Thermal Rearrangement of a 2-Benzylidenecyclobutanone: a Suprafacial [1,3]Shift with Inversion

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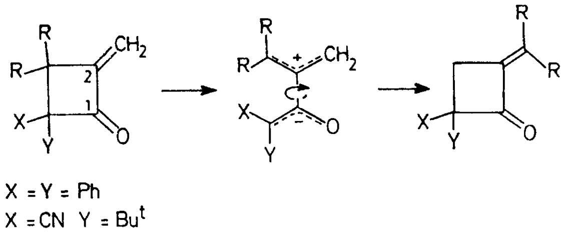
Summary The optically active 2-*E*-benzylidene-4-t-butyl 4-cyano-3-phenylcyclobutanone (**1**) rearranges thermally to the 2-*Z*-benzylidene isomer (**3**) by a [1,3]sigmatropic shift with inversion of the migrating centre; a further thermal isomerisation of (**3**) is also described.

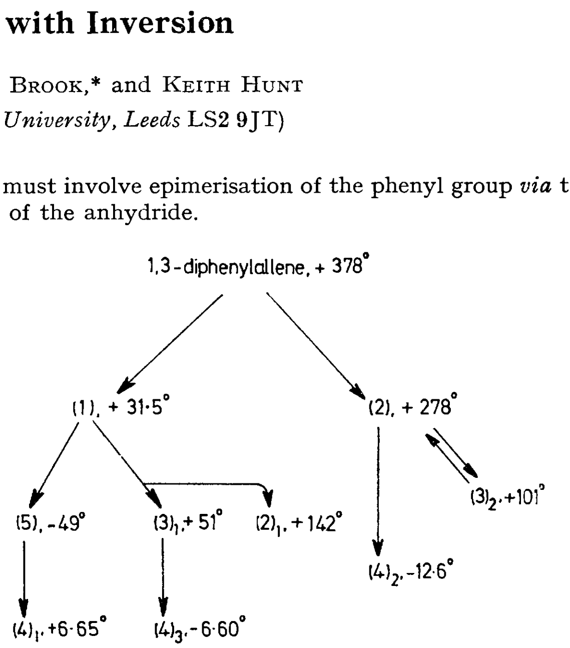
Dipolar intermediates (or their diradical equivalents) have been proposed in the thermal rearrangement of 3,3-dialkyl-2-methylenecyclobutanones (Scheme 1).[1] More recently, Bertrand's group have reported[2] that two adducts, derived from partially resolved 1,3-dimethylallene and dimethylketen, equilibrate at 330 °C by a related process with at least 22% retention of optical activity, a reaction which they interpreted as an antarafacial [1,3]shift with retention at the migrating centre.



Scheme 1

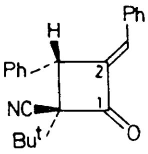
We now report a related highly stereospecific rearrangement where inversion of the migrating centre has been clearly established. The result excludes a planar and hence achiral intermediate (Scheme 1), but allows a twisted conformation as transition state or intermediate in the rearrangement.

The adducts (**1**) and (**2**) have structures clearly established by *X*-ray and n.m.r. studies.[3,4] Steric effects in (**1**) cause it to be more labile thermally than (**2**), and, after 4 h in refluxing 1,2-dichlorobenzene (178 °C), (**1**) gave a new 2-*Z*-benzylidenecyclobutanone (**3**) together with adduct (**2**) in a ratio 82:18 (85% yield after chromatography). The *Z*-geometry in (**3**) follows from its n.m.r. spectrum; the olefinic proton appeared at 0·97 p.p.m. higher field than in (**1**) and (**2**), whilst the aromatic region showed two unusually low field protons, absent in (**1**) and (**2**). These differences are those to be expected when protons close to the carbonyl group are deshielded.[5] The ring stereochemistry of (**3**), with phenyl and t-butyl groups mutually *trans*, was established when catalytic reduction of either (**2**) or (**3**) gave the same dihydro-compound (ν_{max} 1795 cm^{-1}) different from dihydro-(**1**). Confirmation of the last point was obtained when ozonolysis of either (**2**) or (**3**) at −80 °C followed by treatment with peracetic acid gave the same succinic anhydride (**4**). In the same way, adduct (**1**) gave an unstable anhydride (**5**), characterised only spectroscopically, which on crystallisation or sublimation was converted into (**4**). This isomerisation (**5**) → (**4**) relieves steric compression and must involve epimerisation of the phenyl group *via* the enol of the anhydride.

