Dynamic Nuclear Magnetic Resonance Evidence for Acetyl Exchange between *peri*-Oxygens of the Naphthazarin System

By I. C. CALDER,* D. W. CAMERON, and M. D. SIDELL

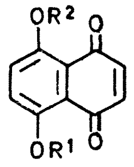
(*Department of Organic Chemistry, University of Melbourne, Parkville, Victoria* 3052, *Australia*)

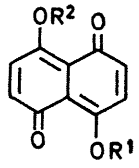
Summary Variable-temperature n.m.r. studies of naphthazarin mono- and di-acetates have shown the occurrence of rapid intramolecular acetyl exchange.

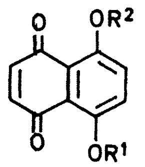
TAUTOMERISM in naphthazarin (I) between various forms (Ia—c) is too rapid to be observed by n.m.r.[1] at room temperature. On the other hand, the spectrum of naphthazarin diacetate (II) is consistent with a single tautomer (IIa).[2] However, recent work on the chemistry of *C*-substituted derivatives of this diacetate indicates that intramolecular acetyl shifts *e.g.* (IIa ⇌ c) can occur under remarkably mild conditions.[3] We present n.m.r. evidence for rapid shifts of this kind in naphthazarin diacetate (II) and monoacetate (III) and have calculated relevant thermodynamic parameters.

The mono- and di-acetates[2] were prepared directly from sublimed naphthazarin, the former being obtained in *ca.* 90% yield by selective acetylation with acetic anhydride

The 100 MHz n.m.r. spectrum of naphthazarin diacetat (II) in $C_6D_5NO_2$ showed signals from the acetate protons at δ 2·24 the quinonoid protons at δ6·56 and the aromatic protons at δ 7·28. On heating, the signals from the ring protons began to broaden at 170° and significant broadening was observed at 200°.


(a)


(b)


(c)

(I) $R^1 = R^2 = H$
(II) $R^1 = R^2 = Ac$
(III) $R^1 = H, R^2 = Ac$

The spectrum of the monoacetate (III) in $C_6D_5NO_2$ showed signals from the acetate protons at δ2·38, the hydroxyl at δ12·34, the quinonoid protons at δ 6·67 and 6·70 (AB quartet; *J* 10·0 Hz) and the aromatic protons at δ 7·10 and 7·20 (AB quartet; *J* 8·5 Hz). Broadening was observed at 120° and almost complete coalescence at 190°C (Figure, a). For both compounds the acetate signals remained sharp throughout the temperature ranges studied.

The exchange broadened spectra were calculated using the DNMR programme of Binsch[4] and those corresponding to the spectra in the Figure (a) are shown in (b). The thermodynamic parameters are listed in the Table.

TABLE

Compound	E_a kcal mole^{-1}	log A	$\Delta G\ddagger$ kcal mole^{-1}
(II)	21·8	12·3	22·3
(III)	22·8	11·5	24·5

While spectra could not be obtained corresponding to the limiting fast-exchange situation, the results are consistent with intramolecular exchange of acetyl groups between *peri*-oxygen atoms. Intermolecular acetyl transfer takes place, but is slow compared to the intramolecular process and only becomes appreciable at temperatures above 180°. The intermolecular process results in an equilibrium mixture of naphthazarin and the mono- and di-acetates. However, at 170° this equilibrium takes at least 8 h to be attained.

