Reactions of Monoölefins and Hexachlorocyclopentadiene

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Monoölefinic compounds react with hexachlorocyclopentadiene at 85–150° to give high yields of Diels–Alder adducts. This new reaction was demonstrated with sixteen compounds. Rates of reaction with 1-octadecene and 4-methylcyclohexene-1 correspond to activation energies of 24 and 20 kcal. per mole. The adducts are new compounds that open a field for future study; two have shown promise as insecticides.

Hexachlorocyclopentadiene readily adds to the olefinic bond of conjugated systems such as maleic anhydride and acrylonitrile.[1] It also adds readily to olefinic compounds containing no conjugated systems. This unexpected reaction goes at temperatures as low as 85°, and the yields of adducts are high. Previous investigators[2] condensed butadiene, dimethylbutadiene and cyclopentadiene with ethylene, but at about 200° and under 5000 pounds pressure.

The new reaction has been demonstrated with 16 olefinic compounds and the adducts have been examined. Besides hydrocarbons, the olefins included halogen and oxygen derivatives. The rates of reaction with two olefins have been determined.

Experimental

Hexachlorocyclopentadiene was obtained from the Hooker Electrochemical Company. Olefins purchased from the sources in Table I were used without processing. Allyl butyrate, b.p. 142–143°, was obtained by reaction of equimolar quantities of butyric anhydride and allyl alcohol at 60° for one-half hour with 1% ethanesulfonic acid.

To obtain the adducts, an equimolar mixture of hexachlorocyclopentadiene and each olefin was heated without stirring until the temperature rose to 135°, where it was held for 4 hours. With high-boiling olefins, the mixture was heated at 145–150° for one hour. The adducts were either distilled under vacuum directly from the reaction flask or crystallized from methanol. There was no evidence of polymer formation. Variants of the procedure are detailed in Table I.

TABLE I
FORMATION OF ADDUCTS

Monoölefin	Source	Technique
1-Hexene	Humphrey–Wilkinson	a,c
1-Octene	Humphrey–Wilkinson	a,c
1-Octadecene	Humphrey–Wilkinson	b
Cyclohexene	Eastman Kodak	a,c,d
4-Methylcyclohexene-1	Phillips Petroleum	a,c
α-Pinene	Eastman Kodak	b
dl-Limonene	Hercules Powder	b
Allyl chloride	Eastman Kodak	a,c
Methallyl chloride	Eastman Kodak	a
Allyl bromide	Eastman Kodak	a,d
Propargyl bromide	General Aniline	a,c
Allyl alcohol	Eastman Kodak	a,d
Allyl butyrate	....	b,c
Dicyclopentenyl alcohol	Rohm and Haas	b
Butadiene monoxide	Columbia	a,c,d
Undecylenic acid	Eastman Kodak	b

 a Slow heating up to 135°, held there 4 hours. *b* Heated at 145–150° for 1 hour. *c* Distilled *in vacuo*. *d* Crystallized from methanol.

To prepare derivatives of one of the adducts, a solution of 19.6 g. (0.05 mole) of the propargyl bromide adduct in

(1) E. A. Prill, THIS JOURNAL, **69**, 62 (1947).

(2) L. M. Joshel and L. W. Butz, *ibid.*, **63**, 3350 (1941).

50 ml. of isopropyl ether was refluxed 6 hours with 0.05 mole of two amines. The white crystals that separated were collected on a filter, washed with isopropyl ether, and dried. From 4 ml. of pyridine, the yield was 22.8 g. (95%); the salt turned black at 250° and decomposed without melting at 270–280°. From 6.75 g. of benzyldimethylamine, the yield was 25.5 g. (97%), m.p. 171°.

To determine the effect of oxidants and antioxidants on the reaction, a mixture of 272.8 g. (1 mole) of hexachlorocyclopentadiene and 112 g. (1 mole) of 1-octene was divided into two equal portions. To one was added 3 ml. of *t*-butyl peroxide; to the other, 2.5 g. of *t*-butylcatechol. Both mixtures were held at 135° for 4 hours. One gave 161 g. (86.6%) of adduct, $n^{20}\text{D}$ 1.5235; the other, 153 g. (79.5%) of adduct, $n^{20}\text{D}$ 1.5230.

