# Decomposition of a Tetrahydromethanophthalazine: Retro-diene Reaction *versus* Nitrogen Elimination, and Electrocyclic Transformation of a Derived Tricyclo[6,1,0,0$^{2,7}$]nonadiene

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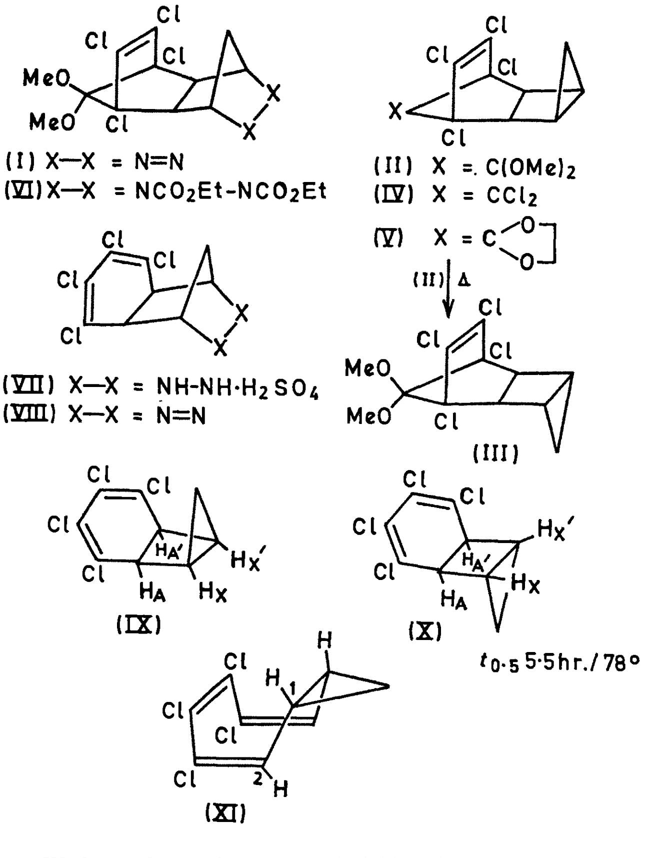
*Summary* *exo*-3,4,5,6-Tetrachloro-9,10-diazatricyclo-[6,2,1,0$^{2,7}$]undeca-3,5,9-triene (tetrachlorotetrahydromethanophthalazine) (VIII) decomposes thermally by retrogressive Diels–Alder reaction: under u.v. irradiation elimination of nitrogen from (VIII) gives *syn*- and *anti*-3,4,5,6-tetrachlorotricyclo[6,1,0,0$^{2,7}$]nona-3,5-diene, (IX) and (X).

WE recently reported isolation of the *syn*-fused bicyclopentane (II) from the product of photolysis of diazanorbornane derivative (I) and commented on its rapid thermal conversion into the *anti*-isomer (III).[1]

Sulphuric acid hydrolysis of the precursor of (I), (VI), and decarboxylation gives the salt (VII)[2] which on neutralization–oxidation (BaO/HgO) yields the azo-compound (VIII). The stereochemistry of (VIII) follows from $^1$H n.m.r. data ($J_{1\text{-H}-2\text{-H}}$ *ca.* 0), and similar data on (II)† and (III)[1] serve to define the stereochemistry of the halogenated ring in these compounds and therefore also in (I) and (VI), which is that expected on the basis of precedent.[3]



