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SPECIFIC ORTHO ORIENTATION IN THE VICARIOUS SUBSTITUTION OF HYDROGEN IN AROMATIC NITRO COMPOUNDS WITH CARBANION OF CHLOROMETHYL PHENYL SULFONE[1]

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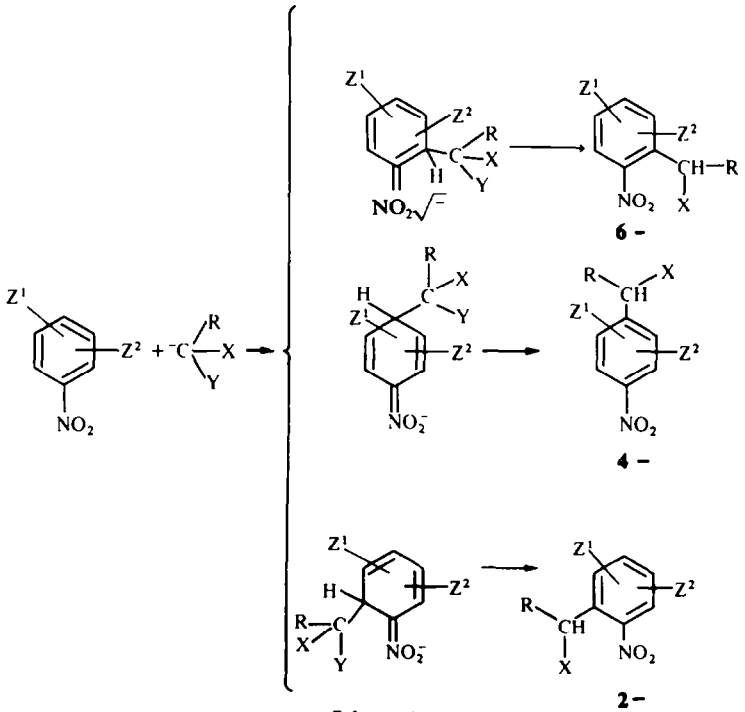
Abstract—Vicarious nucleophilic substitution of hydrogen atoms in nitroarenes with chloromethylphenyl sulfone proceeds selectively ortho to the nitro group when carried out in t-BuOK/THF base/solvent system. In the majority of 3-substituted nitrobenzene derivatives substitution occurs at the most hindered position 2. These conditions offer an efficient method of synthesis of 2,6 and 2,3-disubstituted nitrobenzene derivatives.

In several preceding papers we have presented the general concept of the vicarious nucleophilic substitution of hydrogen in aromatic nitrocompounds and also numerous examples of this process in application to a variety of carbanions and nitroarenes.[2a–f] This new method of introduction of α-functionalized alkyl substituents into nitroarenes is of general character and offers considerable practical possibilities. Main features of this reaction and its scope were presented in our recent review.[3]

The substitution of hydrogen in nitroarenes via the vicarious reaction with carbanions containing leaving groups at the carbanionic centers can take place at the positions ortho and para to the nitro group giving two or even three (in the case of the reaction with *m*-substituted nitrobenzenes) isomeric products.

Hence the problem of the orientation and the possibility to manipulate with the proportion of the isomers are of considerable interest. We have already reported our observations that the orientation of the substitution is strongly influenced by the steric factors: secondary carbanions $YCHX^-$ (Y-carbanion stabilizing group, X-leaving group) react at both ortho- and para positions and the o/p ratio depends on the size of X and Y whereas tertiary carbanions react exclusively at the position para to the nitro group. When position para in nitroarenes is occupied, tertiary carbanions containing small substituents X, Y and R react to some extent in ortho position but as a rule tertiary carbanions do not react with such nitroarenes according to the vicarious substitution scheme. It is reasonable to anticipate that the orien-



Scheme 1.

