6. Nucleophilic Aromatic Substitution. Part XV[1]). Phase-Transfer Catalysis of Sulfodechlorination and Identification of a Primary Product of Sulfite Ion with 1-Chloro-2,4-dinitrobenzene[2])

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Summary

With conventional phase-transfer catalysis using quaternary ammonium salts, yields of 2,4-dinitrobenzenesulfonic acid (**2**) in the sulfodechlorination of 1-chloro-2,4-dinitrobenzene (**1**) with sulfite ions are no better than those obtained with the classical method in aqueous ethanol (80–82%). Yields up to 97% and a very pure product are obtained, however, by using protonated tertiary amines as catalysts. The optimum chain-length of the amine is found with tributylamine. On mixing solutions of the reagents and catalysts a strong bluish-red colour develops immediately, but disappears within *ca.* 1 h. Comparison of the NMR. spectrum of this primary product with model adducts of sulfite ions and di- and trinitrobenzene derivatives demonstrates that the primary addition of the nucleophile to 1-chloro-2,4-dinitrobenzene does not take place at C(1), but at C(5). It is shown that the increments calculated for a C_{sp^3}-SO_3^- group and for the 1,3-dinitro- and 1,3,5-trinitropentadienyl ring moieties can be employed for the approximate calculation of ^{1}H-chemical shifts using *Clerc & Pretsch*'s modification of the *Shoolery* rules [3].

Introduction. – By 1980 more than 1400 publications including 4 books had appeared on phase-transfer catalysis (PTC.), reporting mainly on nucleophilic aliphatic substitutions. In some 20 papers *nucleophilic aromatic substitutions* were treated. With the exception of a communication on thiodehalogenation[3]) [5], all of these papers describe reactions of *mono*anionic nucleophiles with neutral substrates yielding neutral organic products, and an anion.

In contrast to these reactions, in sulfodehalogenations a dianion reacts with an aromatic molecule forming a monoanionic organic product and a halide ion.

[1]) Part XIV: [1].

[2]) Parts of this paper were published in a preliminary communication [2].

[3]) We use the systematic IUPAC-nomenclature for substitution reactions [4].

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This has two fundamental disadvantages for the application of the conventional PTC. technique with quaternary ammonium salts. First, it is difficult to extract a dianion into the organic phase. The anions being formed act as 'catalyst poison', *i.e.*, the anionic product, the aromatic sulfonate Ar-SO_3^-, and even the nucleofuge (the halide anion X^-) form more stable ion pairs [Q^+Ar-SO_3^-] and [Q^+X^-] than does the sulfite dianion which must form an ion triplet [$Q_2^+SO_3^{2-}$]. Second, usual workup procedures which involve separating the catalyst from the neutral product are not applicable as the catalyst cation is tied up as a stable ion pair [$Q^+ArSO_3^-$] in the organic phase.

Finally, S_NAr-sulfodehalogenations of halobenzene derivatives are possible only in the presence of strong -M, -I substituents, particularily nitro groups, which are, however, easily reduced by excess sulfite. This is the main reason why aromatic sulfodehalogenations under conventional conditions give relatively low yields [6] [7].

In the present investigation, first, a modified PTC. method for the synthesis of 2,4-dinitrobenzenesulfonate salts or acid (**2**) by nucleophilic substitution of 1-chloro-2,4-dinitrobenzene (**1**) with sulfite ion is described. This gives yields of up to 97% in contrast to the classical method [7] and to the conventional PTC. procedure which give yields no higher than 81%. Second, the structure of an unexpected primary product from interaction of **1** with sulfite ion is elucidated with the help of NMR. measurements.

Results. – *Conventional PTC. technique.* The main problem in the application of this technique is the low solubility in the organic phase of ion pairs involving sulfite dianions. In principle, a quaternary ammonium ion with large aliphatic chains can be used, *e.g. Aliquat 336* (trioctylmethylammonium salt). As such large cations also form relatively lipophilic ion pairs with the reaction product, 2,4-dinitrobenzenesulfonate ion (**2**), the extraction of this product into the aqueous phase becomes difficult. Therefore we compromised by choosing tetrabutylammonium hydrogen sulfate as catalyst.

