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SOME NEW DIENOPHILES IN THE DIELS–ALDER REACTION WITH ACTIVE CYCLIC DIENES

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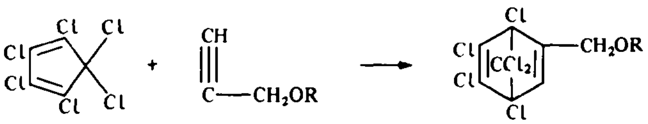
Abstract—A comparative study of the Diels–Alder reaction have been carried out for three types of cyclic dienes: cyclopentadiene (CPD), hexachlorocyclopentadiene (HCP), and tetrachloro-1,2-benzoquinone (TCBQ) with dienophiles of five types: monosubstituted acetylenes (propargyl alcohol and its esters), conjugated amines (allyl acetylene, allyl ethynyldimethylcarbonol and its esters), conjugated dienes (2-methylhexadiene-3,5-ol-2 and its esters, 1-ethoxy- and 1-ethoxycarbonylbutadiene-1,3), and conjugated trienes (hexatriene-1,3,5 and 5-methylhexatriene-1,3,5).

It was found that conjugated trienes react with dienes of all types under mild conditions and give only the monoadducts through the terminal vinyl or ethynyl group.

The diene syntheses have been studied in detail for highly active polychlorinated cyclic dienes of the HCP type with a common dienophiles such as maleic anhydride, *p*-quinones, and allyl derivatives.[1,3] However, the reactions of HCP and TCBQ with dienophiles such as acetylenes, vinyl acetylenes, and conjugated dienes[3–9] are less well documented, while the reactions with dienophiles such as allyl acetylene or conjugated polyenes have not been given any attention. In this connection, we have studied the Diels–Alder reaction of HCP, TCBQ and CPD (for comparison) with a series of dienophiles for synthesis of new functionally substituted di-, tri- and tetracyclic compounds, among which useful derivatives could be expected.

(1) *Reaction of polychlorinated cyclic dienes with monosubstituted acetylenes*

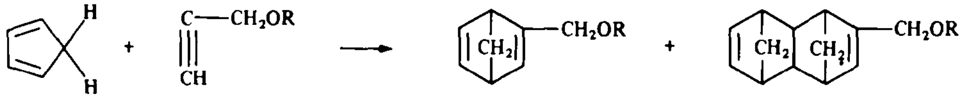
Acetylenes are seldom used as dienophiles in the Diels–Alder reaction with polychlorinated cyclic dienes.[1,3] In addition to propargyl alcohol we have introduced β-oxyethyl, cyanoethyl esters and acetate of propargyl alcohol into the reaction with HCP and CPD. The reaction proceeds under optimal conditions (150–155°, 8 hr, molar ratio—diene:dienophile = 2:1) and gives monoadducts of I type, yield 75–90%.



$R = CH_2CH_2OH, CH_2CH_2CN$ or $COCH_3$

1

In contrast to polychlorinated cyclic dienes, the reaction with CPD proceeds under the stronger conditions (175–180°) and gives the mixture of mono- and bis-adducts of types 2 and 3. The monoadducts 2 are formed in yields of 72–84% when a molar ratio of diene to dienophile 1:2 is used. And the bis-adducts 3 are formed as main products with yields of 75–86%, when this ratio is 2:1. The bis-adducts 3 can be obtained as a result of condensation of CPD with monoadducts 2 at 140–145°, yield being 80–90%.



$R = H, CH_2CH_2OH, CH_2CH_2CN$ or $COCH_3$

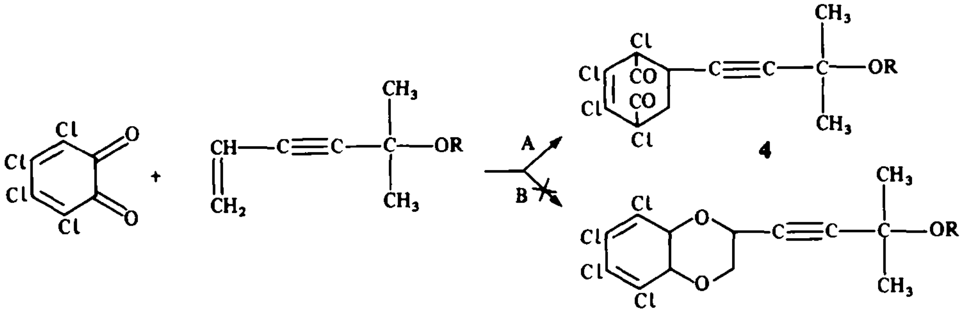
2

3

(2) *Reactions of polychlorinated dienes with conjugated enynes*

The literature states[4,5] that diene synthesis of CPD and HCP with vinyl acetylenes proceeds through the double bond only and results in monoadducts with good yields.

However, TCBQ was not introduced into the reaction. First, the diene synthesis of TCBQ was carried out with vinyl ethynyldimethylcarbinol (VEDC) and its methyl ester. This reaction theoretically is likely to follow two different routes:



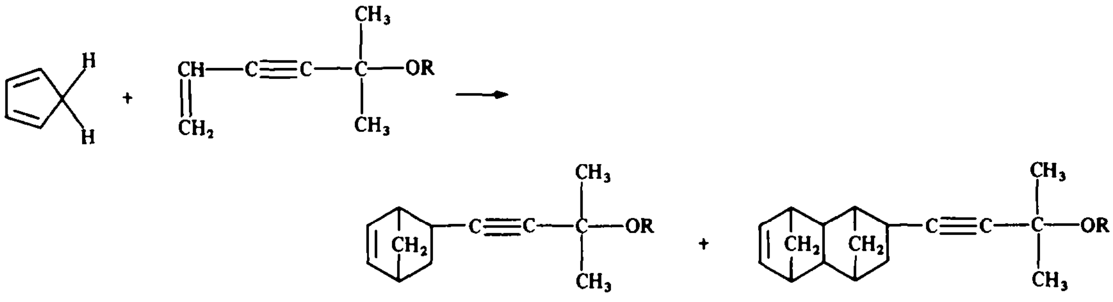
4

R = H or CH_3

At 105–110° VEDC reacted with TCBQ giving adduct 4, its yield being 85% under optimal conditions (108°, 18 hr, TCBQ:VEDC = 1:2). It will be noted that the methyl ester of VEDC reacts with TCBQ in benzene solution at room temperature, giving adduct 4 (R = CH_3) in quantitative yield.

