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HEXAHALOCYCLOPENTADIENES—III

SYNTHESIS AND DIELS–ALDER REACTION OF 1,2,3,4-TETRABROMO-5,5-DIMETHOXYCYCLOPENTADIENE

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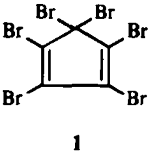
Abstract—Treatment of hexabromocyclopentadiene (**1**) with sodium methoxide in methanol-glyme provides 1,2,3,4-tetrabromo-5,5-dimethoxycyclopentadiene (**6**). The reactivity of this new diene in the Diels–Alder reaction has been determined with a number of dienophiles. The greater reactivity of ketal **6** towards maleic anhydride compared to cyclopentadiene suggests that **6** behaves as an electron-rich diene in the Diels–Alder reaction.

ALTHOUGH hexabromocyclopentadiene (**1**) has been known for almost forty years,[1] the chemistry of **1** has evoked little interest as indicated by the few publications in this area. Riemschneider and Grabitz[2] have claimed the isolation of the Diels–Alder adduct of **1** with cyclopentadiene, and Marvel and Kovacs[3] have reported the synthesis of 1,4,5,6,7,7-hexabromobicyclo-[2.2.1]-5-heptene-2-carboxylic acid (**2**) from the Diels–Alder reaction of **1** and acrylic acid. On reduction with zinc and hydrochloric acid, **1** yields 1,2,3,4-tetrabromocyclopentadiene,[4] whereas hydrogenation of **1** gave 1,2,3,4,5-pentabromocyclopentadiene.[5] In addition to the alkylation of **1** with trialkyl phosphites,[6] the reductive coupling of **1** to octabromofulvalene[7a] (**3**) and its dimerization to dodecabromopentacyclo $[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]$ decane[b,7c] (**4**) were the only reactions in the literature when we initiated our studies in this area. Recently, we have shown that **1** undergoes reaction with fluorosulphonic acid to give the fluoro-



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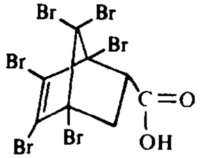

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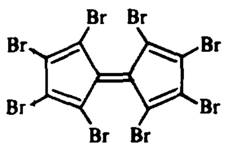

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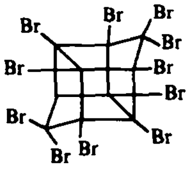

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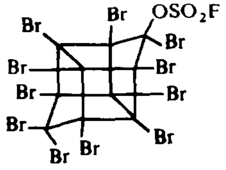

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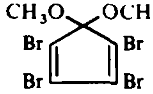
sulphate ester[8] of undecabromopentacyclo $[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]$ decan-5-ol (**5**). We now wish to report the synthesis of 1,2,3,4-tetrabromo-5,5-dimethoxycyclopentadiene (**6**) and its reactivity as a diene in the Diels–Alder reaction



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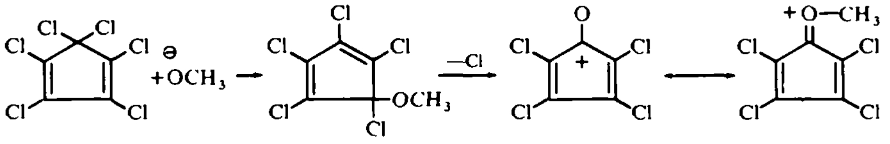
DISCUSSION

Preliminary experiments on the reaction of hexabromocyclopentadiene with nucleophilic reagents were unsuccessful. When an alcoholic solution of an alkali metal iodide, cyanide or acetate was allowed to react with a solution of **1** in the same solvent at room temperature, a blue-green solution formed immediately. After a short period of time, the reaction mixture turned brown, and no identifiable compound could be isolated with the exception of unreacted starting material. Similar results were observed in the reaction of **1** with sodium methoxide at room temperature. The blue-green solutions are probably due to the formation of the pentabromocyclopentadienyl anion as Riemschneider[4] has observed similar color changes when 1,2,3,4-tetrabromocyclopentadiene is allowed to react with base. The decomposition of **1** with methoxide was circumvented by addition of a methanolic solution of sodium methoxide to the precooled solution of **1** in glyme or glyme–methanol at −20° or less. After the addition of the methoxide solution, the reaction mixture was allowed to warm to room temperature and then poured onto ice–water to precipitate the product in greater than 90% yield. Proof of structure of the product as 1,2,3,4-tetrabromo-5,5-dimethoxycyclopentadiene follows from the elemental analyses and spectroscopic data. The mass spectrum gave a mol wt of 438 and the correct isotope ratio of four Br atoms. The NMR spectrum shows only a singlet at 3·29 ppm which is consistentent with the proposed structure. The UV spectrum had λ_{max}^{hexane} 318 mμ (ε 1700), essentially identical with that of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene.[9]