For the isolation of **2** we precipitated the barium salt by addition of $Ba(ClO_4)_2$ or we used a special procedure (based on a suggestion by *Brändström* [8] for the regeneration of tetrabutylammonium salts), involving the addition of toluene, aqueous sulfuric acid and trioctylamine.

Using this method of PT.-catalyzed sulfodehalogenation with either of the two methods of product isolation, we obtained complete conversion of **1** in a shorter time (1 h) and at lower temperature (40°) than by the classical method (4 h, 78° [7]). The yield was, however, not higher (80–81%), and was not increased by changing various parameters in the PTC. procedure [9a].

Use of protonated tertiary amines for PTC. For the specific case of the formation of arenesulfonate ions in PTC. by sulfodehalogenation, protonated tertiary amines have the advantage that, after the substitution, addition of alkali hydroxide will deprotonate the ammonium ions, leave the tertiary amine in the organic phase, and bring the sulfonate ion into the aqueous phase *(Eqn. 1)*.

$$[HNR_3^+\,Ar\text{-}SO_3^-]_{org} + KOH_{aq} \rightarrow NR_{3_{org}} + Ar\text{-}SO_3^-K^+_{aq} \qquad (1)$$

In the choice of a suitable tertiary amine, various factors have to be considered.

1) The pK_a-value of the conjugate acid should not be lower than *ca.* 7 since it does not have to be deprotonated by sulfite ions (pK_a of $HSO_3^- = 6.9$); this criterion excludes aromatic amines; 2) for the protonation of the amine, acids should be used whose conjugate bases do not decrease the extractability of sulfite ions. The simplest choice is potassium hydrogen sulfite ($KHSO_3$) or disulfite ($K_2S_2O_5$) as substitution *and* protonation reagent; 3) the lipophilicity of the tertiary amine and the temperature have to be optimized as usual in PTC. In sulfodehalogenations of nitrated benzene derivatives, temperature not only influences the solubilities of ion pairs, but also the ratio of the rate of nucleophilic substitution to that of the reduction of the nitro groups by sulfite, hydrogen sulfite and/or SO_2.

We worked with mixtures of water with chloroform and methylene chloride, with various amines, at several temperatures *(Table 1).*

The decrease in yield at higher temperature is probably due to reduction of the nitro groups; SO_2 is formed predominantly when the temperature is increased. This limits also the applicability of this PTC. method to substrates which are activated strongly for S_NAr-substitutions. In our experience it cannot be used for the sulfodechlorination of *o*- and *p*-chloronitrobenzene.

The structure, molecular size and basicity of the tertiary amine have a big influence on the yield in this reaction. *N, N*-Diethylaniline is, as expected not basic enough. Furthermore, it is probably not sufficiently lipophilic for its conjugate acid to extract sulfite ions from the aqueous phase. The same is true for DABCO and *N, N, N', N'*-tetramethylethylenediamine (TMEDA). On replacement of the four *N*-methyl groups in TMEDA by ethyl groups the lower limit of lipophilicity is reached. This is also the case for tripropylamine. Tributyl and tripentylamine are

Table 1. *Influence of temperature and type of tertiary amine on the sulfodechlorination of 1-chloro-2,4-dinitrobenzene* (**1**) *with potassium disulfite under PTC. conditions*[a])

