Kurze Mitteilungen

Maximalumfang: 6 Schreibmaschinenseiten (alles inbegriffen).

Synthese und Charakterisierung von Oxadiazolo[5,4-a]Phenoxazin-4-on*

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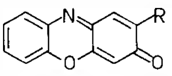
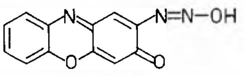
Abstract

The synthesis of oxadiazolo[5,4-a]phenoxazin-4-one, an unexpected reaction product of the nitrosation of 2-amino-phenoxazin-3-one is described. Full ^{1}H-NMR-interpretation and mass-spectral data are given.

Im Rahmen der Untersuchung von Pilzmycel-Produkten [1] wurde nach Möglichkeiten gesucht, in 2-Stellung substituierte Phenoxazin-3-on-Derivate (I) zu synthetisieren.



I



II

Nach [2] kann 2-Amino-phenoxazin-3-on mit Natriumnitrit diazotiert werden. Mehrere Versuche ergaben anstelle des gewünschten 3-Oxo-phenoxazin-2-diazohydroxid (II) in guter Ausbeute eine Substanz (III), die aus Methanol in braunen Nadeln kristallisiert. Das Massenspektrum dieser Verbindung (Abb. 1) zeigt ein Molekülion bei m/z 239. Durch ^{1}H-NMR-Spektroskopie konnte (III) als Oxadiazolo[5,4-a]phenoxazin-4-on identifiziert werden.

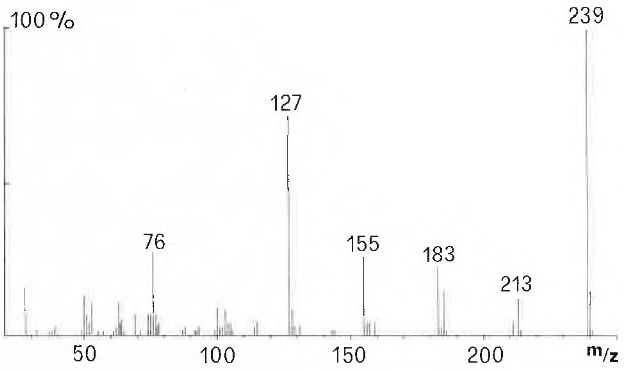


Abb. 1: Massenspektrum von Oxadiazolo [5,4]-phenoxazin-4-on (III)

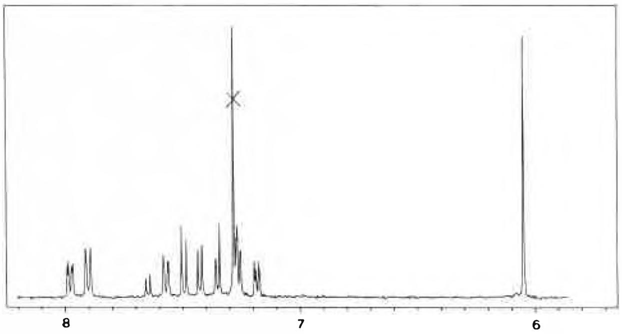
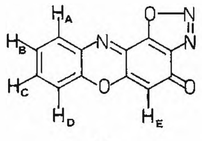
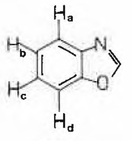


Abb. 2: ^{1}H-NMR Spektrum von Oxadiazolo[5,4]phenoxazin-4-on (III)



