BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (12), 3568—3570 (1978) [Vol. 51, No. 12

The Chlorination of Norbornene and Cyclooctadienes with Sulfuryl Chloride and Phosphorus(V) Chloride. Ionic *vs.* Radical Chlorination with Each Reagent

Sakae UEMURA,* Hajime OKAZAKI, Akira ONOE, and Masaya OKANO
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611

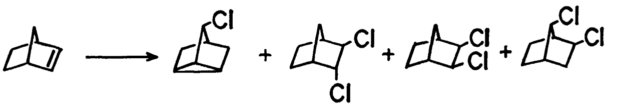
(Received March 31, 1978)

The chlorination of norbornene and cyclooctadienes with sulfuryl chloride and phosphorus(V) chloride has been investigated mainly in carbon tetrachloride under various conditions. From the studies of the product distributions and the effect of radical scavengers, the following facts have been revealed for the first time in olefin chlorination: chlorination with sulfuryl chloride proceeds through an ionic pathway at room temperature or in the presence of silica gel and that with phosphorus(V) chloride through a radical pathway at elevated temperature, and an ionic chlorination with phosphorus(V) chloride in nonpolar solvents does not seem to involve C–P bond formation through the reaction.

Sulfuryl chloride has generally been known to chlorinate olefin through a radical pathway,¹⁾ while it is also known as the effective electrophile in nuclear chlorination of some aromatic compounds.²⁾ Phosphorus(V) chloride, on the other hand, can usually chlorinate olefin *via* an ionic mechanism,³⁾ while it also works as the effective catalyst⁴⁾ or the reagent³⁾ for the radical chlorination of alkanes. In order to know whether each chlorinating agent shows both an ionic and a radical nature in olefin chlorination, we have carried out the chlorination of norbornene and cyclooctadienes under various conditions; these olefins have already been shown to be good substrates to study the nature of chlorination because of clear-cut different distributions in the products between radical and ionic reactions.⁵⁾⁶⁾ We will describe the results and discuss the nature of both reagents.

Results and Discussion

Treatment of norbornene with sulfuryl chloride and phosphorus(V) chloride afforded four products: nortricyclenyl chloride (**1**) and *trans*-2,3- (**2**), *exo-cis*-2,3- (**3**), and *exo*-2-*syn*-7-dichloronorbornane (**4**); their distributions depended very much on reaction conditions. The results are summarized in Table 1, together with



1 2 3 4

the data of typical ionic (Runs 13 and 15) and radical chlorination (Runs 14 and 16) by use of chlorine⁷⁾ and

TABLE 1. CHLORINATION OF NORBORNENE

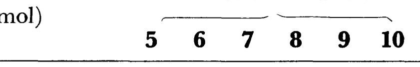
Run	Norbornene (mmol)	Chlorinating agent (mmol)	Solvent (ml)	React. temp (°C)	React. time (h)	Additives *etc.* (mmol)	Products[a]				
							Isomer distribution				Yield (%)
							1	**2**	**3**	**4**	
1	25	SO_2Cl_2 25	CCl_4 50	20	20	—	74	3	1	22	41
2	25	SO_2Cl_2 25	CCl_4 50	76	1	—	15	64	16	5	95
3	25	SO_2Cl_2 25	CCl_4 50	76	1	*m*-DNB[b] 5	61	17	7	15	25
4	25	SO_2Cl_2 25	CCl_4 50	25	2	*hν*	6	78	16	0	97
5	5	SO_2Cl_2 5	Benzene 25	80	2	—	7	74	16	3	97
6	25	SO_2Cl_2 25	CCl_4 50	76	1	SiO_2[c] 39	57	2	0	41	48
7	25	PCl_5 25	CCl_4 50	27	3	—	61	7	3	29	58
8	25	PCl_5 25	CCl_4 50	76	2	—	42	20	7	31	66
9	25	PCl_5 25	CCl_4 50	76	2	*m*-DNB[b] 5	57	5	3	35	72
10	25	PCl_5 25	CCl_4 50	25	3	*hν*	45	25	7	23	92
11	5	PCl_5 5	Benzene 25	80	3	—	45	5	4	46	58
12	5	PCl_5 5	$CHCl_3$ 25	65	2	—	97	trace	trace	3	43
13[d]	—	Cl_2 —	CCl_4 —	25	0.5	O_2	65	6	4	25	95
14[d]	—	Cl_2 —	CCl_4 —	25	0.5	N_2, *hν*	19	37	35	0	—
15[e]	—	$PhICl_2$ —	CCl_4 —	0	47	O_2	79	7	2	12	—
16[e]	—	$PhICl_2$ —	CCl_4 —	74	0.05	—	0	74	26	0	—

