Cyclopropanation of Electron-deficient Olefins with Dibromomethane by Ni(0) Complexes and Zinc

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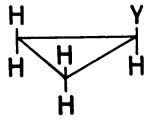
A new method for the synthesis of cyclopropane derivatives is described. It involves treatment of electron-deficient olefins with dibromomethane in the presence of Ni(0) complex/zinc/Lewis acid (or alkali halide) systems. $Ni(PPh_3)_4/Zn/ZnBr_2$ system was effective for the cyclopropanation of methyl acrylate and acrylonitrile, but was ineffective for that of methyl vinyl ketone and acrylaldehyde. $Ni(COD)_2/Zn/NaI$ system was applicable to the cyclopropanation of methyl vinyl ketone as well as to that of methyl acrylate and acrylonitrile. Alternative catalytic systems which were easy to handle were exploited, involving *in situ* generated Ni(0) complexes prepared from $NiBr_2(PPh_3)_2$ and zinc, or nickel bromide, sodium iodide, zinc, and an olefin. Catalytic amounts of nickel compounds are sufficient for the cyclopropanation of methyl acrylate, acrylonitrile, and methyl vinyl ketone, but a 1 : 2 nickel : acrylaldehyde mole ratio results in the best yield. A mechanism is proposed which involves metallacyclobutane as an intermediate.

The Simmons-Smith reaction provides a convenient synthesis of cyclopropane derivatives.[1] Copper has been found to act as an agent for a similar reaction.[2] The metal-carbenoid intermediates of these reactions are electrophilic so that electron-rich olefins are more susceptible to the reactions than electron-deficient ones. Modifications of zinc couples have enabled less reactive *gem*-dihalides and olefins to react: The zinc–copper couple prepared by treating granular zinc with a hot acetic acid solution of copper(II) acetate[3a] and zinc powder prepared by lithium reduction of zinc chloride[3b] can be used in the reactions involving unreactive *gem*-dihalides, and zinc–silver couple can improve yields in the reactions of electron-deficient olefins.[4] However, cyclopropane derivatives of acrylonitrile and acrylaldehyde have been obtained in very low or no yields. We have found a new method for the synthesis of cyclopropane derivatives by the reactions of electron-deficient olefins with dibromomethane by nickel(0) complexes and zinc.[5]

$$CH_2{=}CHY + CH_2X_2 + Zn \xrightarrow[\text{or NaI}]{\text{Ni(0)/Lewis acid}} \quad (1)$$



$+ ZnX_2$

X = Br, I; Y = CO_2CH_3, CN, $COCH_3$, CHO.

Experimental

General. All reactions involving organometallic reagents were carried out under a nitrogen atmosphere. Tetrahydrofuran (THF) was refluxed over sodium, distilled, and stored in a nitrogen atmosphere. Methyl acrylate, acrylonitrile, methyl vinyl ketone, and acrylaldehyde were distilled and stored in N_2 and in a refrigerator. The zinc powder provided by E. Merck was used without further purification. Other chemicals were commercially available and were used without further purification. $Ni(PPh_3)_4$[6] and $Ni(COD)_2$[7] (COD= 1,5-cyclooctadiene) were prepared by literature methods. Analysis and purification of cyclopropanes were run on a Shimadzu 6A gas chromatograph using analytical and preparative columns (PEG, 20% on Celite 545).

Reactions of Olefins with Dibromomethane in the Presence of Ni(0) Complexes and Zinc. In a 100 ml two-necked flask were placed zinc powder (8 mmol) and additives. Tetrahydrofuran (10 ml), an olefin (10 mmol), a Ni(0) complex (0.05—0.90 mmol), and dibromomethane (5 mmol) were added and the reaction mixture was stirred at room temperature for a given period of time.

