Kinetics and Mechanism of Thermal Isomerisation of Aryl Alkanehydrazonates into *N'*,*N'*-Diarylhydrazides. Extension of a Recent Free Radical Analogue of the Chapman Rearrangement

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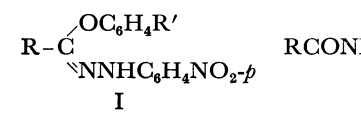
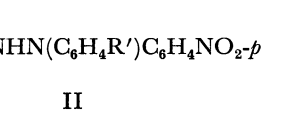
A series of twelve aryl *N*-(*p*-nitrophenyl)alkanehydrazonates (I) have been prepared and their thermal rearrangement into *N*-acyl-*N'*,*N'*-diarylhydrazines (II) was investigated. The structures of I and II were derived from their elemental analyses and spectral properties. Hydrolysis of II afforded the corresponding *N'*,*N'*-diarylhydrazines. Kinetic experiments have shown that electron withdrawing substituents decrease the rate of the rearrangement whereas electron donating groups increase it. The rate of conversion of I into II was also increased by addition of benzoyl peroxide. A free radical mechanism was proposed to account for the results.

We have been exploring the synthesis and thermal isomerization of several hydrazonates of type I (R= aryl, H_5C_2OOC- or C_6H_5NHCO-).[1-4] In continuation of these studies, we have investigated the synthesis of a number of aryl alkanehydrazonates (I, R=alkyl) and examined the kinetics of their rearrangement into the hydrazides (II, R=alkyl).

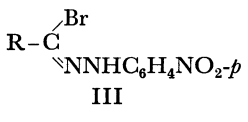


I



II

a, R=CH_3, R'=H
b, R=CH_3, R'=*p*-CH_3
c, R=CH_3, R'=*p*-Cl
d, R=CH_3, R'=*p*-NO_2
e, R=CH_3CH_2, R'=H
f, R=CH_3CH_2, R'=*p*-CH_3
g, R=CH_3CH_2, R'=*p*-Cl
h, R=CH_3CH_2, R'=*p*-NO_2
i, R=$(CH_3)_2CH$, R'=H
j, R=$(CH_3)_2CH$, R'=*p*-CH_3
k, R=$(CH_3)_2CH$, R'=*p*-Cl
l, R=$(CH_3)_2CH$, R'=*p*-NO_2

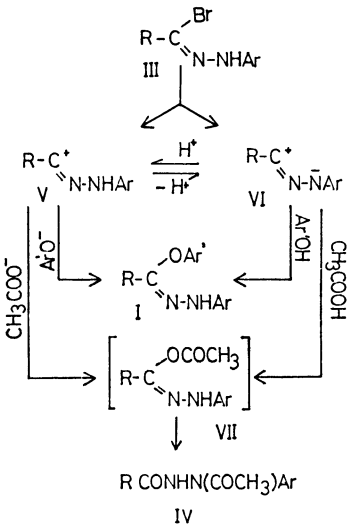


III

IIIa, R=CH_3,; IIIb, R=CH_3CH_2; IIIc, R=$(CH_3)_2CH$

Results and Discussion

Treatment of *N*-(*p*-nitrophenyl)ethanehydrazonoyl bromide (IIIa) with sodium phenoxide in ethanol results in the formation of phenyl *N*-(*p*-nitrophenyl)ethanehydrazonate (Ia). The latter ester was also prepared by treating IIIa with phenol in ethanol in presence of triethylamine at room temperature. These two procedures were found to be general and good yields of the hydrazonate esters, Ib to Il were obtained when other alkanehydrazonoyl bromides and phenols were used. In an attempt to prepare Ia, Ie, and Ii by the reaction of the respective hydrazonoyl bromides with phenol in presence of sodium acetate in ethanol, *N*,*N'*-diacyl-*N*-*p*-nitrophenyl)hydrazines (IVa, IVe, and IVi) were obtained and no hydrazonate was formed (Scheme 1). These results indicate that the formation of I involves the carbonium ion, (V)[5] or the nitrilimine, VI[6] as intermediate. The former ion can be attacked by nucleophilic reagents, namely the phenoxide and acetate



Scheme 1.

ions to form I and the acetate ester VII, respectively. Alternatively, the nitrilimine can add phenol and acetic acid to give I and VII respectively. The acetate ester VII seems to be unstable; it undergoes OAc→NAc rearrangement to form IV as it is formed[7] (Scheme 1).