tation of the vicarious substitution should depend also on the reaction conditions. We have already found that it is necessary for the process to use base/solvent systems in which carbanions are relatively free or are present in the form of loose ion-pairs. Under such conditions (KOH, NaOH in DMSO or NH_3 liq; t-BuOK/DMSO; $R_4N^+OH^-$/benzene) the ratio o/p substitution in nitrobenzene with chloromethylphenyl sulfone does not change considerably. Actually within these base/solvent systems the o/p ratio varies moderately with the reaction procedure: the order of mixing, the excess of base and temperature. These changes are due to rather complicated mechanism of the reaction: fast and reversible addition of the carbanion to the nitroarene molecule followed by the base induced β-elimination.[4] Thus variations of the base concentration or mixing order could change the contributions to the overall orientation pattern, made by the σ-complex formation equilibrium and the elimination rates from the isomeric σ-complexes.

Actually one can have selective substitution at the para position using tertiary carbanions or even secondary carbanions but with bulky substituents X and Y. In this paper we would like to present a method for selective vicarious substitution of hydrogen ortho to the nitro group.

RESULTS AND DISCUSSION

During examination of various base/solvent systems for the reaction of chloromethylphenyl sulfone 1 with nitrobenzene we have observed that t-BuOK/THF at room temperature gave low yields of the product, but with a significantly different isomer ratio as compared to the typical conditions. Since, during the reaction, characteristic deep colouration was observed and the starting materials were totally consumed we supposed that the process was very fast and the low yield was due to the decomposition of the anion of the product. Indeed when the reaction was carried out at the room temperature for very short time (less than 1 min) the yield became much better. The best results were obtained when the reaction was carried out at about $-25°$ for 30 min; the yield of pure o-nitrobenzylphenyl sulfone was 61%. These conditions have been found to be suitable for a variety of substituted nitrobenzene derivatives; in the great majority of cases the hydrogen atom ortho to the nitro group was exclusively or preferentially replaced by the phenylsulfonylmethyl substituent. Since the o/p ratio in this reaction often changes due to small changes in procedure all experiments were performed in an identical way. Results of these experiments are given in Table 1.

In order to compare results obtained when the

Table 1. Reactions of nitrobenzene derivatives with 1 in t-BuOK/THF system (KOH/DMSO in parentheses)

	Z^1	Z^2	Total yield	Product composition		
				2-	4-	6-
1(1a)	H	H	61(82)	100(42)	0(58)	( )
2(2a)	2-NMe_2	H	32(63)	-	0(84)	100(16)
3(3a)	2-OMe	H	56(75)	-	7(96)	93(4)
4(4a)	2-CF_3	H	93(87)	-	trace (44)	100(56)
5(5a)	2-Cl	H	99(77)	-	0(85)	100(15)
6(6a)	2-Me	H	19[a](41)	-	0(81)	100(19)
7(7a)	2-t-Bu	H	0(0)	-	0(0)	0(0)
8(8a)	3-NO_2	H	65(93)	12(0)	88(100)	( )[b]
9(9a)	3-CN	H	93(90)	23(trace)	14(37)	63(63)
10(10a)	3-CF_3	H	82(94)	0(0)	0(22)	100(78)
11(11a)	3-SO_2Me	H	87(90)	0(0)	26(26)	74(74)
12(12a)	3-OMe	H	42(75)	85(25)	0(61)	15(14)
13(13a)	3-NMe_2[c]	H	10(44)	100(0)	0(84)	0(16)
14(14a)	3-Me	H	81(64)	90(0)	0(88)	10(12)
15(15a)	3- 	H	79(66)	36(0)	0(51)	64(49)
16(16a)	3-F	H	90(86)	93(32)	0(57)	7(8)
17(17a)	3-Cl	H	77(93)	60(6)	5(73)	35(21)
18(18a)	3-Br	H	58(83)	50(5)	8(67)	42(28)
19(19a)	3-J	H	66(68)	34(0)	5(74)	61(26)
20(20a)	3-Cl	4-Cl	81(71)	87(37)	-	13(63)
21(21a)	2-Cl	5-Cl	81(80)	-	23(100)	77(0)
22(22a)	4-F	H	92(89)	100(58)	0(42)[d]	-

(a) 2,2'-dinitrobibenzyl was obtained with 15% yield. 2-Nitro-3-methylbenzyl phenyl sulfone was not isolated in pure form.

