The Electrochemical Reduction of Compounds with the $-N=\underset{|}{C}-\underset{|}{C}=N-$ Group. III *as*-Triazines

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Received November 19, 1971

The electrochemical reduction of *as*-triazines 3-one or -thione leads to a 1,4-dihydro derivative which rearranges into a 4,5-dihydro compound which is further reducible to an imidazolone or a tetrahydro *as*-triazine 3-one. In the case of simple *as*-triazine the 1,4-dihydro compound rearranges either to a 1,2- or to a 4,5-dihydro compound. This last derivative can be reduced to an imidazole or a tetrahydro *as*-triazine. The mechanisms are discussed.

La réduction électrochimique des *as*-triazine ones-3 ou thiones-3 conduit à un dérivé dihydro-1,4 qui se transpose en un dérivé dihydro-4,5 lui-même réductible en imidazolone ou en tétrahydro *as*-triazine one-3. Dans le cas des *as*-triazines simples, le dérivé dihydro-1,4 se réarrange en dihydro-1,2 ou 4,5 *as*-triazine. Ce dernier composé peut être réduit en imidazole ou en tétrahydro *as*-triazine. Les mécanismes sont discutés.

Canadian Journal of Chemistry, 50, 1581 (1972)

Introduction

It has already been shown that the $-N=\underset{|}{C}-\underset{|}{C}=N-$ group is electrochemically reduced at a mercury electrode according to eq. 1. The reaction is valid whether this group

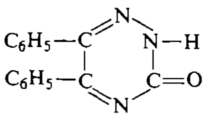
$$[1]\quad -N=\underset{|}{C}-\underset{|}{C}=N- + 2e^- + 2H^+ \rightleftharpoons -HN-\underset{|}{C}=\underset{|}{C}-NH-$$

is included in an aromatic ring (quinoxalines (1)), in a non-aromatic ring (dihydro-5,6 pyrazines (2)), or in an open-chain compound (α-diimines (3)), and even if the substituents on the two carbons are different. It seemed interesting to study the electrochemical reduction of compounds with the same $-N=\underset{|}{C}-\underset{|}{C}=N-$ group, but with different substituents on the two nitrogen atoms; this is the case of *as*-triazines. We have studied both *as*-triazine 3-one (or -thione) and simple *as*-triazines.

Results and Discussion

1. as-Triazines 3-One (or Thione)

We will first describe the polarography and the controlled potential reduction in hydro-organic medium of 5,6-diphenyl *as*-triazine 3-one (**1**), 5,6-diphenyl 2-methyl *as*-triazine 3-one (**2**), and 5,6-diphenyl *as*-triazine 3-thione (**3**). The polarography and the controlled potential electrolysis of the corresponding 4,5-dihydro compounds will then be described.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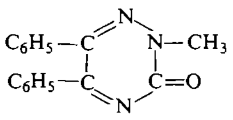
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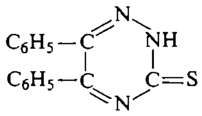
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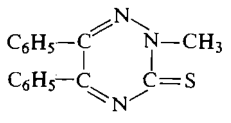
1.1 Reduction of as-Triazines 3-One (or-Thione)

1.1.1. Polarography and behavior in hydro organic medium

The stability of **1**, **2**, and **3** has been examined by u.v. spectroscopy in water–acetonitrile media at different p*H*. Compounds **1** and **2** are stable between p*H* 1 and 12, while **3** is only stable at p*H* > 7. The 5,6-diphenyl 2-methyl *as*-triazine 3-thione decomposes rapidly over the whole p*H* range.



Compound **1** shows over the whole p*H* range studied ($c = 2.10^{-3}\ M$, 20% CH_3CN) a single two-electron wave (3), the half-wave potential of which varies linearly with the p*H* as $E_{1/2} = -0.13 - 0.080$ p*H* (Fig. 1). In the case of **2** a single two-electron wave is observed in acidic medium, the $E_{1/2}$ of which varies linearly with the p*H*. At p*H* higher than 5 the wave height decreases while the height of a second wave, at more negative potential, increases. The $E_{1/2}$ of the second wave does not vary with the p*H*. This can be interpreted by supposing that the first wave corresponds to the reduction of protonated species and the second wave to the reduction of neutral species.

The sum of the heights of the first and the second wave remains constant and above p*H* 6 only the second wave is present.

The polarograms of **3** are strongly perturbed by adsorption phenomena. The half-wave potentials are given in Table 1.

1.1.2. Electrolyses in dilute solutions

We will describe the typical case of **1** at p*H* 1 (50% CH_3CN). The polarograms drawn in the course of electrolyses of dilute solutions under an argon atmosphere show that an anodic wave appears, the half-wave potential of which is close to that of the cathodic wave of **1**, followed by a cathodic wave at more negative potentials. (Fig. 2).

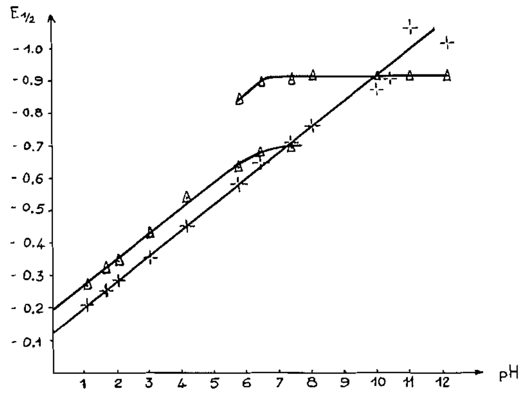


FIG. 1. The p*H* dependence of half-wave potentials $E_{\frac{1}{2}}$ (V/SCE) of **1** (-¦-) and **2** (△).

TABLE 1. Half-wave potentials (V/SCE)

p*H*	1	3	5	7	9	11
1	−0.21	−0.37	−0.53	−0.69	−0.85	−1.01
2	−0.26	−0.44	−0.60	−0.69 −0.90	−0.92	−0.92
3				−0.6	−0.8	−1.0

As the electrolysis proceeds the height of the anodic wave increases until it reaches about a quarter of the height of the cathodic wave of **1** and then decreases.

At the end of the electrolysis (consumption of 2 F/mol) only a cathodic wave, the height of which is close to that of **1**, remains. If the electrolyse is interrupted before the second cathodic wave appears and if the flow of argon is stopped, the anodic wave decreases rapidly and the wave of **1** reappears at its original height.

