methyl-$\Delta^{1(9)}$-octalone-2 (VI) provided the dione II in 50% yield after 15 hr.

VI
R = benzyl, cyclohexyl
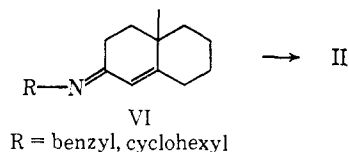
Like the autoxidation of enamines this oxidation is most likely a free-radical chain process which may pro-


VII
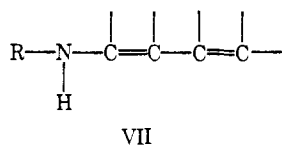
ceed *via* the enamine form VII of the Schiff bases. The slower rate of the uncatalyzed oxidation of the enamine I than that of the similar oxidation of Schiff base VI may be ascribed to steric factors. The methylene groups adjacent to the nitrogen atom in I may tend to prevent the electron transfer in the chain-initiation step.

Autoxidation of Schiff bases is strongly catalyzed by ferric chloride, which may not only act as an electron acceptor from the enamine form VII of the Schiff bases, but being a good Lewis acid may also promote the Schiff base–enamine tautomerism. On the other hand cupric chloride, a weak Lewis acid, proved to be a rather poor catalyst. For example, the cupric chloride catalyzed oxidation of VI, which contains on the basis of nmr spectral data about 35% of the enamine form,[10] gave the dione II in only 40% yield after 1 hr; the ferric chloride catalyzed oxidation of VI under similar conditions led to the dione II in 75–80% yield. The oxidation of the benzylamine Schiff base of 8,10-dimethyl-$\Delta^{1(9)}$-octalone-2, which on the basis of its nmr spectrum contains about 75% of the enamine form, was equally well catalyzed both by cupric chloride and ferric chloride. The preponderance of the enamine form in this case is undoubtedly due to the hyperconjungative effect of the C-8 methyl group which stabilizes the Δ^8 double bond. The product consisted primarily of a 3:1 mixture of the 8β- and 8α-hydroxy derivatives of the ketone showing that the oxygenation at the γ position is subject largely to stereoelectronic control. Interestingly the uncatalyzed oxidation of the benzylamine Schiff base of ergosterone, which according to its nmr spectrum exists entirely in the trienamine form, gave 6-ketoergosterone (mp 176–177°) in 91% yield after 1 hr.[11]

Further work along these lines is in progress.

(10) The Schiff base:enamine ratio did not alter significantly when treated with a catalytic amount of *p*-toluenesulfonic acid in refluxing benzene overnight.
(11) This facile oxidation is most probably due to the intermediacy of a highly resonance-stabilized radical cation VIII.
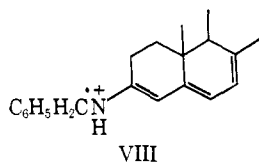
$C_6H_5H_2C\overset{\cdot+}{N}$
H
VIII

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Nonhydrogen Tautomerism and Other Chemical Rate Processes in Cyclohexadienones[1,2]

Sir:

Cyclohexadien-2,5-ones (**1**) and cyclohexadien-2,4-ones (**2** and **2'**) formally are nonhydrogen tautomers where X is the migrating group. Some chemical reactions of quinol ethers (X = OAr)[3] and quinol halogenides (X = Br)[4] show that true equilibria between **1** and **2** should be possible. We have inves-

1   2   2'
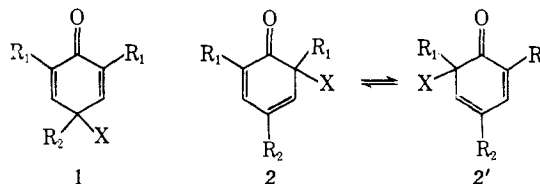
tigated several sterically hindered cyclohexadienones by nmr spectroscopy in the range from 0° to the temperature of decomposition (100–200°) and have found either the *para* form (**1**) or the *ortho* form (**2**). Compounds **1** give one signal for olefinic protons at τ 2.7–4.0 and one signal for R_1, whereas compounds **2** give an AB spectrum (J_{AB} = 2.0–2.8 cps) at τ 2.2–3.5 and two signals for R_1.