(b) Positions 4- and 6- are equivalent.

(c) In standard conditions reaction did not occur so it was carried out at 0° for 30 min.

(d) Substitution of fluorine: 4-nitro-α-chlorobenzylphenyl sulfone

t-BuOK/THF system was applied with those obtained in presence of KOH in DMSO the latter are also included in the Table. These results (yields and orientation patterns) are almost identical to those reported earlier;[2e] some discrepancies are due to somewhat different procedures, which for the above mentioned reasons can change the o/p ratios.

The most important conclusion that can be drawn from the data given in Table 1 is that the driving force for the ortho orientation in t-BuOK/THF system is remarkably strong. It is particularly apparent in the case of o-substituted nitrobenzene derivatives. In spite of the fact that only one ortho position is available the substitution occurred practically exclusively at this position although the products formed are the 2,6-disubstituted, sterically hindered nitrobenzene derivatives (Entries 2–5); with o-t-butyl-nitrobenzene the reaction did not proceed since the secondary steric effect of t-Bu group prevents the formation of the σ-complex (Entry 7).

In the reaction with o-nitrotoluene, 2,2'-dinitrobibenzyl was obtained as the main product (Entry 6) instead of expected hydrogen substitution product. Similar base induced couplings of nitrotoluenes in the presence of electron acceptors are well known and possess some synthetic utility.[5]

The strong tendency for reaction at position ortho to the nitro group is also observed for the majority of 3-substituted nitrobenzene derivatives. In these cases the substitution pattern is much more complicated since all three isomers (2, 4 and 6) can, in principle, be formed. In several cases (Entries 8, 13, 14, 15, 19 and 21) t-BuOK/THF system gave rise to the 2-substituted products which were completely absent when KOH/DMSO was used, and in other cases (Entries 3, 4, 5, 12, 16, 17 and 20) the product distribution in t-BuOK/THF system is reversed compared to that obtained when KOH/DMSO was applied. Comparison of entries 22 and 22a shows that in t-BuOK/THF system the substitution of the hydrogen atom ortho to the nitro group strongly dominates even over such a facile reaction as the fluorine atom substitution in 4-fluoro-nitrobenzene, although the fluorine substitution competes effectively with the vicarious substitution when KOH/DMSO is used. The assignment of the position of phenylsulfonylmethyl substituent ($PhSO_2CH_2$) in the isolated isomers was made on the basis of spectral and chemical evidence. Most of the isomeric substituted nitrobenzyl phenyl sulfones obtained in this work have been recently characterized.[2e] With only one execption for 3-methylsulfonylnitrobenzene (Entry 11) the NMR signals of 2-methylene group protons of the products appear downfield from corresponding methylene group signals of 4-isomers. When both 2- and 6-isomers were present the signal due to the methylene group located in position 2- was observed at lower field.

In several cases the structure of the isomeric products was unambiguously proved by the independent synthesis. Thus: 2-nitro-4-methylsulfonylbenzyl phenyl sulfone was obtained from methyl p-tolylsulfone by subsequent NBS bromination, nitration and reaction with $PhSO_2Na$. 2-Nitro-4-chlorobenzyl phenyl sulfone was obtained from 2-nitro-4-chlorotoluene via NBS bromination and subsequent reaction with $PhSO_2Na$. Analogous procedure was applied for 2-nitro-4-fluorobenzyl phenyl sulfone. 2-Nitro-6-methylbenzyl phenyl sulfone was obtained from 3-nitro-o-xylene by NBS bromination (two isomers are formed), reaction with $PhSO_2Na$ and column chromatography isolation of the required isomer. 2-Nitro-4-methylbenzyl phenyl sulfone was synthesized in a similar manner starting from nitro-p-xylene. 2-Nitro-6-trifluoromethylbenzyl phenyl sulfone was obtained from 4-trifluoromethylbenzaldehyde by $NaBH_4$ reduction to the corresponding alcohol, bromination with concentrated hydrobromic acid, nitration and reaction with $PhSO_2Na$. The above described standards were identical with the corresponding isomeric products isolated from reaction mixtures of substituted nitrobenzene derivatives with I (NMR, GLC, TLC and melting points). In case of 2-nitro-6-methoxybenzyl phenyl sulfone the structure was proved by oxidative degradation with aqueous $KMnO_4$ to 2-nitro-6-methoxybenzoic acid (mp 176–178°; lit[6] 178–180°).

