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HEXABROMOCYCLOPENTADIENE V.[1] THE DIELS-ALDER REACTION OF HEXABROMOCYCLOPENTADIENE

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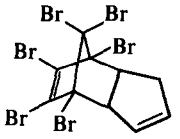
Abstract—The reactivity of hexabromocyclopentadiene (**1**) as a diene in the Diels–Alder reaction has been determined with a number of dienophiles. The results of the present study show that **1** behaves as an electron-poor diene in that cyclopentadiene is a more reactive dienophile than maleic anhydride. Qualitatively, **1** has been found to be a less reactive diene than hexachlorocyclopentadiene. Several new Diels–Alder adducts of 5,5-dibromo-1,2,3,4-tetrachlorocyclopentadiene are also reported.

Since Diels and Alder correctly formulated in 1928 the reaction between a conjugated diene and an olefin, the Diels–Alder reaction has become one of the most fundamental and useful reactions available to the synthetic organic chemist. The mechanism of this reaction, which has enticed the curiosity of many, still remains an area of active research.[2] In addition to the better understanding of the reaction that has been obtained from these mechanistic studies, the reaction has also found utility in the development of physical organic chemistry as exemplified by the development of a solvent polarity scale by Berson *et al.*[3]

Our interest in the Diels–Alder reaction originated from our studies on the chemistry of hexabromocyclopentadiene (**1**). No detailed investigation of the reactivity of **1** as a diene had been reported in the literature although several adducts of the analogous chlorine compound, hexachlorocyclopentadiene, which has been studied in great detail,[4] have found commercial utility either as insecticides or as components of fire retardant polyesters.[5] At the time that we initiated our studies, there did not appear to be any authentic examples of the Diels–Alder reaction of **1**, although the chemistry of **1** is often taught in the abundant patent literature of hexachlorocyclopentadiene.[4] Robitschek and Bean[6] have claimed the synthesis of the Diels–Alder adducts of **1** with maleic anhydride and 2-buten-1,4-diol but experimental methods and physical properties were not reported. The synthesis of **2** from **1** and cyclopentadiene has been reported.[7]



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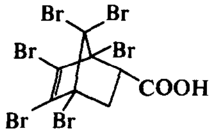

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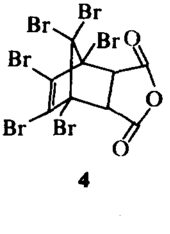
During the course of this study, Marvel and Kovacs[8] reported the synthesis of 1,4,5,6,7,7-hexabromobicyclo-2,2,1-heptene-2-carboxylic acid (**3**) from acrylic acid and **1** and, a brief study was published on the reaction of hexahalocyclopentadienes with long-chain olefins.[9]

DISCUSSION

The initial experiments on the Diels–Alder reaction of **1** were carried out with maleic anhydride since this dienophile is known to condense readily with hexachlorocyclopentadiene.[10] Although the Diels–Alder reaction of **1** with maleic anhydride to give **4** proceeded slowly in refluxing benzene or toluene, the higher boiling chlorobenzene was found to be a more satisfactory solvent. With maleimide, the Diels–Alder reaction of **1** proceeded smoothly in refluxing chlorobenzene to give **5**.



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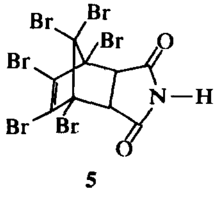

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Table 1. Diels–Alder adducts of hexabromocyclopentadiene and 1,2,3,4-tetrachloro-5,5-dibromocyclopentadiene

