7. A. Ohno and Y. Ohnishi, Int. J. Sulfur Chem., A1, 203 (1971).
8. M. Procházka, Collect. Czech. Chem. Commun., 41, 1557 (1976).
9. J. W. Timberlake and M. L. Hodges, Tetrahedron Lett., 1970, 4147.
10. A. Ohno, Y. Ohnishi, and N. Kito, Int. J. Sulfur Chem., A1, 151 (1971).
11. P. S. Engel and D. J. Bishop, J. Am. Chem. Soc., 97, 6754 (1975).
12. Ya. A. Levin, I. P. Gozman, A. G. Abul'khanov, and B. E. Ivanov, Izv. Akad. Nauk SSSR, Ser. Khim., 1975, 983.
13. A. Sh. Mukhtarov, A. V. Il'yasov, Ya. A. Levin, I. P. Gozman, M. S. Skorobogatova, and E. I. Zoroatskaya, Teor. Eksp. Khim., 12, 831 (1976).
14. E. E. Nifant'ev, N. V. Zyk, and M. P. Koroteev, Dokl. Akad. Nauk SSSR, 218, 1371 (1974).
15. A. Wilson, Rev. Sci. Instrum., 38, 1757 (1967).
16. W. A. Pryor and K. Smith, J. Am. Chem. Soc., 92, 5403 (1970).
17. F. Bernardi, N. D. Epiotis, W. Cherry, N. B. Schlegel, M.-W. Whangbo, and S. Wolfe, J. Am. Chem. Soc., 98, 469 (1976).
18. W. von Doering, G. Horowitz, and K. Sachdev, Tetrahedron, 33, 273 (1977).
19. D. C. McKean, J. L. Duncan, and L. Batt. Spectrochim. Acta, 29A, 1037 (1973).
20. K. D. King and R. D. Goodard, Int. J. Chem. Kinet., 7, 837 (1975).
21. J. Weber, L. Ginet, and M. Geoffroy, Chem. Phys. Lett., 41, 507 (1976).

SYNTHESIS AND ELECTROCHEMICAL OXIDATION OF DERIVATIVES OF 1,4-DIHYDRO-1,2,4,5-TETRAZINE

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Chemical oxidation and electrochemical oxidation (ECO) of compounds (e.g. the 1-arylpyrazolines) containing an $>C{=}N{-}NAr$ arylhydrazone fragment, either in a ring or an open chain, yield different products [1-7]. Electrochemical oxidation of compounds (such as the 1-phenylpyrazolines) with unsaturated phenylhydrazone fragments leads to oxidational dehydrodimerization of the primary cation radicals at the p-position in the phenyl ring [2-6]. Dimer formation does not occur in the chemical oxidation of these compounds [1, 4, 7]. Dimerization at the p-position is not observed in the ECO of compounds which carry a substituted phenyl group in this p-position, since the cation radical is stabilized or the reaction proceeds along other paths [3, 4, 8]. Both chemical [7] and electrochemical oxidation of the 4-R-phenylhydrazones of the benzoylhalides lead to the formation of 1,3,4,6-tetraaryl-1,4-dihydro-1,2,4,5-tetrazine [6], which, in turn, passed over to stable cation-radical salts, either in ECO or under the action of iodine [9], or other oxidizing agents, in the presence of acids [7].

It therefore seemed of interest to carry out a detailed investigation of the electrochemical oxidation of the derivatives of 1,4-dihydro-1,2,4,5-tetrazine, a heterocyclic [3 + 3]-dimer involving two hydrazone fragments and a conjugated system consisting of two π-bonds and two unshared N-atom electron pairs. The effect of the nature and position of the substituents on the structure of the products formed in electrochemical oxidation was studied in 1,3,4,6-tetraphenyl-1,4-dihydro-1,2,4,5-tetrazine (Ib) and its symmetrical disubstituted derivatives with substituents in the phenyl rings attached to either the nitrogen atoms (1,4-diaryl-3,6-diphenyl derivatives (IIb)-(VIIb), see Table 1), or the carbon atoms [1,4-diphenyl-3,5-diaryl derivatives (VIIIb)-(XIIb)], and in 1,4-di(4-nitrophenyl)-3,6-diacetyl-(XIIIb), 1,3,4,6-tetra(4-nitrophenyl)-(XIVb), 1,4-ditosyl-3,6-diphenyl-(XVb), 1,4-ditosyl-3,6-di(3-nitrophenyl)-(XVIb), and 1,3,6-triphenyl-1,4-dihydro-1,2,4,5-tetrazines (XVII).