At p*H* 6.30 (50% methanol) an anodic wave, the height of which remains constant, appears while a white compound precipitates; but no cathodic wave can be seen. At p*H* 11 (50%

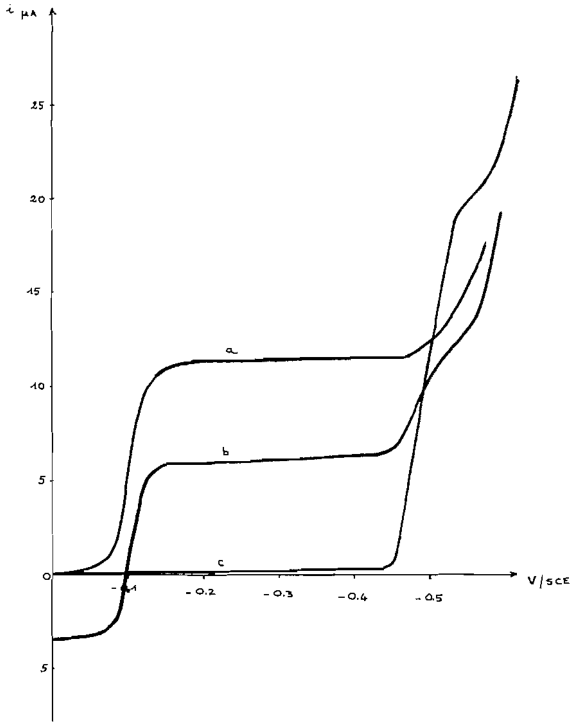
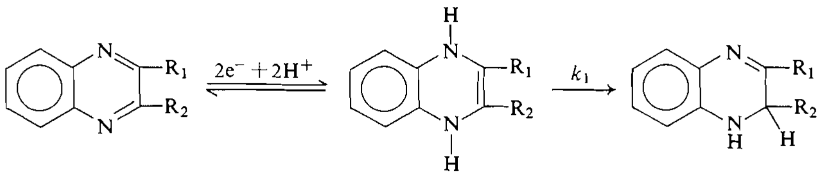


FIG. 2. Polarograms registered during the electrolysis of **1** (p*H* 1, CH_3CN 50%, c 2×10^{-3} *M*); a, beginning; b, $c_1 = 10^{-3}$ *M*; c, end.



SCHEME 1

TABLE 2. Half-wave potentials (V/SCE)

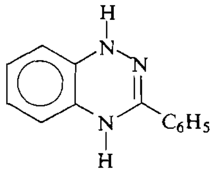
	p*H*	1.0*	6.30†	7.90†	11.0†
1	$E_{\frac{1}{2}c}$	−0.21	−0.50		−0.92
	$E_{\frac{1}{2}a}$	−0.17	−0.47		
2	$E_{\frac{1}{2}c}$	−0.25	−0.57; −0.88		−0.81
	$E_{\frac{1}{2}a}$	−0.21	−0.51		
3	$E_{\frac{1}{2}c}$			−0.71	−1.00
	$E_{\frac{1}{2}a}$			−0.57	

*20% CH_3CN.
†50% CH_3CN.

methanol) for **1** and **2** no anodic or cathodic wave appears; for **3** a cathodic wave is observed at potentials close to that of the background discharge. However, cyclic voltametry carried out on a hanging mercury drop shows that in basic medium the primary reduction compound of **1**, **2**, and **3** presents an anodic peak (*i.e.* for **1** p*H* 10.1, CH_3OH 50%, $v = 0.2\ V\ s^{-1}$, $E_c = -1.00$, $E_a = -0.66$ V, $i_a = 0.7\ i_c$).

Table 2 gives the half-wave potentials of **1**, **2**, and **3** ($E_{1/2c}$) and of the anodic waves of the primary reduction compounds ($E_{1/2a}$).

A similar phenomenon has already been observed in the electrochemical reduction of quinoxalines (1); it has been shown that the anodic wave corresponds to a 1,4-dihydro derivative of type —NH—C=C—NH— which rearranges into a derivative of type —N=C—CH—NH— which is reducible at the dropping mercury electrode at more negative potentials than the starting quinoxaline (Scheme 1). It will be shown that reaction Scheme 2 is proved by preparative electrolyses. This is in good agreement with the fact that the following compound shows an anodic wave and reoxidizes rapidly in the air as has been shown by Kwee and Lund (4).



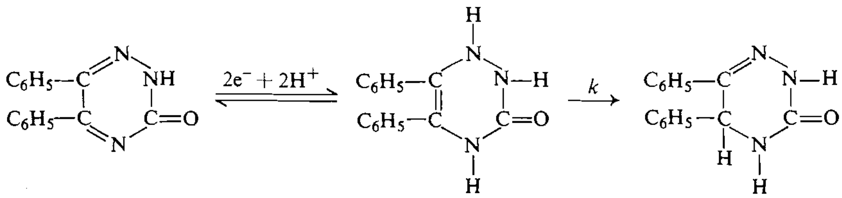
It must be noticed that as in the case of quinoxalines the rearrangement rate (which varies with the solvent, the p*H*, and the buffer composition) is under control of a general acidobasic catalysis.

Thus the electrochemical reduction in dilute solution of compounds **1**, **2**, and **3** yields a very oxidizable compound which shows an anodic wave and rearranges more or less rapidly, according to the p*H*, into a derivative evidencing a cathodic wave.[1]

1.1.3. Preparative electrolyses

Preparative electrolyses are carried out at 25° on a mercury pool, under argon. A saturated calomel electrode was used.

*5,6-Diphenyl as-triazine 3-one (**1**).* In acidic medium (p*H* 1, $E = -0.35$ V), a white compound precipitates in the course of the electrolysis. This compound is identified, by com-



SCHEME 2

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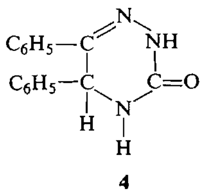
[1] The electrochemical reduction of *as*-triazines into 1,4-dihydro compounds is electrochemically irreversible ($E_{\frac{1}{2}c} \neq E_{\frac{1}{2}a}$).

parison with an authentic sample (5), as the 4,5-dihydro 5,6-diphenyl *as*-triazine 3-one (**4**). In neutral medium (p*H* 6, $E = -0.95$ V) an easily reoxidizable white compound precipitates in the course of the electrolysis. It is the 1,4-dihydro 5,6-diphenyl *as*-triazine 3-one, as shown by its spectroscopic properties. In solution this compound shows the same anodic wave as that observed in the electrolysis of **1** in dilute solution. In basic medium (p*H* 11, $E = -1.10$ V) the same product as in acidic medium is obtained.