The selective substitution of hydrogen ortho to the nitro group when the reaction was carried out in the presence of t-BuOK in THF can be rationalized taking into account the situation of the carbanions in this system. In conditions typical for the vicarious substitution (KOH, NaOH in DMSO or NH_3 liq) the carbanions and cations form loose, solvent-separated ion pairs. Since the carbanions enter the reaction in a relatively free state the influence of the cations on the orientation is not substantial. On the other hand in THF, carbanions form tight ion pairs or high molecular weight aggregates with potassium cations. During the approach of such ion-pair to the nitroarene molecule the negatively charged oxygen atoms of the nitro group attract the potassium cation therefore the associated carbanion is directed into neighbouring ortho position (Fig. 1).

Interaction with the nitro group weakens the cation–carbanion association thus the carbanion adds to the nitroarene in the form of a loose ion-pair. This can be considered as an example of a reaction induced by "solvation of one reactant by another." The above rationalization is supported by following experiments. Addition of equimolar amount of HMPT to the reaction mixture results in the partial solvation of the potassium cations and disfavours the ortho orientation (Table 2, Entries 1 and 1b). Addition of 18-crown-6 in equimolar quantity has much stronger effect promoting para orientation (Table 2, Entry 1c). The vicarious substitution of hydrogen in nitrobenzene with α-chloroethylphenylsulfone practically does not proceed in the presence of t-BuOK in THF. The product formed in very low yield showed o/p isomers ratio around 50. Contrary to this, the

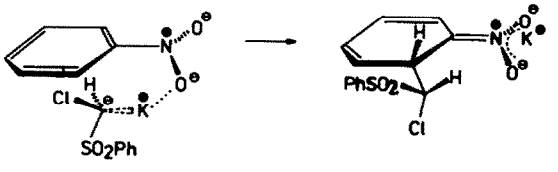


Fig. 1.

Table 2. Reactions of nitrobenzene with 1 in various base/solvent systems

	Solvent	Base	Complexing agent	Total yield	2-/4- isomer ratio
1	THF	t-BuOK	-	61	only 2-
1a	DMSO	KOH	-	82	0.73
1b	THF	t-BuOK	HMPT	68	100
1c	THF	t-BuOK	18-c-6	31	2.3
1d	THF	KOH	-	no reaction	-
1e	THF	KOH	18-c-6	39	1.7[a]
1f	THF	t-BuOLi	-	very low	not determined
1g	THF	t-BuONa	-	16	50
1h	DMSO	t-BuOK	-	96	1.7
1i	benzene	$(nBu)_4N^+OH^-$	-	50	0.44

(a) Reaction was carried out at the room temp. 0.5 h. contrary to the other reactions in THF. Anion of o-nitrobenzyl phenyl sulfone is much more stable when the accompanying cation is complexed by crown ether.

same reactants in presence of KOH in DMSO give satisfactory yields of pure p-isomer. It was already established that tertiary carbanions are unable to replace hydrogen ortho to the nitro group and also that the vicarious substitution occurs only with carbanions relatively free or being in the form of loose ion pairs. Since the "solvation of one reactant by another" can not induce the reaction at the para position, t-BuOK/THF system is inefficient for the reaction of tertiary carbanions.

