# 111. Intermediates in the Dehydrogenation of Hydroaromatic Compounds with Quinones

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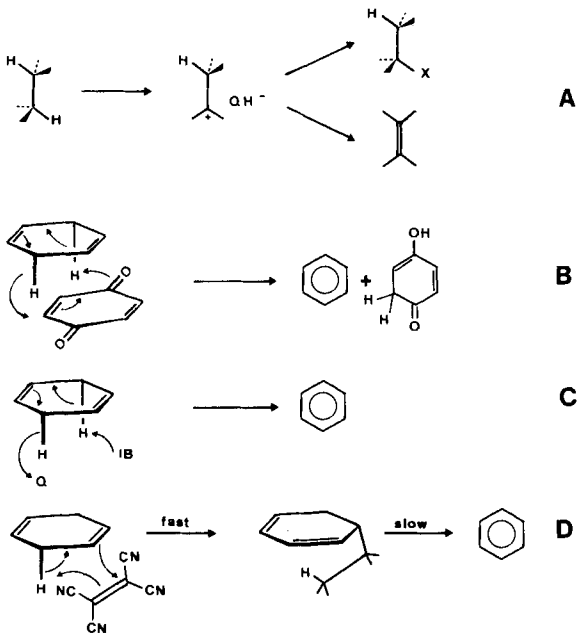
*Summary*

Dehydrogenation of hydroaromatic compounds with quinones was reinvestigated in the light of recent criticism of the reaction mechanism. Kinetic and spectroscopic evidence shows that disappearance of substrate proceeds at the same rate as the product-forming step. A mechanism consisting in fast formation followed by slow decomposition of an intermediate can be ruled out. The order of reactivities of 1,4-cyclohexadiene (**1**), 1,4-dihydronaphthalene (**8**) and 9,10-dihydroanthracene (**11**) changes in going from benzoquinone to chloranil or 2,3-dichloro-5,6-dicyanobenzoquinone. It is suggested that this behaviour could be due to contribution of CT-complexes or HOMO-LUMO interactions for determining the reactivity of the substrates.

Oxidations of hydrocarbons by quinones have been studied extensively since the pioneering work of *Braude* [1]. They are believed to proceed by hydride transfer from the substrate to the quinone to yield an ion pair which undergoes proton loss or nucleophilic attack (*Scheme 1*, path A) [2] [3]. A special mechanism was invoked to explain the abnormally high reactivity of 1,4-dihydrobenzenes, such as 1,4-cyclohexadiene (**1**) [4][1]), which are believed to react by simultaneous transfer of two *cis*-H-atoms either in a cyclic mechanism (path B) [5] or by hydride transfer concomitant with proton loss to the solvent [6] (path C). The concerted mechanisms B and C for dehydrogenation of 1,4-cyclohexadiene is still controversial [3]. In addition, recent evidence suggests that all mechanisms proposed in the *Scheme* might be wrong. *Haselbach & Rossi* [7] found that dehydrogenation of 1,4-cyclohexadiene (**1**) by tetracyanoethylene (TCNE) proceeds in part *via* ene-reaction to an adduct followed by slow, base-induced elimination as shown in path D. This observation was rediscovered by *Jacobson* [8] who suggested that dehydrogenations with quinones could also proceed by an ene-type mechanism; the latter has also been observed for aromatization of **1** with $SO_2$ [9]. Analogous behaviour of TCNE and quinones does indeed occur with metal hydrides [10] although these oxidations

[1]) All compounds with formula numbers are summarized in *Table 1*.

*Scheme*




proceed *via* rate-determining electron transfer in charge-transfer complexes of metal hydride and TCNE or quinone.

In the past we have never explicitly ruled out nor even considered an ene-mechanism for quinone oxidation of hydroaromatic compounds [6] [11]. We considered the question to be sufficiently important, in particular in relation to the significance of quinone oxidations as models for nicotinamide coenzymes [12] [13], to merit a reinvestigation in the light of *Jacobson*'s suggestion.

