Kinetics and mechanism of reactions between 2,4,6-trinitrofluorobenzene and alcohols

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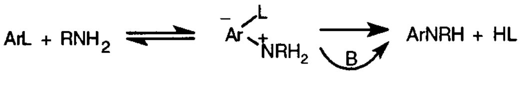
The kinetics of formation of some ethers from alcohols and 2,4,6-trinitrofluorobenzene were studied under first order conditions ($[ROH]_o > [TNFB]_o$). In CCl_4, k (in $dm^3\ s^{-1}\ mol^{-1}$) values are increased on increasing the values of the initial concentrations of the alcohols. This anomalous kinetic behaviour parallels that of reactions between amines and activated aromatic fluoro derivatives. The presence of a substrate–alcohol interaction which precedes the substitution process explains the kinetic behaviour of the alcohols.

Nucleophilic aromatic substitution reactions with neutral nucleophiles have been extensively investigated for amines.[1] Both aliphatic and aromatic amines are well known for showing (in apolar solvents) an increase of the second order rate constant values, k (in $dm^3\ s^{-1}\ mol^{-1}$) {obtained from the $k_{obs}/[amine]_o$ ratios, where k_{obs} (s^{-1}) is the first order rate constant} on increasing the initial concentration value of the amine {$[amine]_o$}. This kinetic behaviour was explained[1] by the leaving group–proton departure in a rate limiting step from the zwitterionic complex (**I**) *via* the usual two-step mechanism shown in Scheme 1, where L is the leaving group and B is a catalyst which may be the same reacting amine.



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Scheme 1

An alternative explanation involves the presence of an equilibrium preceding the substitution reaction and providing a molecular complex (Scheme 2) *via* substrate–amine interaction.[2–4] Another explanation[5] is the self-association of the amines in the 'dimer mechanism'.

$$\mathrm{ArL} + \mathrm{RNH_2} \overset{K}{\rightleftharpoons} \mathrm{ArL{\cdot}RNH_2}$$

Scheme 2

Less attention has been devoted to the neutral oxygenated nucleophiles,[6] such as alcohols, which are less reactive nucleophiles than amines in S_NAr reactions. Alcohols can provide zwitterionic intermediates in S_NAr reactions similar to those of amines.

In order to check the kinetic behaviour of neutral nucleophiles other than amines, we report here some kinetic data on the reactions between 2,4,6-trinitrofluorobenzene (TNFB) and alcohols, in THF and in CCl_4.

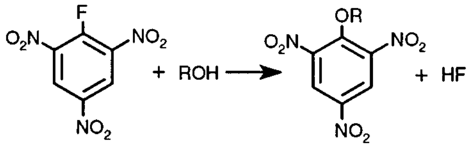
Results

The reaction between TNFB and alcohols affords ethers in almost quantitative yields (see Experimental), as shown in Scheme 3.

Table 1 reports data obtained from reactions between TNFB and H_2O or MeOH in THF. The k ($dm^3\ s^{-1}\ mol^{-1}$) values are unaffected by variations in the initial concentrations of water and methanol. Table 1 also shows data obtained in the presence of two common catalysts of S_NAr reactions with amines:[7] 2-hydroxypyridine (PY) and *δ*-valerolactam (VAL). Both PY and VAL enhance the reactivity of water and methanol, respectively. The addition of tetrabutylammonium bromide (TBAB) enhances water reactivity (see Table 1). The reaction of 2,4,6-trinitrochlorobenzene is too slow to yield kinetic data.

Table 1 Reactions between TNFB and H_2O or MeOH in THF at 25 °C and in the presence of tetrabutylammonium bromide (TBAB), 2-hydroxypyridine (PY) and δ-valerolactam (VAL)

