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AROMATIC NUCLEOPHILIC SUBSTITUTION
REACTIONS WITH CARBANIONS PART. II

by

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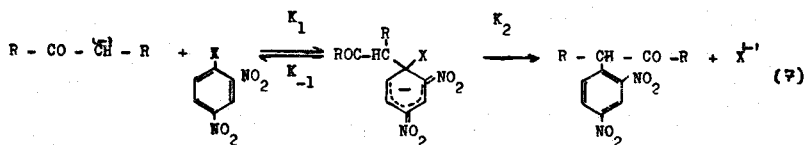# AROMATIC NUCLEOPHILIC SUBSTITUTION REACTIONS WITH CARBANIONS PART. II*

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Reactions of 2,6–dinitro and 2, 4–dinitrohalobenzenes with potassium salts of β–diketones, of α–diketoesters, of β–ketonitriles, of α–cyanoesters were investigated and substitution products were obtained in dimethylsulfokside. Pseudo-first order rate coefficients of some reactions were determined in the same solvent by the photometric method to be confirmed the Two-stage mechanism and $Cl \sim Br > I$, reactivity order was found.

INTRODUCTION

Aromatic substitution reactions of large series of the nucleophiles have been investigated by several workers (1–3). Some workers have advocated a simple one step $S_N 2$ like mechanism (4). Bunnet and coworkers (1), (5) and Miller (2), (6) suggested the two-stage mechanism involving a meta stable Cyclohexadienide intermediate.
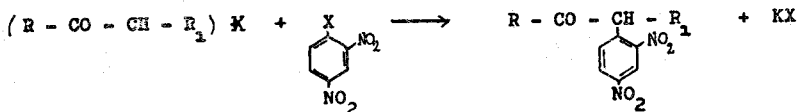
Meisenheimer (7) and recently Crampton (8) and Foster (9) have demonstrated the formations of such compounds. There is evidence for corresponding intermediates also in aromatic nucleophlic substitution (10).

Miller (2) and co-workers have measured substituent effects in reactions of some anions with activated aromatic substrates in methanol. The Reported data are fully in accord with the two stage mechanism. The investigations, including the effects of base-catalysis of Bunnet and co-workers olso support the concept of reaction via an intermediate complex (1), (5). Details of Mechanism have been given previously (3). (1).

The reactions of 2,4 – dinitro and 2,6–dinitrohalobenzenes with carbanions have been videly investigated neither kinetically nor syntetically (11), (12). (1).

In our recent study, reactions of some enol anios with dinitrohalobenzenes in dimethyl sulphoxide (DMSO) have been investigated and utilizing a photometric method the pseudo-first order rate coefficients simply determined. It has been found that the reactions take place in the DMSO faster then other protic and aprotic solvents, possibly, due to the cation solvating ability of this solvent (30). Applied method is suitable as a kinetic measurement method which is a continuos photometry.

In the present work the reactions of 2,6–dinitrohalobenzenes and 2,4–dinitrohalobenzenes with some of the potassioderivetives of enoles, such as β–diketones, ketoesteres, β–ketonitriles, α–cyanoesters, in DMSO were studied.

$$(R - CO - CH - R_1) \, K \; + \; \underset{NO_2}{\overset{X}{\bigcirc}} NO_2 \; \longrightarrow \; R - CO - CH - R_1 \underset{NO_2}{\overset{}{\bigcirc}} NO_2 \; + \; KX$$
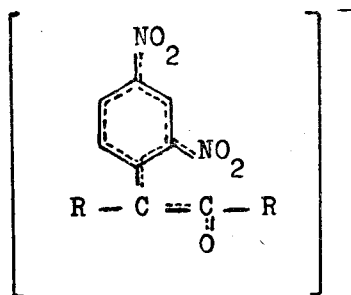
KINETICS

Reaction rates of substitution reactions of 2,4–dinitrohalobenzenes with potassium salts of dietyhlmalonate, of ethylcyanoacetate, of benzoylacetonitril, in dimethylsulphoxide at 20°C and also, only to compare, the rate coefficients of 2,6–dinitro