The condensation of esters of VEDC with CPD proceeds under the stronger conditions (165–170°) through the vinyl group and gives both monoadducts **5** and bis-adducts **6**.

The adducts **5** are formed at 165–170° for 8 hr with molar ratio of diene to dienophile 1:2 in 70–89% yield, and adducts **6** are formed in 5–10% yield; with molar ratio of diene to dienophile 2:1 in 14 hr the adducts **5** are formed in 10–20% yield, and adducts **6** in 55–70% yield.

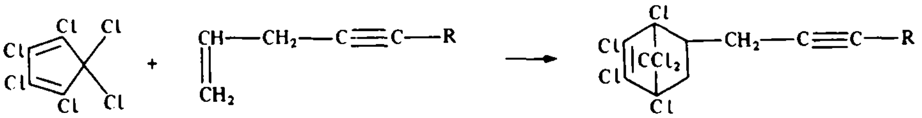


5 **6**

R = CH_3; CH_2CH_2OH

(3) *Reaction of polychlorinated cyclic dienes with unconjugated enines*

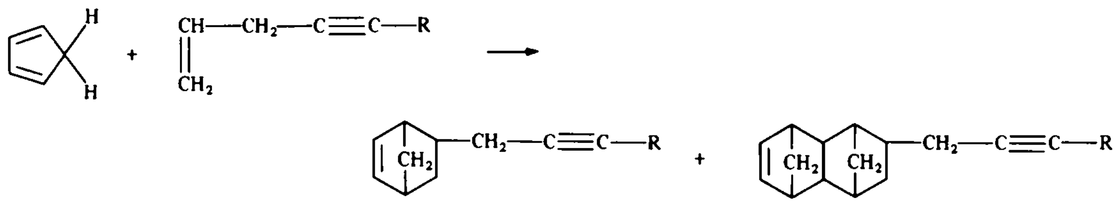
We have introduced allyl acetylene (AA), allyl ethynyldimethylcarbinol (AEDMC), and methyl ester of the latter into the condensation with HCP. The reaction proceeded more readily than in the case of monosubstituted acetylenes at 80–100° and through the vinyl group exclusively, this resulted in monoadducts 7 in 70–90% yield.



7

R = H; $C(CH_3)_2OH$ or $C(CH_3)_2OCH_3$

CPD unlike HCP reacts with AA and AEDMC under the stronger conditions (150–180°) also through end vinyl group, giving both monoadducts **9** and bis-adducts **10**.

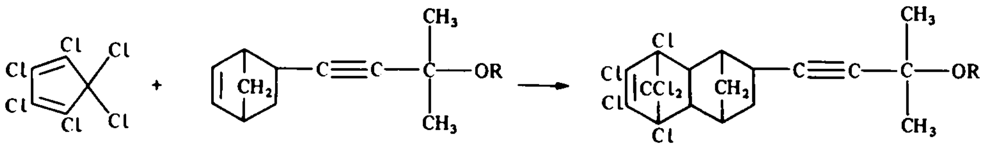


8 9

R = H or $C(CH_3)_2OH$

The yield of adducts depends on the molar ratio of components, duration and temperature of the reaction. For example, under optimal conditions (150–155°, 7 hr, CPD : AA = 1 : 1) the monoadduct **8** (R = H) is formed in 72.7% yield, and bis-adduct **9** is formed in 8.5% yield. Under the same conditions with CPD : AA = 2 : 1 in 16 hr **8** (R = H) and **9** (R = H) are obtained in 20% and 66.6% yields, respectively. Similarly, the reaction of CPD with AEDMC (175–180°, 16 hr, CPD : AEDMC = 1 : 1) gives **8** (R = $C(CH_3)_2OH$) in 76.3% yield and **9** (R = $C(CH_3)_2OH$) in 10% yield. The reaction at the same temperature with CPD : AEDMC = 2 : 1 in 29 hr gives **8** (R = $C(CH_3)_2OH$) in 15% yield and **9** (R = $C(CH_3)_2OH$) in 69.5% yield.

Unconjugated enyne **5** undergoes the diene synthesis with HCP to give polychlorotetracyclic compounds with an acetylenic bond in the side-chain. This method is very useful for the synthesis of polychloro-containing tetracyclic compounds. These adducts **10** are obtained in 45–70% yield at 110° for 8 hr.

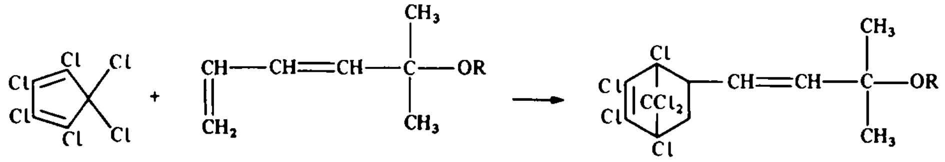


R = CH_3; CH_2CH_2OH 5 10

(4) *Reaction of polychlorinated cyclic dienes with conjugated dienes*

To date 1,3-diene hydrocarbons were used only in the reaction with polychlorinated cyclic dienes.[3] We used *trans*, *trans*-2-methylhexadien-3, 5-ol-2 and its esters in the reaction with HCP and TCBQ.

