# ELECTROCHEMICAL INTERCONVERSION OF
1-(*p*-TOLYL)-6-METHYL-2,4-DIPHENYLPYRIMIDINIUM
PERCHLORATE AND 1-(*p*-TOLYL)-6-METHYLENE-2,4-
DIPHENYLPYRIMIDINE

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It is shown that reduction of the 6-methyl-1-(p-tolyl)-2,4-diphenylpyrimidinium cation proceeds in two one-electron stages. In the first stage, an unstable radical is formed, and in the second stage, an unstable anion. As a result of dehydrogenation of the radical, the anhydro base 6-methylene-1-p-tolyl-2,4-diphenyl-6H-pyrimidine is formed. Oxidation of this compound in a single one-electron stage forms an unstable cation radical, the hydrogenation of which leads to the original pyrimidinium cation. Data obtained by cyclic voltametry and electrosynthesis with subsequent identification of the products have shown that, the same as in the reaction with the hydroxide anion, the methyl-substituted pyrimidinium cation acts as a CH-acid.

Interaction with primary amines has been described exclusively for 2,4,6-triaryl-substituted azapyrylium salts [1]. The compound 6-methyl-2,4-diphenyl-1-(*p*-tolyl)-2,4-diphenylpyrimidinium perchlorate (I) was obtained for the first time, by recyclization of 6-methyl-β-azapyrylium perchlorate with *p*-toluidine [2].
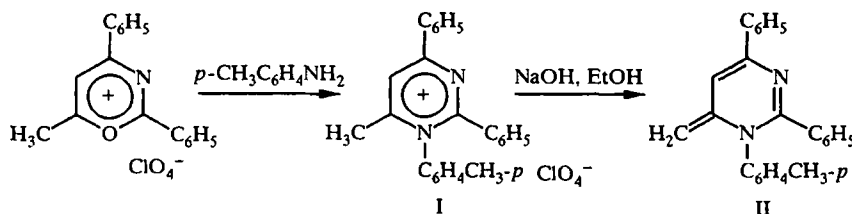

The sole example of obtaining an anhydro base of the pyrimidine series was described in [3] as a result of the reaction of a strong base, namely potassium *tert*-butylate, with 1,4,6-trimethyl-2-phenylpyrimidinium perchlorate. We have obtained for the first time 6-methylene-1-(*p*-tolyl)-2,4-diphenyl-6H-pyrimidine (II) by addition of the 6-methyl-1-(*p*-tolyl)-2,4-diphenylpyrimidinium salt (I) to a boiling ethanol solution of NaOH, with subsequent rapid cooling of the reaction mixture. The purity of the product proved to be adequate for its use in various conversions, even without purification.

No information is available in the literature on the electrochemical behavior of pyrimidinium salts. The closest analogs, pyridinium and pyrylium salts, are reduced in two stages, forming neutral radicals and anions [4-6]. The cation of the salt I that we have investigated, owing to the presence of the methyl substituent, can be regarded as a CH-acid that reacts with a base, splitting off a proton (conversion I → II). At the same time, it has been shown with some models that an alternative is possible, involving electron transfer and subsequent conversions of the electronic pairs [7, 8].

In seeking arguments in favor of one reaction path or the other, we carried out an electrochemical evaluation of the paths for the original compound I and its conversion product, the anhydro base II, by means of cyclic voltametry (CVA) on a platinum disk electrode.
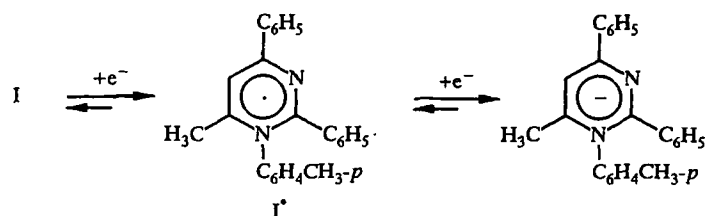
In the electrochemical sense, the pyrimidinium cations behave like pyrylium and pyridinium cations; however, the reduction of the methyl derivatives is partly irreversible [4-6].