The reaction of hexachlorocyclopentadiene with alkoxides has been studied by several groups.[10–12,*] McBee *et al.* found the reaction of hexachlorocyclopentadiene with methanolic sodium methoxide to be first order, both in diene and in base, and secondly, that the dimethoxy derivative was formed exclusively. In a more recent study on the chemistry of the tetrachloroketals, Lemal *et al.* were able to isolate from the reaction of phenoxide and hexachlorocyclopentadiene a monophenoxy deriva-

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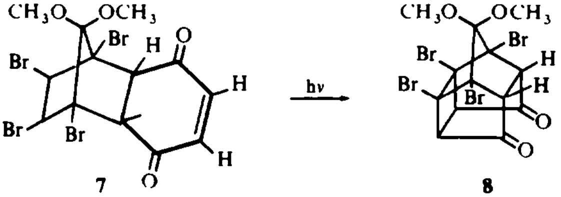
[*] Since the monomethyoxy derivative could not be detected in the reaction mixture by vapor phase chromatography, McBee *et al.* proposed that the second Cl atom is displaced in a fast step unmeasurable by comparison with the first displacement. Presumably, the fast second step is due to the further resonance stabilization by the methoxyl group of the incipient carbonium ion.

TABLE 1 IR AND NMR SPECTRAL DATA OF DIELS–ALDER ADDUCTS

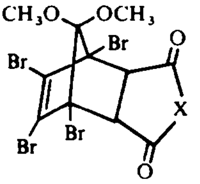
Dienophile	IR	Solvent	NMR
p-Benzoquinone	1570 cm^{-1} (BrC=CBr), 1600 (CH=CH), 1670 cm^{-1} (C=O)	$CDCl_3$	δ3·63 (s, 2, CH), δ3·66 (s, 3, OCH_3), δ3·70 (s, 3, OCH_3), δ6·70 (s, 2, CH=CH)
Maleic anhydride	1565 cm^{-1} (BrC=CBr), 1785 cm^{-1} (C=O)	$CDCl_3$	δ3·92 (s, 2, CH), δ3·68 (s, 3, OCH_3), δ3·64 (s, 3, OCH_3)
Maleimide	1569, 1563 cm^{-1} (CBr=CBr) 1787, 1715 cm^{-1} (O=C—N—C=O) 3245 cm^{-1} (NH)	DMSO-d_6	δ3·53 (s, 3, OCH_3), δ3·58 (s, 3, OCH_3), δ3·77 (s, 2, CH), δ11·3 (s, 1, NH)
Dimethylacetylene dicarboxylate	1750 cm^{-1} (C=O) 1210–1255 (C—O)	CCl_4	δ4·00 (s, 2, OCH_3), δ3·86 (s, 1, OCH_3)
Divinyl sulfone	1129, 1314 cm^{-1} (SO_2), 1515 cm^{-1} (CBr=CBr), 1612, 970 cm^{-1} (C=CH_2), 3001 cm^{-1} (C—H)	$CDCl_3$	δ2·60 (m, 2, CH_2), δ3·62 (s, 3, OCH_3), δ3·67 (s, 3, OCH_3), δ4·00 (m, 1, CH), δ6·1–6·8 (m, 3, CH=CH_2)
cis-1,2-Dichloro-ethylene	1569 cm^{-1} (CBr=CBr)	$CDCl_3$	δ3·62 (s, 3, OCH_3), δ3·66 (s, 3, OCH_3), δ4·86 (s, 2, CH)
Cyclopentadiene	3049 cm^{-1} (=CH), 1614 cm^{-1} (CH=CH), 1572 cm^{-1} (CBr=CBr)	$CDCl_3$	δ2·40 (m, 2, CH_2), δ3·59 (s, 3, OCH_3), δ3·62 (s, 3, OCH_3), δ3·50 (m, 2, CH), δ5·70 (m, 2, CH=CH)
Acrylonitrile	2240 cm^{-1} (C≡N), 1573 (CBr=CBr)		δ3·60 (s, 3, OCH_3), δ3·64 (s, 3, OCH_3), δ2·10 (q, 1, —CH endo), δ2·75 (q, 1, CH, exo), δ3·58 (q, 1, CHCN)
Allyl alcohol	3720 cm^{-1} (OH), 1570 cm^{-1} (CBr=CBr) 1032 cm^{-1} (C—O)	$CDCl_3$	δ3·58 (s, 3, OCH_3), δ3·63 (s, 3, OCH_3), δ1·70 (s, 1, OH), δ3·33, 3·80 (m, 2, CH_2OH), δ2·89 (m, 1, C-5 proton) δ2·52 (m, 1, C-6 proton, exo), δ1·68 (m, 1, C-6 proton, endo)
5-Methylene-2-norbornene	1669 cm^{-1} (C=CH_2), 1579 cm^{-1} (CBr=CBr)	$CDCl_3$	δ2·47 (m, 1, C-6 proton), δ2·22 (m, 1, C-2 proton, exo), δ1·85 (m, 1, C-2 proton, endo), δ2·79 (m, 1, —C-1 proton), δ2·64 (1, s, C-1a proton), δ2·64 (1, —s, C-4a proton), δ1·60 (m, 1, C-10 proton, syn), δ1·09 (m, 1, C-10, proton anti), δ4·64, 4·92 (m, 2, —C=CH_2), δ3·56 (s, 3, OCH_3), δ3·61 (s, 3, OCH_3)

