

## PROTOLYSIS OF SOME *p*-SUBSTITUTED 1,5-DIPHENYL-3-METHYL-1,4-PENTAZDIENES

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Protolysis mechanism of 1,5-diphenyl-3-methyl-1,4-pentazdiene and some of its *p*-substituted derivatives has been studied in 50% ethanolic solutions of perchloric acid of defined acidity values. The reaction has been found to be pseudomonomolecular 1. order with antecedent acid-base equilibrium having activation energy of 15.5 kcal/mol. The rate constants correlate well with the Hammett  $\sigma$  constants. The protolysis mechanism is suggested on the basis of the kinetic data obtained and identification of the reaction products.

1,5-Diphenyl-3-methyl-1,4-pentazdiene is one of the two possible products of N-diazocoupling of benzenediazonium ion with methylamine. So far due attention has not been given to synthetic aspects and physico-chemical properties of these compounds. The parent 1,5-diphenyl-3-methyl-1,4-pentazdiene and its symmetrical substitution derivatives can be prepared generally by reaction of the respective arenediazonium salt with methylamine in alkaline medium<sup>1-3</sup> respecting the antecedent equilibria of the both reagents, arenediazonium ion and alkylamine<sup>4,5</sup>. Dimroth, Eble and Gruhl<sup>1</sup> studied the behaviour of these compounds in hot diluted sulphuric acid and in alcoholic hydrogen chloride, too. The protolysis of the parent substance in the former medium gave methylamine, aromatic amine, phenol, methanol and nitrogen gas, whereas in the latter medium methyl chloride, nitrogen gas, aniline and benzenediazonium chloride were formed.

Within the investigations carried out in our laboratory on the problems of interaction of some cancerogenic compounds in biological substrate we studied besides N-diazocoupling reactions also the protolysis of the respective coupling products *viz.* 1-phenyl-3,3-dimethyltriazene<sup>6</sup> and phenyl-3-methyltriazene<sup>7</sup> derivatives. In the present paper we have focused our attention on protolysis of 1,5-diphenyl-3-methyl-1,4-pentazdiene (*I*) and its derivatives<sup>5</sup>.

### EXPERIMENTAL

1,5-Diphenyl-3-methyl-1,4-pentazdiene (*I*) and its *p*-substituted derivatives were prepared by N-diazocoupling of the respective arenediazonium salts with methylamine in alkaline medium<sup>4-5</sup>. Aniline, 2-naphthol, 2-hydroxynaphthalene-3,6-disulfonic acid and the other reagents used (Analar and Lachema) were commercial products of *p.a.* purity grade.

\* Part IX in the series N-Diazocoupling; Part VIII: Českoslov. farm. 21, 442 (1972).

Protolysis was carried out in mixtures of perchloric acid and water containing 50% ethanol and having defined acidity values<sup>8</sup>. Photometric analyses were carried out with the spectrophotometer Spekol (Zeiss, Jena).

The protolysis products were identified by GLC: Carlo Erba apparatus, Chromosorb W silanized with 10% Versamide 900 at 198°C for identification of aniline and its alkyl derivatives, Synachrom E5 at 144°C for identification of methanol.

The protolysis kinetics was followed by polarography using a mercury dropping electrode of the Smoler type and a saturated calomel reference electrode (s.c.e.). The concentration decrease of the pentazdiene was followed, the substance being reduced under the experimental condition used at the mercury electrode with imposed voltage  $-0.2$  to  $-0.6$  V (according to the acidity of medium). Limit current of this wave has a diffusion character<sup>9</sup>. Course of the kinetic curve was recorded by means of a EZ 2 recorder with a polarograph LP 60, the polarographic filter being set aside.

#### Measurement Procedure

36 ml absolute ethanol, 4 ml 10M-HClO<sub>4</sub> and 36 ml distilled water were put in the tempered reaction vessel of the polarographic apparatus. Pure nitrogen was bubbled through the solution for 10 minutes and then 4 ml 10<sup>-3</sup>M ethanolic pentazdiene solution (through which nitrogen was also bubbled before) was added quickly thereto. During the reaction the stream of nitrogen was decreased and the mixture was stirred with a stirrer having constant rate. At other acidities the kinetic runs were much the same, the overall alcohol content being 40 ml, and the perchloric acid to water ratio being varied to make the total volume of reaction mixture 80 ml. The limit current values, which were directly proportional to the pentazdiene concentration, were read from the kinetic curve record and the rate constants were calculated from the relation (1), where  $k$  is the

$$k = (1/t) 2.303 \log (i_0/i_t) \quad (1)$$

first order rate constant, and  $i_0$  and  $i_t$  ( $\mu$ A) stand for the limit current values at the initial pentazdiene concentration and at a time  $t$ , respectively (under constant conditions).