The structures of the hydrazonates Ia to Il were derived from their elemental analyses and spectral data. Thus, the IR spectra showed, in each case, two characteristic bands at 1264 and 1080 cm^{-1} assignable to an aryl ether linkage. The UV absorption pattern was of typical hydrazones. The data are summarized in Table 1.

On heating the hydrazonates Ia to Il at 125 °C for 60 min in the absence of solvent, rearrangement occurred and the corresponding *N*-acyl-*N'*,*N'*-diarylhydrazines (IIa to III) were obtained. The latter products were characterized by strong absorption band near 1680 cm^{-1} assignable to the CONH grouping. The assigned hydrazide structure for the rearranged products was also indicated by the fact that *N*-phenyl-*N*-(*p*-nitrophenyl)hydrazine (VIII) was obtained upon acid hydrolysis of the rearranged products IIa and IIi. Acetylation of VIII with acetic anhydride gave back IIa.

The thermal isomerization of I was also effected by refluxing the esters in xylene for 1—3 h. The hydrazide

Table 1. Aryl N-(p-nitrophenyl)alkanehydrazonates

Compound No.	Mp, °C	Molecular formula	C, % Calcd	C, % Found	H, % Calcd	H, % Found	N, % Calcd	N, % Found	λ_{max}^{EtOH} nm, (log ε)
Ia	114—115	$C_{14}H_{13}N_3O_3$	61.98	61.80	4.83	4.73	15.49	15.34	395(4.349); 250(4.11)
Ib	151—151.5	$C_{15}H_{15}N_3O_3$	63.15	62.99	5.30	5.34	14.73	14.64	392(4.24); 250(4.17)
Ic	175—176	$C_{14}H_{12}ClN_3O_3$	55.00	55.40	3.96	4.06	13.74	13.47	390(4.43); 248(4.17)
Id	174—175	$C_{14}H_{12}N_4O_5$	53.17	53.09	3.82	4.05	17.72	17.99	382(4.45); 225(4.18)
Ie	113—114	$C_{15}H_{15}N_3O_3$	63.15	63.03	3.29	3.18	14.73	14.83	390(4.45); 250(4.18)
If	111—113	$C_{17}H_{17}N_3O_3$	64.20	64.28	5.73	5.81	14.04	14.11	393(4.43); 250(4.18)
Ig	164—165	$C_{15}H_{14}ClN_3O_3$	56.33	56.21	4.41	4.40	13.14	13.00	384(4.32); 355(3.89) sh; 256(3.85) sh
Ih	156.5—158	$C_{15}H_{14}N_4O_5$	54.57	54.21	4.20	4.15	16.97	17.62	390(4.25); 250(4.00)
Ii	134—135	$C_{16}H_{17}N_3O_3$	64.20	64.13	5.73	5.62	14.03	14.07	390(4.45); 250(4.20)
Ij	121—123	$C_{17}H_{19}N_3O_3$	65.16	64.93	6.11	5.79	13.41	13.53	392(4.46); 250(4.20)
Ik	115—116	$C_{16}H_{16}ClN_3O_3$	57.57	57.33	4.82	4.77	12.59	11.96	386(4.28); 250(4.12)
Il	199—201	$C_{16}H_{16}N_4O_5$	55.80	55.91	4.68	4.55	16.27	16.11	383(4.12); 325(3.71) sh; 255(3.66) sh.

