

σ -Complex Intermediates in Acylation and Sulfonation of 1,3,5-Tripyrrolidinobenzene—Preparation, Reactions, and Structure^[1]

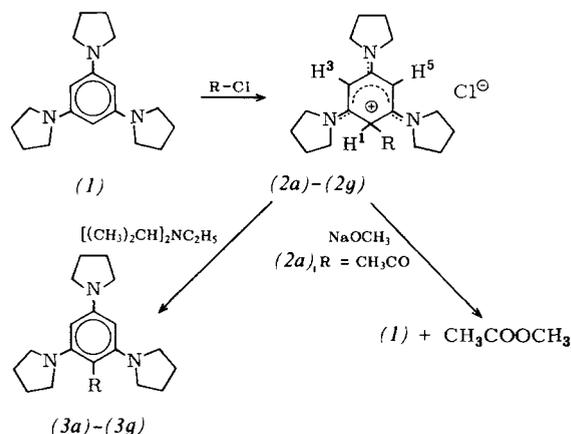
By Peter Menzel and Franz Effenberger^[*]

In the acylation of arenes, σ -complex (Wheland) intermediates have been cited^[2] for the formyl fluoride/boron trifluoride reaction of alkylbenzenes; they have received no mention, however, in more recent spectroscopic work^[3]. σ -Complex intermediates have been established unequivocally by NMR spectroscopy for the sulfonation of persubstituted benzenes^[4]. With the extremely electron-rich 1,3,5-triaminobenzenes, such complexes have even been isolated in the case of protonation^[5], alkylation^[6], and halogenation^[7]; we now report analogous results for the acylation and sulfonation of triaminobenzenes.

If 1,3,5-tripyrrolidinobenzene (*1*) is treated with acetyl or benzoyl chloride in anhydrous dichloromethane at 0°C, the orange-yellow σ -complexes (*2a*) and (*2b*), respectively, can be precipitated with ether from the brownish yellow reaction solutions. Sulfonation of (*1*) with tosyl chloride under similar conditions yields (*2d*), while (*2c*) [formed upon reaction with mesyl chloride in CDCl₃] can be identified only by NMR spectroscopy. Compounds (*2e*), (*2f*), and (*2g*) which have proved essential for assessing the conformation of Wheland intermediates^[8], are prepared analogously (Table 1).

Except for (*2c*), the σ -complexes (*2*) are stable at room temperature for a reasonable time. The chloride ion may be exchanged with either AgClO₄ or AgBF₄.

Deprotonation of (*2*) to (*3*) is effected with *N,N*-diisopropylethylamine; no deprotonation but rather cleavage of the acetyl group is observed with sodium methoxide.



Nonplanarity of the cyclohexadienyl ring has been established by X-ray crystallography for σ -complexes of type (*2*) with $R=CH_3$ and $R=Br$ ^[10]. If (*2a*)–(*2g*) are also nonplanar only two extreme conformations (*syn* or *anti*) are possible for steric reasons. In case of restricted rotation about the C^1-C^7 or C^1-S bonds these two conformations could be differentiated by NMR spectroscopy. There is no significant change, however, in the NMR signals over a wide temperature range, thus ruling out rotation or an alteration of rotational behavior.

For the acyl σ -complexes (*2a*) and (*2b*), the olefinic protons $H^{3,5}$ exhibit nearly identical shifts, while H^1 is less shielded by 1.63 ppm in (*2b*) as compared with (*2a*) (Table 1). The acyl complexes must therefore be assigned the *syn* conformation (A *syn*) where H^1 is strongly deshielded if $R'=phenyl$.

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Table 1. σ -Complexes (2) prepared.