tive.[11] In the present study, all efforts to prepare ketals derived from other alcohols, e.g., ethyl, isopropyl and n-propyl under the conditions for the synthesis of **6** were unsuccessful.

p-Benzoquinone was selected as a dienophile for the initial experiments on the reactivity of **6** as a diene in the Diels–Alder reaction since the known photocyclization of the diene–quinone adducts would provide a facile method to establish the stereochemistry of the adduct.[13] When allowed to react in refluxing toluene, *p*-benzoquinone and **6** gave in good yield ($>80\%$) the Diels–Alder adduct **7**. (The spectral properties of the adducts are summarized in Table 2.) When irradiated in the solid state for several days, **7** photoisomerized to 1,8,9,11-tetrabromopentacyclo $[6.3.0.0^{2,7}.0^{4,11}.0^{5,9}]$ undecane-3,6,10-trione-10,10 dimethyl acetal **8**. The photoisomerization of **7** to **8** is consistent with *endo* addition and all other adducts described below are *assumed to be endo by invocation of Alder's endo addition rule* since spectral data is equally applicable to both *exo* and *endo* addition. The photoisomerization can be followed by the disappearance of the carbonyl band of **7** at 1670 cm^{-1} and the appearance of the carbonyl band of **8** at 1770 cm^{-1}. It is of interest to note that in the NMR spectra of the adducts the OMe groups are nonequivalent and appear as two singlets separated by 2–3 c/s whereas one singlet is observed for the OMe groups in the NMR spectrum of **8**. The nonequivalence is probably due to the π orbitals of the halogen substituted double bond of **7**. The cross-conjugated enediones, maleic anhydride and maleimide gave the adducts **9a** and **9b** on reaction with **6** in refluxing toluene.



