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MAGNESIUM—BUTADIENE ADDITION COMPOUNDS: ISOLATION, STRUCTURAL ANALYSIS AND CHEMICAL REACTIVITY

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Summary

The magnesium—butadiene 1 : 1 (I), 1 : 2 (II) and 1 : 3 (III) addition compounds obtained by the direct metalation of butadiene with metallic magnesium were isolated. These compounds have a polymeric structure. Structural analysis of these compounds by NMR and IR methods was carried out. The process for the formation of II via I and III via II was investigated. The results of protolysis and alkylation of the above magnesium compounds corresponded well to those of crotylmagnesium compounds.

The metals used for the direct metalation of conjugated dienes have been limited to alkali metals [1—5] until the direct metalation by magnesium, which gives "magnesium—diene compounds", was developed by Ramsden [6] and Akutagawa [7]. The reaction of the magnesium—isoprene compound with carbonyl compounds to give terpene alcohols was reported by Takase [8,9]. The addition of ethylene to the magnesium—butadiene compounds was recently investigated by Lehmkuhl [10]. This paper describes (1) the isolation of the magnesium—butadiene 1/1 addition compound $(MgC_4H_6)_n$ (I), the 1/2 addition compound $(MgC_8H_{12})_n$ (II) and the 1/3 addition compound $(MgC_{12}H_{18})_n$ (III); (2) the configurational analysis of these compounds by NMR and IR methods; (3) the process for formation of II from I and of III from II, and (4) the chemical properties of these compounds. The structures and chemical reactivity of these magnesium—butadiene compounds were compared with those of dicrotylmagnesium and crotylmagnesium bromide.

Results and discussion

The reaction between metallic magnesium and butadiene in tetrahydrofuran

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(THF) at 40° C in the presence of a catalytic amount (0.1—1.0 mol % of magnesium) of an organic halide gave magnesium—butadiene compounds. The addition of magnesium to butadiene with a g-atom/mol ratio of 1/1 resulted in the exclusive formation of the magnesium—butadiene 1/1 addition compound $(MgC_4H_6)_n$ (I). When the reaction was carried out with a 1/2 or 1/3 ratio at 40° C, the 1/2 addition compound $(MgC_8H_{12})_n$ (II) or the 1/3 addition compound $(MgC_{12}H_{18})_n$ (III) was obtained as the predominant product. Compounds II and III, respectively, gave reduced butadiene dimers and trimers on hydrolysis. Thus, the chain length of the butadiene oligomer in these magnesium compounds parallels the initial molar ratio of butadiene to magnesium (Fig. 1). Iodine, methyl iodide, iodobenzene, ethyl bromide or t-butyl bromide had an excellent catalytic activity for promoting the metalation whereas a chloride (butyl chloride, chlorobenzene or hexyl chloride) had no activity. Tetrahydropyran also was a useful solvent for carrying out the reaction at 40° C, but no reaction occurred in diethyl ether, 1,4-dioxane or ethylene glycol dimethyl ether even at 80° C for one weak. Under appropriate conditions, the reaction could be initiated in THF at 20° C and the maximum conversion was obtained at ca. 60° C as Fig. 2 shows. This enabled us to isolate each addition compound I, II or III. Compound I could be isolated as a white powdery substance by the reaction of magnesium with butadiene at a g-atom/mol ratio of 2/1 at 40° C; the ratio 2/1 instead of 1/1 is suitable for the preparation of pure I. The solubility of I in THF or other common solvents is extremely small. Compound II was a pale yellow powder; the reaction mixture obtained at a molar ratio of 1/2 at 40° C had been cooled down to —78° C to induce its precipitation. Compound III was prepared by the reaction of magnesium with butadiene at a ratio of 1/3 at 70°C. The compound II contaminant in III was removed by precipitation at —78° C. The chemical constitutions of I, II and III were determined by quantitative analysis of magnesium and also by gas chromatographic analysis of the resulting butadiene derivatives.