III



IV

Zuordnung der NMR-Signale (Abb. 2):
Das Singulett bei 6,04 ppm ist dem Proton H_E zuzuordnen, da alle anderen Protonen Kopplungen mit Nachbarprotonen zeigen. Die beiden Protonen der Signale bei 7,94 und 7,18 ppm müssen in para-Stellung zueinander liegen, da sie im Gegensatz zu den andern beiden Signalen bloss eine relativ grosse ortho-Kopplung von 7,5 Hz zeigen. Für die Zuordnung der Signale wurde die Modellverbindung Benzoxazol (IV) herangezogen.
Nach [3] liegt H_a bei 7,77 ppm und H_d bei 7,67 ppm. Überlegungen zur Elektronendichte mittels Grenzstrukturen lassen erwarten, dass H_A in III einen zusätzlichen Tieffeldshift erfährt. Somit ist H_A im Spektrum von (III) dem Signal bei 7,94 ppm zuzuordnen, dasjenige von H_D liegt demnach bei 7,18 ppm. Durch die gleichen Überlegungen erwartet man weiter, dass H_C stärker entschirmt ist als H_B und somit bei tieferem Feld liegen muss.

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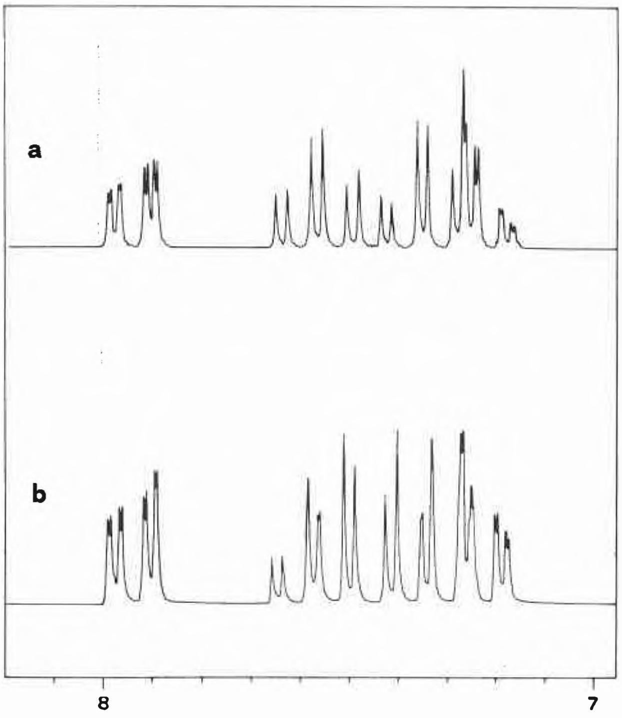

Abb. 3: ^{1}H-NMR-Simulationsspektren a + b für das Benzoxazol-System

Durch Simulationsspektren wurde diese letzte Zuordnung überprüft:

Simulationsspektrum 1 (Abb. 3a)

H_A 7,94 ppm $J_{AB} = J_{BC} = J_{CD} = 7{,}5$ Hz
H_B 7,56 ppm $J_{AC} = J_{BC} = 2{,}0$ Hz
H_C 7,33 ppm $J_{AD} = 0{,}5$ Hz
H_D 7,22 ppm

Simulationsspektrum 2 (Abb. 3b)

H_A 7,94 ppm $J_{AB} = J_{BC} = J_{CD} = 7{,}5$ Hz
H_B 7,33 ppm $J_{AC} = J_{BD} = 2{,}0$ Hz
H_C 7,56 ppm $J_{AC} = 0{,}5$ Hz
H_D 7,18 ppm

Simulationsspektrum 2 stimmt mit dem gemessenen Spektrum von (III) gut überein und bestätigt obige Zuordnung von H_B und H_C.

Synthese von Oxadiazolo[5,4-a]phenoxazin-4-on

4 mg (0,019 mmol) 2-Amino-phenoxazin-3-on [4] werden fein zerrieben, mit 1 ml Salzsäure (1 M) versetzt und auf 0°C gekühlt. Dazu gibt man 0,2 ml (0,29 mmol) einer Natriumnitrit-Lösung (100 mg/ml) und rührt bei 0°C während zwei Stunden. Das Rohprodukt wird abfiltriert und aus Methanol umkristallisiert. Ausbeute 4,2 mg (93% d.T.)

