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Original Scientific Paper

The Mechanism of Aromatization of 7-Norbornadiene Acetals. Evidence for Norcaradiene Formation**

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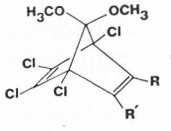
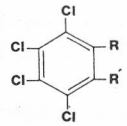
Dicarbomethoxy-tetrachloronorbornadienone acetal *1c* rearranges spontaneously to hemimelitate *3c* while the corresponding anhydride *14* is stable up to 200 °C. This result supports the hypothesis that the thermal rearrangement of substituted norbornadienes to aromatic products occurs by rate determining formation of norcaradiene intermediates.

INTRODUCTION

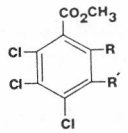
7-Norbornadiene acetals are known to decompose thermally to yield aromatic products.[1] Depending on the mechanism two kinds of products have been observed, as exemplified of the thermal decomposition of the tetrachloro derivative (*1*).[2,3]



1a-c



2a-c



3a-c

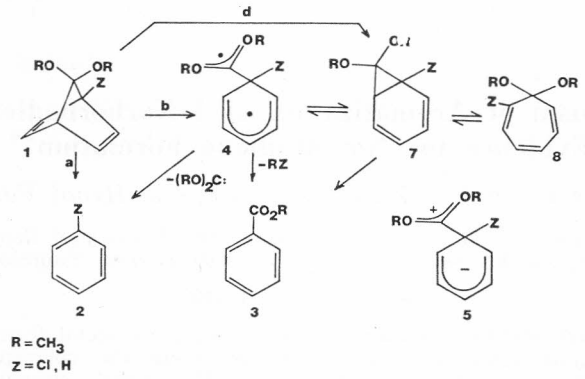
a) R = R′ = H
b) R = H, R′ = C_6H_5
c) R = R′ = $COOCH_3$

Compounds of structure *2* are generated by a cheletropic dimethoxycarbene elimination while *3c* was isolated in the attempted synthesis of *1c* from 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene and dimethyl acetylenedicarboxylate.[2] The primary adduct of this reaction, *i. e. 1c* was never isolated; its decomposition must have occurred well below 110 °C, the temperature required for the Diels-Alder reaction.

** Dedicated to Professor Mihailo Lj. Mihailović on occasion of his 60th birthday.

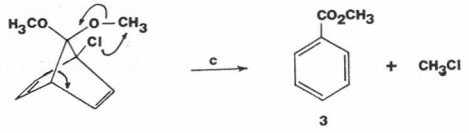
For a preliminary account of this work see D. E. Sunko, Z. Lovrić, and H. Vančik, *J. Chem. Soc., Chem. Comm.* (1985) 1589.

Mackenzie[4] and Hoffmann[3] as well as Lustgarten and Richey[5] proposed the following mechanistic scheme which can account for both types of products (Scheme 1, path b). From the solvent dependence of the product ratio *2* vs. *3* for path b an ionic mechanism was also proposed leading to a zwitterionic



Scheme 1

structure *5* which can subsequently rearrange to *3*. Alternatively a totally concerted decomposition of *1* to yield *3* could also be envisaged (path c):

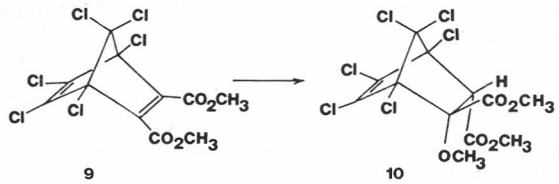


Recent work by Bleasdale and Jones[6] on donor-acceptor accelerated norbornadiene rearrangements favors a fourth pathway (path d) as the most probable mechanism.

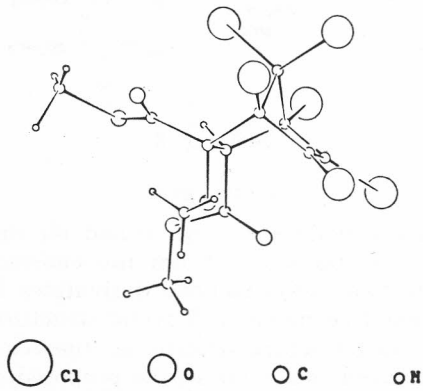
In this paper we describe some experiments which helped to clarify the mechanism of aromatization of substituted norbornadienes and which support the rate determining formation of norcaradiene intermediates as proposed by Bleasdale and Jones.[6].

