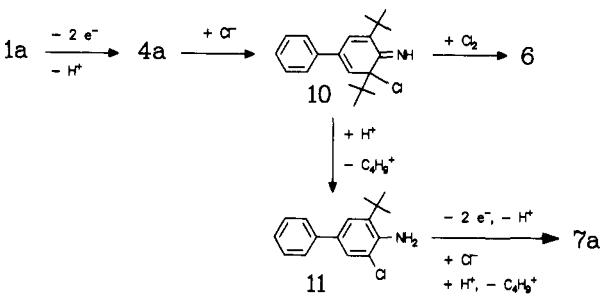


**Figure 1.** Cyclic voltammograms of anilines **1a** (a), **1b** (b), and **1c** (c) in $CH_3CN$ in the presence of lu. Conditions: (a) $c(\textbf{1a}) = 1.27 \times 10^{-3}$ mol $L^{-1}$, $c(lu) = 1.13 \times 10^{-2}$ mol $L^{-1}$, $v = 0.05$ V $s^{-1}$; (b) $c(\textbf{1b}) = 1.44 \times 10^{-3}$ mol $L^{-1}$, $c(lu) = 1.88 \times 10^{-2}$ mol $L^{-1}$, $v = 0.05$ V $s^{-1}$; (c) $c(\textbf{1c}) = 8.81 \times 10^{-4}$ mol $L^{-1}$, $c(lu) = 4.9 \times 10^{-3}$ mol $L^{-1}$, $v = 0.05$ V $s^{-1}$.

### Scheme III



accordance with the reaction mechanism of Scheme II. Two protons are formed during the reaction from one molecule of **1a** and MeOH. If no stronger base is present, two molecules of the starting material are therefore protonated to give anilinium cation **9**. This protonated aniline is not electroactive at the electrode potentials used in this work, as show cyclic voltammograms of **1a** in the presence of perchloric acid.[2] Thus, only one-third of **1a** consumed forms iminoquinol ether **5b**. On the other hand, if lu is added, the protons generated during the oxidation reaction protonate this base. Aniline **1a** is not protonated under these conditions, and the yield of **5b** increases by a factor of 3.

The products of electrogenerated **4a** in the presence of chloride ion are most obviously formed from a common intermediate **10** (Scheme III). This *o*-iminoquinolide chloride is formed by the reaction of **4a** with $Cl^-$. In contrast to the oxygen nucleophiles, $Cl^-$ reacts at the ortho position of the nitrenium ion. The expected chloride **10** may be relatively stable in the presence of the efficient base lu. A potential of +1.0 V vs SCE is high enough[20] to form $Cl_2$ by oxidation of $Cl^-$. By addition of $Cl_2$ to one of the cyclohexadiene double bonds of **10**, trichloride **6** is formed. On the other hand, if $E = +1.0$ V and solid sodium carbonate is used as a base, near the electrode still enough protons may be present to cause acid-catalyzed cleavage of a *tert*-butyl group from **10**. The resulting 3-*tert*-butyl-5-chlorobiphenyl-4-ylamine (**11**) could not be isolated. It is further oxidized in an analogous reaction sequence to the dichloroaniline **7a**. Compound **6** is not found under these conditions. This result leads to the conclusion that the $Cl_2$ addition is slower than the competing cleavage reaction in the presence of protons. The same dichloro product **7a** is found if $E = +0.85$ V. The yield, however, is only 21%. Starting with **1b** only the reaction to **7b** is observed.

If **6** is dissolved in acetone and treated with a solution of $AgClO_4$ in the same solvent, AgCl precipitates. Thus, at least one of the Cl atoms in **6** is fairly labile and cleaved as a $Cl^-$ ion.

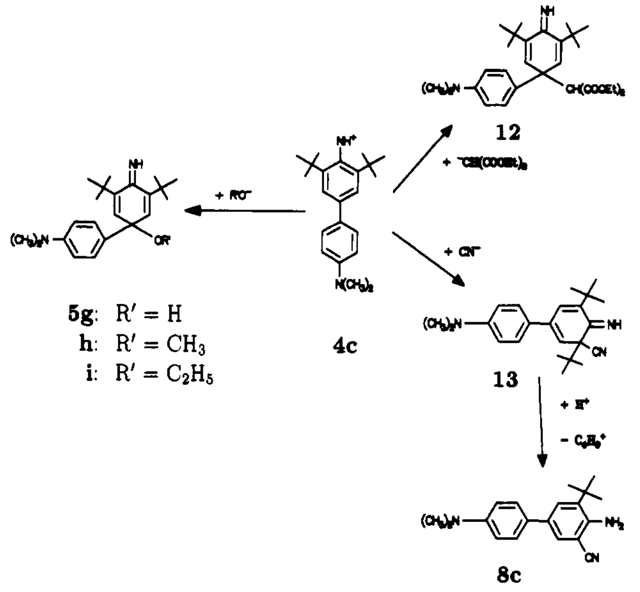
The oxidation of **1a** or **1b** in the presence of base and $Cl^-$ is a process that consumes more charge as the oxidation in the presence of the oxygen nucleophiles, which is in accordance with the previous mechanism: both the formation of $Cl_2$ and the further oxidation of **11** result in an additional flow of electrons.

Cyanide ion did not react with **1a** to give isolable products. To avoid the formation of $(CN)_2$, the potential in these electrolyses was kept at only +0.85 V, 150 mV less

---

(20) Feoktistov, L. G.; Andreev, G. V.; Tomilov, A. P. *Elektrokhimiya* **1988**, *24*, 37–42. A report of $E_{1/2} \approx +0.8$ V vs an Ag/AgCl reference electrode for the oxidation of $Cl^-$ in acetonitrile is given. This value corresponds to ~+0.75 V vs SCE according to the potential difference between these two reference electrodes, see: Bard, A. J.; Faulkner, L. R. *Electrochemical Methods, Fundamentals and Applications*; John Wiley: New York, 1980.

Scheme IV



positive than in most other experiments in this work. In the case of **1b**, a product **8**, similar to **11** in the case of the $Cl^-$ reaction, is formed. No further oxidation of **8** is observed. As the nucleophile $Cl^-$, cyanide obviously prefers to react with the ortho carbon of the nitrenium ion **4b**.

*Preparative electrolyses of **1c** in the presence of lu* yield solutions of **4c**. The nitrenium ion **4c** is stable against the less nucleophilic species used above, as is also shown by the fact that a solution of **4c** can be subjected to moist air without decolorizing. Thus, the solutions were treated with several anionic nucleophiles. Two types of reactions were observed: *nucleophilic attack* gives iminoquinol **5g**, iminoquinol ethers **5h,i** or products **8c**, **12**, and **13** (Scheme IV), and *reduction* of **4c** yields the aniline **1c** ($Ac^-$, $C_6H_5S^-$, and $t$-BuO⁻ as reagents).