5,6-Diphenyl 2-methyl as-triazine 3-one (2). In acidic medium (p*H* 1, $E = -0.35$ V) an easily reoxidizable white compound precipitates in the course of the electrolysis. It is identified by its spectroscopic properties as the 1,4-dihydro 5,6-diphenyl 2-methyl *as*-triazine 3-one. It shows the same anodic wave as that observed in the course of the electrolysis of **2** in dilute solution. In basic medium (p*H* 11, $E = -1.05$ V) a white compound precipitates which is identified by comparison with an authentic sample (5) as the 4,5-dihydro 5,6-diphenyl 2-methyl *as*-triazine 3-one (**5**). This same compound can also be obtained in acidic medium, by leaving the solution under argon several hours after the end of the electrolysis.

5,6-Diphenyl as-triazine 3-thione (3). In neutral medium (p*H* 7.5, $E = -0.90$ V) a yellow compound precipitates in the course of the electrolysis. This easily oxidizable compound which shows in solution the same anodic wave as that observed in the electrolysis of **3** in dilute solutions is the 1,4-dihydro 5,6-diphenyl *as*-triazine 3-thione. In basic medium (p*H* 11, $E = -1.10$ V) the 4,5-dihydro 5,6-diphenyl *as*-triazine 3-thione (**6**) precipitates in the course of the electrolysis.



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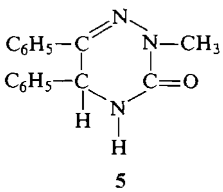

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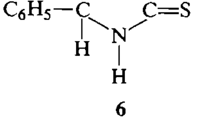

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TABLE 3. Half-wave potentials (V/SCE)

p*H*	1.30	3.05	5.50	10.30
4	−0.97	−1.15	−1.33	
5	−1.00	−1.14	−1.33	
6			−1.60	−1.90

In conclusion, the preparative electrolysis supports Scheme 2. The primary reduction compound is a 1,4-dihydro triazine which presents an anodic wave at the dropping mercury electrode and is easily oxidizable. This 1,4-dihydro triazine rearranges into a 4,5-dihydro triazine with a rate depending on the medium.

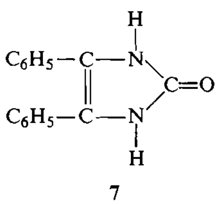
1.2. 4,5-Dihydro as-Triazines 3-One (or Thione)

1.2.1. Polarography of the 4,5-dihydro derivatives

These compounds are reducible in certain p*H* ranges only and then show a single wave the height of which varies with the p*H*. The half-wave potentials are given in Table 3 ($c = 2.10^{-3}$ *M*, 40% CH_3CN).

1.2.2. Electrolysis of 4,5-dihydro derivatives

4,5-Dihydro 5,6-diphenyl as-triazine 3-one (4). In the course of the electrolysis of **4**, in acidic medium (p*H* 0.93, $E = -1.00$ V), a white compound precipitates which is identified by comparison with an authentic sample (5) as the 4,5-diphenyl imidazole 2-one (**7**). By making the filtrate alkaline (p*H* 11) a second compound precipitates: the *trans*-1,4,5,6-tetrahydro 5,6-diphenyl *as*-triazine 3-one (**8*b***) (5). In neutral medium, only the *cis*-1,4,5,6-tetrahydro 5,6-diphenyl *as*-triazine 3-one (**8*a***) is obtained.



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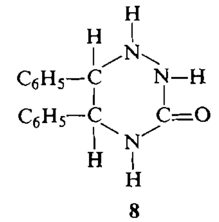

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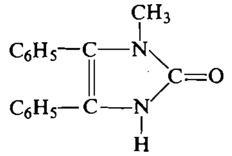
a cis
b trans

4,5-Dihydro 5,6-diphenyl 2-methyl as-triazine 3-one (5). The reduction in acidic medium gives the 4,5-diphenyl 1-methyl imidazole 2-one **9**.

4,5-Dihydro 5,6-diphenyl as-triazine 3-thione



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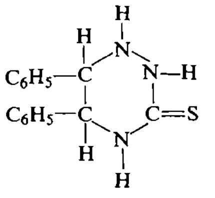
(6). In the course of the reduction of **6** in basic medium (p*H* 10.67, $E = -2.00$ V) the *cis*-1,4,5,6-tetrahydro 5,6-diphenyl *as*-triazine 3-thione **10** precipitates. Thus, the reduction of 4,5-dihydro compounds leads to two different kinds of compounds: the 1,4,5,6-tetrahydro triazines and the 2-imidazolones. It has been shown that under the conditions of the electrolysis, the imidazolone does not come from the corresponding tetrahydrotriazine. No imidazolone can be detected in a solution of the tetrahydrotriazine which has been allowed to stand for a time equivalent to the length of an electrolysis. The reaction scheme can be rationalized as shown in Scheme 3.



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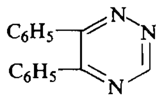
Scheme 3 is in good agreement with the reduction of phenylhydrazones in acidic medium (6) and with the scheme proposed by Kwee and Lund (4) for benzotriazines. The cleavage of the N_1—N_2 bond needs a preliminary protonation of the N_2 nitrogen, a quaternary ammonium then being a good leaving group. In the case of **5** only the imidazolone is obtained in acidic medium, this can be explained by the higher basicity of the N_2 nitrogen which carries a methyl group.

2. *as-Triazines*

We will describe the case of 5,6-diphenyl *as*-triazine (**11**) and 3,5,6-triphenyl *as*-triazine (**12**).

2.1. *Behavior in Hydroorganic Medium and Polarography*

Compounds **11** and **12** are stable in hydroorganic medium over the whole p*H* range.



