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RECENT DEVELOPMENTS IN THE CHEMISTRY OF o-BENZOQUINONE-DIIMINES

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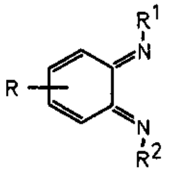
This article presents a survey of recent developments in the chemistry of o-benzoquinone-diimines, especially the achievements thus far realized in the reactions of these compounds.

CONTENTS

1. INTRODUCTION

The chemistry of o-benzoquinone-diimines (1) dates back to the year 1905 when R. Willstätter and A.Pfannenstiel, in their famous paper " On the Oxidation of o-Phenylenediamine ", provided conclusive evidence for the existence of the parent



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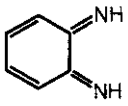

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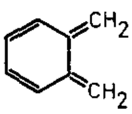
compound, namely o-benzoquinone-diimine (2)[1,2]. These authors - as others (Sect. 3.1) - did not succeed in isolating this rather unstable substance; only dilute ethereal solutions are of moderate stability below 0°C. N,N-Diacylated o-benzoquinone-diimines (1 ; R^1,R^2 = aroyl, arylsulfonyl) are, however, far more stable than 2. In an impressive series of papers, R.Adams and coworkers have elucidated the synthesis and reactions of these compounds. This work has been reviewed[3] and will be dealt with here only cursorily. In recent years o-benzoquinone-diimines have attracted attention as homo- and heterodienes in Diels-Alder reactions[4].Our own work in this field has shown that various types of cycloaddition reactions (normal Diels-Alder reactions,Diels-Alder reactions with inverse electron demand, $[\pi4+\pi4]$-, $[\pi6+\pi4]$-, $[\sigma2+\sigma2+\pi4]$-cycloadditions) are possible; a number of interesting nitrogen heterocycles are accessible which would be obtained only with difficulty on other routes. The main emphasis of this review will lie upon the synthetic applications of o-benzoquinone-diimines.

2. THEORETICAL INVESTIGATIONS

In contrast to the o-benzoquinones[5,6], theoretical investigations of o-benzoquinone-diimines and derivatives are scarce[7]. Our own calculations have shown that even the simple HMO model predicts stabilization of the o-quinonoid system on going from o-quinodimethane (3) over 2 and 4[8] to 5.



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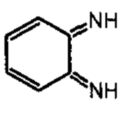

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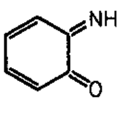

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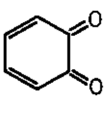

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E_π (in β)[9]: 9.954 10.042 10.228 10.313

Using the ω-technique together with a variable β-procedure[10-13],we have obtained charge distributions (q_i) and bond orders (p_{ij}) as presented in Table 1;together with bond order-bond length relationships[12,13] these latter values lead to distances as shown in Fig.1. As can be seen for the case of o-benzoquinone, these values resemble quite closely those measured except for the extraordinarily long C_5-C_6-distance.

TABLE 1 : Results of quantum chemical calculations on o-benzoquinone-diimine and o-benzoquinone.

method / q_i, p_{ij}	H M O	ω-technique[a]	ω-technique with variable β's[b,c]	CNDO/2[d]	CNDO/2[d,e]
q_1	1.0002	0.9805	0.9989	1.0121	1.0157
q_2	0.9480	0.9727	0.9876	0.9751	0.9581
q_5	0.8738	0.9365	0.8848	0.9349	0.8816
q_7	1.1781	1.1003	1.1287	1.0780	1.1454
p_{12}	0.7773	-	0.9515	0.8682	0.8954
p_{16}	0.4753	-	0.2212	0.3613	0.3138
p_{23}	0.5239	-	0.2273	0.3956	0.3440
p_{56}	0.3621	-	0.1984	0.3161	0.2377
p_{57}	0.7704	-	0.9455	0.8688	0.9029

a: Because of the very slow convergence approximate values[10] are given.

b: $\beta_{C_i-C_j} = \beta_o \cdot \exp(0.96425 \cdot p_{ij} - 0.644525)$

$\beta_{C_i-N_j} = \beta_o \exp(1.050525 \cdot p_{ij} - 0.400925)$; (see ref. 12, 13).

c: In contrast to the ω-technique, this procedure converges rapidly.

d: W.Friedrichsen and I.Schwarz, unpublished data.

e: Data for o-benzoquinone, for comparison.

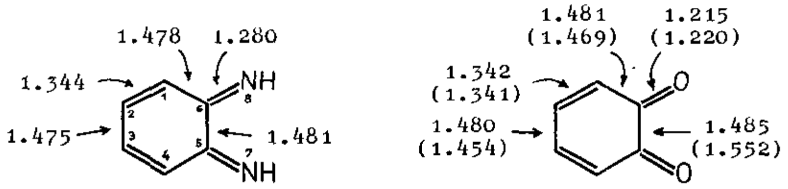
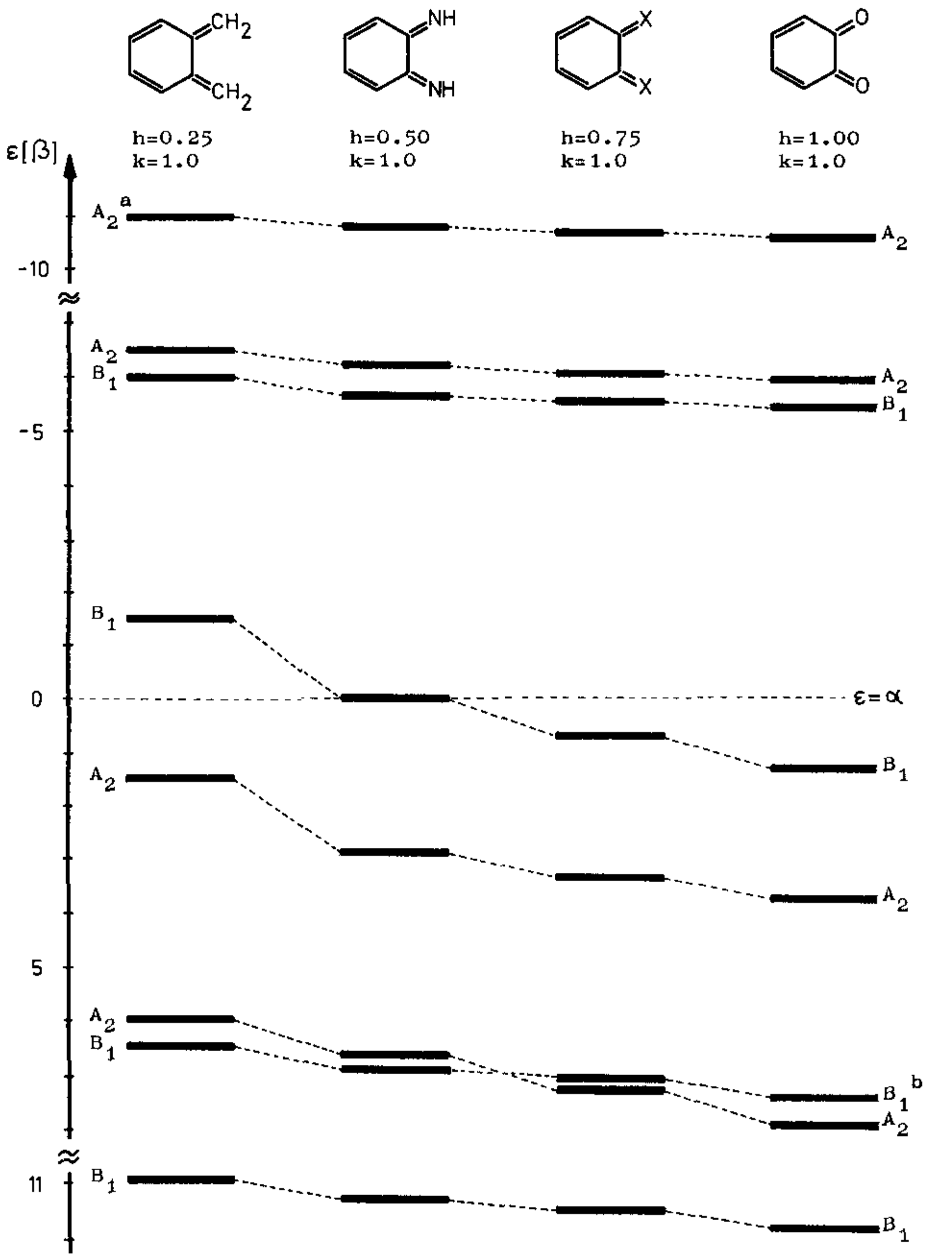


