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THE REACTION OF POLYNITROAROMATIC HALIDES WITH POTASSIUM ALCOHOLATES

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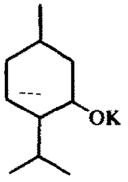
Abstract—Complexes of picryl chloride and 2-chloro-3,5-dinitropyridine with aliphatic potassium alcoholates were isolated and investigated. Structures I and II for these complexes are proposed. The products of the reaction between various potassium alcoholates and picryl chloride, 2-chloro-3,5-dinitropyridine, 2,4-dinitrochlorobenzene, 1-chloro-2,4-dinitronaphthalene and 2,4,6-trinitrofluorobenzene were also investigated. The mechanisms for the formation of Meisenheimer complexes and dialkyl ethers in this reaction are advanced. The effect of silver nitrate and the role of CT complexes in the reaction between potassium alcoholates and polynitroaromatic halogens are discussed.

STUDIES OF THE CHEMISTRY of 2-chloro-3,5-dinitropyridine have demonstrated[1,2] that this compound when treated with sodium or potassium methoxide gives appropriate ethers in moderate yields. Another product isolated was the sodium salt of 2-hydroxy-3,5-dinitropyridine. When higher alcoholates were used the latter product was the major one, and ethers were formed in poor yields. The same is true for the reaction between picryl chloride and sodium and potassium alcoholates. Previous information about the mechanism of nucleophilic substitution of halogens in polynitroaromatic compounds was insufficient to explain these observations. Therefore we decided to investigate the reaction of several polynitroaromatic halides with various potassium alcoholates. In this paper we report our studies of: picryl chloride, 2-chloro-3,5-dinitropyridine (CDNP), 1-chloro-2,4-dinitronaphthalene (CDNN), 2,4-dinitrochlorobenzene (DNCB) and 2,4,6-trinitrofluorobenzene (TNFB). The starting point of our investigation was the observation of the instantaneous and quantitative formation of coloured solid complexes when the listed nitro compounds are treated with potassium alcoholates in hydrocarbon solvents. As a rule the complexes are unstable and decompose spontaneously, but in the case of picryl chloride and CDNP the complexes formed by reaction with aliphatic alcoholates are reasonably stable and may be separated from the reaction mixture by filtration, and their decomposition may be controlled. However, the complexes are not sufficiently stable to be analysed in a conventional manner or to be investigated by methods applied for Meisenheimer complexes.[3] They decompose rapidly in contact with air and in solution, and cannot be completely freed from solvent. The structure of these complexes may be inferred from products resulting from their spontaneous and controlled decomposition.

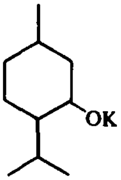
The complexes were prepared by adding a solution of the potassium alcoholates to a solution of the nitro compounds. As solvents for the potassium alcoholates we used in most cases light petroleum (b.p. 40–60°), and sometimes hexane, cyclohexane, benzene and mesitylene. Nitro compounds were dissolved in a mixture of benzene and light petroleum (1:1), hexane or cyclohexane, in accordance with the solvent used for the alcoholate. In some experiments nitro compounds were dissolved in MeCN, in this case when the solutions were mixed two phases were formed, and we believe that the reaction takes place exclusively in the MeCN layer. The colour of the complex varies with the nitro compound and alkoxide used. Picryl chloride, CDNN and TNFB produce red complexes, becoming redish brown for bulky alkoxides. The CDNP complexes are bright orange, and DNCB gives violet and blue complexes. The complexes are soluble in MeCN, acetone, DMSO, DMF and MeNO$_2$. The complexes obtained from picryl chloride and CDNP when treated with trifluoroacetic acid in benzene decompose, giving, as major product, the starting nitro compounds, Table 1 and 2. Other acids can be used instead of TFA. This property

TABLE 1. THE YIELDS OF PRODUCTS FROM THE DECOMPOSITION OF PICRYL CHLORIDE COMPLEXES[a] UNDER THE ACTION OF CF$_3$COOH

ROK	[PicCl]/[ROK][b]	Yield (%)	
		PicCl[c]	PicOR
EtOK	1·5	38·0	—
	1·0	71·0	—
	0·7	67·0	—
	0·5	62·0	—
n-PrOK	1·0	61·0	—
	0·7	44·0	9·3
i-PrOK	1·0	65·0	—
n-BuOK	0·7	48·0	8·5
i-BuOK	1·0	61·5	2·2
	0·7	54·0	4·0
	0·7[d]	50·0	—
	0·7[e]	71·0	5·7
t-BuOK	0·8	45·0	—
i-AOK	0·7	37·0	7·7
t-BuCH$_2$OK	1·0	56·0	—
	0·7	53·0	1·5
	1·0	62·0	—
	0·7	44·0	1·5
$\underset{\text{CH}_3}{\text{t-BuCH}}\text{—OK}$	1·0	36·0	—
$\underset{\text{CH}_3}{\phi\text{-CH}}\text{—OK}^{f}$	1·0	10·4	—

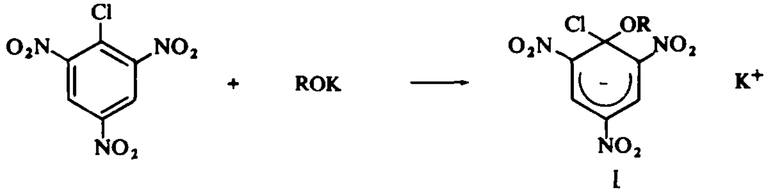
[a] The complexes were obtained in light petroleum if not otherwise stated. [b] Molar ratio of PicCl to ROK. [c] Pic = Picryl. [d] The complex was dissolved in MeCN and treated with TFA. [e] The complex was obtained in MeCN then the petroleum layer discarded and the MeCN layer treated with TFA. [f] Alcoholate was prepared in cyclohexane.

TABLE 2. THE YIELDS OF PRODUCTS FROM THE DECOMPOSITION OF CDNP COMPLEXES[a] UNDER THE ACTION OF TFA

ROK	[CDNP]/[ROK][b]	Yield (%)	
		CDNP	Ether
EtOK	1·0	80·5	—
i-BuOK	1·0	86·0	—
	0·7	94·0	—
	0·5	65·0	4·1
	0·7[c]	81·0	—
ϕ-CH_2OK[d]	1·0	67·0	—
	0·7	94·0	4·2

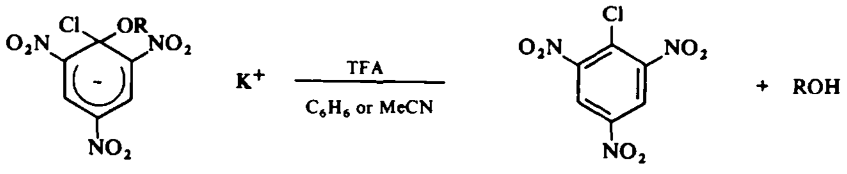
[a] The complexes were obtained in light petroleum if not otherwise stated. [b] Molar ratio CDNP to ROK. [c] The complex was obtained in MeCN, then the petroleum layer discarded and the MeCN layer treated with TFA. [d] Alcoholate was prepared in benzene.

suggests that the structure of the complexes is analogous to that of Meisenheimer complexes (IV). The structure of Meisenheimer complexes has been established by NMR[4–9] and by X-ray crystallography.[10, 11] If this assumption is valid, the formation of the complex may be presented as follows



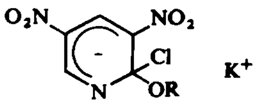
(1)

and its decomposition under the action of TFA:



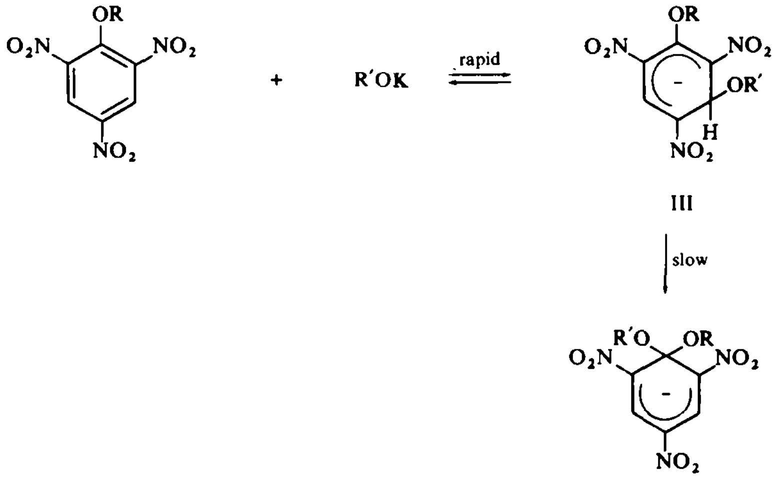
(2)

By analogy the structure of CDNP complex should be:



II

The structures I and II are, to a certain degree, in agreement with present view of the mechanism of nucleophilic displacement of halogens in polynitroaromatic compounds. However there are other possible structures which might be expected to give the same result as in reaction (2). By NMR it has been shown[6, 12] that Meisenheimer complexes are formed in a two step process:



III

IV

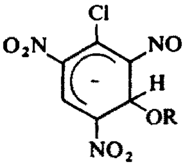
(3)

If the alkoxyl groups are different, complex III when treated with acid should give mainly the starting ether, whereas complex IV should give a mixture of two ethers. Table 3 presents the results obtained when R = Me, R′ = n-Bu and R = n-Bu, R′ = All (allyl). The composition of ethers in the first case is influenced by the period of time which elapsed from the preparation of the Meisenheimer complex to its decomposition by TFA, which favours mechanism (3). However when R = n-Bu and R′ = All the results are less convincing, and in the case of potassium allyloxide there remain two possibilities: either the allyloxide ion adds directly to the 1-position, or the second step of reaction (3) is a fast one.