Again, the oxygen nucleophiles react in the para position of the NH group. Also diethyl malonate anion, a *carbon nucleophile*, attacks **4c** in the para position, giving **12**. The primary product of the reaction with $CN^-$ was found to be the *o*-quinolide cyano compound **13**. Treatment of **13** with $HBF_4$ yields **8c** under cleavage of the *tert*-butyl group. Transformation to **8c** occurs even with traces of protons, e.g., during registration of a $^{13}C$ NMR spectrum in $CDCl_3$. In the case of the reaction with thiophenolate, diphenyl disulfide could be isolated as a product. Here, and with acetate and *tert*-butylate, unidentified side reactions consume most of the nitrenium ion, and only small quantities of **1c** could be recovered.

In all reactions described here, nucleophilic attack is observed only in the positions ortho or para to the NH group. No reaction at the imino nitrogen or in the aromatic ring bearing the substituent R is found, although considerable delocalization of the positive charge is expected. In fact, this has been proven by the $^1H$ NMR spectrum of **4c**.[4] A possible explanation that no reaction occurs in the second ring is as follows: in the reaction both aromatic systems would be destroyed at least temporarily. This would result in an intermediate or end product of high energy.

Both steric and electronic effects may contribute to the observed regioselectivity of the nucleophilic attack (alkoxy nucleophiles react in the para position of **4** while $Cl^-$ and $CN^-$ form bonds with the ortho carbon atom). It has been shown that the positive charge density in the para position of singlet-state phenoxenium and nitrenium ions is much larger than that in the ortho position.[21] From this point of view, reaction of "hard" nucleophiles ($RO^-$) with the para carbon atom is expected, while "soft" reagents ($CN^-$) should attack in the ortho position. On the other hand, the steric requirements of the *tert*-butyl groups in ortho position and the aryl rings in para position should result in a preferable reaction of *large* nucleophiles with the para carbon atom. *Small* nucleophiles could react in the ortho position, as is observed in the experiments.

From the first argument, the "soft" diethyl malonate anion is expected to form the ortho product. In the experiment, however, the para adduct is found. Thus, in this case the steric effect seems to be predominant.

A similar product spectrum has been observed for the reaction of chemically produced *N*-alkylnitrenium ions.[22]

**Spectroscopic Characterization of the Reaction Products.** $^1H$ NMR, IR, and mass data of the products of nucleophile addition to **4** are given in the experimental part under the heading of the respective compound. $^{13}C$ NMR data are listed in Tables II and III. In the following text, the assignment of signals will be discussed and some common features of the iminoquinolide spectra will be pointed out.

The IR spectra of all iminoquinolide compounds synthesized here show a NH valence vibration at 3400–3300 $cm^{-1}$. A characteristic band appears in the C=N region between 1565 and 1560 $cm^{-1}$ for **5** and **12**, which is shifted to 1585 $cm^{-1}$ in the *o*-quinolide compound **13**. A similar shift was observed when a large number of *o*- and *p*-quinolide derivatives was investigated.[24,25] The IR spectra of the other products are in agreement with the proposed structures.

In all mass spectra of **5** and **12** only molecule ion peaks of small intensity were found. Usually, fragmentation of $CH_3$ and/or *tert*-butyl groups can be observed ($M^+ - 15$, $M^+ - 56/57$). In the case of the chlorinated products **6** and **7** the isotope pattern is in accordance with the presence of three or two Cl atoms in the molecule, respectively.

The proton NMR spectra of the iminoquinolide products **5** and **12** show a single signal for the *tert*-butyl groups at 1.30 ± 0.03 ppm. In no case was a splitting into two peaks observed. Another singlet is found for the vinylic protons at 5.78–6.03 ppm, almost independent of the substituents R and R′ in **5**. In the spectrum of **12** this signal is shifted to 6.68 ppm. This may indicate some interaction of these protons with the carbonyl oxygens of the ethoxycarbonyl groups. The NH proton gives rise to a broad signal around 10 ppm. The signals of protons in the aromatic ring and the substituents show splittings and chemical shifts as expected.

In contrast to these *p*-iminoquinolide compounds, the ortho species **13** is characterized by *two tert*-butyl signals. Also, two doublets correspond to the vinylic protons. Again, the NH signal is broad. It is observed at slightly lower field than that of the para compound. The signals of protons in the aromatic ring and the dimethylamino group are found at usual positions.

As expected for the unsymmetrical structure, the proton NMR spectrum of **6** shows two *tert*-butyl signals. For the *o*-quinolide chloride **14** Crozier and Hewitt[26] observed a

---

(21) Li, Y.; Abramovitch, R. A.; Houk, K. N. *J. Org. Chem.* **1989**, *54*, 2911–2914.

(22) Gassman, P. G.; Campbell, G. A.; Frederick, R. C. *J. Am. Chem. Soc.* **1972**, *94*, 3884–3891. Gassman, P. G.; Campbell, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 3891–3896.

(23) Denivelle, L.; Hedayatullah, M. *C. R. Acad. Sci.* **1961**, *253*, 2711–2713.

(24) Rieker, A.; Rundel, W.; Kessler, H. *Z. Naturforsch.* **1969**, *24b*, 547–562.

(25) Crozier, R. F.; Hewitt, D. G. *Aust. J. Chem.* **1972**, *25*, 183–190.