The *o*-quinol halogenides **2a** [R_1 = $C(CH_3)_3$; R_2 = CN; X = Br][5] and **2b** [R_1 = $C(CH_3)_3$; R_2 = NO_2; X = Br][4] show temperature-dependent spectra. At 0° **2a** and **2b** give the expected AB spectrum (**2a**: τ_A 2.72, τ_B 3.26, J_{AB} = 2.0 cps; **2b**: τ_A 2.24, τ_B 2.55, J_{AB} = 2.5 cps; olefinic protons) and two singlets (**2a**: τ 8.71, 8.79; **2b**: τ 8.70, 8.78; *t*-butyl groups). On warming, the signals of H_A and H_B as well as those of the *t*-butyl groups first collapse, then sharpen again on further heating. By using the Eyring equation the free enthalpy of activation can be calculated[6] (Table I).

An explanation for this phenomenon can be given if one assumes a reversible transition **2** $\rightleftharpoons$ **2'**. At sufficiently high temperatures this equilibrium is fast with respect to the nmr time scale. Thus we are able to show that bromine tautomerism indeed takes place in cyclohexadien-2,4-ones.[7]

From our nmr data alone we cannot draw any conclusion as to whether the rearrangement of the

(1) Innermolecular Motion by Nmr Spectroscopy. VII; VI: H. Kessler and W. Rundel, *Ber.*, **101**, 3350 (1968).
(2) The quinonoid state XI; X: A. Rieker and G. Henes, *Tetrahedron Lett.*, 3775 (1968).
(3) N. Zeller, doctoral thesis, 1968, University of Tuebingen.
(4) V. V. Ershov and A. A. Volod'kin, *Izv. Akad. Nauk SSSR, Ser. Chim.*, 336 (1965); *Chem. Abstr.*, **62**, 14520h (1965).
(5) E. Mueller, A. Rieker, K. Ley, R. Mayer, and K. Scheffler, *Ber.*, **92**, 2278 (1959).
(6) H. G. Schmid, H. Friebolin, S. Kabuss, and R. Mecke, *Spectrochim. Acta*, **22**, 623 (1966); A. Rieker and H. Kessler, *Tetrahedron*, **23**, 3723 (1967).

Table I. Nmr Parameters[a] and Free Enthalpy Barriers for Cyclohexadienones

Compd	Process[b]	Obsd on	$\Delta\nu$, cps	T_c, °C	$\Delta G_c^{\ddagger}$, kcal/mol	Solvent
2a	α	H_A; H_B	32	55	16.5	CDCl₃
	α	R_1	5	34	16.5	CDCl₃
	α	R_1	7	35	16.4	C_6H_6
	β	R_1	18	−105	c	CS₂
2b	α	H_A; H_B	19	63	17.2	CDCl₃
	α	R_1	5	47	17.2	CDCl₃
	β	R_1	21	−83	c	CS₂
1c	β	R_2	30	−90	9.0[d]	CS₂
1d	β	R_2	41	−89	8.9[d]	CS₂[e]

[a] Varian A-60 instrument, frequency 60 Mcps. [b] α = tautomer‑ism, β = hindered rotation of the allylic t-butyl group. [c] See text. [d] Obtained by a graphic method for the calculation of k in the case of unequal populations of the invertomers; see A. Jaenhke, H. Muensch, H. G. Schmid, H. Friebolin, and A. Mannschreck, *J. Mol. Spectrosc.*, in press. [e] Frequency 100 Mcps.

bromine atom proceeds by an intramolecular or inter‑molecular path and whether free radicals or ions are involved. However, an intermolecular radical mech‑anism is not unlikely, for solutions of **2a** show weak paramagnetism.[8] The epr spectrum is identical with that of 4-cyano-2,6-di-t-butylphenoxyl.[5] Additional evidence for a radical mechanism could be seen in the fact that reaction of this radical with bromine yields **2a**.[5]

At very low temperatures we observe a new effect in the nmr spectra of **2a** and **2b**. The high-field peak corresponding to the allylic t-butyl group[9] broadens and splits below −100° into at least two peaks. Only one of these is well separated from the peak of the vinylic t-butyl group. Thus, activation parameters cannot be evaluated. A similar effect (duplication of the signal of the t-butyl group at the saturated p-carbon atom) is observed in cyclohexadien-2,5-ones, *e.g.*, **1c** [$R_1 = R_2 = C(CH_3)_3$; X = Br][10] and **1d** [$R_1 = R_2 = C(CH_3)_3$; X = OCH₃].[11] In these cases, the doublet lines are sufficiently separated from the signal of the vinylic t-butyl groups. Their intensity ratio amounts to 1:2.