TABLE — 1

Potassium salt of Carbanion	Substrate	Substitution products	Yield. Calculated. Found.					
			m.p.	%	%C	%H	%C	%H
Ethyl (p-nitrobenzoyl) acetate (13)	2.4 DNCB	Ethyl (2,4-dinitrophenyl-p-nitrobenzoyl) acetate	136	72	50.62	3.22	50.68	3.20
n-Butylactoacetate (14)	2.4 DNCB	n-Butyl (2,4-dinitrophenyl) acetoacetate	79	70	51.86	4.93	51.74	4.89
” ”	2.6 DNBB	n-Butyl (2,6-dinitrophenyl) acetoacetate	101	51	51.86	4.93	51.80	4.87
Ethylcyanoacetate (15)	2.6 DNBB	Ethyl (2,6-dinitrophenyl) cyanoacetate	115	60	47.31	3.22	47.25	3.02
t-Butylcyanoacetate (16)	2.4 DNBB	t-Butyl (2,4-dinitrophenyl) cyanoacetate	74	67	50.81	4.23	50.77	4.27
”	2.6 DNBB	t-Butyl (2,6-dinitrophenyl) cyanoacetate	81	70	50.81	4.23	50.59	4.29
Benzoylacetonitril (17)	2.4 DNBB	Benzoyl (2,4-dinitrophenyl) acetonitril	166d.	69	57.87	2.89	57.90	2.90
”	2.6 DNBB	Benzoyl (2,6-dinitrophenyl) acetonitril	165d.	65	57.87	2.89	57.93	2.89
Mesitoylacetonitril (18)	2.4 DNBB	Mesitoyl (2,4-dinitrophenyl) acetonitril	206	35	62.01	4.24	61.08	4.20
Hexan-2,4-dion (19)	2.4 DNCB	3-(2,4-dinitrophenyl) hexan-,4-dion	109	69	51.42	4.28	51.34	4.30
Heptan-3,5-dion (20)	2.4 DNCB	4-(2,4-dinitrophenyl) hexan-3,5-dion	106	67	53.06	4.76	52.98	4.66
Cyclohexan-1,3-dion (21)	2.4 DNBB	2-(2,4-dinitrophenyl) cyclohexan-1,3-dion	244	71	51.79	3.59	51.29	3.49
5,5-Dimethylcyclohexan-1,3-dion (22)	2.4 DNBB	5,5-dimet. (2,4-dinitrophen.) cyclohexan-1,3-dion	256	73	55.17	4.93	54.99	4.87
Benzoyl-α-Furoylmethane (23)	2.4 DNBB	Benzoyl (2,4-dinitrophenyl)-α-Furoylmethane	135	45	60.00	3.15	59.91	3.22

Reactions of 2,6-dinitro and 2,4-dinitrohalobenzenes with Carbanions.

bromobenzene's reactions with potassio diehylmalonate and ethylcyanoacetate were determined.

Dinitroarylated enoles gave red to violet coloured solutions in the presence of alkali salts of enoles or alkali alkoxides in dimethylsulphoxide. It is observed as a spesific absorbtion at 490–550 nm in DMSO but at lower wavelengths in hydroxylic solvents,(3) most probably, due to the anionic mesomerisim of dinitroarylatedcarbanion, illustrated as:

$$
\left[
\begin{array}{c}
NO_2 \\
\text{(aromatic ring with)} \\
NO_2 \\
R-C=C-R \\
O
\end{array}
\right]^{-}
$$

Kinetic studies were made in dimethylsulphoxide by following the rate of appearance of chromophore, which is the dinitroarylatedcarbanion, at maximumwavelength of absorbtion and set up so as to furnish pseudo frist order reaction rates, Initial concentrations other data are displayed in Table 3. Temperature was at 20°C. Good first order kinetics were observed by the linearity of plots of Log $(A\infty - A)$ versus time, as shown in Figure– 2.

With the change in the concentration of anion [B], which was maintained high relative to substrate [S], it was found that, the ratio between the pseudo-first order rate coefficient, K, and concentration of carbanion [B], was almost constant, as shown following equations (24), (25).

$$d\,[C]/dt = K_r[S]\,[B] \qquad K/[B] = K_r \qquad (5)$$

[C] = Concentration of product formed in reaction. K_r = Rate coefficient of bimoleculer-second order raction.