**Table II. $^{13}$C NMR Spectroscopic Data[a] of Iminoquinolide Products 5, 12, 13, and 15**

| compd | C1 | C2/C6 | C3/C5 | C4 | C7/C9 | C8/C10 |
|---|---|---|---|---|---|---|
| **5a** | 167.0 (t, 8) | 143.0 (m)[b] | 136.1 (d, 165; d, 5) | 71.9 (s) | 34.8 (m) | 30.5 (q, 126; h, 5) |
| **5b**[c] | 167.0 (t, 9) | 147.6 (m) | 135.7 (d, 160; d, 5) | 77.4 (m) | 35.8 (m) | 31.1 (q, 126; h, 5) |
| **5c**[c] | 167.4 (t, 9) | 145.0 (m) | 136.3 (d, 160; d, 5) | 77.9 (s) | 35.7 (m) | 31.1 (q, 126; h, 5) |
| **5d**[c] | 167.7 (t, 8) | 143.1 (m) | 138.2 (d, 160; d, 5) | 71.7 (m) | 35.3 (m) | 31.0 (q, 126; h, 5) |
| **5e** | 166.8 (t, 9) | 146.7 (m) | 134.9 (d, 160; d, 4) | 76.4 (m) | 35.2 (m) | 30.8 (q, 126; h, 5) |
| **5f**[c] | 167.4[d] | 147.4 (m) | 136.4 (d, 160; d, 5) | 76.8[d] | 36.5 (m) | 31.1 (q, 126; h, 5) |
| **5g**[c] | 167.7 (t, 9) | 142.6 (m) | 138.6 (d, 160; d, 5) | 71.6 (m) | 35.6 (m) | 31.0 (q, 126; h, 5) |
| **5h** | 166.9 (t, 9) | 146.8 (m) | 135.1 (d, 165, d, 5) | 76.3 (m) | 35.2 (m) | 30.8 (q, 126; h, 5) |
| **5i** | 167.2 (t, 9) | 146.0 (m) | 136.8 (d, 159; d, 5) | 76.8 (s) | 35.7 (m) | 31.1 (q, 126; h, 5) |
| **12** | 166.5 (t, 10) | 144.2 (m) | 135.2 (d, 161; m) | 46.8 (m) | 35.0 (m) | 30.5 (q, 126; h, 5) |
| **13** | 169.6 (m) | C2, 61.0 (m) | C5,[e] 129.3 (d, 158; d, 9) | 137.3[d] | C7, 36.1 (m)[b] | C8, 30.2 (q, 126; h, 5)[b] |
|  |  | C6, 146.9 (m) |  |  | C9, 31.1 (m)[b] | C10, 25.3 (q, 126; h, 4–5)[b] |
| **15a**[c] | 166.6 (t, 9) | 144.0 (m)[b] | 135.8 (d, 156; d, 5) | 71.2 (s) | 35.3 (m) | 30.8 (q, 126; h, 5) |
| **15b**[c] | 166.0 (t, 9) | 142.6 (m) | 136.2 (d, 160; d, 5) | 73.3 (s) | 35.3 (m) | 30.8 (q, 126; h, 5) |
| **15c**[c] | 167.7[d] | 141.4 (m) | 136.7 (d, 161; m) | 71.6 (s) | 35.2 (m) | 30.9 (q, 126; h, 5) |
| **15d**[c] | 166.3 (t, 9) | 142.5 (m) | 136.7 (d, 160; d, 6) | 73.3 (s) | 35.3 (m) | 30.9 (q, 126; h, 5) |
| **15e**[c] | 167.5 (t, 9) | 143.0 (m)[b] | 138.0 (d, 160; d, 5) | 71.8 (s) | 35.2 (m) | 30.9 (q, 126; h, 5) |

| compd | C11 | C12/C16 | C13/C15 | C14 | substituents |
|---|---|---|---|---|---|
| **5a** | 143.8 (m)[b] | 125.0 (d, 160; m) | 128.4 (d, 154; m) | 127.2 (d, 160; t, 7) |  |
| **5b**[c] | 143.9 (m) | 126.4 (d, 159; m) | 129.1 (d, 166; m) | 128 (d, 157; t, 7) | $\mathrm{O}\mathit{C}\mathrm{H_3}$: 51.6 (q, 141) |
| **5c**[c] | 144.2 (m) | 126.2 (d, 159; m) | 128.8 (d, 160; m) | 127.8 (d, 160; t, ≈ 10) | $\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$: 59.4 (t, 141; q, 4.6)<br>$\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$: 16.7 (q, 126; t, 3) |
| **5d**[c] | 137.2 (m) | 127.2 (d, 159; d, 6) | 114.4 (d, 161; d, 5) | 159.7 (m) | $\mathrm{O}\mathit{C}\mathrm{H_3}$: 55.5 (q, 144) |
| **5e** | 134.7 (t, 6) | 126.7 (d, 160; d, 7) | 113.8 (d, 160; d, 5) | 158.9 (m) | $\mathrm{ArO}\mathit{C}\mathrm{H_3}$: 55.2 (q, 144)<br>$\mathrm{O}\mathit{C}\mathrm{H_3}$: 51.3 (q, 142) |
| **5f**[c] | 135.8 (m) | 127.5 (d, 160; d, 7) | 114.4 (d, 159; d, 4.6) | 159.8[d] | $\mathrm{ArO}\mathit{C}\mathrm{H_3}$: 55.4 (q, 144)<br>$\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$: 59.5 (t, 143; m)<br>$\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$: 16.5 (q, 125; m) |
| **5g**[c] | 132.6 (m) | 126.8 (d, 157; d, 7) | 113.2 (d, 157; d, 6) | 150.6 (m) | $\mathrm{N(}\mathit{C}\mathrm{H_3)_2}$: 40.6 (q, 135; q, 4) |
| **5h** | 130.0 (m) | 126.3 (d, 158; d, 6.9) | 112.4 (d, 158; d, 5.7) | 149.7[d] | $\mathrm{N(}\mathit{C}\mathrm{H_3)_2}$: 40.5 (q, 135; q, 4.6)<br>$\mathrm{O}\mathit{C}\mathrm{H_3}$: 51.3 (q, 141) |
| **5i** | 131.1[d] | 127.1 (d, 158; d, 6.9) | 113.1 (d, 157; d, 5) | 151.0 (m) | $\mathrm{N(}\mathit{C}\mathrm{H_3)_2}$: 40.6 (q, 135; q, 4)<br>$\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$: 59.4 (t, 141; q, 4.6)<br>$\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$: 16.6 (q, 126; m) |
| **12** | 129.9 (m) | 126.5 (d, 154; d, 7) | 112.5 (d, 157; d, 5) | 149.0 (m) | $\mathrm{N(}\mathit{C}\mathrm{H_3)_2}$: 40.2 (q, 135; d, 5)<br>$\mathit{C}\mathrm{H(COOEt)_2}$: 60.2 (d, 133; m)<br>$\mathrm{CH(}\mathit{C}\mathrm{OOEt)_2}$: 166.8 (m)<br>$\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$: 61.0 (t, 135; m)<br>$\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$: 13.9 (q, 126; m) |
| **13** | 131.3 (m) | 126.6 (d, 156; d, 7) | 112.3 (d, 158; d, 6) | 150.6 (m) | $\mathrm{N(}\mathit{C}\mathrm{H_3)_2}$: 41.7 (q ≈ 140; q, ≈4)<br>$\mathit{C}\mathrm{N}$: 119.4[d] |
| **15a**[c] | 142.3 (m)[b] | 136.3[b]<br>127.9 (d, 163; d, 8) | 132.5 (d, 156; m)<br>126.6 (d, 160; m) | 126.6 (d, 160; m)[b] | $-\mathit{C}\mathrm{H_3}$: 20.6 (q, 127; d, 4) |
| **15b**[c] | 140.6[d] | 137.4 (m) | 131.5 (d, 158; m) | 127.2 (d, 159) | $-\mathit{C}\mathrm{H_3}$: 24.3 (q, 125) |
| **15c**[c] | 111.9[d] | 159.4 (m) | 105.7 (d, 162; d, 7) | 129.1 (d, 162) | $-\mathrm{O}\mathit{C}\mathrm{H_3}$: 56.7 (q, 165) |
| **15d**[c] | 137.7[d] | 137.4[d] | 132.4 (d, 153; m) | 136.3[d] | $-\mathit{C}\mathrm{H_3}$ (ortho): 24.2 (q, 129; m)<br>$-\mathit{C}\mathrm{H_3}$ (para): 20.5 (q, 126; m) |
| **15e**[c] | 142.2[c,d] | 125.9 (d, 159; d, 6) | 129.4 (d, 156; m) | 136.8 (m) | $-\mathit{C}\mathrm{H_3}$: 21.0 (q, 129; t, 5) |