TABLE 3. THE YIELDS OF ETHERS FROM THE DECOMPOSITION OF UNSYMMETRICAL MEISENHEIMER COMPLEXES UNDER THE ACTION OF TFA

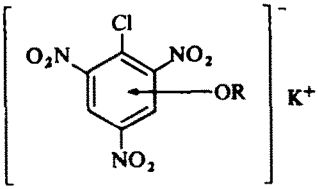
Starting ether	R'OK	Solvent	Time (min.)	Yield (%)	
				PicOR′	Starting ether
$PicOCH_3$	n-BuOK	MeCN	1·5	8·2	84·0
		MeCN	3·0	14·3	76·0
		MeCN	180	57·0	28·0
		Light petrol.	1·5	9·6	80·0
		Light petrol.	180	34·0	37·0
PicOBu-n	AllOK	MeCN	2·0	19·5	78·0
		MeCN	180	24·0	65·0

By analogy to reaction (3) we can suppose that in the case of picryl chloride the alkoxide ion also adds to the 3-position in a preliminary fast step, and then the resulting complex (V) rearranges in a slow process to complex I. If this assumption is correct the isolated complex may be presented as:



V

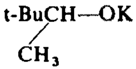
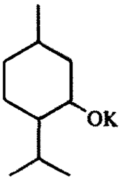
In the case of CDNP the addition may take place at C4 or C6. However, there are substantial differences between polynitroaromatic ethers and polynitroaromatic halides, and analogies in reaction mechanisms to various nitro compounds with nucleophiles have limited application. The inductive effect of chlorine is quite different from that of alkoxy, and we should expect a greater difference in electron density at C1 and C3 in picryl chloride than in trinitrophenethole. Moreover, steric requirements of the chlorine atom are less than those of alkoxyl groups. There are known Meisenheimer complexes with fairly sizable substituents bonded to the 1-position.[13, 14] The decreased electron density at C1 compared with C3 and the steric factor can favour kinetically and thermodynamically the addition to the 1-position of picryl chloride and to the 2-position of CDNP compared to the nitro ethers. But there is another structure which should be taken into consideration. This is the charge-transfer (CT) type structure:



VI

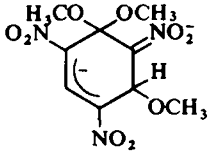
Data in Table 1 show that the amount of picryl chloride recovered from complex I in reaction (2) falls as the alkoxyl becomes more sizable. This can be rationalized in two ways. The free energy of complex I with a bulky alkoxyl is increased and it is less stable. Five to ten minutes elapsed from the formation of the complex to its decomposition by TFA, and during this period substantial decomposition may occur. The lowering of the yields is also caused by a change in the stoichiometry of the reaction for bulky alkoxyls, Table 4. The practical stoichiometry depends on the molar ratio of potassium alcoholate to nitro compound in the reaction mixture and on the nature of the substrates, but mainly on the size of the alkoxyl group. One mole of nitro compound always bonds more than one mole of potassium alcoholate. The bulkier the alkoxide the higher the practical stoichiometry (the number of moles of potassium alcoholate bonded by one mole of nitro compound), Table 4.

TABLE 4. THE PRACTICAL STOICHIOMETRY OF THE REACTION BETWEEN POLYNITROAROMATIC COMPOUNDS AND POTASSIUM ALCOHOLATES[a]

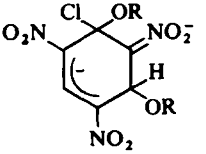
Nitro compound	ROK	[Nitro comp.]/[ROK][b]	Stoichiometry[c]
PicCl	EtOK	0·5	1·75
		1·0	1·10
		1·5	1·02
	n-PrOK	1·0	1·15
	i-PrOK	1·0	1·15
	i-BuOK	0·5	1·95
		1·0	1·15
		1·5	1·05
	t-BuCH$_2$OK	1·0	1·32
	 t-BuCH(CH$_3$)—OK	1·0	1·59
	 ϕ-CH(Me)—OK[d]	1·0	1·63
	 OK	1·0	1·10
CDNP	EtOK	1·0	1·10
	i-BuOK	0·5	1·89
		1·0	1·13
	ϕ-CH$_2$OK[e]	1·0	1·16
PicOEt	EtOK	0·5	1·55
		1·0	1·05
2,4-Dinitrophenethole	EtOK	0·5	1·20
		1·0	1·03
1-Ethoxy-2,4-dinitronaphthalene	EtOK	1·0	1·14

[a] The complexes were obtained in light petroleum if not otherwise stated. [b] Molar ratio of nitro compound to ROK. [c] Number moles of alcoholate reacting with one mole of nitro compound. [d] Alcoholate was prepared in cyclohexane. [e] Alcoholate was prepared in benzene.

Potassium 1-mentholate stands as an exception to the rule. Also the practical stoichiometry of Meisenheimer complex formation in hydrocarbon solvents is always greater than unity. If the structure of the picryl chloride complex with potassium alcoholates is VI, the stoichiometry of reaction (1) should be near unity. Foster and Fyfe[5] and Servis[6] have found that trinitroanisole in the presence of excess potassium or sodium methoxide forms a diadduct presented by formula VII:

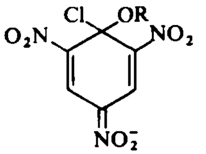


VII

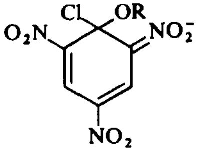


VIII

From the data of Table 4 it is suggested that some diadduct is formed even if the nitro compound is in excess. The formation of the 1:2 complex (VIII), when some of the nitro compound remains unchanged in the reaction mixture, indicates that the activation energy of the reaction by which the second molecule adds to the complex I is lower than the activation energy of reaction (1). This is in accordance with a simple HMO calculation[10] of π-electron density at C3 for diethoxy Meisenheimer complex and trinitrophenothole. The former indicates lower π-electron density at C3 than in the latter. Crystallographic studies[10] have revealed that in diethoxy Meisenheimer complexes the bond distances in the 4-nitro group are different from those of the 2- and 6-nitro groups. Especially the C4—N bond is much shorter than the C2—N bond. Moreover the C3—C4 bond is longer than C2—C3. This suggests that contribution of structure IX to the hybrid is greater than structure X.



IX



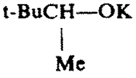
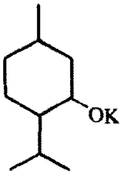
X

The same conclusion can be drawn from MO calculations,[10, 15] which indicate a greater electron density on the 4-nitro group compared to the 2- and 6-nitro groups. The steric interaction between the geminal alkoxyl and the nitro groups in the 2- and 6-positions results in a twisting of the nitro groups out of the plane, and mesomeric interaction between the ring and the nitro groups is reduced. Thus, the increased spatial requirements of the alkoxyl group brings about destabilization of the complex. HMO calculations carried out by Caveng *et al.*[16] for various angles of nitro group twist in Meisenheimer complexes, showed that the *para*-nitro-group must carry the bulk of the negative charge when the 2- and 6-nitrogroups are substantially rotated out of the plane. Thus, steric interference between alkoxyl and nitro groups would increase the contribution of the canonical structure IX to the hybrid, and as a result the C2—C3 and C5—C6 bonds become more olefinic and more reactive towards nucleophiles. Thus, the increased stoichiometry for a more sizable alkoxyl might be justified.

The spatial requirements of the 1-mentholate ion are so severe that a diadduct cannot be formed, or in this case the complex is of the CT type (VI). The picryl chloride and CDNP complexes in MeCN solution, when treated with TFA produce starting nitro compound in substantially the same yield as in benzene. However, in DMSO solution the starting nitro compound is recovered in only minute yield. In DMSO the complex suffers rapid decomposition to undefined products. Among the TFA decomposition products, besides starting nitro compound, are nitro arylalkyl ethers, picric acid in the case of picryl chloride and 2-hydroxy-3,5-dinitropyridine in the case of CDNP. Ethers can result either by spontaneous decomposition of complex I and II or TFA decomposition of Meisenheimer complexes which are formed in a small amount during the reaction (1).