Reactions of Olefins with Dibromomethane in the Presence of in situ *Generated $Ni(PPh_3)_3$ and Zinc.* In a two-necked flask were placed $NiBr_2(PPh_3)_2$ (0.5 mmol), PPh_3 (0.5 mmol), and zinc (8 mmol). Tetrahydrofuran (10 ml) was added and the mixture was stirred at room temperature. After a few minutes, the color changed from green first to yellow and soon to red-brown. The yellow color is due to the formation of $NiBr(PPh_3)_3$,[8] which is subsequently reduced to red-brown $Ni(PPh_3)_3$.[9] After 30 min, an olefin (10 mmol) and dibromomethane (5 mmol) were added and the mixture was stirred at r.t. for 24 h.

Reactions of Olefins with Dibromomethane in the Presence of in situ *Generated Nickel(0) Complexes and Zinc.* Nickel bromide (0.25—5.0 mmol), alkali halide (0—10 mmol), and zinc powder (8 mmol) were placed in the standard reaction flask. Tetrahydrofuran (10 ml) and an olefin (10 mmol) were added. The mixture was stirred and turned brown in a few minutes. After 20—30 min, dibromomethane (5 mmol) was added and the mixture was stirred at r.t. for a given period of time. If necessary, the flask was thermostated at the desired temperature before dibromomethane was added.

All cyclopropane derivatives were isolated with a Shimadzu 6A preparative gas chromatograph. Their NMR spectra and gas chromatograms agreed well with those of the authentic samples.

Results

Cyclopropanation of Electron-deficient Olefins with Dibromomethane by Ni(0) Complexes and Zinc. Electron-deficient olefins such as methyl acrylate, acrylonitrile, and methyl vinyl ketone (abbreviated as MA, AN, and MVK, respectively) were allowed to react with dibromomethane in the presence of Ni(0) complexes ($Ni(PPh_3)_4$ or $Ni(COD)_2$) to give cyclopropane drivatives.[5] The addition of Lewis acids or sodium iodide is necessary for the reactions. The effects of zinc bromide and sodium iodide on the cyclopropanation of MA, AN, and MVK are shown in Table 1. No cyclopropanation

TABLE 1. CYCLOPROPANATION OF ELECTRON-DEFICIENT OLEFINS WITH DIBROMOMETHANE BY Ni(0) COMPLEX/ZINC/LEWIS ACID (OR SODIUM IODIDE) SYSTEMS[a]

Olefin[b]	Catalytic system: Ni(0) complex (mmol)		Additive (mmol)		Zn (mmol)	Yield[c] of cyclopropane %
MA	$Ni(PPh_3)_4$	0.05	$ZnBr_2$	0.57	8.1	51
		0.10	$ZnBr_2$	0.10	8.1	84[d]
		0.10	$ZnBr_2$	0.61	5.0	27
		0.10	$ZnBr_2$	0.69	8.1	55
		0.10	$ZnBr_2$	0.56	12	79
		0.50	$ZnBr_2$	0.16	8.1	86[e]
		0.50	$ZnBr_2$	1.0	8.2	23
		0.61	NaI	4.4	8.0	24
	$Ni(COD)_2$	0.79	$ZnBr_2$	0.50	8.0	14
		0.43	NaI	4.0	8.0	63
		0.66	phen[f]	0.5	8.1	21
			NaI	5.0		
AN	$Ni(PPh_3)_4$	0.90	$ZnBr_2$	0.95	8.0	18
		0.40	NaI	1.0	8.0	33
		0:37	NaI	6.0	8.0	50
	$Ni(COD)_2$	0.30	$ZnBr_2$	0.51	8.0	14[g]
		0.58	NaI	4.1	8.0	21
MVK	$Ni(PPh_3)_4$	0.41	$ZnBr_2$	1.1	8.0	4.1
			NaI	6.0		
	$Ni(COD)_2$	0.43	$ZnBr_2$	0.51	8.0	20
		0.65	NaI	4.1	8.1	39
		0.43	bpy[h]	0.53	8.0	28
			NaI	4.0		

a) A mixture of an olefin (10 mmol), dibromomethane (5 mmol), Ni(0) complex, Zn, and Lewis acid or sodium iodide in THF (10 ml) was stirred at r.t. for 24 h.b) MA: Methyl acrylate; AN: acrylonitrile; MVK: methyl vinyl ketone. c) Vpc yield based on CH_2Br_2. d) 48 h. e) 46 h. *f*) phen: 1,10-Phenanthroline. g) 18 h. h) bpy: 2,2'-Bipyridyl.