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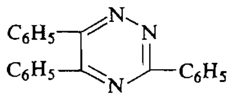

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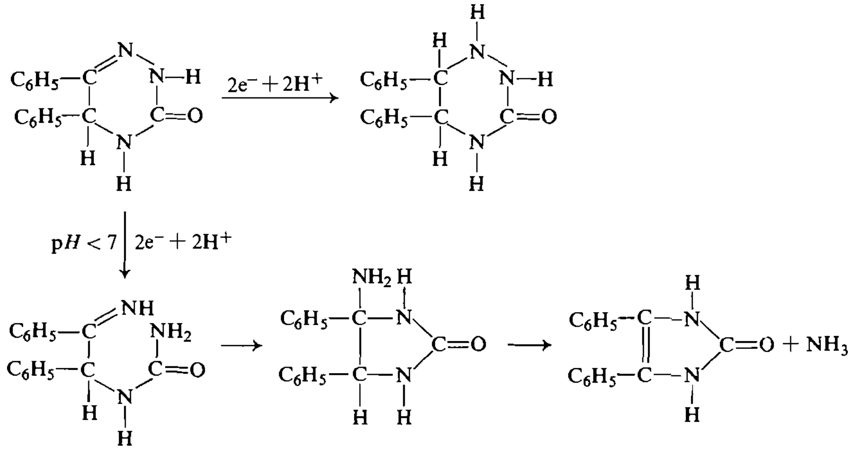
Compound **11** ($c = 10^{-3}$ *M*, 40% CH_3OH) shows two two-electron waves up to p*H* 7; at higher p*H* only the first wave remains; its half-wave potential (V/SCE) varies linearly with the p*H* as $E_{1/2} = -0.14 - 0.066$ p*H*. Compound **12** ($c = 10^{-4}$ *M*, 40% MeOH) behaves similarly; the second wave exists only up to p*H* 8. The half-wave potential of the first wave varies linearly with the p*H* as: $E_{1/2} = -0.23 - 0.062$ p*H*. The half-wave potentials are presented in Table 4.

2.2. *Electrolysis in Dilute Solutions*

An electrolysis of **11** under argon at a potential corresponding to the first plateau ($c = 2.10^{-3}$ *M*, p*H* 3.65, 50% CH_3OH, $E = -0.60$ V) gives



Scheme 3

TABLE 4. Half-wave potentials (V/SCE)

p*H*	1	3	5	7	9	11	
11	−0.21	−0.34	−0.47	−0.60	−0.74	−0.87	1st wave
	−0.88	−0.97	−1.15	−1.36			2nd wave
12	−0.29	−0.41	−0.54	−0.66	−0.79	−0.91	1st wave
	−0.77	−0.88	−1.05	−1.42			2nd wave

a compound which shows an anodic wave at a potential slightly more positive than the cathodic wave of the starting compound. The height of the anodic wave never exceeds about a tenth of the height of the cathodic wave of **11**. At the end of the electrolysis, after consumption of about 2 F/mol, only a cathodic wave, the half-wave potential of which is slightly different from that of the second wave of **11**, remains. The same phenomenon is observed at p*H* 6.20 ($E = -0.80$ V), while at p*H* 12.83 ($E = -1.20$ V) no anodic wave appears. Cyclic voltametry carried out on a hanging mercury drop shows that in alkaline medium the primary reduction compound also shows an anodic peak (p*H* 12.96, CH_3OH 50%, $v = 0.2$ V s^{-1}, $E_c = -1.00$, $E_a = -0.72$ V, $i_a = 0.9\, i_c$). The same behavior is observed for **12**. Table 5 gives the half-wave potentials of **11** and **12** ($E_{1/2c}$) and of the anodic waves of the primary reduction compounds ($E_{1/2a}$).

The similarity of the results obtained in the electrolysis in dilute solutions of **11** and **12** with those of compounds **1**, **2**, and **3** indicates that a 1,4-dihydro derivative is obtained as the primary reduction compound. This 1,4-dihydro compound then undergoes a rearrangement.

2.3. *Preparative Electrolysis*

3,5,6-Triphenyl as-Triazine (12)

Reduction on the first plateau. In the course of an electrolysis at p*H* 3.60 ($E = -0.70$ V) a white compound precipitates which is identified as the 1,2-dihydro 3,5,6-triphenyl *as*-triazine **13**. By extracting the filtrate with ether a second compound, the 4,5-dihydro 3,5,6-triphenyl *as*-triazine **14**, is obtained. A reduction at p*H* 13.5 ($E = -1.30$ V) leads only to the 4,5-dihydro 3,5,6-triphenyl *as*-triazine **14**. The spectroscopic properties of **14** do not allow a definite choice between a 4,5-dihydro structure and a 5,6-dihydro structure. However the analogy of polarographic behavior between **14** and **4**, **5**, and **6** points to a 4,5-dihydro compound. Besides, the 5,6-dihydro derivative would probably be irreducible at the dropping mercury electrode.

Reduction on the second plateau. By adding water to the electrolysis solution (p*H* 3.60, $E = -1.30$ V, 4 F/mol) the 2,4,5-triphenyl imidazole **15** is obtained and by neutralizing the filtrate with sodium bicarbonate the *cis*-1,4,5,6-tetrahydro 3,5,6-triphenyl *as*-triazine **16** precipitates. The reduction at p*H* 6.20 ($E = -1.40$ V) only leads to the 2,4,5-triphenyl imidazole **15**. The 5,6-diphenyl *as*-triazine **11** gives similar results.

2.4. *Reduction of 4,5-Dihydro Compounds*

The 1,2-dihydro derivatives are not reducible at the dropping mercury electrode, but the 4,5-dihydro *as*-triazine shows a two-electron wave ($E_{1/2}$ given in Table 6).

A preparative electrolysis of **14** at p*H* 3.60 ($E = -1.20$ V) yields the *cis*-1,4,5,6-tetrahydro 3,5,6-triphenyl *as*-triazine **16**.