METHOD AND RESULTS

In the course of our mechanistic studies of 7-norbornyl derivatives we attempted the synthesis of *1c* by alternative routes. The obvious choice was the base-hydrolysis of the easily accessible 7,7-dichloro derivative *9* under conditions similar to the ones used in the preparation of 5,5-dimethoxytetrachlorocyclopentadiene from the corresponding hexachloro derivative.[7] The

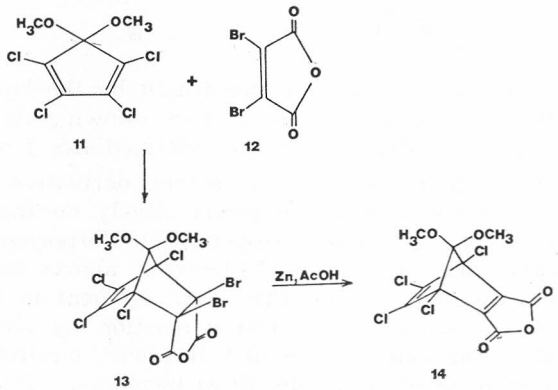


reaction proceeded smoothly but the isolated product *10* proved to be the result of a Michael addition to the activated double bond in *9*.
The structure of *10* was confirmed by X-ray analysis on the single crystal[8] (Figure).



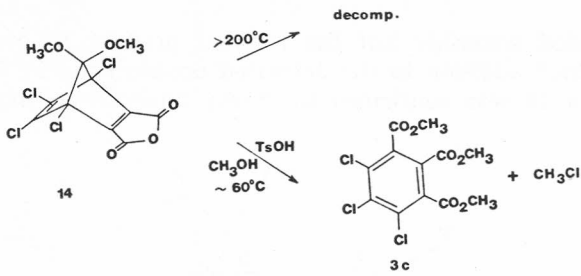
A careful repetition of the reported[2] attempted synthesis of *1c* confirmed the original observation: below 110 °C both reactants, *i. e.* acetylenedicarboxylate and dimethoxytetrachlorocyclopentadiene, are stable regardless of changes of the medium (neat, polar or nonpolar) or addition of potential catalysts ($BF_3 \cdot Et_2O$). At higher temperature a fast reaction occurs with almost quantitative evolution of methyl chloride and the formation of *3c*.

Eventually, a successful entry into the norbornadiene system related to *1c* was achieved by the following series of reactions leading to anhydride *14* (Scheme 2).



Scheme 2

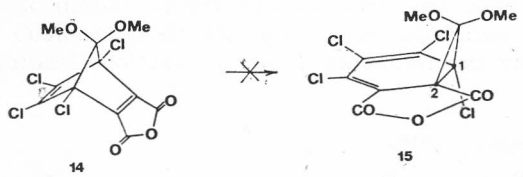
In contrast to *1c* which could not be isolated the anhydride *14* proved to be a thermally stable compound slowly decomposing above 200 °C, presumably by the carbene forming mechanism to the aromatic anhydride related to the diester *2c*. However, on acid hydrolysis with catalytic amounts of *p*-toluene sulfonic acid in methanol the anhydride *14* converted easily to the benzene derivative *3c* (Scheme 3):



Scheme 3

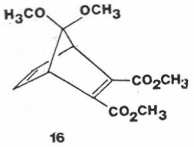
DISCUSSION

Several important conslusions can be drawn on the basis of the results obtained in the course of this work. From the enormous differences in the thermal stability of the two norbornadiene derivatives *1c* and *14* respectively the presence of the rigid five membered cyclic structure in the anhydride *14* emerges as the crucial factor which determines the reaction pathway and by implication the reaction mechanism. Of all the proposed reaction intermediates, *4*, *5*, 7 or *8* only the norcaradiene derivative 7 has the necessary structural requirements which can account for the different behavior of *1c* and *14*. The presence of the five membered ring in *14* precludes a 1,3-sigmatropic shift to the norcaradiene *15* (or 7 in Scheme 1). The strain imposed to C-2 by the cyclopropane ring in *15* is apparently too high to allow for its formation.