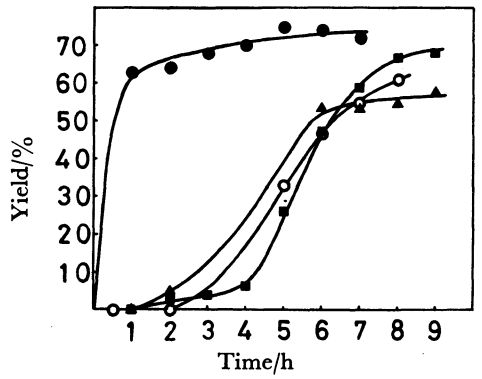


Fig. 1. Time dependence of the yields of methyl cyclopropanecarboxylate in the reaction of MA (10 mmol) with dibromomethane (5 mmol) in THF (10 ml) by the following systems; ○: $Ni(PPh_3)_4$ (0.5)/Zn (8.1)/$ZnBr_2$ (0.56); ▲: $Ni(PPh_3)_4$ (0.3)/Zn (8.1)/$ZnBr_2$ (0.15); ■: $Ni(PPh_3)_4$ (0.1)/Zn (12)/$ZnBr_2$ (0.56); ●: $Ni(COD)_2$ (0.5)/Zn (8.2)/NaI (5.0) where the number in parentheses is given as mmol values.

occurred in the absence of nickel complexes. The yields of methyl cyclopropanecarboxylate slightly increased with an increase in the amount of $Ni(PPh_3)_4$. Although zinc bromide is essential for the reaction, its increase lowers the yield. Lewis acids such as zinc chloride and iodide, and aluminium chloride were also effective,[5] but tin(IV) chloride was ineffective. Sodium iodide played a role similar to that of Lewis acids. In $Ni(PPh_3)_4$/Zn/$ZnBr_2$ or NaI system cyclopropane derivatives from MA, AN, and MVK were obtained in good, moderate, and very low yields, respectively.

The reaction of AN and MVK with dibromomethane gave cyclopropane derivatives in the presence of $Ni(COD)_2$ and NaI.[5] Zinc is required for the cyclopropanation of MA, AN, and MVK by the $Ni(COD)_2$/$ZnBr_2$ system. Sodium iodide is more effective than zinc bromide. An advantage of sodium iodide is the lack of retardation of the reaction by its excess. In $Ni(COD)_2$/Zn/NaI system a further addition of ligands *e.g.* PPh_3, 2,2'-bipyridyl (bpy), 1,10-phenanthroline (phen), lowered the yields of cyclopropanes.

The induction periods were observed in the cyclopropanation of MA by $Ni(PPh_3)_4$/Zn/$ZnBr_2$ system (Fig. 1). The decrease in the amount of $ZnBr_2$ shortens the induction period. It takes about 24 h for the consumption of dibromomethane since the rates after 6 h are very slow. With the elapse of time, zinc bromide is produced (Eq. 1), resulting in a gradual inhibition. On the other hand, the initial rate is very fast in the cyclopropanation of MA by $Ni(COD)_2$/Zn/NaI system. Three-quarters of the total yield is obtained in less than one hour.