**Results and discussion.** – *Reactivity study. Jacobson*'s criticism is based on the observation that in virtually all kinetic investigations of quinone oxidation the reaction rate was measured by following the disappearance of quinone by some spectroscopic or titrimetric method, while product formation was not monitored. If the ene-mechanism outlined in *Scheme 1* (path D) also applies to quinones, the rate of disappearance of the quinone is not necessarily related to that of product formation, because the second step of the reaction may be rate-determining. This situation holds for TCNE and **1**. However, inspection of the rate data summarized in *Table 1* and *Figure 1* shows that the ene-mechanism is unlikely for quinone oxidations. We first note roughly parallel behaviour of the substrates under investigation towards dichlorocyanoquinone (DDQ) and triphenylmethylfluoroborate, which indicates similar mechanisms. The benzannelated compounds appear to react at enhanced rates with DDQ. This unexpected behaviour will be discussed below. Several observations are incompatible with the ene-mechanism for quinones; **1** reacts *ca.* 50 times faster than **5**. The ene-mechanism would lead to 1,3-cyclohexa-

Table 1. *Relative rates of dehydrogenation with quinones*

| No. | Substrate | $k_{rel}$ DDQ[a]) | $k_{rel}$ Chloranil[d]) | $k_{rel}$ BQ[g]) | $k_{rel}$ $\Phi_3C^{+i}$) |
|---|---|---|---|---|---|
| **1** | 1,4-Cyclohexadiene | 100 (100)[c]) | 100 | 100 (100)[h]) | 100 |
| **2** | 3,3-Dimethyl-1,4-cyclohexadiene | 0.2 | | | 2.3 |
| **3** | *cis*-3,6-Dimethyl-1,4-cyclohexadiene | 143 | | | |
| **4** | *trans*-3,6-Dimethyl-1,4-cyclohexadiene | 6.8 | | | |
| **5** | 1,4-Cycloheptadiene | 1.7 | | | |
| **6** | Cycloheptatriene | 378 | | | 1240 |
| **7** | 1,2-Dihydronaphthalene | | (0.7)[e]) | (0.9)[h]) | |
| **8** | 1,4-Dihydronaphthalene | 240[b]) (290)[c]) | 135 (135)[e]) | 43 (57)[h]) | 11.7[b]) |
| **9** | 5*H*-Benzocycloheptene | 166[b]) | | | 19[b]) |
| **10** | Acenaphthene | | (0.2)[f]) | | |
| **11** | 9,10-Dihydroanthracene | 63[b]) (100)[c]) | 40 (40)[e]) | 11 (15)[h]) | 1.5[b]) |
| **12** | 5*H*-Dibenzo[*a*,*d*]-cycloheptene | 1.5[b]) | | | 0.1[b]) |
| **13** | 10,11-Dihydro-5*H*-dibenzocycloheptene | <0.7[b]) | | | <0.02[b]) |
| **14** | 1,2,3-Tri-*t*-butylcyclopropene | 2.4[b]) | | | 3.8[b]) |
| **15** | 1,2,3-Triphenylcyclopropene | 113 | | | 708 |

[a]) In AcOH, 25° [5] [6]. [b]) This work. [c]) [3]. [d]) By competition experiments in anisole, 60°. [e]) In phenetole, 100° [14]. [f]) Extrapolated from data in chlorobenzene, 131° [15]. [g]) By competition experiments in anisole, 60°. [h]) In dioxane, 80° [1]. [i]) In $CH_3CN$, 25° [6].

and 1,3-cycloheptadiene derivatives. The heat of isomerization from 1,4- to 1,3-cyclohexadiene is negligible [16] [17], for **5** to the conjugated isomer it is −6 kcal/mol [17]. On thermodynamic grounds ene-reaction with **5** should be faster than with **1** if part of this energy change is reflected in the transition state of the reaction. The observed reactivity sequence of **1** and **5** is the opposite of that predicted and therefore does not support the ene-mechanism. Similar arguments can be applied to the dibenzannelated homologues **11** and **13**. Reaction of both **11** and **13** would involve a double bond of one of the aromatic rings and lead to loss of