2.5. *Reduction Mechanism*

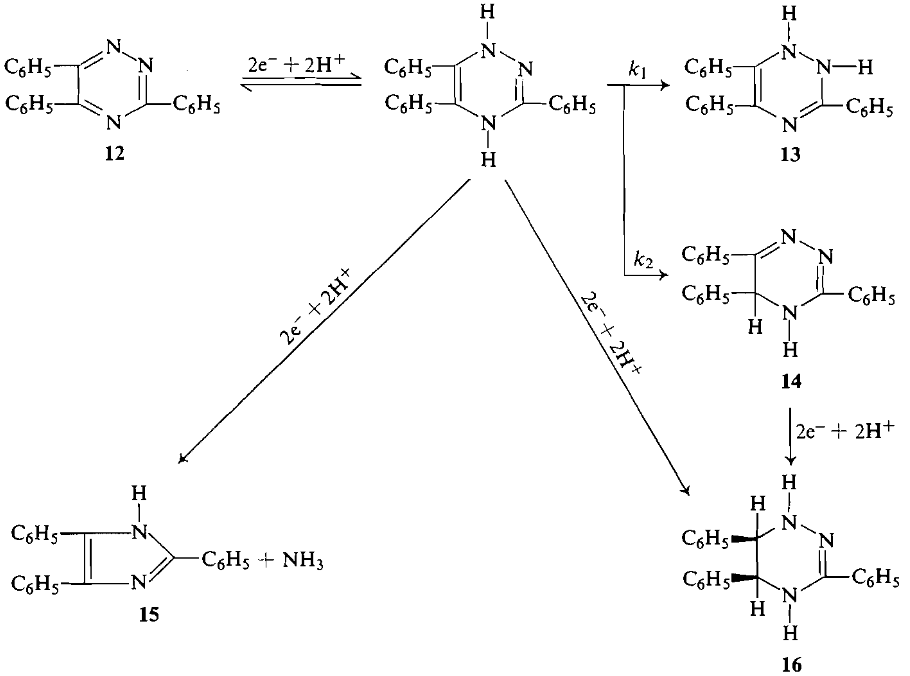
The different steps of the electrochemical reduction of **12** are given in Scheme 4. The primary reduction compound for **11** and **12** is the 1,4-dihydro derivative characterized by its

TABLE 5. Half-wave potentials (V/SCE) (50% CH_3OH)

	p*H*	3.6	6.0	13.0
11	$E_{\frac{1}{2}c}$	−0.38	−0.53	−1.00
	$E_{\frac{1}{2}a}$	−0.34	−0.51	—
12	$E_{\frac{1}{2}c}$	−0.45	−0.60	−1.04
	$E_{\frac{1}{2}a}$	−0.40	−0.57	—

TABLE 6. Half-wave potentials (V/SCE) (50% CH_3OH)

p*H*	3.60	6.00	13.00
4,5-Dihydro 5,6-Diphenyl *as*-Triazine	−0.95	−1.32	−1.40
4,5-Dihydro 3,5,6-Triphenyl Triazine **14**	−0.97	−1.06	−1.45

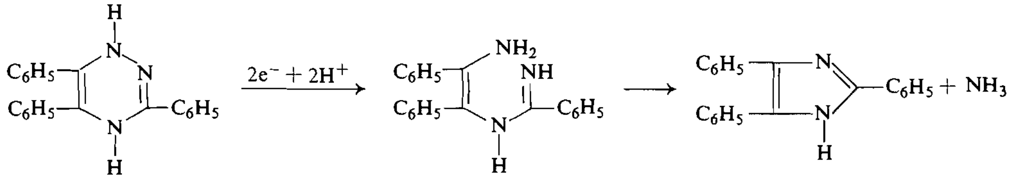


SCHEME 4

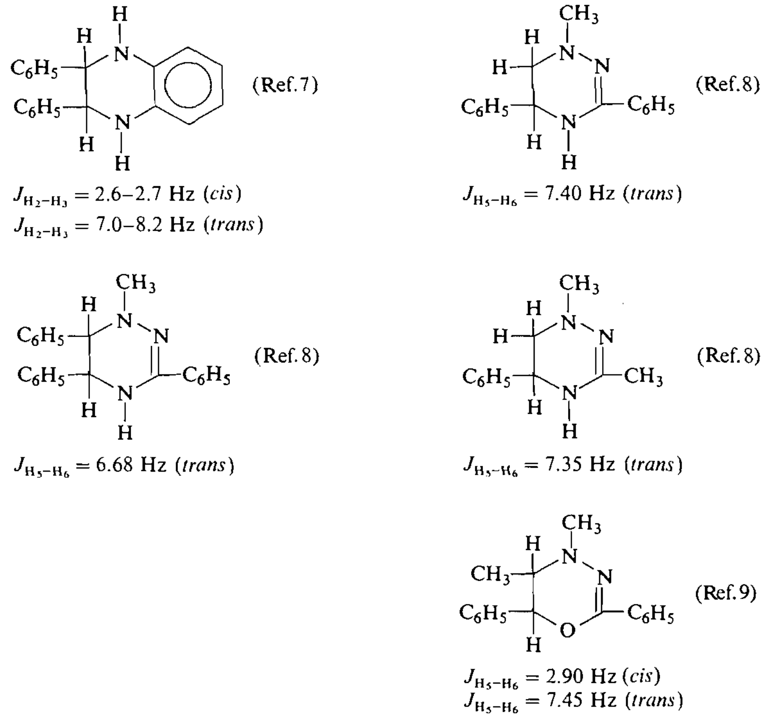
anodic wave, but it rearranges too quickly to be isolated. The 1,2- and 4,5-dihydro derivatives are obtained through two competitive reactions; it has been shown that under the conditions of the electrolysis these two compounds do not transform into each other; in the solution and during the time of the electrolysis the 1,2-dihydro compound does not give the 4,5-dihydro compound; in the same way the 4,5-dihydro compound does not give the 1,2-dihydro compound. The relative amount of these two compounds is strongly dependent on the p*H*. The 1,4-dihydro *as*-triazine shows two polarographic waves: an anodic wave (corresponding to the reoxidation into the starting compound) and a cathodic wave (the second wave observed on the polarograms of *as*-triazine). The reduction of the 1,4-dihydro *as*-triazine leads either to an imidazole or to a 1,4,5,6-tetrahydro triazine; here also the relative amount of the two compounds depends strongly on the p*H*. Scheme 5 could explain the formation of the imidazole. At last the 4,5-dihydro *as*-triazine is itself reducible, it corresponds to the cathodic wave observed at the end of the electrolysis of **11** and **12** in dilute solutions, and leads to a 1,4,5,6-tetrahydro *as*-triazine.