FIG. 1 : Calculated bond lengths (in Å) for o-benzoquinone-diimine and o-benzoquinone (values in parentheses : measured values corrected for thermal motion[14]).

Furthermore HMO calculations show that the lowest unoccupied molecular orbital (LUMO) for 2 - as for 5 - lies at a particularly low level, which indicates a pronounced reactivity as an electrophile (Fig.2). These results could be substantiated by a CNDO/2 treatment (Fig.3). According to Fukui[15] the electron distributions in HOMO and LUMO (squared coefficients of the corresponding molecular orbitals) indicate the point of attack of, respectively, electrophilic and nucleophilic agents.



a : Symmetry in C_{2v}.

b : This crossing (for h=0.706) is also observed in CNDO/2 calculations, see Fig. 3.

FIG. 2: Correlations of molecular orbitals for o-quinodimethane, o-benzoquinone-diimine and o-benzoquinone (HMO level).

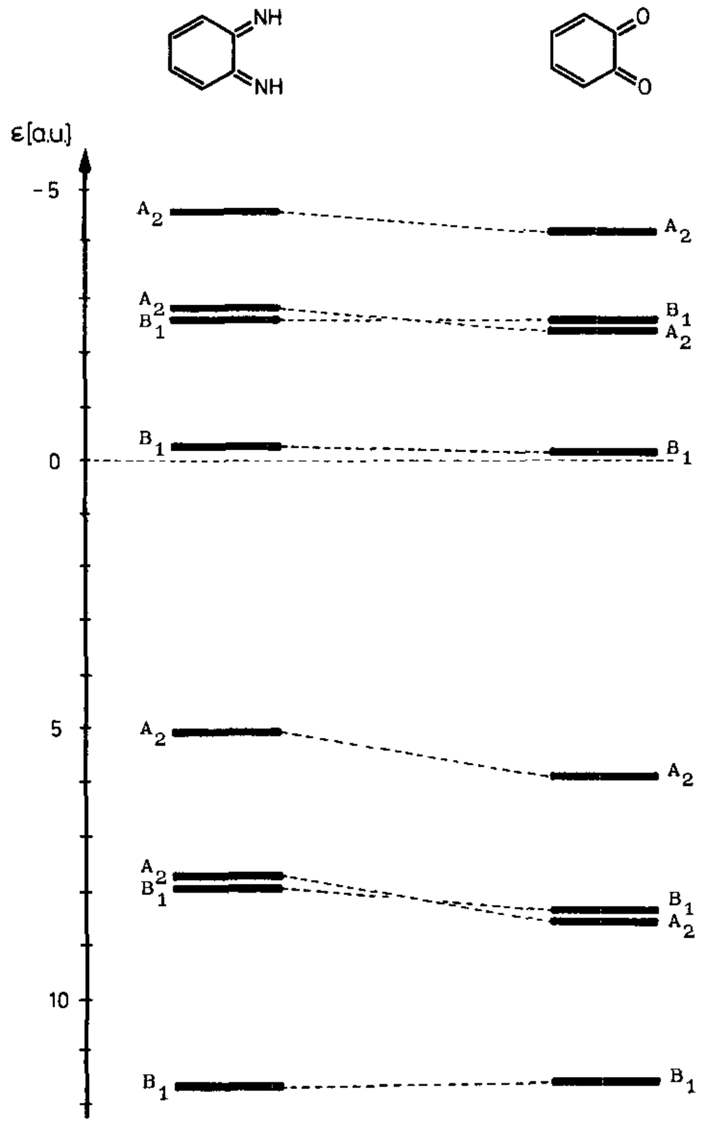


FIG. 3 : Correlation of molecular orbitals for o-benzoquinone-diimine and o-benzoquinone (CNDO/2 - level; W.Friedrichsen and I.Schwarz, unpublished data).

As can be seen from the values in Fig.4,o-benzoquinone-diimine should show a more or less equal reactivity for nucleophilic attack at positions 3 and 4. In summary these calculations reveal the expected and observed strong similarity between o-benzoquinone-diimine and o-benzoquinone.

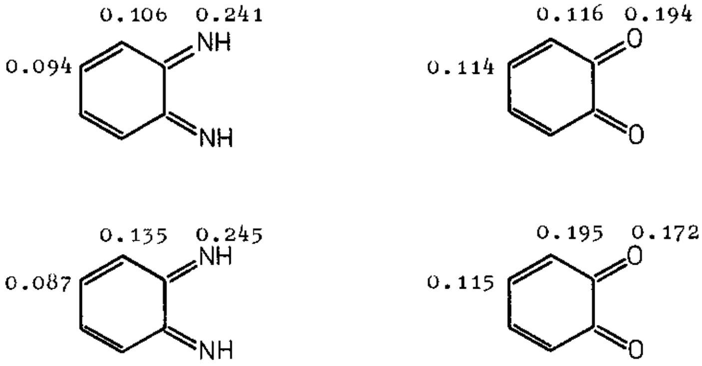
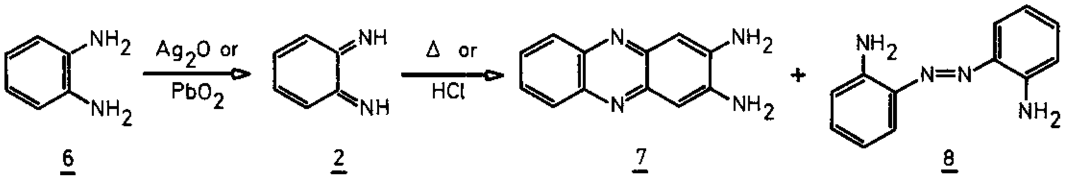


FIG. 4 : Squared coefficients at centers μ in π-LUMO (top) and π-HOMO (bottom) (CNDO/2 values).