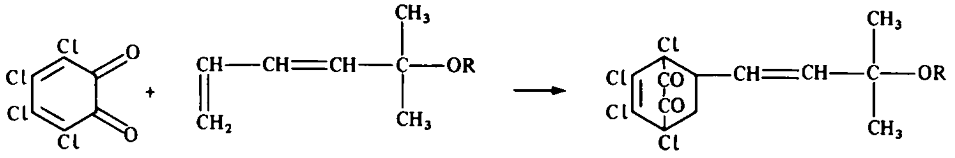
2-Methylhexadien-3,5-ol-2 condenses with HCP at 95–100° through the terminal double bond giving the corresponding adduct **11** (R = H) in 60–90% yield. The reaction with esters of diene carbinol proceeds analogously.



R = H; CH_3; CH_2CH_2OH; CH_2CH_2CN; $CH_2CH(OH)CH_2Cl$

11

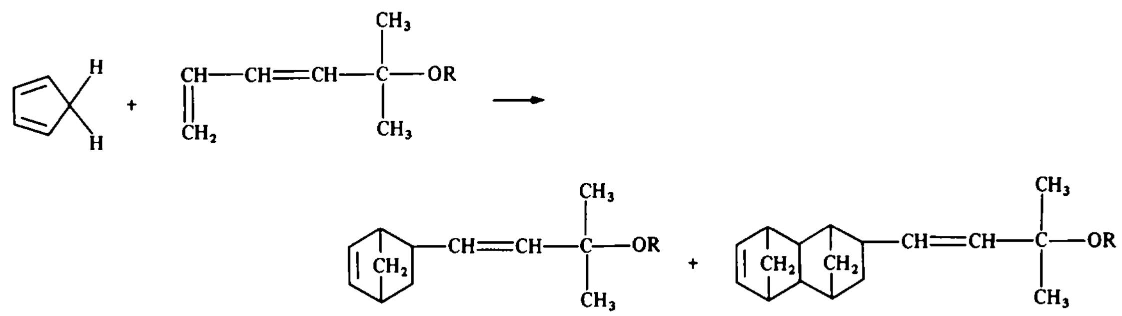
2-Methylhexadien-3, 5-ol-2, its oxyethyl and cyanoethyl esters react with TCBQ in toluene at 108–110°, but the methyl ester condenses with TCBQ at room temperature. In all cases the reaction proceeds only through end vinyl group. The adducts **12** are formed in high yield.



12

R = H; CH_3; CH_2CH_2OH; CH_2CH_2CN

CPD reacts with 2-methylhexadien-3,5-ol-2 and its esters react at 135–140° to form monoadducts **13** and bis-adducts **14**, the ratio of which depends on the molar ratio of reagents and temperature of reaction.

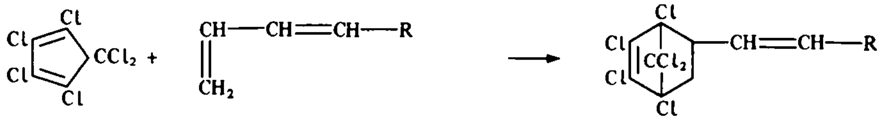


13

14

R = H; CH_3; CH_2CH_2OH; CH_2CH_2CN

The diene condensation of 1-ethoxybutadiene-1,3 and 1-ethoxycarbonylbutadiene-1,3 with HCP proceeds at 95–100° to form **15**:



15

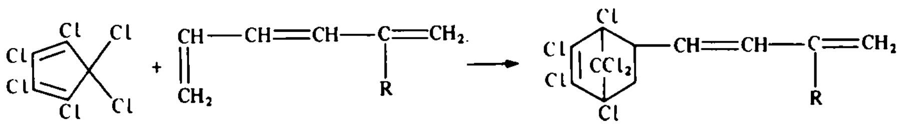
R = OC_2H_5, $COOC_2H_5$

(5) *Reactions of polychlorinated cyclic dienes with polyenes*

It is known[5] that conjugated polyenes add different dienophiles in 1,4 position, and diene-1,3 can act as dienophile (see preceding section). We have found that conjugated polyenes such as hexatriene-1,3,5 and 5-methylhexatriene-1,3,5 act as dienophiles with HCP. The reaction proceeds at 95–100° through the terminal vinyl group and yields the adducts **16** in 70–75% yields.

It should be noted that disubstituted trienes of $p\text{-}XC_6H_4(CH{=}CH)_3COOC_2H_5$ type (wherein X = H, Cl, Br, MeO) do not react with HCP and dimethoxytetrachlorocyclopentadiene (DMTCCPD).

The structure of the adducts obtained (**1**–**16**) has been confirmed by elemental analysis and PMR spectroscopy. According to the endo-rule all the adducts represent endo-isomers. Traces of exo-isomers were observed only in the case of **8** (R = H). It was demonstrated by H^5 signals both in the endo- and exo-field; the same sample exhibited a small second peak on GLC.



16

R = H or CH_3

Table 1. Characteristics of energy levels of HOMO and LUMO for CPD, HCP and some dienophiles

Compound	$HOMO_{eV}$	$LUMO_{eV}$
Cyolopentadiene	-8.617	0.976
Hexachlorocyclopentadiene	-9.268	-1.423
Butadiene-1,3	-8.853	1.125
Hexatriene-1,3,5	-8.236	0.657
Octatetraene-1,3,5,7	-7.883	0.389
Decapentaene-1,3,7,9	-7.659	0.218
Vinyl acetylene	-9.261	1.466
Allyl acetylene	-9.758	1.737
Pentadiene-1,4	-9.526	1.695