3. Remarks on the Stereochemistry of 1,4,5,6-tetrahydro as-Triazines

The n.m.r. spectra of **8**, **10**, and **16**, after addition of D_2O, show that either one or the other of the two possible isomers is obtained. The molecular models show that the ring takes a half chair conformation as cyclohexene and the two phenyl groups can be either *cis* or *trans* to each other. The coupling constants are: $J_{H_5-H_6} = 4.0$ for **10**, 8.2 for **8***b*, 4.0 for **8***a*, and 4.0 Hz for



SCHEME 5



$J_{H_2-H_3}$ = 2.6–2.7 Hz (*cis*)
$J_{H_2-H_3}$ = 7.0–8.2 Hz (*trans*)

$J_{H_5-H_6}$ = 7.40 Hz (*trans*)

$J_{H_5-H_6}$ = 6.68 Hz (*trans*)

$J_{H_5-H_6}$ = 7.35 Hz (*trans*)

$J_{H_5-H_6}$ = 2.90 Hz (*cis*)
$J_{H_5-H_6}$ = 7.45 Hz (*trans*)

CHART 1

16. Chart 1 shows the values found in the literature. Therefore **8***b* is a *trans* derivative. The 5 and 6 protons are *trans* axial–axial with a dihedral angle of about 180°, and the two phenyl groups are in equatorial position. On the contrary **8***a*, **10**, and **16** are certainly *cis*-tetrahydro triazines. The coupling constant of 4.0 Hz obtained for **8***a*, **10**, and **16** is somewhat greater than the coupling constants given above. This may be due to a deformation of the ring which decreases the dihedral angle $C_5H—C_6H$ and thus increases the J_{H_5}–J_{H_6} coupling constant.

Thus, these results are different from that obtained in the electrochemical reduction of quinoxalines. These last compounds always yield *cis*-tetrahydro quinoxalines (1). These differences can be explained in the following way: the dihydroquinoxalines, **4** (in neutral medium), **6**, and **14** would be adsorbed when the last proton is fixed. On the contrary, the stereochemically determining step in the reduction of **4** in acidic medium, that is the fixation of the last proton, would take place in the bulk of the solution. The most stable isomer where the two phenyl groups are equatorial would then be obtained.

Conclusion

(*1*) Although the two substituents on the nitrogen atoms of the studied compounds are very different, the observed primary reduction mechanism is similar to that of the compounds with the $—N{=}\underset{|}{C}—\underset{|}{C}{=}N—$ group previously studied (eq. 1).

(*2*) The electrochemical reduction of *as*-triazines allows selective preparation of some compounds which cannot be obtained by chemical reduction (5,10,11,16): the 1,4-dihydro *as*-triazines 3-one (or -thione), the 4,5-dihydro *as*-triazines, and the 1,4,5,6-tetrahydro *as*-triazines or *as*-triazinones. These last compounds are obtained stereoselectively.

Experimental

The apparatus and techniques used have been described previously (1). The cathodic compartment of the electrolytic cell is a glass cylinder of 85 mm diameter and the anodic compartment which fits in the cathodic compartment is a glass cylinder of 50 mm diameter closed at its lower end by a fine fritted glass. The organic cosolvents used in the electrolyses are either methanol or acetonitrile (for solubility reasons). It has been checked that the nature of the cosolvent does not change the results of the electrolyses. All the compounds gave correct elemental analysis.

1. Controlled Potential Electrolysis of as-Triazines 3-One (or -Thione)

1.1 Reduction of 5,6-Diphenyl as-Triazine 3-One (1)

Compound **1** is prepared according to Biltz and Stellbaum (12) by condensation of semicarbazide hydrochloride with benzile in boiling acetic acid. Yellow crystals, m.p. 224°, are obtained.

Reduction of 1 in acidic medium

A solution is prepared from 100 cm^3 CH_3CN, 40 cm^3 1 *N* H_2SO_4, 60 cm^3 of water. Three grams of **1** are dissolved in 150 cm^3 of this solution (p*H* 0.97). In the course of the electrolysis ($E = -0.35$ V, 2.0 F/mol) a white compound precipitates, m.p. 176°, 2 g (yield 67%) identified as **4** (4,5-dihydro 5,6-diphenyl *as*-triazine 3-one) by comparison (i.r., n.m.r.) with an authentic sample.

Reduction at pH 6.3

A solution (200 cm^3) is prepared from 100 cm^3 CH_3OH, 40 cm^3 1 *N* NaOH, 3.6 g of succinic acid, and water. Compound **1** (0.5 g) is dissolved in 150 cm^3 of this solution, the rest of it being used as anolyte. In the course of the electrolysis ($E = -0.95$ V, 2.0 F/mol) a white compound precipitates, recovered under nitrogen in a glove box. The product is identified as the 1,4-dihydro 5,6-diphenyl *as*-triazine 3-one (370 mg, yield 75%, m.p. 150°). The n.m.r. spectrum (DMSO-d_6): NH 1 proton(s) δ 6.30, 1 proton(s) 8.05, and 1 proton(s) 8.26 p.p.m. which can be displaced by D_2O; C_6H_5 10 protons(m) 7.00–7.60 p.p.m. The i.r. spectrum (KBr pellet) ν_{NH} 3280 (m), 3200 cm^{-1} (m), $\nu_{C=O}$ 1680 cm^{-1} (s). The product reoxidizes rapidly in the air.

1.2 Reduction of 5,6-Diphenyl 2-Methyl as-Triazine 3-One

Compound **2** is prepared according to Biltz and Stellbaum (12).

Reduction in acidic medium

Compound **2** (0.5 g) is dissolved in 150 cm^3 of a solution prepared from 100 cm^3 CH_3CN, 40 cm^3 1 *N* H_2SO_4, and 60 cm^3 H_2O. In the course of the electrolysis (p*H* 0.97; $E = -0.35$ V, 2.0 F/mol) a white compound precipitates, recovered under nitrogen in a glove box (350 mg, yield 70%, m.p. 153° (alcohol)). This compound is easily oxidized in the air. The n.m.r. spectrum (DMSO-d_6) N—CH_3 3 protons(s) δ 2.91, N_1—H 1 proton(s) 6.60, N_4H 1 proton(s) 8.46 p.p.m., both NH protons are displaced by addition of D_2O; C_6H_5 10 protons(m) 7.0–7.5 p.p.m. The i.r. spectrum (KBr pellet) ν_{NH} 3.200 (m), $\nu_{C=O}$ 1670 cm^{-1} (s). This allows assignment of the 1,4-dihydro 2-methyl *as*-triazine 3-one formula to this compound (in particular, there is no C—H protons in the n.m.r. spectrum).

