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THE ADDITION OF TETRACHLOROCYCLOPENTADIENE TO DIENOPHILES

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Despite the fact that tetrachlorocyclopentadiene is fairly easily prepared (1), no careful study of the structure of its reaction products with dienophiles appears to have been reported. McBee et al. (2) obtained adducts with benzoquinone (1:1), cyclopentadiene (reported as a liquid), and maleic anhydride. Roedig and Hörnig (1) obtained similar results with the same dienophiles, and also prepared products from acrylonitrile and 1,4-naphthoquinone, and made a 2:1 adduct with benzoquinone. Mel'nikov and Volodkovitch (3) obtained adducts with diethyl maleate, methyl acrylate, norbornene, and norbornadiene, and Goldman and Kleinman (4) prepared a solid adduct with cyclopentadiene. In cases where structures were given for the reaction products, little or no supporting evidence was provided.

While investigating the Diels-Alder reactions of benzocyclobutadiene (I) (5), we generated this reactive species in the presence of tetrachlorocyclopentadiene (II), and after chromatography on alumina isolated two adducts, III and IV, the latter being the major product. [The precise stereochemistry of the compounds is undefined, although endo-addition is to be expected (5b)]. Two isomers (V, and VI or VII) were isolated from the reaction of II with dimethyl acetylenedicarboxylate, with the symmetrical structure (V) predominating. Maleic anhydride also gave mostly a symmetrical adduct, but, due to isomerisation to the fumarate, dimethyl maleate gave a complex mixture of products which were not separated. Benzoquinone gave the symmetrical 1:1 adduct (VIII) in good yield, in an exothermic reaction; no unsymmetrical product was found. Methyl phenylpropiolate also formed only the symmetrical compound (IX); the yield in this case was rather poor.

The structure of tetrachlorocyclopentadiene was confirmed as II by its N.M.R. spectrum (in CCl_4); no trace of any unsymmetrical isomer (X or XI) could be detected. Benzocyclobutadiene is generally regarded as being a very

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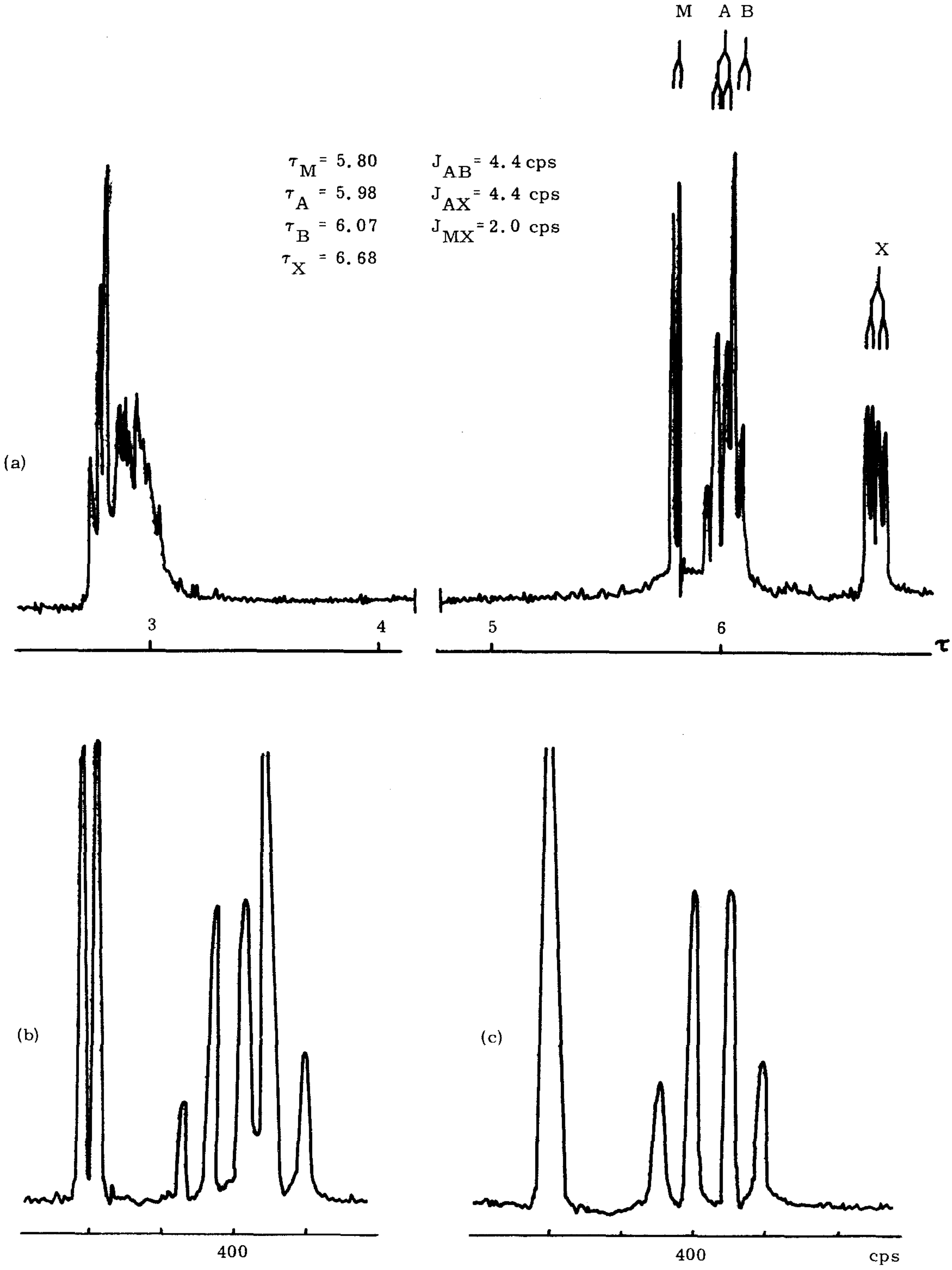
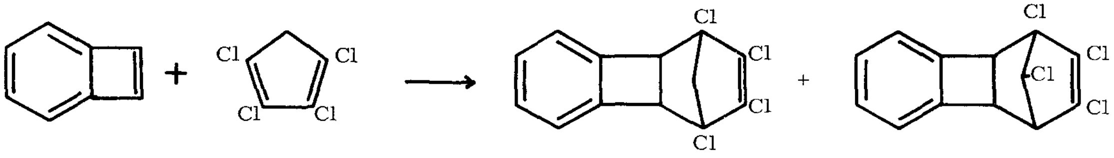
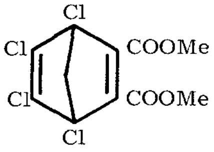
FIGURE