Table 2. Difference in energy levels of HOMO and LUMO for dienophiles and dienes

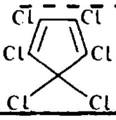
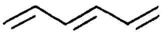
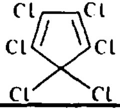
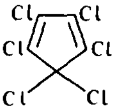
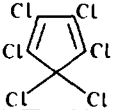
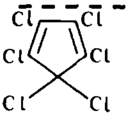
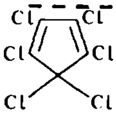
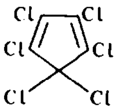
Dienophile A	Diene B	$\varepsilon_A^{LUMO}-\varepsilon_B^{HOMO}$ eV	$\varepsilon_B^{LUMO}-\varepsilon_A^{HOMO}$ eV	$\varepsilon_A^{LUMO}-\varepsilon_A^{HOMO}$ eV	$\varepsilon_B^{LUMO}-\varepsilon_B^{HOMO}$ eV
		ε_1	ε_2	ε_3	ε_4
		9.74	9.83	9.98	9.59
		10.39	7.43		7.84
		9.27	9.21	8.89	9.59
		9.93	6.81		7.84
		9.01	8.86	8.28	9.59
		9.66	6.46		7.84
		8.84	8.64	7.88	9.59
		9.49	6.23		7.84
$CH_2=CH-C\equiv CH$		10.24	10.24	10.79	9.59
		7.84	7.84		7.84
$CH_2=CHCH_2C\equiv CH$		10.34	10.73	11.50	9.59
		8.34	8.34		7.84
$CH_2=CHCH_2CH=CH_2$		10.51	10.51	11.22	9.59
		8.11	8.11		7.84

Table 3. Conditions for reactions between dienes and dienophiles

Compounds	Molar ratio diene:dienophile	T, °C	Time, hour
1	2:1	150–155	8
2	1:2	170–175	14
3	2:1	180–185	14
4 (R = H)**	1:2	108	18
4 (R = Me)*	1:2	25–30	40
5 (R = Me; CH_2CH_2OH)	1:2	165–170	14
6 (R = Me; CH_2CH_2OH)	2:1	165–170	14
7 (R = H)	2:1	85–90	20
7 (R = CMe_2OH; CMe_2OMe)	2:1	95–100	30
8 (R = H)	1:1	150–155	7
8 (R = CMe_2OH)	1:1	175–180	16
9 (R = H)	2:1	150–155	16
9 (R = CMe_2OH)	2:1	175–180	20
10 (R = Me, CH_2OH)	2:1	110	8
11	2:1	95–100	18
12 **	1:2	108–110	15
12 (R = Me)*	1:2	25–30	44
13	1:2	125–140	5
14	2:1	160–165	10
15	1:1	95–100	18
16	1:1	95–100	18

* Reaction was carried out in benzene;

** Reaction was carried out in toluene.

Table 4. Constants and elemental analysis data

Adduct No.	(R)	Yield, %	B.p. °C (mm Hg) or m.p.	n_D^{20}	d_4^{20}	Found, % (Calculated, %) C	H	Cl	Formula
1	(CH_2CH_2OH)	86	186–188(1)	1.5492	1.5870	32.10 (32.17)	2.33 (2.14)	57.32 (57.10)	$C_{10}H_8O_2Cl_6$
1	(CH_2CH_2CN)	84.2	157–158(1)	1.5500	1.5426	34.10 (34.29)	1.95 (1.80)	55.60 (55.75)	$C_{11}H_7OCl_6N$
1	($COCH_3$)	78.4	140–141(1)	1.5617	1.6170	31.95 (32.08)	1.69 (1.60)	56.82 (56.90)	$C_{10}H_6O_2Cl_6$
2	(H)	72.1	65–67(1)	1.5366	1.0890	78.50 (78.68)	8.26 (8.19)	-	$C_8H_{10}O$
2	(CH_2CH_2OH)	82.2	84–86(1)	1.4999	1.0697	72.09 (72.28)	7.98 (7.83)	-	$C_{10}H_{14}O_2$
2	(CH_2CH_2CN)	84.6	125–126(1)	1.4900	1.0176	70.36 (70.28)	7.51 (7.42)	-	$C_{11}H_{13}ON$
2	($COCH_3$)	79.8	84–85(1)	1.5036	1.0724	70.01 (70.31)	7.23 (7.03)	-	$C_{10}H_{12}O_2$
3	(H)	76.2	108–110(1)	1.5437	1.1017	82.10 (82,29)	8.75 (8,51)	-	$C_{13}H_{16}O_2$
3	(CH_2CH_2OH)	80.5	164–165(1)	1.5290	1.1123	77.34 (77.58)	8.85 (8.62)	-	$C_{15}H_{20}O$
3	(CH_2CH_2CN)	86.6	164–165(1)	1.5240	1.0971	79.24 (79.66)	7.06 (7.48)	-	$C_{16}H_{19}ON$

3	(COCH$_3$)	76.4	104–105(1)	1.5116	1.5283	70:60 (70.82)	7.15 (7.08)	-	$C_{15}H_{18}O_2$
4	(H)	85.3	140–141	-	-	39:82 (40.01)	2:88 (2.80)	39:82 (38.87)	$C_{13}H_{10}Cl_4O_3$
4	(CH$_3$)	93	120–121	-	-	45.25 (45.40)	3.30 (3.24)	38.22 (38.37)	$C_{14}H_{12}Cl_4O_3$
5	(CH$_3$)	82.1	88–89(6.5)	1.4815	0.9440	82:33 (82.11)	9:22 (9.47)	-	$C_{13}H_{18}O$
5	(CH$_2$CH$_2$OH)	75.4	104.5–105(1)	1.4990	1.0185	75.94 (76.36)	9.35 (9.09)	-	$C_{14}H_{20}O_2$
6	(CH$_3$)	75.8	120–121(1)	1.5190	1.0277	84.05 (84.38)	9:79 (9.38)	-	$C_{18}H_{24}O$
6	(CH$_2$CH$_2$OH)	71.3	156–157(1)	1.5220	1.0581	80.17 (79.72)	8.89 (9.09)	-	$C_{19}H_{26}O_2$
7	(H)	78.	65–66	-	-	35:30 (35.39)	1.89 (1.77)	69.91 (62.83)	$C_{10}H_6Cl_6$
7	(CMe$_2$OH)	90.5	95.5–96.5	-	-	39.35 (39.28)	2.98 (3.02)	53.52 (53.65)	$C_{13}H_{12}Cl_6O$
7	(CMe$_2$OMe)	95	172–174(3)	1.5386	1.4083	40:84 (40.87)	3.44 (3.40)	51.89 (51.82)	$C_{14}H_{14}Cl_6O$
8	(H)	73	140–141	0.4894	0.9221	90:96 (90.91)	9.18 (9.09)	-	$C_{10}H_{12}$