a) Determined by GLC. b) *m*-Dinitrobenzene. c) Silica gel, Wakogel C-300, 2.35 g, 100 wt % to norbornene. 2-Chloronorbornane (*ca.* 10%) and a small amount of unidentified compound were also formed. d) Ref. 7. The amounts of olefin and chlorine were not described. e) Ref. 8. Olefin (0.15—0.8 M) and $PhICl_2$ (0.13—0.2 M) were used. The yields of the products were not stated.

(dichloroiodo)benzene.[8] The chlorination with sulfuryl chloride in carbon tetrachloride gave a mixture of **1** and **4** or of **2** and **3** as the main products at room (Run 1) or reflux (Run 2) temperature, respectively. The comparison of the product distribution with that of Runs 13—16 reveals that the reaction has a radical nature at reflux temperature as expected, while it has an ionic nature at room temperature. In fact, when *m*-dinitrobenzene (*m*-DNB) was added as a radical scavenger in the reaction at reflux temperature (Run 3), the yields of the products decreased profoundly and the isomer distribution became similar to that in an ionic reaction, showing that the radical reaction was almost completely suppressed. A quite similar phenomenon was observed using phenol or *t*-butylcatechol instead of *m*-DNB. Under irradiation of UV light (Run 4) or in the presence of benzoyl peroxide, an almost complete radical reaction occurred even at room temperature. The reaction in benzene under reflux also showed a radical nature, as expected (Run 5). Since olefin chlorination with sulfuryl chloride has already been recognized as a radical reaction, as described above, the finding described here seems to be the first clear-cut example of ionic chlorination of olefins with sulfuryl chloride. The attempts of the chlorination in more polar solvents such as acetonitrile and nitromethane, in which the result of a more ionic reaction is expected, resulted in the low yield of products and/or the formation of various unidentified compounds. It has been found that electrophilic chlorination of aromatic compounds by sulfuryl chloride occurs if silica gel is added to the reaction system.[9] When we applied such a reaction to norbornene by using silica gel (Wakogel C-300, 300 mesh), the products whose distribution was clearly characteristic of an ionic reaction were obtained even in the reaction at refluxing temperature (Run 6).

The product distributions in the chlorination of norbornene by phosphorus(V) chloride in carbon tetrachloride, chloroform, and benzene suggest that all reactions proceeded mainly through an ionic pathway (Runs 7, 8, 11, and 12). Considering the results of Runs 8 and 10, however, it may be possible to say that the reaction has a slightly radical nature at refluxing temperature or under UV irradiation in carbon tetrachloride. In fact, the addition of *m*-DNB to a reaction system at refluxing temperature in carbon tetrachloride suppressed the formation of **2** and **3** (Run 9). These results revealed that both a homolytic and a heterolytic chlorination were operative at 76 °C (refluxing temperature of CCl_4) by use of phosphorus(V) chloride. Wyman *et al.*[3] have suggested the presence of a radical nature in the chlorination of *trans*-stilbene at more elevated temperatures (at 124 °C in chlorobenzene as solvent).

Treatment of 1,5-cyclooctadiene with sulfuryl chloride and phosphorus(V) chloride gave *trans*- (**5**) and *cis*-5,6-dichlorocyclooctene (**6**), together with a small amount (<1%) of an unidentified compound. Typical results are shown in Table 2. It has already been clarified that an ionic reaction favored the formation of



5 6

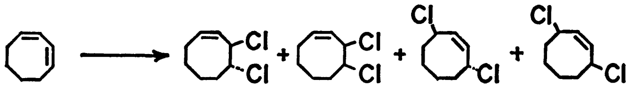
Table 2. Chlorination of 1,5- and 1,3-cyclooctadienes