Reactants							Analysis									
						Yield	Carbon		Hydrogen		Bromine		Chlorine		Nitrogen	
Diene	Dienophile	Solvent	Temp (hr)	Product	m.p. °C	%	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
1	Maleimide	Chlorobenzene	Reflux (14)	9	295° (dec)[a]	92	16·98	17·00	0·47	0·45	75·32	75·10	—	—	2·20	2·24
1	Dimethylacetylene dicarboxylate	Toluene	Reflux (72)	11	138–140°[b]	27	19·35	19·40	0·88	0·92	70·37	70·40	—	—	—	—
1	Maleic anhydride	Chlorobenzene	Reflux (24)	4	250–252°[c]	93	16·93	17·00	0·32	0·16	17·23	75·40	—	—	—	—
1	Cyclopentadiene	Chloroform	−8 (8 days)	2	220–230 (dec)[d]	73	19·83	19·70	1·00	1·32	79·25	79·10	—	—	—	—
9	*p*-Benzoquinone	Benzene	150° (150°)	10	218–220	40	20·37	20·43	0·62	0·87	74·07	73·70	—	—	—	—
9	Maleic anhydride	Benzene	150 (3)	—	242–243°[e]	18										
9	Maleimide	Toluene	Reflux	—	250 (dec)[f]	38	23·72	23·60	0·66	0·75	34·80	34·25	30·86	30·80	3·07	2·90
9	Cyclopentadiene	Chloroform	−8° (8 days)	—	198–200 (dec)[g]	72	28·06	28·40	1·40	1·75	37·37	37·10	33·16	32·9		
9	*p*-Benzoquinone	Chlorobenzene	150° (2 hrs)	6		20	28·10	27·90	0·85	0·63	30·18	30·0	34·06	34·2		

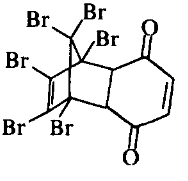
Solvent for recrystallization: [a]methylene chloride-hexane; [b]ether-hexane; [c]ethyl acetate-hexane; [d]ether-methanol; [e]See reference 12; [f]methylene chloride-hexane; [g]ether-methanol; [h]ether-methanol.

Table 2. IR and NMR spectral data of Diels–Alder adducts

Diene	Dienophile	IR[a]	Solvent	NMR
1	Maleimide	3245 cm^{-1} (N–H), 1569 and 1563 cm^{-1} (O=C-N-C=O)	Acetone-d_6	δ 10·36 (S,1,NH), δ 4·17 (S,2,CH)
1	Dimethylacetylene dicarboxylate	3040 and 3013 cm^{-1}, (C–H), 2960 cm^{-1} (OCH_3), 1722 and 1732 cm^{-1} (C=O), 1627 cm^{-1} (C=C) and 1553 cm^{-1} (CBr=CBr)	$CDCl_3$	δ 3·87 (S,OCH_3)
1	Maleic anhydride	1561 (CBr=CBr) and 1781 and 1789 cm^{-1} (O=C–O–C=O)	Acetone-d_6	δ 4·58 (S,CH)
1	Diclopentadiene	3065 cm^{-1} (=CH), 1603 cm^{-1} (CH=CH), 1574 cm^{-1} (CBr=CBr)	$CDCl_3$	δ 2·40 (m,1,CH_2), δ 3·70 (m,1,methine) δ 5·70 (m,1,vinyl)
1	*p*-Benzoquinone	1570 cm^{-1} (BrC=CBr), 1600 (CH=CH), 1670 cm^{-1} (C=O)	$CDCl_3$	δ 3·63 (S,2,CH), δ 6·70 (S,2,CH=CH)
9	Maleic anhydride	1593 cm^{-1} (CCl=CCl), 1831 and 1814 cm^{-1} (O =C —O —C =O)	$CDCl_3$	δ 4·16 (S,CH)
9	Maleimide	3199 cm^{-1} (NH), 1590 and 1582 cm^{-1} (CBr=CBr), 1732 and 1782 cm^{-1} (O=C-N-C=O)	Acetone-d_6	δ 4·17 (S,2,CH), δ 10·36 (S,1,N-H)
9	Cyclopentadiene	3065 cm^{-1} (=CH), 1603 cm^{-1} (CH=CH), 1595 cm^{-1} (CBr=CBr)	$CDCl_3$	δ 2·40 (m,l,CH_2), d, 3·70 (m,l,methine) and δ 5·70 (m,1,vinyl)
9	*p*-Benzoquinone	1685 cm^{-1} (C=O), 1610 cm^{-1} (CH=CH), 1598 cm^{-1} (CCl=CCl)	$CDCl_3$	δ 3·82 (5,2,CH), δ 6·68(S,2,vinyl)