Complexes I and II, separated by filtration and washed with hydrocarbon solvents, decompose giving several compounds when allowed to stand in hydrocarbon solvents or in MeCN. We have estimated the half life of I in MeCN, (R = i-Bu or Et)

TABLE 5. THE YIELDS OF THE DECOMPOSITION PRODUCTS OF THE PICRYL CHLORIDE COMPLEXES

			Yield (%)		
ROK	Solvent	[PicCl]/[ROK][a]	PicOR	Meisenheimer complex	PicCl
EtOK	Light Petrol.	0·5	15·0	18·0	0·0
	Light Petrol.	0·7	15·5	16·5	—
	Light Petrol.	1·0	17·2	17·6	—
	Light Petrol.	1·5	12·0	1·3	—
	MeCN	1·0	16·5	6·3	25·0
	EtOH	0·5	11·5	47·5	0·0
	EtOH	0·7	22·0	31·0	—
	EtOH	1·0	39·0	18·8	—
n-PrOK	Light petrol.	0·7	12·0	4·6	6·6
n-BuOK	Light petrol.	0·7	12·7	4·1	8·0
i-BuOK	Light petrol.	0·7	9·1	6·1	6·3
	Light petrol.	1·0	9·3	1·9	21·1
	Light petrol.	1·5	1·5	0·0	19·5
	MeCN	0·5	6·4	2·2	0·0
	MeCN	0·7	12·5	1·2	11·2
	MeCN	1·0	15·3	0·5	23·0
	i-BuOH	0·7	24·0	7·2	7·5
	Dioxan	0·7	3·7	0·0	3·0
t-BuOK	Light petrol.	0·8	0·0	0·0	16·0
i-AmOK	Light petrol.	0·7	7·8	2·1	0·7
t-BuCH$_2$OK	Light petrol.	0·7	5·3	0·0	8·4
	MeCN	0·7	2·8	0·0	11·8
 $\underset{\text{Me}}{\text{t-BuCH}}\text{—OK}$	Light petrol.	0·7	0·1	0·0	0·5
	Light petrol.	0·7	3·1	0·0	7·5
	MeCN	0·7	1·7	0·0	5·0

[a] Molar ratio of PicCl to ROK.

TABLE 6. THE YIELDS OF THE DECOMPOSITION PRODUCTS OF THE CDNP COMPLEXES

ROK	Solvent	[CDNP]/[ROK][a]	Yield (%)		
			Nitro ether	Meisenheimer complex	CDNP
EtOK	Light petrol.	0·7	13·3	1·9	6·3
	Light petrol.	1·0	12·0	1·3	14·3
	MeCN	1·0	5·5	0·0	10·5
	MeCN + $AgNO_3$	1·0	17·8	0·0	4·0
iBuOK	Light petrol.	0·7	6·8	0·0	14·3
	Light petrol.	1·0	4·7	0·0	24·0
	MeCN	1·0	2·6	0·0	14·3
	MeCN + $AgNO_3$	1·0	7·2	0·0	2·9
ϕ-CH_2OK	Benzene	1·0	21·0	0·0	20·0

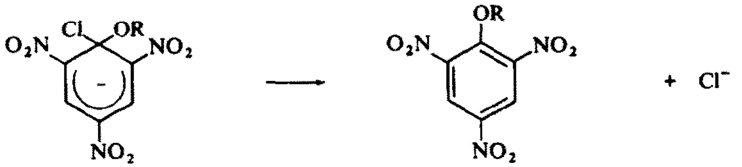
[a] Molar ratio of CDNP to ROK.

to be 30–40 minutes. Decomposition products of I are alkylpicryl ethers, picryl chloride, potassium picrate, Meisenheimer complexes and tarry and amorphous compounds. Analogous products have been found in the case of II. The yields of the decomposition products of I and II are presented in Tables 5 and 6, respectively. The yields of nitrophenols are displayed in Table 10. The yields of ethers are rather low, and fall rapidly as the size of alkoxide increases. If the complexes have the structures I and II, one would expect that when they decompose, ethers should be produced as major products. Inspection of crystallographic data obtained by Gramaccioli *et al.*[10,17] for trinitrophenethole and diethoxy Meisenheimer complex shows clearly that there is no reason to expect a high yield of ether in reaction (4). From these data, it is evident that steric strain in the Meisenheimer complex is much less important than in trinitrophenethole. Thus, in trinitrophenethole the two nitro groups, in the *ortho* positions with respect to the ethoxyl group, are significantly rotated out of the plane of the phenyl ring; rotation up to 61·3° has been observed. Whereas in the Meisenheimer complex the nitro groups are almost coplanar with the cyclohexadienate ring. If we take into account that the steric requirements of the chlorine atom are less than those of the ethoxyl group, the difference in steric strain in complex I and in the appropriate ether should be greater than in the diethoxy Meisenheimer complex and in trinitrophenethole. This steric effect will be much more important for more sizable alkoxyls.

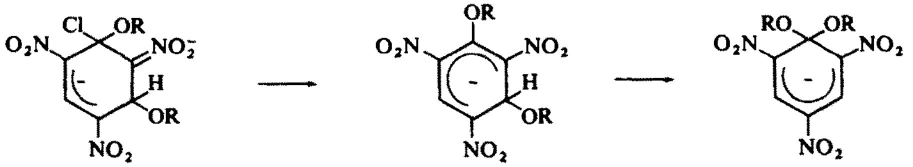
Besides complex I other species may be formed, such as V, VI and VIII. The formation of these species is favoured as the spatial requirements of the alkoxyls rise. We suppose the 1:2 adduct VIII will not decompose directly to the appropriate ether. When bearing sizable alkoxyls it will decompose with rupture of the ring.

The Meisenheimer complex formation can be explained in two ways. A less plausible explanation is based on the reversibility of reaction (1). This assumption is less probable when the reaction is carried out in hydrocarbon solvents. Ether formed by the decomposition of complex I reacts with alkoxide ions which are in equilibrium with complex I. The presence of picryl chloride among the decomposition products is in agreement with this explanation. If the explanation is correct, the amount of

Meisenheimer complex should depend on the equilibrium constant of reactions of (1) and (3) and on the rate of reaction (4).

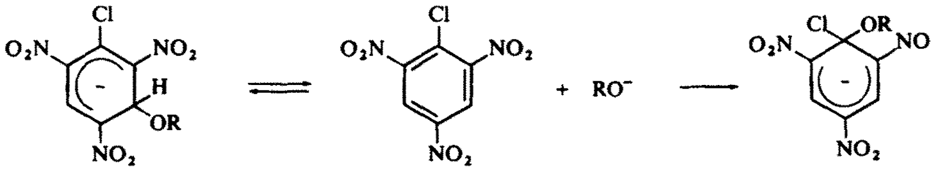

(4)

If the complex is represented by formula V, the additional equilibria and reactions should be considered. Another explanation assumes the Meisenheimer complex is formed from diadduct VIII by the sequence:


(5)

Complex III is not necessarily the intermediate in reaction (5). It is very probable that the ring of complex VIII, bearing six bulky substituents, is not planar. Puckering of the ring makes possible an intramolecular route for reaction (5). This explanation does not assume the competition between picryl chloride and picryl ether for alkoxide ions. Such competition is assumed in the first explanation. Picryl chloride is much more reactive towards potassium alcoholates than picryl ether and there would be little reason for the formation of Meisenheimer complexes as long as picryl chloride is present in the reaction mixture.

Alcoholates obtained from alcohols having π-bonds produce much less stable complexes with picryl chloride and CDNP than aliphatic alcoholates. The complexes obtained by using such alcoholates decompose rapidly and may not be isolated from the reaction mixture. In the case of potassium allyloxide the complex decomposes instantaneously, other unsaturated alcoholates produce more stable complexes. The CDNP complex with potassium benzyloxide decomposes slowly, and may be isolated from the reaction mixture. In spite of the impossibility of separating the complexes there is some reason to investigate their decomposition products. The results obtained in the case of picryl chloride and CDNP are shown in Table 7. The rapid decomposition of the complexes obtained from alcoholates having π-bonds argues in favour of structure I at least for potassium allyloxide and benzyloxide. If addition occurs initially at C3 the overall reaction should not be so rapid. If we assume reaction (4) to be rapid for saturated alcoholates then the rearrangement of V to I should be slow, otherwise the complex could not be isolated. The rearrangement of V to I can be represented by the following scheme:



(6)

It is a two step intramolecular process. The first step is assumed to be reversible, but in the case of picryl chloride, CDNP and TNFB it appears less likely because, when the complex is obtained in petroleum ether or other hydrocarbon solvents, the red precipitate is formed instantaneously as the reagents are mixed and potassium alcoholate is completely bonded if it is not in considerable excess. It is rather improbable that the rearrangement (6), which should take place in the solid state, can be a rapid reaction. And it would be difficult to find the reason why this rearrangement is rapid in the case of alcoholates with π-bonds. Therefore it is more reasonable to assume that the addition initially occurs at C1 in the cases of saturated as well as unsaturated

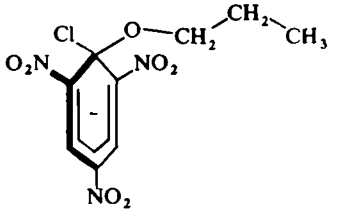
TABLE 7. THE YIELDS OF THE DECOMPOSITION PRODUCTS WHEN THE COMPLEX WAS NOT SEPARATED FROM THE REACTION MIXTURE

ROK	Solvent	[Nitro comp.]/[ROK][a]	Yield (%)		
			Nitro ether	Meisenheimer complex	Starting nitro compound
		PicCl			
AllOK	Light petrol.	0·5	6·5	53·0	1·1
	Light petrol.	0·7	14·3	34·0	14·2
	Light petrol.	1·0	20·0	13·0	40·0
	MeCN	0·5	5·0	45·0	0·0
	MeCN	0·7	17·0	35·0	13·0
	MeCN	1·0	27·0	10·7	35·0
	MeCN + $AgNO_3$	0·7	38·0	5·5	0·0
	MeCN + $AgNO_3$	1·0	30·5	1·0	21·0
ϕ-CH_2OK	Benzene	1·0	4·5	29·0	41·0
$\phi CH{=}CHCH_2OK$	Benzene	1·0	2·5	0·0	49·0
ϕ_2CHOK	Benzene	1·0	0·0	0·0	38·0
	Benzene	1·0	13·3	0·0	37·0
		TNFP			
EtOK	Light petrol.	0·7	63·0	20·0	0·0
i-BuOK	Light petrol.	0·7	50·0	7·0	0·0
	Light petrol.	1·0	54·5	3·7	0·0
		CDNP			
EtOK	Light petrol.	1·0	24·0	0·0	27·0
AllOK	Light petrol.	1·0	28·0	0·0	22·6
ϕ-CH_2OK	Benzene	1·0	33·5	0·0	32·0
ϕ_2CHOK	Benzene	1·0	0·0[b]	0·0	24·0

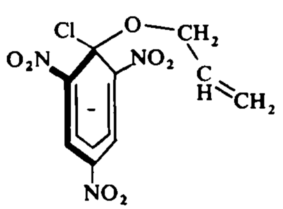
[a] Molar ratio of nitro compound to ROK. [b] Instead of ether, N-benzyhydrylo-3,5-dinitropyridone-2 is formed in 15·0% yield.

alcoholates, and that there is a difference in the rate of reaction (4) for both groups of alcoholates.