The increasing size of leaving group at the secondary carbanionic center (Cl < Br < I Entries 1, 23 and 24) also lowers the yield obtained in t-BuOK/THF system although the strong ortho preference is still retained.

Preferential ortho orientation was reported earlier by Traynellis in the methylation of nitroarenes with sulfoxonium methylide in DMSO.[7] The authors have suggested that this is due to the attractive interaction between the positive pole of the ylide and the oxygen atoms of the nitro group. Contrary to our case here the carbanion centre and the cationic centre are connected with covalent bond; thus this effect operates in DMSO.

Another important problem is the influence of substituents in 3-substituted nitrobenzene derivatives on the orientation of the substitution of hydrogen which can occur at positions 2, 4 and 6. With such nitroarenes also the reaction proceeds mostly ortho to the nitro group (at positions 2- or 6-) although there are a few cases in which para isomer is also formed. In m-dinitrobenzene (Entry 8) positions 4- and 6- are equivalent.

Substituents $-SO_2Me$ and CN seem to be able to provide, to some extent, the reactant solvation of the potassium cations thus promoting the reaction in position 4-(Entries 9 and 11). The question 2- vs 6-substitution and the influence of 3-substituent on it, is the most interesting. In the great majority of cases the substitution occurs mainly at position 2- thus the most sterically hindered 2,3-disubstituted nitrobenzene derivatives are formed. Taking into account 2-vs-6-substitution in 3-Z nitrobenzenes substituents Z can be organized in the following order in which 2-/6- ratio increases:$-CF_3$(0); $-SO_2Me$(0); $-NO_2$(0.27); -CN(0.38); $-\overline{CHOCH_2CH_2O}$ (0.56; I (0.56); Br(1.2); Cl(1.7); OMe(5.5); Me(9.0); F(13.3); NMe_2(only 2-).

The observed orientation pattern is a result of a variety of factors affecting the orientation of the initial attack of the carbanion on the nitroarene ring, the relative stabilities of the resulting σ-complexes, the rates of the β-elimination of HCl from these complexes etc. Existing data are insufficient to discuss this problem in details. So far the rationalization of the preferential substitution at position 2- should be based mainly on two conceivable types of attractive interactions between carbanion–cation pairs and a substituent in position 3-. The possibility of complexation of cations by groups like $-SO_2Me$ and –CN has already been mentioned. Another type of effect was

Table 3. Reactions of nitrobenzene with α-haloalkyl phenyl $XRCHSO_2Ph$ in t-BuOK/THF system (KOH/DMSO in parantheses)

	X	R	Total yield	Product composition 2-	4-
23(23a)	Br	H	55(65)	92(6)	8(94)
24(24a)	J	H	28(38)	90(2)	10(98)
25(25a)	Cl	CH_3	8(51)	98(0)	2(100)

suggested by Bunnett[8] who formulated the hypothesis that polarizable substituents can promote an addition of polarizable nucleophiles at the vicinal position due to the action of attractive London forces. Thus the substitution of fluorine with thiolate anion proceeds faster in 4-fluoro-3-methyl-nitrobenzene than in 4-fluoronitrobenzene. Similar explanation of the directing effect of 3-alkyl substituents in the addition of organometallic compounds to substituted pyridines was given by Abramovitch.[9] These attractive interactions favour the addition of the carbanion to the nitroarenes and affect the position of the σ-complex formation equilibrium.

Since σ-complexes formed via addition of nucleophiles to mononitroarenes are short lived intermediates, no data concerning their stability are available. On the other hand, this problem was thoroughly studied for di- and trinitroarenes which form much more stable σ-complexes. A considerable body of data was collected in recent reviews by Terrier[10] and Beletskaya.[10a]

In particular Fendler[11] has shown that log of the equilibrium constants for addition of OH^- or CH_3O^- to di and trinitroarenes were in good correlation with σ^s-sum of substituent constants of all substituents present in the ring (with the slope 5.8). Since these σ-constants do not account for such substituent effects as London attractive forces or the influence of the substituent on rates of the β-elimination step it is no surprise that in the vicarious substitution no correlation between calculated relative stabilities of the intermediate isomeric σ-complexes and the orientation pattern is observed. These rather complicated problems are now under investigation.