3. SYNTHESES

3.1 PARENT COMPOUND

R.Willstätter and A.Pfannenstiel[1], in their initial synthesis of o-benzoquinone-diimine (2), found that o-phenylenediamine (6), on dehydrogenation with Ag_2O or PbO_2 in cold ether, yielded a yellow solution of 2. Upon subsequent heating or treatment with HCl, 2,3-diaminophenazine (7) and 2,2'-diaminoazobenzene (8) were produced, with 16 % and 24-65 % yields, respectively.



The findings of these authors have been substantiated numerous times[16-20]. The dehydrogenation should be carried out with freshly prepared[21] lead dioxide[20]; the reaction can also be carried out in toluene, chloroform, acetone, acetonitrile, and even in buffered aqueous solutions[20]. The reaction of 2 with 6, which yields 7, 8, and mucodinitrile, has been studied mechanistically in some detail[18,20]. In the formation of 7 and 8, 2-amino-N-(2-aminophenyl)-p-benzoquinone[22] is probably involved as an intermediate compound[20].

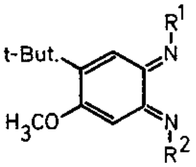
Physical data on 2 are lacking except an UV maximum at 350 nm[20] (352 nm[19]) with an extinction coefficient of 1300.

The synthesis of pure o-benzoquinone-diimine clearly remains a challenge to the preparative organic chemists.

3.2 SUBSTITUTED DERIVATIVES

3.2.1 Simple N-Substituted Compounds; Benzannelated 2H-Imidazoles

Attempts to prepare 9 (R^1=R^2=H) were unsuccessful[23].



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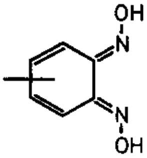
Compound 9 (R^1=2,6-$(OCH_3)_2$-4-t·but.-C_6H_2, R^2=H) has been obtained as a maroon material by dehydrogenation of the corresponding diamine[23];it could not be crystallized.Hydrogenation yielded the parent diamine.9 (R^1=R^2=2,6-$(OCH_3)_2$-4-t·but.-C_6H_2) has been formulated as an intermediate in dehydrogenation reactions of 2,5-dimethoxy-4-tert.-butylaniline in the presence of ammonia[24].

A tremendous stabilization of the o-benzoquinone-diimine system occurs when the nitrogen atoms carry further heteroatoms. o-Benzoquinone-dioximes (10) have been known for a long time[25a] and have been investigated extensively, especially as ligands in transition metal complexes[25b]. Recently compounds of type 11 have become available by reactions of substituted anilines with trisbenzenesulfenamide[26].Compounds of these types, however, will not be dealt with in this review.



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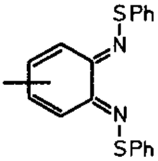

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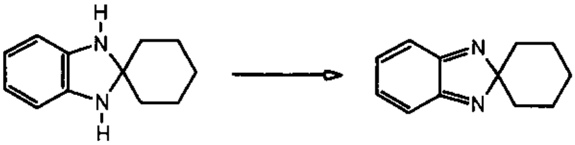
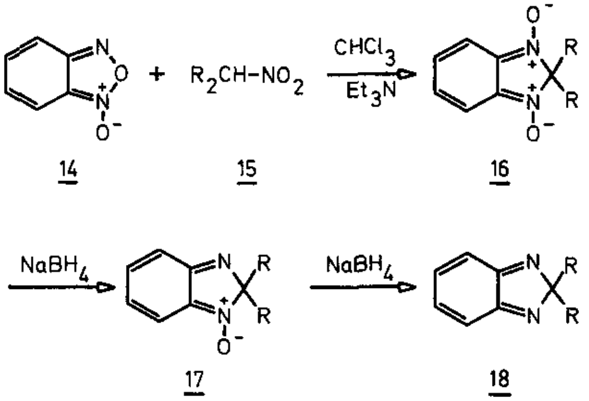
Unexpectedly, even the bridging of the two nitrogen atoms in 2 by an sp^3-hybridized carbon atom is accompanied by a remarkable stabilization of the o-quinonoid moiety. As has been reported by H.Suschitzky and coworkers[27,28], dehydrogenation of 12 with manganese dioxide gives the 2H-benzimidazole (13). This transformation could also be affected with methanolic sodium methoxide[28], and even occurs on the TLC plate[29].



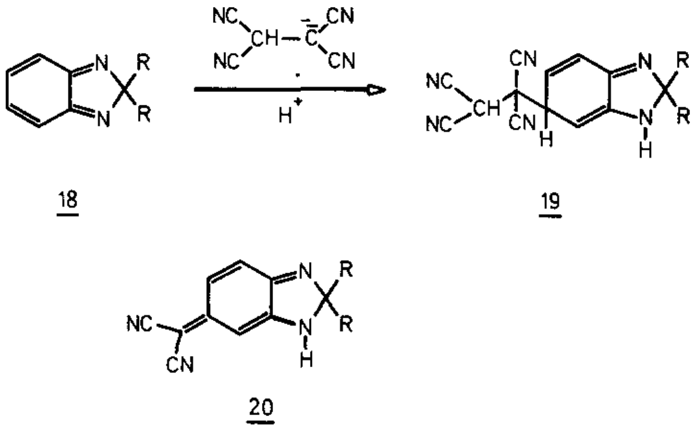
12 13

Compounds of this type (18) have also been obtained upon treatment of benzofuroxane (14) with secondary nitroalkanes (15) and subsequent reduction of the resulting red, crystalline 2H-benzimidazole-1,3-dioxides (16) with sodium borohydride; the mono-N-oxides (17) are isolatable intermediates in this reaction sequence[30,31].



$\underline{a}$: R = CH_3 , $\underline{b}$: RR = $(CH_2)_4$, $\underline{c}$: RR = $(CH_2)_5$

18a shows a methyl singlet at δ=1.45 ppm ($CDCl_3$)[30]; the vinylic protons appear as AA'BB'-system[30] at 6.30-7.34 ppm ($CDCl_3$)(for 18c)[29]. Similar values have been reported for other systems[32]. The vinylic protons appear in a region which has also been observed for other o-quinonoidal heterocycles (benzo[c]furan[33,34], benzo[c]indole[34], benzo[c]thiophene[34]). The UV spectrum of 18c is - as expected - completely different from that of 12; whereas 12 shows maxima at 211.5 (ε=18670) and 304 nm (4650), the spectrum of 18c shows maxima at 240.5 (9680) and 343 nm (4690) with an impressive fine structure (measured in cyclohexane)[29]. The 2H-benzimidazoles exhibit properties of quinones in as much as they form deeply colored (purple black) complexes in the solid state, probably of charge transfer type[32]. Additionally, they undergo a reaction with cold, alcoholic tetracyanoethylene yielding purple products of structure 20. These compounds are probably formed in a Michael-type reaction via 19 by the addition of deprotonated tetracyanoethane (generated under the reaction conditions) with subsequent loss of malodinitrile[35].



