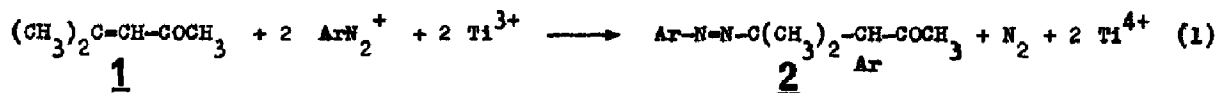


STERIC AND POLAR EFFECTS IN FREE-RADICAL REACTIONS. - AN UNUSUAL TYPE OF AZOCOUPLING BY FREE
RADICAL DECOMPOSITION OF DIAZONIUM SALTS

Atilio 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 reported¹ the reductive arylation of α, β -unsaturated ketones via aryl-diazonium 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 (Cr²⁺, V²⁺)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):



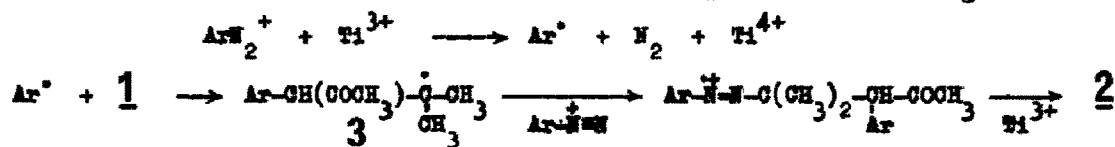
In a typical experiment, a cold solution of p-chlorobenzendiazonium salt (20 ml, 1.01 M) was added to a magnetically stirred solution of TiCl₃ (40 ml of the commercially 15% solution (1.05 M)) and 4-methyl-3-penten-2-one (7 ml) in methanol (50 ml) under N₂ at 0°C. N₂ evolution is immediate and it is complete in 1/2 hr. A small amount of Ti³⁺ (2% by Ce(IV) titration) was present at the end, indicating that two moles of Ti³⁺ 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 (Ti³⁺, Cu⁺, Fe²⁺, H₃PO₂) and aryl-diazonium salts gave the azocoupling product 2. The results are summarized in the Table.

TABLE - Diazo coupling 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	"	
CuCOOCH ₃	p-Cl	32	"	As acetonitrile complex
H ₃ PO 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 summarized in the following Scheme :



The results with H₃PO₂ (a well known reducing reagent of diazonium salts via free-radicals³) excludes the formation of intermediate organometallic compound during the azocoupling.

The change of behaviour between 3-penten-2-one and 1 can be reasonably explained taking into account steric and polar effects. The orientation in the addition of aryl radicals to olefin is determined more by steric effects 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 faster the addition to the diazonium ion, due to favourable contribution of polar form to the transition state: $[\overset{\cdot}{C}-N=N-Ar] \longleftrightarrow [C^+-N=N-Ar]$.

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

References

- 1) A. Citterio, E. Vismara, *Synthesis*, 291 (1980)
- 2) Unpublished results of this laboratory.
- 3) G.P. Mikiukin 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. Packer 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)