The substantial increase in the rate of reaction (5) in the case of unsaturated alcoholates may be conceivable if we take into account the steric course of the reaction leading to complex I. If picryl chloride reacts, for example with potassium n-propoxide, the resulting complex should be represented by structure XI. Whereas, in the case potassium allyloxide the complex is presumably represented by structure XII.



XI



XII

Structure XI is *exo* and XII is *endo*. Picryl chloride exerts a strong affinity towards π-electrons, so the molecule of potassium allyloxide approaches it in such manner that in a transition state a CT interaction might take place. The situation is analogous to that in the case of a Diels–Alder condensation.[18] As long as the normal bond is not formed between Cl and oxygen of alkoxide, the CT interaction prevails over the steric repulsion. However, in complex XII there is no further CT interaction, instead there is steric repulsion which destabilizes it compared to the *exo* complex. Inspection of molecular models shows there is some steric inhibition of the conversion of the *endo* configuration to *exo*. As the free energy of the *endo* complex is increased, the activation energy of reaction (4) might decrease. In the transition state of reaction (4) the aromaticity of the ring is partially restored and the CT interaction appears again. This CT interaction remains in the resulting allylpicryl ether, which is evident from its UV spectrum, Table 12 and Fig. 1. As a result of the CT interactions we have a flattening of the energy profile of the overall reaction between picryl chloride and potassium allyloxide, *i.e.* reaction (1) + reaction (4). The increased free energy of complex XII enhances its reactivity towards the allyloxide anion and as a result a greater amount of 1:2 adduct is formed. The greater amount of the diadduct is manifested by higher yields of Meisenheimer complexes, which are formed in the case of potassium allyloxide and benzyloxide. TNBF in spite of giving especially unstable complexes, produces essentially the same amounts of Meisenheimer complexes as picryl chloride, Table 7.

The increased reactivity of the complexes formed by unsaturated alcoholates can be explained more conventionally. It has been shown by high-resolution photoelectron spectroscopy[19] that there are strong interactions between lone pair AO's and π-MO's separated by a number of σ-bonds. The same has been shown by theoretical investigation.[20–22]

We should expect an interaction between the AO of the allyloxyl oxygen and the π-MO of the double bond through the methylene group. This interaction should

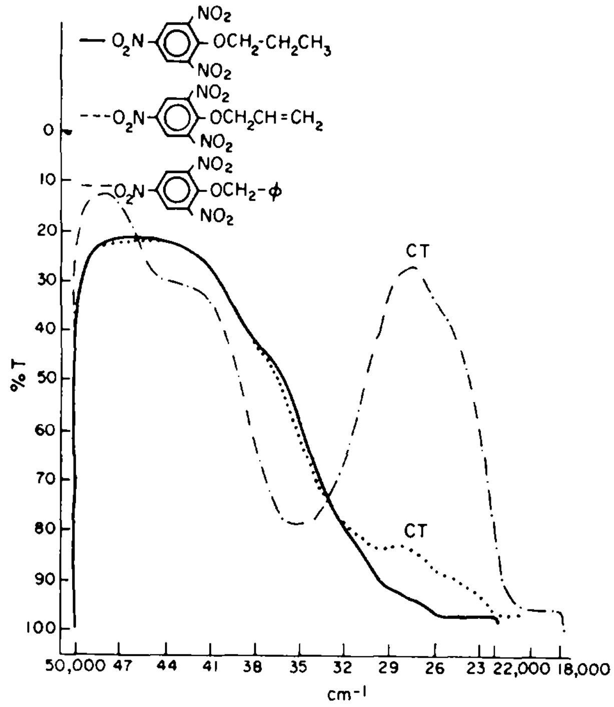


FIG. 1. UV spectra of picryl ethers in ethyl alcohol

stabilize the bonding orbitals of oxygen, and as a result the Cl–oxygen bond should be stronger. Moreover, this interaction should influence the nonbonding orbitals of oxygen *i.e.* the AO occupied by the lone pair of electrons, and as a consequence there is obtained a picture similar to that advanced by Kloppman *et al.*[23] for the explanation of supernucleophility, but instead of an alpha effect there we have a beta effect. This beta effect should be observed in reaction (4) as it is much slower than reaction (1). If this explanation is correct the yields of ethers should be much higher than for saturated alcoholates and the yields of Meisenheimer complexes should be little changed. But it is not true, and we believe that the first explanation is more probable. The results in the case TNFB, Table 7, indicate that such reasoning is valid. CDNP reacting with unsaturated alcoholates yields greater amounts of the appropriate ethers than with saturated alcoholates, whereas Meisenheimer complexes are formed in minute amounts or are not formed at all in both cases. The small yield of Meisenheimer complexes may be the result of low stability of the heterocyclic ring of the diadduct. DNCB and CDNN, when treated with potassium alcoholates, saturated as well as unsaturated, produce complexes which decompose immediately. The situation is similar to that in the case of TNFB and in the case of the complexes obtained from picryl chloride or CDNP and unsaturated alcoholates. DNCB reacts with potassium alcoholates to produce analogous products as in the case of picryl chloride, but there are substantial differences in the yields, Table 8. It seems likely that the reaction mechanism in the case of DNCB is essentially the same as for picryl

Table 8. The yields of the reaction products of DNCB and CDNN with potassium alcoholates[a]

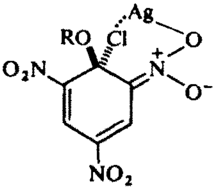
ROK	Solvent	Yields (%)		
		Nitro ether	Meisenheimer complex	Starting nitro compound
		DNCB		
EtOK	Light petrol.	81·5	0·4	10·4
	MeCN	81·0	1·9	11·5
	MeCN + $AgNO_3$	3·6	0·0	93·0
i-BuOK	Light petrol.	67·0	0·0	10·4
	MeCN	64·0	0·0	13·4
	MeCN + $AgNO_3$	4·7	0·0	87·0
AllOK	MeCN	78·0	4·0	8·4
	MeCN + $AgNO_3$	6·7	0·0	88·0
ϕ_2CHOK	Benzene	68·0	0·0	17·2
		CDNN		
EtOK	Light petrol.	5·0	47·0	43·0
	MeCN	21·0	28·0	35·0
	MeCN + $AgNO_3$	21·0	0·8	74·0
i-BuOK	Light petrol.	0·0	31·2	57·0
AllOK	MeCN	22·3	13·0	30·0
	MeCN + $AgNO_3$	13·5	3·0	72·0
ϕ_2CHOK	Benzene	21·0	0·0	40·5

[a] A 1:1 molar ratio of nitro compound to alcoholate was used in all cases.

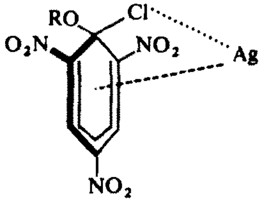
chloride. The picture is different in the case of CDNN. The major products of the CDNN reaction with potassium alcoholates are Meisenheimer complexes, however some ethers are formed when the reaction is performed in MeCN. If Meisenheimer complexes were to be formed by the reaction between the appropriate ether which should result from the rapid sequence of reactions (1) and (4) and potassium alcoholates, then we must assume that the ether is much more reactive towards potassium alcoholate than CDNN itself. This assumption is rather improbable. On the other hand, if Meisenheimer complexes are formed as result of reaction (5) it implies that complex I is much more reactive towards potassium alcoholates than CDNN itself. The practical stoichiometry of the reaction of 1-ethoxy-2,4-dinitronaphthalene with potassium ethoxide is higher than in the case of 2,4-dinitrophenethole, 1·14 and 1·03 resp. and it is even higher than in the case of trinitrophenethole (1·05) and picryl chloride (1·10), Table 4. These results indicate that the relative reactivity of the Meisenheimer complex towards potassium alcoholate in the case of 1-ethoxy-2,4-dinitronaphthalene is greater than in the case of 2,4-dinitrophenethole and trinitrophenethole. For the corresponding chlorides this difference may be more significant, and it is probable that the reaction of the complex of type I derived from CDNN with another molecule of potassium alcoholate would be much faster than reaction (1).