For use in measuring reaction rates, the diene and two olefins were distilled to give fractions having the constants:

|	B.p. °C.	Mm.	$n^{20}\text{D}$
Hexachlorocyclopentadiene	88–89	3	1.5639
1-Octadecene	172–174	10	1.4415
4-Methylcyclohexene-1	101.5–102	753	1.4432

Mixtures of equimolar quantities of the diene with each olefin were held at three temperatures within 0.1°. Samples were withdrawn at regular intervals and bromine absorptions were determined. No bromine was taken up at 0° by the hexachlorocyclopentadiene or the adduct; the bromine absorbed was consequently a direct measure of the concentration of the olefin. Reaction rates were calculated according to the usual integrated form of the second-order rate equation. Table II gives the data for a mixture of 25.23 g. (0.1 mole) of 1-octadecene and 27.28 g. (0.1 mole) of hexachlorocyclopentadiene at 110°.

TABLE II
RATE OF REACTION OF 1-OCTADECENE

$t \times 10^3$, seconds	Bromine absorbed, moles per liter $(a - x)$	$k \times 10^{-5}$, liters mole^{-1} sec.$^{-1}$
0	2.02	...
3.6	1.81	1.6
7.2	1.54	2.1
14.4	1.33	1.8
27.0	1.03	1.8
82.8	0.51	1.8

Discussion

The adducts are viscous light-yellow distillable liquids or white crystalline solids soluble in all common solvents. Composition data and physical properties are given in Table III. The analyses agree well with those for compounds that would be expected from a Diels–Alder condensation.
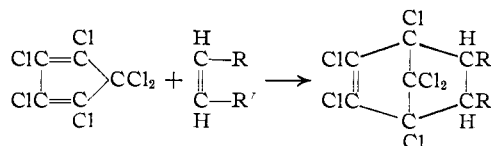
The rates of reaction and yields were about the same whether or not peroxides or antioxidants were

TABLE III
EXAMINATION OF ADDUCTS

Monoölefin	Yield, %	Chlorine, % Calcd.	Found	B.p. °C.	Mm.	Ref. index n^{20}D	M.p., °C.	Mol. wt.
1-Hexene	65	59.8	59.8	149–151	3	1.5309	.....	...
1-Octene	86	55.3	54.7	152–153	3	1.5235	.....	...
1-Octadecene	97	40.1	40.5	.....	...	....	.....	527
Cyclohexene	88	60.0	60.2	154	0.8	1.5647	76.7	...
4-Methylcyclohexene-1	97	57.8	57.2	146–147	0.7	1.5555	.....	...
Allyl chloride	43	71.0	69.6	142–144	3.7	1.5600	.....	...
Allyl bromide	87	74.3[a]	74.8	.....	...	....	77	389
Propargyl bromide	95	74.7[a]	74.1[b]	137	1.6	1.5860	.....	403
Allyl alcohol	98	64.3	64.5	.....	...	....	165	...
Allyl butyrate	80	53.0	53.3	158–159	0.5	1.5273	.....	...
Butadiene monoxide	97	59.8	60.0	137	1.3	....	101–104	342

[a] Total halogen. [b] Calcd.: C, 24.50; H, 0.76. Found: C, 24.75; H, 1.17; d^{20}_4 1.8563.

present. Free radicals can play little part in the mechanism of the reaction.