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TABLE 1. Oxidation Times for the Halohydrazones; Yields, Melting Points, UV Spectra, and ECO Data for the 1,3,4,6-Tetrasubstituted 1,4-Dihydro-1,2,4,5-tetrazines

Compound	R^1	R^2	Reaction time, h	Yield, %	mp, C° (solvent)	ECO		UV spectra, λ_{max}, nm (log ε)		Empirical formulas of the dihydrotetrazines[a]
						$E'_{1/2}$, V	$E''_{1/2}$, V	Dihydrotetrazines in ethanol	cation-radical perchlorates in CH_3CN	
(Ib)	Ph	Ph	0,5	90	204–205 (EtOH)	0,28	1,28	272 (4,31), 333 (4,15)	276 (4,30), 333 (4,11)[b], 423 (3,52), 582 (3,32)	$C_{26}H_{20}N_4$ [9, 10]
(IIb)	Ph	$4\text{-}BrC_6H_4$	1,5	88	264,5–265 (AcOH)	0,34	1,29	227 (4,54), 275 (4,26), 329 (4,25)	227 (4,63)[b], 278 (4,36), 340 (4,20), 454 (3,54), 623 (3,42)	$C_{26}H_{18}Br_2N_4$ [11]
(IIIb)	Ph	$3\text{-}ClC_6H_4$	1,5	63	148–150 (ether)	0,40	1,22	272 (4,20), 335 (4,14)	286 (4,44), 340 (4,27)[b], 412 (3,80), 580 (3,44)	$C_{26}H_{18}Cl_2N_4$
(IVb)	Ph	$4\text{-}O_2NC_6H_4$	1,5	96	317–318 ($CHCl_3$: EtOH)	0,53	1,40	225, 240, 261, 414[c]	263 (4,48), 290 (4,32)[b], 350 (4,30), 560 (3,28)	$C_{26}H_{18}N_6O_4$ [10, 12]
(Vb)	Ph	$4\text{-}(4\text{-}O_2NC_6H_4N{=}N)C_6H_4$	2,0	90	302–307[d,e]	c	—	345, 490[c]	—	$C_{38}H_{26}N_{10}O_4$
(VIb)	Ph	$2,4\text{-}Br_2C_6H_3$	4,0	30	254,5–255 (AcOH)	—	—	—	—	$C_{26}H_{16}Br_4N_4$ [11]
(VIIb)	Ph	$2\text{-}Br\text{-}4\text{-}O_2NC_6H_3$	2,0	90	278–279	0,53	0,98	224, 243, 263, 410[c]	263 (4,63), 290 (4,52)[b], 38_5 (4,41), 420 (4,26), 555 (3,48)	$C_{26}H_{16}Br_2N_6O_4$ [10, 12]
(VIIIb)	$4\text{-}BrC_6H_4$	Ph	1,5	93	205–206 (THF : MeOH)	0,28	1,35	242 (4,45), 276 (4,41), 340 (3,04)	276 (4,47), 313 (4,36)[b], 435 (3,70), 590 (3,40)	$C_{26}H_{18}Br_2N_4$
(IXb)	$4\text{-}ClC_6H_4$	Ph	3,0	70	155–156 (ether) : $CHCl_3$)	0,28	1,33	236 (4,44), 275 (4,34), 340 (3,04)	276 (4,42), 312 (4,36)[b], 430 (3,67), 580 (3,40)	$C_{26}H_{18}Cl_2N_4$