Potassium benzyloxide reacts with picryl chloride to give results similar to those observed in the case of the reaction of CDNN with other potassium alcoholates. There also we have a low yield of ether and an increased yield of Meisenheimer complex. The explanation of that can be also analogous. The practical stoichiometry of the reaction of CDNP with potassium benzyloxide is 1·16.

The increased reactivity of the complexes in some cases and their higher stability in others, may be taken as an indication that in the former cases the additions take place directly at C1 and at C3 in the latter cases. It would be in agreement with the failure of Fendler *et al.*[8,9] to observe a two step reaction of 2,4-dinitrophenethole, 2,6-dinitrophenethole and 1-ethoxy-2,4-dinitronaphthalene with potassium ethoxide. On the basis of our results, Table 3, we cannot say that the case of the reaction of picryl ethers with potassium allyloxide the preliminary reaction is addition at C3. However, there is an observation which strongly argues that in the case of picryl chloride and CDNP the preliminary reaction is addition at Cl and that the complex obtained is represented by formula I, as otherwise, it would be difficult to conceive of the influence of silver nitrate on the decomposition reaction of the complex. If we allow the complex to decompose in MeCN solution containing silver nitrate, the amount of ether is increased, Table 6, 7, 8 and 9. This effect decreases notably as the size of the alkoxyl group increases. Potassium 1-mentholate is an exception to this rule. The effect of silver nitrate may be understood if we assume that complex I reacts with silver ions to produce a silver salt having the silver ion bonded to an oxygen of one of the three nitro groups. If silver is bonded to the nitro group at the 2-position, then in the resulting complex (XIII) there is the possibility of an intramolecular interaction between the silver atom and chlorine. Such interaction should facilitate reaction (4).



XIII

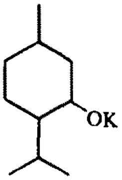


XIV

As the size of the alkoxy increases the electron density on the nitro group at the 4-position also increases, and silver ions would be likely to be bonded to this group mainly. It is also probable that silver ion is complexed by the cyclohexadienate ring. If this is true the silver cation should occupy the intermediate position between the C2 and C6, (XIV). Such a conclusion can be drawn if we consider the interaction of the lowest unoccupied AO (5s) of silver cation with the highest occupied MO of trinitro-cyclohexadienate ion. The MO's of trinitrocyclohexadienate ion have been calculated by Hosoya.[15] In complex XIV the silver atom may also interact with chlorine, moreover formation of the silver cation complex should change significantly the MO levels of trinitrocyclohexadienate ion.

The silver nitrate effect is most markedly manifested when a petroleum solution of potassium alcoholate is added to the solution of picryl chloride in MeCN containing dissolved silver nitrate. In this case the resulting complex immediately reacts with silver nitrate. The presence of silver nitrate in the mixture substantially decreases the amount of Meisenheimer complex formed.

TABLE 9. THE YIELDS OF THE DECOMPOSITION PRODUCTS OF THE PICRYL CHLORIDE COMPLEXES IN THE PRESENCE OF $AgNO_3$

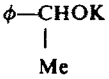
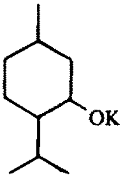
ROK	[PicCl]/[ROK][a]	Yield (%)		
		PicOR	Meisenheimer complex	PicCl
EtOK	0·5	37·5	2·4	—
	0·7	49·0	2·3	—
	1·0	25·0	0·3	—
i-BuOK	0·5	22·0	1·5	0·0
	0·7	33·0	0·0	0·0
	1·0	14·7	0·0	7·7
	0·7[b]	47·0	2·1	0·0
	1·0[b]	30·5	1·2	13·3
	1·0[c]	36·0	0·0	9·5
	1·0[d]	8·0	0·0	28·0
$t\text{-}BuCH_2OK$	0·7	2·5	0·0	3·6
 $t\text{-}Bu\text{-}\underset{\displaystyle Me}{\underset{\vert}{C}}HOK$	0·7	0·3	0·0	0·0
	0·7	30·0	0·0	0·0

[a] Molar ratio of PicCl to ROK. [b] Both PicCl and $AgNO_3$ were dissolved in MeCN and then a solution of alcoholate was added. [c] The complex was not separated, a solution of $AgNO_3$ in MeCN was added to the complex obtained in light petroleum. [d] To the solution of $AgNO_3$ in MeCN was added the solution of potassium isobutoxide and then the solution of picryl chloride in benzene was added.

We can suppose that silver nitrate does not react with complex I but with alkoxide ions and the resulting silver alcoholate reacts subsequently with picryl chloride or CDNP, giving the appropriate ether. In such a case the mechanism would be different from that proposed above. We performed an experiment adding firstly to the solution of silver nitrate in MeCN the solution of potassium isobutoxide in petroleum ether and then the solution of picryl chloride in benzene. The yield of picryl ether was only 8%, Table 9. This result confirms the supposition that silver ions react with the complex I, otherwise a sequence of solution mixing should not influence the yield of ether.

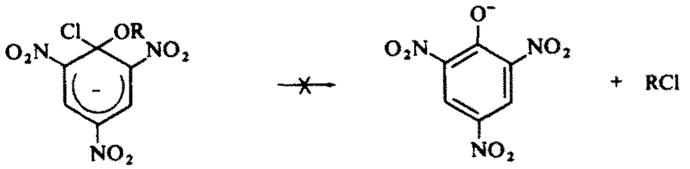
When DNCB reacts with potassium alcoholates in the presence of silver nitrate we observe a considerable lowering in the yield of ether. This is understandable since DNCB is less reactive towards potassium alcoholates than picryl chloride, and it is not able to compete with silver nitrate for alkoxide ions successfully, and the silver alcoholate is not a sufficiently strong nucleophile to react with DNCB. In the case of CDNN, silver nitrate exerts no effect upon the yield of ethers but it significantly decreases the yield of Meisenheimer complexes. Silver nitrate reacts with complex I or alkoxide ions, shifting the equilibrium of the reaction by which the diadduct is formed to the left, and as a result we observe a considerable lowering in the yield of Meisenheimer complexes.

TABLE 10. THE YIELDS OF POLYNITRO PHENOLS

Nitro compound	ROK	Solvent	Yield of polynitro phenol (%)
PicCl	i-BuOK	Heptane	34·0
	AllOK	Light petrol.	35·0
	$\phi\text{—}CH{=}CHCH_2OK$	Cyclohexane	46·7
	$\phi\text{—}CH_2OK$	Benzene	30·0
	ϕ_2CHOK	Benzene	38·5
	 $\phi\text{—}\underset{\text{Me}}{\underset{\vert}{C}}HOK$	Benzene	35·0
		Benzene	27·0
TNFB	ϕ_2CHOK	Benzene	67·0
CDNP	AllOK	Mesitylene	23·0
	$\phi\text{—}CH_2OK$	Mesitylene	7·0
	ϕ_2CHOK	Benzene	15·0
DNCB	i-BuOK	Light petrol.	3·5
	i-BuOK	CH_3CN	8·3
	ϕ_2CHOK	Benzene	9·2
CDNN	ϕ_2CHOK	Benzene	16·5

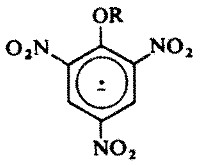
Potassium polynitrophenolates are always present among the reaction products of polynitroaromatic halogens with potassium alcoholates. This statement is valid for the reaction of polynitroaromatic ethers with potassium alcoholates also, as noted earlier.[24] The actual yield of nitrophenols formed in the reaction is somewhat higher than that presented in Table 10, since they have not been determined analytically, but the reported yields are based on product isolated and purified by recrystallization. The amounts of polynitrophenols increase as the alcoholate molecule becomes larger. It is reasonable that the phenolic oxygen originates from the alcoholate molecule. If this is true, the alcoholate molecule should give products characteristic of the loss of oxygen. The only products we have identified which could be formed as a result of oxygen transfer from alkoxide to picryl chloride are dialkyl ethers, but the ethers are not always present and in most cases are present in minute amounts,

Table 11, so the yield of phenols cannot be compared with the ether yields. An alternative possibility for the production of phenols is indicated below.

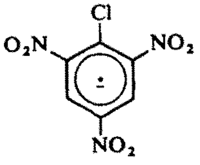


(7)

This is the SNi reaction similar to that observed when cyanuric chloride reacts with alcoholates,[25] but we have not found the appropriate alkyl chlorides, and reaction (7) appears to be ruled out. Only potassium benzyloxide, reacting with picryl chloride or CDNP, forms small amounts of benzyl chloride (4·5% and 2·6%, respectively). We have not found saturated and unsaturated hydrocarbons which may originate from the alcoholates. Thus, the phenolic oxygen may originate from the nitro group of another species present in the reaction medium. Unidentified products are always present during the decomposition of the complexes. It is also probable that phenolic oxygen originates from the air. During our experiments we did not take special precautions to avoid contact with air. However, solutions of aromatic alcoholates were prepared avoiding the presence of molecular oxygen and solutions of other alcoholates were at least partially deoxygenated by evolved hydrogen. Thus, the solutions applied should not contain much oxygen, and in some cases the complex was formed and decomposed within a few seconds; in spite of that, the amounts of polynitrophenols were significant, for example when picryl chloride or CDNP reacts with potassium allyloxide or potassium cinnamylate, Table 10. The assumption that phenolic oxygen may originate from the air is based on the well-known observation[26] that during the reaction of nitroaromatic compounds with alcoholates free radical species are formed as a rule. The free radical species would be able to react with molecular oxygen giving as a result replacement of chlorine by oxygen. Shein *et al.*[26, 27] have proved recently that free radical species formed when nitroaromatic ethers or nitroaromatic halides react with potassium or sodium alkoxides, are radical anions exemplified by formulae:



XV



XVI

In the reaction mixtures they have been observed the anion radical derived from the substrates as well from the products, i.e. XV and XVI, are formed when an excess of picryl chloride reacts with alcoholate.