Cyclopropanation of Electron-deficient Olefins with Dibromomethane by in situ Generated Ni(0) Complexes and Zinc. When $NiBr_2(PPh_3)_2$ was reduced with zinc in the presence of PPh_3, $Ni(PPh_3)_3$, or $Ni(PPh_3)_4$ was produced *via* $NiBr(PPh_3)_3$.[8b,9] The method serves a double

$$NiBr_2(PPh_3)_2 + PPh_3 \xrightarrow{Zn} NiBr(PPh_3)_3$$
$$\xrightarrow{Zn} Ni(PPh_3)_3 \quad \xrightarrow{PPh_3} Ni(PPh_3)_4 \quad + ZnBr_2 \qquad (2)$$

TABLE 2. CYCLOPROPANATION OF METHYL ACRYLATE AND ACRYLONITRILE WITH DIBROMOMETHANE BY THE *in situ* GENERATED $Ni(PPh_3)_3$/Zn SYSTEM[a]

Olefin	X in $NiX_2(PPh_3)_2$	PPh_3 mole ratio to Ni	Conversion of CH_2Br_2 %	Yield[b] of cyclopropane %
MA	Br	1.0	100	73
	Br[c]	3.0	100	63
	Br[c]	5.0	100	44
	Br[c,d]	1.0	77	6.6
	Br[e,f]	1.0	96	45
	I[g]	1.0	100	18
	I[g,h]	1.0	100	52
AN	Br	1.0	100	49

a) To the *in situ* generated $Ni(PPh_3)_{3-4}$ from $NiBr_2(PPh_3)_2$ (0.5 mmol), PPh_3, and Zn (8 mmol) in THF (10 ml) were added an olefin (10 mmol) and dibromomethane (5 mmol) and the mixture was stirred at r.t. for 24 h. b) Vpc yield based on CH_2Br_2. c) 25 h. d) Mn powder (8 mmol) was used instead of Zn. e) CH_3CN (10 ml) was used as solvent. f) 18 h. g) CH_2I_2 was used instead of CH_2Br_2. h) 0 °C.

TABLE 3. CYCLOPROPANATION OF ELECTRON- DEFICIENT OLEFINS WITH DIBROMOMETHANE BY THE *in situ* GENERATED Ni(0) COMPLEX/Zn/NaI SYSTEMS

Olefin	$NiBr_2$ (mmol)	NaI (mmol)	Temp °C	Time h	Conversion of CH_2Br_2 %	Yield[d] of cyclopropane %
MA	0.5	0	r.t.	24	100	9.9
	0.5	10	r.t.	24	100	67
	1.0	10	r.t.	20	100	73
	1.0	10	0	24	100	90
	1.0[c]	10	0	69	100	83
	3.0	10	r.t.	20	100	71
AN	0.25	6	20	43	100	62
	0.5	1	r.t.	24	100	35
	0.5	6	20	43	100	70
	1.0	6	0	42	100	92
	1.0	6	20	43	100	67
	1.0	6	25	66	98	53
	1.0	KI 7	r.t.	96	41	26
	2.0	6	20	43	98	74
MVK	0.5	LiI 7	0	64	56	7
	0.5	7	0	67	100	58
	0.5	10	0	96	72	67
	0.5	KI 7	0	93	31	16
	1.0	6	r.t.	65	100	78
	1.0	10	r.t.	52	100	82
	1.0	10	0	96	100	97
	5.0	10	0	163	71	67
AC[d]	1.0	5	r.t.	46	64	46
	1.0	LiBr 5	r.t.	48	41	tr
	1.0	LiI 5	r.t.	48	56	36
	1.0	KI 5	r.t.	48	6	3
	1.0[e]	5	r.t.	48	39	30
	1.0[f]	5	r.t.	120	31	17
	1.0	10	r.t.	48	83	60
	3.0	5	r.t.	46	77	71
	5.0	5	r.t.	46	93	81
	5.0	5	r.t.	120	—	48

a) To Ni(0)–olefin complex prepared *in situ* from $NiBr_2$, an olefin (10 mmol), NaI, and Zn (8 mmol) in THF (10 ml) was added dibromomethane (5 mmol); the mixture was stirred for a given period of time. b) Vpc yield based on CH_2Br_2. c) MA (20 mmol), CH_2Br_2 (10 mmol), Zn (15 mmol), and THF (20 ml). d) AC: Acrylaldehyde. e) 1,2-Dimethoxyethane (10 ml) was used as solvent. f) Acetonitrile (10 ml) was used as solvent. g) CH_2I_2 (5 mmol) was used instead of CH_2Br_2.