TABLE — 2

Spectral Characteristics of Some Dinitroarylatedcarbanions at Visible Range in DMSO.				
Dinitroarylated carbanions	Position at Fig. 1	Carbanion concent.	Maximum wave length (nm.)	Molar extinc. coefficient.
Benzoyl (2,4–dinitrophenyl) acetonitril	I	4.10^{-3} M.	505	14560
Ethyl (2,4 –dinitrophenyl) – α –cyanoacetate	II	8.10^{-4} M.	495	27640
Diethyl (2,4–dinitrophenyl) malonate	III	8.10^{-4} M.	518	19875
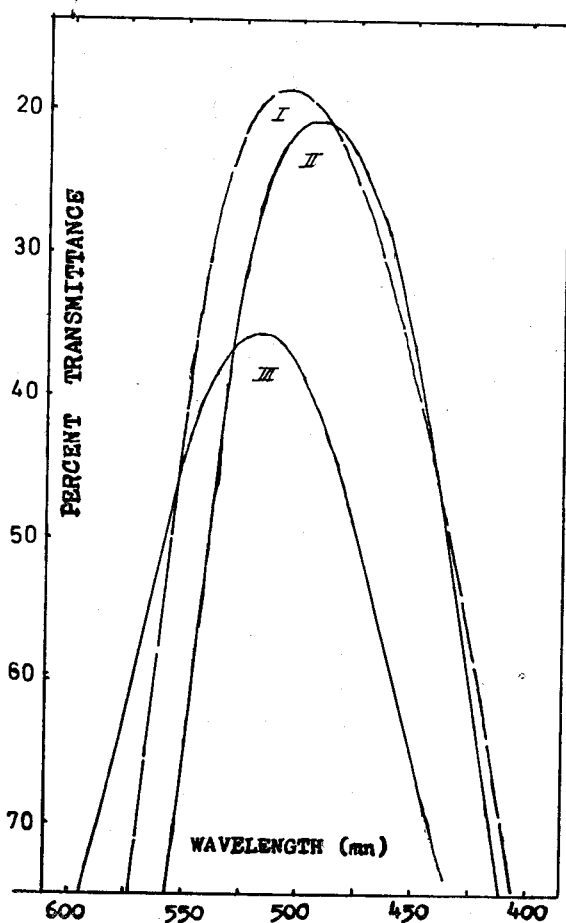
Figure– 1. Transmittance spectrum of dinitroarylatedcarbanions in the presence
of their corresponding anions'potassium derivatives in dimethylsulphoxide solutions.

I. Benzon 1 (2,4-dinitrohenyl) acetonitril

II. Ethyl (2,4-dinitrophenyl)-α-cyanoacetate

III. Diethyl (2,4-dinitrophenyl) malonate

EXPERIMENTAL

Materials: 2,4–dinitrohalobenzenes   were prepared by the
standart methodes and repurified by several crystalcisations
from ethanol (3). 2,6–dinitrobromobenzene was also available
from another study(26).
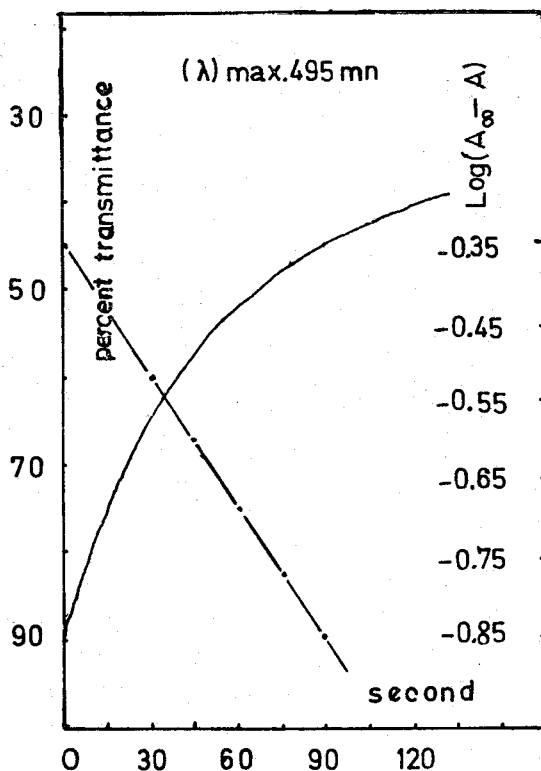
Figure– 2. Plot of experimental data for typical run in dmethylsulfoxide is of 2, 4–dinitroiodbenzen and (CNCHCOOC$_2$H$_5$) K, at 20° C. (A). Spectrophotometer recording, dependence between transmittance and time. B). Log (A∞ –A), as fonction of time.

