Photochemical Behaviour of Biased Homo-conjugated Ketones: Details of an Oxa-di-π-methane Rearrangement

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The acetone sensitized irradiation of the three spiro[5.5]undeca-1,3-dien-7-ones (1),(2), and (3) leads to two types of annelated bicyclo[3.1.0]hexen-2-yl ketone products, the structures of which were assigned by n.m.r. spectroscopy and confirmed by X-ray crystallography; the results are interpreted in terms of a substitution-influenced 1,2-acyl shift, involving one or both double bonds, with an oxa-di-π-methane type mechanism.

We are currently studying the photochemical behaviour of cyclohexa-1,3-dien-5-yl ketones as a function of the geometry of the two homo-conjugated chromophores.[1,2] Here we discuss this with respect to the oxa-di-π-methane (ODPM) rearrangement.

Our results[1] suggested that 2-methylspiro[5.5]undeca-1,3-dien-7-one (1) undergoes electrocyclic opening from the π,π^* excited state and α-cleavage from the n,π^* singlet excited states, but rearranges from triplet excited states by a 1,2-acyl shift to give two annelated bicyclo[3.1.0]hexen-2-yl systems
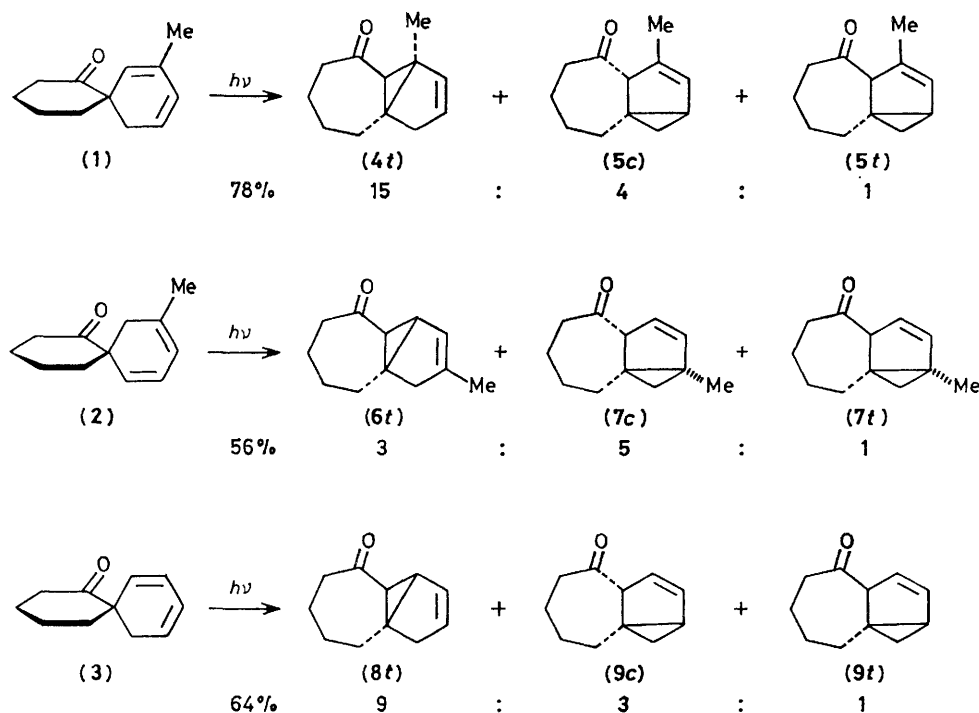
Scheme 1

(4) and (5). We wished to determine (i) the scope and generality of the rearrangement and (ii) why and to what extent is this a normal ODPM rearrangement (*i.e.* involving only one of the two available double bonds) as opposed to one in which the whole diene is involved, as was shown to be the case for the 1,2-dihydrophthalimides.[3]

Comparison of the photochemical behaviour of (1), (2), and (3)[4] was interesting. While the products from singlet excited states (λ254 and 300 nm) were as expected,[1] and will be reported in a full paper, triplet energy transfer (acetone; 300 nm) to (1), (2), and (3) yielded various rearranged products (Scheme 1)†whose structures were assigned unequivocally. All were found to be 1,2-acyl shift products of (1), (2), and (3): (4*t*), (6*t*), and (8*t*), respectively, are *trans*-tricyclo[5.4.0.0^{7,11}]undec-9-en-2-ones formed by involvement of only one double bond in the ODPM rearrangement while the isomeric products (5), (7), and (9) (*cis* and *trans* pairs in each case) are tricyclo[5.4.0.0^{7,9}]-undeca-10-en-2-one derivatives. On direct irradiation at 350 nm, only the corresponding *trans*-tricyclo[5.4.0.0^{7,11}]-undeca-9-en-2-ones (4), (6), and (8) were isolated.[1] Gross structural assignment was achieved spectroscopically, in particular by detailed n.m.r. studies which showed a consistent pattern for the series (4), (6), and (8) and (5), (7), and (9).†However, the ring-junction geometry could not be assigned readily, and so we studied one compound from each series by *X*-ray crystallography. The oximes of (7*c*) and (8*t*) had the expected structures with the *cis*- and *trans*-configuration, respectively. Chemical interconversion within all the *trans*–*cis*-pairs proved the correctness of all the assignments shown (Scheme 1).