Adduct No.	(R)	Yield, %	B.p., °C (mm Hg) or m.p.	n_D^{20}	d_4^{20}	Found, % (Calculated, %) C	H	Cl	Formula
8	(CMe$_2$OH)	76.5	86.5–87.5(1)	1.5020	0.9788	82:17 (82.10)	9:34 (9.47)	-	$C_{13}H_{18}O$
9	(H)	66.5	87–88 (27)	1.5326	1.0224	90:88 (90.91)	9.12 (9.09)	-	$C_{15}H_{18}$
9	(CMe$_2$OH)	69.5	121–122(1)	1.5284	1.0189	84:14 (84.37)	9.62 (9.75)	-	$C_{18}H_{24}O$
10	(CH$_3$)	76.3	184–185(1)	1.5520	1.3956	46:28 (46.65)	4:16 (3.89)	46.27 (46.00)	$C_{18}H_{18}Cl_6O$
10	(CH$_2$CH$_2$OH)	70.7	170–171	-	-	46.64 (46.25)	4:21 (4.06)	42:84 (43.20)	$C_{19}H_{20}Cl_6O_2$
11	(H)	82	164–165(0.5)	1.5515	1.4582	37:53 (37.40)	3.21 (3.17)	54.90 (55.32)	$C_{12}H_{12}Cl_6O$
11	(CH$_3$)	89	144–145(1.5)	1.5550	1.4446	39.49 (39.10)	3.20 (3.51)	53.51 (58.38)	$C_{13}H_{14}Cl_6O$
11	(CH$_2$CH$_2$OH)	70.6	183.5–184.5 (1)	1.5490	1.4614	39.51 (39.16)	4.05 (3.73)	49.39 (46.95)	$C_{14}H_{16}Cl_6O_2$
11	(CH$_2$CH$_2$CN)	60.2	192–193(1)	1.5440	1.4308	40.71 (41.10)	3:63 (3.42)	48:16 (48.63)	$C_{15}H_{15}Cl_6NO$
12	(H)	89.4	147–148	-	-	43.47 (43.58)	3.54 (3.35)	39.62 (39.66)	$C_{13}H_{12}Cl_4O_3$

DISCUSSION

This comparative study of the Diels–Alder reactions between dienes and dienophiles reveals that the most reactive diene is TCBQ, which reacts with some enynes and conjugated dienes at room temperature. Next to TCBQ is HCP which reacts with the same dienophiles at 95–100°. Finally, the condensation with CPD requires the strongest conditions. We wish to emphasize the high reactivity of enynes which form part of the dienophile group. So, vinyl acetylenes react with HCP at 85–90°, whereas the reaction with allyl acetylenes and dienes proceeds at 95–100° and with monosubstituted acetylenes at 150–155°. In the case of CPD allyl acetylene reacts at 175–180°.

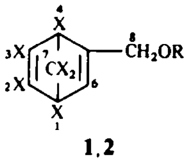
This reactivity of dienes and dienophiles depends on a difference in the energy levels of LUMO and HOMO. We calculated these energy levels for HCP, CPD, 1,3-butadiene, 1,3,5-hexatriene, 1,3,5,7-octatetraene, 1,3,5,7,9-decapentaene, 1,4-pentadiene, vinyl acetylene and allyl acetylene using the MINDO/3 technique[10] (Table 1).

The difference ($\Delta\epsilon$) between LUMO and HOMO of the above molecules and differences between LUMO and HOMO of dienes and dienophiles are

12	(CH_3)	93	-	-	-	45.63 (45.16)	3.52 (3.76)	37.90 (38.07)	$C_{14}H_{14}Cl_4O_3$
12	(CH_2CH_2OH)	64.2	160–161	-	-	44:25 (47.78)	4:41 (3.98)	34:93 (35.32)	$C_{15}H_{16}Cl_4O_4$
12	(CH_2CH_2CN)	60.8	189–190	-	-	46.18 (46.72)	3.86 (3.65)	34.80 (34.55)	$C_{16}H_{16}Cl_4NO_3$
13	(H)	77	103–104(4)	1.5020	0.9812	80.50 (80.89)	10.82 (10.11)	-	$C_{12}H_{15}O$
13	(CH_3)	79.8	69–70(4.5)	1.4800	0.9308	80.96 (81.25)	10.06 (10.42)	-	$C_{13}H_{20}O$
13	(CH_2CH_2OH)	73	117–118	1.9982	0.9975	75:68 (76.80)	9:91 (9.69)	-	$C_{14}H_{22}O_2$
13	(CH_2CH_2CN)	80.2	109–110(1,5)	1.4870	0.9836	78.25 (77.92)	9.26 (9.09)	-	$C_{15}H_{21}NO$
14	(H)	80	131–132(1)	1.5280	1.0368	82.98 (88.61)	10.15 (9.84)	-	$C_{17}H_{24}O$
14	(CH_2CH_2OH)	69.4	158.5–159.5 (1)	1.5200	1.0373	78.69 (79.17)	9.51 (9.72)	-	$C_{19}H_{28}O_2$
14	(CH_2CH_2CN)	63.7	65.–66	-	-	80.54 (80.4)	9.40 (9.09)		$C_{20}H_{27}NO$