EXPERIMENTAL

General. ^{1}H NMR spectra were determined with Varian EM-360 (60 MHz) spectrometer in $CDCl_3$ unless otherwise stated. Chemical shifts are given in δ ppm downfield from internal TMS. GLC analyses were performed on Chromatron GCHF 18/3 instrument equipped with 1.5 m stainless-steel column packed with 5% OV-17 on Chromosorb W. For column chromatography silica gel Merck 230-400 mesh was used. TLC analyses were made on foil plates Merck 60F 254. Visualisation of TLC chromatograms was accomplished by spraying with MeOH–DMSO (10 : 1) solution of KOH.

Materials. Commercial aromatic nitrocompounds were used in most cases. Commercially unavailable substrates have been synthesized by known procedures which are cited in Ref. 2c.

α-Chlorethyl phenyl sulfone. Chloromethyl phenyl sulfone (9.5 g, 50 mmol) in benzene (30 mL) was vigorously stirred with 50% aqueous NaOH (100 mL) and TEBA chloride (0.2 g, 1 mmol) at 10°. Methyl bromide (6.0 g, 65 mmol) in benzene (10mL) was added dropwise (over 30 min) and stirring was continued for 2 h. The reaction mixture was diluted with H_2O and extracted with benzene. The extract was dried over $NaSO_4$ and evaporated in vacuum. The oily crude product solidified upon cooling (9.2 g, 89%). Recrystallisation from hexane gave white crystals (5.5 g, 54%) m.p. 52–54° (lit.[12] 53°).

Reactions of nitroarenes with α-haloalkyl phenyl sulfones in t-BuOK/THF system

Potassium t-butoxide (1.2 g, 11 mmol) was dissolved in dry THF (20mL) and cooled to about −50°. To this solution nitroarene (5 mmol) and α-halosulfone (5 mmol) dissolved in THF (2 mL) were added in one portion (20 mL of THF were necessary for entry 11). The reaction mixture was maintained at −30° to −20° for 30 min, quenched with glacial acetic acid (1.0 mL), warmed up to room temp. and poured on water. The products were extracted with methylene chloride (2 × 50 mL) the extracts dried over Na_2SO_4 and small portions were examined by ^{1}H NMR and/or GLC in order to determine the ratio of isomers. The solvent was evaporated and the products isolated and purified by column chromatography using chloroform as eluent.

Reactions of nitroarenes with α-haloalkyl phenyl sulfones in KOH/DMSO system. To stirred solution of nitroarene (5 mmol) and α-halosulfone (5 mmol) in DMSO (20 mL) powdered KOH (2.0 g, 36 mmol) was added in one portion. The reaction was carried out at 20–25° for 30 min (cooling with ice—water bath was necessary). The mixture was poured on diluted HCl and extracted with methylene chloride (2 × 50 mL). The workup of the extract was the same as in the preceding procedure.

Preparations of the standards. 4 - trifluoromethyl - benzyl bromide was prepared according to lit.[13]

Brominations with N-bromosuccinimide. The equimolar amounts of corresponding substituted toluene and NBS with small amounts of benzoyl peroxide were refluxed for 4 h in CCl_4. (In case of 4-chloro-2-nitrotoluene and 4-fluoro-2-nitrotoluene 24 and 100 h respectively.) The succinimide formed was filtered off, the solvent was evaporated, the residue was dissolved in chloroform and filtered through silica gel to remove the residual succinimide. After evaporation of chloroform the crude product was used without further purification. (Brominations of 3-nitro-o-xylene and 2-nitro-p-xylene gave mixtures of benzyl bromides which were used in the next step without separation.)