7 **8**



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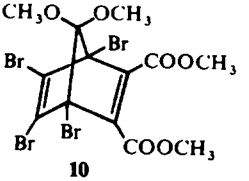
9a: X = O
b: X = N—H

Dimethyl acetylene dicarboxylate was the only acetylenic dienophile investigated in this study. The reaction product was not the norbornadiene **10**, but, trimethyl tribromohemimellitate (**11**). The aromatization of **10** to **11** has been reported for the analogous chlorine compound.[14] Although dimethyl acetylene dicarboxylate reacts



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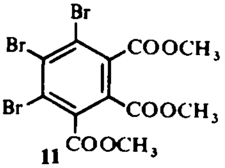

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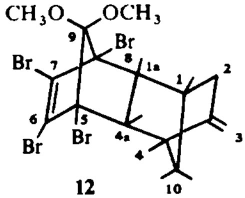
TABLE 2 DIELS–ALDER ADDUCTS OF 1,2,3,4-TETRABROMO-5,5-DIMETHOXYCYCLOPENTADIENE

Dienophile	Solvent	Temp (hr)	Product	M.p., °C	% Yield	Analysis C		H		Br		Cl, N or S	
						Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
p-Benzoquinone	Toluene	reflux (2·5)	**7**	195–196^{a}	81	28·36	28·45	1·83	1·75	58·17	58·00	—	—
Maleic Anhydride	Toluene	reflux (3)	**9a**	244–245^{b}	86	24·44	24·60	1·49	1·45	59·25	59·10	—	—
Maleimide	Toluene	reflux (2)	**9b**	254–256^{c}	97	24·50	24·50	1·68	1·95	59·36	59·40	2·62	2·75
Dimethylacetylene dicarboxylate	Toluene	reflux (48)	**11**	111–112^{d}	23	29·44	29·60	1·85	1·86	49·30	49·07	—	—
Divinyl Sulfone	Benzene	165° (4)		104–106^{e}	80	23·60	24·00	2·18	2·16	57·09	57·30	5·72	5·60
cis-1,2-Dichloroethylene	Dienophile	160° (18)		135–137^{f}	65	20·03	20·40	1·50	1·46	59·37	59·90	13·16	12·80
Acrylonitrile	Dienophile	180° (4)		95–96^{g}	54	24·24	24·30	1·83	1·78	64·64	64·85	13·16	13·00
Cyclopentadiene	Benzene	190° (2)		141–143^{h}	71	28·34	28·50	2·38	2·14	62·90	63·20		
5-Methylene-2-norbornene	Benzene	165° (4)	**12**	72–74^{i}	22	32·87	33·20	2·94	3·12	58·36	58·63		
Allyl alcohol	Benzene	200° (1·5)		89–90^{j}	46	24·02	24·30	2·42	2·53	63·99	63·60		
Dichloromaleic anhydride		180° (60)		No Reaction									
Tetrachlorobenzoquinone		180° (60)		No reaction									

Solvent for recrystallization: [a] ether methanol; [b] carbon tetrachloride-methylene dichloride; [c] methanol; [d] methylene dichloride-methanol; [e] ether-hexane; [f] ether-methanol; [g] methanol; [h] ether-methanol; [i] methanol; [j] hexane with **6** in refluxing toluene, the reaction was considerably slower than with *p*-benzoquinone.

Good yields of the Diels–Alder adducts were obtained when either divinyl sulphone, *cis*-1,2-dichloroethylene or acrylonitrile were used as dienophiles. In these cases, higher temperatures (165–180°) and longer reaction times (4–20 hr) were required. Two hydrocarbons, cyclopentadiene and 5-methylene-2-norbornene were examined as dienophiles. The former gave in good yield the Diels–Alder adduct of **6** after heating for about 2 hr at 190°. With 5-methylene-2-norbornene, the cycloaddition took place through the internal olefin to give the adduct **12**. The compound was assigned the *endo* adduct on the basis of the NMR experiment. No splitting of the C-1a and C-4a could be observed. If the same protons were *endo* (relative to the ketal moiety) a coupling of 3 c/s or greater would be expected with C-1 and C-4 protons. The C-10 bridge was assigned the anti-position relative to the C-9 bridge from steric considerations on examination of the molecular models.



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Allyl alcohol and cyclopentadiene were found to be the least reactive dienophiles to give Diels–Alder adducts with **6** under the several conditions used.