Hexachlorocyclopentadiene is far more reactive than unchlorinated alkadienes; it gave 27% of adduct with cyclohexene at 82°, whereas 2-methyl-1,3-pentadiene gave none. The rates of reaction with 1-octadecene and 4-methylcyclohexene-1 are shown in Table IV. Wassermann[3] found that the rate of the cyclopentadiene–quinone reaction in carbon tetrachloride at 20.4° is 3.1×10^{-1} liter mole^{-1} min.$^{-1}$. The octadecene reaction at 97° is 1/1,000 as fast, and the methylcyclohexene reaction at 85° is 1/25,000 as fast. The large difference in the rates of reaction is probably due to the lower reactivity of monoölefins than of conjugated systems.
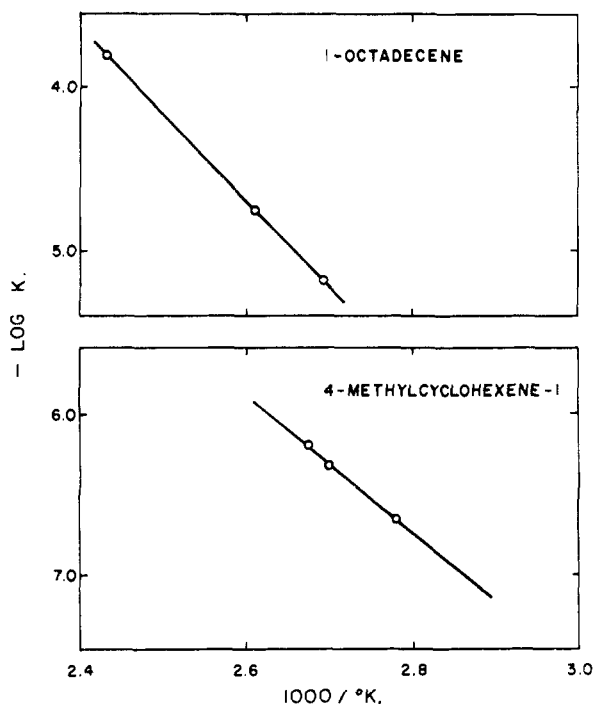
Fig. 1.—Activation energy plot.

(3) A. Wassermann, Ber., 66, 1392 (1933).

TABLE IV
RATES OF REACTION

Temp., °C.	k, liters mole^{-1} sec.$^{-1}$	Temp., °C.	k, liters mole^{-1}sec.$^{-1}$
	1-Octadecene		4-Methylcyclohexene-1
97	$6.7 \times 10^{-6} \pm 0.4$	85	$1.9 \times 10^{-7} \pm 0.3$
110	$1.8 \times 10^{-5} \pm .3$	97	$4.9 \times 10^{-7} \pm .5$
138	$1.7 \times 10^{-4} \pm .2$	101	$6.6 \times 10^{-7} \pm .6$

An activation energy plot for the reaction with these two olefins is shown in Fig. 1. The energies calculated from the slopes of the straight lines are 24.1 ± 0.3 and 20.3 ± 0.2 kcal. per mole. These values are much higher than the 9.2 kcal. obtained by Wassermann[3] and the 8.4 obtained by Fairclough and Hinshelwood.[4]

As found by Prill[1] the chlorine atoms of the adducts are unreactive; boiling 10% alcoholic potassium hydroxide removes only 2–7% of the total chlorine in 8 hours. The halogen inertness extends even to the bromine in the side chain of the allyl bromide adduct. This compound shows no appreciable reaction with pyridine or benzyldimethylamine in 60 hours at 100–110°. On the other hand, the adduct from propargyl bromide,[5] as expected from its allylic structure, rapidly forms quaternary salts with tertiary amines and instantly precipitates sodium bromide from an acetone solution of sodium iodide.
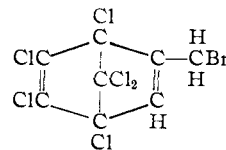
The monoölefin reaction has opened a promising field for future study and development. Many interesting new compounds can be made. For example, the allyl alcohol adduct is a stable alcohol containing 64% chlorine. The adducts from cyclohexene and 4-methylcyclohexene-1 have exceptional insecticidal activity.

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(4) R. A. Fairclough and C. N. Hinshelwood. J. Chem. Soc., 236 (1938).

(5) 1,4,5,6,7,7-Hexachloro-2-bromomethylbicyclo[2,2,1]-2,5-heptadiene.