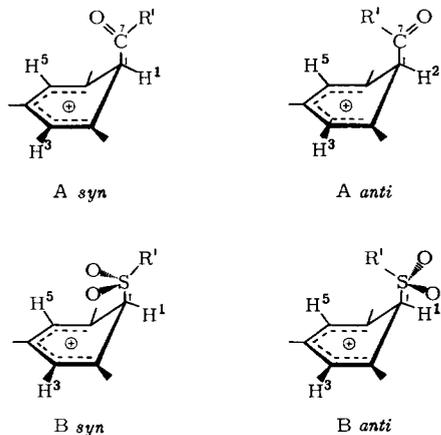
R	$^1\text{H-NMR}, \delta$ [ppm] [a]		$\text{H}^{3,5}$	IR [cm^{-1}] [b] C=N and C=C
	H^1			
(2a)	CH_3CO	4.86	5.07	1610; 1520; 1435
(2b)	$\text{C}_6\text{H}_5\text{CO}$	6.49	4.92	1615; 1523; 1430
(2c)	CH_3SO_2	5.66	5.00	
(2d)	$p\text{-CH}_3\text{-C}_6\text{H}_4\text{SO}_2$	5.55	4.63	1620; 1540; 1430
(2e)	9-Anthryl- SO_2	5.75	3.84	1620; 1540; 1430
(2f)	1-Naphthyl- SO_2	5.66	4.21	1620; 1545; 1427
(2g)	2-Methyl-1-naphthyl- SO_2	5.58	$\left\{ \begin{array}{l} 4.59 \\ 3.93 \end{array} \right.$	1620; 1545; 1425

[a] 0.1 M in CDCl_3 , 30°C, internal reference TMS.[b] KBr pellet. The three intense bands listed are characteristic of 1,3,5-triaminobenzene σ -complexes [9].

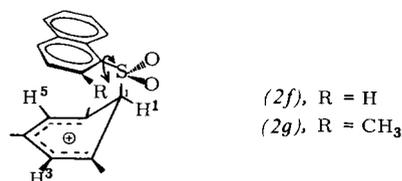
In contrast, the analogous sulfonyl complexes (2c) and (2d) exhibit different shifts for $\text{H}^{3,5}$ and almost identical shifts for H^1 , and must therefore exist in the *anti* conformation (B

exist in a nonplanar conformation with the substituent at C^1 in axial position, both in solution and in the solid state.

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anti). In this arrangement, the olefinic protons of (2d) come to lie within the diamagnetic shielding cone of the tolyl ring, and thus experience an upfield shift as compared with (2c). If this rationalization is correct, the effect should be much more pronounced for an anthracenesulfonyl complex: indeed, $\text{H}^{3,5}$ of (2e) appear better shielded by another 0.8 ppm while the H^1 signal is shifted slightly downfield. For the naphthalene-sulfonyl compound (2f) where only one proton experiences additional shielding by the annelated benzene ring, separate resonances are expected for H^3 and H^5 . Due to rapid oscillation of the naphthyl moiety about the S-aryl bond, however, the spectrum shows only one singlet of intermediate shift.



Upon introduction of a methyl group in the β position of (2), this oscillation is no longer possible for steric reasons; accordingly, the $\text{H}^{3,5}$ signal of (2g) is split into two resonances. Concomitant with the increasing shielding by larger and larger π -systems, the ^1H signal shows a systematic downfield shift in the series (2d) \rightarrow (2f) \rightarrow (2e), thus providing further confirmation that the aryl rings are fixed above the cyclohexadienyl system. Differing conformations of acyl and sulfonyl σ -complexes would be impossible in a planar structure; furthermore, the marked influence of the aryl substituents upon the $\text{H}^{3,5}$ signal of (2d)–(2g) would be hard to explain. The σ -complexes, at least of triaminobenzenes, must therefore

CAS Registry numbers:

(1), 16857-93-5; (2a), 53973-55-0; (2b), 53973-56-1; (2c), 53973-57-2; (2d), 53973-58-3; (2e), 53973-59-4; (2f), 53973-60-7; (2g), 53973-61-8; acetyl chloride, 75-36-5; benzyl chloride, 98-88-4; mesyl chloride, 124-63-0; tosyl chloride, 98-59-9; 9-anthrylsulfonyl chloride, 53973-96-9; 1-naphthylsulfonyl chloride, 85-46-1; 2-methyl-1-naphthylsulfonyl chloride, 53973-97-0

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[10] Dihedral angle between the planar cyclopentadienyl part and the tetrahedral C^1 ca. 15°; J. J. Stezowski, personal communication.