Nitration of benzyl bromides. The crude benzyl bromide was dissolved upon cooling with ice–water in HNO_3 (100%; d = 1.50) and left overnight at the room temp. The reaction mixture was poured on ice–water, the product extracted with chloroform and the extract dried with Na_2SO_4. After evaporation of the solvent crude nitrobenzyl bromides were used without purification.

Reactions with sodium benzenesulfinate. The crude nitrobenzyl bromides were added to a warm solution (about 60°) of equimolar amount of $PhSO_2Na$ in DMSO. The reaction was left overnight at room temp, poured on water and extracted with methylene chloride. The corresponding nitrobenzyl phenyl sulfones were purified after evaporation of the solvent by column chromatography and/or recrystalisation.

Other compounds were characterized as follows. 2,6-Dinitrobenzyl phenyl sulfone, m.p. 218–219° (ethanol). NMR,/$(CD_3)_2CO$/: 5.39 (s, 2H), 7.57–8.49 (m, 8H). (Found: C, 48.41; H, 2.99; N, 8.70. Calc for $C_{13}H_{10}N_2O_6S$: C, 48.44; H, 3.13; N, 8.69%). 2-Cyano-6-nitrobenzyl phenyl sulfone, m.p. 174–176° (ethanol). NMR: 5.23 (s, 2H), 7.40–8.12 (m, 7H), 8.29(d.d, J = 2; J = 8; 1H). (Found: C, 55.69; H, 3.19; N, 9.10. Calc for $C_{14}H_{10}N_2O_4S$: C, 55.61; H, 3.33; N, 9.27%). 2 - N,N - Dimethylamino - 6 - nitrobenzyl phenyl sulfone, m.p. 103–105° (ethanol). NMR: 2.30 (s, 6H), 5.23 (s, 2H), 7.14–7.99 (m, 8H). (Found: C, 56.25; H, 5.05; N, 8.45. Calc for $C_{15}H_{16}N_2O_4S$: C, 56.23; H, 5.03; N, 8.75%). 2-/2-(1.3-Dioxolanyl)/-6-nitrobenzyl phenyl sulfone, m.p. 107–108°(methanol). NMR: 3.98 (s, 4H), 5.30 (s, 2H), 6.12 (s, 1H); 7.27–8.09 (m, 8H). (Found: C, 55.13; H, 4.30; N, 3.78. Calc. for $C_{16}H_{15}NO_6S$; C, 55.00; H, 4.33; N, 4.01%). 2-Nitro-4-fluorobenzyl phenyl sulfone, m.p. 108–109° (hexane/ethyl acetate). NMR: 4.90 (s, 2H), 7.24–7.99 (m, 8H). (Found: C, 52.82; H, 3.31; N, 4.52. Calc for $C_{13}H_{10}FNO_4S$: C, 52.87; H, 3.41; N, 4.71%). 2-Iodo-6-nitrobenzyl phenyl sulfone, m.p. 152–153° (hexane/ethyl acetate). NMR: 5.26 (s, 2H), 7.10–8.03 (m, 8H). (Found: C, 38.48; H, 2.32; N, 3.36. Calc for $C_{13}H_{10}INO_4S$: C, 38.71; H, 2.49; N, 3.46%). 2,3 - Dichloro - 6 - nitrobenzyl phenyl sulfone, m.p. 169–171° (ethanol). NMR: 5.26 (s, 2H), 7.40–8.03 (m, 7H). (Found: C, 45.12; H, 2.37; N, 4.12. Calc

