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SHORT COMMUNICATIONS

10-Methyl-9-phenylacridinium Iodide and 2,4,6-Triphenylpyrylium Perchlorate as Catalysts for Reduction of Aromatic Ketones

B. S. Tanaseichuk[a], **A. I. Azrapkina**[a], **M. K. Pryanichnikova**[a], **and A. V. Dolganov**[b]

[a] *Ogarev Mordovian State University, ul. Bol'shevistskaya 68, Saransk, 430000 Russia*
e-mail: orgchem@mrsu.ru

[b] *Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
ul. Vavilova 28, Moscow, 119991 Russia

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Methyl viologen and its analogs are capable of undergoing multiple redox transformations dication ⇄ radical cation [1]. The resulting radical cation may be regarded as an electron-rich radical [2] which tends to donate electron to an appropriate acceptor and return to the initial aromatic cation. This property was widely utilized in various electrochemical, photochemical, and other processes [3, 4], including reduction [5–7]. It may be presumed that other heterocyclic cation which can undergo reversible reduction to the radical, e.g., triphenylpyrylium (**1**) [8] or 10-methyl-9-phenylacridinium (**2**) [9], can also act as electron carrier.

We made an attempt to use cations **1** and **2** (as perchlorate and iodide, respectively) in the reduction of aromatic ketones with zinc. As model substrates we selected benzil, benzophenone, and acetophenone. All reactions were carried out in aqueous acetonitrile under argon at the same reactant ratio.

Our results, as well as published data on the reduction of aromatic ketones in the presence of propyl viologen (**3**) as catalyst [5], are given in table. It is seen that benzil was reduced most readily; next followed benzophenone, while acetophenone failed to react. The different results of the reduction of aryl ketones are determined by the substituent on the carbonyl group: the stronger the electron-withdrawing power of the substituent, the more facile is the reduction. On the other hand, the yield of the reduction product also depends on the redox potential of the initial ketone. Comparison of the data for benzil and benzophenone shows that the yield increases in parallel with the redox potential of the corresponding cation.

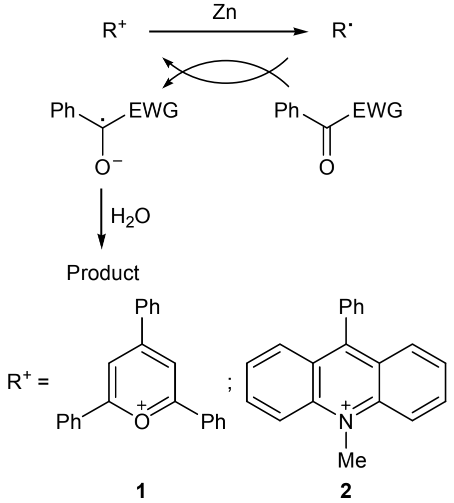
Thus, the ability to act as electron carrier in reduction processes is a characteristic feature of heterocyclic cations. A probable mechanism of this reaction is shown below.

The catalytic activity of cations **1** and **2** (as perchlorate and iodide, respectively) was studied under standard conditions: a mixture of 1.5 mmol of zinc, 1.0 mmol of aryl ketone, 0.05 mmol of the catalyst, and 20 mL of 98% acetonitrile was stirred for 24 h at 20°C under argon.

Yields of the reduction products (%) of aryl ketones with zinc in the presence of heterocyclic cations **1**–**3**

Substrate	$E_{1/2}$,[a] V [10]	Product	**1** $E_{1/2}^{b} = -0.35$ V	**2** $E_{1/2}^{b} = -0.5$ V	**3** $E_{1/2} = -0.43$ V [1]
PhCOCOPh	–0.54	PhCH(OH)COPh	50	99	92
PhCOPh	–1.25	$Ph_2C(OH)C(OH)Ph_2$	0	62	13
PhCOMe	–1.54	–	0	0	0

[a] Ionization potential of ketone.
[b] Reduction potential of the cation (data of this work).



EWG = Ph, COPh.

The products were identified and quantitated with an accuracy of ~5% by ^{1}H NMR according to the procedure described in [5]. The ^{1}H NMR spectra were recorded in $CDCl_3$ on a Jeol JNM-ECX400 spectrometer (400.1 MHz). The electrochemical redox potentials were measured using a three-electrode cell and an IPC Pro-M digital potentiostat/galvanostat (*Vol'ta*, Russia). A stationary platinum electrode with a diameter of 2 mm was used as working electrode, a saturated AgCl electrode was used as reference, and a Pt electrode was used as auxiliary. The cells were purged with dry argon to remove oxygen. The substrate concentration was 10^{-3} M. After recording each curve, the Pt electrode was thoroughly cleaned.

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