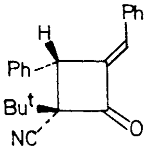


Scheme 2

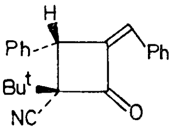
The rearrangement, (**1**) → (**3**), results in change of stereochemistry both at the double bond and the ring, and we consider this strong evidence for migration of C-4 across the allyl system.[6]



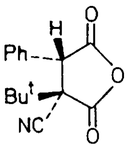
(1)



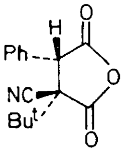
(2)



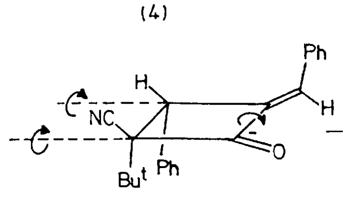
(3)



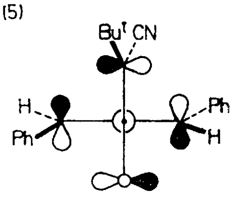
(4)



(5)



(6)



(7)
HOMO of enolate
LUMO of allyl cation

If the reasonable assumption is made that in the oxidative degradation of (**1**), (**2**) and (**3**) to the common derivative (**4**) there is no configurational change in the quaternary carbon bearing the cyano group, it is possible to use optically active adducts to determine the stereochemistry and optical yields in the above reactions. Scheme 2 shows the specific rotations of the various products starting from partially resolved[7] *S*-1,3-diphenylallene, $[\alpha]_D^{25} + 378°$. [The subscripts on formulae numbers denote the precursors; *i.e* $(\mathbf{4})_1$ = (**4**) derived from (**1**)].

The first conclusion, from specific rotations of $(\mathbf{4})_1$ and $(\mathbf{4})_2$, is that (**1**) and (**2**) differ in configuration at C-4 and therefore have the same configuration† at C-3, and (**1**) has $6{\cdot}65/12{\cdot}6 = 53\%$ of the optical purity of (**2**).‡ Secondly, considering $(\mathbf{4})_1$ and $(\mathbf{4})_3$, the rearrangement $(\mathbf{1}) \rightarrow (\mathbf{3})$, involves inversion at C-4 and proceeds with $6{\cdot}60/6{\cdot}65 = 99\%$ optical purity. Finally, for the minor pathway $(\mathbf{1}) \rightarrow (\mathbf{2})$, although a direct conversion has not been ruled out it is more probable that (**3**) is an intermediate. On heating for 4 days under the conditions for rearrangement (**2**) and (**3**) approach equilibrium [*ca.* 66% of (**2**)].

$$(\mathbf{3})_1, + 51° \longrightarrow (\mathbf{3}), + 50° \text{ and } (\mathbf{2})_3 + 139°$$

$$(\mathbf{2}), + 278° \longrightarrow (\mathbf{3})_2, + 101° \text{ and } (\mathbf{2}), + 273°$$

The negligible loss of specific rotation in recovered material, and the ratio of specific rotations: $(\mathbf{3})_1/(\mathbf{3})_2 = 0{\cdot}51$, $(\mathbf{2})_3/(\mathbf{2}) = 0{\cdot}50$ [close to the ratio of optical purity in (**1**) and (**2**)] show this equilibration to be highly stereospecific. We cannot yet distinguish between simple *cis-trans* isomerism at the double bond, or a [1,3]shift of C-4 with retention.

As shown in (**6**), the initial rotations needed to convert (**1**) to (**3**) are just those which give maximum relief of steric strain; conrotatory opening of the C-3–C-4 bond with inward movement of the ring phenyl group (to escape the benzylidene group) and outward movement of the t-butyl group. The synchronous twist about the C-1–C-2 bond avoids steric interaction between the cyano- and ring phenyl groups and leads to the orthogonal species (**7**).

The large phenyl and t-butyl substituents may be responsible for the difficulty in reaching the planar intermediate in this case. We suggested earlier that the planar species was the cause of loss of optical activity in certain keten–allene cycloadditions. The present results raise the possibility that, even with smaller substituents present, this planar species may not be at an energy minimum.

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† From the *S*-allene, the mechanism proposed earlier[3] leads to cycloadducts with absolute configuration represented in (**1**) [and (**2**)]. In the epimerisation (**5**) to $(\mathbf{4})_1$ a positive change in rotation is found. The same configuration change in phenylsuccinic anhydride, *R* to *S*, also gives a positive change.[8] This suggests the absolute configuration in (**1**) is correct, but the additional chiral centre in (**5**) makes this assignment tentative.

‡ The mechanism proposed[3] gave one possible reason why (**1**) could have a lower optical purity than (**2**).

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