(Xb)	3-$O_2NC_6H_4$	Ph	1,5	84	231–233 (DMFA : MeOH)^{d}	0,35	1,31	265, 333 ^{c}	263(4,33), 333(3,90) ^{b}, 400(3,48) ^{b}, 500(3,20)	$C_{26}H_{18}N_6O_4$
(XIb)	4-$O_2NC_6H_4$	Ph	3,0	56	277–278 (DMFA : MeOH, 2 : 1)d	0,36	1,28	265(4,32), 302(4,45), 406(3,74)	267(4,61), 305(4,55), 405(4,00), 550(3,49)	$C_{26}H_{18}N_6O_4$
(XIIb)	4-$MeOC_6H_4$	Ph	2,0	90	95–96^{f}	0,15	1,06	272(4,43), 332(4,11)	227(4,34), 278(4,30), 330(4,45), 470(3,61), 670(2,28)	$C_{28}H_{24}N_4O_2$
(XIIIb)	McCO	4-$O_2NC_6H_4$	2,0	95	284–286 (DMFA : MeOH) ^{d}	0,86	—^{g}	240(4,08), 262(4,08), 394(4,36)	—	$C_{18}H_{14}N_6O_6$
(XIVb)	4-$O_2NC_6H_4$	4-$O_2NC_6H_4$	3,0	95	275–278 (DMFA : MeOH)^{d,h}	0,68^{c}	—	270(4,40), 418(1,90)^{i}	—	$C_{26}H_{16}N_8O_8$ [10]
(XVb)	Ph	$SO_2C_6H_4Me$-4	24,0	57	156–157 (EtOH)^{j}	1,10	—^{g}	230(4,48), 255(4,44)	—	$C_{28}H_{24}N_4O_4S_2$
(XVIb)	3-$O_2NC_6H_4$	$SO_2C_6H_4Me$-4	24,0	87	198–199 (EtOH)	1,31	—^{g}	225, 252^{c}	—	$C_{28}H_{22}N_6O_8S_2$
(XVII)	Ph	– k	—	—	125–126	0,25	1,25	236(4,37), 264(4,30), 315(3,99)		$C_{20}H_{16}N_4$

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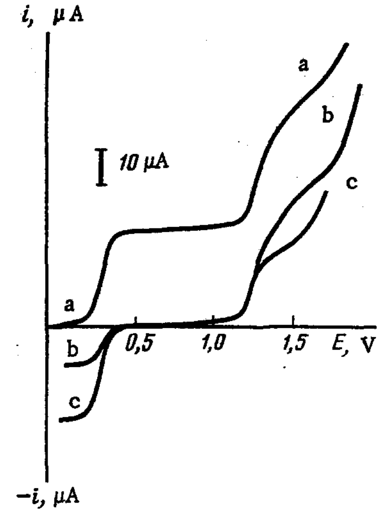
a) The measured and calculated values of the content of the various elements differed by 0.02–0.2%. The empirical formulas for the cation radical perchlorates would show the ClO_4 content. b) Shoulder. c) Only slightly soluble. d) With decomposition. e) Purified by treatment with boiling ethanol or ether. f) Precipitated from ethanol solution by ether. g) Second wave masked by discharge background. h) For recrystallization from PhCN or oxidation in PhCN, mp, 340–345°C. i) In MeCN. j) Prepared by the method of [13]. k) 3,4,6-Triphenyl-1,4-(or 4,5)-dihydro-1,2,4,5-tetrazine.



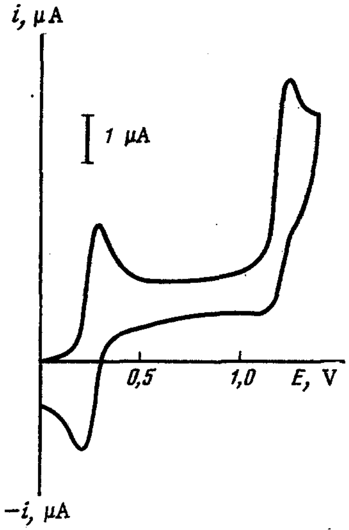
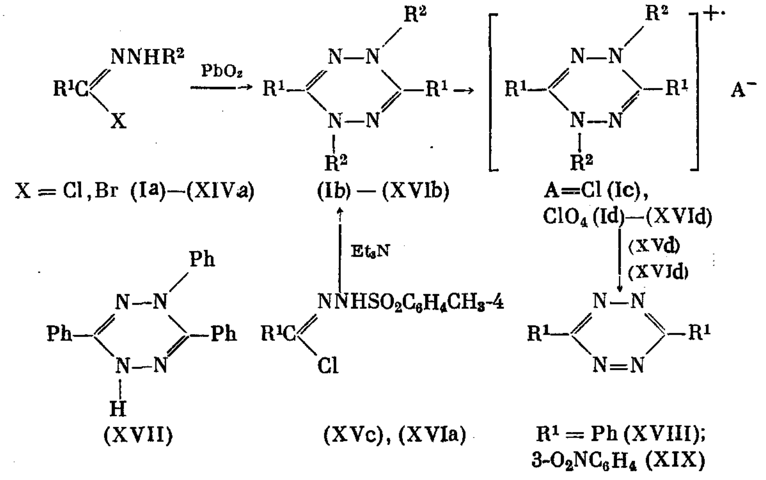


Fig. 1. Polarogram for a 0.001 M solution of 1,3,4,6-tetraphenyl-1,4-dihydro-1,2,4,5-tetrazine (Ib) on the rotating disk electrode, ω = 293 sec^{-1} (a); polarogram for the same solution after passage of 1 Faraday/mole at E = 0.6 V (c), polarogram of the same solution after CPE at E = 1.5 V (b).