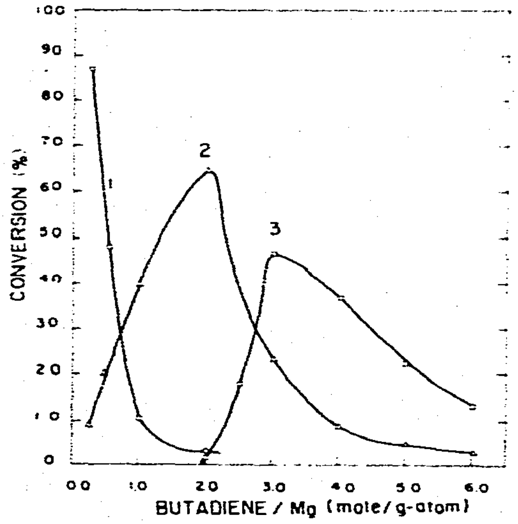


Fig. 1. The variation in conversion to the magnesium—butadiene compounds with mol/g-atom ratio of butadiene to magnesium. Reaction condition; 40° C for 48 h. 1, (MgC_4H_6); 2, $(MgC_8H_{12})_n$; 3, $(MgC_{12}H_{18})_n$.

The success in isolation of a series of these magnesium—butadiene compounds made it possible to investigate the structural and chemical properties of each individual magnesium compound.

Structural analysis of the magnesium—butadiene compound

Deuterolysis of I with deuterium oxide in toluene gave a mixture of 3,4-dideuterio-1-butene, 1,4-dideuterio-*trans*-2-butene and 1,4-dideuterio-*cis*-2-butene in 69, 3 and 28 mol % yields, besides the two mol of THF which had been coordinated to the magnesium atom. Deuterolysis of II gave 3,6-dideuterio-1,7-octadiene, 3,8-dideuterio-1,6-octadiene and 1,8-dideuterio-2,6-octadiene (25, 54 and 21 mol %, respectively). The two mol of THF coordinated to II were recovered also in this case. A mixture of dideuteriocyclododecadienes was obtained by deuterolysis of III. These results show that two carbon atoms of a butene, octadiene or cyclododecadiene moiety in the compound bind to the magnesium atom(s).

In the IR spectra (nujol mull), two absorptions assigned to the C=C vibration were observed at 1604 and 1575 cm^{-1} for I and at 1619 and 1593 cm^{-1} for II. The frequency difference between the two absorptions of I and II corresponds well to those of *trans* and *cis* isomers of pentenylsodium (35 cm^{-1}) [11], crotylmagnesium bromide (21 cm^{-1}) [12] and crotylzinc bromide (18 cm^{-1}) [12]. The absorptions at 1575 and 1593 cm^{-1} are, therefore, assigned to the *cis* C=C vibration and absorptions at 1604 and 1619 cm^{-1} to the *trans* C=C vibration. The *cis/trans* isomer ratio calculated from the IR absorption intensities was 15.5 for I and 1.4 for II. This ratio is consistent with the results obtained from a quenching reaction of these magnesium—butadiene compounds. Thus I gave *cis*-2-butene and *trans*-2-butene in a ratio of 14.5 and II gave *cis*- and *trans*-1,6-octadiene in a ratio of 1.3. It may be concluded that the *cis* conformation is more stable

