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FRAGMENTATION OF TETRAHYDROMETHANONAPHTHALENES AND THEIR DIAZA- AND BENZO-ANALOGUES.

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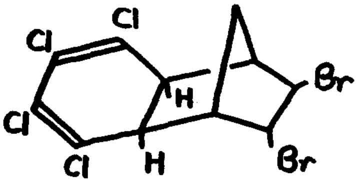
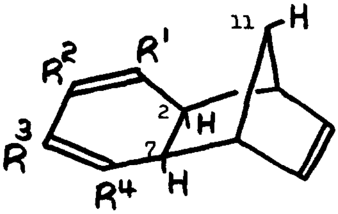
In a previous paper [1] one of us showed that the zinc dehalogenation of dibromo- compound (1) in boiling ether gives 1,2,3,4-tetrachlorobenzene and cyclopentadiene by retro- Diels-Alder reaction of the presumed intermediate (2), which therefore resembles its analogues (3)-(4) derived by decarbonylation of cyclopentadienone adducts of norbornadiene. Isolation of (2) has enabled us to compare its properties quantitatively with those of compounds (6) and (7) and to unambiguously confirm its previously assumed stereochemical features.

Stirring (1) with zinc in ethanol-acetic acid at 0° and cautious work-up at 0-5° gives triene (2), m.p. 66° (decomp.) $\nu_{max.}$ 1617vs, 712vs cm.$^{-1}$ (conj. ClC=CCl and *cis*- CH=CH) τ 3.84(t) (J 2 Hz), 6.61(m), 7.35(d) (J 1.5Hz), centred near 8.38, 8.66 (complex AB doublets) (vinyl, bridgehead, ring-junction and bridge methylene protons).[†] The ring junction nmr spin coupling confirms the *exo* assignment for the diene ring in (2) and double resonance experiments indicate that 'W' mode long range coupling occurs with the higher field anti related bridge methylene proton [2] and not to the bridgehead proton (dihedral angle *ca.* 90°); a coupling constant of at least twice the value of that observed would be expected for *exo* ring junction-bridgehead spin coupled protons [3] (*cf.* also (6),below). Characteristic 1,2,3,4-tetrachlorocyclohexadiene uv absorption [1,4] at $\lambda_{max.}$ (266), 277.5, 289, 301.5, and 314.5 nm ($\varepsilon \times 10^{-3}$: (2.9), 3.8, 5.4, 5.8, 3.4) (EtOH*) is useful in following the decomposition of (2); the solid is stable several days at *ca.* -25° but at 5° 1,2,3,4-tetrachlorobenzene slowly sublimes from the decomposing solid; in solution (EtOH) $t_{0.5}$ varies from 10.5 min. at 54.5° to 106 min. at 34.5°. (Compare the parent systems,transiently observed at 60-70°, McCulloch,ref.1).

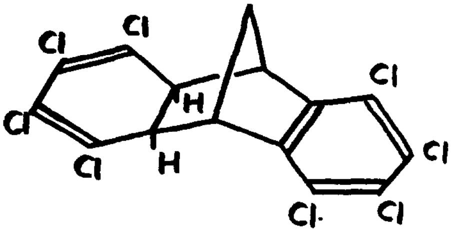
The physical and chemical properties of (2) are closely paralleled by those of its diaza analogue (6) [5] m.p.70°- 72° (decomp.) $\nu_{max.}$ 1612vs cm.$^{-1}$ (conj. ClC=CCl) τ 4.39(m), 7.39(s w/2 3Hz) centred near 8.22(d), 8.64(complex d) (bridgehead, ring-junction and bridge methylene). The stereochemistry shown for (6) is supported by these and other data;[6] uv absorption: $\lambda_{\text{max.}}$ 284sh, 295, 307.5, and 322 nm ($\varepsilon \times 10^{-3}$ 3.3, 4.7, 5.3 and 2.2) (EtOH*). Azo compound (6) rapidly decomposes at the m.p. into 1,2,3,4-tetrachlorobenzene and pyrazole, both identified by reference to the authentic compounds; it has $t_{0.5}$ 16 min. at 56.5° and 98 min. at 40°