[a] All samples were recorded as split mulls (Nujol-Flurolube) with the exception of the cyclopentadiene adducts which were obtained in CCl_4 solution.

p-Benzoquinone and dimethyl acetylene dicarboxylate with **1** gave the Diels–Alder adducts **6** and **7** respectively. No attempt was made to optimize the yields of these dienophiles.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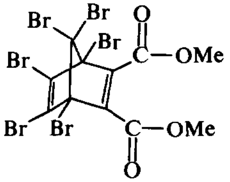
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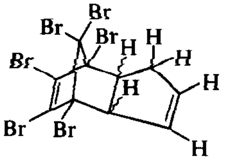
The *p*-benzoquinone adduct, **6** was found difficult to purify. Perhaps this was due to the cyclopentadiene-quinone photoisomerization reaction which has been described by Cookson.[11] 5,5-Dibromo-1,2,3,4-tetrachlorocyclopentadiene (**9**)[12] also gave Diels–Alder adducts with *p*-benzoquinone, dimethyl acetylene dicarboxylate, maleimide and maleic anhydride (Table 1).

Any study on the Diels–Alder reaction of hexabromocyclopentadiene would be incomplete without determining its classification as either an electron-rich or an electron-poor diene.[2b] Hexachlorocyclopentadiene, which is an electron-poor diene, reacts some 500 times faster with the electron-rich dienophile, cyclopentadiene than with the electron-poor dienophile, maleic anhydride. The reaction of **1** and cyclopentadiene in refluxing heptane has been reported to give **2** as a pale yellow solid, m.p. 144–145°. We have been unable to prepare **2** by this procedure or at various temperatures between 120° and 180°. However, using mild conditions (−8°, two weeks) in order to minimize the dimerization of cyclopentadiene, we have obtained a product, m.p. > 220° (dec) whose mass spectrum and elemental analysis were consistent with a Diels–Alder adduct of cyclopentadiene and **1** (see below). 5,5-Dibromo-1,2,3,4-tetrachlorocyclopentadiene was also found to react with cyclopentadiene under similar conditions. Only starting materials can be recovered from solution of maleic anhydride and **1** under conditions identical for the preparation of **2**. These results demonstrate that **1**, like hexachlorocyclopentadiene is an electron deficient diene in the Diels–Alder reaction.

The NMR analysis[13] of the hexabromocyclopentadienecyclopentadiene adduct is of interest since four possible structures exist, i.e. the *exo* and *endo* adducts of **2** and **8**.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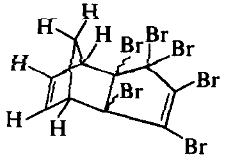
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The analysis of a 100 MHZ pMR spectrum of the $C_{10}H_6Br_6$ adduct allowed an unambiguous differentiation between **2** and **8**. The geminal protons are easily identified from the chemical shifts and the large coupling constants of −18·4 Hz. The methine and the olefinic protons are also easily identified from their chemical shifts. The coupling constant between the two methine protons was found to be 8·5 Hz, which is expected for the vicinal coupling constant in **2**, but completely unreasonable for the corresponding coupling in **8**.