Table 2. N-Acyl-N',N'-diarylhydrazines

Compound No.	Mp, °C	Molecular formula	C, % Calcd	C, % Found	H, % Calcd	H, % Found	N, % Calcd	N, % Found	λ_{max}^{EtOH} nm, (log ε)
IIa	197—197.5	$C_{14}H_{13}N_3O_3$	61.98	62.00	4.83	4.96	15.96	15.55	365(4.23); 250(3.85)
IIb	193—194	$C_{15}H_{15}N_3O_3$	63.15	62.98	5.30	5.36	14.73	14.85	366(4.21); 250(3.89)
IIc	233—235	$C_{14}H_{12}ClN_3O_3$	55.00	55.40	3.96	4.13	13.74	13.68	366(4.28); 250(4.02)
IId	239—241	$C_{14}H_{12}N_4O_5$	53.17	52.90	3.82	3.90	17.72	17.61	380(4.31); 325(4.00) sh; 258 (3.92) sh
IIe	176—177	$C_{15}H_{15}N_3O_3$	63.15	63.01	3.29	3.11	14.73	14.66	361(4.21); 250(3.87)sh
IIf	203—204	$C_{16}H_{17}N_3O_3$	64.20	64.30	5.73	5.76	14.04	14.20	366(4.23); 250(3.91)sh
IIg	190—192	$C_{15}H_{14}ClN_3O_3$	56.33	56.20	4.41	4.51	13.14	13.00	361(4.26); 260(3.92)sh
IIh	246—247.5	$C_{15}H_{14}N_4O_5$	54.57	54.32	4.20	4.01	16.97	16.81	382(4.39); 325(3.93) sh; 255(3.89) sh
IIi	183—184	$C_{16}H_{17}N_3O_3$	64.20	64.09	5.73	5.77	14.03	13.98	366(4.22); 250(3.88)
IIj	189.5—190	$C_{17}H_{19}N_3O_3$	65.16	65.23	6.11	6.24	13.41	13.10	368(4.21); 250(3.88)
IIk	191—192	$C_{16}H_{16}ClN_3O_3$	57.57	57.20	4.80	4.60	12.59	12.42	364(4.19); 255(3.86)
IIl	246—248	$C_{16}H_{16}N_4O_5$	55.80	55.72	4.68	4.52	16.27	16.01	372(4.40); 266(3.90)

obtained from a given ester by this method was identical in all respects with that obtained by the above procedure. The compounds prepared and their physical constants are listed in Table 2.

To shed more light on the mechanism of the rearrangement of I, the kinetics of the rearrangement of the esters Ia to Il were studied in p-xylene spectrophotometrically. In this solvent both the ester and the respective hydrazide have absorption maxima in the region 350—390 nm. However, the molar absorptivity of the ester, at a given wavelength, is higher than that of the hydrazide at the same wavelength. The data are summarized in Table 3. Therefore the absorbance in the region 350—390 nm decreases with the progress of the rearrangement. Accordingly, the rates of the isomerization of I were followed spectrophotometrically at the wavelength where maximum absorbance difference was observed. In case of the p-nitrophenyl esters (Id, Ih, and Il) a tight isosbestic point in the UV spectra was observed. This indicates that the rearrangement occurred without the formation of intermediates which absorb in the same region.

For the rearrangement of all esters, the following first order rate equation was obtained;

$$-\log(A_t - A_\infty) = k_1 t/2.3 - \log(A_0 - A_\infty),$$

where A_0, A_t, and A_∞ are the absorbance values of the reaction mixture at time 0, t, and ∞, respectively. The rate constant was calculated from the slope of the plot

Table 3. UV data of aryl alkanehyrazonates (I) and N',N'-diarylhydrazides (II) in p-xylene and rate constants for conversion of I into II at 110 °C

Ester-I Compound No.	Ester-I λ_{max}	Ester-I ε	Hydrazide-II Compound No.	Hydrazide-II λ_{max}	Hydrazide-II ε	$10^4 k_1$ (s^{-1})
Ia	370	25119	IIa	360	13489	1.67
Ib	373	25119	IIb	360	16982	1.87
Ic	370	23442	IIc	360	11220	1.32
Id	362	20417	IId	384	16218	0.79
Ie	370	24547	IIe	360	14125	0.93
If	371	25119	IIf	360	16982	1.18
Ig	370	23442	IIg	360	11749	0.71
Ih	361	19952	IIh	380	16596	0.37
Ii	376	19952	IIi	360	15135	0.52
Ij	370	25119	IIj	360	15849	0.69
Ik	367	23442	IIk	360	15849	0.30
Il	360	16218	IIl	380	15135	0.23