$[TNFB]_o = 2.30 \times 10^{-4}$ mol dm^{-3}					
$[H_2O]_o$/mol dm^{-3}	0.111	0.148	0.178	0.200	
$k/10^{-3}$ dm^3 s^{-1} mol^{-1}	0.909	1.02	1.07	1.02	
$[TNFB]_o = 2.60 \times 10^{-4}$ mol dm^{-3}					
$[MeOH]_o$/mol dm^{-3}	0.372	0.452	0.558	0.569	0.696
$k/10^{-4}$ dm^3 s^{-1} mol^{-1}	2.74	2.67	2.85	2.88	2.72
$[TNFB]_o = 2.60 \times 10^{-4}$ mol dm^{-3}, $[H_2O]_o = 0.111$ mol dm^{-3}					
$[TBAB]/10^{-3}$ mol dm^{-3}	—	1.36	2.44	3.27	4.08
$k/10^{-3}$ dm^3 s^{-1} mol^{-1}	1.03	2.17	3.03	5.14	6.37
$[TNFB]_o = 2.50 \times 10^{-4}$ mol dm^{-3}, $[H_2O]_o = 0.111$ mol dm^{-3}					
$[PY]/10^{-2}$ mol dm^{-3}	—	0.401	1.00	1.40	
$k/10^{-3}$ dm^3 s^{-1} mol^{-1}	1.03	1.20	1.75	2.69	
$[PY]/10^{-2}$ mol dm^{-3}	1.81	2.02	2.37	2.90	
$k/10^{-3}$ dm^3 s^{-1} mol^{-1}	2.91	3.97	4.79	5.00	
$[TNFB]_o = 2.50 \times 10^{-4}$ mol dm^{-3}, $[MeOH]_o = 0.509$ mol dm^{-3}					
$[VAL]/10^{-2}$ mol dm^{-3}	0.561	1.12	1.54	1.96	
$k/10^{-4}$ dm^3 s^{-1} mol^{-1}	6.19	6.86	7.54	9.25	



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Scheme 3 R = Me, Pr^i, Bn, $3\text{-}ClC_6H_4CH_2$, $3\text{-}MeC_6H_4CH_2$, $4\text{-}MeC_6H_4CH_2$.

Table 2 shows kinetic data for some alcohols toward TNFB in carbon tetrachloride. The reactions of *tert*-butyl alcohol with TNFB and benzyl alcohols with 2,4,6-trinitrochlorobenzene are too slow to provide kinetic data, in agreement with neutral solvolysis data: TNFB is 2 × 10^4 times more reactive than 2,4,6-trinitrochlorobenzene.[8]

Table 2 Reactions between TNFB and alcohols in CCl_4 at 25 °C; $[TNFB]_o = (5–6) \times 10^{-4}$ mol dm^{-3}

$[MeOH]_o$/mol dm^{-3}	0.124	0.163	0.185	0.231	0.247	0.262	0.308	0.371	0.435	0.523	0.618
$k/10^{-3}$ dm^3 s^{-1} mol^{-1}	1.87	2.09	2.37	2.60	2.96	3.00	3.17	3.75	3.80	4.02	4.13
$[MeOD]_o$/mol dm^{-3}	0.107	0.214	0.321	0.432	0.535	0.696	0.803				
$k/10^{-3}$ dm^3 s^{-1} mol^{-1}	0.592	1.07	1.42	1.71	1.90	2.12	2.36				
$[Pr^iOH]_o$/mol dm^{-3}	0.129	0.204	0.255	0.307	0.438	0.515	0.613	0.695			
$k/10^{-3}$ dm^3 s^{-1} mol^{-1}	0.528	0.716	0.796	0.928	1.06	1.18	1.21	1.24			
$[TBATS^a] = 3.33 \times 10^{-2}$ mol dm^{-3}											
$[MeOH]_o$/mol dm^{-3}	0.107	0.214	0.321	0.432	0.535	0.696	0.803				
$k/10^{-3}$ dm^3 s^{-1} mol^{-1}	0.652	1.07	1.42	1.71	1.90	2.11	2.16				
$[BnOH]_o$/mol dm^{-3}	0.124	0.128	0.165	0.187	0.248	0.311	0.348	0.403	0.497		
$k/10^{-4}$ dm^3 s^{-1} mol^{-1}	1.93	1.98	2.59	2.80	3.35	3.62	3.85	4.19	4.27		
$[4\text{-}MeC_6H_4CH_2OH]_o$/mol dm^{-3}	0.152	0.172	0.202	0.205	0.263	0.287	0.344	0.390	0.437	0.492	
$k/10^{-4}$ dm^3 s^{-1} mol^{-1}	5.34	5.56	5.88	6.10	6.44	6.50	6.66	7.12	7.37	7.81	
$[4\text{-}MeC_6H_4CH_2OD]_o$/mol dm^{-3}	0.156	0.222	0.251	0.295	0.399						
$k/10^{-4}$ dm^3 s^{-1} mol^{-1}	3.54	4.03	4.20	4.46	4.63						
$[3\text{-}MeC_6H_4CH_2OH]_o$/mol dm^{-3}	0.237	0.307	0.324	0.356	0.427	0.474					
$k/10^{-4}$ dm^3 s^{-1} mol^{-1}	3.69	3.71	3.81	4.00	4.22	4.32					
$[3\text{-}ClC_6H_4CH_2OH]_o$/mol dm^{-3}	0.156	0.163	0.243	0.292	0.365	0.414					
$k/10^{-5}$ dm^3 s^{-1} mol^{-1}	1.85	1.93	3.02	3.31	4.16	4.52					

