BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (5), 1437—1438 (1976)

The Chlorination of 1,3- and 1,5-Cyclooctadienes with Various Chlorinating Agents

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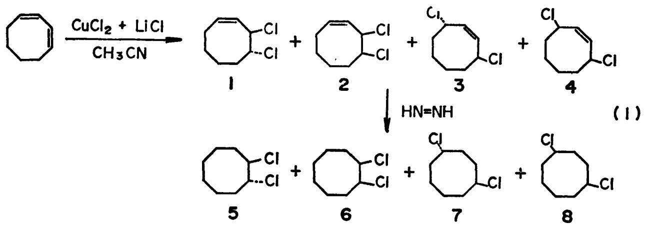
(Received October 13, 1975)

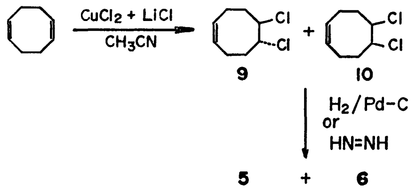
Synopsis. The chlorination of 1,3-cyclooctadiene with various chlorinating agents gave an isomeric mixture of *trans*-3,4-, *cis*-3,4-, *trans*-3,8-, and *cis*-3,8-dichlorocyclooctene. From 1,5-cyclooctadiene an isomeric mixture of *trans*- and *cis*-5,6-dichlorocyclooctene was obtained. The isomer distribution depended a great deal on chlorinating agents in both cases.

Recently Lasne and Thuillier1) have reported the chlorination of 1,3-cyclooctadiene (1,3-COD) with (dichloroiodo)benzene or copper(II) chloride which gave both 1,2- and 1,4-addition products. Since it has previously been reported2) that 1,3-COD was chlorinated with copper(II) chloride to give only two isomeric 1,2-addition products, we reexamined the reaction products in the previous paper2) and also carried out the chlorination of both 1,3- and 1,5-COD with many other chlorinating agents with which norbornene3) and norbornadiene4) were treated.



Scheme 1.

The product mixtures obtained from the reaction of 1,3-COD with CuCl$_2$2) were hydrogenated with diimide in methanol5) to the mixture of four isomeric dichlorocyclooctanes (**5**—**8** in Scheme 1). Each isomer was identified by comparison of retention time in GLC and the spectroscopic data with those of each authentic sample by the reported method.6—8) From this result four isomers were revealed to be *trans*-3,4-(**1**), *cis*-3,4-(**2**), *trans*-3,8-(**3**), and *cis*-3,8-dichlorocyclooctene (**4**), respectively. Since we confirmed in separate experiments that no isomerization occurred during hydrogenation, the isomer ratio in **1**—**4** is considered to be the same as that in **5**—**8**. This isomer ratio was reproducible in each run and was not affected so much by prolonging the reaction time. The ratio of 1,2- to 1,4-addition was 53—51 : 47—49, being nearly the same as the reported value.1) In order to compare with the reported data1) chlorination with PhICl$_2$ was carried out under several conditions. It was revealed that the proportion of 1,4-addition was quite high (69—81%) in our case under any conditions, compared with the reported value1) of 30%. Typical results are shown in Table 1. The chlorination was also carried out with several other chlorinating agents in which PbCl$_4$, SeCl$_4$, and Cl$_2$ gave **1**—**4** (Table 1). Tetrachlorocyclooctane was not formed under any conditions shown in



Scheme 2.

Table 1. Chlorination of 1,3-cyclooctadiene

1,3-COD (mmol)	Chlorinating agents (mmol)	Solvent (ml)	React. Temp (°C)	React. Time (h)	Products Isomer distributiona) 1	2	3	4	Yield (%)b)
50	CuCl$_2$ 100+LiCl 100	CH$_3$CN 100	82	4	22	31	2	45	44
50	CuCl$_2$ 100+LiCl 100	CH$_3$CN 100	82	22	21	30	2	47	70
10	PhICl$_2$ 5	CHCl$_3$ 25c)	25	1	17	4	62	17	42
10	PhICl$_2$ 5	CHCl$_3$ 25	25	1	27	4	54	15	41
10	PhICl$_2$ 5	CHCl$_3$ 25c)	61	1	20	3	58	19	66
10	PhICl$_2$ 5	CHCl$_3$ 25	61	1	16	3	67	14	66
50	PbCl$_4$ 10	CH$_2$Cl$_2$ 50	−40	2	31	4	21	44	82
10	SeCl$_4$ 3	CCl$_4$ 50c)	76	5	49	12	33	6	79
10	SbCl$_5$ 4	CCl$_4$ 50c)	5	0.1	19	35	0	46	33
50	Cl$_2$ 50	CH$_2$Cl$_2$ 100	−50	0.1	44	4	22	30	9
50	Cl$_2$ 50	CH$_2$Cl$_2$ 100	−50	0.5	45	3	24	28	44

a) Determined by GLC after diimide reduction of concentrated organic extract. b) Based on chlorinating agents charged as determined by GLC. c) Under N$_2$.

