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The Chlorination of Cyclooctadiene with Cupric Chloride in Acetonitrile Containing Lithium Chloride

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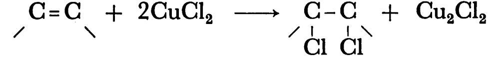
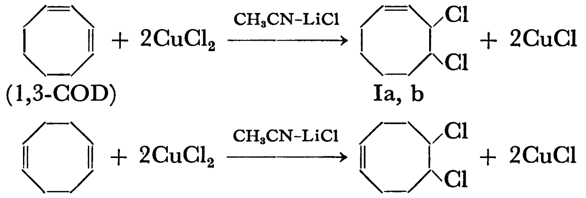
In previous papers, it was demonstrated that olefins can be chlorinated to form dichloroparaffins with cupric chloride under rather mild conditions.[1] The reaction of butadiene in acetic acid containing sodium acetate, however, gave 3,4-diacetoxy-1-butene and 1,4-diacetoxy-2-butene in place of the expected dichlorobutenes.[2] In this paper, the results of applying the method to cyclooctadienes and acrylonitrile and *trans*-crotyl chloride as reference substrates will be reported, and the results will be compared with those obtained by conventional chlorine gas-chlorination. In the presence of lithium chloride, anhydrous cupric chloride dissolves into acetonitrile to make a clear solution. In this solution, *cis*, *cis*-1,3-, and 1,5-cyclooctadienes were chlorinated (Table 1). In the cases of both 1,3- and 1,5-dienes, dichlorocyclooctenes were the main products, along with a high-boiling resinous residue. Only a small amount of tetrachlorocyclooctane (bp 164°C/10 mmHg; NMR, τ5.2—6.0, 4H, τ7.2—8.3, 8H) was obtained, even when more than four moles of cupric chloride were used for one mole of diene.



$$>C{=}C< + 2CuCl_2 \longrightarrow >C(Cl){-}C(Cl)< + Cu_2Cl_2$$



(1,3-COD) Ia, b

(1,5-COD) IIa, b

(a: *trans*, b: *cis*)

This is not due to the formation of an inactive complex which might be formed between dichlorocyclooctene and the resulting cuprous chloride, but to the low reactivity of the chloroolefin, since the further reaction of dichlorocyclooctene (isolated and purified)

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[1] K. Ichikawa, S. Uemura, T. Hiramoto, and Y. Takagaki, *Kogyo Kagaku Zasshi*, **71**, 1657 (1968); S. Uemura, T. Hiramoto, Y. Takagaki, and K. Ichikawa, *ibid.*, **72**, 2390 (1969); S, Uemura, Y. Takagaki, and K. Ichikawa, *ibid.*, **72**, 2577 (1969); K. Ichikawa, S. Uemura, Y. Takagaki, and T. Hiramoto, *Bull. Japan Petrol. Inst.* **12**, 77 (1970).

[2] S. Uemura, T. Hiramoto, and K. Ichikawa, *Kogyo Kagaku Zasshi*, **72**, 1096 (1969).

Table 1. Chlorination of cyclooctadienes and related compounds with cupric chloride[a]

Olefin	mol	Solv. CH_3CN m*l*	$CuCl_2$ mol	Time hr	Product	Yield[b] %	*trans*:*cis*	Residue *g*
Cyclooctene	0.05	100	0.1	4	1,2-dichlorocyclooctane	9	53:47	—
Acrylonitrile	0.3	200	0.3	22	2,3-dichloropropionitrile	42		—
trans-Crotylchloride	0.05	100	0.1	22	1,2,3-trichlorobutane	trace		0.1
1,3-COD	0.05	100	0.1	4	I	44		0.6
1,3-COD	0.05	200	0.3	22	I	58	71:29	1.9
1,3-COD	0.15	200	0.3	22	I	58	69:31	1.8
1,5-COD	0.05	100	0.1	4	II	26		1.0
1,5-COD	0.05	200	0.3	22	II	65	38:62	1.2
					1,2,5,6-tetrachlorocyclooctane	6		
1,5-COD	0.15	200	0.3	22	II	46	38:62	1.5
I	0.05	100	0.1	22	—			0.7
II	0.05	100	0.1	22	1,2,5,6-tetrachlorocyclooctane	8		0.1
In HOAc (200 m*l*) containing NaOAc (0.3 mol) at 82°C								
1,3-COD	0.15		0.3	3	I	1	80:20	
1,5-COD	0.15		0.3	3	II	trace		

a) Equimolar amounts of lithium chloride were added to cupric chloride, and the reaction was carried out under refluxing (at about 82°C).