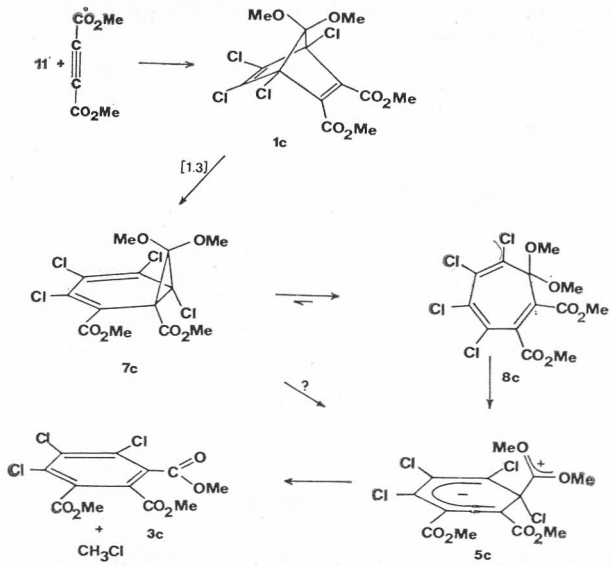
Once this strain is circumvented as demonstrated by the hydrolysis of *14*, a norcaradiene intermediate can easily be formed allowing its subsequent fast rearrangement to the aromatic product *via* intermediates *4* or *5*.

The choice of the pathway a norbornadiene derivative will take in its rearrangement to aromatic products depends largely on the nature of substituents at carbon atoms 2, 3 and 7, respectively. Norbornadiene itself rearranges to cycloheptatriene above 325 °C.[9] Phenyl or alkoxy substitution at C-7 lowers the temperature required for this rearrangement to 175 °C.[5] 7,7-Dialkoxy norbornadienes undergo a cheletropic reaction by eliminating dialkoxycarbenes at 150 °C (Scheme 1, path a).[10] However, electron-accepting substituents at the double bond as in the di-carbomethoxy derivative *16* cause a change in the mechanism with cycloheptatriene becoming the preferred product (Scheme 1, path d). As recently shown by Bleasdale and Jones,[6] this



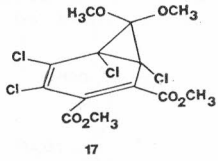
reaction occurs at temperatures as low as 45—55 °C. The corresponding monoester shows the same enhanced reactivity indicating the importance of this particular acceptor group. Simple conjugation with the endocyclic double bond is not enough, because with only a vinyl group at C-2 the decomposition occurs with the extrusion of dimethoxycarbene above 120 °C (path a).[5]

Several authors[1,4,10] proposed the formation of a biradical or zwitterionic intermediate of structure *4* or *5*, respectively, as first formed intermediates (path b). No clear preference could be given to either the radical or zwitterionic structures, because only minor effects with solvents of different polarity were observed. The results of this work clearly rule out the rate determining formation of such intermediates, because both *4* and *5* should form with equal ease from either *1a* or *14*. We propose that the Diels-Alder cycloaddition of 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene and dimethyl acetylenedicarboxylate proceeds by the following mechanism (Scheme 4).



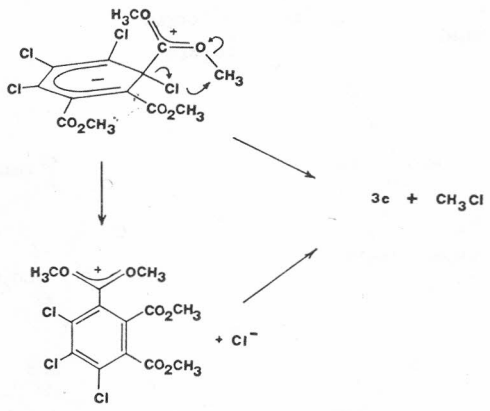
Scheme 4

The formation of *7c* is rate determining and its formation cannot be bypas sed as shown by the relative inertness of 14. The carbomethoxy group acts as a efficient electron-acceptor causing the preferred formation of *7c* relative to its isomer *17*. This isomer would lead to identical products as isomer *7c*



but here steric factors which prevent the formation of *15* from *14* are not present. Nevertheless its formation from *14* does not occur which demonstrates