Reduction in basic medium pH 11

A solution is prepared from 100 cm^3 CH_3OH, 1.7 g CO_3HNa, 4 cm^3 1 *N* NaOH, and 100 cm^3 of water. Compound **2** (0.5 g) is dissolved in 150 cm^3 of this solution. A white precipitate appears in the course of the electrolysis ($E = -1.05$ V, 2.1 F/mol); 350 mg, yield 70%, m.p. 195° (alcohol); n.m.r. spectrum (DMSO-d_6): N—CH_3 3 protons(s) δ 3.31, C_5—H 1 proton(d) 5.78, N_4H 1 proton(d) 8.13 p.p.m. $J_{C_5H-N_4H} = 4.0$ Hz; the addition of D_2O transforms the doublet of C_5H in a singlet and N_4H is displaced. The i.r. spectrum (KBr pellet) ν_{NH} 3200, $\nu_{C=O}$ 1680 cm^{-1}. This compound is identical (t.l.c., i.r., m.p., n.m.r.) to the compound obtained by hydrogenation of **2** in the presence of Raney nickel (5) and to that obtained by electrolysis of **2** in acidic medium when the solution is kept under argon several hours after the end of the electrolysis. Thus this compound is the 5,6-diphenyl 2-methyl 4,5-dihydro *as*-triazine 3-one **5**.

1.3. Reduction of 5,6-Diphenyl as-Triazine 3-Thione (3)

Compound **3** is prepared according to Klosa (13)

Reduction in neutral medium

A solution is prepared from 120 cm^3 CH_3OH, 50 cm^3 1 *N* NaOH, 30 cm^3 H_2O, and 3.9 g citric acid. Compound **3** (0.5 g) is dissolved in 150 cm^3 of this solution. In the course of the electrolysis (p*H* 7.42, $E = -0.90$ V, 1.8 F/mol) a yellow compound precipitates which is recovered in a glove box under nitrogen (350 mg, yield 70%), m.p. 210° (alcohol). The n.m.r. spectrum (DMSO-d_6): N_1H 1 proton(s) δ 6.5, N_4H 1 proton(s) 9.5, both NH are displaced by addition of D_2O, C_6H_5 10 protons(m) 7.0–7.6 p.p.m. The i.r. spectrum (KBr pellet) ν_{NH} 3150, $\nu_{N-C=S}$ 1530 (s), $\nu_{C=S}$ 1220 cm^{-1}. In solution this compound is easily oxidized by air to **3**. Thus, this compound is the 1,4-dihydro 5,6-diphenyl *as*-triazine 3-thione **6**.

Reduction in basic medium

A solution is prepared from 100 cm^3 CH_3OH, 100 cm^3 of water, 1.7 g CO_3HNa and 4 cm^3 1 *N* NaOH. Compound **3** (0.5 g) is dissolved in 150 cm^3 of this solution (p*H* 10.64). In the course of the electrolysis ($E = -1.00$ V, 1.9 F/mol) a white compound precipitates (350 mg, yield 70%) F = 222° (alcohol). The n.m.r. spectrum (DMSO-d_6): C_5H 1 proton (d) δ 5.71, N_4H 1 proton (d) 9.70, $J_{C5H-N4H} = 4.0$ Hz, N_2H 1 proton(s) 11.50 C_6H_5 10 protons(m) 7.0–8.0 p.p.m. The addition of D_2O displaces the peaks at 11.50 and 9.70 p.p.m. and transforms into a singlet the doublet at 5.71 p.p.m. The i.r. spectrum (KBr pellet) ν_{NH} 3150 and 3350 (m), $\nu_{N-C=S}$ 1550 (s) and $\nu_{C=S}$ 1180 cm^{-1} (s). The compound thus obtained is identical (n.m.r., i.r., t.l.c., and m.p.) to the compound obtained by hydrogenation of **3** by Raney nickel (11), this ascertains the structure of this compound: 4,5-dihydro 5,6-diphenyl *as*-triazine 3-thione (**6**).

2. Controlled Potential Electrolysis of 4,5-Dihydro as-Triazines

2.1 4,5-Dihydro 5,6-Diphenyl as-Triazine 3-One (4)

Reduction in acidic medium

A solution is prepared from 100 cm^3 CH_3CN, 60 cm^3 H_2O, and 40 cm^3 *N* H_2SO_4; 1.5 g of **4** are dissolved in 150 cm^3 of this solution. In the course of the electrolysis ($E = -1.00$ V, p*H* 0.93) white crystals precipitate (700 mg, yield 50%), m.p. 318° (alcohol) n.m.r. spectrum (DMSO-d_6): 2 NH 2 protons(s) δ 10.51 which are displaced by addition of D_2O, C_6H_5 10 protons (s) 7.33 p.p.m. The i.r. spectrum (KBr pellet) ν_{NH} 3200 (s), $\nu_{C=O}$ 1690 cm^{-1} (s). This compound is identical (n.m.r., t.l.c.) to the 4,5-diphenyl imidazole 2-one (5). When the filtrate is concentrated and made slowly alkaline to p*H* 11, a second white compound precipitates: the *trans*-1,4,5,6-tetrahydro 5,6-diphenyl *as*-triazine 3-one **8*b*** (700 mg, yield 45%), m.p. 220° (alcohol). The n.m.r. spectrum (DMSO-d_6 + D_2O) C_5H or C_6H 1 proton (d) δ 3.83, C_6H or C_5H 1 proton (d) 4.70 ($J_{H_5-H_6} = 8.2$ Hz),

C_6H_5 10 protons (m), 7.1–7.4 p.p.m. The i.r. spectrum (KBr pellet) ν_{NH} 3400 (m) and 3200 (s), $\nu_{C=O}$ 1655 cm^{-1} (s).

Reduction in neutral medium

A solution is prepared from 125 cm^3 CH_3CN, 50 cm^3 1 *N* NaOH, 3.9 g citric acid, and 75 cm^3 H_2O; 0.5 g of **4** is dissolved in 200 cm^3 of this solution. The compound which precipitates during the electrolysis (p*H* 5.98, $E = -1.50$ V) is the *cis*-1,4,5,6-tetrahydro 5,6-diphenyl *as*-triazine 3-one **8*a*** (150 mg, yield 30%), m.p. 240° (alcohol). The n.m.r. spectrum (DMSO-d_6 + D_2O): C_5H or C_6H 1 proton (d) δ 4.50, C_6H or C_5H 1 proton (d) 4.93 ($J_{H_5-H_6}$ = 4.0 Hz), C_6H_5 10 protons (m) 6.8–7.3 p.p.m. The i.r. spectrum (KBr pellet): ν_{NH} 3200 (m) $\nu_{C=O}$ 1670 cm^{-1} (s).