#### Identification of Protolysis Products of 1,5-Diphenyl-3-methyl-1,4-pentazdiene (I)

0.01 mol compound *I* was mixed with 100 ml 1M-HClO<sub>4</sub> and the mixture was left to stand at 20°C until the evolution of nitrogen ceased. Then the reaction mixture was neutralized with 1M-NaOH with cooling, the protolysis products were extracted with 50 ml ether and the extract was analyzed by GLC.

#### Gasometric Determination of 1,5-Diphenyl-3-methyl-1,4-pentazdiene (I)

The method adopted was analogous to that used for determination of arenediazonium compounds<sup>10</sup>. 0.5 mmol compound *I* was dissolved in 5 ml dioxane and added into 10 ml 1N-H<sub>2</sub>SO<sub>4</sub> and 50 ml water. The nitrogen gas evolved was collected in gasometric burette and its volume converted to normal conditions.

#### Determination of Arenediazonium Salt in Protolysis Products of 1,5-Diphenyl-3-methyl-1,4-pentazdiene (I)

0.1 mmol compound *I* was mixed with 3 ml 10M-HClO<sub>4</sub> in a 50 ml calibrated flask. After the nitrogen gas evolution had ceased, the volume was adjusted at 50 ml with water. From the solution

TABLE I

Dependence  $\log k + H'_0$  vs  $\sigma$  Constants for Protolysis of *p*-Substituted 1,5-Diphenyl-3-methyl-1,4-pentazdiene Derivatives at 25°C

Substituent	$\log k + H'_0$	$\sigma$
CH <sub>3</sub>	0.474	-0.17
H	0.043	0.00
F	-0.267	0.05
Cl	-0.541	0.23
Br	-0.594	0.23
J	-0.581	0.28

TABLE II

Temperature Dependence of Protolysis Rate Constants of 1,5-Diphenyl-3-methyl-1,4-pentazdiene at  $H'_0$  1.430

<i>t</i> , °C	25	35	45	55
<i>k</i> , min <sup>-1</sup>	0.184	0.449	1.014	2.115

obtained 0.5 ml samples were withdrawn and added to 40 ml 0.2M borax and 4.5 ml 0.01M 2-hydroxynaphthalene-3,6-disulfonic acid solution in a 50 ml calibrated flask. After adjusting the 50 ml volume with 0.2M borax the extinction was measured at  $\lambda_{\max}$  of the corresponding azo dyestuff. Percentage of the azo compound was calculated by means of a calibration line.

Similarly the C-diazocoupling with 2-naphthol was carried out. The dyestuff formed was extracted with benzene and chromatographed on a silica gel thin layer (Silufol UV 254) along with the model substance. All the procedures were carried out in red light with respect to high photochemical lability of pentazdiene.

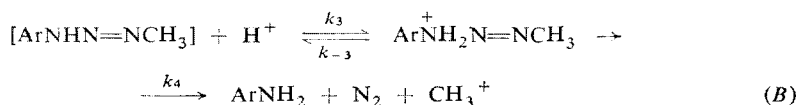
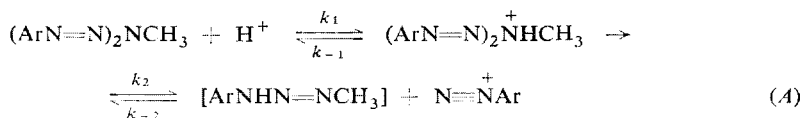
## RESULTS AND DISCUSSION

The following substances were found among the protolysis products of 1,5-diphenyl-3-methyl-1,4-pentazdiene (*I*): benzenediazonium ion, aniline, small amounts of its *N*-alkyl derivatives, methanol, nitrogen gas. Quantitative analysis showed that 1 mol of the compound *I* gave 1 mol benzenediazonium salt and 1 mol nitrogen gas at room temperature.

