Oxyanion-assisted Retro-Diels–Alder Reactions in the Tricyclo[3.3.1.0^{2,8}]nona-3,6-diene (Barbaralane) System

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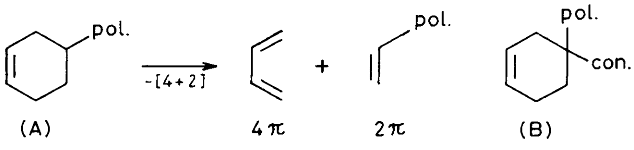
9-Vinyl- and 9-aryl-tricyclo[3.3.1.0^{2,8}]nona-3,6-dien-9-olates (**1c**—**h**) underwent the retro-Diels–Alder reaction to give cycloheptatrienes (**2c**—**h**) in excellent yields, indicating that it is not necessary for the fragmented 4π component to be incorporated into an aromatic nucleus.

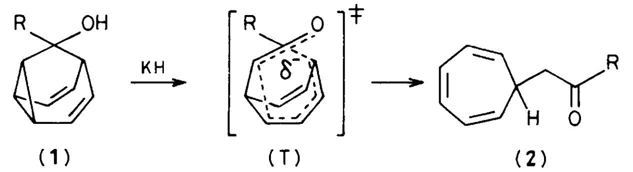
Since Evans found that the anionic oxy-Cope rearrangement takes place readily,[1] oxyanion-assisted pericyclic reactions have attracted much synthetic and mechanistic attention, and various [1,3]-,[2] [1,5]-,[3] and [3,3]-[4] sigmatropic rearrangements and retro-Diels–Alder reactions[5] have been reported. To predict the substituent effect of an oxyanion on these reactions, Carpenter recently proposed a convenient theoretical model which, for instance, predicts that the retro-Diels–Alder reaction represented by (A) would be accelerated by a polar substituent such as an oxyanion group.[6] The recently reported retro-Diels–Alder reactions in the bicyclo[2.2.2]octadiene[5a] and 9,10-ethano-bridged anthracene[5b] systems are essentially in good accord with Carpenter's prediction. In contrast with those reactions in which the 4π components comprise part of an aromatic system such as the phenolate anion, anthracene, or naphthalene, bicyclo[2.2.1]hept-5-en-2-olates were found to be inert.[5b] On this basis, RajanBabu *et al.* claimed that the retro-Diels–Alder reaction occurs only if the substrate is capable of fragmenting so that the 4π-component is incorporated into an aromatic nucleus.[5b] If so, the synthetic applicability of oxyanion-assisted retro-Diels–Alder reactions would not be reliable. In order to test this, we have investigated retro-Diels–Alder reactions in the barbaralane (a formal [4 + 2] cycloadduct of 7-vinylcycloheptatriene) and norbornene ring systems, (**1**) and (**3**), respectively.

Upon treatment of (**1c**) with KH followed by addition of 18-crown-6 in tetrahydrofuran (THF) at room temperature the retro-Diels–Alder product (**2c**) was isolated in 60% yield. In contrast, neither (**1a**) nor (**1b**) cycloreverted, showing the importance of the geminal conjugation group. The 9-aryl derivatives (**1d**—**h**) likewise underwent the same reaction to give (**2d**) (86%), (**2e**) (98%), (**2f**) (90%), (**2g**) (91%), and (**2h**) (81%), repectively. This was further demonstrated in the norbornene system. In contrast with the inertness of bicyclo[2.2.1]hept-5-en-2-olates,[5b] the 2-aryl derivative (**3**) quantitatively afforded *p*-chloroacetophenone under the same conditions.†



pol.: polar group; con.: conjugation group.

These results clearly indicate that the incorporation of the fragmented 4π component into an aromatic nucleus is not a necessary requirement if a group capable of conjugation is introduced at the carbon atom bearing the oxyanion as shown in (B).



(**1**) (T) (**2**)

a; R = H
b; R = Me
c; R = CH_2=CH
d; R = *p*-BrC_6H_4
e; R = *p*-ClC_6H_4
f; R = Ph
g; R = *p*-MeC_6H_4
h; R = *p*-$MeOC_6H_4$

Table 1. First-order rate constants and activation parameters.

	(**1d**)	(**1e**)	(**1f**)	(**1g**)	(**1h**)
$10^4 k$/s^{-1} [a]	7.98	7.82	6.03	4.72	4.27
E_a/kcal mol^{-1} [b]	15.8	16.2	17.9	—	22.5
log (A/s^{-1})	8.28	8.44	9.72	—	12.9

[a] At 30 °C. [b] T 30—50 °C. 1 cal = 4.184 J.

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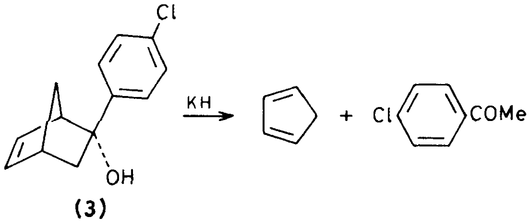
† Under the reaction conditions used, cyclopentadiene decomposed and could not be isolated as either the monomer or dimer.



(3)

In order to study the effect of the conjugation groups, the first-order rate constants were measured for **(1d—h)**. As shown in Table 1, electron-withdrawing substituents accelerate the reaction, obeying the Hammett relation, log $k^X/k^H = 0.55\sigma_p$ ($r = 0.997$). The stabilization of the partially anionic 6-membered ring transition state (T) by the electron-withdrawing substituent readily accounts for the observed rate acceleration. This finding in conjunction with the fact that both vinyl and phenyl substituents facilitate the retro-Diels–Alder reaction, shows that the vinyl and phenyl groups are evidently effective in conjugation in the transition state rather than in the product. Our results thus suggest that strain release would facilitate the retro-Diels–Alder reaction of systems of type (B) incorporated into a strained molecule, even if the fragmented 4π component is not incorporated into an aromatic nucleus.

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