[a] In ppm, multiplicity and $J_{\mathrm{C\text{-}H}}$ in Hz given in parentheses; recorded in $CDCl_3$, except where otherwise noted; numbering of C atoms is given in Scheme V, it has been chosen to facilitate comparison to cyclohexadienone systems and does not conform to IUPAC rules. [b] Assignment questionable. [c] Recorded in acetone–$d_6$. [d] Unresolved peak, multiplicity not determined. [e] Assignment impossible due to overlapping.

**Table III. $^{13}$C NMR Spectroscopic Data[a] of Ortho Substitution Products 8**

| compd | C1 | C2 | C3 | C4 | C5 | C6 | C7 | C8 |
|---|---|---|---|---|---|---|---|---|
| **8b**[b] | 148.3 (m) | 99.2 (m) | 130.8 (d, d)[c,d] | 131.1 (m) | 128.7 (d,d)[c,d] | 135.5 (m) | 35.4 (m) | 29.7 (q, 127; m) |
| 8c | 146.1 (t, 8) | 98.5 (m) | 127.5 (d, m)[c,d] | *e* | 127.0 (d, m)[c,d] | 134.2 (m) | 34.5 (m) | 29.6 (q, 126; h, 5) |

| compd | C9 | C11 | C12/C16 | C13/C15 | C14 | substituents |
|---|---|---|---|---|---|---|
| **8b**[b] | 119.1[f] | 133.4[f] | 128.3 (d,d)[d] | 115.4 (d, 160; d, 4.6) | 160.3 (m) | $\mathrm{O}\mathit{C}\mathrm{H_3}$: 55.9 (q, 140) |
| 8c | 118.6 (d, 6) | 128.4 (m) | 129.8 (d, 156; d, 7) | 113.0 (d, 158; d, 6) | 149.3 (m) | $\mathrm{N(}\mathit{C}\mathrm{H_3)_2}$: 40.7 (q, 137; m) |

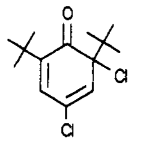
[a] In ppm; recorded in $CDCl_3$, except where otherwise noted; numbering of C atoms according to Scheme V. [b] Recorded in acetone-$d_6$. [c] Assignment questionable. [d] Coupling constants not determined due to overlapping. [e] Not identified due to overlapping. [f] Unresolved peak, multiplicity not determined.

chemical shift difference of 0.15 ppm for the two *tert*-butyl signals in very good accordance with the value of 0.16 ppm found for **6**. The assignment of the high-field signal to the sp$^3$ carbon follows in analogy to ref 25. The signal of the vinylic proton is in the range given previously. The proton with two vicinal and one geminal Cl atom as neighbors absorbs at 5.17 ppm.

It is well-known that Cl shifts the signals of $\alpha$-protons

---

(26) Pretsch, E.; Clerc, T.; Seibl, J.; Simon, W. *Tabellen zur Strukturaufklärung organischer Verbindungen mit spektroskopischen Methoden*; Springer: Berlin, 1976.



**14**

downfield by ~0.5 ppm.[27] Taking as a reference the resonance of the proton at the central carbon atom in isopropyl chloride at 4.14 ppm and considering two such vicinal Cl atoms, a chemical shift of ~5.14 ppm is calculated in good accordance with the value found for **6**. In a series of polychlorocyclohexenones, Hartshorn et al. found shift values of 4.71–5.07 ppm for the signals of protons in similar chemical environments.[28,29] The exact stereochemistry of **6** was not determined.

For both dichloroanilines **7** the signal of the *tert*-butyl groups has disappeared, as expected. The broad resonance of the amino proton is no longer detectable in the case of **7b** in $CD_3OD$ due to exchange of the protons. The *o*-cyanoanilines **8**, on the other hand, are characterized by a *tert*-butyl signal corresponding to nine protons and, in particular, an AB system corresponding to the two aromatic protons in the ring bearing the *tert*-butyl, amino, and cyano functions. In the case of **8c** the corresponding quartet is superimposed onto the $A_2B_2$ quartet of the second aromatic ring.

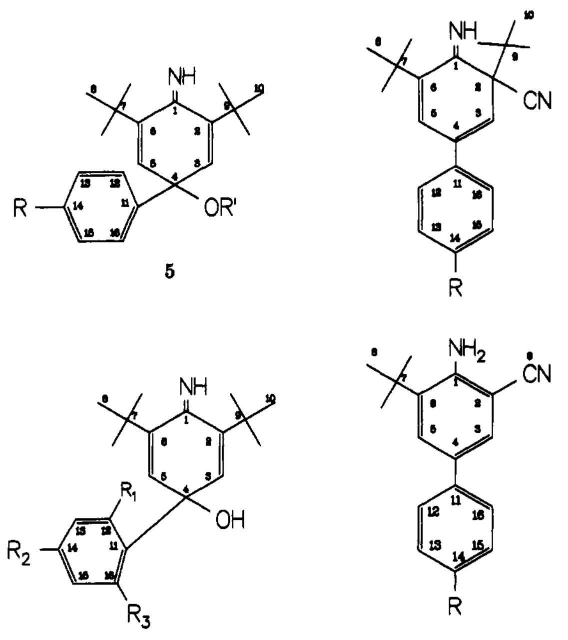
Table II lists the $^{13}C$ NMR spectroscopic data of the iminoquinolide products **5**, **12**, and **13** synthesized in this work and iminoquinols **15** whose synthesis has already been reported.[23]

The signals were assigned by comparison to the values calculated from an increment system[27] and consideration of the splitting pattern in coupled spectra (in Table II given by the multiplicity and the coupling constant, $J_{C-H}$, if appropriate).