The qualitative results on the relative reactivity of the dienophiles discussed above are readily understood in light of Alder's Rule.[15] The electron deficient dienophiles, e.g., maleimide, maleic anhydride and benzoquinone are far more reactive than the electron rich dienophiles, e.g., cyclopentadiene and allyl alcohol. The replacement of hydrogen by chlorine in maleic anhydride or *p*-benzoquinone inhibits the reaction. After 60 hours at 180°, both the ketal and dienophile, either dichloromaleic anhydride or tetrachloro-*p*-benzoquinone can be recovered quantitatively. Since dichloromaleic anhydride and tetrachloro-*p*-benzoquinone are also electron poor dienophiles, the failure to observe the Diels–Alder reaction in these two cases may be due to steric factors. The greater reactivity of **6** toward electron deficient dienophiles permits its classification as an electron rich diene in the Diels–Alder reaction. This is in contrast to hexachlorocyclopentadiene which behaves as an electron-poor diene. Kinetic studies have shown that hexachlorocyclopentadiene is 500 times more reactive toward cyclopentadiene than maleic anhydride.[16] However, the classification of a diene as electron rich or electron poor must be made with reservation since steric and/or electronic effect in dienophiles not yet investigated may alter the proposed classification.

EXPERIMENTAL

UV spectra were determined with a Cary recording spectrophotometer, Model 15 and are reported in millimicrons. NMR spectra were obtained with a Varian A-60 using TMS as an internal standard. IR spectra were obtained with a Beckmann IR-9 spectrometer. The mass spectrum was obtained for each compound on a CEC 21-110B (Direct Probe) instrument. In every case, the spectrum was consistent with the proposed structure and gave the correct mol wt and isotope ratios for the number of halogens present in the molecule. All m.p.s were taken on a Thomas–Hoover m.p. apparatus and are uncorrected.

1,2,3,4-*Tetrabromo*-5,5-*dimethoxycyclopentadiene* (**6**). Hexabromocyclopentadiene[1] (54 g, 0·1 m) was dissolved in dimethoxyethane (250 ml) and the soln cooled to −78° in a 3-necked, round-bottomed flask (500 ml) equipped with magnetic stirrer, dropping funnel, condenser, thermometer and N_2 inlet. After the temp had decreased to −78°, a NaOMe soln, prepared from 12·8 g of 85% NaOMe and anhyd MeOH (75 ml) was added dropwise. When the addition was complete, the cooling bath was removed and the homogeneous soln allowed to warm to room temp. At approximately 0°, the NaBr began to precipitate from the reaction. After 2 hr at room temp, the reaction mixture was poured onto acidified ice-water mixture. The off-white ppt was collected on a filter and dried to give 42·6 g (96%) of crude ketal (m.p. 95–100°). Recrystallization from ether–MeOH gave pure ketal: m.p. 104–105°; IR (split mull) 2999, 2952, 1450 and 1450 cm^{-1} (C—H), 1573 cm^{-1} (CBr═CBr), 1080–1200 cm^{-1} (C—O); NMR (CCl_4) δ3·29 (s, OCH_3); UV max (hexane) 318 mμ (ε 1700). (Found: C, 19·10; H, 1·36; Br, 72·08. Calc. for $C_7H_6Br_4O_2$: C, 19·00; H, 1·37; Br, 72·39.)

1,8,9,11 *Tetrabromopentacyclo* $[6.3.0.0^{2,7}.0^{4,11}.0^{5,9}]$ *undecane*-3-6,10-*trione*-10,10-*dimethyl Ketal* (**9**). 1,4-Methanonaphthalene-5,8,9-trione, 1,2,3,4-tetrabromo-4,4-dimethyl acetal (2·0 g) was placed in a Fisher–Porter reactor degassed and attached to a Rinco evaporator. The sample was rotated and irradiated (2537 Å) for several days. The material, on recrystallization from ether–hexane yielded 1 g (50%) of product, m.p. 253–254°; IR, 1770 cm^{-1} (C═O); NMR ($CdCl_3$), δ 3·78 (s, 3, OCH_3), δ 3·40 (s, 2, methine hydrogen). (Found: C, 28·60; H, 1·95; Br, 57·8. Calc. for $C_{13}H_{10}Br_4O_2$; C, 28·35; H, 1·83; Br, 58·17.)

General procedure for preparation of the Diels–Alder adducts

The reaction for the more reactive dienophiles was carried out by refluxing equimolar amounts of diene and dienophile in toluene as indicated in Table 2. The remaining were carried out in sealed tubes using benzene or excess dienophile as solvent.

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