This phenomenon can be caused either by slow ring inversion, I ⇌ II, and, simultaneously, fast rotation of the t-butyl group around the single bond s, or by slow rotation around s with the ring planar on the nmr time scale (III).

There is good evidence for the validity of the latter alternative (slow rotation around s). (1) The intensity ratio of split t-butyl signals is *ca.* 1:2 for the cyclo‑hexadien-2,5-ones mentioned in Table I.[12] According

(7) From our measurements one cannot conclude, however, that the *para* form (**1**) is involved in this equilibrium.

(8) Conditions used for epr measurements are the same as used for nmr measurements, *e.g.*, 0.2 M solutions of **2a** in benzene (atmosphere of nitrogen) contain 0.02% of 4-cyano-2,6-di-t-butylphenoxyl (DPPH as reference).

(9) This assignment results from comparison with a large number of o-quinonoid and p-quinonoid compounds.
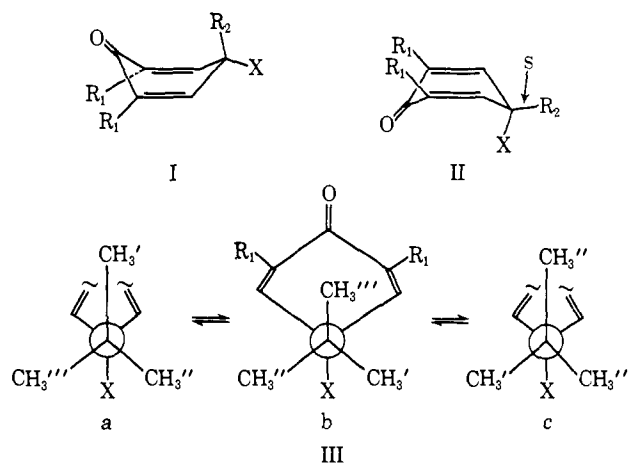
(10) E. Mueller, K. Ley, and W. Kiedaisch, *Ber.*, **87**, 1605 (1954).

(11) A. Rieker and N. Zeller, *Z. Naturforsch.*, **23b**, 463 (1968).

(12) During the preparation of this manuscript we have investigated further compounds of type **1** [$R_1=C(CH_3)_3$; X = OH, OC₆Cl₅]
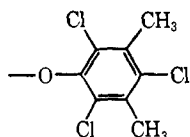
For these compounds the intensity ratio is also nearly 1:2.

to III, this ratio would be expected in the case of slow rotation around s, because each rotamer (a, b, c) comprises two magnetically equivalent methyl groups. For the ring inversion I ⇌ II, on the other hand, the intensity ratio should vary by altering the *para* sub‑stituent X. (2) The methoxy signal of **1d** shows no broadening down to −100° (100 Mcps). Ring inver‑sion should, however, produce two signals for the methoxy group. (3) The signals of the vinylic t-butyl groups are unaffected by lowering the temperature. For ring conformational interconversions (I ⇌ II) R_1 in I would not be equivalent to R_1 in II. In prin‑ciple, then, the spectra at −100° of **1c** and **1d** might be expected to show also two signals for these groups.[13] (4) The $\Delta G_c^{\ddagger}$ value of approximately 9 kcal/mol for **1c** is unexpectedly high for ring inversion,[14] whereas hindered rotation around single bonds may involve such high barriers.[17] Our observations concerning the o-quinonoid derivatives **2a** and **2b** should be interpreted analogously.

Unequivocal proof for the discussed rotation mech‑anism would be obtained if compounds could be investigated which in any one rotamer contain three methyl groups in magnetically nonequivalent positions (three signals, 1:1:1). Such compounds would be of the type **1** with two different R_1's or of the type **2a**, **2b**. In the last two cases, peak splitting cannot be observed for practical reasons, as described above. With the data available so far, we prefer the mechanism of hindered rotation around bond s for the low-tem‑perature nmr effects.

(13) Because of the structural similarity of R_1 in I and II this effect might, however, be too small to be observable.

(14) For cyclohexadienes a low barrier of ring inversion has been proposed.[15] As far as we know, ring inversion, as observed by nmr, has been found only in methylenecyclohexadienes, showing a particular steric hindrance.[16]

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(16) D. Y. Curtin, C. G. Carlson, and C. G. McCarty, *Can. J. Chem.*, **42**, 565 (1964).

(17) R. A. Newmark and C. H. Sederholm, *J. Chem. Phys.*, **43**, 602 (1965); J. P. N. Brewer, H. Heaney, and B. A. Marples, *Chem. Commun.*, 27 (1967).

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