We examined our reaction mixtures by ESR, and have found in all cases the presence of free radicals in hydrocarbon solvents. We failed to detect free radicals when the

TABLE 11. THE YIELDS[a] OF DIALKYL ETHERS (ROR) AND CARBONYL COMPOUNDS

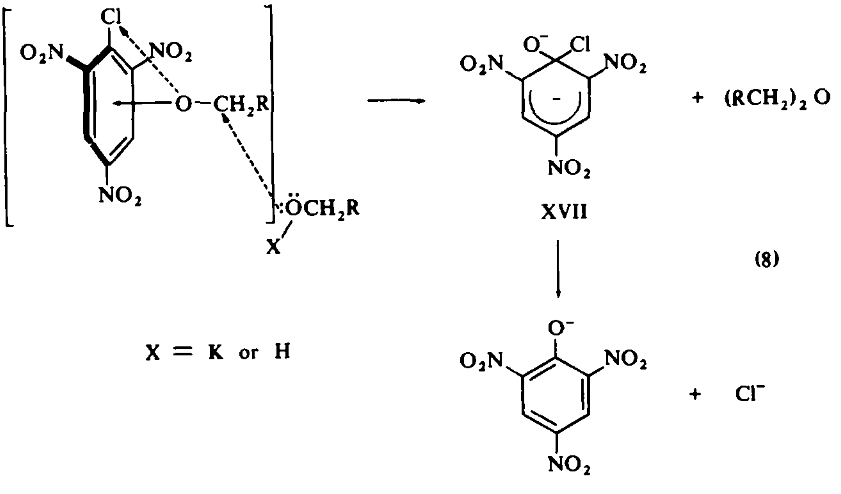
Nitro compound	ROK	Solvent	Yield (%)	
			Ether	Carbonyl compound
PicCl	i-BuOK	Mesitylene	6·9	0·0
	AllOK	Mesitylene	12·9	0·0
	ϕ—CH_2OK	Mesitylene	0·0	4·4
	ϕ—CH_2OK	Benzene	0·0	6·1
	ϕ_2CHOK	Benzene	52·0	17·0
	ϕ—$CH{=}CHCH_2OK$	Benzene	22·6	7·5
TNFB	ϕ_2CHOK	Benzene	94·0	—
CDNP	i-BuOK	Mesitylene	7·4	0·0
	AllOK	Mesitylene	28·4	0·0
	ϕ—CH_2OK	Mesitylene	0·0	0·75
	ϕ—CH_2OK	Benzene	0·0	2·9
	ϕ_2CHOK	Benzene	2·8	9·8
DNCB	i-BuOK	Mesitylene	6·0	0·0
	ϕ_2CHOK	Benzene	0·0	5·2
CDNN	i-BuOK	Mesitylene	5·0	0·0
	ϕ_2CHOK	Benzene	47·0	18·0
PicOBu-i	i-BuOK	Mesitylene	traces	0·0
2,4-Dinitrobenzene isobutyl ether	i-BuOK	Mesitylene	5·4	0·0
1-Isobuthoxy-2,4-dinitronaphthalene	i-BuOK	Mesitylene	3·0	0·0

[a] The yields are based on the potassium alcoholate.

reaction was carried out in MeCN. Picryl chloride and CDNP form free radicals in much lower concentrations than DNCB and CDNN. Especially long lived radicals are formed when CDNN reacts with potassium isobutoxide and potassium diphenylmethoxide. The life-time of radicals formed by picryl chloride and CDNP is rather short, about 20 minutes. We do not yet know the role of free radical species in the reaction of nucleophilic substitution of halogens in polynitroaromatic compounds.

In the case of aromatic alcoholates we have found among the reaction products appropriate aldehydes and ketones, Table 11. Aliphatic alcoholates are not oxidized to carbonyl compounds. The carbonyl compounds may be a result of a free radical side reaction. Tertiary aromatic alcoholates, such as potassium dimethylphenylmethoxide and diphenylmethoxide, do not give any carbonyl compound. We searched for isobutylene oxide among the products when potassium isobutoxide was used, but we failed to find it. Isobutylene oxide may be present if during the reaction isobutoxide free radical is formed.

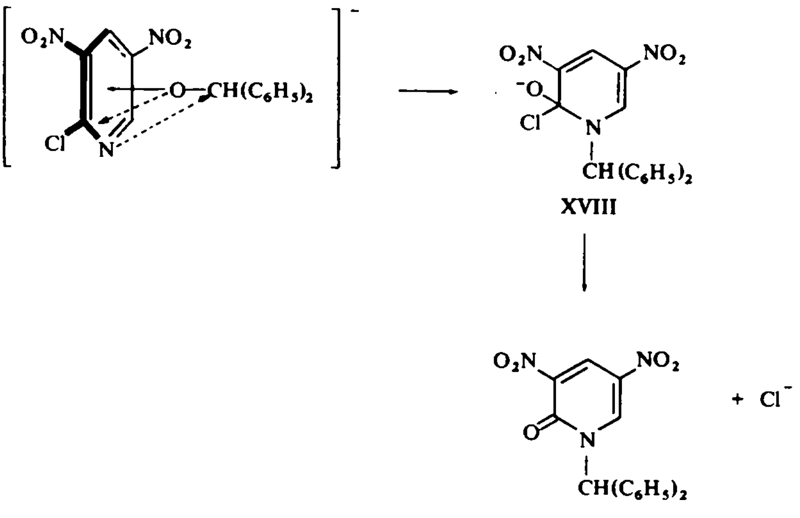
The formation of dialkyl ethers is difficult to understand on the basis of our knowledge about the mechanism of nucleophilic substitution of halogens in polynitroaromatic compounds. Alcoholates obtained from allyl, benzhydryl and cinnamyl alcohols give considerable amounts of appropriate ethers when they react with picryl chloride, Table 11. Potassium isobutoxide forms isobutyl ether in a small yield, whereas potassium benzyloxide does not form benzyl ether at all. The presence of dialkyl ethers among the reaction products sheds new light on the mechanism of nucleophilic substitution of halogens in polynitroaromatic compounds. The ethers are formed, presumably, in a SN_2 reaction. If they would be formed in a SN_1 reaction other compounds beside them should be present in the reaction mixture, for example unsaturated hydrocarbons. Moreover, such tertiary alcoholates as potassium dimethylphentlmethoxide and diphenylmethylmethoxide do not give ethers. It is less probable that the ethers are formed as a result of nucleophilic attack at the α-carbon of the alkoxyl bonded in complex I, since there is no reason to expect considerable preference at this position. However, the necessary preference of electron density on the α-carbon would be achieved in CT complex VI. There the electron density on alkoxyl oxygen should be substantially decreased and as a result the electron density on the α-carbon should be also decreased. Picryl chloride is a strong π-acid towards potassium alcoholates, and we have an analogous situation as in the case of the reaction in which ethers are formed from alcohols under the influence of H-acids. The nucleophile attacking the α-carbon of alkoxyl may be the potassium alcoholate or the free alcohol, since the alcoholate solutions always contained some free alcohol (0·25–0·8 moles/l). The solubility of alcoholates in hydrocarbon solvents considerably falls as the amount of free alcohol decreases. As a result of the above considerations we propose the following mechanism of ether formation:



(8)

Reaction (8) is the transfer of oxygen from the potassium alcoholate to the picryl moiety. The transfer is assisted by nucleophilic attack on the α-carbon atom of the alkoxyl. The bond making and the bond breaking is presumably a concerted, multicentre process and species XVII would not be formed explicitly.

When TNFB reacts with potassium diphenylmethoxide, benzhydryl ether is obtained almost quantitatively, based on the quantity of alcoholate used. The dialkyl ethers are formed in substantial yields when rather sizable alcoholates are used (potassium diphenylmethoxide and potassium cinnamyloxide) which favours the proposed mechanism. The proposed mechanism (8) is strongly supported by the result obtained from the reaction between CDNP and potassium diphenylmethoxide. In this case benzhydryl ether is formed as a minor product (in 3·2% yield) instead N-benzhydryl-3,5-dinitropyridine-2, XIX, in 15% yield is formed, based on the quantity of alcoholate. It is rather improbable that compound XIX is formed either as a rearrangement product of 2-benzhydryloxy-3,5-dinitropyridine or as a rearrangement product of the complex of type I. Since the known 3,5-dinitro-2-pyridyl ethers are stable compounds, and in the complex of type I the C2-oxygen bond is more likely to be broken than the α-carbon–oxygen bond in the alkoxy group. It would be better to suppose that compound XVIII is formed by a mechanism analogous to mechanism (8), but in this case when a molecule of CDNP receives two electrons from potassium alcoholate it becomes a nucleophile with a nucleophilic centre upon heterocyclic nitrogen. The resulting nucleophile competes in the intramolecular process with the alcoholates or alcohols.