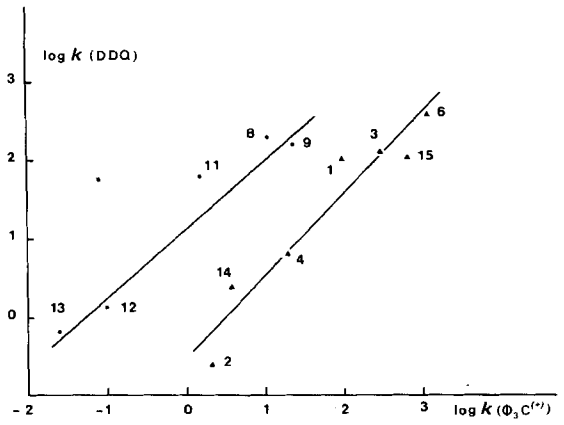



Fig. 1. *Rates of dehydrogenation with DDQ* vs. *triphenylmethylfluoroborate* (Data from *Table 1*)

aromaticity. While the low reactivity of **13** is compatible with the ene-mechanism, the reactivity of **11** nearly as high as that of **1** is not compatible. The reactivity of **1** and of its dimethyl derivatives provide further evidence against the ene-mechanism. Introduction of two *cis*-methyl groups in the 3,6-positions increases the rate from 100 for **1** to 143 for **3**. The *trans*-isomer **4** reacts at a relative rate of 6.8, but the 3,3-dimethyl compound **2** is very unreactive. These trends have been interpreted in favour of simultaneous transfer of two H-atoms *(Scheme 1B)* [5] [6]. They could also be due to steric effects operating in the hydride mechanism A. For the ene-mechanism we would expect similar steric hindrance for **2** and **4** and therefore the same rate. Taking into account a factor of 1.4 for reactivity of a secondary *vs.* a tertiary substrate (from **1** and **3**) we find the reactivity of **2** *ca.* 15 times less than that of **4**. Although this factor is small, it provides additional evidence against the ene-mechanism. A last discrepancy between DDQ and TCNE is found in aromatization of **1**, **8** and **11**. Diene **1** reacts at 35.5° with TCNE in THF with a rate constant $k_2 = 5.3 \times 10^{-3}\ \text{M}^{-1}\ \text{min}^{-1}$ [8]. Rate constants for **8** and **11** have not been determined with TCNE, but these reactions require heating at reflux for 4–6 h [18] in dioxane. In contrast with DDQ the reactivity sequence is **8** > **1** > **11**. Thus, we conclude that the reactivity of hydroaromatic substrates towards DDQ provides no support for the ene-mechanism.

*Role of intermediates in quinone oxidation.* The UV. spectrum of DDQ in dioxane shows bands with maxima at 270 and 375 nm *(Fig. 2)*. Upon addition of **1** these bands disappear while a new band corresponding to the hydroquinone,