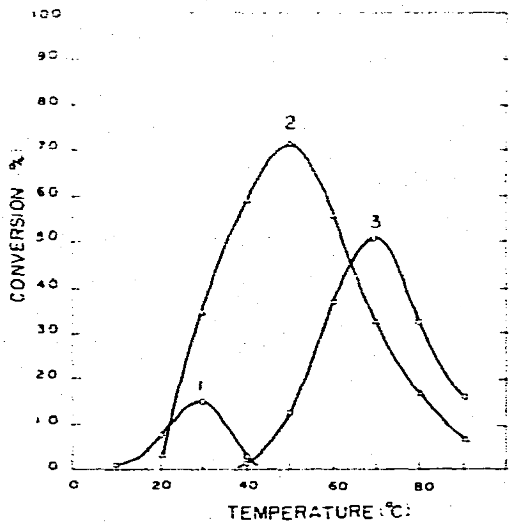
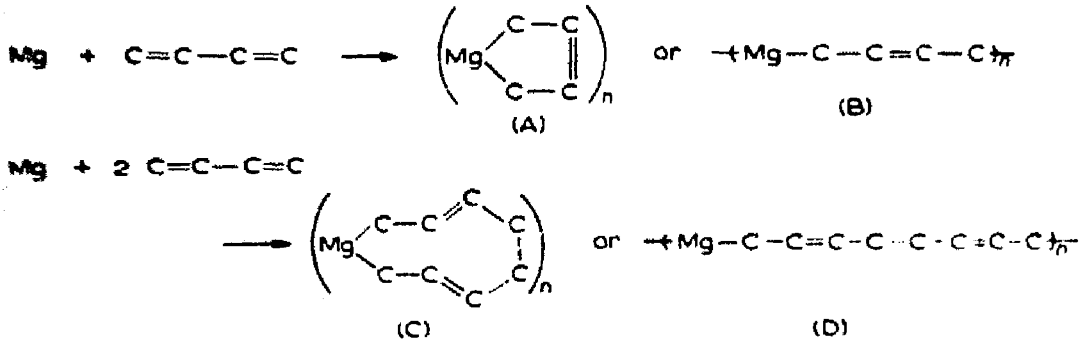


Fig. 2. Temperature dependence of the variation in conversion to the different magnesium—butadiene compounds obtained from a mixture of butadiene and magnesium in a 2/1 (mol/g-atom) ratio. Reaction time, 48 h. 1. (MgC_4H_6); 2, $(MgC_8H_{12})_n$; 3, $(MgC_{12}H_{18})_n$.

than the *trans* one. Thus, one can see the empirical "*cis* rule" in this system that has been shown to be applicable in other allylic systems [13,14]. Summarizing the above results of deuterolysis and IR measurements, either associated structures (A and C) or polymeric structures (B and D) can be considered as the structures of I and II. The molecular weight of II determined in THF by an ebullioscopic method is 2960—3040 (n = ca. 11), irrespective of the concentration of II. This result sharply contrasts to the behavior of usual Grignard reagents [15] or dialkylmagnesium compounds [16] which have monomeric structures in THF. Therefore, the insolubility of I in THF and high molecular weight of II should be ascribed to their polymeric nature (i.e., B and D) rather than to an associated structure.



The NMR spectrum of II is very similar to those of dicrotylmagnesium and crotylmagnesium bromide (Table 1). The chemical shift data suggest that the primary σ-bonded structure exists predominantly in II as well as in crotylmagnesium compounds. Any signals of the other stereoisomer which has the secondary σ-bonded structure have not been detected in the ^{1}H NMR spectrum. The coupling constant J_{23} of 11.8 Hz is an intermediate value between *cis* and *trans* proton—proton couplings [17,18]. The *cis/trans* isomer ratio calculated from the magnitude of the coupling constant with a linear equation [18] is 60/40, in good accordance with the data obtained by the IR and quenching reaction studies. Variable-temperature studies have been done in order to freeze out individual stereoisomers. However, the coupling constant remained unchanged (within a range of ±0.4 Hz) over temperatures from −80 to 50° C. This suggests that a rapid *cis—trans* interconversion is taking place even at −80° C. On the ba-

