

The Role of Norcaradiene Intermediates in the Thermal Rearrangement of Norbornadien-7-one Acetals

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The bis(methoxycarbonyl)tetrachloronorbornadienone dimethyl acetal (1) rearranges spontaneously to the hemimellitate (2) via the norcaradiene intermediate (6); the corresponding anhydride (5) is stable below 200 °C because steric strain prevents its conversion into an analogous intermediate (9).

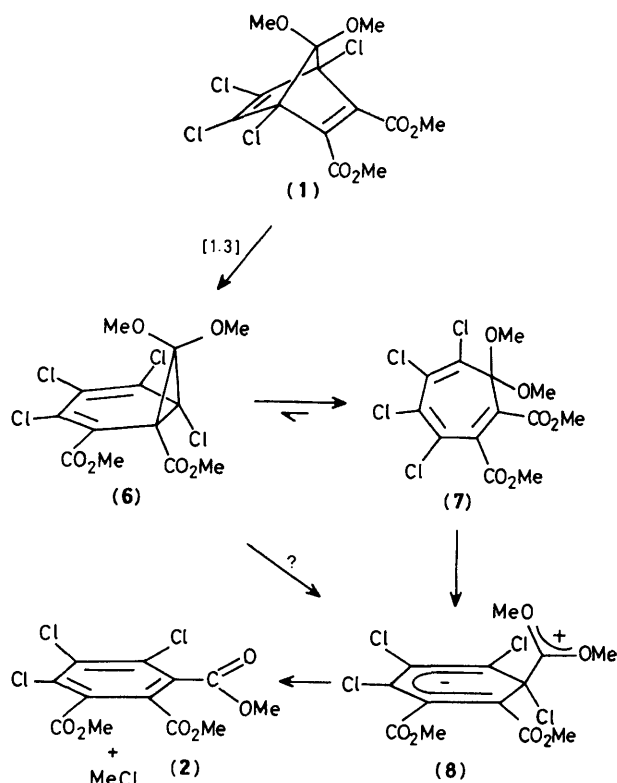
It has recently been demonstrated¹ that donor-acceptor interactions strongly accelerate the rearrangement of substituted norbornadienes to cycloheptatrienes. It was assumed that this reaction proceeds via norcaradiene intermediates. Our present work supports this conclusion and provides further evidence for the transitory rate determining formation of norcaradienes in the thermal rearrangement of the norbornadienone dimethyl acetal (1).

As shown by Diekmann² and others³⁻⁶ the Diels-Alder cycloaddition of dimethyl acetylenedicarboxylate to the cyclopentadiene (3) affords only the trimethyl trichlorohemimellitate (2). Thus, the fragmentation of (1) must occur below the temperature (110 °C) required for its formation. We prepared the anhydride (5) by zinc debromination of (4) which is in turn easily accessible as an *exo-endo* mixture from dibromomaleic anhydride and (3). † The anhydride (5) proved to be a stable compound decomposing slowly above 200 °C. However, when treated in methanol at 60 °C with a trace of toluene-*p*-sulphonic acid, it rapidly fragments to give the triester (2). On the basis of these results the mechanism in Scheme 1 for the rearrangement of (1) to (2) is proposed.

The rate-determining formation of a norcaradiene intermediate is crucial for the outcome of this reaction. It is the only structure which can explain the thermal stability of (5). The strain imposed on C-2 by the cyclopropane ring in an analogous norcaradiene derivative (9) derived from (5) is seemingly too high to allow for its formation. Once this strain is circumvented as demonstrated by the hydrolysis of (5), the 1,3-shift to yield (6) can easily occur leading to subsequent formation of intermediates (7) and (8) resulting in the formation of the aromatic product (2).

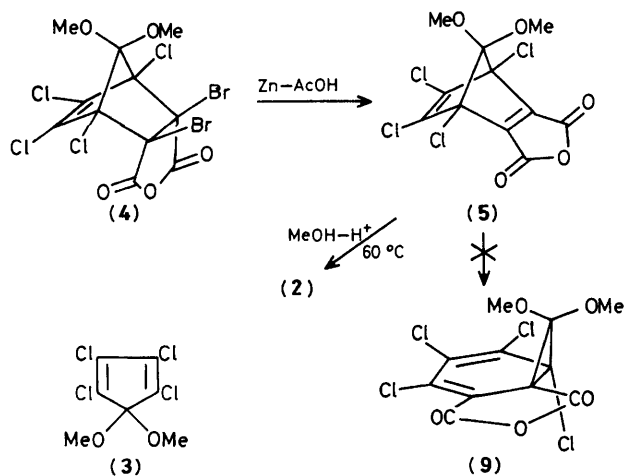
On the basis of the present work we cannot decide the

relative importance of the intermediates (7) and (8). The triene (7) is included in Scheme 1 only because it is known that alkoxy substituents strongly favour a rapid rearrangement of



Scheme 1

† Satisfactory elemental analyses and mass spectra and ¹³C n.m.r. data were obtained for compounds (4) and (5).



norcaradiene derivatives to cycloheptatrienes.⁶ A direct conversion of (6) into (8) is also feasible. For intermediate (8) both zwitterionic and biradical structures have been suggested.⁵ It is not clear to what extent donor-acceptor interactions of substituents at C-7, C-2, and C-3 would favour a biradical intermediate.⁷ The zwitterion structure is similar to the intermediate formed in acetal hydrolysis which is known to proceed by an ionic mechanism.⁸ The driving force for the

formation of the Meisenheimer type complex (8) from the cycloheptatriene (7) could be provided by both the lone electron pairs on oxygen⁸ and the electron delocalization of the cyclic part of the molecule. The proposed³⁻⁵ initial formation of (8) (zwitterion or biradical) in the slow step of the investigated rearrangement must be rejected.

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