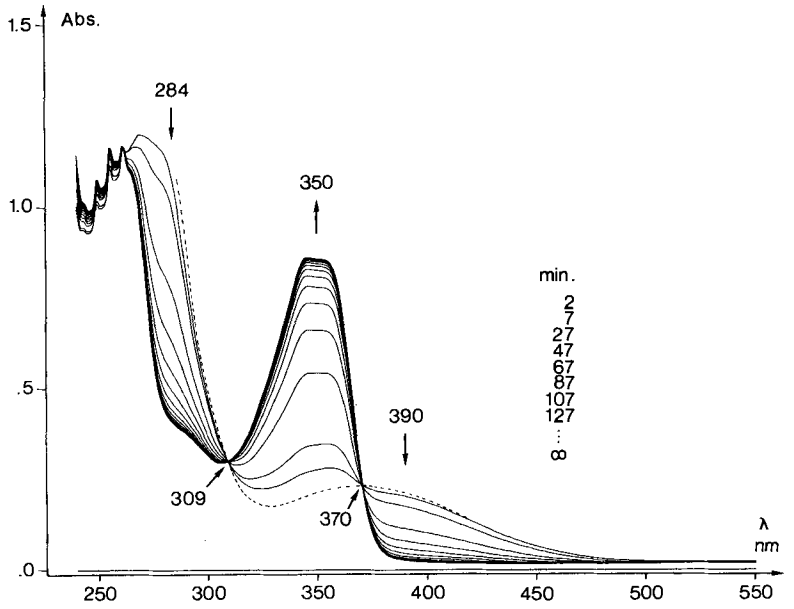



Fig. 2. *UV. spectrum for oxidation of* **1** ($2.54 \times 10^{-2}$ M) *with DDQ* ($1.46 \times 10^{-4}$ M) *in dioxane, 25°* (The broken line is that of DDQ before addition of **1**, adjusted to the isosbestic points)

$DDQH_2$ arises at 350 nm. The second-order rate constants for disappearance of DDQ and that for formation of $DDQH_2$ determined from the change in absorbance at 284, 390 and 345 nm, respectively are 0.919 ($r^2=0.999$), 1.003 ($r^2=0.999$) and 0.963 ($r^2=0.997$) $M^{-1}\,min^{-1}$. Together with the isosbestic points at 309 and 370 nm, they provide evidence against the formation of an intermediate at high concentrations. Similarly, the reaction of **1** and chloranil was investigated in ($D_8$)dioxane at 100° by $^1$H-NMR. *Figure 3* shows the time course of the reaction.

Only **1** and the product, benzene, are present. The material balance amounts to $100\pm5\%$ which is within experimental error. Similarly, aromatization of **8** by chloranil was followed at 120° in $CD_2Cl_2$. The $^1$H-NMR. spectra taken after 10, 30 and 75 min showed only **8** and naphthalene, but no intermediate could be observed. The reaction rates for disappearance of **8** ($k_r=0.74\,M^{-1}\,min^{-1}$) and formation of naphthalene ($k_r=0.70\,M^{-1}\,min^{-1}$) were determined in 1,2-dichloroethane at 120° by GC. analysis of the reaction mixture *(Fig. 4)* at appropriate time intervals. Their identity within experimental error does not support the stepwise mechanism of *Jacobson*.

In summary, all available evidence suggests that dehydrogenation with quinones does not proceed *via* an intermediate as observed in the case of TCNE. However, these results cannot rule out a mechanism where an intermediate is formed in a fast equilibrium preceding the rate-determining step:

$$AH_2+Q \overset{\text{fast}}{\rightleftharpoons} \mathbf{I} \overset{\text{slow}}{\longrightarrow} AH^+$$

This would lead to the same kinetics and would also accommodate the reactivity sequence as well as the isotope effects measured for the reaction [10] [11]. The intermediate **I**, present only at low (steady-state) concentrations, could easily escape detection. We believe that charge-transfer (CT) complexes are more likely intermediates than ene-adducts in reactions with quinones. CT-complexes have been repeatedly reported to occur during dehydrogenation with quinones [19] [20], but only recently *Lai & Colter* [21] were able to trap the *N*-methylacridanyl radical from oxidation of *N*-methylacridan by 2,3-dicyanobenzoquinone. This and additional

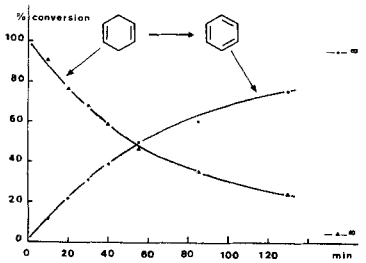



Fig. 3. *Time-course of reaction between* **1** ($1.82\times10^{-1}$ M) *and chloranil* ($1.65\times10^{-1}$ M) *in* ($D_8$)*dioxane, 100°, followed by* $^1$*H-NMR. with* $CH_3CN$ *as internal standard*