[a] Tetrabutylammonium trifluoromethanesulfonate.

Table 3 Dissection of the data for reactions between TNFB and alcohols at 25 °C

Nucleophile	Solvent	A^a	B^a	k'/dm^3 s^{-1} mol^{-1}	K^b/dm^3 mol^{-1}	R^c	n^d
H_2O	THF	—	—	$(1.0 \pm 0.1) \times 10^{-3\,e}$	—	—	4
MeOH	THF	—	—	$(2.8 \pm 0.1) \times 10^{-4\,e}$	—	—	6
MeOH	CCl_4	$(1.53 \pm 0.1) \times 10^2$	49 ± 2	6.5×10^{-3}	3.1	0.990	11
MeOD	CCl_4	$(2.31 \pm 0.1) \times 10^2$	155 ± 2	4.3×10^{-3}	1.5	0.999	7
$MeOH^f$	CCl_4	$(1.10 \pm 0.1) \times 10^2$	44 ± 2	9.1×10^{-3}	2.5	0.996	6
Pr^iOH	CCl_4	$(5.35 \pm 0.2) \times 10^2$	175 ± 4	1.9×10^{-3}	3.1	0.998	8
BnOH	CCl_4	$(1.20 \pm 0.1) \times 10^3$	474 ± 24	8.3×10^{-4}	2.5 (2.7)	0.991	9
$4\text{-}MeC_6H_4CH_2OH$	CCl_4	$(1.09 \pm 0.03) \times 10^3$	121 ± 7	9.2×10^{-4}	9.0 (6.0)	0.986	10
$4\text{-}MeC_6H_4CH_2OD$	CCl_4	$(1.49 \pm 0.01) \times 10^3$	224 ± 6	6.7×10^{-4}	6.7	0.999	5
$3\text{-}MeC_6H_4CH_2OH$	CCl_4	$(1.49 \pm 0.04) \times 10^3$	367 ± 12	6.7×10^{-4}	4.1 (6.3)	0.998	6
$3\text{-}ClC_6H_4CH_2OH$	CCl_4	$(1.94 \pm 1.2) \times 10^3$	8071 ± 302	5.2×10^{-4}	0.2 (0.67)	0.997	10

[a] *A* and *B* are the intercept and slope, respectively, of eqn. (2). Errors are standard deviations. [b] The values in parentheses were obtained (by Benesi–Hildebrandt plot) from absorbance extrapolation values at zero reaction times (see Tables 4 and 5). [c] Coefficient of correlation. [d] Number of points. [e] Mean of the determinations. Errors are standard deviations. [f] In the presence of tetrabutylammonium trifluoromethanesulfonate (TBATS).

Table 4 Absorbance values, at zero reaction time (A_o), for the reactions between TNFB and benzyl alcohol in CCl_4 at 25 °C; $[TNFB]_o = 5.5 \times 10^{-4}$ mol dm^{-3}

$[BnOH]_o$/mol dm^{-3}	0.124	0.128	0.147	0.147	0.165	0.187	0.220	0.248
A_o	0.114	0.115	0.120	0.121	0.128	0.150	0.170	0.175
$[BnOH]_o$/mol dm^{-3}	0.311	0.348	0.373	0.403	0.497	0.621		
A_o	0.207	0.210	0.213	0.238	0.242	0.274		

In a solvent of low permittivity, such as CCl_4, the *k* values (dm^3 s^{-1} mol^{-1}) are increased on increasing $[ROH]_o$ values. Under first order conditions, $[ROH]_o > [TNFB]_o$, kinetic runs follow a first order kinetic law up to high reaction percentages. This fact contrasts with the possibility that the reactive species is the anion of the alcohol. The reactions of Scheme 3 produce HF which depresses the amount of alkoxide ion arising from the equilibrium of Scheme 4, with the consequence that the concentration of RO^- will be depressed as the substitution reaction progresses. In conclusion, there are indications that the reactive species is the alcohol molecule.