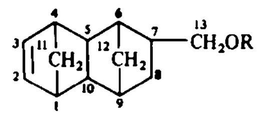
15	(OC_2H_5)	81	141–142(1)	1.5382	1.3869	35.62 (35.57)	2.77 (2.69)	57.38 (57.41)	$C_{11}H_{10}Cl_6O$
15	($CO_2C_2H_5$)	86	165–166.5(1)	1.5386	1.4900	36.00 (36.09)	2.55 (2.50)	53.48 (53.38)	$C_{12}H_{10}Cl_6O_2$
16	(H)	68	182–182(2)	1.5633	1.4190	37.37 (37.41)	2.37 (2.28)	60.44 (60.31)	$C_{11}H_8Cl_6$
16	(CH_3)	75	155–156(1)	1.5476	1.4335	39.40 (39.23)	3.01 (2.72)	58:09 (58.03)	$C_{12}H_{10}Cl_6$

Table 5. PMR-spectroscopic data of adducts investigated (1–16)



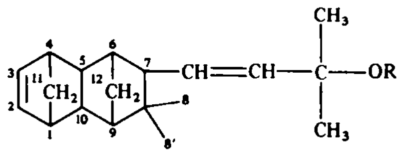
1,2

Compound		Proton signals, ppm relative to internal HMDS					
X	R	H_1,H_4	H_2,H_3	H_6	H_7,H_7'	H_8,H_8'	R
Cl	CH_2CH_2OH	-	-	6,45(m)	-	4.12 (m)	δ=3.30–3.70(m,OCH_2CH_2O) δ=2.90 (s,OH)
Cl	CH_2CH_2N	-	-	6.40(m)	-	4.12 (m)	δ=3.45 (t, OCH_2) δ= 2.45 (t,CH_2CN)
Cl	$COCH_3$	-	-	6.20(m)	-	3.87 (m)	δ= 2.00 (s,$OCOCH_3$)
H	CH_2CH_2OH	3.25–3.70(m)	6.50–6.73(m)	6.35(m)	1.95(m)	4.05 (m)	δ=3.25–3.70(m,OCH_2CH_2O) δ= 2.75 (s,OH)
H	CH_2CH_2CN	3.32–3.60(m)	6.58–6.80(m)	6.35–6.45 (m)	1.90(m)	4.05 (m)	δ=3.50 (t,OCH_2) δ=2.42 (t, CH_2CN)
H	$COCH_3$	3.70–4.10(m)	6.50–6.75(m)	6.30(m)	2.00(m)	4.00 (m)	δ=1.95 (s, $OCOCH_3$)



3

Compound	Proton signals, ppm relative to HMDS								
R	H^1,H^4	H_2,H_3	H^5,H^{10}	H^6	H^8	H^9	$H^{11},H^{11'}$, $H^{12},H^{12'}$	$H^{13},H^{13'}$	R
CH_2CH_2OH	2.60–3.00 (m)	6.45–6.60(m)	2.00–2.30 (m)	2.30–2.55(m)	5.70–6.00(m)	2.30–2.55(m)	1.15–2.00(m)	3.80–4.15(m)	δ=3.30–3.75(m, OCH_2CH_2O), δ=2.85 (s,OH)
CH_2CH_2CN	2.55–2.95 (m)	6.55–6.70(m)	1.95–2.25 (m)	2.28–2.60(m)	5.75–6.00(m)	2.28–2.60(m)	1.20–2.00(m)	3.85–4.10(m)	δ=3.55 (t,OCH_2) δ=2.48(t,CH_2CN)
$COCH_3$	2.50–2.95 (m)	6.50–6.68(m)	2.05–2.28 (m)	2.30–2.50(m)	5.75–6.05(m)	2.30–2.50(m)	1.40–2.10(m)	3.82–4.20(m)	δ= 1.95(s,$\overset{O}{C}$–CH_3)



14

Compound	Proton signals, ppm relative to internal HMDS												
R	H^1,H^4	H^2H^3	H^5H^{10}	H^6	H^7	H^8	$H^{8'}$	H^9	$H^{11},H^{11'}$, $H^{12},H^{12'}$	H^{13}	H^{14}	H^{15} $(CH_3)_2$	R
H	2.60–2.90 (m)	5.95 (m)	2.00–2.30 (m)	1.70–2.40 (m)	2.45 (m)	0.80 (m)	2.60 (m)	2.60–2.90 (m)	1.05–1.92 (m)	5.45 (m)	5.00 (m)	1.32 (s)	2.10(s)
CH_2CH_2OH	2.65–2.90 (m)	6.00 (m)	1.90–2.25 (m)	1.65–2.45 (m)	2.55 (m)	0.85 (m)	2.65 (m)	2.65–2.90 (m)	1.10–2.00 (m)	5.55 (m)	5.05 (m)	1.35 (s)	δ=3.40(m, OCH_2CH_2O) δ=2.05(s,OH)

given in Table 2. The data analysis presented in Table 1 is consistent with expectation, namely that:

(a) Introduction of chlorine into the cyclopentadiene molecule decreases the levels of HOMO and LUMO significantly thus increasing the activity of HCP as a diene against CPD in the reverse diene synthesis (i.e. when LUMO of diene and HOMO of dienophile interact and combine in the reaction).

(b) An extension of the conjugated chain of double bonds in the aliphatic series $H(CH{=}CH)_nH$ increases the HOMO level and decreases the LUMO level thus increasing their ability as dienes in the normal diene synthesis, and possibly their use as dienophiles in the reverse diene synthesis (i.e. when LUMO and HOMO of dienophiles interact and combine in the reaction);

(c) Introduction of a methylene link between vinyl and ethynyl groups, i.e. a transition from vinyl acetylene to allyl acetylene increases the LUMO level and decreases the HOMO level, thus decreasing dienophilic activity of allyl acetylene in the normal diene synthesis. Hence allyl acetylene reacts with HCP at 80–100°, whereas vinyl acetylene reacts at 60–80°.

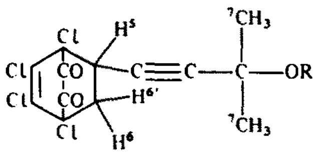
Similarly, the introduction of a methylene link between vinyl groups, decreases the HOMO level and increases the LUMO level, i.e. decreases the dienophile activity of 1,4-pentadiene as against 1,3-butadiene.