Whether 2H-benzimidazoles show a tendency to react with electron-poor dienes in a Diels-Alder manner is not yet clear[35,36]. With bromine in carbon tetrachloride, 13 yields a tetrabromo compound (no experimental details given)[28]. The increased stability of 2H-benzimidazoles as compared with o-benzoquinone-diimine may have an analogy in the o-quinodimethane and 2H-indene chemistry[37,38].

3.2.2 Benzannelated o-Benzoquinone-diimines

Whereas linear benzannelation seems to destabilize o-quinonoidal compounds, angular benzannelation strongly stabilizes these systems[33,39]. A simple HMO calculation shows this fact for 21 and 22.

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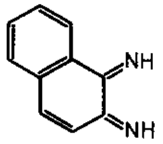
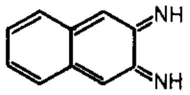


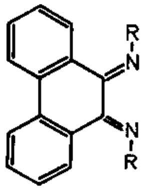


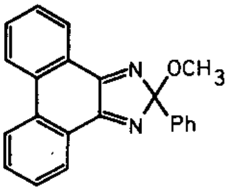
22

E_π (in β) : 16.909 16.616

The reported[40] formation of 9,10-phenanthrenequinone-diimine (23, R=H) has shown to be an error[41]. 9,10-Phenanthrenequinone-dianile (23, R=Ph) is known, however. It has been prepared by the action of lithium on benzildianile with subsequent oxidation of the resulting dianion. Upon hydrolysis with 20% HCl, 23 (R=Ph) yields 9,10-phenanthrenequinone[42].

23





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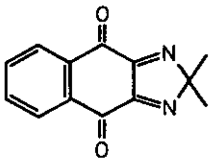

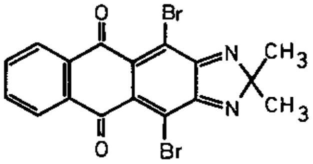

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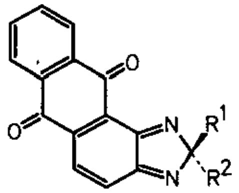

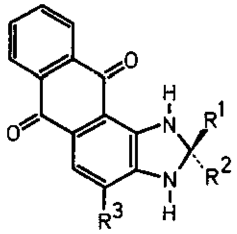

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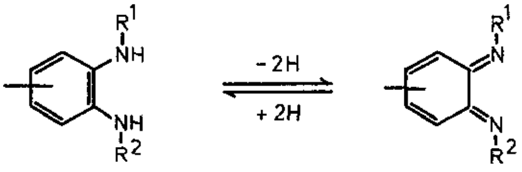
A number of benzannelated 2H-benzimidazoles (24[43], 25[44], 26[45], 27[45-48]) is known. Reaction of 27 with HCl, HBr, or $C_6H_5SO_2H$ in dioxane at room temperature produced 28 (R^3=Cl,Br,SO_2Ph)[46].

3.2.3 N-Acyl Substituted o-Benzoquinone-diimines

The introduction of N-acyl groups greatly increases the stability of o-benzoquinone-diimines; even N-monobenzoylated derivatives have been described (Table 2). The diimines almost always have been prepared by dehydrogenation of the corresponding diamide (Eq.(1)). This reaction is reversible; reduction with -for example- zinc/acetic acid converts the diimine back to the starting material.



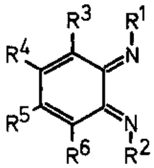
(1)

R^1 = aroyl, arylsulfonyl ; R^2 = aroyl, arylsulfonyl, H

The dehydrogenation is carried out with lead-(IV)-acetate in either chloroform or benzene or - as in the case of dibenzenesulfonyl-o-benzoquinone-diimines - in acetic acid, acetic anhydride, or ether.

The diimines usually (for exceptions see Table 2) are obtained as yellow to orange crystalline compounds; upon attempted recrystallisation a pronounced detorioration is sometimes observed. Fortunately the diimines are almost always obtained in a state pure enough for subsequent reactions. Previously described compounds are presented in Table 2.

TABLE 2 : N-Acylated o-Benzoquinone-diimines



R^1	R^2	R^3	R^4	R^5	R^6	mp	references and footnotes
Ph-CO	H	H	CH_3	H	H	65.5-66	3
Ph-CO	H	H	CH_3	H	CH_3	oily	3
Ph-CO	H	H	CH_3	Cl	CH_3	133-134	3
Ph-CO	Ph-CO	H	H	H	H	136-137[3], 142[49]	3,49
Ph-CO	Ph-CO	CH_3	H	H	H	126	4,50,51;a

TABLE 2 (Continued)

R^1	R^2	R^3	R^4	R^5	R^6	mp	references and footnotes
Ph-CO	Ph-CO	H	CH_3	H	H	191	3
Ph-CO	Ph-CO	CH_3	CH_3	H	H	128-129	52;b
Ph-CO	Ph-CO	CH_3	H	CH_3	H	215-220	52;b
Ph-CO	Ph-CO	CH_3	H	H	CH_3	187-188	52;b
Ph-CO	Ph-CO	H	CH_3	CH_3	H	157	53
Ph-CO	Ph-CO	CH_3	CH_3	H	CH_3	180	54;b
Ph-CO	Ph-CO	CH_3	H	H	$CH(CH_3)_2$	113-114	54;b,c
Ph-CO	Ph-CO	H	Cl	H	H	98.5-99.5	3
Ph-CO	Ph-CO	Br	H	Br	H	181-182	50;b
Ph-CO	Ph-CO	H	OCH_3	H	H	-	3
Ph-CO	Ph-CO	H	NO_2	H	H	83-97	55
$(p\text{-}NO_2)C_6H_4CO$	$(p\text{-}NO_2)C_6H_4CO$	H	H	H	H	185	56
$(p\text{-}NO_2)C_6H_4CO$	$(p\text{-}NO_2)C_6H_4CO$	H	CH_3	CH_3	H	272	56
$PhSO_2$	$PhSO_2$	CH_3	H	H	H	133-135	3
$PhSO_2$	$PhSO_2$	H	CH_3	H	H	155-160[3], 160-162[49]	3,49
$PhSO_2$	$PhSO_2$	CH_3	H	CH_3	H	177-183	3
$PhSO_2$	$PhSO_2$	H	CH_3	CH_3	H	181-186[3], 195-200[49]	3,49
$PhSO_2$	$PhSO_2$	H	Cl	H	H	176-178[3], 152[49]	3,49;e
$PhSO_2$	$PhSO_2$	H	Cl	Cl	H	185-186[3], 190-192[49]	3,49
$PhSO_2$	$PhSO_2$	Cl	Cl	Cl	H	155-157	3
$PhSO_2$	$PhSO_2$	H	OCH_3	H	H	139	53;d
$(p\text{-}NO_2)C_6H_4SO_2$	$(p\text{-}NO_2)C_6H_4SO_2$	H	CH_3	CH_3	H	188-190	56
$(p\text{-}OCH_3)C_6H_4SO_2$	$(p\text{-}OCH_3)C_6H_4SO_2$	H	CH_3	CH_3	H	170-180	56

a : Mp of the dimer.

b : This diimine has been described as colorless.