Fig. 2. Cyclic voltamperogram for a 1,3,4,6-tetraphenyl-1,4-dihydro-1,2,4,5-tetrazine (Ib) solution, developed on the stationary electrode. Sweep rate, 20 mV/sec.

Compounds (Ib)-(XIVb) were prepared by oxidizing the respective arylhydrazones of the acylhalides (Ia)-(XIVa) by PbO_2 in THF, following the procedures of [7], compound (XVb) by the method of [13], and compound (XIVb) by the action of Et_3N on the tosylhydrazones of benzoyl chloride and 3-nitrobenzoyl chloride.



R^1 and R^2 are identified in Table 1.

EXPERIMENTAL

The methods used in purifying the MeCN and $NaClO_4$, the procedures followed in the preparative electrolyses, and the apparatus were as described in [6]. The working electrode was either a stationary disk or a rotating polished platinum disk 5 mm in diameter; the cyclic voltamperograms were developed with a Pt wire auxilary electrode and a Ag/0.1 N $AgNO_3$ reference electrode. The UR spectra were recorded with a Specord UV-VIS spectrometer. Melting points were determined on a Boetius stage. The purity of the various compounds was checked through TLC using Silufol UV-254 sheets. The eluent was a mixture of petroleum ether with either benzene or ether; the developer, iodine vapors.

1,4-Di(4-bromophenyl)-3,6-diphenyl-1,4-dihydro-1,2,4,5-tetrazine (IIb). A. To a solution containing 0.62 g (2 mmoles) of the 4-bromophenylhydrazone of benzoylchloride in 50 ml of THF there was added 12 g of PbO_2 and the suspension agitated at 20-25°C. The resulting sludge was filtered off, the THF removed by vacuum evaporation, the residue treated with 3-5 ml methanol, and recrystallized. Table 1 lists reaction times, yields, melting points, solvents for recrystallization, empirical formulas, and UV spectra not only for compound (IIb) but for compounds (Ib) and (IIIb)-(XIVb) as well. The latter compounds were prepared in the same manner as (IIb), starting respectively from the phenyl- (Ia), 3-chloro- (IIIa), 4-nitro- (IVa), and 4-(4-nitrophenylazo-(Va))-phenylhydrazones of benzoyl chloride, from the 2,4-dibromo-(VIa), and 2-bromo-4-nitro-(VIIa)-phenylhydrazones (VIIa) of benzoyl bromide, from the phenylhydrazones of 4-bromo-(VIIIa), 4-chloro- (IXa), 3-nitro- (Xa), 4-nitro- (XIa), and 4-methoxy- (XIIa)-benzoyl chloride, and from the 4-nitrophenylhydrazones of the bromoanhydride of pyroracemic acid (XIIIa) and 4-nitrobenzoyl bromide (XIVa). Compound (XIVb) was obtained in two polymorphic forms.

B. To a solution containing 0.4 g (1 mmole) of compound (Ib) dissovled in 15 ml of AcOH there was added 0.2 g of AcOK, and the mixture refluxed for 1 h while adding a solution containing 0.052 ml (1 mmole) of Br_2 dissolved in 10 ml of AcOH. This mixture was diluted with 150 ml water during the following 10-15 min, and then filtered to obtain 0.5 g (96%) of (IIb) as a yellowish powder, mp, 265°C (from AcOH), which proved to be identical with the product described in A.