Solvent (+H_2O)	Amine[b])	Temperature °C	Duration h	Yield[c]) %	Purity[c]) %
$CHCl_3$	Bu_3N	0–8	2	82[d])	–
$CHCl_3$	Bu_3N	20–32	2	66	–
$CHCl_3$	Bu_3N	60	2	56	–
CH_2Cl_2	$PhNEt_2$	25	23	0	–
CH_2Cl_2	TMEDA	25	23	0	–
CH_2Cl_2	DABCO	20	24	0	–
CH_2Cl_2	TEEDA	25	23	58	91
CH_2Cl_2	Pr_3N	0–8	3	81	96
CH_2Cl_2	Bu_3N	0–8	3	97	96
CH_2Cl_2	$(n\text{-}C_5H_{11})_3N$	0–8	3	95	99
CH_2Cl_2	$(n\text{-}C_6H_{13})_3N$	0–8	3	85	78
CH_2Cl_2	$(n\text{-}C_8H_{17})_3N$	0–8	3	76	87

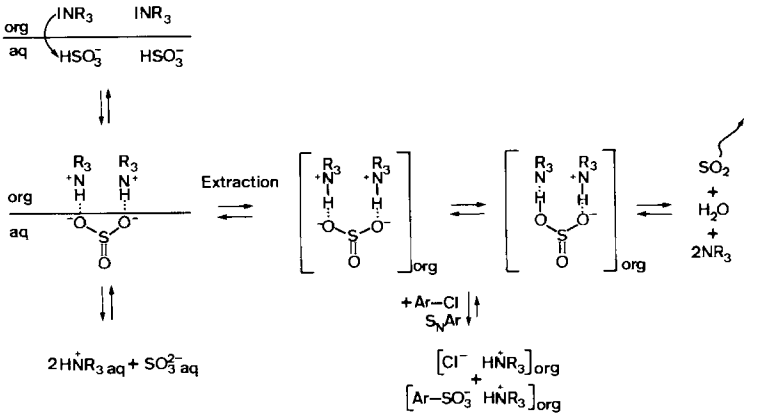
[a]) Ratio **1**/$K_2S_2O_5$/amine = 1:1:2.

[b]) TMEDA = tetramethylethylenediamine, DABCO = diazabicyclo[2.2.2]octane, TEEDA = *N, N, N', N'*-tetraethylethylenediamine.

[c]) Determined by UV./VIS. spectroscopy.

[d]) Reaction not finished after 2 h.

Scheme 1



optimal, whereas higher tertiary aliphatic amines are already too large for this reaction.

The mechanism of the various phase transfer processes is described in *Scheme 1*. The tertiary amine ($pK_a = 10$–11) deprotonates the hydrogen sulfite ion ($pK_a = 6.9$) through the phase boundary; an ion triplet is extracted into the organic phase where the S_NAr-reaction takes place. An increase in temperature favours reduction of nitro groups and formation and evolution of gaseous SO_2 from the organic phase.

It is likely that this PTC. method with protonated tertiary amines as catalysts is also applicable to the sulfodehalogenation of other aromatic compounds which are highly activated for S_NAr-reactions by suitable substituents if the lipophilicity is appropriately adjusted.

When the two solutions of the reagents are mixed, a bluish-red colour develops instantly; the rate of disappearance of this colour (up to 1 h) depends on concentrations, temperatures *etc.* The final colour of the system, slightly orange-yellow, is due to traces of decomposition products.

Structure of the primary product. – *Electronic and NMR. spectra of the primary product.* The bluish-red colour occurred in all our experiments with **1** in two-phase systems with all protonated tertiary amines, with quarternary ammonium ions and also (not described here) with crown ethers. It was found also when K_2SO_3 was added to a solution of **1** in dimethyl sulfoxide, but not in the classical sulfodechlorination in aqueous ethanol [6]. The ions and molecules of the PTC. are therefore not part of the primary product.

As this transient primary product decomposes relatively rapidly, we were not able to determine its absorption maximum accurately (λ_{max} *ca.* 540–545 nm[4])). In the ^{1}H-NMR. signals *(Table 2)* could be detected besides the signals of **1** and **2**. Unfortunately, we were not able to obtain ^{13}C-NMR. spectra because the lifetime

[4]) The real λ_{max} is probably somewhat smaller, as the spectrophotometer used measures slowly from longer to shorter wavelengths.