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TABLE 2. CHLORINATION OF 1,5-CYCLOOCTADIENE

1,5-COD (mmol)	Chlorinating agents (mmol)	Solvent (ml)	React. Temp (°C)	React. Time (h)	Products Isomer distribution$^{a)}$		Yield (%)$^{b)}$
					9	10	
50	$CuCl_2$ 100+LiCl 100	CH_3CN 100	82	4	61	39	26
50	$CuCl_2$ 100+LiCl 100	CH_3CN 100	82	22	62	38	65
6	$PhICl_2$ 5	$CHCl_3$ 25$^{c)}$	25	1	23	77	53
6	$PhICl_2$ 5	$CHCl_3$ 25$^{c)}$	61	1	27	73	65
6	$PhICl_2$ 5	CCl_4 25$^{c)}$	76	1	20	80	47
50	$PbCl_4$ 10	CH_2Cl_2 50	−40	2	84	16	49$^{d)}$
11	$SeCl_4$ 3	CCl_4 50$^{c)}$	76	5	82	18	34$^{d)}$
21	$MoCl_5$ 4	CCl_4 100	27	3	8	92	48
50	Cl_2 50	CH_2Cl_2 50	−50	0.1	93	7	6
50	Cl_2 50	CH_2Cl_2 50	−50	0.5	93	7	18

a) Determined by GLC before reduction. b) Based on chlorinating agents charged as determined by GLC. c) Under N_2. d) No improvement of the yield by prolonging the reaction time to 10 h.

Table 1, while variable amounts of high-boiling resinous products were always produced. In the case of $SbCl_5$ the yield of **1**—**4** was decreased by prolonging the reaction time or raising the temperature, producing the resinous products. In the case of Cl_2 it was necessary to carry out the reaction at low temperature. Otherwise very many unidentified products were formed as reported previously.[2] The reaction with $TlCl_3 \cdot 4H_2O$, VCl_4, and $MoCl_5$ at room or refluxing temperature gave only a trace amount of **1**—**4** together with lots of polymerized products.

The product mixtures obtained from chlorination of 1,5-COD with $CuCl_2$[2] were hydrogenated catalytically or with diimide to afford an isomeric mixture of **5** and **6** (Scheme 2), the ratio between two isomers being the same as that in the starting unsaturated compounds. The result showed that the products were *trans*-(**9**) and *cis*-5,6-dichlorocyclooctane (**10**). This means that both isomers have been assigned erroneously and reversely in the previous report.[2] Typical results were shown in Table 2 together with those of chlorination with some other metal chlorides and chlorine gas. The reactions were slow as compared to those of 1,3-COD and did not give tetrachlorocyclooctane in any cases. Although the chlorination of 1,5-COD with $SbCl_5$ gave an isomeric mixture of 2,8-dichlorobicyclo[3,2,1]octanes as the products,[9] such compounds were not formed by the use of chlorinating agents shown in Table 2. The characteristic *cis*-chlorination with $MoCl_5$ which has been observed with various olefins[10] was also found in this case.

Experimental

Experimental procedures were almost the same as those reported.[2–4] The IR and NMR spectra were recorded with a Hitachi EPI-S2 and a Varian A-60 or T-60 apparatus respectively. Gas chromatographies were carried out on Shimadzu 4BMPF apparatus using SE-30(3%)-Chromosorb-W (3 m) and EGSS-X(15%)-Chromosorb-W (3 m) columns (N_2 as carrier gas; ethyl benzoate as internal standard).

Anthentic Samples for GLC. **5** was prepared by the addition of chlorine to *cis*-cyclooctene.[6] A mixture of **5** and **6** (**5**:**6**=75:25) was prepared by the reaction of $PhICl_2$ with *cis*-cyclooctene.[7] A mixture of **7** and **8** (**7**:**8**=20:80) was prepared by the reaction of *cis*-cyclooctene with $PbCl_4$.[8]

Diimide Reduction of a Mixture of **1**—**4**. To a methanol (50 ml) solution of a mixture of **1**—**4** (0.6 g, 3.3 mmol, bp 62—69 °C/3 Torr) and hydrazine hydrate (80%, 10 g) was added 30% H_2O_2 (10 g) drop by drop at room temperature and then the mixture was heated to reflux for 1 h. The reaction mixtures were worked up by the following successive treatments; dilution with water, extraction with benzene, and then evaporation of benzene. The residue was analyzed by GLC on EGSS-X (3 m) column at 150 °C: **5** (21.7%), **6** (31.3%), **7** (2.2%), and **8** (44.8%); total yield, 3.1 mmol, 92%.

Similary a mixture of **9** and **10** was reduced to a mixture of **5** and **6** in a 95% yield as determined by GLC [EGSS-X or SE-30 (3 m) column at 150 °C].

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