$$ROH \rightleftharpoons RO^- + H^+$$

Scheme 4

With substituted benzyl alcohols in CCl_4, UV/VIS spectrophotometric inspection of the reaction mixtures at zero reaction time reveals the presence of an absorbance value which cannot be attributed to the starting materials or to the reaction products. This absorbance increases as the initial concentration of ROH increases (see Experimental), and may be related to the presence of a substrate–nucleophile interaction; a similar mechanism has been observed in similar reactions of amines.[9] Benesi–Hildebrand treatment[10] of the 'extra absorbance' at zero reaction time allows the evaluation of the apparent stability constant *K* (dm^3 mol^{-1}) of the substrate–alcohol complexes (see Tables 4 and 5).

Discussion

The kinetic behaviour of alcohols in THF should be a bimolecular process, typical of a simple S_NAr reaction. In effect, the reactions of TNFB with water or methanol follow a second order kinetic law, first order in each reagent.

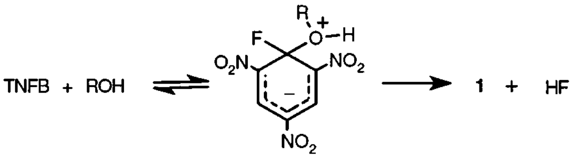
There is a moderate salt effect on the reactivity of water (see Table 1), of the type expected when neutral reagents cause the formation of a transition state with strong charge separation before the formation of the zwitterionic intermediate in the usual two-step mechanism of a S_NAr reaction (Scheme 5).

The scale of reactivity F ≫ Cl confirms the usual two-step mechanism of S_NAr reactions, in which the addition step is

Table 5 Apparent stability constant K (calculated *via* a Benesi–Hildebrand plot from spectrophotometric data at $\lambda = 320$ nm) of the molecular complexes between TNFB and substituted benzyl alcohols ($RC_6H_4CH_2OH$) in CCl_4 at 25 °C; [TNFB] = 5.5×10^{-4} mol dm^{-3}

R	ε/dm^3 mol^{-1} cm^{-1}	K/dm^3 mol^{-1}	R^a	n^b
H	787	2.7	0.993	14
4-Me	893	6.0	0.989	12
3-Me	763	6.3	0.943	11
3-Cl	1718	0.67	0.997	7

[a] Correlation coefficient. [b] Number of points.



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Scheme 5

rate limiting. The positive catalytic effect of the addition of 2-hydroxypyridine or δ-valerolactam, which is usually observed with amines,[7] also confirms the usual S_NAr mechanism.

The reactions in CCl_4 are complicated by 'anomalous' behaviour; the k value increases when the $[ROH]_o$ value is increased. This kinetic behaviour parallels that reported for similar reactions with aliphatic amines.[11] When amines react with fluoronitrobenzenes, in apolar solvents, the deprotonation (or the departure of HF) has been indicated as a rate determining step.

Our previous findings[2,9] support a mechanism for the base catalyzed step which is different from that usually accepted. In the present case, the movement of the proton from the oxonium ion (**2**) to the alcohol in a rate determining step is unlikely owing to the very high acidity of the oxonium ion.[12] Moreover, the proton transfer is favoured by the large excess of alcohol with respect to the zwitterionic intermediate **2**. Consequently, the deprotonation of the zwitterionic intermediates (**2**) is a fast step in the catalyzed substitution process.

It should also be noted that the reactivity scale F ≫ Cl does not support the idea of the leaving group departure as the rate limiting step. The autocatalytic behaviour of the alcohols cannot be explained *via* the HF abstraction from the zwitterionic intermediate (**2**) of Scheme 5, in agreement with literature reports on acid-catalyzed decomposition of some σ-adducts.[13]