purpose: The *in situ* generated $Ni(PPh_3)_3$ contaminates the zinc bromide formed, and then catalytic species are completely supplied in Eq. 2 in the presence of excess of zinc.

In the *in situ* generated $Ni(PPh_3)_3$/Zn system, the cyclopropane derivatives from MA was obtained in high yields and that from AN was obtained in moderate yields, but no cyclopropanes from MVK and acrylaldehyde (abbreviated as AC) were produced (Table 2).

Tetrahydrofuran is the most suitable solvent among several examined: The yield decreased in acetonitrile and none was obtained in benzene and diethyl ether.

Dibromomethane gave higher yields than diiodomethane. The yield increased appreciably for reactions with diiodomethane at 0 °C. No reaction occurred with dichlomethane. Zinc could be replaced by manganese, which was a milder reductant, to give a drop in the yield.

We have exploited an alternative catalytic system for $Ni(COD)_2$/Zn/NaI system (Table 3). When the mixture of nickel bromide, sodium iodide, and zinc was stirred in THF in the presence of an electron-deficient olefin, a red-brown solution was obtained after a few minutes. Dibromomethane was added and aliquots were analyzed at various times. A cyclopropane derivative was gradually produced with the elapse of time, in contrast to the case of the $Ni(COD)_2$/Zn/NaI system. This may be due to the slow rate of the formation of a Ni(0)–olefin complex.[10,11] The amount of sodium iodide needed for the reaction is nearly that of the cyclopropane derivative produced. Further addition of sodium iodide brought a slight increase of the yield. Sodium iodide is the most favorable promoter among the alkali halides investigated.

The yields were almost invariable or rather decreased for the cyclopropanation of MA, AN, and MVK with

an increase in the amount of nickel bromide. However the highest yield was obtained at a 1 : 2 nickel : olefin mole ratio for the cyclopropanation of AC. Lower temperatures gave higher yields of cyclopropane derivatives, due to the decrease of the ethylene formation.[12]

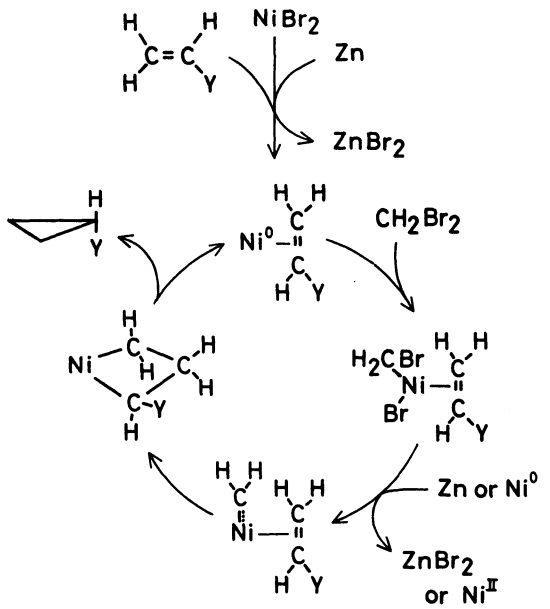
Discussion

The cyclopropanation of electron-deficient olefins with *gem*-dihalides by Ni(0) complex/Zn/Lewis acid systems has some characteristics different from the Simmons-Smith reaction:[1,3,4] (1) Electron-deficient olefins are more susceptible than electron-rich ones; (2) dibromomethane is more suitable than diiodomethane; (3) no cyclopropanation occurs in diethyl ether.