for $C_{13}H_9Cl_2NO_4S$: C, 45.10; H, 2.62; N, 4.05%). 4,5 - Dichloro-2-nitrobenzyl phenyl sulfone, m-p. 170–172° (ethanol). NMR: 4.87 (s, 2H), 7.53–7.90 (m, 6H); 8.12 (s, 1H). (Found:C, 45.16; H, 2.38; N, 4.02. Calc for $C_{13}H_9Cl_2NO_4S$: C, 45.10; H, 2.62; N, 4.05%). 2,5 - Dichloro-6 - nitrobenzyl phenyl sulfone, m.p. 177–179 (acetone). NMR/$(CD_3)_2CO$/: 4.61 (s, 2H), 7.53–8.09 (m, 7H). (Found: C, 44.89; H, 2.48; N, 4.07. Calc for $C_{13}H_9Cl_2NO_4S$: C, 45.10; H, 2.62; N, 4.05%), 2,5 - Dichloro - 4 - nitrobenzyl phenyl sulfone, m.p. 138–140° (acetic acid). NMR: 4.54 (s, 2H), 7.57–7.86 (m, 7H). (Found: C, 45.07; H, 2.50; N, 3.82. Calc for $C_{13}H_9Cl_2NO_4S$: C,45.10; H, 2.62; N, 4.05%). 2 - Nitro-α-methylbenzyl phenyl sulfone, m.p. 95–96° (hexane/methyl ethyl ketone). NMR: 1.78 (d, J = 7, 3H), 5.43 (q, J = 7, 1H), 7.24–7.96 (m, 9H). (Found: C, 57.64; H, 4.44; N, 5.00. Calc for $C_{14}H_{13}NO_4S$: c, 57.71; H, 4.50; N, 4.81%). 4-Nitro-α-methylbenzylphenyl sulfone, m.p. 120–122° (methanol). NMR: 1.74 (d, J = 8, 3H); 4.34 (q, J = 8, 1H), 7.33–7.76 (m, 7H), 8.12 (d, J = 9, 2H). (Found: C, 57.68; H, 4.39; N, 4.85. Calc for $C_{14}H_{13}NO_4S$: C, 57.71; H, 4.50; N, 4.81%).

Reactions of nitrobenzene with **1** *in different base/solvent systems · t-BuOK/THF system in presence of a complexing agent* (*Entries* 1b, c). To a solution of nitrobenzene (0.063 g, 0.5 mmol) **1** (0.095 g, 0.5 mmol) and complexing agent (HMPT or 16-c-6, 1.0 mmol) cooled to −20° the solution of t-BuOK in THF (0.5M, 2.2mL, 1.1 mmol) was added in one portion. After 15 min the reaction was quenched with few drops of acetic acid and after addition of internal standard the mixture was analyzed by GLC to determine the yields of ortho and para isomers.

KOH/THF system in presence of a complexing agent (*Entry* 1e). To stirred suspension of powdered KOH (0.13 g, 2.5 mmol) and 18 - c - 6 (0.13 g, 0.5 mmol) in THF (12 mL) nitrobenzene (0.063 g, 0.5 mmol) and **1** (0.0095 g, 0.5 mmol) in THF (2 mL) was added at room temp. and stirring was continued for 30 min. The reaction mixture was poured on diluted HCl, extracted with methylene chloride and after addition of internal standard the extract was analyzed by GLC.

t-BuOLi (*t-BuONa*)*/THF system* (*Entries* 1f, g). The reactions were carried out according to the general procedure described for t-BuOK/THF system. In the course of the reaction with t-BuOLi only faint colouration appeared.

t-BuOK/DMSO system (*Entry* 1h). To a stirred suspension of t-BuOK (1.2 g, 11 mmol) in DMSO (20 mL) **1** (0.95 g, 5 mmol) was added while the temp. was kept below 25° with ice-water bath. After 3 min nitrobenzene (0.63 g, 5 mmol) in DMSO (2 mL) was added in one portion. Stirring was continued for 5 min. and the reaction mixture was poured on diluted HCl, extracted with methylene chloride and the extract was analyzed as above.

50% aqueous NaOH/benzene/$(Bu)_4N^+HSO_4^-$ *system* (*Entry* 1i). nitrobenzene (0.12 g, 10 mmol) and **1** (0.19 h, 10 mmol) in benzene (10 ml) and $(Bu)_4N^+HSO_4^-$ (0.35 g, 10 mmol) were vigorously stirred with 50% aqueous NaOH (2 mL) for 30 min. at room temp. The reaction mixture was poured on diluted HCl and worked up in usual manner.

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