Carbon atom C1 of the C=N group absorbs at 166.0–167.7 ppm throughout in the *p*-iminoquinolide compounds. In all cases, except for **5f** and **15c**, a triplet is observed due to coupling with the protons in the meta position. The resonance of C1 is shifted to lower field in the case of the ortho product **13** by approximately 3 ppm, where a multiplet is found. A similar shift has been observed in the case of *N*-acyliminoquinolide derivatives[30] and *o*- and *p*-quinolide compounds,[31] where, however, the effect is much stronger. The carbon atoms C2 and C6 do not show separate signals in the para compounds. The same is true for C3 and C5. The variations of the chemical shifts with the substituents in both cases are very small. In the ortho product **13** carbons C2 and C6 give two separate peaks each, as expected. Due to overlapping only one signal is observed for C3 and C5. Coupling of C2 and C6 with the NH proton (in **5**, **12**, **13**, and **15**) or of C3 and C5 with the OH proton (in **5a,d,g** or **15**) was not found.

The signals of C2/C6 and C11 both form hardly resolved multiplets. The assignment was made after inspection of the peak shape (C2/C6 couple with 9 protons in the *tert*-butyl groups, resulting in a broader signal, while C11 couples with the protons at C3/C5 and C13/C15 to give a more narrow peak) and on the basis of the signal half-width and intensity (2 atoms C2/C6 vs 1 atom C11).

**Scheme V**



**5**

**15** a: $R_1 = H, R_2 = H, R_3 = CH_3$
b: $R_1 = CH_3, R_2 = H, R_3 = CH_3$
c: $R_1 = OCH_3, R_2 = H, R_3 = OCH_3$
d: $R_1 = R_2 = R_3 = CH_3$
e: $R_1 = H, R_2 = CH_3, R_3 = H$

For C4 small differences in chemical shift are found in iminoquinolides **5** and **15**, having an oxygen atom bound to the carbon. The iminoquinols **5a,d,g** and **15** show a signal slightly upfield compared to the corresponding peak in the iminoquinol ethers. In **12**, where another carbon is bound to C4, the signal appears at much higher field. The carbon at the quinol center (C2) in **13**, bearing two carbon substituents (*tert*-butyl and CN), absorbs at 61.0 ppm. Compared to the *p*-iminoquinolide compound **12**, the upfield shift is similar to that found for quinol derivatives.[32] For all *p*-iminoquinolide products **5**, **12**, and **15** similar chemical shifts were found for the carbon atoms in the *tert*-butyl groups (C7–C10). In the case of **13**, two peaks each are recorded, confirming the unsymmetrical structure of the ortho compound. The signal of the *tert*-butyl group at the $sp^3$ carbon (C10) is shifted upfield.

For the 6-*tert*-butyl-2-cyanoanilines **8** (see Table III) the chemical shifts for carbon atoms in the attached aryl system are assigned by comparison to standard increment values.[27] Also, the other signals can be assigned in most cases from their chemical shifts and multiplicities. Only the peaks of C3 and C5 could not be attributed to their respective carbon atoms.

Although the iminoquinolide compounds investigated here are expected to be asymmetrical due to the bent =NH group, splitting of the signals (C2/C6, C3/C5, *tert*-butyl) could not be observed in the NMR spectra. In the case of the persistent nitrenium ion **4c**, on the other hand, two *tert*-butyl signals were found in the $^1H$-NMR spectrum.[4] Obviously, fast exchange reactions of the NH proton occur in the iminoquinolides and only the time averaged signal is found.

Only one example of an *o*-iminoquinolide compound could be investigated here. Comparing the spectra to those

---

(27) Hartshorn, M. P.; Martyn, R. J.; Vaughan, J. *Aust. J. Chem.* **1984**, *37*, 795–808.

(28) Hartshorn, M. P.; Hayman, K. A.; Martyn, R. J.; Robinson, W. T.; Vaughan, J.; Wells, B. A.; Wright, G. J. *Aust. J. Chem.* **1990**, *43*, 1729–1744.

(29) Bracht, J.; Rieker, A. *Synthesis* **1977**, 708.

(30) Perst, H. Private Communication. Eckhardt, H. Thesis Universität Marburg, 1980.

(31) Rieker, A. In *Methoden der organischen Chemie*, Grundmann, C., Ed. Houben-Weyl, Thieme: Stuttgart, 1979; Vol. VII/3b, Chinone, Part II, p 765.

(32) Rieker, A.; Berger, S. *Org. Magn. Reson.* **1972**, *4*, 857–873.

of the para analogues, we observe similar effects as have been reported for quinols and their derivatives.[25] The extent of the signal shifts, however, is smaller.

## Conclusion

Nitrenium ions of type 4 may be produced by anodic oxidation of the corresponding anilines 1 in acetonitrile in the presence of a base. The reactivity of these species toward nucleophiles decreases with increasing electron donating power of the substituent R. The main reaction of the ions 4 observed is nucleophilic attack at the position para or, in a few cases, ortho to the NH group. Only the most stabilized nitrenium ion in the series, 4c, undergoes in some cases electron-transfer reactions to an appreciable amount, resulting in the formation of aniline 1c. It can easily be concluded from the NMR spectra if ortho or para substitution has occurred.

## Experimental Part

**Cyclic voltammetry** was performed in approximately $10^{-3}$ M solutions of the anilines in acetonitrile/0.1 M $NEt_4ClO_4$ at a platinum disk electrode (electroactive area $A = 0.29$ cm$^2$) by means of a Princeton Applied Research PAR 170 Electrochemistry System. Solutions were deaerated with pure nitrogen (bubbling for 10 min) prior to the experiments. The counter electrode was separated by a frit; the reference electrode was an SCE with a Luggin capillary.

**Preparative Electrolyses.** Species 4 were generated by anodic oxidation of the corresponding anilines in acetonitrile at platinum electrodes in the presence of a base (2,6-lutidine (lu) or suspended $Na_2CO_3$). All preparative electrolyses were carried out at +1.0 V vs SCE with the exception of the experiments where $CN^-$ was added to **4a** and **4b** as well as some electrolyses in the presence of $Cl^-$ as a nucleophile, where a potential of +0.85 V vs SCE was used, see Table I. The cell consisted of a glass beaker with a magnetic stirrer, two cylindrical Pt/Ir (90/10) net electrodes (Degussa) separated by a ceramic diaphragm (Haldenwanger, ABS) and a Haber–Luggin capillary. The potential was controlled with a Wenking HP72 or a Princeton Applied Research PAR 373 potentiostat. The current through the working and counter electrodes was integrated with a Wenking SSI 70. Approximately 0.8 mmol of the aniline and 1.0 g (10 mmol) of 2,6-lutidine were dissolved in 200 mL of the electrolyte and electrolyzed at the potential indicated.