As can be seen from Fig. 1a, the cation I can be reduced in two one-electron stages, in the same manner as pyridinium salts. The conclusion that each stage is a one-electron process was based on a comparison of the magnitude of the diffusion current with that for a ferrocene solution having the same concentration, with comparatively low voltage sweep rates. The first stage of the reduction is partly reversible; upon taking cathodic polarograms from 0.0 to -2.2 V, the first-stage peak is distinct, with peak potential 1.0 V. The existence of a second stage can be judged from indirect considerations. In the presence of the cation I, the reduction current at -2.0 V is considerably higher in comparison with the background; the reverse branch of the voltamperogram also changes, and an anodic peak can be seen. The first stage corresponds to the formation of a radical species I* that is unstable under the conditions of the experiment. Upon lowering the temperature, the ratio between the forward current (reduction) and the reverse current (oxidation) increases from 0.33 at 21°C to 0.55 at -70°C, indicating an increased stability of this radical. The second stage, corresponding to anion formation, was not further investigated.
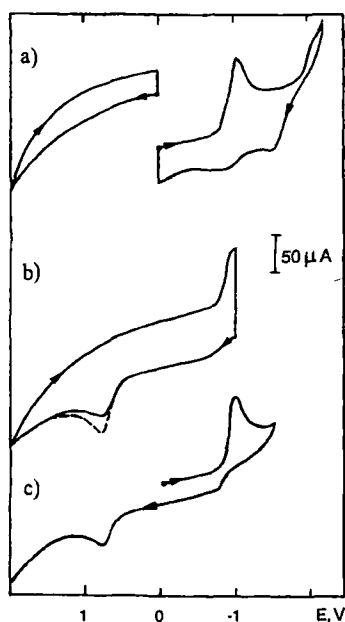

Fig. 1. Cyclic voltamperograms of compound I with E_{ini} = 0.0 V (anodic and cathodic) (a), -1.0 V (anodic) (b), and -1.0 V (cathodic) (c).
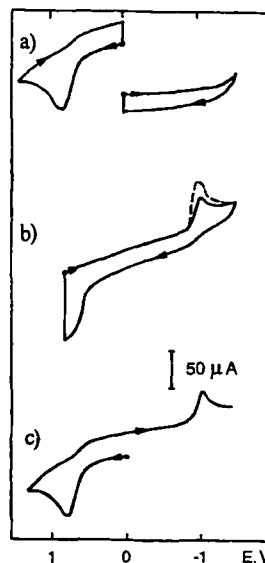
Fig. 2. Cyclic voltamperograms of compound II with E_{ini} = 0.0 V (anodic and cathodic) (a), +0.8 V (cathodic) (b), and 0.0 V (anodic) (c).

The height of the first peak varies linearly with the cation concentration in solution, over a range from 0.4×10^{-3} to 1.4×10^{-3} M, following the equation $i = ac$ with a 0.995 coefficient of correlation. The rate coefficient for the cation is 0.56 ± 0.02 (coefficient of correlation 0.996), with a variation of the rate from 0.25 to 4.00 V/sec. The

excess of the cation rate coefficient above the value 0.5 indicates that adsorption contributes slightly to the reduction process. The anodic/cathodic current ratio, as the voltage sweep rate is increased from 0.25 to 4.00 V/sec, increases from 0.28 to 0.36, corresponding to fast transfer of the electron, with a subsequent irreversible chemical reaction of conversion to the anhydro base.

A second possible source of the irreversibility is the formation of dimeric compounds, similar to what takes place in the case of pyrylium salts [9, 10].

In recording anodic polarograms from 0 to +2 V, no oxidation peaks were observed. The pyrimidinium cations are not susceptible to oxidation. The anhydro base II can be oxidized and cannot be reduced. When taking anodic polarograms from 0 to +1.5 V, an irreversible oxidation peak is observed at a potential of +0.80 V (Fig. 2a). The number of electrons, determined by comparison with ferrocene, is 1; consequently, the oxidation product is an unstable cation radical. The peak height varies linearly with the concentration of anhydro base in solution from 0.4×10^{-3} to 1.4×10^{-3} M. The rate coefficient for the anhydro base is 0.59 ± 0.03 with a 0.993 coefficient of correlation. The excess of the rate coefficient for the anhydro base in comparison with the cation indicates a slightly greater contribution from adsorption. The peak of the anhydro base is practically irreversible; therefore, we did not perform any measurements of the reverse peak. In taking cathodic polarograms from 0 to -1.5 V (and further into the cathodic region), no reduction peaks were observed (Fig. 2a); the anhydro base cannot be reduced.