Apparatives:

NMR: 100 MHz Varian XL-100 Spektrometer
Fouriertransformationsspektren. Angabe der chemischen Verschiebung bezogen auf Tetramethylsilan.

MS: Massenspektrometer Varian MAT CH-7A
Ionisierungsenergie 70 eV, Quellentemperatur 250°C, Direktprobeneinlasse 135°C.

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Steric Effects on Reaction Rates. VII. Application of a New MM2 Force-Field for Carbenium Ions to Solvolysis of Bridgehead Substrates*

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Abstract

The changes in steric energies ($\triangle E_{st}$) associated with the solvolysis of bridgehead halides and *p*-toluenesulfonates are calculated by means of an empirical force-field for carbenium ions, incorporated into *Allinger*'s MM2 programme. The reactivities, relative to 1-adamantyl, of bridgehead derivatives are correlated with the equation: $\triangle G^{\neq} = 0.71\ \triangle E_{st} - 4.61$ ($r = 0.997$).

We have recently described a force-field compatible with *Allinger*'s MM2 molecular mechanics programme for calculation of steric energies of secondary carbenium ions [1]. This force-field was successfully applied for the correlation of reactivities with strain changes occurring upon solvolysis of secondary *p*-toluenesulfonate esters reacting *via* the k_c-mechanism. In *Allinger*'s approach [2] the angle strain of trigonal centers is accounted for by two different terms, the first one considering deviation of the calculated from the «ideal» bond angle at the trigonal center, and the second one considering the degree of pyramidalization (out of plane bending) of this center. For secondary carbenium ions, only the contributions of the first term are important, since they should achieve planarity without much restriction. Therefore a poor choice of parameter for out of plane bending would be of no harmful consequences as long as only secondary ions are considered, and it would remain undetected. Accordingly our reported correlation for reactivity of secondary *p*-toluenesulfonates is of limited value with respect to the general applicability of the force-field, in particular to tertiary carbenium ions. We have now performed tests with a series of bridgehead carbenium ions, where the degree of pyramidalization is expected to contribute significantly to their energy.

In their pioneering work on application of molecular mechanics, *Bingham* and *Schleyer* [3] associated bridgehead reactivities for solvolysis with the strain difference between substrate and the respective carbenium ion. Since at the time of their work parameters for leaving groups were not available, the latter were replaced by hydrogen for the computer calculations. Thus eventual strain due to the presence of sterically demanding leaving groups (F-strain) was omitted. For reasons of consistency, we have used the same substrates and the same model reaction for our calculations. The results are summarized in the table 1. Rate

Table 1: Steric energies (E_{st})$^{a)}$ *and rates of solvolysis*$^{b)}$ *of tertiary halides and p*-toluenesulfonates$^{c)}$

Entry	*Compound*	E_{st} (RH)	E_{st} (R+)	$\triangle E_{st}$	$\triangle G^{\neq}$ (chloride)	$\triangle G^{\neq}$ (tosylate)
1	1-Norbornyl	23.09	50.22	27.13	-	15.62
2	1-Bicyclo[2.2.2]octyl	19.64	33.88	14.24	5.26	5.79
3	1-Bicyclo[3.2.1]octyl	19.27	36.03	16.76	-	7.42
4	1-Bicyclo[3.3.1]nonyl	18.26	22.76	4.50	- 1.59	-
5	1-Bicyclo[3.2.2]nonyl	24.35	29.78	5.43	- 0.44	-
6	1-Noradamantyl	28.02	46.95	18.93	-	8.66
7	1-Bicyclo[3.3.2.]decyl	29.96	27.99	- 1.97	- 5.46	-
8	1-Adamantyl	17.09	24.80	7.71	0	0
9	7-Methyl-3-noradamantyl	27.80	51.15	23.35	-	11.74
10	10-Tricyclo[5.2.1.0^{4,10}]decyl	26.55	45.94	19.39	-	8.86
11	1-Bicyclo[3.3.3]undecyl	37.29	29.27	8.02	10.76	-
12	3-Homoadamantyl	28.04	28.19	0.15	3.65	-
13	*trans-trans, trans*-13-tricyclo [7.3.1.^{1,9}0^{5,13}]tridecanyl	15.51	18.18	2.67	- 1.96	-
14	*trans-cis-trans*-13-tricyclo [7.3.1.^{1,9}0^{5,13}]tridecanyl	19.20	20.68	1.48	- 3.92	-

a) Ref. [4].

b) Relative to 1-adamantyl, [3].

c) Energies in kcal/mol.