1,4-Ditosyl-3,6-di(3-nitrophenyl)-1,2-dihydro-1,2,4,5-tetrazine (XVIb). To a solution containing 0.9 g (2.5 mmole) of the tosylhydrazone of 3-nitrobenzoyl chloride (XIVa) (mp, 149-159°C, from a mixture of benzene and petroleum ether; prepared from 1-tosyl-2-(3-nitrobenzoyl) hydrazine and $SOCl_2$, following the procedure of [14]) in 50 ml of benzene there was added 0.7 ml of Et_3N, and the mixture allowed to stand for 24 h. The precipitate which had fallen out at the end of this time was filtered off and washed with H_2O and EtOH. This procedure gave 0.7 g (87%) of bright yellow crystals of (XVIb), mp, 198-199°C (from ethanol). Data on the UV spectrum of the compound and its empirical formula are given in Table 1.

1,3,4,6-Tetraphenyl-1,4-dihydro-1,2,4,5-tetrazinyl Chloride (Ic). [Chloride of the Cation-Radical of Compound (Ib)]. Fifty ml of benzene were saturated with dry HCl at 10-15 °C. One gram (2.5 mmole) of (Ib) and a solution containing 1.26 g (5 mmoles) of benzoyl peroxide dissolved in 50 ml of benzene was then added. The dark violet crystals of the cation-radical salt which precipitated out over the following 10-15 min were allowed to stand for 1 h, filtered off, washed with benzene to disappearance of the color, and then dried in the air. Yield of (Ic), 0.75-0.8 g (75-80%). The crystals swelled and became yellow at 130-135°C, finally recrystallizing to a product, contaminated with the parent compound, which melted at 190-195°C. The UV spectrum of the (Ic) salt in MeCN showed the following optical absorption, λ_{max}, nm (log ε): 284 (4.20), 312 (4.146) shoulder, 333 (3.95) shoulder, 430 (3.58) 585 (3.40). ESR spectrum in THF: $\alpha_1N = 7.5 + 0.2$; $\alpha_2N = 4.1 + 0.2$; g-factor, 2.00247. Found: C 73.36; H 5.01; Cl 8.21; N 13.07%. $C_{26}H_{20}ClN_4$. Calculated: C 73.70; H 4.72; Cl 8.39; N 13.23%.

Electrochemical Oxidation of Derivatives of 1,4-Dihydro-1,2,4,5-tetrazine. The cyclic voltamperograms of compounds (Ib)-(IVb), (VIIb)-(XIIb), and (XVII) showed two anodic waves with the half-wave potentials indicated in Table 1. The second wave merged with the discharge background on the voltamperograms of compounds (XIVb)-(XVIb). Compounds (Vb) and (XIVb) were so slightly soluble in MeCN that their electrochemical oxidation could not be studied.

The perchlorates of the (Id)-(IVd), and (VIId)-(XId) cation-radical perchlorates were prepared by subjecting 40-ml solutions containing compounds (Ib)-(IVb), (VIIb)-(XIb) at 10^{-3} 10^{-2} mole/liter concentration and 2.45 g (0.5 mole/liter $NaClO_4$ to anodic oxidation on a Pt sheet of 7.7 cm^2 surface area, working at first wave saturation current potentials. Oxidation was considered to be complete when the anodic current fell to zero. The solvent was evaporated off, the residue washed with water, and then dried to obtain brilliant black or dark violet crystals of the (Id) — (IVd), (VIId) — (XId) salts with metallic luster.

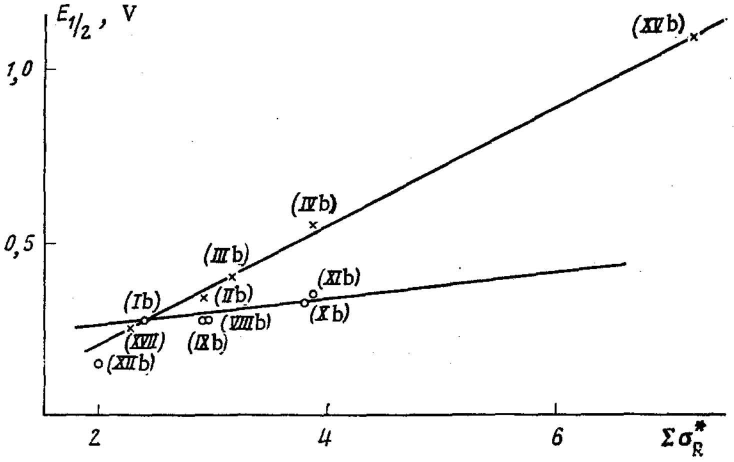


Fig. 3. Correlation between $E_{1/2}$ values for the substituted 1,4-dihydro-1,2,4,5-tetrazines and the sum of the Taft substitutent constants. Point designation in accordance with Table 1: a) Substituent at the N atom; b) substituent at the C atom.