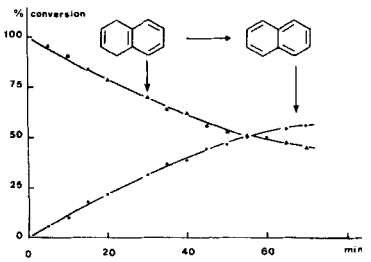



Fig. 4. *Kinetics for disappearance of* **8** *and formation of naphthalene with chloranil* (1,2-dichloroethane, 120°)

evidence was interpreted with a sequential electron-proton-electron transfer, which most likely occurs *via* a CT-complex:

$$AH + Q \rightleftarrows [AH \ldots Q] \rightleftarrows AH^+ A^- \xrightarrow{\text{slow}} A\cdot AH\cdot \rightarrow A^+ AH^-$$

This scheme does not necessarily apply to dehydrogenation of hydrocarbons. However, we made some observations which could suggest a similar mechanism.

In their early work *Braude et al.* [1] measured the rates of dehydrogenation of **1**, **8** and **11** and found the sequence **1** > **8** > **11** *(Table 1)*. The sequence with triphenylmethylfluoroborate is the same. It is in agreement with the hydride-transfer mechanism *(Scheme 1A)* since the change in $\pi$-energy in the simple *Hückel* model (1.46, 1.38, 1.30 $\beta$) leads to the same order [22]. Incidentally, the change in $\pi$-energy of 4.0, 3.68 and 3.31 $\beta$ [22] predicts the same sequence for mechanism B [1]. *Braude et al.* stated that this reactivity sequence applied to all quinones [1]. This is however incorrect. With DDQ the sequence is **8** > **1** > **11**. Although the relative reactivities of the substrates are somewhat solvent dependent the reactivity order is retained in AcOH, benzene, dioxane and $CHCl_3$, and also holds for chloranil. In view of these conflicting results the reaction of benzoquinone was reinvestigated by competition experiments. Our results fully confirm the sequence **1** > **8** > **11** reported by *Braude et al.* [1].

The inversion of the reactivity sequence upon changing the quinone is inconsistent with the mechanism discussed above, so that the intervention of an additional factor must be considered. The analogy with *N*-methylacridan [13] [20] suggests that CT-complexes could be involved. Complexation could, in principle, lower the energy of hydride or proton transfer which occurs in the rate-determining step in any one of the mechanisms proposed. Unfortunately, reactions of our substrates with DDQ are too fast to allow identification of CT-complexes during dehydrogena-

Table 2. *Compilation of characteristics of CT-complexes from the literature*

| Donor | TCNE[a] | | DDQ[b] | | Chloranil | | Benzoquinone[f] |
|---|---|---|---|---|---|---|---|
| | $\tilde{\nu}$ (cm$^{-1}$) | $K_{ap}$ | $\tilde{\nu}$ (cm$^{-1}$) | $K$[c] | $\tilde{\nu}$ (cm$^{-1}$) | $K$[e] | $K$ |
| Hexamethylbenzene | 18350 | 302 | 16000 | 574 (47.3)[d] | 19400 | 28.9 | 0.66 |
| Pentamethylbenzene | 18330 | 106 | 16800 | (25.4)[d] | 20200 | 16.5 | 0.49 |
| | 19730 | | | | | | |
| Durene | 19200 | 39 | 17200 | 72.3 (14.2)[d] | 20900 | 10.4 | 0.40 |
| | 22700 | | | | | | |
| Mesitylene | 21690 | 22 | 19600 | 19.2 | 23300 | 5.9 | 0.24 |
| Xylene | 22100 | 11.3 (*o*) | 21100 (*o*) | | 24700 | 2.9 (*m*) | 0.21 (*p*) |
| | 23850 (*o*) | | | | | | |
| Toluene | 23530 | 4.7 | 22700 | | 27000 | 1.7 | |
| | 25330 | | | | | | |
| Benzene | 26040 | 2.1 | 24600 | | 29900 | 0.56 | |
| 1,3-Cyclohexadiene | 22500 | 0.91 | - | | | | |
| | 28600 | | | | | | |
| Cyclohexene | 24500 | 0.45 | - | | | | |