Potassium derivatives of carbonacids: They were prepared, under dry and carbondioxide free nitrogen atmosphere, reacting the metallic potassium with enol in absolute dimethoxyethane at 30° – 40° C. The formed salts were filtered and washed under nitrogen atmosphere and dried over CaH$_2$. Solutions of carbanions in dimethylsulphoxide were promptly used.

Dimethylsulphoxide: It was commercial product and redistiled at 73° – 74° C/11 mm Hg. then chromatographed on neutral alumina.

Preparations of dinitroarylated derivatives: The dinitroarylation of carbanions was carried out according to general procedure described previously (3). 10 mmol. potassium derivative of carbonacid was placed in a reaction flask with 5–6 ml DMSO then 10 mmol. dinitrohalogenbenzene was aded. The mixture acidified after it had heated 40 °C for ten or fifteen minutes. Male product was filtered and washed then mostly crystallised from methanol or acetic acid.

Kinetic procedure: The formation rate of dinitroarylatedcarbanion was followed with a BECKMAN spectrophotometer, model DB-G, at appriopriate wavelength in which any of other components does not absorb appreciably. The cells and reactions solutions were thermostated to $\pm 0,5°$ C. Since the half life of some of the reactions were only ten or fifteen seconds a special device was constructed for mixing of reactants. The solutions of carbanion and dinitrohalobenzene before mixing were stored in separate compartments, both of them thermostated to the same temperature as cells of the spectrophotometer. Through two combined pistons a definit amount of the reactant solutions could be effetively mixed in the reaction cell in less then 0,2 sec. The appearance of dinitroarylatedcarbanion was being recorded by the 5 inch recorder unit of spectrometer as lowering of transmittance by the time.

Last measurement was made for 'infinitive value', (A∞), one hour later. The calculated Log (A∞–A) values were ploted against the time.

The resulting lines were straight and pseudo-first order rate coefficients were calculated from the slope of line according to the following equation,

$$Kt = 2,303 \ Log \ A∞ - 2,303 \ Log \ (A∞-A) \qquad (6)$$

A good proportion of reactions was followed usually between the % 3 – % 80 since they obey appropriate pseudo-first order law. Data from a typical run are displayed in Table-3 which is represented as an experimental data in Figure – 2.
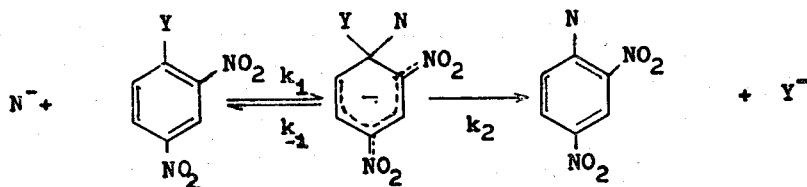
T A B L E 3

Reaction of 2,4–dinitroiodbenzene with the potassium derivative of ethylcyano-acetate at 20°C. Initial concentrations: 2, 4DNIB, $2,0.10^{-5}$ M. Potassium ethylcyano-acetate, $8,0.10^{-4}$ M. Solvent, dimethylsulphoxide. The rate coefficient, calculated for this run, is $12,4.10^{-3}$ sn^{-1}.

Time (sec.	Transmittance	Absorbance (A)	(A∞ – A)	Log (A∞ – A)
0	0,890	0,05038	0,44447	–0,35213
15	0,755	0,12189	0,37296	–0,42829
30	0,647	0,18893	0,30592	–0,51442
45	0,575	0,24030	0,25455	–0,59414
60	0,520	0,28398	0,21087	–0,67592
75	0,480	0,31869	0.17616	–0,75399
90	0,448	0,34967	0,14518	–0,83803
∞	0,315	0,49485	—	—

RESULTS AND DISCUSSION

Results within experimental errors of applied techinque in the reactions of 2,4–dinitro and 2,6–dinitrohalobenzenes with carbanions are summerized in Table-4. The ease of displeacement of aromatic halogen is found to be Cl $\approx$ Br > I, which is in accord with our recent experimental results (3), and kinetics of substitution show first order rate dependence in substurate as well as in carbanion concentration, i. e. overall second order kinetics. In general, the carbanion, most probably, reacts with activated aromatic halides via two-stage mechanism.