XVIII

(9)

XIX

Again intermediate XVIII is not indispensable. If the mechanisms (8) and (9) are correct, we have CT catalysis which can be assumed to be a special case of general acid-base catalysis. The formation of CT complex VI in the preliminary step of the reaction of polynitroaromatic compounds with alcoholates is very probable and accounts for the rapidity of the reaction. Even very bulky alkoxides, such as potassium di-t-butylmethoxide and triphenylmethoxide, react with picryl chloride or CDNP in benzene instantaneously and quantitatively, giving solid complexes. The preliminarily formed CT complex VI would undergo subsequent change to complex I. But in the case of very sizable alkoxyls rearrangement VI to I may not occur.

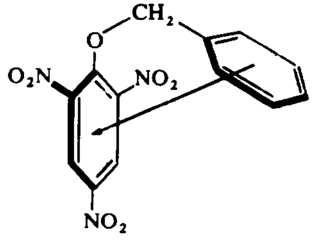
When potassium cinnamyloxide reacts with picryl chloride, nearly the same amounts of cinnamyl ether are formed in hydrocarbon solvents as in MeCN. The presence of silver nitrate slightly decreases the amount of cinnamyl ether formed, and from that we may infer that the nucleophile is the free alcohol rather than the alcoholate.

Table 12. The charge-transfer absorption bands of polynitroaromatic ethers in ethanol

Compound	of CT band $\nu(\mathrm{cm}^{-1})$	ε
PicOAll	28800	2022
$\mathrm{PicOCH_2{-}\phi}$	27800	14015
2,4-Dinitrophenyl allyl ether	—	—
2,4-Dinotrophenyl benzhydryl ether	28100	3122
	24700	2105
1-Allyloxy-2,4-dinitronaphthalene	22400	1027
1-Benzhydryloxy-2,4-dinitronaphthalene	23000	1190
	20500	1071

As in complex VI, when electrons are shifted toward the aromatic ring there occurs the possibility of a 1-2 hydride shift from the α-carbon atom to the oxygen atom of the alkoxide, and as a result there is oxidation of alcoholate to aldehyde or ketone and reduction of the nitro compound.

As was mentioned above, some polynitroaromatic ethers prepared during this investigation have structural features which enable the intramolecular CT interaction to occur. The situation is analogous to that in the case of N-(*p*-nitrobenzyl)-aniline.[28] For benzyl picryl ether the CT interaction can be represented as in diagram XX.



XX

Ethers which can show a CT band in the UV spectra are listed in Table 12. The UV spectra of ethers derived from CDNP do not show a CT band. In the case of ethers derived from benzhydrol two CT bands appear in the UV spectrum, which in the UV spectrum, which indicates that the phenyl rings of the benzhydryl moiety occupy unequal positions in space.

EXPERIMENTAL

Capillary m.ps. are uncorrected. Ir spectra were taken with a Zeiss UR-10 spectrophotometer. UV absorption spectra were obtained in EtOH (4×10^{-5} M) with a Unicam SP 700 spectrophotometer. NMR spectra were recorded with a Tesla 80 spectrometer using 10–15% solns in $\mathrm{CCl_4}$ or $\mathrm{CDCl_3}$ using HMDS as internal standard. Coupling constants, *J*, are expressed in hertz.

GLPC was carried out on a Willy Giede GCDF 18·3 chromatograph equipped with a flame ionization detector. Columns were packed with 20% Hallcomid M-18 on Chromosorb W and 20% Carbowax M-20 on Chromosorb W for reaction mixtures resulting from potassium isobutoxide and potassium benzyloxide respectively. H_2 was used as the carrier gas. The percent of each compound of interest in the mixture was calculated from peak area. Isobutyl and allyl ethers, benzaldehyde and benzylchloride were determined in this way; other ethers and carbonyl compounds were determined by isolation after column chromatographic separation. Column chromatography was carried out on Silica Gel (less than 0·08 mm) (Merck). Plates for TLC were prepared with Silica Gel G (Merck). Visualization of the spots of nitro compounds was carried out with 1% fluorescein aq. spray and a UV lamp. Other compounds were visualised by spraying with 50% H_2SO_4 and heating.

Materials. Solvents and reagents were purified by standard methods.[29] Trinitrofluorobenzene was prepared according to Parker and Read.[30] 2-Chloro-3,5-dinitropyridine was prepared according to Płażek.[31]

Procedure for the preparation of potassium alcoholates

To 5 ml of EtOH, n-PrOH and AllOH, or 6 ml of higher alcohol (n-BuOH, i-BuOH, benzyl alcohol, etc.) in 100 ml hydrocarbon solvent, was added 1–1·5 g clean potassium in small pieces. When the alcohol was a solid, 5–7 g per 100 ml of solvent was used. In the case of reactive ethyl and allyl alcohols, the mixture was cooled with water in the initial stages of reaction. In the case of higher or sterically hindered alcohols, the reaction was speeded up by maintaining the mixture at 40–50°. In the case of aromatic alcoholates the mixture was degassed after potassium addition by applying a vacuum, then the flask was connected to a mercury pressure relief valve. In the case of reactive alcohols the mixture was filtered through a sintered glass funnel after 2 hr and the remaining potassium washed with solvent, the time period was 20 hr in the case of the slow reacting alcohols. The filtrate was measured and a 10 ml aliquot was added to 50 ml of water and titrated with 0·2 N HCl using phenolphthalein as indicator. 10 ml of the alcoholate soln. consumed 5–13 ml of 0·2 N HCl. The soln. obtained was immediately used in a subsequent reaction.

Preparation of the complexes of picryl chloride and CDNP with potassium alcoholates

The calculated amount of picryl chloride or CDNP was dissolved in 20 ml of benzene in a wide-neck Erlenmeyer flask, which was placed in a beaker containing water. 20 ml of light petroleum or other hydrocarbon solvent was added and the mixture stirred. The alcoholate soln. (about 100 ml) was added during ½ min. The mixture was stirred for an additional ½–1 min and was filtered through a Buchner funnel and washed two times with petroleum or other solvent which had been used as the reaction medium. All operations were ended within 3–5 min. and the complex was used immediately in a subsequent operation. The filtrate was evaporated to dryness and the residue separated by column chromatography or analysed otherwise.

Decomposition of the complex with CF_3COOH

The complex obtained above was quickly put in a wide-neck Erlenmeyer flask and 7·5 ml of TFA in 50 ml of benzene was added with stirring. The stirring was continued until the complex was completely decomposed. Then the benzene soln was shaken with water, Na_2CO_3 aq, water again and finally dried ($MgSO_4$) and evaporated to dryness. The residue was separated by column chromatography using $CHCl_3$ as an eluent. Trinitrophenethole and picryl chloride could not be separated by column chromatography. Thus, in the case of reaction between potassium ethoxide and picryl chloride, the mixture of trinitrophenethole and picryl chloride was dissolved in 25 ml of benzene, the soln was warmed near boiling and 3 ml of pyridine added. The mixture was allowed to stand for 4 hr at room temp. The resulting precipitate was filtered and washed with benzene, dried and weighed. The amount of picryl chloride in the mixture was calculated assuming that it reacted with pyridine in 1:1 molar ratio, and the MW of the resulting compound was 326·56. This method is reasonably accurate (the relative error ±3% for 0·3–2 g picryl chloride), and sometimes it was used to determine the picryl chloride amount in other cases. This method does not give good results when trinitrophenethole is present in considerable amount in the mixture.

Spontaneous decomposition of the complex

After filtration the complex was quickly added to the appropriate solvent (50 ml) and stirred for 10–15 min, then the flask was stoppered and allowed to stand overnight. The colour of the mixture turned from red to brown in the case of picryl chloride or from orange to brown in the case of DNCP. Then the precipitate was filtered and washed thoroughly with benzene. The filtrate was evaporated to dryness and the residue separated by column chromatography. In the case of the reaction between picryl chloride and potassium ethoxide the residue after crystallization from MeOH gave almost pure trinitrophenethole.

The precipitate was treated with 30 ml of HCl (10%) and extracted into benzene. The benzene extract was shaken once with water and twice with Na_2CO_3 aq and then with water again, dried ($MgSO_4$) and evaporated to dryness. The residue was separated by column chromatography. It is assumed that all picryl ether obtained from the precipitate originates from a Meisenheimer complex.

When the complex was decomposed in MeCN, the resulting mixture, without filtration, was evaporated to dryness in vacuo. The residue was treated with benzene and filtered. The filtrate and the precipitate were treated as above.

When the decomposition was carried out in the presence of $AgNO_3$ (10 g/50 ml of MeCN) the procedure was the same as in the case of pure MeCN but the precipitate was treated with HNO_3 (10%) instead of HCl.

