Tetrahedron, 1957, Vol. 1, pp. 169–171. Pergamon Press Ltd., London

NOTES

Dehydrobrucinolone, *iso*brucinolone, and *iso*strychinolones-I and -II

(*Received* 28 *December* 1956)

LEUCHS and Brewster[1] oxidised crude brucinolone-B acetate with permanganate in acetone and obtained a small amount of a compound analysing as $C_{23}H_{22}O_6N_2$ or $C_{23}H_{24}O_6N_2$. Later, this substance was obtained by heating brucinolone-C in acetic anhydride containing sodium acetate. It was suggested[2] that it was the acetate of either a dehydrobrucinolone or of an unknown brucinolone. The acetyl group could be removed with methanolic ammonia to give a compound $C_{21}H_{20}O_5N_2$ or $C_{20}H_{22}O_5N_2$.

In attempting to repeat this work we obtained only brucinolone-C acetate on heating brucinolone-C in acetic anhydride as directed. However, when brucinolone-C acetate was heated with one equivalent of benzoyl peroxide in acetic anhydride, a good yield of an acetate $C_{23}H_{22}O_6N_2$ was obtained, which from its analysis and mode of formation must be dehydrobrucinolone acetate. Similarly, brucinolone-B or -C, heated with benzoyl peroxide in acetic acid, gave dehydrobrucinolone, agreeing closely in properties with Leuchs' ammonolysis product.

The ultra-violet absorption curves of dehydrobrucinolone and its acetate were identical (λ_{max} 237, 311, 350 mμ; log ε_{max} 4·3, 3·7, 3·9 respectively). These resemble the absorption curve for dehydrostrychninolone[3] (λ_{max} 340 mμ; log ε_{max} 3·9); the additional peak at 311 mμ is to be ascribed to the effect of the methoxyl groups.[4] Dehydrobrucinolone must consequently possess the *N*-phenyl-α-pyridone structure like dehydrostrychninolone.

*iso*Brucinolone[1] has the same ultra-violet absorption as brucine and so must be a $\beta\gamma$-unsaturated amide,[5] confirming some rather tentative evidence from oxidation experiments.[6]

*iso*Brucinolone must, consequently, be epimeric with brucinolone-B at $C_{(21)}$. The shift in molecular rotation (Δ) attendant on the inversion at this centre is approximately the same as that in going from strychninolones-B and -C to the *iso*strychninolones-I and -II[7] as shown below. Hence, the two latter compounds probably have the $\beta\gamma$- and $\alpha\beta$-unsaturated amide structures respectively.

MOLECULAR ROTATIONS

				Δ value
Brucinolone-B	−91·7°	*iso*Brucinolone	+129·9°	+221·6°
Strychninolone-B[6]	−77·3°	*iso*Strychninolone-I[7]	+148·1°	+225·4°
Strychninolone-C[5]	−565·5°	*iso*Strychninolone-II[7]	−504·7°	+157·8°

EXPERIMENTAL

Brucinolone-C. The following method was found to be considerably more convenient than that published.[2] Crude brucinolone-B (4·0 g) in pyridine (40 c.c.) and 2·5% sodium hydroxide solution (160 c.c.) was heated on the steam-bath for 90 min. The acidified solution was extracted with chloroform (5 × 10 c.c.), and the dried chloroform-extract passed through a short column of alumina. The residue crystallised from methanol in needles (1·1 g), m.p. 180–184°, raised to 185–186° by a second crystallisation from methanol, $[\alpha]_D^{18}$, −147° (*c.* 0·184 in acetic acid).

Dehydrobrucinolone. Brucinolone-C (0·40 g) and benzoyl peroxide (0·25 g) in glacial acetic acid (5 c.c.) were heated on the steam-bath for 30 min. The solution, on dilution with water, gave brown needles of dehydrobrucinolone (0·1 g), m.p. 299–301°. Recrystallisation from ethanol (charcoal)

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[1] Leuchs and Brewster *Ber.* **45**, 201 (1912).

[2] Leuchs and Pierce *ibid.* p. 2653; Leuchs, Hellriegel, and Heering *Ber.* **54**, 2177 (1921).

[3] Prelog, Kocor, and Taylor *Helv. Chem. Acta* **32**, 1052 (1949).

[4] Prelog and Szpilfogel *ibid.* **28**, 1669 (1946).

[5] Prelog, Szpilfogel, and Battegay *ibid.* **30**, 366 (1947).

[6] Leuchs, Gladkorn, and Hellriegel *Ber.* **56**, 2472 (1923).

[7] Leuchs and Ritter *Ber.* **52**, 1583 (1919).

furnished pale fawn needles, sintering at 295°, m.p. 307–310° (dec.), $[\alpha]_D^{30}$? −388° (c. 0·34 in acetic acid) (Found in air-dried material: C, 58·7, 58·9; H, 5·9, 6·0. Calc. for $C_{21}H_{20}O_5N_2$, 2·5 H_2O: C, 59·0; H, 6·4%. Found in material dried at 130°/15 mm: C, 65·9; H, 5·2; N, 7·4. Calc. for $C_{21}H_{20}O_5N_2$: C, 66·3; H, 5·3; N, 7·4%). Dehydrobrucinolone gave a yellow colour, rather than the usual orange-red of brucine derivatives, with nitric acid.