The first requisite for the cyclopropanation of electron-deficient olefins with dibromomethane is the formation of Ni(0)–olefin complexes which are not too much stabilized. Twice as much olefin as dibromomethane was used to complete the reaction of the latter. Ni(0) complexes in the form of $Ni(olefin)_2$ are isolated for olefins with highly electron-deficient groups such as CN, CHO, and $COCH_3$.[10,11] $Ni(MA)_2$ has not been isolated, but its formation in solution may be conceivable on the basis of the results in Tables 1 and 3. The Ni(0) complex of MA is suitably stabilized by further coordination of PPh_3. On the other hand, cyclopropanation of AN, MVK, and AC was inhibited in the presence of PPh_3, bpy, and phen. The inhibition may be caused by the increased stabilization due to their coordination,[13,14] or because olefins are expelled from the sphere of coordination when dibromomethane oxidatively adds to the Ni(0)–olefin complexes.[15] No reaction occurred with electron-rich olefins such as cyclohexene and vinyl acetate because of the absence of nickel–olefin complexes.[14b,17] No cyclopropanation occurred with α- or β-methyl-substituted olefins with polar groups such as methyl crotonate, methyl methacrylate, methacrylonitrile, and 4-methyl-3-penten-2-one due to their weak coordination to nickel complexes.[14b]

The reaction of ethylene with dibromomethane in the presence of Ni(0)–PPh_3 or –bpy complex gives large amounts of propylene and very little cyclopropane.[12] No olefinic products were obtained in the presence of electron-deficient olefins and dibromomethane by Ni(0) complex/Zn/Lewis acid (or sodium iodide) systems.[18] Methylene species formed from dibromethane and Ni(0) complexes[12] or alkylnickel complexes[19] have been thought to be nickel–carbene complexes on the basis of the reactions between metal–carbene complexes and olefins or alkyl groups.[20]

Metallacyclobutane complexes produced from metal–carbene species and olefins are key intermediates for the metathesis of olefins.[21] Metallacyclobutanes undergo metathesis, cyclopropanation, and olefin formation, which are affected by the nature of metals, carbene species, and olefins.[22] The reaction of metal–carbenes and electron-deficient olefins gives reductive elimination products rather than metathesis ones.[20b,c] It seems reasonable to assume that the cyclopropane derivatives from the reactions of electron-deficient



Scheme 1.

olefins and dibromomethane by Ni(0) complex/Zn/Lewis acid (or sodium iodide) systems are produced *via* nickellacyclobutanes. We have not been able to detect any nickel–carbene species.

We propose a mechanism for the cyclopropanation *via* nickellacyclobutane intermediates which are formed from Ni(0)–olefin complexes and dibromomethane. Dibromomethane oxidatively adds to a nickel metal center followed by debromination with a reduced nickel complex or zinc to produce a nickel–methylene complex. The role of Lewis acids or sodium iodide has not been clarified. Lewis acids are necessary cocatalysts in some metathesis reactions.[23] Grubbs *et al.* have found that Me_2AlCl or $AlCl_3$ interacts with titanacyclobutane to facilitate its isomerization and C–C bond cleavage.[24] Lewis acids such as zinc halides and aluminium chloride effectively promoted the cyclopropanation, but their excess hindered the reaction and lengthened the induction period. The basicity of low-valent transition-metal complexes is manifested in many examples.[25] Lewis acids may form adducts involving nickel complexes to saturate coordination sites and/or to deactivate nickel complexes. An excess of sodium iodide, which is the most effective alkali halide, is desirable, but an excess of lithium iodide is not. It is not clear now whether sodium iodide plays the same role as Lewis acids do.

Suitable solvents such as THF may give stabilization to Ni(0)–olefin and/or nickel–carbene and/or nickellacyclobutane complexes by interacting the nickel metal center, and may be easily replaced by olefins. The interaction of Lewis acids with THF may not be neglected completely.[26]

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