Now let us consider the anodic voltamperograms of the cation I if the initial potential is changed to that where we should expect the formation of the radical I* and its decomposition products. On polarograms taken from -1 to +2 V, we observe a signal with an oxidation peak potential +0.8 V (Fig. 1b). Addition of the anhydro base II increases the peak height. This indicates that the decomposition of the radical species I* is accompanied by ejection of H by the radical and the formation of the anhydro base II:

$$ I \xrightarrow{+e^-} I^{\bullet} \xrightarrow{-H^{\bullet}} II $$
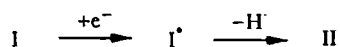
This hypothesis is further supported by the polarogram shown in Fig. 1c. An oxidation peak is observed with a potential sweep from 0 to -1.5 V and then to +2 V. The hydrogen that is formed may interact with the solvent, or it may be adsorbed on the electrode.
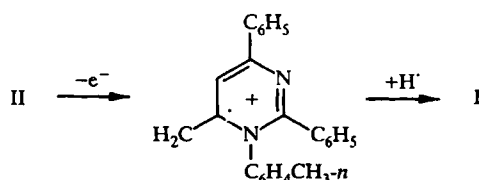
In turn, as shown in the scheme, the product from oxidation of the anhydro base is the cation I.

This can be seen from the voltamperograms for reduction of the anhydro base with an initial potential of +0.80 V, where the cation I is formed (Fig. 2b). On such voltamperograms, we find a reduction peak at -1.00 V, the height of which increases upon adding the cation I. Formation of this cation is also evidenced by the voltamperograms taken from 0 to +1.5 V and then to -1.5 V (Fig. 2c). The detachment of atomic hydrogen may result from the solvent or traces of water that are usually present in acetonitrile at a concentration up to 5×10^{-3} M. Direct confirmation of the formation of compound II from the cation I was obtained in the electrolysis of a 0.1 M solution of the salt I on a Microfisher platinum screen electrode at a potential of -1.2 V over the course of 6-7 h. The electrolysis process was monitored electrochemically, so that it was possible to evaluate the product yield. As time passed, we observed a gradual decrease of the reduction peak of the original cation, as well as the appearance and subsequent increase of the oxidation peak of the anhydro base.

The product II was recovered from the solution in pure form. In various experiments, the yield varied from 50% to 80%. Analogously, we carried out the anodic oxidation of the anhydro base II to form the cation I. The results of our experiments by the fact that, for both of these compounds, the PMR and IR spectra of the products II and I were identical with those of the corresponding synthetic samples.

EXPERIMENTAL

The IR spectra were taken on a Specord IR-71 spectrometer in a thin layer of white mineral oil; the PMR spectra were taken on a Varian Unity 300 instrument, internal standard HMDS, solvent $CDCl_3$. The scheme of cyclic voltamperograms was performed on a PI-50-1 potentiostat with a PI-8 programmer and an OP-3 oscillographic polarograph. The working electrode used in taking the cyclic voltamperograms was a platinum electrode with a diameter of 2 or 0.2 mm.

The auxiliary electrode was platinum, the comparison electrode a saturated calomel electrode equipped with an insulating water-impermeable partition made of asbestos impregnated with aluminum isopropylate, with subsequent hydrolysis and drying. The acetonitrile used in this work was distilled twice over CaH_2 and P_2O_5. The background electrolyte, tetraethylammonium perchlorate, was dried 24 h at 80°C.

Under the conditions of experiment, the oxidation of 5×10^{-3} M ferrocene proceeds with a half-peak potential of +0.35 V; the maximum current is 110 µA with a voltage sweep rate of 0.5 V/sec. Electrolysis at a controlled potential was performed in a PR-50-1 potentiostat using a Microfisher platinum screen electrode, an auxiliary zinc electrode, and a saturated calomel comparison electrode. After the electrolysis was completed, the reaction mixture was allowed to stand for natural evaporation of the solvent (acetonitrile); the dry mixture was dissolved in chloroform. With this procedure, all of the salt-like compounds remained in the residue. After evaporation of the chloroform and purification, PMR spectra were taken on the dried residues.

1-(p-Tolyl)-2,4-diphenyl-6-methylene-6H-pyrimidine (II). To a boiling solution of 12 g (30 mmole) of NaOH in 12 ml of H_2O and 100 ml of alcohol, 20 g (45 mmole) of the pyrimidinium salt I was added, and the mixture was again brought to boiling. After cooling, the precipitate was filtered off, washed with water and alcohol, and recrystallized from isopropyl alcohol. Yield 42%, mp 153-154°C. Found, %: C 85.58; H 6.04. $C_{24}H_{20}N_2$. Calculated, %: C 85.61; H 5.99. IR spectrum: 1623, 1540 cm^{-1}. PMR spectrum: 2.18 (3H, s, CH_3); 3.11 and 3.68 (2H, two s, CH_2); 6.50 (1H, s, 5-H); 6.00 – 8.00 ppm (14H, m, H_{arom}).

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