Dehydrobrucinolone acetate. Brucinolone-C acetate (0·6 g) and benzoyl peroxide (0·35 g) in acetic anhydride (5 c.c.) were warmed on the steam-bath for 1 hour. The yellow solid (0·4 g) which separated was crystallised from ethanol as fine yellow needles, sintering at 290°, m.p. 304°, $[\alpha]_D^{20}$, −429° (c. 0·892 in acetic acid) (Found: C, 65·5; H, 4·9; N, 6·4. Calc. for $C_{23}H_{22}O_6N_2$: C, 65·4; H, 5·2; N, 6·6%).

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Note on the transmission of free radical character through a conjugated system

225.

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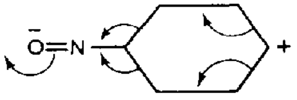
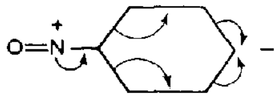
IN an early paper entitled Polarisation of Nitrosobenzene[1] the author drew attention to the possible overlapping "enoid" and "onoid" conjugated systems in nitrosobenzene and suggested that they might be present together in this and simliar cases



enoid displacement
or polarisation



onoid displacement
or polarisation

Although the interpretation which follows was not excluded by the language used, the intention was to postulate *activations* in two different senses, both of which were feasible. The emphasis was on the *electron displacements* responding to the approach of a reagent rather than on the hybridisation within the normal molecules resulting from the opposing tendencies. Subsequently, in lectures and university teaching the idea of polarisation in the course of a reaction was always prominent. It is by no means the present intention to abandon this conception, which certainly must always apply to the completion stages of a reaction process. But it is now desired to point out that the electronic conditions may be such that a reaction can be *initiated* in either sense in the normal molecules, identifiable sites in which may possess free radical character and hence may be at the same time electron-donor and electron-acceptor in quality.

Furthermore, free radical character may be transmitted along a conjugated chain exactly as we originally postulated the transfer of unshared electrons or electron defect.[2]

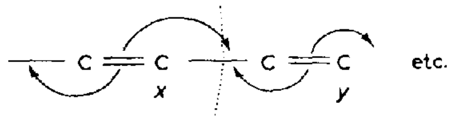
The fundamental character of a free radical site is that the atom concerned has both (1) unshared electron or electrons and (2) an incomplete electron configuration. In regard to (1), every atom is potentially an electron-donor if it bears an unshared electron (or electrons), even if the electrical field at the point considered is positive. It is generally true that an adverse electrical field will diminish in varying degree the ease with which electron coupling or electron-nucleus coupling occurs but it does not totally prohibit such events. It is even possible for an atom site to have an actual electrical charge and to accept or donate electrons in the opposite sense. A^+ can donate electrons if it bears any that are unshared, and B^- can accept electrons if the B configuration is incomplete.

The well-known fact that free radical reagents attack the *p* position of monosubstituted benzenes whatever the reaction of the substituent, is clearly due to the two circumstances (1) that conjugated aromatic systems are always activated in the *p* (or *o*) position, which either acquires unshared electron value or becomes configurationally defective in electrons and (b) that free radicals can either accept or donate electrons.

It should be noted that when two identical atoms or free radicals unite, $R\cdot$ and $R\cdot$ giving $R{:}R$, the question of electron donor or acceptor becomes meaningless. However, when $A\cdot$ joins with $B\times$ to $A\overset{\times}{\cdot}B$, there may be a recognisable distinction.

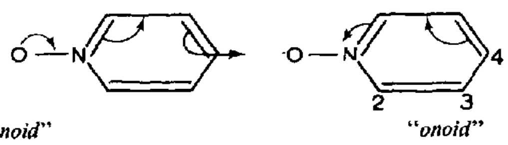
Free radicals can therefore be classified in accordance with these proclivities, but this interesting side-issue need not be pursued for the present purpose. It may, however, be noted that a classification could be predicted on theoretical grounds, or based on experimental observation of the relative proneness of a series of free radical reagents to attack systems with unshared electron sites, or those defective in electron configuration. Returning to the case of nitrosobenzene, it will now be clear that the *p*-carbon atom has free radical character in accordance with the above analysis. The "enoid" and "onoid" systems are now assumed to operate together and reach a hybrid.

This type of "push-pull" double displacement originates in the peculiar nitroso group, but it will be apparent that conjugated relay is theoretically feasible beyond the *p*-position, as shown in the symbol:



Here C-*x* corresponds to the *p*-position in nitrosobenzene and its character is relayed to C-*y*.

There are many applications of these views which will later be considered in more detail. An interesting example is pyridine-*N*-oxide



The simultaneous occurrence of the two types of displacement shown gives free-radical character to C-4.

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[1] R. Robinson *J. Soc. Chem. Ind. XLIV*, 456 (1925).

[2] W. O. Kermack and R. Robinson *J. Chem. Soc.* **121**, 427 (1922).