

THE BEHAVIOUR IN ACID OF 2-BROMO-4,4-DIMETHYLCYCLOHEXA-2,5-DIENONE:

A SURPRISINGLY RAPID DIENONE-PHENOL REARRANGEMENT

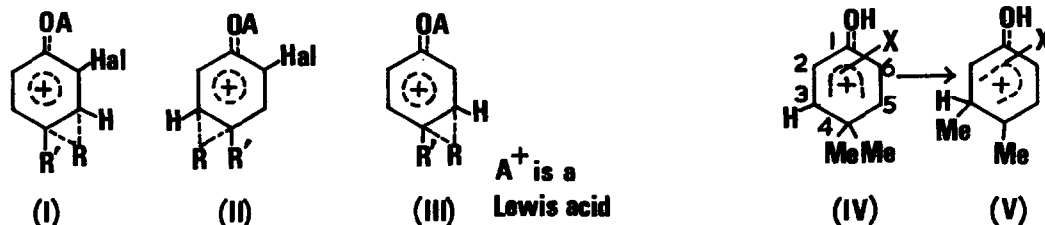
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(Received in UK 28 November 1974; accepted for publication 5 December 1974)

In dienone-phenol rearrangements of monocyclic¹ and steroidal² 2-chloro- and 2-bromocyclohexa-2,5-dienones and particularly of the 2,6-dibromo-analogues,^{1,3} using acetic or propionic anhydride with mineral acid catalysis, the halogen atom causes a significant rate reduction compared to the non-halogenated compounds. It has been suggested² that the halogen atom may reduce the carbonyl basicity and hence the amount of reactive dienone cation present in an acidic medium, or¹ destabilise transition state (I) relative to (II) and, presumably, (III).



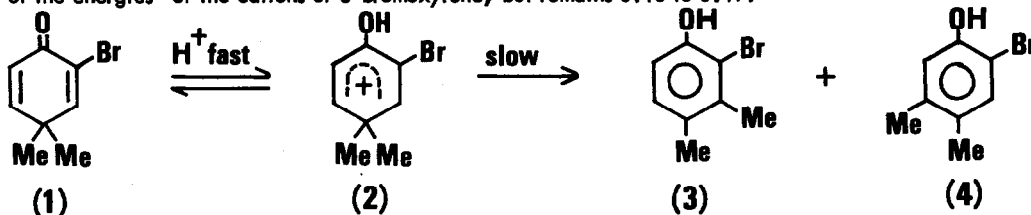
We have measured the basicity and kinetics of rearrangement of the title bromodienone (1) in aqueous sulphuric acid at 25°C using the methods of refs. 4 and 5. The results are used in a correlation of rearrangement rates with cyclohexadienone structure.

Dienone (1) has a protonation equilibrium which closely follows the amide acidity function H_A with a pK , or H_A at half-protonation, -4.1 ± 0.15 . It is thus much less basic than its 2,4,4-trimethyl⁵ and 4,4-dimethyl⁴ analogues (pK -2.7 ± 0.2 , and -2.4 ± 0.05).

The rate constant k_1 for rearrangement of the cation (2) which is present in the acid (see Eqn. 1) is remarkably large. In 70% H_2SO_4 (H_0 -5.80), which we take⁵ as a standard acid for comparing such rates, $k_1 = (3.2 \pm 0.4) 10^{-3} \text{ sec}^{-1}$, which is four times faster than the 2,4,4-trimethyl analogue, and ten times faster than the 4,4-dimethyl analogue. The acidity dependence of k_1 is unusually steep, but (2) rearranges

faster than the 4,4-dimethyl analogue at all acidities studied. Clearly, arguments that the bromine atom destabilises (I) or (II) are unimportant. The energies of (I) and (II) with $A=H$ are almost equal; n.m.r. analysis of the products gives a ratio of (3) to (4) of 54 ± 6 to 46 ± 6 , with no obvious trend with acidity or reaction time.

The rate constants k_1 for rearrangement of cations (IV) to (V) in the standard acid, 70% H_2SO_4 , at 25°C are related to substituent σ^+ values by Eqn. 2, for all cations (IV) we have studied. A group X at C-2 requires σ^+_{meta} in (IV) and σ^+_{ortho} in (V). Values of σ^+_{ortho} are known for many groups X, for reactions which do not suffer strong steric effects,^{6,7} but we believe the value given for Br⁶ may be unreliable. Studies of the stabilities of the isomeric cations of 5-bromo-1,3-xylene⁸ give $\sigma^+_{ortho, Br} = \sigma^+_{para, Br} + \sigma^+_{ortho, Me} - \sigma^+_{para, Me}$ i.e. +0.184. This value is modified slightly by consideration of the energies⁸ of the cations of 3-bromoxylene, but remains 0.18 to 0.19.*



$$\text{Rate} = d[(1) + (2)]/dt = k_{\text{obs.}} [(1) + (2)] = k_1 [(2)] \quad \text{and} \quad k_1 = k_{\text{obs.}} \left\{ 1 + \frac{[(1)]}{[(2)]} \right\} \quad \text{Eqn. 1}$$

$$\log k_1 = -0.62 (H_0 + \log [H_2SO_4]) - 5.47 \pm 0.05; \quad k_1 \text{ in sec.}^{-1}, \quad \text{correlation coefficient } 0.997$$

$$\log k_1 = -3.97 \pm 0.24 - 3.96 \left[\left(\sum \sigma^+_{X(V)} \right) - \left(\sum \sigma^+_{X(IV)} \right) \right] \text{ in } 70\% H_2SO_4 \text{ at } 25.0^\circ C \quad \text{Eqn. 2}$$

Correlation coefficient 0.96, over a 300 fold range of rates.

References

- 1 F. G. Bordwell and K. M. Wellman, *J. Org. Chem.*, 1964, **29**, 509.
- 2 D. N. Kirk and V. Petrow, *J. Chem. Soc.*, 1959, 788.
- 3 H. H. Inhoffen and W. Becker, *Chem. Ber.*, 1953, **86**, 116.
- 4 K. L. Cook and A. J. Waring, *J. Chem. Soc., Perkin II*, 1973, 84 and 88.
- 5 M. J. Hughes and A. J. Waring, *J. Chem. Soc., Perkin II*, 1974, 1043.
- 6 C. W. McGary, Jr., Y. Okamoto and H. C. Brown, *J. Amer. Chem. Soc.*, 1955, **77**, 3037.
- 7 H. V. Ansell, J. LeGuen and R. Taylor, *Tetrahedron Letters*, 1973, 13.
- 8 D. M. Brouwer, *Rec. Trav. Chim.*, 1968, **87**, 335 and 342.
- 9 S. W. Benson, 'Thermochemical Kinetics', *J. Wiley and Sons*, 1968.

*When X is a 2-methyl group the change (IV) to (V) introduces a gauche Me-Me interaction⁹ of 0.5 kcal mol.⁻¹. We assume that this affects the transition state also, reducing $\log k_1$ by up to 0.36 (from the Eyring equation) compared to the value given by Eqn. 2. We assume that the steric interaction between a 2-bromine atom and the 3-methyl group in (V, X=2-Br,) the precursor of (3), is negligibly small, [steric hindrance seems to be relatively unimportant in nuclear bromination in toluene, as reflected in the ortho/para ratio (see ref. 7)].