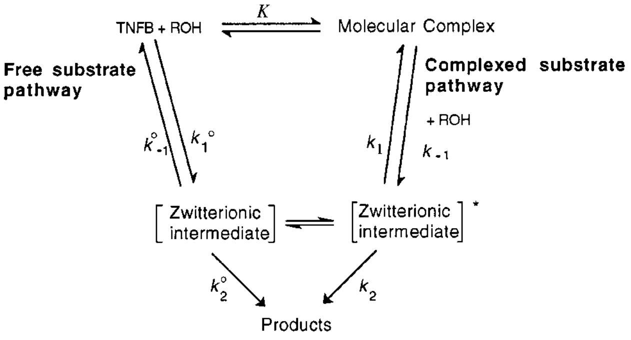
We should emphasize that the behaviour of the alcohols is very close to that of the amines not only from the kinetic point of view, but also with respect to the substrate–nucleophile interaction present in the reaction mixtures at zero reaction time. Benzyl alcohols also show the formation of a complex with the substrate in a step preceding the substitution process. The nature of this interaction requires clarification. Probably, in apolar solvents, alcohols form complexes *via* two main interactions: a hydrogen bonding interaction and an electron donor–acceptor interaction. In the present case, complex formation is observed (by the spectrophotometric method) for benzylic alcohols only.

A possible explanation for the kinetic behaviour observed in alcohols is shown in Scheme 6 and is similar to that previously proposed for amines.[2,9]

From Scheme 6, eqn. (1) may be used for data dissection,

$$k\,\{1 + K[ROH]_o\} = k_o + Kk'[ROH]_o \qquad (1)$$

where K is the apparent stability constant of the complex, $k_o = (k^\circ_1/k^\circ_{-1})k^\circ_2$ is the rate of the uncomplexed substrate and $k' = (k_1/k_{-1})k_2$ refers to the reactivity of the complexed substrate.



Scheme 6

Eqn. (1) may be reduced to eqn. (2) under the conditions

$$1/k = 1/k' + 1/\{Kk'[ROH]_o\} \qquad (2)$$

$k_o \ll k'K[ROH]_o$. For benzylic alcohols, K values are known from the Benesi–Hildebrand treatment (see Tables 4 and 5). Consequently, eqn. (1) enables the evaluation of k_o (rate of the uncatalyzed reaction) and of k' (rate of the reaction of complexed substrate). The k_o values are very near to zero and k are very near to the k values calculated using eqn. (2). The conditions $k_o \ll kK[ROH]_o$ are also indicated to be correct by considering the approximate k_o values calculated as the intercept of the simple plot of k values against $[ROH]_o$ values. The k and K values obtained using eqn. (2) are shown in Table 3.

The K values obtained using the eqn. (2) match the K values obtained independently using spectrophotometric analysis of the reaction mixtures at zero reaction time. This similarity (as in previous cases of the amine reactions) can hardly be considered as casual.

Even if the number of substituents is low, the substituent electronic effect on the K values (calculated from k values) shows a linear Hammett plot $\rho = -2.5 \pm 0.1$, $R = 0.995$. This negative ρ value confirms that the formation of the molecular complex involves an electron donor–acceptor interaction. In addition, the H/D isotope effect on the K values indicates the presence of hydrogen bonding interactions. K_H/K_D ratios are 2.07 and 1.34 for methanol and for 4-methylbenzyl alcohol, respectively. These values agree with previous findings. The K_H/K_D ratio for complexes between 2-hydroxypyridine and TNFB (in chlorobenzene), 2,4-dinitrofluorobenzene, and 4-nitrofluorobenzene (in benzene-d_6) were 1.75,[14] 1.7 and 3.4,[15] respectively. Also the association between amines and aromatic fluoro-derivatives was related to the hydrogen bonding interaction[4] as the main interaction. In CCl_4, the kinetic isotope effect, measured by the k'_H/k'_D ratio, is 1.5 and 1.0 for methanol and 4-methylbenzyl alcohol, respectively. These weak isotopic effects match those observed in the reactions of amines.[1,16]

Methanol is more reactive in CCl_4 than in THF ($k'_{CCl_4}/k'_{THF} = 23$). This ratio is unexpected because THF is a more polar solvent than CCl_4 and the reaction shows a transition state preceding the intermediate **I** with strong charge separation.[17] This is further confirmed by adding tetrabutylammonium trifluoromethanesulfonate which shows weak enhancement of k' values (see Table 3). The k'_{CCl_4}/k'_{THF} ratio may be explained by the fact that the k' value in CCl_4 is related to the reactivity of the substrate complexed by the nucleophile. As a consequence the substrate is surrounded by molecules more polar than those of either THF and CCl_4.