In the case of **4a** and **4b** the nucleophiles were present during the electrolysis. Chloride ion was added in the form of tetraethylammonium chloride (from $NEt_4OH$ solution by neutralization with aqueous HCl, recrystallization from water, and subsequent drying in vacuo for 60 h), while tetrabutylammonium cyanide (Fluka) was used as a source of $CN^-$. The electrolyses were continued until the current had reduced to the background value. The solvent was evaporated. The residue was extracted with petroleum ether from which the products were isolated and purified as described in the following text.

In the case of **4c**, the nitrenium ion solution was treated with a solution of the nucleophile. Usually, the deep purple color of the solution disappeared immediately. The solvent was evaporated and the residue extracted with petroleum ether. The crude products were recyrstallized.

Those products that have been described previously (**5a,b,d,g**)[6,19,23] were identified by TLC, with comparison of the melting point with that of an authentic sample as well as $^1$H NMR spectroscopy. For the other products details are given in the following text. Samples of iminoquinols **15**[23] were recrystallized and used for $^{13}$C NMR spectroscopic experiments.

**2,6-Di-*tert*-butyl-4-ethoxy-4-phenyl-2,5-cyclohexadien-1-imine (5c)** was recrystallized from petroleum ether (60/90) (yield, 58%): mp 61 °C; MS *m/z* 325 (1, M$^+$), 296 (5), 280 (100), 268 (25), 248 (26); $^1$H NMR (90 MHz, $CCl_4$) $\delta$ 1.20 (t, 3 H, $J$ = 7 Hz, $OCH_2CH_3$), 1.28 (s, 18 H, *tert*-butyl), 3.43 (q, 2 H, $J$ = 7 Hz, $OCH_2CH_3$), 6.03 (s, 2 H, vinylic protons), 7.2–7.4 (m, 5 H, aromatic protons), 10.09 (s, 1 H, NH); IR (KBr) 3390 (NH), 2950 (CH), 1570 (C═N), 1070 (CO) cm$^{-1}$. Anal. Calcd for $C_{22}H_{31}NO$: C, 81.18; H, 9.60; N, 4.30. Found: C, 81.07; H, 9.78; N, 4.32.

**2,6-Di-*tert*-butyl-4-methoxy-4-(4-methoxyphenyl)-2,5-cyclohexadien-1-imine (5e)** was recrystallized from petroleum ether (60/90) as colorless crystals (yield, 73%): mp 104 °C; MS *m/z* 341 (3, M$^+$), 326 (4), 310 (35), 284 (100); $^1$H NMR (90 MHz, $CCl_4$) $\delta$ 1.30 (s, 18 H, *tert*-butyl), 3.21 (s, 3 H, $OCH_3$), 3.71 (s, 3 H, $OCH_3$), 5.78 (s, 2 H, vinylic protons), 6.95 (q, $A_2B_2$, $J$ = 9 Hz, aromatic protons), 10.10 (s, broad, 1 H, NH); IR (KBr) 3400–3300 (NH), 2940 (CH), 1580–1565 (C═N), 1250 (CO), 1078 (CO) cm$^{-1}$. Anal. Calcd for $C_{22}H_{31}NO_2$: C, 77.38; H, 9.15; N, 4.10. Found: C, 77.41; H, 9.15; N, 3.99.

**2,6-Di-*tert*-butyl-4-ethoxy-4-(4-methoxyphenyl)-2,5-cyclohexadien-1-imine (5f)** was recrystallized from petroleum ether (60/90) (yield, 77%): mp 97 °C; MS *m/z* 355 (0.5, M$^+$), 311 (4), 298 (10), 261 (39), 246 (100); $^1$H NMR (90 MHz, $CCl_4$) $\delta$ 1.24 (t, 3 H, $J$ = 7 Hz, $OCH_2CH_3$), 1.32 (s, 18 H, *tert*-butyl), 3.41 (q, 2 H, $J$ = 7 Hz, $OCH_2CH_3$), 3.73 (s, 3 H, $OCH_3$), 6.00 (s, 2 H, vinylic protons), 6.98 (q, $A_2B_2$, $J$ = 9 Hz, aromatic protons), 10.03 (s, 1 H, NH); IR (KBr) 3350 (NH), 2940 (CH), 1578/1565 (C═N), 1255 (CO), 1070 (CO) cm$^{-1}$. Anal. Calcd for $C_{23}H_{33}NO_2$: C, 77.70; H, 9.36; N, 3.94. Found: C, 77.93; H, 9.50; N, 3.76.

**2,6-Di-*tert*-butyl-4-[4-(dimethylamino)phenyl]-4-methoxy-2,5-cyclohexadien-1-imine (5h)** was recrystallized from petroleum ether (60/90) (yield, 74%): mp 134–135 °C; MS *m/z* 354 (19, M$^+$), 324 (37), 323 (27), 297 (100), 241 (47); $^1$H NMR (90 MHz, $CCl_4$) $\delta$ 1.30 (s, 18 H, *tert*-butyl), 2.90 (s, 6 H, $(CH_3)_2N$), 3.21 (s, 3 H, $OCH_3$), 5.97 (s, 2 H, vinylic protons), 6.80 (q, $A_2B_2$, $J$ = 9 Hz, aromatic protons), 10.00 (s, 1 H, NH); IR (KBr) 3380 (NH), 2920 (CH), 1565 (C═N), 1068 (CO) cm$^{-1}$. Anal. Calcd for $C_{23}H_{34}N_2O$: C, 77.92; H, 9.67; N, 7.90. Found: C, 78.18; H, 9.83; N, 8.01.

**2,6-Di-*tert*-butyl-4-[4-(dimethylamino)phenyl]-4-ethoxy-2,5-cyclohexadien-1-imine (5i)** was recrystallized from petroleum ether (60/90) (yield, 75%): mp 124 °C; MS *m/z* 368 (11, M$^+$), 324 (76), 311 (100), 255 (43); $^1$H NMR (90 MHz, $CCl_4$) $\delta$ 1.21 (t, 3 H, $J$ = 7 Hz, $OCH_2CH_3$), 1.33 (s, 18 H, *tert*-butyl), 2.89 (s, 6 H, $(CH_3)_2N$), 3.36 (q, 2 H, $OCH_2CH_3$), 5.97 (s, 2 H, vinylic protons), 6.80 (q, $A_2B_2$, $J$ = 9 Hz, aromatic protons), 9.95 (s, 1 H, NH); IR (KBr) 3360 (NH), 2940 (CH), 1560 (C═N), 1068 (CO) cm$^{-1}$. Anal. Calcd for $C_{24}H_{36}N_2O$: C, 78.21; H, 9.85; N, 7.60. Found: C, 78.07; H, 9.67; N, 7.47.