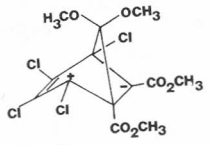
the importance of suitable donor-acceptor substituents.[6] The dimethoxy substituents in *7c* should strongly favor its rapid rearrangement to the cycloheptatriene derivative *8c*. However, we did not observe the formation of *8c*, and its inclusion in the mechanistic scheme is warranted only on the basis of the demonstrated[5,11] rapid rearrangement of 7-alkoxy norcaradienes to cycloheptatrienes. A direct conversion of *7c* to *5c* is also feasible. In the next step *8c* (or *7c*) rearranges to *5c*. We prefer the zwitterionic structure for this intermediate on the basis of its formation at temperatures below 100 °C, and the reported solvent effects. This rearrangement can be regarded as an acetal decomposition which was shown to proceed by an ionic mechanism,[12] where the necessary driving force is provided by both the lone electron pairs on the oxygen and the electron delocalization in the departing fragment. In the absence of the ketal function, the reaction assumes a different path (path a); the hexachloro derivative *9* is perfectly stable up to 200 °C. Intermediate *5c* can be regarded as a Meisenheimer type complex, which should easily fragment to give *3c*. This final step could proceed either by a concerted reaction or in a stepwise manner (Scheme 5).



Scheme 5

Which path is actually being taken cannot be decided on the basis of this work. A concerted reaction appears to be less likely because of entropy factors and the steric requirements for a backside attack of the departing chloride on the methoxyl carbon atom. The same applies for the earlier mentioned concerted decomposition of *1c* (path c).*

* Referees of the preliminary communication of this work pointed out the difficulties associated with the distinction between a biradical and a zwitterionic mechanisms. Intermediates such as *18* cannot be *a priori* excluded, but are not probable.



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EXPERIMENTAL

General Methods

Melting points are uncorrected. IR spectra were taken on a Perkin-Elmer 167 spectrometer. ^{1}H NMR spectra were measured in $CDCl_3$ as a solvent on a Varian T-60 spectrometer. ^{13}C NMR spectra were recorded with a Jeol FX-100 spectrometer with $(CH_3)_4Si$ as internal standard. Mass spectra were obtained on a Varian CH-7 spectrometer. Thin-layer chromatography (TLC) was performed on Merck silica gel 60 F-254 plates. Elemental analyses were carried out at the Ruđer Bošković Institute, Zagreb.

Dimethyl 2-Methoxy-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]-hept-5-ene-2,3-dicarboxylate (10)

In a round bottom flask equipped with a reflux condenser and a dropping funel are placed 2 g (4.8 mM) of dimethyl 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (*9*)[13] in 6.5 ml of methanol. To the stirred solution a solution of KOH (0.54 g, 9.6 mM) in methanol (5 ml) was added in the course of one hour. After stirring for one additional hour ice (25 ml) was added and the mixture extracted with five 10-ml portions of dichloromethane. The combined extracts were dried over $MgSO_4$, the solvent evaporated, and the residue crystallized from petroleum ether. Yield 0.95 g (48%), m. p. 132.5—133 °C. IR: 2955, 1750, 810 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 3.4 (3H, CH_3), 3.7 (3H, CH_3), 3.9 (3H, CH_3), 4.5 (1H, CH). ^{13}C NMR ($CDCl_3$) δ 165, 164 (C=O), 130 (C=C), 101 (H_3CO—)C—(—CO_2CH_3), 88 (CCl), 85 (CCl_2), 51—60 (CH_3).

Anal. calc'd: C 32.25; H 2.26; Cl 47.60.
found: C 32.23; H 2.26; Cl 47.68.