The steric requirement of the reaction of ROH is indicated by the ratio (in CCl_4) $k'_{methanol}/k'_{isopropanol} = 3.4$. The reactions of alkoxide ions and 2,4-dinitrofluorobenzene show $k'_{methoxide}/k'_{isopropoxide} = 4.9$.[18] The low reactivity of *tert*-butyl alcohol confirms the importance of the steric requirement usually observed in S_NAr reactions.

In conclusion, our data confirm the role played by hydrogen bond interactions in assisting fluoride ion departure. The hydrogen bond interactions are active on the free substrate in a step prior to nucleophilic attack and *not* on the zwitterionic intermediate; this is shown by the complexed substrate pathway in Scheme 6.

Experimental

Materials

Trinitrofluorobenzene was prepared by nitration of 2,4-dinitrofluorobenzene according to the literature.[19] The crude product was crystallized from cold ethanol; mp 122–123 °C. TNFB was stored at −20 °C. Benzyl alcohol, 4-methylbenzyl alcohol, methanol and isopropanol (Carlo Erba) were purified by distillation.[20] 3-Methylbenzyl alcohol and 3-chlorobenzyl alcohol were purified using a chromatographic column of silica gel (eluant: light petroleum–diethyl ether 8:2) followed by distillation. THF (Carlo Erba) was dried over sodium, distilled, and then redistilled from $LiAlH_4$, immediately before use, in a nitrogen atmosphere.[20] Tetrabutylammonium bromide was recrystallized from anhydrous THF. δ-Valerolactame and 2-hydroxypyridine (Carlo Erba) were purified by the usual procedures.[6]

General

All products gave satisfactory elemental analyses. Mps are uncorrected. UV/VIS spectra were recorded with Perkin-Elmer Lambda 5 and Lambda 12 spectrophotometers. NMR data were recorded on a Varian Gemini 300 MHz spectrometer; J values are in Hz. Kinetic runs were performed by following the appearance of the reaction product at $\lambda = 320$ nm in CCl_4 and $\lambda = 360$ nm in THF. The reproducibility of k_{obs} values was ±4%.

Reaction products

These were prepared by mixing appropriate solutions (in THF or in CCl_4) of TNFB (0.1 g, 0.4 mmol) in 1 mL of solvent and alcohol (4 mmol) in 1 mL of solvent. The reaction was monitored by TLC (silica gel, eluant: light petroleum–diethyl ether 8:2) The solid trinitrophenyl derivatives were separated on a silica gel column (light petroleum–diethyl ether 7:3) and purified by crystallization from methanol. 2,4,6-Trinitrophenyl methyl ether,[21] 2,4,6-trinitrophenyl isopropyl ether[21] and 2,4,6-trinitrophenyl benzyl ether[22] were prepared following procedures reported in the literature.

2,4,6-Trinitrophenyl 3-methylbenzyl ether

Mp 124–126 °C; $\delta_H(CDCl_3)$ 8.90 (2H, s, NO_2CCH), 7.2–7.4 (4H, m, Ar), 5.30 (2H, s, OCH_2), 2.40 (3H, s, CH_3); $\delta_C(CDCl_3)$ 150.41, 145.43, 141.56, 130.57, 138.86, 132.90, 130.07, 128.86, 126.39, 124.09, 80.32, 21.31.

2,4,6-Trinitrophenyl 4-methylbenzyl ether

Mp 108–110 °C; $\delta_H(CDCl_3)$ 8.87 (2H, s, NO_2CCH), 7.48 (2H d, J 7.9, $C\mathit{H}CCH_2$), 7.30 (2H, d, J 7.9, $C\mathit{H}CCH_3$), 5.31 (2H, s, OCH_2), 2.38 (3H, s, CH_3); $\delta_C(CDCl_3)$ 150.391, 145.37, 141.50, 129.66, 140.02, 138.93, 129.52, 124.00, 80.17, 21.32.

2,4,6-Trinitrophenyl 3-chlorobenzyl ether

Mp 111–112 °C; $\delta_H(CDCl_3)$ 8.80 (2H, s, NO_2CCH), 7.48 (1H, s, $CH_2CC\mathit{H}Cl$), 7.3–7.4 (3H, m, Ar), 5.30 (2H, s, OCH_2); $\delta_C(CDCl_3)$ 150.18, 145.42, 141.99, 130.23, 135.15, 134.79, 129.83, 129.07, 127.07, 124.31, 79.24.

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