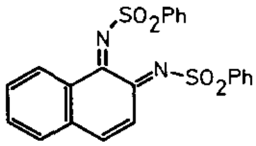
c : The solutions of this diimine are yellow (in benzene, ethylacetate, petroleum ether, chloroform, alcohol).

d : The compound could not be purified.

e : *Probably dimorph.*

A benzannelated o-benzoquinone-diimine is also known; 29 has been prepared in the usual way by dehydrogenation of the corresponding bisamide.

29



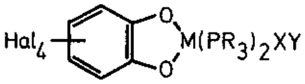
Spectroscopic properties of o-benzoquinone-diimines have not been investigated systematically; some data have been reported, however. In this context it is of interest that there has been no report concerning the stereochemistry of the N-acylimino groups; in the p-benzoquinone series there are some ^{1}H-NMR observations which are interpretable in terms of mixtures of syn- and anti-isomers[57] (as in the case of an acyclic N-benzenesulfonylimine[58]).

3.3 METAL COMPLEXES

Whereas a great number of o-quinone complexes of type 30 (o-quinone:o-benzoquinone, 3,5-di(t.butyl)-o-benzoquinone,tetrachloro-o-benzoquinone, 9,10-phenanthrenequinone;M=Zn[59a,b],Ni[59b,c], Co[59c,d], Fe[59c,e,f], Cr[59e,f,g,h,o], Mo[59g,i], W[59e,f,g]), type 31 (X=Y=CO; X=CO, Y=Cl : M=Ir, Ru, Rh; no X,Y : M=Pd, Pt)[59j,k,l,m,r], and others[59n,q] (including metal 1,2-dithiolene and related complexes[59p]) have been studied extensively, analogous investigations in the o-benzoquinone-diimine field have been far less common. Reaction of Ni^{2+} and o-phenylenediamine in concentrated ammonia leads to a crystalline, diamagnetic complex[16,60-63], which is identical to the reaction product formed from o-benzoquinone-diimine (2) and $Ni(CO)_4$ in ether (32, M=Ni); other metal complexes (32; M=Pd,Pt,Co) are also known. Polarographic experiments in nonaqueous solutions have established the existence of the complete five-membered series (Eq.(2)) with M=Ni,Pd,and Pt and the existence of z=-2,-1,0, and +1 with M=Co. Salts of type 33 and 34 have been obtained from 32, with one and two equivalents of iodine, respectively. The crystal structure of 32 (M=Ni) is known[64]. The nickel atom is four-coordinated in a monomeric,planar $[C_6H_4(NH)_2]_2Ni$ molecule; the bond lengths in the chelate rings indicate a more substantial delocalisation (with only a slight o-diimine character) of the π-bonds than in complex 35[65],which has been prepared by the reaction sequence shown in Eq.(3). Chemical and structural data demonstrate that salt 35 contains a stabilized o-benzoquinone-diimine unit. Quite recently the preparation of the Co(II)-complex of o-phenylenediamine (36) has been described[66]. Controlled oxidation with oxygen yields an un-

$$(\text{o-quinone})_m M_n$$

30



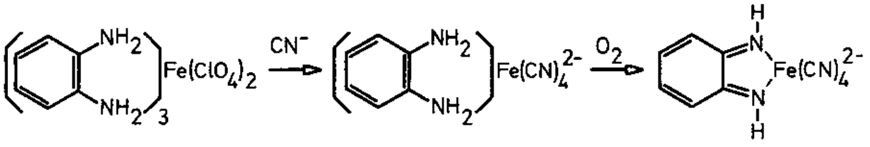
31

$$[C_6H_4(NH)_2]_2M \qquad [C_6H_4(NH)_2]_2MJ \qquad [C_6H_4(NH)_2]_2NiJ_2$$

32 33 34

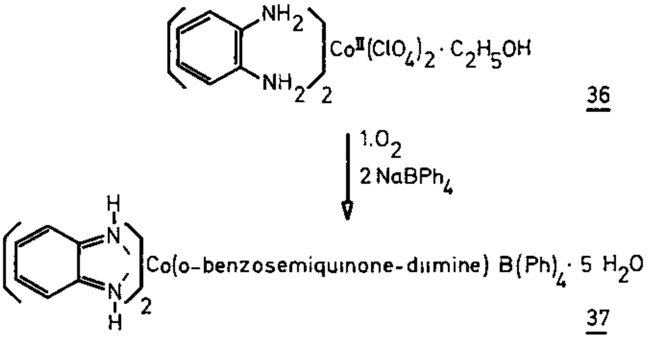
$$[M\text{-}N_4]^{2-} \rightleftharpoons [M\text{-}N_4]^{-} \rightleftharpoons [M\text{-}N_4]^{0} \rightleftharpoons [M\text{-}N_4]^{+} \rightleftharpoons [M\text{-}N_4]^{2+} \qquad (2)$$

$$N_4 = [C_6H_4(NH)_2]_2$$



35

(3)



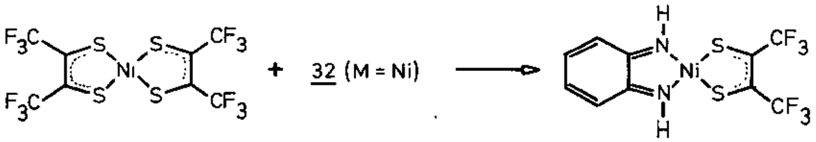
36

37

(4)

stable, crystalline, paramagnetic o-benzosemiquinone-diimine complex which on further oxidation gives a stable, diamagnetic, dark blue o-benzoquinone-diimine complex (37) (Eq.(4)).An X-ray investigation shows that two ligands have the oxidation state of an o-benzoquinone-diimine while the third,coordinated by one amino group only, is pseudosemiquinonoid; the o-benzoquinone-diimine moieties are in a square pyramidal arrangement.

The square-planar dithiolene-o-benzoquinone-diimine complex 38 has been prepared in a ligand exchange reaction (Eq.(5));cyclic voltammetry of this high melting,intensively colored, diamagnetic compound reveals the existence of a one-electron oxidation state and two one-electron reduction states[67].