**2,6-Di-*tert*-butyl-4-phenyl-4,5,6-trichloro-2-cyclohexen-1-imine (6)** was recrystallized from petroleum ether (30/50) (yield, 32%): mp 140 °C dec; MS *m/z* 387 (0.2), 385 (0.2) (peaks at 391 and 389 are expected to be too small and could not be observed), 354 (0.2), 352 (1.5), 350 (2.3), 326 (4.8), 316 (2.4), 314 (6.9), 295 (10.6), 293 (15.6), 278 (19), 258 (22), 236 (100); $^1$H NMR (90 MHz, $CCl_4$) $\delta$ 1.20 (s, 9 H, *tert*-butyl), 1.36 (s, 9 H, *tert*-butyl), 5.17 (s, 1 H, CHCl), 6.30 (s, 1 H, vinylic proton), 7.3–7.8 (m, 5 H, aromatic protons), 11.50 (s, broad, 1 H, NH); IR (KBr) 3500 (NH), 3000 (CH) cm$^{-1}$. Anal. Calcd for $C_{20}H_{28}Cl_3N$: C, 62.11; H, 6.78; Cl, 27.50; N, 3.62. Found: C, 62.27; H, 6.92; Cl, 27.43; N, 3.65.

**3,5-Dichlorobiphenyl-4-ylamine (7a)** was recrystallized from methanol: mp 101 °C; MS *m/z* 241 (13), 239 (72), 237 (100), 203 (3), 201 (9), 167 (21); $^1$H NMR (90 MHz, $CCl_4$) $\delta$ 4.43 (s, broad, 2 H, $NH_2$), 7.39 (m, 7H, aromatic protons); IR (KBr) 3280 (NH) cm$^{-1}$. Anal. Calcd for $C_{12}H_9Cl_2N$: C, 60.53; H, 3.81; Cl, 29.78; N, 5.88. Found: C, 60.37; H, 3.73; Cl, 29.59; N, 5.76.

**3,5-Dichloro-4′-methoxybiphenyl-4-ylamine (7b)** crystallizes from methanol in long colorless needles of mp 102 °C; MS *m/z* 271 (13), 269 (66), 267 (100), 256 (9), 254 (18), 252 (70), 228 (4), 226 (20), 224 (30); $^1$H NMR (90 MHz, $CCl_4$) $\delta$ 3.78 (s, 3 H, $OCH_3$), 4.37 (s, broad, 2 H, $NH_2$, disappears in $CD_3OD$), 7.09 (q, $A_2B_2$, $J$ = 9 Hz) and 7.39 (s) (aromatic protons); IR (KBr) 3480/3390 (2 sharp bands, NH), 1250 (CO) cm$^{-1}$. Anal. Calcd for $C_{13}H_{11}Cl_2NO$: C, 58.23; H, 4.13; Cl, 26.44; N, 5.22. Found: C, 58.38; H, 4.27; Cl, 26.31; N, 5.20.

**4-Amino-5-*tert*-butyl-4′-methoxybiphenyl-3-carbonitrile (8b)** was isolated by preparative TLC on silica gel with petroleum ether/acetone (9:1) and recrystallized from petroleum ether (30/50): mp 78 °C; MS *m/z* 280 (100, M$^+$), 265 (80); $^1$H NMR (90 MHz, $CDCl_3$) $\delta$ 1.47 (s, 9 H, *tert*-butyl), 3.85 (s, 3 H, $OCH_3$), 4.66 (s, broad, 2 H, $NH_2$), 7.19 (q, $A_2B_2$, $J$ = 9 Hz), 7.53 (q, AB, $J$ = 2 Hz) (aromatic protons); IR (KBr) 3505/3415 (NH), 2205 (CN), 1245 (CO) cm$^{-1}$. Anal. Calcd for $C_{18}H_{20}N_2O$: C, 77.11; H, 7.19; N, 9.99. Found: C, 76.95; H, 7.31; N, 10.15.

**4-Amino-5-*tert*-butyl-4'-(dimethylamino)biphenyl-3-carbonitrile (8c)** was prepared from 0.17 g (0.49 mmol) of 13 in 25 mL of $CH_3CN$ by addition of 1 mL of $HBF_4$ (40% in ether). After being stirred for 45 min, the solution was treated with lu until an aqueous extract was no longer acidic. The solvent was evaporated, and the residue was several times extracted with ether. The resulting colorless material was recyrstallized from methanol and yielded 70 mg (51%) of **8c**: mp 137–138 °C; MS *m/z* 293 (100, $M^+$), 278 (28), 263 (10); $^1H$ NMR (90 MHz, $CCl_4$) $\delta$ 1.44 (s, 9 H, *tert*-butyl), 2.95 (s, 6 H, $N(CH_3)_2$), 4.49 (s, 2 H, $NH_2$), 6.5–7.6 (m, 6 H, aromatic protons); IR (KBr) 3470/3390 (NH), 2900 (CH), 2205 (CN). Anal. Calcd for $C_{19}H_{23}N_3$: C, 77.78; H, 7.90; N, 14.32. Found: C, 77.61; H, 7.71; N, 14.02.

**Diethyl 2-[3,5-Di-*tert*-butyl-1-[4-(dimethylamino)-phenyl]-4-imino-2,5-cyclohexadien-1-yl]malonate (12).** A 2.55-g (16-mmol) portion of diethyl malonate was treated with 0.12 g (5.2 mmol) of Na dissolved in 20 mL of EtOH. The resulting solution was added to a solution of **4c** (from anodic oxidation of 0.28 g (0.86 mmol) of aniline **1c**) in acetonitrile. After immediate decolorization, the excess of diethylmalonate was evaporated at 100 °C (0.1 Torr). The product **12** was isolated as an oil (yield, 93%): MS *m/z* 482 (6, $M^+$), 426 (13), 324 (100), 309 (44), 173 (68); $^1H$ NMR (90 MHz, $CDCl_3$), $\delta$ 1.13 (t, 6 H, $J = 7$ Hz, $OCH_2CH_3$), 1.31 (s, 18 H, *tert*-butyl), 2.89 (s, 6 H, $N(CH_3)_2$), 4.02 (q, $J = 7$ Hz, $OCH_2CH_3$), 4.17 (s, $CH(COOEt)_2$; the integration of the signals at 4.02 and 4.17 corresponds to 5 H), 6.68 (s, vinylic protons), 6.84 (q, $A_2B_2$, $J = 9$ Hz, aromatic protons; the integration of the signals between 6.56 and 7.11 corresponds to 6 H), a signal for the NH proton was not found, in $C_6D_6$ it was detected at 9.98 (s, broad, 1H); IR (KBr) 3400 (NH), 2960 (CH), 1760/1735 (C=O), 1565 (C=N) $cm^{-1}$. Anal. Calcd for $C_{29}H_{42}N_2O_4$: C, 72.17; H, 8.77; N, 5.80. Found: C, 71.95; H, 8.61; N, 5.72.