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* Received September 26, 1984.

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constants for chlorides (80% EtOH, 70°) and *p*-toluenesulfonates (AcOH, 70°) [3] are expressed in units of $\triangle G^{\neq}$, relative to the respective 1-adamantyl derivative. The plot of $\triangle G^{\neq}$ *vs.* $\triangle E_{\mathrm{st}}$ (Fig. 1) shows that both chlorides and *p*-toluenesulfonates can be correlated by one and the same straight line by means of the equation: $\triangle G^{\neq} = 0.71\ \triangle E_{\mathrm{st}} - 4.61$ ($r = 0.997$).

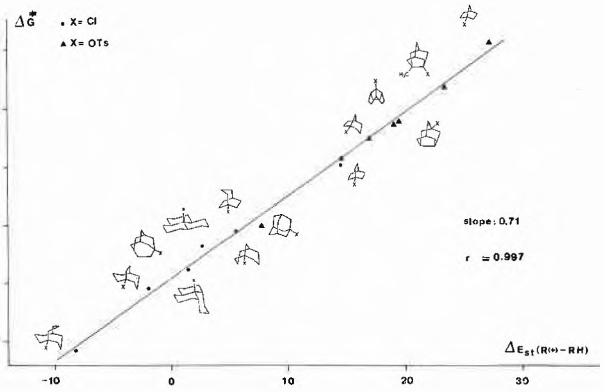

Fig. 1: Correlation of reactivities ($\triangle G^{\neq}$) for bridgehead chlorides and *p*-toluenesulfonates with steric energy differences ($\triangle E_{\mathrm{st}}$) between hydrocarbons and the respective carbenium ions.

In contrast, *Bingham* and *Schleyer* observed different correlation lines for chlorides and sulfonates, with the slopes varying by a factor of ca. 3. The change in slope has been ascribed to F-strain, present in the *p*-toluenesulfonates, but not considered in the calculations. This would lead to underestimation of energy in the substrate and an overestimation of $\triangle E_{\mathrm{st}}$. Since this systematic error does not appear to the same extent with halide leaving groups, they must correlate with a different slope than sulfonates. This discrepancy with our correlation may have two causes: If the F-strain hypothesis is valid in this series, then our result must be due to some fortuitous compensation caused by an inadequate carbenium ion force-field. Alternatively if the force-field describes carbenium ion stabilities adequately, then the F-strain hypothesis must be abandoned. There are not sufficient experimental data available to invalidate one or the other force-field; however work is in progress to thest with MM2 calculations the question of F-strain within this series of substrates.

Among the compounds investigated in this work, the perhydrotriquinacene derivative **10** represents a particular problem. In the treatment of *Bingham* and *Schleyer* [3] it falls out of the correlation by a factor of 10^9, but in our calculation it appears quite normal. The discrepancy is striking because it concerns just this compound alone. The particular geometry of the cation derived from **10** brings out differences between the treatments, which require more detailed examination.

Despite of these inconsistencies which we consider minor, our force-field reproduces the general correlation between strain and reactivities for bridgehead derivatives as originally proposed by *Schleyer* and his school. We are currently examining if adjustments of the force field in light of the F-strain hypothesis or the comportment of **10** is indeed warranted.

Acknowledgment

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4 For the time being we have not developed increments allowing transformation of steric energies (E_{st}) into enthalpies of formation and strain energies [2].