38

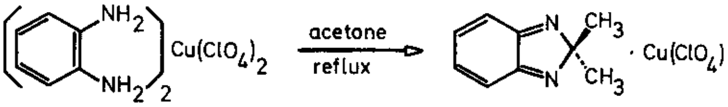
(5)

The Co-cyclopentadienyl complex 39 is obtainable by several methods[17], e.g. by

a

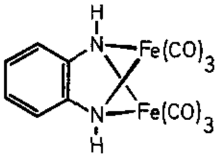
39

b



40

reaction of o-benzoquinone-diimine and (π-C_5H_5)Co(CO)$_2$ in ether. The appropriate formulation (a,b) is open to question. There has also been report of a 2H-benzimidazole complex; o-phenylenediamine with Cu(ClO_4)$_2$ gives a salt which on treatment with acetone yields the red diamagnetic complex 40; 40 forms deeply colored, well crystallized solvates with both acetonitrile and benzonitrile[68]. Dinuclear iron complexes of type 41 have also been described[69].

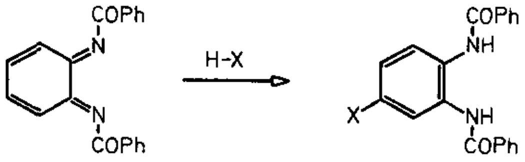


41

4. REACTIONS

4.1 NUCLEOPHILIC ATTACK

As expected, o-benzoquinone-diimines combine fairly readily with nucleophilic agents- as do the p-isomers and the corresponding benzoquinones- to produce substituted amides[3]. Reaction of acetic acid, hydrazoic acid, and methanol with 42 produces a single isomer (43); presumably the adducts with active methylene compounds have the same orientation. Hydrogen chloride forms a mixture of two monochloro compounds.

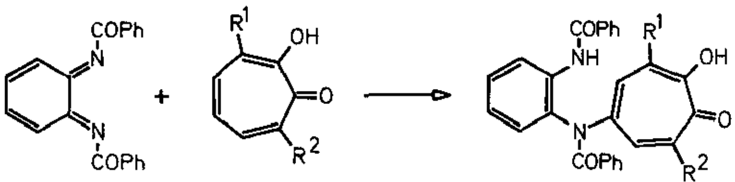


42 43

(6)

X = OAc, N_3, OCH_3 (with BF_3 Et_2O)

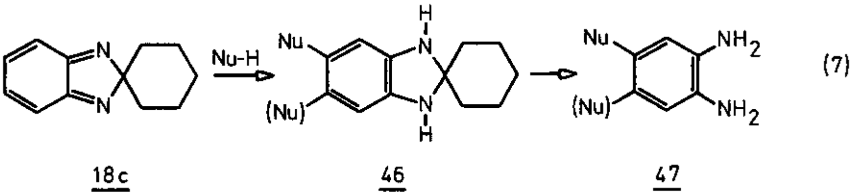
4-Substituted o-benzoquinone-diimines may form 3-,5-, or 6-substituted bisamides. In a number of cases the orientation of the substituents has not been clarified definitely. Tropolone and brominated derivatives (44a,b,c) in the presence of ca-



42 44a,b,c 45a,b,c

a : R^1=R^2=H ; b : R^1=H , R^2=Br ; c : R^1=R^2=Br

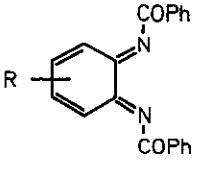
talytic amounts of triethylamine combines with 42 to produce N-tropolonyl-o-phenylenediamides (45a,b,c)[70,71]; phenol reacts in an analogous manner[72].
Addition of nitrogen, oxygen, sulfur, and carbon nucleophiles to 18c, with subsequent reductive cleavage, has been described as a procedure for introducing substituents into o-phenylenediamine (Eq.(7))[73];this reaction sequence is of special interest because o-phenylenediamine serves as a versatile source for a wide range of heterocycles.



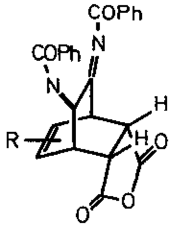
4.2 [π4+π2] CYCLOADDITIONS

4.2.1 Normal Diels-Alder Reactions

Diels-Alder reactions of o-benzoquinone-diimine were described for the first time by R.Adams and coworkers[3];subsequent investigations[49] have shown that some of the structures given by these authors must be revised (Sect.4.2.2).o-Benzoquinone-diimines may react as dienes in a twofold manner,either as homodienes or as heterodienes. With electron-poor olefins, such as maleic anhydride and p-benzoquinone, 42 and its alkyl-substituted derivatives (48) react at the homodiene moiety to produce compounds of type 49 and 50[4,50-52,54]. An analogous reaction takes place with pyridazindione and phthalazindione[74]. The stereochemistry of the adducts 49 and 50 is not known in all cases[4,50,51]; in the majority of these reactions endo-addition (as indicated) seems to occur[52,54,74,75]. Kinetic investigations in these systems are lacking, but phenomenologically these reactions can be considered as normal Diels-Alder reactions (electron-rich diene, electron-poor olefin)[76]. The synthetic possibilities of these reactions have yet to be explored.



48



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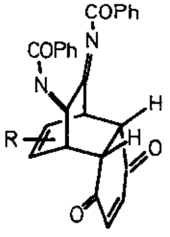
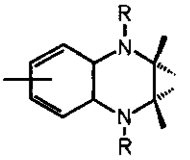


50

R = H, alkyl (s)

4.2.2 Diels-Alder Reactions with Inverse Electron Demand

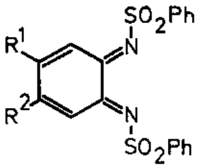
Both N,N-diaroyl-and N,N-diarylsulfonyl-o-benzoquinone-diimines react with simple (normal, strained, electron-rich) compounds (cyclopentadiene[77], cyclopentene, furan, ethyl vinyl ether, butadiene[77], styrene, acenaphthylene, indene[78], norbornene, norbornadiene) to yield adducts at the heterodiene moiety (51).With norbornadiene, both stereoisomers (endo and exo) can be obtained[49].



51

R = COPh, SO_2Ph

The reaction of 52a and 52b with cyclopentadiene has been investigated kinetically. Both the kinetic data, and the only moderate dependence of k (determined for 52b) on the solvent polarity, are in accord with the assumption that a Diels-Alder reaction with inverse electron demand is operating.



52a,b

a: R^1=H , R^2=Cl ; b: R^1=R^2=CH_3

	k ($lmol^{-1}s^{-1}$) [a]
52 a	$1.63\ 10^{1}$
52 b	$1.51\ 10^{-1}$

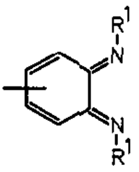
a : In toluene.

for 52b :

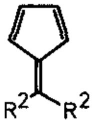
$\Delta H^{\ddagger} = 8.1 \pm 0.4$ kcal·mol^{-1}

$\Delta S^{\ddagger} = -34.7 \pm 1.4$ e.u.

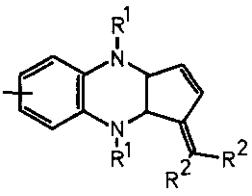
The reactions of N,N-dibenzoyl- and N,N-dibenzenesulfonyl-o-benzoquinone-diimines with fulvenes (54) are of special interest. Whereas both types of diimines form [π4+π2] cycloadducts at the endocyclic double bond of the fulvene nucleus (55a,b), 53b also yields [π4+π6] adducts (56)[79] (Sect.4.3).