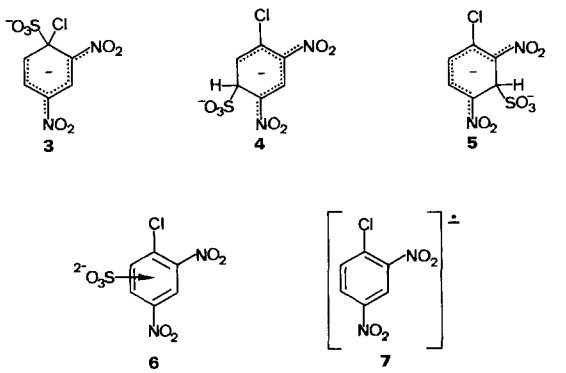
Table 2. *^{1}H-NMR. spectra of the primary product of the reaction of 1-chloro-2,4-dinitrobenzene* (**1**) *with ammonium sulfites in CD_2Cl_2*

Temperature	Reagent	Primary product		Assignment
		δ (ppm)[b]	J (Hz)	
– 30°	$(NBu_4)_2SO_3$	8.58*d*	1.84	H–C(3)
		5.07*d*×*d*	7.14/1.84	H–C(5)
		5.64*d*	7.15	H–C(6)
– 50°	$(NHBu_3)_2SO_3$	8.58*m*		H–C(5)
		5.13*d*	6.95	H–C(5) or H–C(6)[a]
		5.6*d*	7.2	H–C(6) or H–C(5)[a]

[a]) Because of the broadening of these bands, the peaks cannot be assigned to H–C(5) and H–C(6).
[b]) Standard: tetramethylsilane.

of the primary product is too short. Therefore, we investigated the structure by comparing the proton spectra with those of suitable model compounds.

Potential structures of the primary product. Our sulfodechlorination follows probably the classical S_NAr-mechanism [10] *via Jackson-Meisenheimer*-type intermediate **3**. As shown originally by *Servis* [11] and confirmed by *Gold et al.* [12], nucleophiles may add to derivatives of trinitrobenzenes primarily not at the C-atom substituted by a potential leaving group of an S_NAr-substitution, but at other C-atoms in *o*- or *p*-position to the nitro groups. Furthermore, π-complexes and radical anions are known in certain cases [13]. Therefore, at least the following five structures **3**–**7** have to be considered for the primary product.



Structures **6** and **7** can almost certainly be excluded without comparison with models. As *Günther* [14] has pointed out a radical anion shows additional couplings of the unpaired electron with the protons and a significant broadening of the peaks. This is not the case for the spectrum of our primary product, so **7** can be excluded. The signals for H–C(5) and H–C(6) of the primary product are shifted by 2.40 and 3.48 ppm to higher field relative to **1**, whereas the signal for H–C(3) is shifted only by 0.27 ppm. Such large and very different shifts for various protons in the same aromatic ring are unusual in the NMR. spectra of π-complexes. Structure **6**

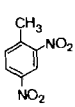
is therefore also unlikely. Differentiation between **3**, **4** and **5** is possible by comparison with model σ-adducts.

Comparison of the NMR. spectrum with those of model compounds. Besides 1-chloro-2,4-dinitrobenzene (**1**), adduct formation of *m*-dinitrobenzene (**8**), 1-chloro-2,6-dinitrobenzene (**9**) and 2,4-dinitrotoluene (**10**) with sulfite ions was studied. Owing to the different reactivity of these compounds, a system had to be chosen in which adducts were sufficiently stable to be studied by NMR. We decided upon the six component mixtures $D_2O/CDCl_3/D_6$-DMSO/18-crown-6/K_2SO_3/benzene derivative at 0°. In *Table 3* key features of the NMR. spectra of the four dinitrobenzene derivatives **1**, **8**, **9** and **10** are given together with those of their adducts with sulfite ions[5]).