2.2 4,5-Dihydro 5,6-Diphenyl 2-Methyl as-Triazine 3-One

Reduction in acidic medium

A solution is prepared from 100 cm^3 CH_3CN, 40 cm^3 1 *N* H_2SO_4, 60 cm^3 H_2O; 300 mg of **5** are dissolved in 150 cm^3 of this solution. In the course of the electrolysis (p*H* 0.93 $E = -1.00$ V, 2 F/mol) the 4,5-diphenyl 3-methyl imidazole 2-one precipitates (150 mg, yield 50%), m.p. 228° (alcohol). The n.m.r. spectrum (DMSO-d_6): N—CH_3, 3 protons (s) δ 2.95, N—H 1 proton(s) 10.71 displaced by addition of D_2O, C_6H_5 10 protons (m) 7.18 and 7.45 p.p.m. The i.r. spectrum (KBr pellet) ν_{NH} 3100 (s), $\nu_{C=O}$ 1730 cm^{-1} (s).

2.3. 4,5-Dihydro 5,6-Diphenyl as-Triazine 3-Thione (6)

Reduction in basic medium

A solution is prepared from 100 cm^3 CH_3OH, 100 cm^3 H_2O, 4 cm^3 1 *N* NaOH, and 1.7 g CO_3HNA; 0.5 g of **6** is dissolved in 150 cm^3 of this solution (p*H* 10.67). In the course of the electrolysis ($E = -2.00$ V) the *cis*-1,4,5,6-tetrahydro 5,6-diphenyl *as*-triazine 3-thione **10** precipitates (300 mg, yield 60%), m.p. 215° (alcohol). The n.m.r. spectrum (DMSO-d_6): C_5H and C_6H 2 protons (m) δ 4.20 and 4.90, N_1H 1 proton (d) 5.36 (J_{NH-CH} = 11 Hz), N_4H 1 proton (d) 8.73 ($J_{N_4H-C_5H}$ = 4.0 Hz), N_2H 1 proton(s) 9.56 p.p.m. By addition of D_2O the spectrum becomes more simple, the N—H are displaced, the C_5H and C_6H appear as doublets δ = 4.44 and 4.83 p.p.m., $J_{C_5H-C_6H}$ = 4.0 Hz. The i.r. spectrum (KBr pellet), ν_{NH} 3150 (s), $\nu_{N-C=S}$ 1560 (s), $\nu_{C=S}$ 1220 cm^{-1} (s).

3. Controlled Potential Electrolysis of as-Triazines

3.1. 5,6-Diphenyl as-Triazine (11)

Compound **11** is prepared according to ref. 14.

3.2. 3,5,6-Triphenyl as-Triazine (12)

Compound **12** is prepared according to Metze (15).

Electrolysis on the First Plateau

A solution is prepared from 5.3 g of citric acid, 15 cm^3 1 *N* NaOH, 110 cm^3 H_2O, 125 cm^3 CH_3CN, and 2 g $NaClO_4$. Compound **12** (700 mg) is dissolved in 200 cm^3 of this solution (p*H* 3.60). The temperature of the solution is maintained at about 10°. In the course of the electrolysis ($E = -0.70$ V) a white compound precipitates, m.p. 264.5° (washed with alcohol and ether) 163 mg (yield 23%). This compound is the 1,2-dihydro 3,5,6-triphenyl *as*-triazine **13**. The n.m.r. spectrum (DMSO-d_6): C_6H_5 (m) δ 7.40 p.p.m., no C—H proton appears on this spectrum. The i.r. spectrum (KBr pellet): ν_{NH} 3180 (m) and 3380 cm^{-1}. Water (200 cm^3) is added to the filtrate which is extracted with ether. A white compound is thus obtained, m.p. 249.5° (alcohol) 440 mg (yield 63%). This compound is the 4,5-dihydro 3,5,6-triphenyl *as*-triazine **14**. The n.m.r. spectrum (DMSO-d_6): C_5H 1 proton(s) δ 5.93, C_6H_5 15 protons (m) 7.2–8.2 p.p.m. The i.r. spectrum (KBr pellet) ν_{NH} 3260 cm^{-1} (m). Compound **14** is also obtained alone (98 mg) by reduction of **12** (124 mg) in basic medium (0.1 *N* NaOH, 50% CH_3CN, p*H* 13.47, $E = -1.30$ V) (yield 80%).

Electrolysis on the Second Plateau

Compound **12** (700 mg) is dissolved in the same solution as above (p*H* 3.60). At the end of the electrolysis ($E = -1.30$ V, 4.1 F/mol) 200 cm^3 of water are added and 300 mg (yield 80%) of a white compound m.p. 282° are filtered. This compound is identified (n.m.r., i.r., t.l.c.) by comparison with an authentic sample (16) as the 2,4,5-triphenyl imidazole **15**. The filtrate is neutralized with sodium bicarbonate and a second product precipitates (145 mg, yield 20%): the *cis*-1,4,5,6-tetrahydro 3,5,6-triphenyl *as*-triazine **16**. The n.m.r. spectrum (DMSO-d_6 + D_2O): C_5H or C_6H 1 proton (d) δ 4.31, C_6H or C_5H 1 proton (d) 4.81 ($J_{H_5-H_6}$ = 4.0 Hz), C_6H_5 15 protons (m) 6.7–8.0 p.p.m.

A reduction of **12** at p*H* 6.20 (700 mg of **12** in 200 cm^3 of a solution of 5.3 g citric acid, 6 ml 1 *N* NaOH, 125 cm^3 H_2O, and 125 cm^3 CH_3CN; $E = -1.40$ V, 4.2 F/mol) gives only the 2,4,5-triphenylimidazole **15** (yield 55%).

3.2. Electrolysis of the 4,5-Dihydro 3,5,6-Triphenyl as-Triazine (14)

The electrolysis of 300 mg of **14** at p*H* 3.60 (same solution as above) ($E = -1.20$ V, 2.2 F/mol) gives, after neutralization of the solution with sodium bicarbonate, 135 mg (yield 45%) of *cis*-1,4,5,6-tetrahydro 3,5,6-triphenyl *as*-triazine **16**.

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