Donor–Acceptor Accelerated Norbornadiene Rearrangements

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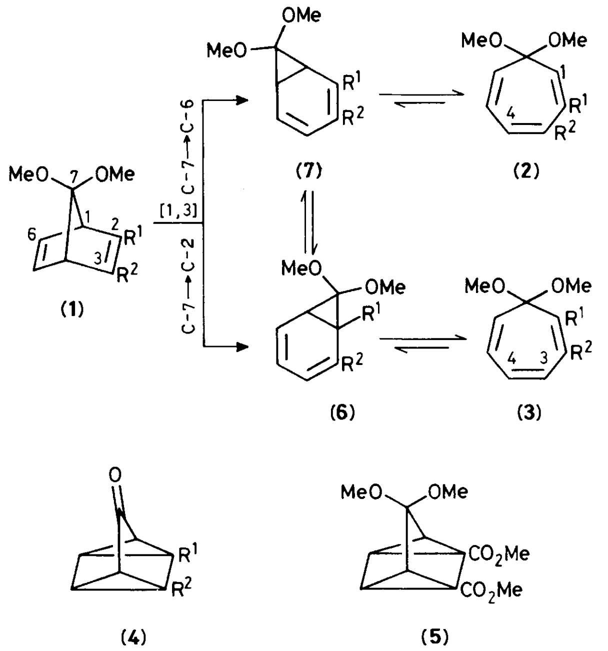
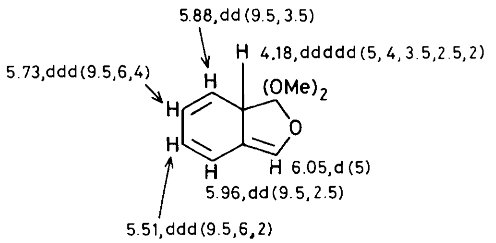
The norbornadienone acetals (**1**) with CO_2Me, $CONMe_2$, or CHO substituents at C-2 undergo rearrangement *via* formal 1,3-shift to norcaradienes under very mild conditions; strong donor–acceptor acceleration of either 1,3-sigmatropic rearrangement or C–C bond homolysis is indicated.

Norbornadiene rearranges to cycloheptatriene[1] above 325 °C, and 7-phenyl- and 7-alkoxy-norbornadienes undergo similar rearrangement[2] at 170 °C. In contrast 7,7-dialkoxynorbornadienes do not normally rearrange but extrude dialkoxycarbenes at *ca.* 150 °C.[3] We describe the exceptional and remarkably easy rearrangement (>40 °C) of the dimethoxynorbornadienes (**1**) to the cycloheptatrienes (**2**). Only at higher temperatures (>100 °C) do the norbornadienes (**1**) and the cycloheptatrienes (**2**) lose dimethoxycarbene. The strong acceleration of the formal 1,3-shift involved in this trans-



a; R^1 = R^2 = CO$_2$Me
b; R^1 = CO$_2$Me, R^2 = H
c; R^1 = CO$_2$Me, R^2 = D
d; R^1 = CONMe$_2$, R^2 = H

Scheme 1



(8)

δ (C$_6$D$_6$) and J values (Hz); additional splittings (*ca.* 1 Hz) omitted.

formation (Scheme 1) is in agreement with predictions for a concerted forbidden process aided by donor and acceptor substituents.[4]†