NMR. spectra of (1:1)- and (2:1)-adducts of nucleophiles to *1,3,5-trinitrobenzene* and its derivatives [15] show that the chemical shifts of sp^2- and sp^3-bonded H-atoms at the six-membered rings are not significantly influenced by the nucleophiles OH^-, OCH_3^- and SO_3^{2-}: δ-values for sp^2- and sp^3-bonded H-atoms are 8.3 to 8.8 ppm and 6.00 to 6.15 ppm, respectively. Considerably lower δ-values were found for hydride ion adducts [16] [17]; they are lower by 1.5 to 2.5 ppm. Therefore we can use data for adducts of OH^- and OCH_3^- with *m*-dinitrobenzene and its derivatives for comparison with our sulfite complexes.

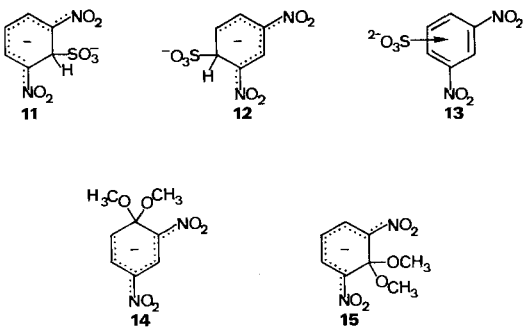
For the (1:1)-adduct of sulfite ions to m-*dinitrobenzene* (**8**) the three structures **11**, **12** and **13** must be considered; **11** and **13** have a plane of symmetry and only three signals are expected for the four protons in these two structures. We found *four* signals *(Table 3)*. This result is compatible only with structure **12**. Also, our

Table 3. *^{1}H-NMR. spectra of* m-*dinitrobenzene and its derivatives and their adducts with sulfite ions* (solvent see text) *at 0°*

		Reagent			Adduct with SO_3^{2-}		
		δ (ppm)[b]	J (Hz)		δ (ppm)[b]	J (Hz)	
	**8**	8.94$d\times d$	2.1/2.0	H–C(2)	8.36–8.33m		H–C(2)
		8.74–8.63m		H–C(6,4)	6.82$d\times d$	9.9/1.5	H–C(6)
		8.04$d\times d$	8.6/7.7	H–C(5)	5.65$d\times d$	9.7/5.7	H–C(5)
					5.15d	5.5	H–C(4)
	**9**	8.3$d\times d$	8.1/0.8	H–C(3,5)	7.03d	9.3	H–C(3)
		7.88$d\times d$	9.0/7.3	H–C(4)	5.52$d\times d$	9.4/5.9	H–C(4)
					5.28d	5.7	H–C(5)
	**1**	8.85d	2.6	H–C(3)	8.56d	1.8	H–C(3)
		8.55$d\times d$	8.9/2.7	H–C(5)	5.6d	7.15	H–C(6)
		8.04d	8.8	H–C(6)	5.08$d\times d$	7.0/1.7	H–C(5)
	**10**	8.76d	2.4	H–C(3)	8.52d[a])	1.3	H–C(3)
		8.46$d\times d$[a])	8.6/2.4	H–C(5)	5.35$d\times d$	6.1/1.2	H–C(5)
		7.85d	8.4	H–C(6)	5.01d	6.1	H–C(6)
		2.71s		CH_3–C(1)	2.2s		CH_3–C(1)

[a]) Overlapping. [b]) Standard: tetramethylsilane.

[5]) The spectra are published elsewhere [9b].



results resemble the δ-values reported [18] for the methoxide adduct to 1-methoxy-2,4-dinitrobenzene (**14**), but not those for the isomeric adduct **15**.

The two significantly different vicinal coupling constants for H–C(5) in the adduct with sulfite, $J = 9.7$ Hz with H–C(6) and $J = 5.7$ Hz with H–C(4), support structure **12**; they are hardly compatible with **11** or **13**[6]).