Attempted Synthesis of Dimethyl 7,7-Dimethoxy-1,4,5,6-tetrachlorobicyclo-[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (1c)

a) Dimethyl acetylenedicarboxylate (1.76 g, 12.4 mM), 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene[7] (4.64 g, 17.7 mM) and 2.5 g of boron trifluoride etherate were stirred at 0 °C for 48 hours.

b) The same mixture was stirred at room temperature for 8 days.

c) Ten ml of benzene were added to the above mixture which was then refluxed for 24 hours.

In all three experiments IR analysis showed no changes in the original composition of the reactants.

7,7-Dimetoxy-2,3-dibromo-1,4,5,6-tetrachlorobicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (13)

Dimethoxy tetrachlorocyclopentadiene (1.98 g, 7.5 mM) and dibromomaleic anhydride[14] (1.92 g, 7.5 mM) were heated in a sealed and evacuated ampoule to 160 °C for 10 hours. To the cooled mixture 10 ml of methanol were added. After standing overnight the precipitated crystals were filtered off and recrystallized from methanol. Colorless crystals 1.30 g (33%), m. p. 151—151.5 °C. IR: 2955, 1830, 1740, 1600 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 3.83 (3H, CH_3), 3.78 (3H, CH_3). MS, *m/e* 437 (M^+-Br).

7,7-Dimethoxy-1,4,5,6-tetrachlorobicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic anhydride (14)

13, (0.95 g, 1.83 mM) is dissolved in hot glacial acetic acid (5.5 ml) and the solution cooled in an ice bath. Activated zink powder (0.17 g) and a few crystals of iodine were added and the mixture stirred at room temperature for 18 hours. Water (10 ml) is added and the product extracted with three 10-ml portions of methylene chloride. The combined extracts are neutralized with $NaHCO_3$ (0.8 g) and dried

over Na_2SO_4. The solvent is removed in vacuo and the residue recrystallized from pentane. Colorles crystals (0.54 g, 82%) were obtained. M. p. 100—102 °C. When heated in the capillary to 255 °C, the melt suddenly darkens turning into tar under evolution of gas. IR: 2965, 1830, 1750, 1595 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.8 (CH_3). ^{13}C NMR ($CDCl_3$) δ 164 (C=O), 136 (=CCl_2), 130 (=C<), 114 ($C(OCH_3)_2$), 66 (CCl), 53, 55 (CH_3). MS, *m/e* 359 (M^++1).

Anal. calc'd: C 36.70; H 1.68; Cl 39.39.
found: C 36.73; H 2.00; Cl 40.51.

Trimethyl 4,5,6-Trichlorophenyltricarboxylate (3c)

14, (1,62 g, 4.5 mM), p-toluenesulfonic acid (0.1 g) and 25 ml of MeOH were refluxed for 3 days. The solution was concentrated to a small volume, ice was added and the product extracted with four 10-ml portions of ether. The extracts were washed successively with diluted sodium hydrogen carbonate solution and water. The crude product was dissolved in methylene chloride and passed through a short column of silica gel. The yellow oil obtained after removal of solvent was crystallized from pentane. Yield 0.9 g (50%), m. p. 88—90 °C. Mixed melting point with an original sample prepared according to Diekmann[2] was undepressed. ^1H NMR ($CDCl_3$ δ 3.96 (6H, CH_3), 3.90 (3H, CH_3).

Acknowledgement. — We thank Professor Barry Trost for stimulating discussion and Dr. Z. Meić for his help with the ^{13}C NMR spectra. Support for this work came from the Research Council of Croatia (SIZ-II).

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SAŽETAK

Mehanizam aromatizacije 7-norbornadien acetala. Dokaz nastajanja norkaradienskih međuprodukata

D. E. Sunko, Z. Lovrić i H. Vančik

Dikarbometoksi-tetraklornorbornadien acetal *1c* spontano se pregrađuje u hemimelitat *3c*. Odgovarajući anhidrid *14* stabilan je do iznad 200 °C. Taj rezultat potvrđuje hipotezu prema kojoj termička pregradnja supstituiranih norbornadiena u aromatske produkte teče preko norkaradienskih međuprodukata koji nastaju u sporom stupnju reakcije.