The calculated spectra are for the exchanges (IIa $\rightleftharpoons$ IIc) and (IIIa $\rightleftharpoons$ IIIc), with no allowance for a contribution from (IIb) or (IIIb). The close similarity between observed and calculated spectra indicates that the lifetime of any 1,5-quinone intermediate must be very small. The similarity of the two activation energies suggests that the rate-determining step is the transfer of a single acetyl group, transfer of the second group, acetyl or proton, following rapidly As far as we are aware this is the first

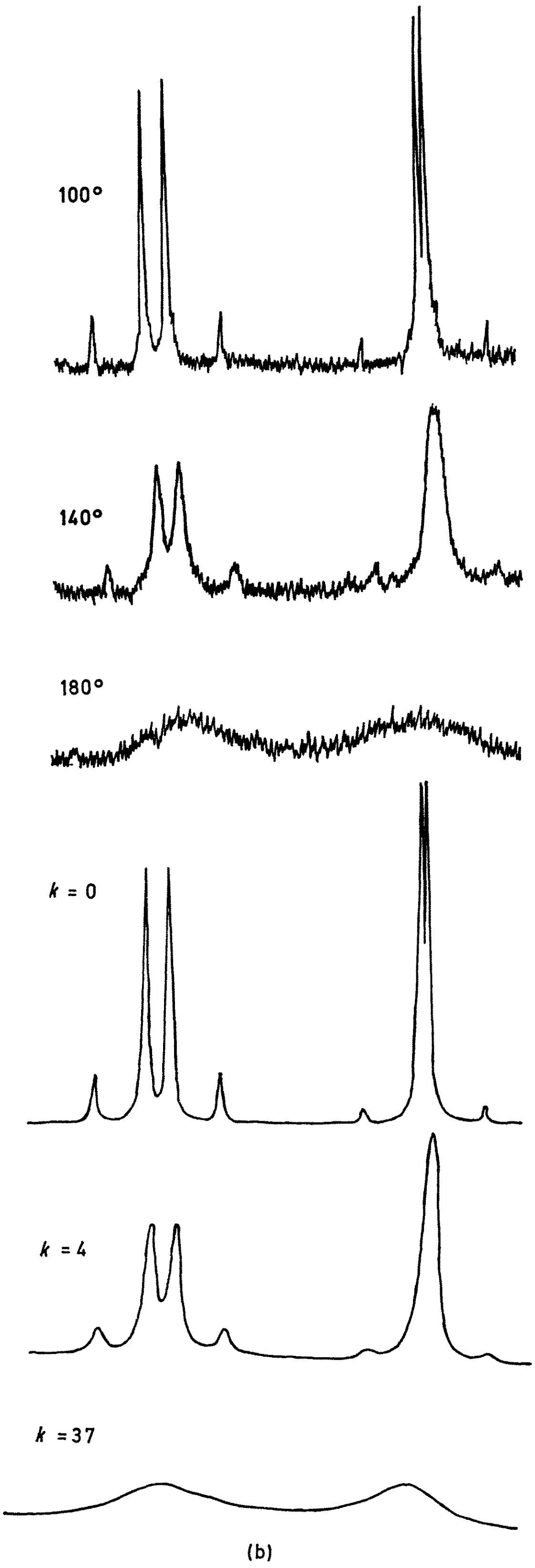


FIGURE. 100 *MHz spectra of naphthazarin monoacetate* (II); (a) *observed*, (*b*) *calculated*.[6]

reported rapid transfer of acetyl groups on the n.m.r. time-scale and further work is being carried out on related systems.

We are indebted to the Australian Research Grants Committee for a Research Fellowship (to M.D.S.).

(*Received, December 29th,* 1970; *Com.* 2255.)

---

[1] R. E. Moore and P. J. Scheuer, *J. Org. Chem.*, 1966, **31**, 3272.

[2] L. A. Cort and P. A. B. Rodriguez, *J. Chem. Soc.* (*C*), 1967, 949.

[3] S. Alvarado, F. Farina, and J. L. Martin, *Tetrahedron Letters*, 1970, 3377; H. Brockmann and A. Zeek, *Chem. Ber.*, 1968, **101**, 4221; R. G. Cooke and J. B. Robinson, personal communication.

[4] G. Binsch, *J. Amer. Chem. Soc.*, 1969, **91**, 1304. The programme was obtained from the Quantum Chemistry Program Exchange.