b) Based on $CuCl_2$ used.

proceeded only slowly in the absence of cuprous chloride. The cyclic structure of the substrate cannot be the reason for the low reactivity, since *trans*-crotyl chloride also resisted the same reaction. Chlorine at the allylic position appers to decrease the reactivity of the double bond towards cupric chloride.

The reaction was slow in acetic acid containing sodium acetate, which is a convenient reaction medium for the chlorination of simple monoolefins with cupric chloride.[1]

The structures of the dichlorocyclooctenes were inferred to be 3,4-dichloro- (I, from 1,3-COD) and 5,6-dichlorocyclooctene (II, from 1,5-COD) on the basis of the analytical data and the IR spectra. The results obtained so far show that only addition occurs and that no isomerization nor substitution proceeds in the liquid-phase chlorination of an isolated double bond with cupric chloride. Since 1,5-diene is not a conjugated one, the normal addition product, II, can be expected unless a transannular reaction occurs to form saturated bicyclic products. Although gas-chromatographical analysis gave two peaks with retention times close to one another, the results do not appear to show the presence of positional isomers, but only that of geometrical isomers resulting from *cis* and *trans* addition. Since the retention times of *trans* isomers of dichlorocycloparaffins are shorter than those of *cis* isomers in the gas chromatogram using Apz-L or PEG columns, the data in Table 1 were calculated on this assumption. Each of two isomers was separated by preparative gas chromatography. Their NMR spectra can be explained in term of these structures.

1,3-Cyclooctadiene is not a usual conjugated diene because of its cyclic structure. The two peaks with retention times close to each other on the gas chromatogram of the chlorinated product appear to show also the presence of *cis* and *trans* isomers, as in the case of 1,5-diene. The NMR spectrum of I is also consistent with these structures.

The *cis* and *trans* ratios in the chlorinated products of cyclooctene and cyclooctadienes, especially in the case of 1,5-diene, are much larger than that of cyclohexene, where the *cis* content was only 2% under the same reaction conditions.

Several attempts to hydrogenate the dichlorocyclooctenes by palladium and platium catalysts in order to confirm the structure further were unsuccessful. These compounds resisted hydroboration by Brown's method,[3] also. The reason for the low reactivities is not yet clear.

A conventional chlorination of both diene with chlorine gas was carried out in acetonitrile (at 6–11°C) and in acetic acid (at 16–26°C). With 1,5-diene, the products were so complicated (16 or 17 peaks in gas chromatograms) that no definite compounds could de isolated, probably because of facile substitution at the allylic positions and transannular reaction.[4] Although the products with 1,3-diene were also complicated (12 peaks in gas chromatograms), I(*trans*: *cis*=95:5) and 5-chlorocycloocta-1,3-diene (bp 75–79.5°C/11 mmHg; NMR τ 3.9—4.6, 4H, τ 5.05—5.45, 1H, τ 7.4—8.9, 6H: IR $\nu_{C=C}$ 1620 cm^{-1}) could be isolated in an almost pure form in this case.

Experimental

Materials. The organic materials were commercial products of the purest grade and were distilled and checked by gas chromatography. The 1,3-cyclooctadiene, bp 142—144°C, and 1,5-cyclooctadiene, bp 150—152°C, (distilled in the presence of *t*-butylcatechol) were both *cis*, *cis*- diene, since

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[3] H.C. Brown and K. Murray, *J. Amer. Chem. Soc.*, **81**, 4108 (1959).

[4] see, for example, S. Moon, and C. R. Ganz, *J. Org. Chem.*, **35**, 1241 (1970).

the IR spectra of both diene showed absorptions at 1660 and 1410 cm^{-1} due to a *cis* double bond, but not at 1675 and 965 cm^{-1} due to a *trans* double bond. The inorganic materials were also commercial materials of an analytical grade and were used without purification. The chlorine gas was prepared by the conventional oxidation of hydrogen chloride with potassium permanganate; it was washed with water and then conc. H_2SO_4 before being introducing into the reaction mixture.