1-Chloro-2,6-dinitrobenzene (**9**) and its σ-adduct at C(1) have also a plane of symmetry. As for **9**, such an adduct should show only two proton signals with an intensity ratio of 1:2 and δ-values similar to those of **15**. We found three proton signals with an intensity ratio 1:1:1 *(Table 3)*. The chemical shifts are comparable to those of **14** [18] and **12**.

As mentioned already, there are three σ-complexes possible, **3**, **4** and **5**, for the addition of sulfite ions to *1-chloro-2,4-dinitrobenzene* (**1**). Two of the three proton signals which we found for the chemical shifts of the complex *(Tables 2* and *3)* correspond to those of the adducts **12** and **14**. For a sulfite adduct at C(1), **3**, the third signal, *i.e.* that for H–C(5), would be expected between 6.85 and 7.20 ppm by comparison with the OH^- and OCH_3^- addition complexes. It is found at 5.07–5.13 ppm. We conclude that sulfite addition to **1** does not lead to **3** as primary product.

The chemical shifts for H–C(3) and H–C(5) which we found differ by 2.5 to 3.0 ppm from those which were found for **15** and the sulfite adduct to 1,3,5-trinitrobenzene [19]. Structure **5** is therefore also very unlikely.

Structure **4**, however, is consistent with the model complexes **12** and the sulfite adduct to 1-chloro-2,6-dinitrobenzene (**9**). *We conclude that* in the primary product *the sulfite ion is attached to C(5) of* **1**. This conclusion is based solely on NMR. data. The bluish-red colour which one observes visually is probably, but not definitely, related to that primary product. It should be kept in mind, however, that this absorption in the visible may be due to another primary product formed simultaneously in low concentration, but having a very high molar extinction coefficient. Such an additional intermediate would be detectable in the visible spectrum, but not in NMR.

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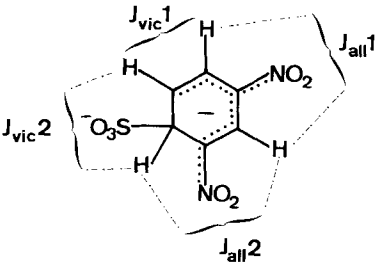
[6]) See also the general argument mentioned previously against the possibility that our adducts have a π-complex structure.

The conclusion that the sulfite ion is attached to C(5) of **1** is further supported by the comparison of the addition product of sulfite ions to 2,4-dinitrotoluene (**10**). The δ-values are consistent with an addition at C(5). It is remarkable that in this adduct it is not the signal for the proton H–C(5) which appears at highest field, as is the case for the other complexes, but that for H–C(6). This increased shielding is probably due to the (+I)-effect of the neighbouring methyl group.

The magnitude of the coupling constants in all adducts which we investigated are consistent with the proposed structures.



$J_{vic}1 = 9.4\text{–}9.9$ Hz
$J_{vic}2 = 5.5\text{–}7.2$ Hz
$J_{all}1,2 = 1.2\text{–}1.7$ Hz

The coupling of two vicinal and coplanar protons ($J_{vic}1$) is in the range comparable to aromatic *o*-couplings. The second vicinal coupling constant is smaller because the two protons are not coplanar and because one of them is bonded to an sp^3-hybridized C-atom. The two possible allylic couplings are, as expected, also smaller than aromatic *m*-couplings.

The fact that most proton signals in the adducts of sulfite appear at much higher field than those of the respective protons in the parent aromatic reagents is understandable. It is, however, remarkable that the signals for the protons with two vicinal nitro groups are shifted only 0.3–0.6 ppm to higher field. This effect is probably due to the paramagnetic anisotropy and the strong electron attracting properties of the nitro groups.