Based on the data given in Table 2 it might be concluded:

(a) The ability of aliphatic dienes ($H(CH{=}CH)_nH$) to polymerization is higher than that of cyclic dienes and increases with extension of the conjugated chain ($\epsilon_1 < \epsilon_2$).

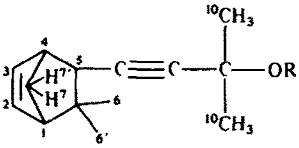
(b) The aliphatic dienes must react as dienophiles with HCP ($\epsilon_1 < \epsilon_4^{HCP}$), but do not with CPD ($\epsilon_1 < \epsilon_4^{CPD}$) with the exception of 1,3-butadiene ($\epsilon_1^{Butadiene} > \epsilon_4^{CPD}$).

This satisfies the experiment[11] and explains why butadiene reacts with CPD and HCP as dienophile



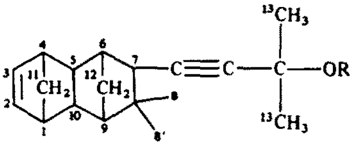
4

Compound	Proton signals, ppm relative to internal HMDS				
R	H^5	H^6	$H^{6'}$	$H^7(CH_3)_2$	R
H	3.73 (m)	1.75 (m)	2.80 (m)	1.38 (s)	2.15 (s)
CH_3	3.70 (m)	1.80 (m)	2.75 (m)	1.35 (s)	3.25 (s)



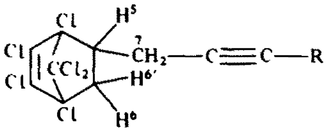
5

Compound	Proton signals, ppm relative to internal HMDS						
R	H^1H^4	H^2H^3	H^5	H^6	$H^{6'}$	$H^7H^{7'}$	H^{10}	R
CH_3	2.83(m)	5.85-6.20(m)	3.38 (m)	2.00 (m)	0.95 (m)	1.20-1.60 (m)	1.25(s)	δ=3.15(s,OCH_3)
CH_2CH_2OH	2.80(m)	5.90-6.20(m)	3.75 (m)	2.03 (m)	0.82-1.10 (m)	1.30-1.60 (m)	1.30-1.38(m)	δ=3.40-3.60 (m, OCH_2CH_2O); δ=2.58 (s,OH)



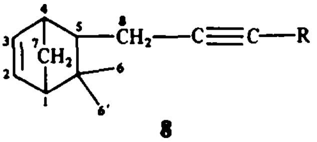
6

Compound	Proton signals, ppm relative to internal HMDS									
R	H^1,H^4	H^2,H^3	H^5,H^{10}	H^6	H^7	H^8	$H^{8'}$	H^9	$H^{11},H^{11'}$ $H^{12},H^{12'}$	$H^{13}(CH_3)_2$	R
CH_3	2.65-3.00(m)	5.80-6.15(m)	1.90-2.20(m)	1.70-2.50(m)	2.55 (m)	0.85 (m)	2.55 (m)	2.65-2.90(m)	1.10-2.00(m)	1.20(s)	3.17(s)
CH_2CH_2OH	2.70-3.00(m)	5.85-6.10(m)	1.95-2.30(m)	1.60-2.40(m)	2.50 (m)	0.75 (m)	2.50 (m)	2.70-2.95(m)	1.10-2.05(m)	1.25(s)	δ=3.35-3.65(m, OCH_2CH_2O); δ=2.45(s,OH)



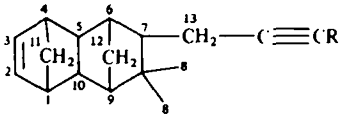
7

Compound	Proton signals, ppm relative to internal HMDS				
R	H^5	$H^{6'}$	H^6	H^7	R
H	3.05(m)(1H)	2.85(m)(1H)	1.95(m)(1H)	1.87(m)(2H)	2.47(m)(1H)
$C(CH_3)_2OH$	2.90(m)(1H)	2.60(m)(1H)	1.90(m)(1H)	2.02(m)(2H)	2.05(s)(1H) 1.40(s)(6H)
$C(CH_3)_2OMe$	3.05(m)(1H)	2.85(m)(1H)	1.95(m) (3H,H^6+CH_2)	1.95(m) (3H,H^6+CH_2)	3.25(s)(3H)(OCH_3) 1.35(s) (6H)



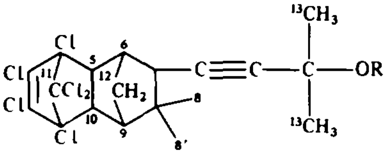
8

Compound	Proton signals, ppm relative to internal HMDS						
R	H^1+H^4	H^2+H^3	H^5	H^6	$H^{6'}$	$H^7+H^{7'}$	H^8	R
H	2.60-2.95(m)	5.80-6.15(m)	2.10(m)	0.60(m)	1.80 (m)	1.10-1.50(m)	1.54-1.90(m)	1.54-1.90(m)
$C(CH_3)_2OH$	2.65-2.95 (m)	5.90-6.15(m)	2.15(m)	0.56(m)	1.60-2.00 (m)	1.10-1.50(m)	1.90(m)	3.00(s)



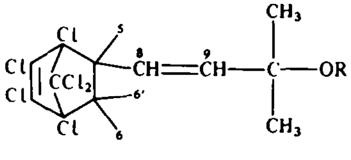
9

Compound	Proton signals, ppm relative to internal HMDS										
R	H^1,H^4	H^2,H^3	H^5,H^{10}	H^6	H^7	H^8	$H^{8'}$	H^9	$H^{11},H^{11'}$, $H^{12},H^{12'}$	H^{13}	R
H	2.7-3.0 (m)	5.85 (m)	1.7-2.3 (m)	1.7-2.3 (m)	2.4 (m)	0.9 (m)	2.0 (m)	1.6-2.0 (m)	1.1-1.35 (m)	2.2 (m)	1.85(s)
$C(CH_3)_2OH$,	2.6-3.3 2.60-3.20 (m)	5,95-6.15 (m)	2.0-2.4 (m)	1.5-2.5 (m)	2.5 (m)	0.7 (m)	2.5 (m)	2.7-3.0 (m)	1.1-2,0 (m)	2.2 (m)	1.1-2.0(m) 3.5 (s)