[a]) $CH_2Cl_2$, 25° [7] [26]. [b]) $CH_2Cl_2$ [25]. [c]) $CCl_4$, 25° [28]. [d]) $C_2H_4Cl_2$, 49° [20]. [e]) $C_6H_{12}$, 18–20° [29]. [f]) $CCl_4$, 33.5° [27].

tion. For chloranil, *Hashish & Hoodless* report a slight enlargement of the absorption band upon addition of **8**, but no association constants could be determined [19]. Complexation of compounds related to ours has however been investigated.

The limited amount of data available *(Table 2)* precludes definite conclusions. Nevertheless, some trends are clearly visible. The constants $K$ for complexation are higher with the strong acceptors DDQ and chloranil (half-wave potentials $\varepsilon_{red}^{1/2} = +0.51$ and 0.01, respectively) than for benzoquinone ($\varepsilon_{red}^{1/2} = -0.51$) [23] [24], and they are spread over a larger range with the former. In addition, the analogy with TCNE suggests stronger complexation with *o*-xylene, a reasonable model for **8**, than with **1** [25]. Although these trends constitute no proof, they are at least consistent with the hypothesis that complexation could lead to rate accelerations with the benzannelated compounds such as **8** and **11** but also with **9** and **12** *(Fig. 1)* in reactions with strong acceptors such as DDQ and chloranil, but less with benzoquinone. An alternative explanation for the inversion of the reactivity sequence must also be considered. Our expectation of the 'normal' sequence of **1** > **8** > **11** is based on the assumption of a late transition state on the reaction coordinate. This is only in part supported by experimental evidence. A plot of $\log k$ for dehydrogenation with DDQ *vs.* the $pK_R^{\oplus}$ [22] [30] of the corresponding carbenium ions *(Fig. 5)* gives a slope of *ca.* 0.3. Thus only a fraction of the energy difference between substrate and carbenium ion is reflected in the energies of activation. The hypothesis of a late transition state on the reaction coordinate is therefore questionable. On the other hand, reactions with early transition states on the reaction coordinate are subject to frontier orbital control [31]. Intermediate situations are conceivable where reactivity is determined by a blend of frontier orbital and product stability control. For the substrates under consideration the HOMO-energies, determined by photoelectron spectroscopy are as follows: **1**: – 8.80 eV [32], **8**: – 8.67, and **11**: – 8.78 eV [33]. Although the differences are small they lead to clearly different reactivity predictions from the changes in $\pi$-energies mentioned above. Typically, **8** is predicted to be the most reactive substrate for frontier-orbital controlled reactions. On these grounds we speculate that the inversion of the reactivity sequence upon introduction of electronegative substituents in the quinone is due to increasing predominance of frontier-orbital control over product stability control.

Substitution of the quinones with electron-withdrawing substituents increases their oxidation potential, and this corresponds to a lowering of the LUMO energies. For a constant donor, the HOMO-LUMO interaction will therefore increase with the oxidation potential of the quinone. The interaction will be weakest between benzoquinone and **1** and strongest between DDQ and **8** and so on. We suggest that

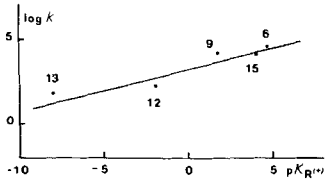



Fig. 5. *Plot of* log k *for dehydrogenation with DDQ* vs. *the* $pK_R^{\oplus}$ *of the corresponding carbenium ions*

these tendencies, superimposed on the trends predicted from changes in total $\pi$-energies (see above) could be responsible for the observed irregularities within the series of our substrates.