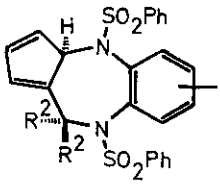
53a,b



54



55a,b

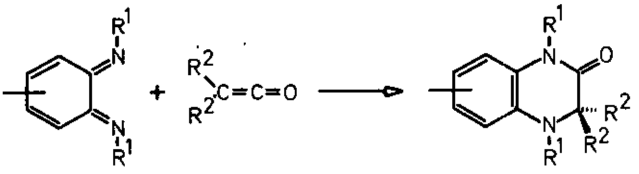


56

a : R^1 = COPh ; b : R^1 = SO_2Ph

R^2 = alkyl, cyclopropyl, aryl

o-Benzoquinone-diimines react with ketenes (57) to give [$\pi 4+\pi 2$] adducts (58)[53]; in this manner they resemble the o-benzoquinones[53,80].



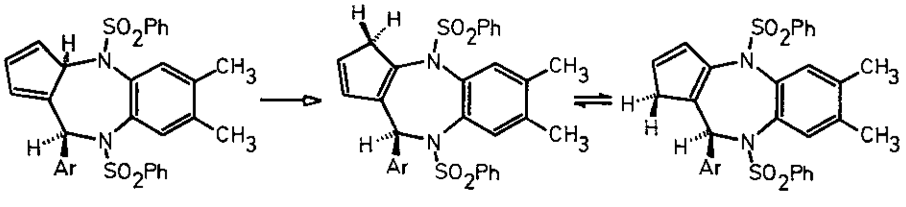
53 57 58

R^1 = COPh, SO_2Ph ; R^2 = Ph, $(p\text{-}NO_2)C_6H_4$

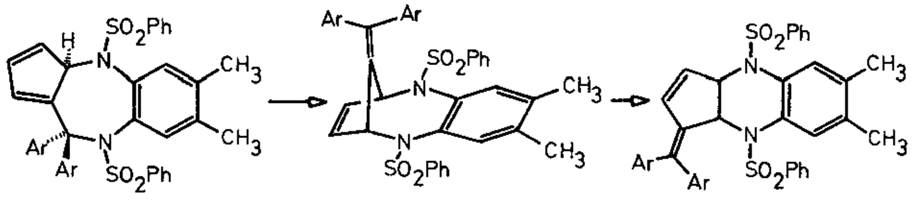
This sequence is of particular interest because it represents one of the rare examples where ketenes act as olefinic compounds in a [$\pi 4+\pi 2$] manner[81]. Kinetic investigations (influence of substituents, determination of activation parameters, solvent dependence of reaction rates) have again shown that this reaction belongs to a type of cycloaddition with an only moderate polar transition state, where the diimine acts as an electron-deficient and the ketene as an electron-rich reactant. Thus the criteria of a Diels-Alder reaction with inverse electron demand are also met in these cases.

4.3 [$\pi 4+\pi 6$] CYCLOADDITIONS

As mentioned in the previous section N,N-dibenzenesulfonyl-o-benzoquinone-diimines may react with fulvenes to yield [$\pi 4+\pi 2$] and [$\pi 4+\pi 6$] adducts (55b, 56); the reason for the different behavior between 53a and 53b remains unclear. Compounds of type 56 (e.g. 59) may rearrange. The adducts resulting from 6-monosubstituted fulvenes suffer from a 1.5-H-shift to give 60; at higher temperatures these compounds are in equilibrium with 61. Remarkably, this equilibrium is also attained in the solid state.



59 60 61



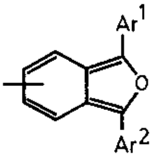
62 63 64

6,6-Bis(4-methoxyphenyl)-fulvene produces an adduct (62) which is unstable at room temperature and rearranges to 63, and which can be formally considered as an [π4+π4] adduct of an o-benzoquinone-diimine (for a further example of this type of reaction see Sect.4.4). Compound 63 is also unstable; even at room temperature it rearranges to 64. Further examples of these complex rearrangements together with a mechanistic scheme which accommodates these peculiar reactions have been published[82].

4.4 [π4+π4] CYCLOADDITIONS

4.4.1 With Benzo[c]furans

Surprisingly, benzo[c]furans (65) react with o-benzoquinone to give [π4+π4] adducts and/or dioxoles (66,67)[6a,83]. N,N-Dibenzoyl- and N,N'-dibenzenesulfonyl-o-benzoquinone-diimines react with 65 in an analogous manner to produce 68; these compounds may rearrange thermally to yield 2H-benzimidazoles (69).



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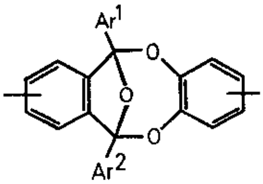
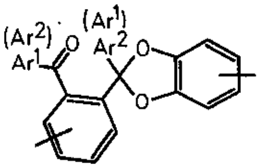


66



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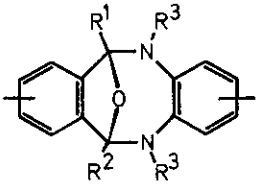

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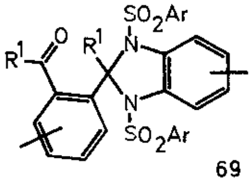
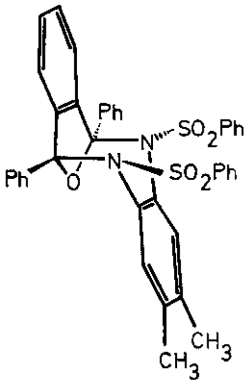


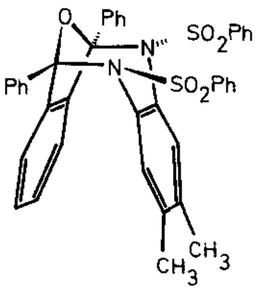
69

R^1, R^2 = aryl ; R^3 = COAr, SO_2Ar

As can be seen by inspection of models, eight-membered rings of type 66 and 68 can



70

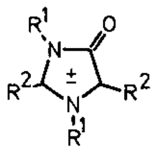


71

exist in both rigid chair and boat conformations. Whereas there is no indication for such an isomeration in the oxygen series (66), both conformations have been isolated in the nitrogen series (70,71); the structures of these compounds have been determined by X-ray diffraction[85].

4.4.2 With Mesoionic Compounds

It is of interest that mesoionic five-membered heterocycles may react with o-benzoquinone-diimines, as well as with o-benzoquinones, to produce $[\pi 4+\pi 4]$ cycloadducts. 1,3-Diazolium-4-olates (72) and a 1,3-oxazolium-4-olate (73) yield (in a rather smooth reaction even at room temperature) products of type 74[86]. Further reactions with mesoionic compounds are described in Sect. 4.6 .