Qualitatively, hexachlorocyclopentadiene appears to be a more reactive diene than hexabromocyclopentadiene. When allowed to react with maleimide under identical conditions for one hour (Experimental), hexachlorocyclopentadiene gave a 33% yield of the adduct compared to 26% for hexabromocyclopentadiene. After 2 hours the yields were 46 and 40% respectively. These results are in good agreement with those of Lyon *et al.*[9] who found the second-order constants to be $3·5 \times 10^{-6}$ l/mole sec. for hexabromocyclopentadiene and $5·3 \times 10^{-6}$ l/mole sec. for hexachlorocyclopentadiene toward long chain alkenes in the Diels–Alder reaction.

EXPERIMENTAL

The NMR spectra were obtained with a Varian A-60 spectrophotometer using TMS as an internal standard. IR spectra were obtained on a Beckmann IR-9 spectrometer. The mass spectra were obtained with a CEC 21-110B (Direct Probe) instrument. All m.ps were taken on a Thomas-Hoover m.p. apparatus and are uncorrected. Fisher "Certified" maleic anhydride was found to be of satisfactory purity for the Diels–Alder reaction.

Hexabromocyclopentadiene (**1**). This material was prepared from either cyclopentadiene and sodium hypobromite[14] or from hexachlorocyclopentadiene and boron tribromide as described.[15] In both cases the crude reaction product was purified by filtration through silica gel followed by recrystallization from MeOH to give material, m.p. 86–88°.

*5,5-Dibromo-*1,2,3,4-*tetrachlorocyclopentadiene* (**9**). This material was prepared by a modification of the procedure reported.[12] Tetrachlorocyclopentadiene (30·0 g, 0·147 mol) was dissolved in benzene-dimethyl formamide (90:10) and N-bromosuccinimide (52·3 g, 0·294 mol) was added to the soln. The mixture was heated to reflux. After 15 min dissolution of the N-bromosuccinimide had taken place. The reaction was refluxed for an additional 20 min, cooled to room temp and diluted with 500 ml water. The organic layer was separated and washed with an additional 500 ml warm water, dried and the benzene removed *in vacuo* to give 52·0 g of product which was contaminated with a trace of a carbonyl material (preseumably succinimide). Attempts to remove this by distillation alone were unsuccessful. Pure material was obtained by recrystallization (0° or less) from MeOH. The product obtained in this manner is a pale yellow solid and melts at room temp.

Reaction of hexahalocyclopentadienes with maleimide. Maleimide (2·43 g, 0·025 mol) and hexabromocyclopentadiene (13·49 g, 0·025 mol) were heated in refluxing toluene (30 ml) for 60 min. The reaction was cooled to room temp or less by a dry-ice acetone bath and the ppt removed by filtration to give 11·48 g of solids (mixture of product and starting materials). The unreacted maleimide was removed by vacuum drying and, the hexabromocyclopentadiene by washing with hexane to give 5·33 g (26%) of **9**. The material balance of hexabromocyclopentadiene was greater than 95%. Under identical conditions, hexachlorocyclopentadiene and maleimide gave a 33% gield the corresponding adduct. After 120 min the yield of **9** increased to 40% and the yield of the adduct of hexachlorocyclopentadiene increased to 46%.

Reaction of 1,2,3,4-*Tetrahalo*-5,5-*dimethoxycyclopentadienes with maleic anhydride.* Maleic anhydride (0·5 g, 0·005 mol) and 1,2,3,4-tetrabromo-5,5-dimethoxycyclopentadiene (2·26 g, 0·005 mol) were refluxed in toluene for 100 min. The reaction was cooled to room temp or less by a dry ice acetone-bath and the ppt removed by filtration and dried to give 1·97 g (71%) of 1,4,5,6-tetrabromo-7-oxo-dimethyl acetal-5-norbornene-2,3-dicarboxylic anhydride.[1] Evaporation of the mother liquor gave only recovered starting material. The material balance for the reaction was greater than 92%.

Under identical conditions, 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene and maleic anhydride gave a 74% 1,4,5,6-tetrachloro-7,7-dimethoxy-5-norbornene-2,3-dicarboxylic anhydride.[16] The material balance was better than 95%.

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