Tetrahedron Letters Vol. 21, pp 2909 - 2910 0040-4039/80/0722-2909$02.00/0
© Pergamon Press Ltd. 1980. Printed in Great Britain

STERIC AND POLAR EFFECTS IN FREE-RADICAL REACTIONS. - AN UNUSUAL TYPE OF AZOCOUPLING BY FREE RADICAL DECOMPOSITION OF DIAZONIUM SALTS

Attilio Citterio*, Francesco Minisci, Alberto Albinati and Sergio Bruckner
Istituto di Chimica del Politecnico di Milano, P.za L. da Vinci 32, 20133 Milano (ITALY)

Summary - A new free-radical azocoupling has been accomplished by decomposition of diazonium salts with monoelectronic reducing agents in the presence of 4-methyl-3-penten-2-one. Steric and polar factors are responsible of the unusual behaviour.

Recently we have reported[1] the reductive arylation of α,β-unsaturated ketones via aryldiazonium salts decomposition induced by titanous salts. The reaction has a general character for diazonium salts and α,β-unsaturated ketones in which R = H or alkyl group (R-CH=CHCOR'). An analogous behaviour has been observed with α,β-unsaturated nitriles, acids, esters, amides and other reducing metal ions (Cr^{2+}, V^{2+})[2]. However, when 4-methyl-3-penten-2-one was used under the same conditions, no reductive arylation was observed but the azocoupling product **2** has been obtained (reaction 1):

$$\underset{\mathbf{1}}{(CH_3)_2C{=}CH{-}COCH_3} + 2\ ArN_2^{+} + 2\ Ti^{3+} \longrightarrow \underset{\mathbf{2}}{Ar{-}N{=}N{-}C(CH_3)_2{-}\underset{Ar}{CH}{-}COCH_3} + N_2 + 2\ Ti^{4+} \qquad (1)$$

In a typical experiment, a cold solution of p-chlorobenzenediazonium salt (20 ml, 1.01 M) was added to a magnetically stirred solution of $TiCl_3$ (40 ml of the commercially 15% solution (1.05 M)) and 4-methyl-3-penten-2-one (7 ml) in methanol (50 ml) under N_2 at 0°C. N_2 evolution is immediate and it is complete in 1/2 hr. A small amount of Ti^{3+} (2% by Ce(IV) titration) was present at the end, indicating that two moles of Ti^{3+} were consumed for mole of diazonium salt. The yellow crystals, separated in the reaction, were collected by filtration, washed (water:methanol), dried and crystallized from methanol. The structure of **2** was established by X-ray analysis. The reaction is quite clean as concerns the olefin. Side-products are the arene and the arylhydrazine arising from reduction of the aryl radical and the diazonium ion, respectively.

Various monoelectronic reducing agents (Ti^{3+}, Cu^{+}, Fe^{2+}, H_3PO_2) and aryldiazonium salts gave the azocoupling product **2**. The results are summarised in the Table.

TABLE - Diazocoupling products in decomposition of aryldiazonium salts ($X{-}ArN_2^+$) induced by various reducing agents in the presence of 4-methyl-3-penten-2-one.

Reducing agent	X	yield (%)	m.p.(°C)	Notes
$TiCl_3$	p-Cl	51	96-97	
$Ti_2(SO_4)_3$	p-Cl	45	"	
$FeSO_4$	p-Cl	39	"	
$CuOCOCH_3$	p-Cl	32	"	As acetonitrile complex
H_3PO_2	p-Cl	25	"	In five molar excess
$TiCl_3$	$p{-}OCH_3$	48	72-73	
$TiCl_3$	H	52	84- 85	

The results are consistent with the mechanism summarised in the following Scheme :

$$ArN_2^+ + Ti^{3+} \longrightarrow Ar^\bullet + N_2 + Ti^{4+}$$

$$Ar^\bullet + \underline{1} \longrightarrow \underset{\underline{3}}{Ar{-}CH(COCH_3){-}\underset{CH_3}{\dot{C}}{-}CH_3} \xrightarrow[Ar{-}\overset{+}{N}{\equiv}N]{} Ar{-}\overset{+\bullet}{N}{-}N{-}C(CH_3)_2{-}\underset{Ar}{CH}{-}COCH_3 \xrightarrow[Ti^{3+}]{} \underline{\underline{2}}$$

The results with H_3PO_2 (a well known reducing reagent of diazonium salts via free-radicals[3]) excludes the formation of intermediate orgamometallic compound during the azocoupling.

The change of behaviour between 3-penten-2-one and **1** can be reasonably explained taking i account steric and polar effects. The orientation in the addition of aryl radicals to olefin is determined more by steric affects than by resonance, so that a reverse addition takes place with these two substrates. The electrophilic character of the radical adduct to 3-penten-2-one, due to the proximity of the carbonyl group, favours its reduction and at the same time makes slower the addition to the diazonium salt. Opposite effects influence the reactivity of the radical adduct **3** : its nucleophilic character makes slower the reduction and faste the addition to the diazonium ion , due to favourable contribution of polar form to the transition state : $\left[-\overset{|}{\underset{|}{C}}{}^\bullet \quad N{\equiv}\overset{+}{N}{-}Ar\right] \longleftrightarrow \left[-\overset{|}{\underset{|}{C}}{}^+ \quad {}^\bullet N{=}N{-}Ar\right]$.

This, as far as we known, is the first synthetic report concerning the addition of alkyl radicals to diazonium ions, supporting previous kinetic interpretations in radiolitic studie

References

1) A. Citterio, E. Vismara, Synthesis, 291 (1980)
2) Unpublished results of this laboratory.
3) G.P.Miklukin and A.F.Reskashova, Dokl. Akad. Nauk. SSSR, 85, 827 (1952)
N. Kornblum, G.D.Cooper and J.E.Taylor, J. Amer. Chem Soc., 72, 3013 (1950)
4) G.J.Heighway, J.E.Paker and R.K.Richardson, Tetrahedron Letters, 4441 (1974)
J.E.Packer and R.K.Richardson, J.Chem. Soc. Perkin II, 751 (1975)

(Received in UK 19 May 1980)