With these results, disaplayed on Table-4, the groups attached to carbon can be arranged in the following order as to their nucleophilic ability $CN > COOC_2H_5 > COCH_3$. However data concerning relative nucleophilites of enolates are not available, this order can be attributed to resonance stabilisation of the enolate anion. The carbanion, consisted of two activating groups has a doubled permanent polarization, and it is a resonance hybrid of three forms (27).

T A B L E 4

Pseudo-first order rate coefficients for the reactions of dinitrohalobenzenes with potassium carbanions in DMSO.

DİNİTROHALOBENZEN	CONCENT.	$(C_6H_5\ COCHCN)K$		$CH(COOC_2H_5)_2\ K$		$(CNCHCOOC_2H_5)\ K$	
		CONCENT.	R.C.(Sn^{-1})	CONCENT.	R. C. (Sn^{-1})	CONCENT.	R. C. (Sn^{-1})
2, 4–dinitrochlorbenzene	10^{-4}	4.10^{-4}	$2,7.10^{-3}$				
	10^{-4}	8.10^{-4}	$5,5.10^{-3}$				
	2.10^{-5}			8.10^{-4}	$15.8.10^{-3}$	8.10^{-4}	$17,5.10^{-3}$
	,,			12.10^{-4}	$23,7.10^{-3}$	16.10^{-4}	$34,9.10^{-3}$
	,,			16.10^{-4}	$31,9.10^{-3}$		
2, 4–dinitrobromobenzene	$10.^{-4}$	4.10^{-3}	$4,3.10^{-3}$				
	10^{-4}	8.10^{-3}	$8.7.10^{-3}$				
	2.10^{-5}			8.10^{-4}	$15.1.10^{-3}$	8.10^{-4}	$19,7.10^{-3}$
	,,			12.10^{-4}	$22,6.10^{-3}$	16.10^{-4}	$39.9.10^{-3}$
	,,			16.10^{-4}	$30,3.10^{-3}$		
2, 4–dinitroiodbenzen	10^{-4}	4.10^{-3}	$2,3.10^{-3}$				
	10^{-4}	8.10^{-3}	$4,8.10^{-3}$				
	2.10^{-5}			8.10^{-4}	$8,8.10^{-3}$	8.10^{-4}	$12,4.10^{-3}$
	,,			12.10^{-4}	$13.1.10^{-3}$	16.10^{-4}	$26,2.10^{-3}$
	,,			16.10^{-4}	$17,4.10^{-3}$		
2, 6–dinitrobromobenzene	10^{-4}			4.10^{-3}	$1,3.10^{-3}$	4.10^{-3}	$2,1.10^{-3}$
	,,			$8,10^{-3}$	$2,7.10^{-3}$	8.10^{-3}	$4,3.10^{-3}$

Common to all active methylene compounds is possibility that the negative charge of the carbanion may be distributed among several atoms of carbanion. The reactivity seems to be related with a combination of the inductive effect with electron-withdrawing ability of the substituent and the ability of these substituents to delocalize the negative charge. As a consequence, the cyano compounds reacts faster than carbonyl carbanions. In these anions charge is probably less delocalised than in carbonyl stabilized carbanions, which largely determine the reactivity (28) and also –CN group is more effective in stabilizing negative charge than –COOC$_2$H$_5$ group and cyano compounds react more readily than esters (29). With these arguments, the mechanism of reactions of dinitrohalobenzenes with carbanions is agreeably explained in terms of the intermediate complex mechanism, Class-A, in which the rate is retermined by the rate of formation, K$_1$. (3), (1).

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Ö Z E T

Bu çalışmada dinitrohalojenbenzerlerin karbon nukleofilleri ile dimetilsulfoksitli ortamda verdikleri reaksiyonlar sentetik ve kinetik verileri yönünden incelenmiş ve reaksiyonların iki basamaklı bir mekanizma üzerinden cereyan ettiği ortaya konulmuştur.

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