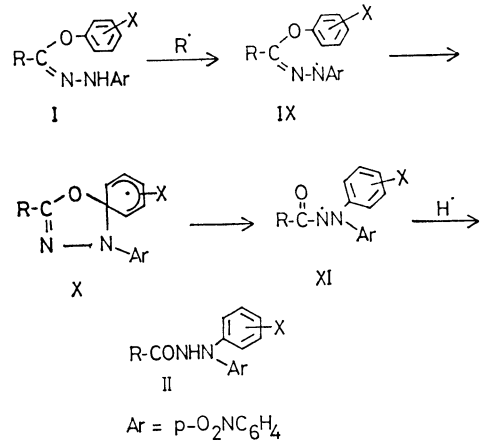
of log $(A_t - A_\infty)$ *versus* time using the least squares method. In Table 3 are listed the first-order rate constants obtained for the esters investigated. The values reported are the average of those obtained in duplicate or triplicate experiments. The data indicate that the rate of the rearrangement is influenced by the nature of both the substituent on the phenolic moiety and the C-alkyl group. In a given series of esters, electron withdrawing substituents decrease the reactivity, whereas electron donating ones increase it. The esters having the same OAR group, and different R's, their rates follow the sequence: $CH_3 > CH_3CH_2 > (CH_3)_2CH$.

TABLE 4. RESULTS OF STATISTICAL TREATMENT OF THE KINETIC DATA[a)]

Series	$-\rho \pm s$	$-\log k_H \pm s$	r	n
Ia—d	0.396±0.012	3.79±0.005	0.999	4
Ie—h	0.522±0.009	4.02±0.004	0.994	4
Ii—l	0.497±0.013	4.29±0.053	0.939	4

a) ρ, reaction constant; log k_H, intercept of the Hammett plot; r, correlation coefficient; s, standard deviation; n, number of points.

The values of log k_1 for each series of esters were then correlated with the Hammett substituent constant, σ, as taken from the compilation of Ritchie and Sager.[8)] The results of statistical analysis of the rate data by the least squares method are summarized in Table 4. The rho values obtained are in agreement with a free radical pathway because their absolute value is small, and with an electron deficient transition state because they are negative.



Scheme 2.

The sequence that probably accounts for the foregoing results is presented in Scheme 2. It is assumed that a radical initiator, R·, removes the amino hydrogen atom to give the hydrazonate radical, IX; this then undergoes intramolecular rearrangement possibly *via* the cyclic radical species X to give the more stable hydrazide radical XI. Hydrogen abstraction from the solvent or from another hydrazonate ester then gives the hydrazide II. The intermediacy of hydrazyl radicals has been postulated for several reactions of hydrazones,[9)] and their stability has been examined by Goldschmidt *et al.*[10)]. Under the conditions which we have used to investigate the kinetics of the conversion of I into II, the radical initiator is probably the trace of oxygen[11)] which might be present. This was substantiated by the observation that the rate of the rearrangement was increased by addition of the free radical initiator namely benzoyl peroxide. For example, the rate constant of the isomerization of the ester Ie in xylene at 110 °C in presence of 4.95×10^{-5} M benzoyl peroxide has a value of 2.08×10^{-4} s^{-1}; whereas in the absence of the peroxide the value of the rate constant was 0.93×10^{-4} s^{-1}. The suggested mechanism (Scheme 2) is also consistent with the recent observation by Hegarty *et al.*[9)] that the rate of the rearrangement of the related aryl arenecarbohydrazonates in dioxane–water mixture is accelerated by the addition of oxidizing agents such as manganese dioxide.

Experimental

All melting points are uncorrected and were measured on a Gallenkamp Electrothermal melting point apparatus, model 1A6301. Elemental analysis was performed by Alfred Bernhardt Mikroanalytisches Chemie Laboratorium, West Germany. Infrared and ultraviolet spectra were measured with Unicam SP1000 and SP8000 spectrophotometers respectively. The solvent *p*-xylene was Analar grade and redistilled twice before use in kinetic study.