We mentioned above that the chemical shifts of comparable adducts of OH^-, OCH_3^- and SO_3^{2-} to di- and trinitrobenzene derivatives are very similar, but that respective hydride ion addition products show signals at significantly lower field (1.5 to 2.5 ppm). As discussed in more detail elsewhere [9c], this difference can be explained empirically by the application of the *Shoolery* rules as modified by *Clerc & Pretsch* [3]. Based on the NMR. data for the addition products of OH^-, OCH_3^- and SO_3^{2-} to 1,3,5-trinitrobenzene the following increments are obtained: for SO_3^- 1.5 to 1.7 ppm, for 1,3,5-trinitropentadienyl ring rest 2.8 to 3.0 ppm.

The hydride ion addition complexes differ from the complexes mentioned by the fact that the sp^3-C-atom is a substituted methylene group and not a methine group. Taking the basic value for CH_2 instead of CH and the increment for the 1,3,5-trinitropentadienyl ring rest, one obtains a δ-value of 4.05 to 4.25 ppm. This corresponds reasonably well with the experimental value of *Taylor* [16] (3.88 ppm).

With the data of *Gold et al.* [17] for the hydride ion adduct to *m*-dinitrobenzene at C(4), the increment for the 1,3-dinitropentadienyl ring rest can be calculated: 2.15 to 2.25 ppm. It can be tested for the sulfite ion adducts to *m*-dinitrobenzenes which we measured:

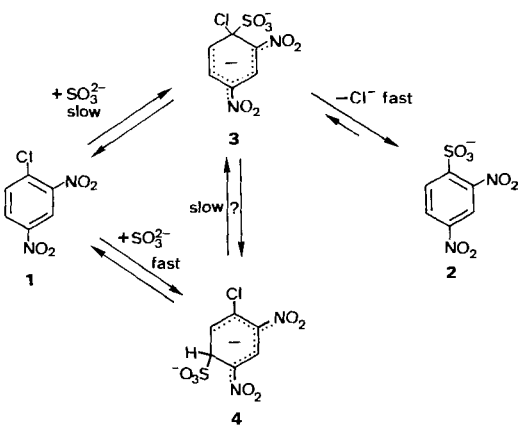
δ (calculated) 5.15 to 5.45 ppm

δ (measured) 5.08 to 5.35 ppm[7])

In conclusion we see that the modified *Shoolery-Clerc-Pretsch* rules can well be applied to *Jackson-Meisenheimer*-type complexes of di- and trinitrobenzenes with various nucleophiles.

Mechanism of sulfodechlorination of 1-chloro-2,4-dinitrobenzene under PTC. conditions. – In two-phase systems with suitable catalysts as well as in dimethyl sulfoxide, sulfite ions react with 1-chloro-2,4-dinitrobenzene (**1**) rapidly to form the complex **4**. The final product is, however, the 2,4-dinitrobenzenesulfonate ion (**2**). Is **4** the product of a side equilibrium, with **2** being formed by an S_NAr-reaction *via* **3**, present only in steady state concentration, *or* is **4** an intermediate in the literal sense on the pathway from **1** to **2**? If so, **4** would rearrange intramolecularily into **3** *(Scheme 2)*.

Scheme 2



We emphasize that our data do not allow a decision as to which of these two alternatives is correct. Our results are consistent with both. The S_NAr-mechanism **1**→**3**→**2** is well documented. There is also good evidence that adducts of the type of **4** are often formed more rapidly than those of type **3**. The problem of whether or not compounds of type **4** can rearrange intramolecularly ('directly') into **3** is, however, to our knowledge still an open question.

We thank Prof. *V. Gold* for a stimulating discussion.

7) The range of δ-values refers to spectra of the dinitrobenzene derivatives being measured.