The norbornadienes (**1**) were prepared from the known[5] quadricyclanones (**4**). Acetalisation of (**4a**) (MeOSiMe$_3$, Me$_3$SiOSO$_2$CF$_3$) gave (**5**) which could be isomerised to (**1a**) at 20 °C [Pd/C or Pd(OAc)$_2$]. Rearrangement of (**1a**) occurred cleanly and completely (<1.5 h) in boiling benzene to give the tropone acetal (**2a**). The transitory appearance of (**3a**) during this transformation was established by heating (**1a**) (50 °C, 30 min, C$_6$D$_6$) when the 400 MHz ^{1}H n.m.r. spectrum revealed the presence of (**1a**) (*ca.* 56%), (**2a**) (*ca.* 33%), and (**3a**) (*ca.* 11%). Spin decoupling experiments allowed the firm assignment of the following spectrum to (**3a**); δ 7.22 (1H, dt, J 11 and 1 Hz, 3-H), 6.51 (1H, ddd, J 11, 6, and 1 Hz, 4-H), 6.07 (1H, ddd, J 10.5, 6, and 1 Hz, 5-H), 5.70 (1H, dt, J 10.5 and 1 Hz, 6-H), 3.65 (3H, s), 3.31 (3H, s), and 3.07 (6H, s). Continued heating led to complete conversion into (**2a**). This presumably involves valence-tautomerism (**3a**) $\rightleftarrows$ (**6a**), walk rearrangement of (**6a**) to (**7a**), and ring-opening to (**2a**) (Scheme 1). The remarkable ease of this walk rearrangement,‡ and the ease of the initial 1,3-shift are associated with donor substituents on the migrating carbon atom and acceptor substituents on the migration frame. The conversion of (**1a**) into (**2a**) at 40—55 °C (C$_6$D$_6$) provided good first order kinetics [k (55 °C) = 2.4 × 10^{-4} s^{-1}; E_a = 24.0 ± 0.3 kcal mol^{-1}. $\Delta H^‡$ = 23.4 ± 0.3 kcal mol^{-1}, $\Delta S^‡$ = −4.6 ± 2 cal mol^{-1} K^{-1}§]. Rearrangement of the monoester (**1b**) to (**2b**) was also rapid [k (55 °C) = 1.2 × 10^{-4} s^{-1} (C$_6$D$_6$)] indicating that only the C-2 methoxycarbonyl group is important for easy rearrangement. A possible rearrangement path for (**1b**) involving migration of C-7 to C-3 rather than to C-6 and/or C-2 was discounted by rearrangement of (**1c**) to give (**2c**) with total deuterium integrity at C-3.

Several observations militate against zwitterionic intermediates in these rearrangements; (**1a**) rearranges only 1.2 times faster in CD$_3$CN than in C$_6$D$_6$ (40 °C), and methanol fails to divert rearrangement. The aldehyde (**1**; R^1 = CHO, R^2 = H) rearranges only *ca.* 4 times more rapidly than (**1b**). The non-isolable product is tentatively assigned structure (**8**) on the basis of u.v. absorption (C$_6$H$_{12}$ $\lambda_{max.}$ 325 nm), the 400 MHz ^{1}H n.m.r. data (C$_6$D$_6$) appended to structure (**8**), and conversion into phthalide and related products (55%) on treatment with CF$_3$CO$_2$H. One possible route to (**8**) would be by vinylcyclopropane type rearrangement of (**6**; R^1 = CHO, R^2 = H). Even the dimethylamide (**1d**), in which steric factors severely hamper conjugation between the amide carbonyl group and the C-2–C-3 double bond,¶ and which is deactivated towards rearrangement by this factor as well as the reduced electron accepting ability of the amide carbonyl group, rearranges only *ca.* 15 times more slowly than (**1b**). Interestingly (**1d**) gave both (**2d**) and (**3d**). Since the latter was isolable and failed to give (**2d**) under the conditions of the original rearrangement the 1,3-shift must occur to both C-2 and C-6 (Scheme 1). Steric and electronic effects can account for less easy interconversion of (**6d**) and (**7d**) compared with (**6a**) and (**7a**).

Despite the lack of evidence for a dipolar intermediate in these reactions it is not sufficient that the C-2 substituent be only a conjugating one; (**1**; R^1 = CH=CH$_2$, R^2 = H) fails to rearrange below *ca.* 120 °C at which temperature it ejects dimethoxycarbene. The substituent and solvent rate effects described here seem most consistent with a pericyclic rearrangement. However, polar effects in radical reactions are well known[7] and we cannot at present rule out rearrangement *via* homolysis favoured by donor–acceptor substitution. In either case the synergistic substituent effect is interestingly large and therefore potentially useful.

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† Although the allowed 1,3-shift of suprafacial inversion (s,i) geometry and the forbidden suprafacial retention (s,r) process should both be accelerated by appropriately placed donor and acceptor substituents, the forbidden antiaromatic transition state with its higher energy HOMO and lower energy LUMO should be better stabilised.

‡ Walk rearrangement of norcaradienes has been observed at 100 °C (ref. 6).

§ 1 kcal = 4.184 kJ.

¶ The C-3 proton in (**1b**) appears at δ 7.50 whilst that in (**1d**) resonates at δ 6.73.

We thank the S.E.R.C. and Fisons Pharmaceuticals PLC for a C.A.S.E. studentship and Dr. B. E. Mann and Dr. Catriona Spencer (Sheffield University) for 400 MHz ^{1}H n.m.r. spectra. We thank Dr. J. Bantick (Fisons) for much helpful discussion and proposing the experiment involving (**1c**).

Received, 27th June 1984; Com. 874

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