The alkanehydrazonoyl bromides (III, R=CH_3, CH_3CH_2, and $(CH_3)_2CH$) used in synthesis of I were prepared by literature method, and their constants (mp's) corresponded to liserature data.[12)]

Aryl Alkanehydrazonates, Ia to Il. Method-A. To an ethanolic sodium ethoxide solution (prepared from sodium (0.11 g, 0.005 g atom) and ethanol (20 ml) was added the appropriate phenol (0.005 mol) followed by the hydrazonoyl bromide (0.005 mol). The mixture was stirred for 5 min and left overnight at room temperature. The crude ester that precipitated was collected, washed with water and finally crystallized from methanol. The results are summarized in Table 1.

Method-B. Equivalent amounts (0.005 mol each) of hydrazonoyl bromide and phenol were stirred in ethanol or acetonitrile (30 ml) containing triethylamine (0.01 mol) at room temperature for 2 h. The product was collected by filtration, washed with water and dried. Crystallization from methanol gave the hydrazonates Ia to Il in 50 to 75% yield. The results are given in Table 1.

Reaction of III with Phenol in Presence of Sodium Acetate. To a suspension of III (R=CH_3) (0.003 mol) in ethanol (20 ml) was added a solution of sodium acetate and phenol (0.003 mol each) in water (5 ml). The reaction mixture was stirred for 5 min and left overnight at room temperature. The solid was collected and crystallization from ethanol gave IVa, mp 184—185 °C, Found: C, 50.60; H, 5.07; N, 18.02%. Calcd for $C_{10}H_{11}N_3O_4$: C, 50.63; H, 4.67; N, 17.70%.

Similar treatment of III (R=CH_3CH_2) and III (R=$(CH_3)_2CH$) with phenol and sodium acetate afforded IVe and IVi respectively. Compound IVe, mp 133.5—134 °C; Found: C, 52.98; H, 5.12; N, 16.50%. Calcd for $C_{11}H_{13}N_3O_4$: C, 52.58; H, 5.21; N, 16.72%. Compound IVi, mp 192 °C, Found: C, 54.10; H, 5.66; N, 15.62%. Calcd for $C_{12}H_{15}N_3O_4$: C, 54.32; H, 5.69; N, 15.84%.

Thermal Rearrangement of Aryl Alkanehydrazonates. Method-A: The hydrazonate (0.5 g) was heated in a test tube

in an oil bath at 120 °C for 1 h. The crude product was extracted with acetone. The solvent was then evaporated and the residue was boiled with benzene (20 ml), cooled, then filtered. Crystallization from methanol–water mixture gave II in 60—70% yield.

Method-B: The hydrazonate (0.5 g) was refluxed in xylene for 3 h. The pale yellow solid that precipitated on cooling was collected (0.45 g). Crystallization from methanol–water mixture gave II (*ca.* 0.4 g). The hydrazides prepared are listed in Table 2 together with their physical constants.

Hydrolysis of IIa and IIi. The hydrazide IIa (0.5 g) was refluxed in 95% ethanol (20 ml) and concentrated hydrochloric acid (20 ml) for 10 h. The reaction mixture was then concentrated to its 1/4 volume and cooled. The solid formed was collected, and washed with dilute solution of sodium acetate. Crystallization from dilute methanol gave *N*-phenyl-*N*-(*p*-nitrophenyl)hydrazine, VIII, yellow needles, mp 100—102 °C, Found: C, 62.42; H, 4.85; N, 17.73%. Calcd for $C_{12}H_{11}N_3O_2$: C, 62.86; H, 4.84; N, 18.33%.

Following the same procedure the hydrazide IIi yielded the hydrazine VIII in 55% yield.

Kinetic Experiments. A stock solution 10^{-4} to 10^{-5} M (suitable for UV analysis) in hydrazonate was prepared in xylene at room temperature. The resulting solution was distributed among ampules (15 at minimum). The ampules were placed in an oil bath at 110 ± 1 °C. At suitable time intervals, the ampule was taken out of the bath, quenched in ice and the UV spectrum of its contents was recorded. The first spectrum was usually taken after 10 min to allow temperature equilibration. Complete spectra taken at the end of each kinetic run corresponded to the spectra of hydrazide solution in xylene of the same concentration. Under these conditions reasonable first order plots of log (A_t-A_∞) *vs.* time, *t*, min were obtained. Each kinetic run was repeated at least twice and the average rate constants are reported. The average deviation was $<\pm8\%$.

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