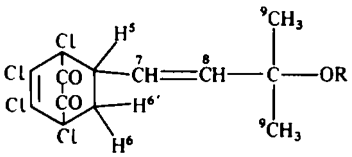
10

Compound	Proton signals, ppm relative to internal HMDS						
R	H^5,H^{10}	H^6,H^9	H^7	H^8	$H^{8'}$	H^{12}	$H^{13}(CH_3)_2$	R
CH_3	2.00-2.90(m)	2.10-2.85(m)	2.50(m)	0.95(m)	2.50(m)	1.05-1.75(m)	1.25(s)	
CH_2CH_2OH	2.00-2.90(m)	2.00-2.80(m)	2.50(m)	0.90(m)	2.50(m)	1.10-1.85(m)	1.20(s)	$\delta=3.45$(m, OCH_2CH_2O) $\delta=2.35$(s,OH)



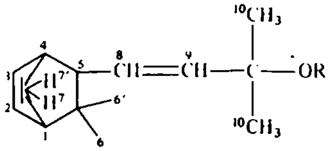
11

Compound	Proton signals, ppm relative to internal HMDS						
R	H^5	H^6	$H^{6'}$	H^8	H^9	$(Me)_2$	R
H	4.74 (m)	1,68(m)	2,72(m)	4.74(m)	5.53(m)	1.30(s)	$\delta=1.70$ (s, OH)
CH_2CH_2OH	4.42 (m)	1.58(m)	2.70(m)	4.90(d)	5.45-6.10 (m)	1.30(m) 1.32(m)	$\delta=3.45$ (m, $(OCH_3)_2$) $\delta=2.42$ (s, OH)



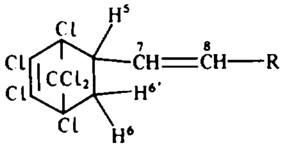
12

Compound R	Proton signals, ppm relative to internal HMDS						
	H^5	H^6	$H^{6'}$	H^7	H^8	$H^9(CH_3)_2$	R
H	3.95(m)	1.68(m)	2.87(m)	4.78(d)	5.55(m)	1.30(s)	1.65 (s)
CH_2CH_2OH	3.88(m)	1.70(m)	2.78(m)	4.85(d)	5.50(m)	1.30(s)	δ =3.50(m, OCH_2CH_2O); δ =1.75(s, OH).



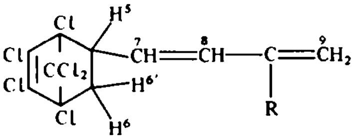
13

Compound R	Proton signals, ppm relative to internal HMDS									
	H_1H_4	H_2H_3	H_5	H_6	$H_{6'}$	$H_7H_{7'}$	H_8	H_9	H_{10}	R
H	2.75 (m)	6.0 (m)	4.56 (m)	0.65 (m)	3.38 (m)	1.30 (m)	4.75 (d)	5.00 (d)	1.30 (s)	δ =2.15 (s, OH) $J_{\widehat{H^8,H^9}}$ =.12 (Hz)
CH_2CH_2OH	2.72 (m)	5.95 (m)	2.95 (m)	0.75 (m)	3.30-3.40 (m)	1.30 (m)	5.10 (d)	4.92 (d)	1.32 (s)	δ =3.40(m. OCH_2CH_2O) δ =2.08 (s, OH)
CH_2CH_2CN	2.80 (m)	6.05)m)	3.18 (m)	0.95 (m)	3.45 (m)	1.60 (m)	5.58 (m)	5.10 (m)	1.40 (s)	δ =3.63(t, CH_2CN) δ =2.45(t, OCH_2)



15

Compound R	Proton signals, ppm relative to internal HMDS				
	H^5	H^6	$H^{6'}$	H^7, H^8	R
OC_2H_5	4.60(m)	1.50(m)	2.88(m)	5.70-6.30(m)	δ = 3.50 (m, OCH_2); δ = 1.00(m, CH_3)
$COOC_2H_5$	4.56(m)	1.57(m)	2.80(m)	5.65-6.40(m)	δ = 4.15 (m, OCH_2); δ = 1.45(t, CH_3)



16

Compound R	Proton signals, ppm relative to internal HMDS					
	H^5	H^6	$H^{6'}$	H^7, H^8	H^9, H^9	R
H	4.75 (m)	1.70 (m)	2.67 (m)	5.40-6.50 (m)	4.90 (m)	5.40-6.50 (m)
CH_3	4.80 (m)	1.60 (m)	2.70 (m)	5.60-6.45 (m)	4.87 (m)	1.75 (s)

and hexatriene reacts as dienophile only with HCP and does not react with CPD. The diene synthesis between dienophiles of $H(CH=CH)_nH$ type and cyclic dienes refers to the reverse type.

(c) The diene synthesis between vinyl acetylene, allyl acetylene, allyl ethylene and CPD or HCP proceeds by neutral diene synthesis (diene and dienophile can play the role of HOMO and LUMO components).

These results have been presented partly in preliminary communications.[12-16]

EXPERIMENTAL SECTION

PMR spectra were recorded on a "Tesla" Model BS-497 spectrometer (100 MHz) in CCl_4 using HMDS as internal standard. The purity of compounds was checked by GLC (Khrom-3, LKHM-8, 1.4 × 0.003 m column, with 5% SE-30 on chromatone N-AW-DMC).

General procedure. A mixture of diene and dienophile was heated in the presence of small amounts of hydroquinone in sealed ampoules at a certain temp. and a given time. The adducts were isolated by vacuum distillation of the mixture. The conditions, yields, constants, elemental analysis and PMR data are presented in Tables 3–5, respectively.

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