The *X*-ray measurements were carried out on a CAD 4F diffractometer. Intensity data were collected using mono-chromatized Mo radiation, in the range $1° \leqslant \theta \leqslant 27°$ using the

θ–2θ scan technique. The structures were solved by MULTAN 78[5] and were refined with the aid of local least-squares programs.[6] All the hydrogen atoms were located on the difference map, except the hydroxy-hydrogen in the oxime of (7*c*).‡

Figure 1 shows parallel projections of the two molecules. The pattern of the dihedral angles shows that (i) the ring junction at the C(1)–C(7) bond is *cis* for the (7*c*) oxime and *trans* for the (8*t*) oxime (Figure 1), (ii) the seven-membered rings adopt somewhat distorted chair conformations, the distortion in (7*c*) being greater, and (iii) the cyclopentene rings are very nearly planar, as expected. A detailed analysis of these structures will be reported elsewhere.

Three mechanistic pathways may be invoked to account for the rearrangements (Scheme 2; by analogy with those proposed for β,γ-unsaturated ketones[7d,8]): (i) α-cleavage to give an acylcyclohexadienyl diradical, (ii) a concerted ($_\sigma 2 + _\pi 2$ and $_\sigma 2 + _\pi 4$) rearrangement, and (iii) intermediacy of a carbonyl–C-2-bonded diradical.[7]

We believe that mechanism (i) is not favoured [owing to the lack of electron density in the 2-position of the pentadienyl radical[7] and the high energy content of the cyclopropyl radical (Scheme 2, pathway α)[7d,9] although the energy content is less for the cyclopentenyl radical (pathway β) intermediate[3,10]] and

‡ *Crystal data:* for the oxime of (7*c*), $C_{12}H_{17}NO$, $M = 191.27$, monoclinic, space group $P2_1/n$, $a = 8.665(1)$, $b = 10.201(3)$, $c = 12.374(2)$ Å, $\beta = 91.61(1)°$, $Z = 4$, 2077 measured reflections, 1283 independent reflections, $I > 3\sigma(I)$, $R = 0.045$, $R_w = 0.058$, number of parameters $= 191$; for the oxime of (8*t*), $C_{11}H_{15}NO$, $M = 177.25$, monoclinic, space group $P2_1/n$, $a = 6.902(3)$, $b = 13.182(2)$, $c = 10.722(2)$ Å, $\beta = 101.44(2)°$, $Z = 4$, 1976 measured reflections, 1412 independent reflections, $I > 3\sigma(I)$, $R = 0.036$, $R_w = 0.047$, number of parameters $= 178$. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

(a)

(b)
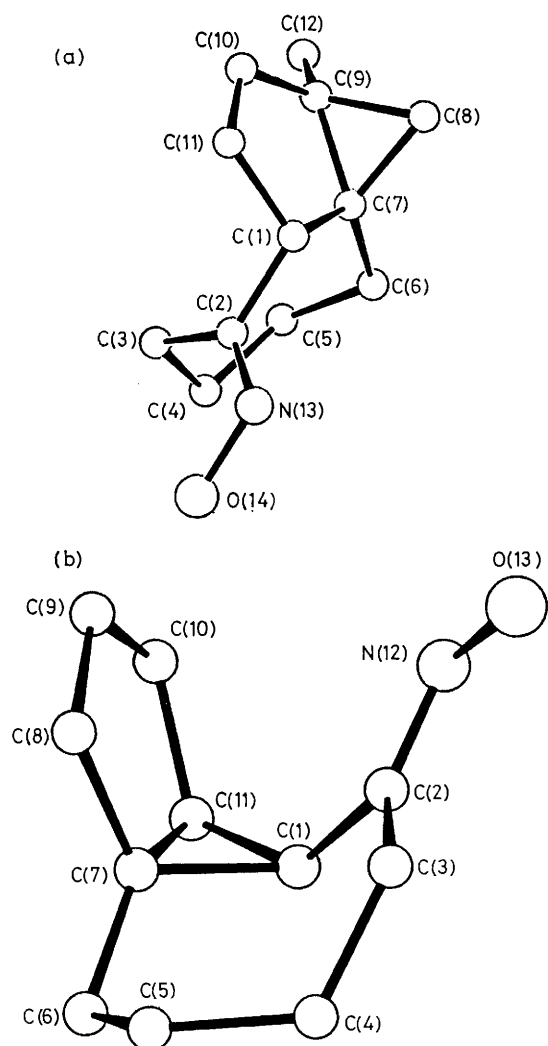
Figure 1. Molecular structure of (a) the oxime of *cis*-9-methyl tricyclo[5.4.0.0⁷,⁹]undeca-10-en-2-one (**7c**) and (b) the oxime of *trans*-tricyclo[5.4.0.0⁷,¹¹]undeca-9-en-2-one (**8t**).