We are not yet in a position to prove unambiguously one or the other of these hypotheses nor can we rule out another factor which could be involved. In view of these uncertainties mechanistic extrapolations from these simple molecules to the more complex systems involved in biological reactions should be considered with caution.

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## Experimental Part

*Products.* Unless mentioned otherwise, the compounds used were purchased from *Fluka* and purified before use. 1,4-Dihydronaphthalene (**8**) was obtained by reduction of naphthalene with Na/EtOH [34]. 5*H*-Benzocycloheptene (**9**) was synthesized from benzosuberene [35] by the method of *Srivastava & Sukh Dev* [36]. 5*H*-Dibenzo[*a,d*]cycloheptene (**12**) was obtained in 85% yield by reduction of dibenzo[*a,d*]cyclohepten-5-one *(Aldrich)* with $NaBH_4$ in $CF_3COOH$ [37]. Catalytic hydrogenation afforded the dihydro derivative **13**. The synthesis of tri-*t*-butylcyclopropene (**14**) has been described [38].

*Kinetic measurements.* The spectrophotometric methods used for measuring reaction rates with DDQ [4] [5] and $Ph_3C^{\oplus}$ [6] have been reported previously. The spectra with repetitive scanning *(Fig. 2)* were recorded on a *UVIKON* 820 spectrophotometer.

*Reaction of* **1** *with chloranil.* A solution of 0.10 mmol of chloranil, 0.11 mmol of **1**, and 9 mg of acetonitrile as internal standard was heated in 0.6 ml of ($D_8$)dioxane to 100° in the probe of a *Varian XL-100* spectrometer. The integrals were recorded at regular time intervals. The results are displayed in *Figure 3.* From the data the ratio of the rate constants for disappearance of **1** and formation of benzene was found to be 1.01.

*Reaction of* **8** *with chloranil.* The reaction rate was determined by sealed ampoule techniques. The ampoules containing 0.5 ml of dichloroethane, $1.03 \times 10^{-2}$M in **8** and $1.93 \times 10^{-2}$M in chloranil were heated to 120° in a thermostatted oil bath. Samples were withdrawn at 5 min intervals and analyzed by GC. (*Hewlett-Packard 5830* instrument with *FFAP* column 5% on *Chromosorb G*) using phenetole as internal standard.

*Competition experiments.* Ampoules containing weighed amounts of benzoquinone or chloranil (*ca.* 1.0 mmol) and pairs of **1**, **8** and **11** in ratios of 2:1, 1:1 and 1:2 (*ca.* 0.5–1.0 mmol) in 3 ml of anisole containing an appropriate internal standard (toluene or triphenylmethane) were heated at 60° during 4–12 h. The content of the samples was analyzed by GC. and the relative rate constants determined from the relative variation of concentration of the substrates. *Table 3* summarizes the results.

Table 3. *Results of competition experiments*

| Substrate | Benzoquinone | | | Chloranil | | |
|---|---|---|---|---|---|---|
| | Ratio | $k_{comp}$ | $k_{rel}$ | Ratio | $k_{comp}$ | $k_{rel}$ |
| **1** | 2:1 | 2.4 | 100 | 2:1 | 0.80 | 100 |
| | 1:1 | 2.4 | | 1:1 | 0.69 | |
| | 1:2 | 2.3 | | 1:2 | 0.74 | |
| **8** | | | 43 | | | 135 |
| | 2:1 | 3.2 | | 1:1 | 2.46 | |
| | 1:1 | 4.2 | | | | |
| **11** | 1:2 | 3.9 | 11 | | | 40 |

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