Experimental Part

Reagents and products. – *1-Chloro-2,4-dinitrobenzene* (**1**)[8]): *Fluka* product 97%; m.p. 48–50° ([20]: 53°). – ^{1}H-NMR.: see *Table 3.*

2,4-Dinitrobenzenesulfonic acid, potassium salt (**2**). The reference compound was synthesized by the classical method in aqueous ethanol [6]; it was recrystallized three times from water (3 ml/g), precipitated by addition of ethanol, and dried (P_2O_5). The C-, H- and N-determination correspond to the formula $C_6H_3KN_2O_7S$ [9d]. – UV.: $\lambda_{max} = 254$ nm, $\varepsilon = 1.141 \times 10^4$ l · mol^{-1} cm^{-1}. – ^{1}H-NMR. (90 MHz, *Bruker HX-90E* and *WH-90*, D_2O, hexadeuteriotrimethylsilylpropionic acid): 8.74 (*d*, $J = 2.19$, H–C(3)); 8.62 (*d* × *d*, $J = 8.61$ and 2.2, H–C(5)); 8.30 (*d*, $J = 8.61$, H–C(6)).

m-*Dinitrobenzene* (**8**), recrystallized from ethanol, m.p. 89–90° ([20]: 90.02°). – ^{1}H-NMR.: see *Table 3.*

1-Chloro-2,6-dinitrobenzene (**9**), synthesized according to *Gunstone & Horwood* [21]; m.p. 87° (ethanol) ([20]: 88°). – ^{1}H-NMR.: see *Table 3.*

2,4-Dinitrotoluene (**10**); m.p. 69° (methanol) ([20]: 71°). – ^{1}H-NMR.: see *Table 3.*

Sulfodechlorinations with PTC. – a) *With tetrabutylammonium sulfate.* In a 250 ml flask with magnetic stirrer and reflux cooler a solution of 2.8 g KOH (0.05 mol) and 8.1 g potassium sulfite (0.05 mol) in 25 ml water is added to a solution of 5.2 g **1** (0.025 mol) and 17.3 g tetrabutylammonium hydrogen sulfate (0.05 mol) in 50 ml CH_2Cl_2. The organic phase becomes bluish-red instantly. The mixture is heated to reflux. The organic phase becomes brownish-red. After 1 h the mixture is cooled to RT. and the two phases are separated. For the isolation of **2** as barium salt a solution of 12 g $Ba(ClO_4)_2$ (0.03 mol) in 15 ml water is added to the organic phase. After stirring (15 min) the yellowish-brown precipitate is isolated, washed with 10 ml CH_2Cl_2 and dried (P_2O_5). Yield: 6.35 g (*ca.* 80%).

For the isolation using trioctylamine the organic phase is evaporated. The residue is mixed with 12.5 ml 1M H_2SO_4, 12.1 ml trioctylamine and 50 ml toluene. After stirring (15 min) and separation the organic phase is washed with water (4 × 12.5 ml) and then added to 25 ml aqueous 1M NaOH. After 15 min the precipitate (sodium arenesulfonate) is separated and dried. Yield: 4.35 g (*ca.* 65%).

b) *With protonated tributylamine.* A solution of 4.9 ml tributylamine in 10 ml CH_2Cl_2 is added to a solution of 2.27 g $K_2S_2O_5$ (0.01 mol) in 10 ml water. The mixture is cooled to 0° in an ice-bath. Immediately after adding 10 ml of a freshly prepared 1M **1** in CH_2Cl_2 the organic phase becomes bluish-red. If the temperature exceeds 8–10°, slower stirring is necessary (slower phase-transfer!). After 3.5 h the mixture is yellowish-orange; the ice-bath is removed and 30 to 35 ml 0.8M KOH are added. The *pH* value of the aqueous phase should be 11.0 ± 0.5. The potassium salt of **2** precipitates. After 5 min it is separated, washed with 25 ml CH_2Cl_2 and dried. Yield: 2.87 g, purity 96%, corresponding to a yield of 97%. Tributylamine can be regenerated from the organic phase (82% yield, see [9e]). Experiments with other tertiary amines were made analogously.

Mixtures of solutions for spectroscopic purposes. – The details of the solutions used for UV. and NMR. spectroscopy are described elsewhere [9f].

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[8]) Compound **1** is strongly irritating to the skin, even if handled with rubber gloves. We used gloves made from neoprene *('Neofloc').*

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