3,6-Di(3-nitrophenyl)-1,2,4,5-tetrazine (XIX). A. To a solution containing 0.1 g (XVIb) dissolved in 40 ml MeCN there was added 2.45 g $NaClO_4$, and the mixture electrolyzed at 1.5 V. The solvent was removed by vacuum evaporation, the residue washed with hot water, dried, and then recrystallized from ethanol. This procedure gave 46 mg (90%) of raspberry colored crystals of compound (XIX), mp, 217-219°C. UV spectrum in MeCN, λ_{max} nm (log ε): 260 (4.65). 540 (2.74). Found: C 51.75; H 2.56; N 26.0%. $C_{14}H_8N_6O_4$. Calculated. C 51.85; H 2.47; N 25.93%.

B. Addition of 0.64 g of compound (XVIb) to 10 ml of 56% HNO_3 gradually brought down raspberry colored crystals. These were allowed to stand for 10-15 min, and then filtered off and washed with water. This procedure gave 0.3 g (95%) of compound (XIX) which was identical with the product described in the A procedure; mp 217-219°C (from ethanol).

A similar procedure was followed in preparing the 3,6-diphenyl-1,2,4,5-tetrazine (XVIII), mp, 191-192°C [15]. UV spectrum, MeCN, λ_{max}, nm (log ε): 222 (4.57), 292 (4.61), 550 (2.70).

DISCUSSION OF RESULTS

Curve a of Fig. 1 is a typical voltamperogram for the oxidation of compounds (Ib)-(IVb), (VIIb)-(XIIb) on the rotating disk electrode. The $i_{sat}/\omega^{1/2} = f(\omega^{1/2})$ function for the first oxidation wave at fixed concentration was plotted up to a straight line parallel to the axis of abscissas, the indication being that the observed current did not arise from coupled reactions but was purely diffusional at disk rotation rates ranging from 600 to 9000 rpm. Cyclic voltamperograms obtained on the stationary electrode showed the first wave oxidation to be a reversible process, $E_{p.a} - E_{p.c} = 60$ mV and $i_{p.a}/i_{p.c} = 1$ (Fig. 2 even at low sweep rates (10 mV/sec). Preparative electrolysis at controlled first wave saturation current potentials (CPE) involved the expenditure of one Faraday per mole of compounds (Ib)-(XIIb) oxidized and led to the formation of cation-radicals which could be detected by ESR methods and separated out as the (Id)-(IVd) and (VIId)-(XIId) perchlorates. The ESR spectrum of the (Id) cation-radical was identical with the ESR spectrum of the (Ic) cation radicals obtained by chemical oxidation (Bz_2O_2 in PhH + HCl: see Experimental section). The same was also true of the spectrum of the cation radicals formed by treating compound (Ib) with iodine [9].

The UV spectra of a (Ic) chloride prepared by electrochemical methods and of MeCN solutions of the (Id)-(IVd) and (VIId)-(XIId) perchlorates prepared by CPE, showed all of the absorption bands appearing in the spectra of the parent (Ib)-(XIIb) compounds, plus two additional bands in the 400-600 nm region (see Table 1), the latter arising from low-frequency transitions from the lower orbitals to the upper half-filled orbital.

The tetraaryldihydrotetrazine oxidation—reduction system is reversible and highly stable, its cation-radicals being capable of withstanding controlled potential coulometry without breakdown. Oxidation of compounds (Ib)-(IVb), (VIIb)-(XIIb) gave rise to a single cathode—anode wave with normal half-wave potential ($E_{1/2} = E^{\circ}$) and form corresponding to the concentrations of the oxidized and reduced forms present in the system. In the 2 h following generation of the (Id)-(IVd), (VIId)-(XIId) cation-radicals, the height of the cathodic radical reduction wave was the same as the height of the anodic parent compound oxidation wave (see Fig. 1, curves a, b). This, plus the lack of electrode passivation and good reproducibility of measurements, suggest the use of the 1,3,4,6-tetraaryl-1,4-dihydro-1,2,4,5-tetrazines as standards for determining electron numbers by the comparison method.

The cation radical salts (Id)-(IVd), (VIId)-(XIId) were stable, in the presence of water and oxygen, in solution (more than a month), and in the solid state (more than a year).