**1,5-Di-*tert*-butyl-3-[4-(dimethylamino)phenyl]-6-imino-2,4-cyclohexadiene-1-carbonitrile (13)** was obtained after addition of a 7% excess of $NBu_4CN$ to the electrogenerated solution of **4c** (from 0.27 g (0.83 mmol) of **1c**). It was recrystallized from petroleum ether (30/50), giving yellow crystals (yield, 64%): mp 98 °C dec; MS *m/z* 349 (1, $M^+$), 324 (2), 293 (100), 278 (36); $^1H$ NMR (90 MHz, $CCl_4$) $\delta$ 1.06 (s, 9 H, *tert*-butyl), 1.33 (s, 9 H, *tert*-butyl), 2.99 (s, 6 H, $N(CH_3)_2$), 5.97 (d, 1 H, $J = 2$ Hz), 6.60 (d, $J = 2$ Hz, vinylic protons), 6.91 (q, $A_2B_2$, $J = 9$ Hz, aromatic protons, the integration of the signals between 6.50 and 7.50 corresponds to 5 H), 10.69 (s, broad, 1 H, NH); IR (KBr) 3390 (NH), 2890 (CH), 2225 (CN), 1585/1525 (C=N) $cm^{-1}$. Anal. Calcd for $C_{23}H_{31}N_3$: C, 79.04; H, 8.94; N, 12.02. Found: C, 79.25; H, 9.12; N, 12.23.

**Reaction of 4c with Thiophenolate Ion.** To a solution of cation **4c** (derived from 0.28 g (0.86 mmol) of **1c**) in acetonitrile were added 1 g of powdered $Na_2CO_3$ and 1 g (9.0 mmol) of thiophenol. From the resulting colorless solution the solvent was evaporated. The resulting oil was separated by preparative TLC on silica gel (petroleum ether/acetone (5:2)) to give 60 mg (34%) of diphenyl disulfide and 45 mg (17%) of aniline **1c**.

**Reaction of 4c with Acetate and *tert*-Butylate Ion.** A solution of cation **4c** in acetonitrile was treated with an excess of sodium acetate or KO-*t*Bu until decolorization occurred (24 h under reflux and 15 min at room temperature, respectively). From the reaction mixtures only small amounts of **1c** could be isolated.

**Acknowledgment.** We thank the Fonds der Chemischen Industrie and the Land Baden-Württemberg for financial support through fellowships.

**Registry No.** **1a**, 65624-10-4; **1b**, 86385-58-2; **1c**, 86385-59-3; **5a**, 65624-04-6; **5b**, 134006-25-0; **5c**, 134006-26-1; **5d**, 86385-64-0; **5e**, 134006-27-2; **5f**, 134006-28-3; **5g**, 86385-65-1; **5h**, 134006-29-4; **5i**, 134006-30-7; **6**, 134006-31-8; **7a**, 134006-32-9; **7b**, 134054-76-5; **8b**, 134006-33-0; **8c**, 134006-34-1; **12**, 134006-35-2; **13**, 134006-36-3; **15a**, 65624-05-7; **15b**, 65624-06-8; **15c**, 65624-08-0; **15d**, 65624-07-9; **15e**, 134006-37-4.

---

# Positional Reactivity of Dibenzofuran in Electrophilic Substitutions

Takashi Keumi,* Naoto Tomioka, Kozo Hamanaka, Hirohito Kakihara, Masahiko Fukushima,
Toshio Morita, and Hidehiko Kitajima

*Department of Applied Chemistry and Biotechnology, Faculty of Engineering, Fukui University, Bunkyo, Fukui 910, Japan*

*Received December 10, 1990*

Isomer distributions of dibenzofuran (DBF) in Friedel–Crafts acylations, Friedel–Crafts alkylations, and nitrations have been determined. The 2- and 3-positions of DBF represents most of the total reactivity. However, the ratio of 2- to 3-isomers greatly varied, depending on the nature of the electrophile. The positional reactivities have been found to be in the following sequence: 2- > 3- > 1- > 4-positions for Friedel–Crafts acylations, Friedel–Crafts benzylations, and nitrations with alkyl nitrate/Lewis acid or nitronium tetrafluoroborate. The ratios for acylations varied over a range from 13.1 to 2.9, while for benzylations and nitrations from 2.0 to 1.0. In contrast, for nitrations of DBF with nitric acid a different reactivity order was found: 3- > 2- > 1- > 4-, with the ratio varying from 0.8 to 0.03 depending on the nature of solvents used. The selectivity for the 3-substitution increased with increase in nitronium ion-like character of nitrating reagents. In particular, nitration with nitric acid in dichloromethane gave mostly 3-nitro-DBF (95% of the four possible isomeric mixture). The charge-transfer nitration with tetranitromethane under the UV irradiation has shown a similar isomer distribution to that in nitration with nitric acid. The MNDO calculations predicts that the late transition-state model (by $\sigma$-complex) favors reactions at the 2-position while the early transition-state model (by HOMO electron density) leads to the 3-substitution.

Dibenzofuran (DBF) is not only a key industrial intermediate but also a compound being investigated in heteroaromatic chemistry. Recently, DBF's chemistry has attracted much attention.[1] Positional reactivity of DBF in electrophilic substitutions is anomalous. Friedel–Crafts acylations,[2] Friedel–Crafts alkylations,[3] sulfonation,[4] and halogenations[5] of DBF give predominantly 2-substituted products. In contrast, nitrations with nitric acid in a

---

[1] Sargent, Melvyn, V.; Stransky, Peter O. *Advances in Heterocyclic Chemistry* **1984**, *35*, 1.

[2] (a) Keumi, T.; Simakawa, S.; Oshima, Y. *Nippon Kagaku Kaishi* **1977**, 1518. (b) Whaley, W. H.; White, C. *J. Org. Chem.* **1953**, *18*, 309. (c) Johnson, R. G.; Willis, H. B.; Gilman, H. *J. Am. Chem. Soc.* **1954**, *76*, 6407.

[3] Abbott, R. K. U. S. Patent 2,500,732.

[4] Wendland, R.; Smith, C. H.; Muraca, R. *J. Am. Chem. Soc.* **1949**, *71*, 1593.