Run	Olefin (mmol)	Chlorinating agent (mmol)	Solvent (ml)	React. temp (°C)	React. time (h)	Additives *etc.* (mmol)	Products[a]						
							Isomer distribution						Yield (%)
							5	6	7	8	9	10	
	1,5-COD[b]												
17	50	SO_2Cl_2 50	CCl_4 50	76	2	—	12	88					63
18	50	SO_2Cl_2 50	CCl_4 50	76	2	*m*-DNB[c] 10	75	25					38
19	50	SO_2Cl_2 50	CCl_4 50	25—35	2	SiO_2[d] 90	79	21					34
20	50	SO_2Cl_2 50	CCl_4 50	20	20	—	96	4					6
21	50	PCl_5 25	CCl_4 50	76	5	—	30	70					79
22	50	PCl_5 25	CCl_4 50	76	5	*m*-DNB[c] 5	80	20					54
23	50	PCl_5 25	CCl_4 50	20	5	—	48	52					20
24	50	PCl_5 25	$CHCl_3$ 50	65	2	—	98	2					65
25	50	PCl_5 25	CH_2Cl_2 50	40	6	—	99	1					88
26	50	PCl_5 25	Benzene 50	80	2	—	91	9					70
27	6[e]	$PhICl_2$ 5	CCl_4 25	76	1	N_2	20	80					47
28	50[f]	Cl_2 50	CH_2Cl_2 50	−50	0.5	—	93	7					18
	1,3-COD[g]												
29	100	SO_2Cl_2 100	CCl_4 100	76	2	—			19	2	58	21	62
30	50	PCl_5 50	CCl_4 50	76	5	—			17	9	49	25	63
31	25	PCl_5 25	CH_2Cl_2 50	40	5	—			40	7	18	35	56
32	10[e]	$PhICl_2$ 5	$CHCl_3$ 25	61	1	N_2			20	3	58	19	66
33	50[f]	Cl_2 50	CH_2Cl_2 100	−50	0.5	—			45	3	24	28	44

a) Determined by GLC. The yield is based on the chlorinating agent charged. b) 1,5-Cyclooctadiene. c) *m*-Dinitrobenzene. d) Silica gel, Wakogel C-300, 5.41 g, 100 wt % to 1,5-COD. Two unidentified compounds, probably HCl addition products, were also formed (*ca.* 5%). e) Ref. 6. Radical reaction. f) Ref. 6. Ionic reaction. g) 1,3-Cyclooctadiene.

5 (Run 28), while a radical reaction preferred that of **6** (Run 27).⁽⁶⁾ The reaction with sulfuryl chloride at reflux temperature in carbon tetrachloride (Run 17) gave mainly **6**, as expected, while that at room temperature (Run 20) gave mainly **5**, although the yield was very low. The addition of silica gel promoted the ionic chlorination profoundly (Run 19), as in the case of norbornene. On the other hand, the reaction with phosphorus(V) chloride afforded mainly **5** in almost all cases (Runs 23—26), except in carbon tetrachloride in which the formation of **6** predominated (Runs 21 and 23). This result seems to be another and much clearer example of a homolytic olefin chlorination with phosphorus(V) chloride. In all cases where a radical reaction seems to prevail, the addition of *m*-DNB suppressed the yield of **6** markedly and increased that of **5** (Runs 18 and 22).

Although a detailed study was not carried out, the results of some reactions of 1,3-cyclooctadiene with both chlorinating agents were worth noting. The products were four dichlorocyclooctenes, **7**—**10**. Typical results are shown in Table 2, together with the results under ionic (Run 33) and radical conditions (Run 32).⁽⁶⁾ If we compare the isomer distributions in Runs 30 and 31 with those in Runs 32 and 33, it seems that chlorination with phosphorus(V) chloride has a radical nature in carbon tetrachloride at refluxing temperature, while it proceeds mainly through ionic pathway in dichloromethane.



7 8 9 10

Contrary to the case of radical chlorination with sulfuryl chloride, where it has already been clarified that sulfuryl chloride decomposed to chlorine atoms and chlorosulfonyl radicals, both acting as chain carriers,⁽¹⁾ there should be the polarization of sulfuryl chloride shown below in an ionic olefin chlorination. The

$$SO_2Cl_2 \longrightarrow SO_2\overset{\delta-}{Cl}\overset{\delta+}{Cl} \rightleftarrows SO_2Cl^- + Cl^+$$

addition of silica gel clearly enhances such polarization. On the other hand, in the radical chlorination of olefin with phosphorus(V) chloride the dissociation shown below seems to occur at elevated temperatures in carbon tetrachloride; such a dissociation was proposed by Olah *et al.*⁽⁴⁾ in the phosphorus(V) chloride catalyzed radical chlorination of several alkanes.

$$PCl_5 \rightleftarrows PCl_4\cdot + Cl\cdot$$
$$PCl_5 \rightleftarrows PCl_3 + Cl_2$$
$$PCl_5 + Cl_2 \rightleftarrows PCl_4\cdot + Cl_3\cdot \ (Cl\cdot + Cl_2)$$