It can be seen from Fig. 2 that our studies on the second-wave electrochemical oxidation of compounds (Ib)-(XIIb) were less extensive. It was merely noted that the number of electrons transferred in the second wave process was unity at high rates of electrode rotation, increasing as the rate of rotation was reduced. The UV and ESR spectra of solutions which had been subjected to electrolysis at second wave saturation current potentials showed the presence of the (Id)-(IVd), (VIId)-(XIId) cation-radicals, the height of their cathodic waves being only half that of the first wave in each electrolysis. The data obtained here suggest an ECE mechanism of second wave oxidation, the primary cations being unstable and breaking down to (Id)-(IVd) and (VIId)-(XIId) cation-radicals and an unknown product.

The cyclic voltamperograms, for the 3,6-diacetyl derivative (XIIIb) and for the unsymmetrical derivative (XVII), were similar to the voltamperograms for the (Ib)-(XIIb) derivatives (see Fig. 2), the products from the single-electron oxidation being sufficiently long-lived to permit development of the cyclic curve, even at a sweep rate of 10 mV/sec. However, the products from the single-electron oxidation, i.e., the (XIIId) and (XVIId) cation radicals, were not stable enough to permit preparative generation in the electrolytic cell. In fact, voltamperograms similar to those shown in Fig. 1b could not be obtained, nor could the presence of the (XIId) and (XVIId) radicals be detected by UV and ESR methods, in solutions which had been subjected to ECO. However, the (XIIId) cation-radical could be detected in the cell of the ESR spectrometer after electrochemical oxidation of compound (XIIIb), its lifetime being of the order of several minutes.

Thus the stability of the cation-radicals formed in ECO is markedly reduced, either by replacing one of the aryl groups at the N atom with a hydrogen atom or by replacing two of the aryl groups at the C atoms by acetyl groups.

The replacement of two of the aryl groups at the N atoms with tosyl groups markedly inhibits ECO (cf. $E_{1/2}$ values in Table 1) by reducing the electron density in the dihydrotetrazine. Although the first oxidation waves for compounds (XVb) and (XVIb) arise from single-electron processes, just as in the case of the tetraaryl derivatives (Ib)-(XIIb), cyclic voltamperograms similar to those of Fig. 2 could be obtained for the tosyl derivatives (XVb) and (XVIb) only at sweep rates of 80 mV/sec, or better. A cathodic current for (XVd) and (XVId) cation-radical reduction could not be detected at v = 10 mV/sec, the lifetimes of these radicals being comparable to the time required for recording the cyclic curve (∿ 10-20 sec).

Thus the stability of the dihydrotetrazine cation radicals is determined by the nature of the substituents at the N and C atoms, falling off in the order: 1,3,4,6-tetraaryl (months), 1,4-diaryl-3,6-diacetyl and 1,3,4-triaryl (minutes), 1,4-ditosyl-3,6-diaryl derivatives (seconds).

The originally colorless solutions of the ditosyl derivatives (XVb) and (XVIb) took on a raspberry coloration during electrolysis at the first wave saturation current potential. Electrolysis brought down 1,3-diphenyl- (XVIII) and 1,3-di(3-nitrophenyl)-1,2,4,5-tetrazine (XIX) quantitatively, these same compounds could be obtained by oxidizing (XVb) and (XVIb) with 56% HNO_3. From this it was concluded that the instability of the (XVd) and (XVId) cation radicals was due to rupture of the N—S bond with elimination of the tosyl group.

Since reversible transfer of an electron from the higher occupied orbital is the potential-determining step in the electrode reaction, the half-wave potential for oxidation should be fixed by the electronic character of the substituent at the dihydrotetrazine ring. Analysis of $E_{1/2}$ values showed that the substituent effect in the 1,3,4,6-tetraaryl derivatives

(Ib)-(XIIb) is more pronounced for substitution in the phenyl ring attached to the N atom (1,4-diaryl derivatives) than for substitution in the phenyl ring attached to the C atom (3,6-diaryl derivatives). The difference here clearly reflects the fact that the upper occupied orbital is more largely localized on the N atoms in the 1,4 positions while the interaction of the phenyl substituent with the dihydrotetrazine ring is similar to the phenyl group interaction in the hydrazones [16].