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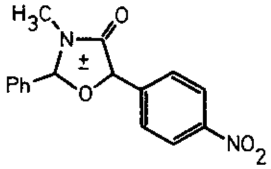

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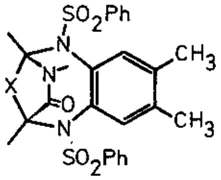

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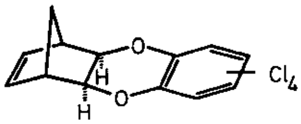
4.5 REACTIONS WITH QUADRICYCLANES

As discussed earlier, tetrachloro-o-benzoquinone reacts with quadricyclane (75) to yield products (76,77) which can be considered as $[\sigma 2+\sigma 2+\pi 4]$ cycloadducts[87,88]. In an analogous manner, the diimines 78a,b react with quadricyclane (75), quadricy-

75



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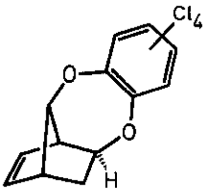

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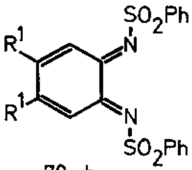
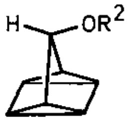


78a,b

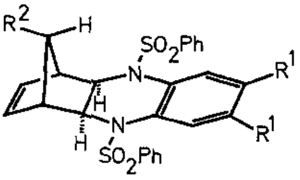
a: R^1=Cl ; b: R^1=CH_3



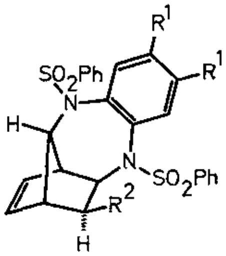
79a,b

a: R^2=H ; b: R^2=Ac

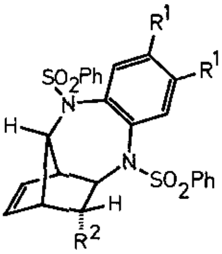
80



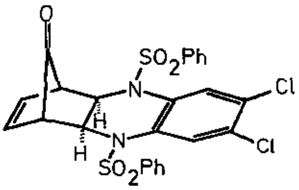
81a-d,f



82a,b,d,e



83b,c,e



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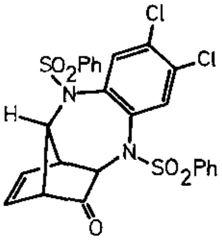


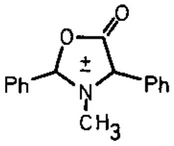
85

81,82,83	R^1	R^2
a	Cl	H
b	Cl	OH
c	Cl	OAc
d	CH_3	H
e	CH_3	OH
f	CH_3	OAc

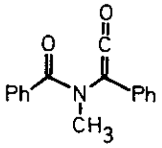
clanol (79a), 7-acetoxyquadricyclanol (79b), and quadricyclanone (80) to produce the adducts 81 - 85[89]. As we have observed, the electron-deficient diimine 78a is more reactive than 78b; whereas 78a and 80 yield the adducts 84 and 85 only sluggishly, 78b does not react at all[89].

4.6 FURTHER REACTIONS WITH MESOIONIC COMPOUNDS

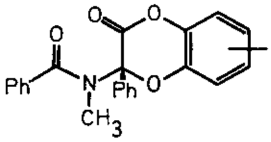
Five membered mesoionic heterocycles of type A[90] not only act as 1.3-dipolar compounds but may also give adducts which can be formally derived from a valence tautomeric ketene (e.g. 87)[91,92]. o-Benzoquinones react with 1,3-oxazolium-5-olates (86) and other mesoionic compounds[93] in this same manner. o-Benzoquinone-diimines show an analogous behavior;with 86, 90, and 91, the 1:1-adducts 89, 92,and 93 are obtained. The mechanism of these remarkably simple reactions remains obscure.



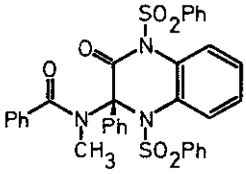
86



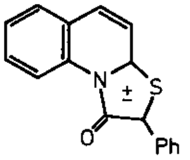
87



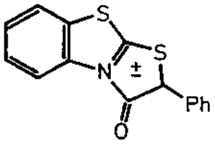
88



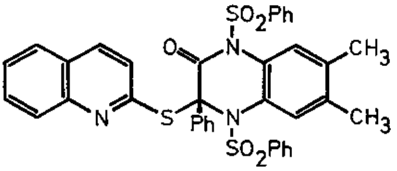
89



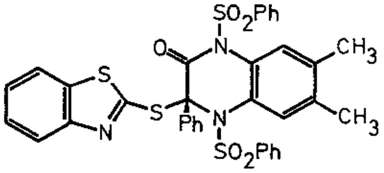
90



91



92

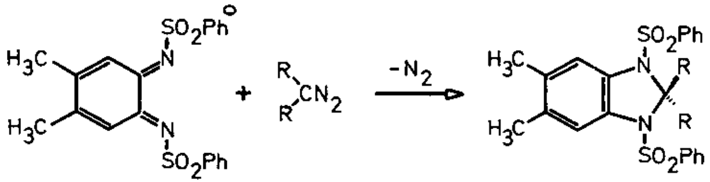


93

4.7 MISCELLANEOUS REACTIONS

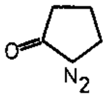
It is well known that o-benzoquinones with high redox potentials (e.g.tetrachloro-o-benzoquinone) may serve as dehydrogenation agents[94].o-Benzoquinone-diimines may act in the same manner. This is suggested by the observation that reactions with these compounds often lead to products contaminated with small amounts of the corresponding amides.Quantitative experiments have shown that N,N-dibenzoyl-o-benzoquinone-diimine dehydrogenates 9,10-dihydroanthracene, and 1,4-cyclohexadiene to produce, respectively, anthracene and benzene[53].

The reaction of o-benzoquinone-diimine with diazoalkanes also parallels the corresponding transformations of o-benzoquinones[95]. N,N-Dibenzenesulfonyl-4,5-dime-

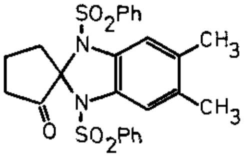


94a,b 95a,b

a : R = C_6H_5 ; b : R = $(4\text{-}OCH_3)C_6H_5$



96



97

thyl-o-benzoquinone-diimine reacts with diaryldiazoalkanes (94a,b) to yield dihydrobenzimidazoles (95a,b).An analogous reaction takes place with α-diazocyclopentanone (96)[29,82] to produce 97.

4.8 CONCLUSION

Systematic and intensive studies in the o-benzoquinone-diimine field were first conducted by R.Adams and coworkers[3].Since then these compounds have been investigated far less extensively than the corresponding o-benzoquinones.In the last few years a renewed interest has developed; the results of these investigations have shown that o-benzoquinone-diimines - in particular the stable N,N-diaroyl- and N,N-diarylsulfonyl substituted derivatives - may serve as an interesting source for new heterocyclic compounds.

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