For an ionic olefin chlorination with phosphorus(V) chloride, it has been proposed⁽³⁾ that phosphorus(V) chloride (in the form of $PCl_4^+PCl_6^-$) added across the double bond to afford the β-chlorophosphorus(V) compound,⁽¹⁰⁾ followed by the S_Ni attack of the chlorine of the PCl_4 moiety and the elimination of phosphorus(III) chloride. Although phosphorus(V) chloride is known to exist in two competing equilibria, (1) $2PCl_5 \rightleftarrows PCl_4^+ + PCl_6^-$ and (2) $PCl_5 \rightleftarrows PCl_4^+ + Cl^-$, in polar solvents, it exists as a monomer in nonpolar solvents such as benzene and carbon tetrachloride.⁽¹¹⁾ Therefore, a mechanism which does not involve C–P bond formation should also be conceivable in the ionic chlorination of olefins with phosphorus(V) chloride in nonpolar solvents. By comparing the product distribution in the case of phosphorus(V) chloride with that in an ionic chlorination with chlorine, one possible scheme may be the ionic attack of chlorine which may be formed by the equilibrium $PCl_5 \rightleftarrows PCl_3 + Cl_2$.⁽³,⁴⁾

The following two points were revealed. The chlorination with sulfuryl chloride proceeds through a radical pathway at elevated temperature, as has been reported, but also through an ionic pathway at lower temperature or in the presence of silica gel. The chlorination with phosphorus(V) chloride is mainly an ionic reaction, but it showed some radical nature in carbon tetrachloride at refluxing temperature.

Experimental

All organic materials and sulfuryl chloride were commercial products and distilled just before use. Commercial phosphorus(V) chloride was used without further purification. The reactions were carried out by mixing all the reagents at room temperature and then keeping the mixture at reaction temperature for appropriate times under the presence of atmospheric oxygen unless otherwise stated. After reaction the mixture was cooled and washed with water and then the organic layer was separated and dried over $MgSO_4$. The identifications of each product, **1**—**4**⁽⁵,¹²⁾ and **5**—**10**⁽⁶⁾ were described previously. The product mixtures were analyzed by GLC by the use of Shimadzu 4BMPF apparatus on EGSS-X (15%)-Chromosorb-W (1 or 3 m) column (carrier gas, N_2; ethyl benzoate as internal standard).

References

1) M. S. Kharasch and H. C. Brown, *J. Am. Chem. Soc.*, **61**, 2142 (1939); D. C. Nonhebel and J. C. Walton, "Free-radical Chemistry," Cambridge Univ. Press, Cambridge (1974), p. 189.

2) See for example, P. B. D. de la Mare, "Electrophilic halogenation," Cambridge Univ. Press, Cambridge (1976), p. 106.

3) D. P. Wyman, J. Y. C. Wang, and W. R. Freeman, *J. Org. Chem.*, **28**, 3173 (1963).

4) G. A. Olah, P. Schilling, R. Renner, and I. Kerekes, *J. Org. Chem.*, **39**, 3472 (1974).

5) S. Uemura, A. Onoe, and M. Okano, *Bull. Chem. Soc. Jpn.*, **48**, 3702 (1975).

6) S. Uemura, A. Onoe, H. Okazaki, M. Okano, and K. Ichikawa, *Bull. Chem. Soc. Jpn.*, **49**, 1437 (1976).

7) M. L. Poutsma, *J. Am. Chem. Soc.*, **87**, 4293 (1965).

8) D. D. Tanner and G. C. Gidley, *J. Org. Chem.*, **33**, 38 (1968).

9) M. Hojo and R. Masuda, *Synth. Commun.*, **5**, 169 (1975).

10) In some cases such intermediates have been formed and converted into the known derivatives: for example, W. H. Woodstock, U. S. Patent 2471471, *Chem. Abstr.*, **43**, 7499 (1949); G. M. Kosolapoff and J. F. McCullough, *J. Am. Chem. Soc.*, **73**, 855 (1951).

11) R. W. Suter, H. C. Knachel, V. P. Petro, J. H. Howatson, and S. G. Shore, *J. Am. Chem. Soc.*, **95**, 1474 (1973).

12) S. Uemura, A. Onoe, and M. Okano, *Bull. Chem. Soc. Jpn.*, **47**, 692, 3121 (1974).