It has been shown that the tetraaryl derivatives of 1,4-dihydro-1,2,4,5-tetrazine and their cation-radicals are not planar structures [9]. Thus it seems most reasonable to attempt to establish correlations in the Taft constants for the substituents bound to the dihydrotetrazine ring, using the equation $E_{1/2} = \rho\pi^*(\sigma^*_{1}\text{-}R^1 + \sigma^*_{3}\text{-}R_2 + \sigma^*_{4}\text{-}R_1 + \sigma^*_{6}\text{-}R^2)$, in which $\rho\pi^*$ is the polarographic constant for the reaction. The value of $\sigma^*_{C_6H_4X}$ for the m and p substituted phenols were calculated from the equation $\sigma^*_{C_6H_4X} = \sigma_{X}° + 0.600$. Developed by the method of least-squares, the correlation equation for the 3,6-diphenyl derivatives, with R^1 = Ph and different H atom substituents (Fig. 3, curve a), has the form: $E_{1/2} = 0.174\, \Sigma\sigma^* - 0.148$ ($r = 0.993$, $s = 0.007$). From it σ^*, the inductive constant for the tosyl group was calculated to be 2.99. The presence of two N atoms each with an unshared electron pair and in conjugation with two π-bonds, makes the 1,4-dihydrotetrazine derivatives more readily oxidizable than the corresponding pyrazoline derivatives [4]. The possibility of unpaired electron delocalization is still higher in the 1,4-dihydro-1,2,4,5-tetrazine system, the cation radicals formed through electrochemical oxidation are stabilized, and there is no possibility of dimerization at the p-position in the N-phenyl group.

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CONCLUSIONS

1. Oxidation of the arylhydrazones of the acetylhalides by PbO_2 leads to the formation of 1,3,4,6-tetraaryl-1,4-dihydro-1,2,4,5-tetrazines, which, in turn, form stable cation-radicals under electrochemical oxidation.

2. The stability of the dihydrotetrazine cation-radicals can be reduced, either by replacing the phenyl group at the nitrogen atom with a tosyl group or a hydrogen atom, or by replacing the phenyl groups at the carbon atoms with acetyl groups.

3. Substituents at the amine N atom are more influential than substituents at the C atoms in fixing the first wave potential for the electrochemical oxidation of 1,4-dihydro-1,2,4,5-tetrazine.

LITERATURE CITED

1. Yu. P. Kitaev and B. I. Buzykin, The Hydrazones [in Russian] Nauka (1974), p. 291.
2. G. Barbey, M. Genies, M. Libert, and C. Caullet, Bull. Soc. Chim. France, 1973, 1942.
3. F. Pragst, J. Prakt. Chem., 315, 549 (1973).
4. F. Pragst and B. Siefke, J. Prakt. Chem., 316, 267 (1974).
5. W. Jugelt and M. Rauh, Z. Chem., 16, 488 (1976).
6. V. Kh. Ivanova, B. I. Buzykin, and Yu. P. Kitaev, Izv. Akad. Nauk SSSR, Ser. Khim., 1977, 393.
7. B. I. Buzykin, A. Sh. Mukhtarov, A. V. Il'yasov, and Yu. P. Kitaev, Izv. Akad. Nauk SSSR, Sr. Khim., 1973, 2167.
8. G. Barbey and C. Caullet, C. R. Acad. Sci., C280, 89 (1975).
9. W. M. Tolles, W. R. McBride, and W. E. Thun, J. Am. Chem. Soc., 91, 2443 (1969).
10. R. Huisgen, K. Adelsberger, E. Aufderhaar, H. Knupfer, and G. Wallbillich, Monatsh. Chem., 98, 1618 (1967).
11. F. D. Chattaway and A. J. Walker, J. Chem. Soc., 1925, 975.
12. G. Ponzio, Gazz. Chim. Ital., 39, II, 538 (1909); Beilstein's Handbuch der Organ. Chemie, Berlin, 26, 373 (1937).
13. S. Wawsonek and J. N. Kellen, J. Org. Chem., 38, 3627 (1973).
14. J. F. King, A. Hawson, B. L. Huston, L. J. Danks, and J. Kamery, Can. J. Chem., 49, 943 (1971).
15. R. Huisgen, H. J. Sturm, and M. Seidel, Chem. Ber., 94, 1555 (1961).
16. V. V. Zverev, V. I. Vovna, T. N. Pylaeva, F. I. Vilesov, and Yu. P. Kitaev, Zh. Org. Khim., 11, 1719 (1975).