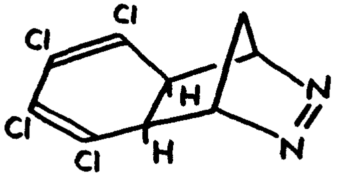
(1)



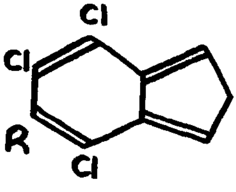
(2) R^{1-4} = Cl, $J_{\textit{endo}\text{-2,7-}\textit{anti}\text{-11}}$~1.5Hz
(3) R^{1-4} = Ph (or Ar)
(4) $R^{1,4}$ = Me, $R^{2,3}$ =Ph
(5) $R^{1,4}$ = Ph, $R^{2,3}$ = 9,10-phenanthro-



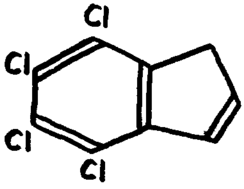
(7)



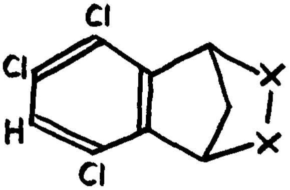
(6)

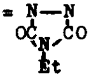


(8) R = Cl
(9) R = H



(10)



(11) X—X = N=N
(12) X—X = 
$\mathrm{N{-}N\,(CO)_2NEt}$

Earlier, attention was drawn to the contrasting stability of benzotricycloundecatriene (7) (a tetrahydromethanoanthracene) compared to the assumed intermediates (2) - (5); [1] (7) is quite stable at room temperature over several years and decomposes rapidly only at 150-180° (e.g. at 165°, $t_{0.5}$ ca. 20 min.) giving 1,2,3,4-tetrachlorobenzene and 4,5,6,7-tetrachloroindene (10), the indene being presumed formed from isoindene (8). Unimolecular rate constants for decomposition of (2) and (6) evaluated from $t_{0.5}$ at five temperatures in the range 34-56° by taking the average of two half lives at each of the four principal absorption maxima gives for (2) E_a 22.74 ∓ 0.69 Kcal/mole and similarly for (6) E_a 22.29 ∓ 0.46 Kcal/mole. Redetermination of the rate constants by the graphical method suggests that these figures may be a little high, but this method applied to the decomposition of (7) gives E_a 34.75 ∓ 2.21 Kcal/mole.

The preliminary kinetic data clearly confirm that retro-diene reaction is characteristically facile for compounds having the skeletal features of e.g. (2) and (6), but the stability of (7) and related compounds [1] suggests that molecules of this type may in general fragment less easily. For the former types, fragmentation represents reversal of the orbital symmetry allowed (but unobserved [7]) thermal concerted ortho cyclo addition to benzenes, the direction of reaction observed here being hardly surprising; as pointed out earlier however the more difficult scission of (7) (mean rate ratio for (2):(7), 3.5×10^6 at 35°) can readily be understood if isoindene (8) is necessarily formed in a similar process. The intermediacy if isoindene in the Diels-Alder addition of maleic anhydride to indene seems fairly certain [8] and we have adduced evidence for the transient formation of e.g. (9) from the isolation of (12) when azo compound (11) is thermally decomposed in the presence of N-ethyltriazolindione.[9] The decomposition of (11) is expected to be a concerted reaction [10] (rather than a biradical process [11]) and one could reason that the existence of (11) at room temperature when 2,3-diazanorbornadiene is expected to resemble in its instability the corresponding diazabicyclo[2,2,2]-octadiene (which decomposes very rapidly even at -78° [10]) reflects the necessity of unfavourably disturbing the aromatic 6-π system in order to achieve the transition state for formation of (9); analogy with the comparitive stability of (7) can clearly be drawn, insofar as both decompositions represent retro- $(4n+2)\pi$ cyclo-additions.

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FOOTNOTES AND REFERENCES.

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† Nmr signals mentioned had the correct area integrations.

* Molar extinction coefficients are subject to uncertainty due to instability, but are of the correct order of magnitude.[1,4]