1-Phenyl-3-methyltriazene, C<sub>6</sub>H<sub>5</sub>N=N—NHCH<sub>3</sub> (*IIa*) could not be identified in the reaction product due to the high hydroxonium ion concentration. The tautomer C<sub>6</sub>H<sub>5</sub>NH—N=NCH<sub>3</sub> (*IIb*) of the substance *IIa* undergoes rapid protolysis already

at pH 5.5 (ref.<sup>7</sup>) when the compound *I* is still entirely stable. Thus it can be presumed that aniline eventually its N-alkyl derivatives, methanol and nitrogen gas are formed in a subsequent reaction step by protolysis of the compound *II*.

Kinetic results suggest that pentazdiene *I* is first protonated and then decomposed to give arenediazonium salt and 1-aryl-3-methyltriazene *II*. The latter substance is protonated<sup>7</sup> and decomposed to give aromatic amine, nitrogen gas and methyl cation which reacts immediately with nucleophiles present in the reaction medium:



Protolysis of the pentazdiene *I* is anteceded by acid-base equilibrium, thus  $k_1$  must be much greater than  $k_2$ . Protolysis study of substance<sup>7</sup> *II* also points to  $k_3 \gg k_4$ , and N-diazocoupling study<sup>4</sup> of arenediazonium salts with methylamine indicates that the rate constant  $k_2$  of the equilibrium reaction is much greater than  $k_{-2}$  under the conditions of protolysis of pentazdiene. The rate constant of protolysis of pentazdiene can then be expressed by Eq. (2) which involves the dependence on acidity of medium; for the compound *I* it is given in Fig. 1 (rate constants in  $\text{min}^{-1}$ ).

$$k = k_1 k_2 h'_0 / k_{-1} \quad (2)$$

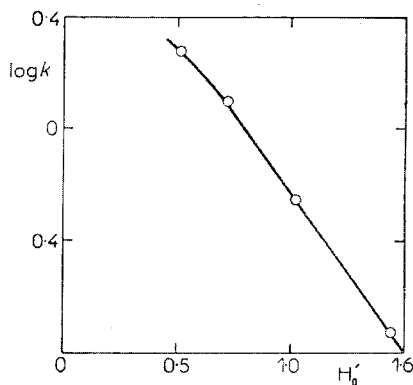
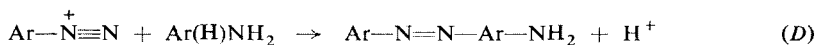


FIG. 1  
Dependence  $\log k$  vs  $H'_0$  of Protolysis of  
1,5-Diphenyl-3-methyl-1,4-pentazdiene at  
25°C

The dependence  $\log k$  vs  $h'_0$  is linear in a sufficiently broad acidity range, the slope being unity, which makes it possible to calculate the  $\log k_2 + pK_a$  values and use them for the Hammett correlation. The protolysis rate decreases with increasing  $\sigma$  value (Table I), the slope  $\rho$  being  $-2.42$ .

Kinetic measurements indicate that the protolysis of the compound *I* and its *p*-substituted derivatives is a pseudomonomolecular 1. order reaction depending markedly on the acidity of reaction medium. Interaction between the arenediazonium ion formed and aromatic amine (Eq. (C)) can be considered as a subsequent reaction. In the case of protolysis of the non-substituted 1,5-diphenyl-3-methyl-1,4-pentazdiene the N-diazocoupling could be accompanied by C-diazocoupling (Eq. (D)).



However, neither of the two subsequent reactions mentioned occurs in the medium of the given hydroxonium ion concentration, which was proved by the absence of products of the reactions (C) and (D) among the protolysis products.

The temperature effects were studied with the compound *I*, and the rate constants obtained fit very well the Arrhenius relation. The activation energy calculated by the least squares method is 15.5 kcal/mol. For illustration Table II gives the values measured with the parent pentazdiene.

In conclusion it must be stated that a more precise expression of substituent effects is impossible without determination of equilibrium constants of the antecedent acid-base equilibria which are, however, inaccessible due to high lability of the protonated pentazdienes.

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