Procedure when the complexes were not separated from the reaction medium

To the nitro compound dissolved in a mixture of benzene and an appropriate solvent, as above, or in MeCN (50 ml) was added the alcoholate soln (about 100 ml) with stirring and cooling with water. CDNN was dissolved in 50 ml of benzene. The mixture was stirred for an additional 10 min, stoppered and allowed to stand at room temperature for 0·5–3 hr. It was filtered and the precipitate was washed thoroughly with benzene. The filtrate was evaporated to dryness and the residue separated by column chromatography. In the case of CDNN and DNCB the column was eluted with benzene or a benzene–cyclohexane mixture. In the case of aromatic alcoholates there were several compounds of interest in the mixture (starting nitro compound, nitro ether, dialkyl ether and carbonyl compound) and to separate them quantitatively some fractions were rechromatographed. 2,4-Dinitrophenylbenzhydryl ether and benzophenone were separated when the column was eluted with ethylene chloride. Benzophenone was freed from 1-benzhydryloxy-2,4-dinitronaphthalene on a column packed with aluminium oxide (calcinated p. A., Serva) and eluted with cyclohexane–benzene. On the other hand, pure 2,4-dinitronaphthalene–benzhydryl ether can be isolated using a column packed with silica gel and eluting with a $CHCl_8$–CCl_4 mixture (1:1).

The precipitate was treated with HCl or HNO_3 as before. In some cases the precipitate was treated with acetone containing 1–15% conc HCl, then filtered. The filtrate was evaporated to dryness and the residue crystallized from a H_2O–EtOH mixture, giving almost pure polynitrophenol. When the reaction was carried out in MeCN the resulting mixture was evaporated to dryness in vacuo and the residue treated with benzene and filtered, further manipulation was the same as described above. Allylpicryl ether could not be separated from picryl chloride by column chromatography. The mixture of these two compounds was purified by column chromatography using benzene as eluent and then allyl picryl-ether was determined by bromine addition to the double bond of allyl group.[31] This method gives satisfactory and reproducible results for pure mixtures of allylpicryl ether and picryl chloride when the established procedure is followed exactly (especially the reaction time).

Precipitation and decomposition of asymmetric Meisenheimer complexes

A calculated amount of picryl ether was dissolved in 50 ml of MeCN or 50 ml of benzene–light petroleum mixture. The soln was cooled with water and stirred and about 100 ml of potassium alcoholate soln was added. After an appropriate period of time (Table 3) 5 ml of TFA in 20 ml benzene was added and the mixture was worked up as before. The products were separated by column chromatography using benzene–cyclohexane mixture as eluent.

Determination of stoichiometry

The complex was obtained as described above. All unbonded picryl or other nitro compound was in the filtrate and was determined by isolation on a chromatographic column, and the practical stoichiometry was calculated. In the cases when the molar ratio of nitro compound to alcoholate was 0·5 the stoichiometry was calculated by determination of the amount of potassium alcoholate in the filtrate. The determination was performed by measuring the filtrate volume and titrating a 20 ml aliquot as described above.

The majority of the compounds obtained during our investigations are well known and may be found in Beilstein's Handbook. But some of them are not described or are described insufficiently in the literature. They are listed below, all were isolated by column chromatography.

Neopentyl picryl ether. Crystallized from hexane, m.p. 60°. NMR (CCl_4), δ 0·79 (3H, Me, s); 3·80 (2H, CH_2, s); 8·73 (2H, aromatic, s). (Found: C, 44·34; H, 4·44; N, 14·05. $C_{11}H_{13}N_3O_7$ requires: C, 44·15; H, 4·38, N, 14·04%).

1-*Menthyl picryl ether*. Crystallized from hexane, m.p. 133°. NMR (CCl_4), δ 0·85 (13H, $3CH_3 + 2CH_2$, m); 1·62 (2H, CH_2, m); 8·78 (2H, aromatic, s). (Found: C, 52·20; H, 5·60; N, 11·74. $C_{16}H_{21}N_3O_7$ requires: C, 52·31, H, 5·76, N, 11·44%).

2,4-*Dinitrophenyl benzhydryl ether*. Crystallized from cyclohexane–benzene, m.p. 149°. NMR ($CDCl_3$), δ 6·38 (1H, CH, s); 7·40 (10H, aromatic, m), 8·12 (2H, d, $J = 9$, protons at the 5 and 6 positions); 8·61 (1H, d, $J = 3$, proton at the 3 position). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2900 ($-\overset{|}{\underset{|}{C}}-H$ group). (Found: C, 64·78, H, 3·88, N, 8·10. $C_{19}H_{14}N_2O_5$ requires: C, 65·14, H, 4·03, N, 8·00%).

1-*Isobutoxy*-2,4-*dinitronaphthalene*. Crystallized from cyclohexane, m.p. 65°. NMR ($CDCl_3$) δ 1·10 (6H, Me, d, $J = 7$); 2·25 (1H, –CH, m); 3·96 (2H, OCH_2, d, $J = 7$); 7·20 (2H, m, naphthalene protons); 7·45 (3H, m, naphthalene protons). (Found: C, 58·22, H, 4·53, N, 10·00. $C_{14}H_{14}N_2O_5$ requires: C, 57·93, H, 4·86, N, 9·65%).

1-*Allyloxy*-2,4-*dinitronaphthalene*. Crystallized from cyclohexane, m.p. 89°, NMR ($CDCl_3$) δ 4·61 (2H, $=CH_2$, d, $J = 6$); 5·73 (2H, OCH_2, m); 6·10 (1H, $=CH-$, m); 7·85 (2H, naphthalene protons, m); 8·56 (3H, naphthalene protons, m). UV ν_{max}^{EtOH} cm^{-1} 47400 (ε, 28875), 39800 (ε, 18440), 34800 (ε, 8245), 27200 (ε, 5547), 22400 (ε, 1027). (Found: C, 56·71, H, 3·39, N, 10·07. $C_{13}H_{10}N_2O_5$ requires: C, 56·94, H, 3·68, N, 10·22%).

1-*Benzhydryloxy*-2,4-*dinitronaphthalene*. Crystallized from cyclohexane–benzene, m.p. 195°. NMR ($CDCl_3$) δ 5·84 (1H, s); 6·50 (1H, s); 7·17 (10H, aromatic protons, m); 7·65 (2H, aromatic protons, m); 8·03 (2H, aromatic protons, m); 8·03 (2H, aromatic protons, m). IR $\nu_{max}^{CCl_4}$ cm^{-1} 2930 ($-\overset{|}{\underset{|}{C}}-H$ group). UV ν_{max}^{EtOH} cm^{-1} 47400 (ε, 40492), 40100 (ε, 29500), 38200 (ε. 19175), 30700 (ε, 5710), 2300 (ε, 1071), 20500 (ε, 1190).

2-*Isobutoxy*-3,5-*dinitropyridine*. Pale yellow liquid. Purified by column chromatography; silica gel/$CHCl_3$. NMR (CCl_4) δ 1·04 (6H, Me, d, $J = 6$); 2·10 (1H, CH, octet); 4·35 (2H, CH_2, d, $J = 6$); 8·94 (1H, pyridine, H, d, $J = 2$); 9·20 (1H, pyridine, H, d, $J = 2$). UV ν_{max}^{EtOH} cm^{-1} 47400 (ε, 14525), 42100 (ε, 7857), 3500 (ε, 10622). (Found: C, 44·51, H, 4·58, N, 16·75. $C_9H_{11}N_3O_5$ requires: C, 44·82, H, 4·60, N, 16·75%).

2-*Allyloxy*-3,5-*dinitropyridine*. Crystallized from cyclohexane, m.p. 64°. NMR ($CDCl_3$) δ 5·12 (2H, CH_2, d, $J = 6$); 5·46 (2H, CH_2, m); 6·05 (1H, CH, m); 8·91 (1H, pyridine, H, d, $J = 2$); 9·22 (1H, pyridine, H, d, $J = 2$). UV ν_{max}^{EtOH} cm^{-1} 47500 (ε, 15052), 42400 (ε, 8692), 35000 (ε, 10592). (Found: C, 42·81, H, 3·67, N, 18·52. $C_8H_7N_3O_5$ requires: C, 42·68, H, 3·43, N, 18·66%).

2-*Benzyloxy*-3,5-*dinitropyridine*. Crystallized from cyclohexane, m.p. 164°. UV ν_{max}^{EtOH} cm^{-1} 47500 (ε, 24265). 41900 (ε, 8915), 35000 (ε, 12545). (Found: C, 51·90, H, 3·92, N, 15·42. $C_{12}H_9N_3O_5$ requires: C, 52·37, H, 3·30, N, 15·27%).

1-*Benzhydryl*-3,5-*dinitro*-2-*pyridone* (XIX). Crystallized from cyclohexane–benzene, m.p. 179°. NMR ($CDCl_3$) δ 6·20 (1H, CH, s); 7·20 (4H, aromatic protons, m); 7·35 (6H, aromatic protons, m), 8·70 (1H, pyridine H, d, $J = 4$); 8·95 (1H, pyridine H, d, $J = 4$). IR ν_{max}^{KBr} cm^{-1} 1680 (C=O), 2955 ($-\overset{|}{\underset{|}{C}}-$ H group). UV ν_{max}^{EtOH} 48300 (ε, 30912), 31800 (ε, 11842), 2200 (ε, 13630). (Found: C, 61·60, H, 3·54, N, 12·04. $C_{18}H_{13}N_3O_5$ requires: C, 61·54, H, 3·73, N, 11·96%).

The compound XIX was prepared by heating at reflux an equimolar mixture of the sodium salt of 2-hydroxy-3,5-dinitropyridine and diphenylmethyl chloride for 12 hr. The pure compound was isolated by column chromatography in 65% yield, using a column packed with silica gel and benzene–ethyl acetate mixture (10:1) as eluent.

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