Analytical Instruments. The IR and NMR spectra were determined by the use of a HITACHI EPI-S2 apparatus and a JEOL JNM MH-60 or a Varian A-60 apparatus respectively. Gas chromatographies were carried out by the use of HITACHI K53 (PEG-20M 1 m or Apiezon-L 1 m columns) and SHIMADZU 5APTF (PEG 600 25%-Chromosorb-W 3 m column) apparatuses.

Procedure. Olefinic substrates were added to mixtures of solvents, cupric chloride (anhyd.) and lithium chloride at a reaction temperature. At proper intervals, small portions of the mixture were withdrawn and the decreases in the cupric chloride concentration were determined by iodometry. The reaction mixtures were worked up by the following successive treatments; filtration from the resulting inorganic materials, the evaporation of the solvents, dilution with water, extraction with benzene, and then distillation. Each fraction was analyzed by gas chromatography. The yields of the chlorinated products were calculated on the basis of the weights of the distillates and the g.l.c. analysis data.

trans *and* cis-*1,2-Dichlorocyclooctane.* Bp 103—109°C/11 mmHg, NMR ($CDCl_3$) τ 5.35—5.80 (m, 2H), 7.40—8.10 (m, 4H) and 8.0—8.80 (m, 8H).

1,2-Dichloropropionitrile. Bp 59—60°C/11 mmHg (lit[5], bp 58°C/10 mmHg). IR 2950 (s), 2240 (m), 1440 (s), 1210 (s), 760 (s), 730 (s), and 660 (s),cm^{-1}. NMR ($CDCl_3$) τ 6.15 (d, J=5.5 Hz, 2H) and 5.3 (t, J=5.5 Hz, 1H).

Found: C, 29.08; H, 2.68; N, 11.40; Cl, 57.19%. Calcd for $C_3H_3NCl_2$: C, 29.07; H, 2.44; N, 11.30; Cl, 57.40%.

trans *and* cis-*3,4-Dichlorocyclooctene (Ia,b).* Bp 101°C/10 mmHg and 62—69°C/3 mmHg. NMR [τ 3.9—4.6, 2H (vinyl proton), 4.85—6.0, 2H ($C\underline{H}Cl$) and 7.5—9.0, 8H ($C\underline{H}_2$)].

Found: C, 53.86; H, 6.73; Cl, 39.05%. Calcd for $C_8H_{12}Cl_2$: C, 53.65; H, 6.75; Cl, 39.60%.

trans *and* cis-*5,6-Dichlorocyclooctene (IIa,b).* Bp 119°C/15 mmHg and 88—92°C/6 mmHg. NMR [τ 4.0—4.7, 2H (vinyl proton), 5.35—5.7, 2H ($C\underline{H}Cl$) and 7.0—8.5, 8H ($C\underline{H}_2$)].

Found; C, 53.66; H, 6.81; Cl, 39.50%. Calcd for $C_8H_{12}Cl_2$: C, 53.65; H, 6.75; Cl, 39.60%. IIa and IIb were separated into pure components by preparative gas chromatography (PEG 6000 25%-Chromosorb-W, 1.5 m column; carrier gas, He 120 m*l*/min at 150°C).

trans-*5,6-Dichlorocyclooctene (IIa).* Bp 74.5—75°C/6 mmHg. NMR [τ 4.2—4.5, 2H (vinyl proton), 5.35—5.6, 2H ($C\underline{H}Cl$) and 7.0—8.5, 8H ($C\underline{H}_2$)].

Found; C, 54.32; H, 6.88%. Calcd for $C_8H_{12}Cl_2$: C, 53.66; H, 6.71%.

cis-*5,6-Dichlorocyclooctene (IIb).* Bp 75—79°C/5 mmHg. NMR [τ 4.0—4.7, 2H (vinyl proton), 5.4—5.7, 2H($C\underline{H}Cl$) and 7.0—8.5, 8H, ($C\underline{H}_2$)].

Found; C, 54.09, H, 6.86%. Calcd for $C_8H_{12}Cl_2$: C, 53.66, H, 6.71%.

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[5] N. B. Lorette, *J. Org. Chem.*, **26**, 2324 (1961).