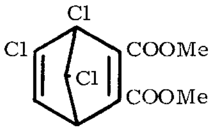
N.M.R. Spectrum of Adduct (IV), in $CDCl_3$. (a) Complete spectrum. (b) and (c), ABM protons, (c) decoupled from X proton (lower scales graduated in 10 cps intervals, from TMS).



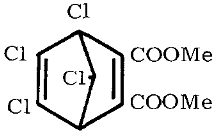
(I) (II) (III) (IV)



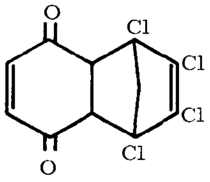
(V)



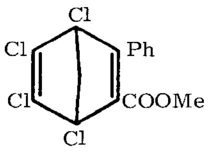
(VI)



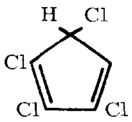
(VII)



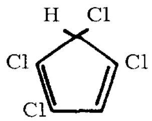
(VIII)



(IX)



(X)



(XI)

TABLE

Diels-Alder Adducts of Tetrachlorocyclopentadiene

Dienophile	Symmetrical Adduct	Unsymmetrical Adduct
Benzocyclobutadiene	III, m.p. 129-130°; 6%	m.p. 150-151°; 11%
Dimethyl acetylene-dicarboxylate	V, m.p. 104-104°; 21%	m.p. 113-114°; 4%
Maleic anhydride	m.p. 177°; 46%[a]	(not isolated); 15%[a]
Benzoquinone	VIII, m.p. 175-176°;[b] 82%	none
Methyl phenylprop-iolate	IX, m.p. 129-130°; 10%	none

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[a] Estimated by conversion into the methyl esters, m.p. 130° (symm.), 152-153° (unsymm.).

[b] Lit. m.p. 168-173° (dec.) (1), 167-168° (2).

reactive transient species, and it is therefore remarkable that it apparently forms more adduct from the unstable tautomer (X); a much lower selectivity would normally be expected than in the reactions of the stable dienophiles. The results are scarcely less surprising on the hypothesis that bond formation is not synchronous in the diene reaction, and that reaction occurs on the symmetrical diene (II), with subsequent rearrangement before cyclisation. It is also noteworthy that all the symmetrical adducts have lower melting points than their less symmetrical isomers.

The yields of products isolated, based on starting dienophile, with their melting points, are listed in the Table. Satisfactory analytical, I. R., N. M. R., and, for compounds III and IV, mass spectrometric, data were obtained for all the compounds prepared. The N. M. R. spectrum of (IV) (at 100 Mc/s) is shown in the Figure.

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