Compound (VIII) is much more stable than its carbocyclic analogue[4] but its rapid decomposition by retrogressive Diels–Alder reaction at the m.p. (70—71°) into 1,2,3,4-tetrachlorobenzene and pyrazole follows the expected course.[4] On photolysis of (VIII) however, de-azetation yields among other products the isomeric bicyclo-[2,1,0]pentane derivatives (IX) m.p. 71—72° and (X) m.p. 85—86°. $^1$H n.m.r. and i.r. spectral data for (IX) and (X) resemble those for (II) and (III). [(IX): $\nu_{\max}$ 1610vs, 1020ms, 1048ms cm$^{-1}$ conj. ClC=CCl and cyclopropane ring;[5] $\tau$ 6·52—6·58 (m, *w*/2 4Hz), 7·94—8·06 (complex), cyclobutane AA′XX′ protons; centred at 8·85, 9·15 (m), cyclopropyl CH$_2$, former signal doublet of triplets ($J_{exo\text{-H}-endo\text{-H}}$ *ca.* 6Hz, $J_{endo\text{-H}-\text{X}-\text{H}}$ *ca.* 1Hz) and the latter signal sextuplet (?) ($J_{exo\text{-H}-\text{X}-\text{H}}$ 5Hz). (X): $\nu_{\max}$ 1622vs, 1038vs cm$^{-1}$ conj. ClC=CCl and cyclopropane; $\tau$7·15 ('s',*w*/2 2Hz) 8·00—8·08 (complex), cyclobutane AA′XX′ protons, AA′ shielded compared to those in (IX) and prominent lines in coupling pattern less well separated due to term $J_{\text{AX}} + J_{\text{AX}'}$ with $J_{\text{AX}'}$ negative,[6] 9·25, 9·4 (overlapping m) cyclopropyl CH$_2$]. Both (IX) and (X) display u.v. absorption typical of 1,2,3,4-tetrachlorocyclohexa-1,3-dienes[4,7] with the band pattern of (IX) hypsochromically shifted 3 nm compared to (X) [$\lambda_{\max}$ 270sh, 283sh, 294, 305·5, 320sh nm, $\epsilon$ 2930, 4010, 4970, 4510, 2020; $\lambda_{\max}$ 274sh, 286sh, 297, 308·5, 323sh nm, $\epsilon$ 2590, 3960, 5020, 4670, 2350, EtOH, $\epsilon \pm 5\%$]. Mass spectra of (IX) and (X) are also closely similar; both show *m*/*e* 254 ($C_9H_6Cl_4^{+\cdot}$), 255 ($M^+$ + H.), 214 ($C_6H_2Cl_4^{+\cdot}$), 219 $C_9H_6Cl_3^+$), 184 ($C_9H_6Cl_2^{+\cdot}$), and 183 ($C_9H_5Cl_2^+$) (100%) with the correct halogen isotopic abundances.

Whilst compound (IX) appears relatively stable (even on brief heating at 160°)‡ isomer (X) slowly rearranges in boiling benzene, and rapidly at 100° in toluene, to give *exo*-3,4,5,6-tetrachlorobicyclo[6,1,0]nona-2,4,6-triene, (XI) m.p. 87—88°, $\tau$ 4·05 (s, *w*/2 2Hz) 2,7-vinylic H, centred at 8·28 (d) and 8·36 (d) 1,8-methine H coupled to cyclopropyl CH$_2$, ($J_{1\text{-H}-9exo\text{-H}} \gg J_{1\text{-H}-9endo\text{-H}}$), 8·87—9·10 (complex m) overlapping CH$_2$ sextuplets. The absence of significant 1-H-2-H coupling accords with *exo*-structure (XI);[8] $\lambda_{\max}$ 250 nm $\epsilon$ *ca.* 4400, $\nu_{\max}$ 3030w, 3075w, 1598vs, 1040ms cm$^{-1}$, HC=, cyclopropane HC, ClC=CCl, cyclopropane ring.[5] The mass spectrum is almost identical to that of (X).§

The difference in stability of (IX) and (X) might be interpreted as follows: considering only realistic electrocyclic transformations, whilst the former isomer must necessarily transform into the higher energy *endo*-conformer of (XI) if it is to rearrange in a concerted reaction, (X) can give directly the stable *exo*-conformer. In contrast

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† We have also made compounds (IV) and (V) whose properties resemble those of (II).

‡ Heating compound (IX) at 115° overnight resulted in extensive decomposition.

§ Satisfactory analytical or accurate mass data have been obtained for all compounds mentioned except the known (ref. 2) (I), (VI), and (VII).

to (II) and (III) where relative ground state energies appear to be an important factor in determining relative stabilities, differences in transition state energies may be crucial in comparing (IX) and (X) (although some relief of non-bonded C-2–H, C-7–H–cyclopropyl methylene interactions could also be a factor[9]).

As to why (XI) does not rearrange further into tetrachlorodihydroindenes under the reaction conditions[10] is obscure, but both steric and electronic effects of chlorine might be expected to modify the facility of required electrocyclic reactions. Such transformation followed by hydrogen chloride elimination could account for the slow charring of neat (IX) at 115°.

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