this is supported by the absence of any of the expected hydrogen abstraction products[1] and by the fact that *trans*-fused rearranged products prevail over the more stable, unstrained *cis*-isomers (Scheme 1). Mechanisms (ii) and (iii) fit the experimental results well, and it is difficult to distinguish between them. Thus, (ii) may also be envisaged as a 'concerted' triplet mechanism[11] taking place as shown in Scheme 3, *i.e.* in ($_\sigma 2_a + \pi 2_a$)[12] fashion to yield (**4t**), (**6t**), or (**8t**) and in ($_\sigma 2_s + _\pi 4_a$ or $_\sigma 2_a + _\pi 4_s$) fashion to give (**5t**, *c*), (**7t**, *c*), and (**9t**, *c*) respectively. The occurrence of the C-2, C-6 bonding mode may be attributed mainly to proximity effects, in contrast with the electron density effects causing the C-4, C-6 bonding mode. Moreover, the exclusive isolation of *trans*-isomers in the series (**4t**), (**6t**), and (**8t**) and the favoured formation of the *cis*-isomers in the series (**5c**), (**7c**), and (**9c**) seem to indicate preferred $_\sigma 2_a$ involvement (Scheme 3) with inversion of configuration at C-6;[8] with C-2, C-6 bonding, the absence of $_\sigma 2_s$ products may be due to avoidance of electron density accumulation, while with C-4, C-6 bonding this is a less severe requirement. However, mechanism (iii), with its excited diradical intermediate, can equally well accommodate both types of
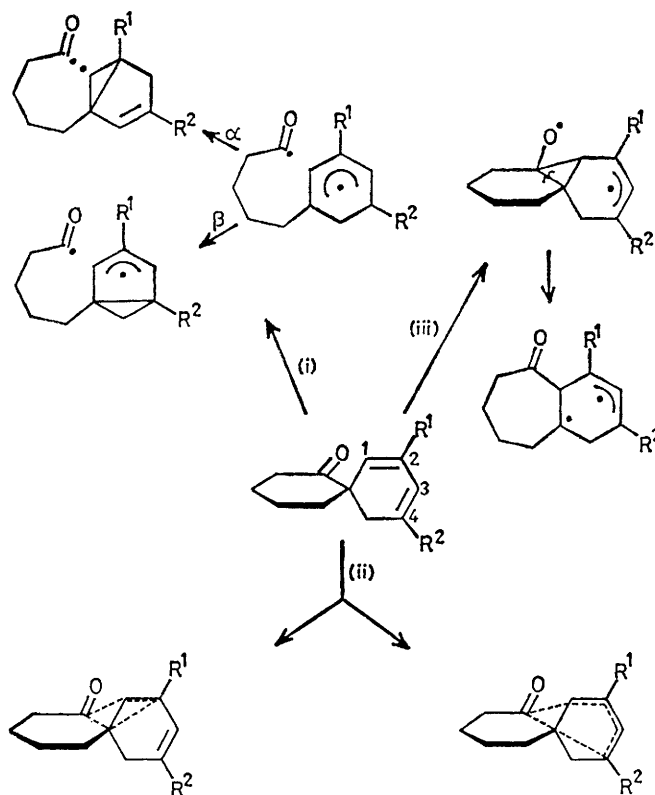
Scheme 2
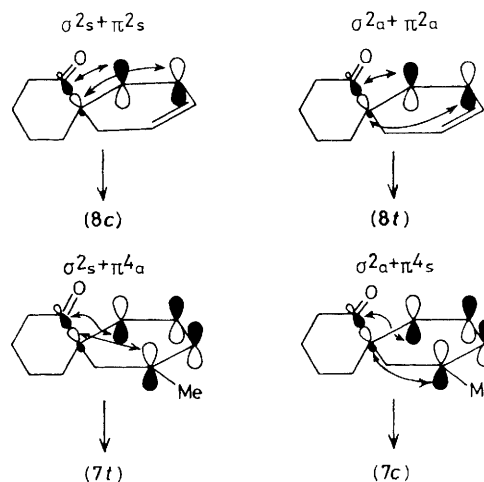
Scheme 3

products obtained (Schemes 1—3).[8c,d] Furthermore, the significant substituent effect, as reflected in the relative yields in Scheme 1, can be rationalized in both mechanisms (ii) and (iii) (Scheme 2), since in both the methyl group increases the electron density on the corresponding carbon atom, increasing the probability of cyclopropane bond formation to that carbon atom.

with some of the *X*-ray diffraction work is gratefully acknow-
ledged.

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