TABLE 1

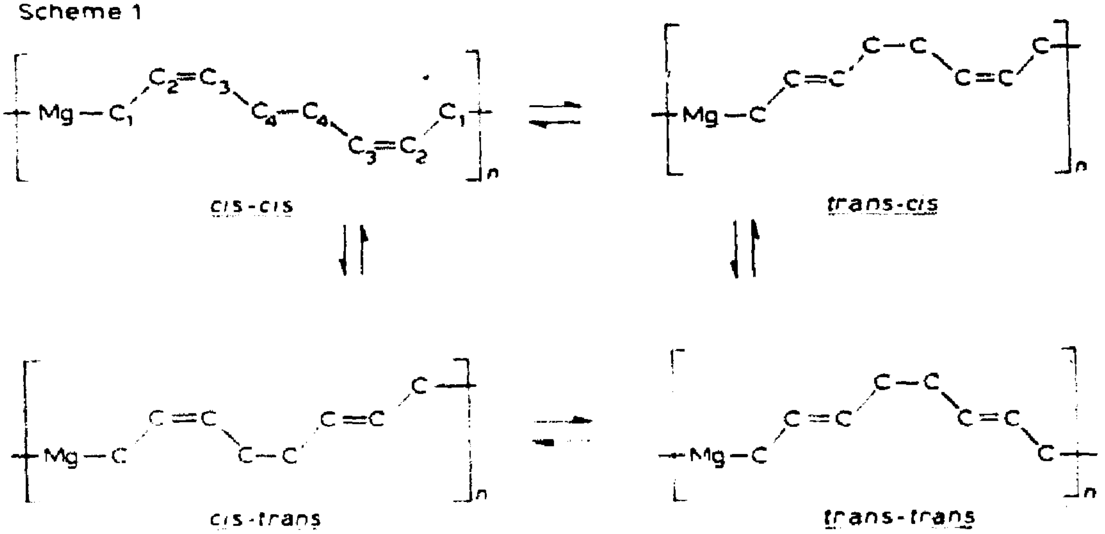
^{1}H NMR DATA FOR $(MgC_8H_{12})_n$, DICROTYLMAGNESIUM AND CROTYLMAGNESIUM BROMIDE [a]

	Chemical shift (ppm)			Coupling constant (Hz)	
	$\tau(H_1)$	$\tau(H_2)$	$\tau(H_3)$	J_{12}	J_{23}
$(MgC_8H_{12})_n$	9.22 (d)	4.04 (double-t)	5.53 (double-t)	9.5	11.8
$Mg(C_4H_7)_2$	9.28 (d)	3.98 (double-t)	5.60 (double-t)	9.6	11.7
$Mg(C_4H_7)Br$	9.33 (d)	4.08 (double-t)	5.54 (double-t)	9.8	11.7

[a] Data were collected at 38° C in THF-d_8. Chemical shifts were calibrated using the upfield THF signal assumed to be 8.15 ppm.

sis of NMR data and the results of the protolysis of II, the equilibrium shown in Scheme 1 is suggested. One and probably all of these species must be in equilibrium with the corresponding stereoisomers. The exact ratio of the *cis—cis*, *cis—trans* and *trans—trans* forms cannot be found from the coupling constant without some idea as to the relative stability of individual isomers.

Scheme 1



The NMR spectrum of I could not be observed due to its extremely low solubility in THF. However, IR and quenching reaction data strongly suggest that the primary σ-bonded structure with *cis* configuration exists in I predominantly.

The process for the formation of II and III from I

The chain growth of the butadiene oligomer contained in the present magnesium—butadiene compounds was dependent on the initial g-atom/mol ratio of magnesium to butadiene. This indicates that III was formed via II and II via I. In practice, the reaction of I with an equimolar amount of butadiene at 0°C in THF gave II in a 90% yield. The reaction between an equimolar amount of II and butadiene proceeded to give III in 50% yield. The compound III thus obtained was identical to that which was produced directly in the reaction between magnesium and butadiene in a 1/3 (g-atom/mol) ratio at 70°C in THF. Thus, stepwise insertion of butadiene into I gave II and then into II gave III. In contrast to I and II, compound III was unreactive to butadiene. The addition of excess (5 molar equivalents) of butadiene to III at 70°C did not result in the formation of butadiene tetramer or a higher oligomer *. Compound III was recovered quantitatively from the mixture. The addition of large excess (10 molar equivalents) of butadiene to magnesium at 70°C resulted in the formation of III as a main product. Butadiene tetramer or a higher oligomer could not be ob-

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* In sharp contrast to the reaction of butadiene, the reaction of magnesium metal with excess of isopropene gave an oligomer having 10—20 units [20] of isoprene. The formation of the ring compounds of the type reported by Ford [21] and Lehmkuhl [10] was not detected in this case.

TABLE 2

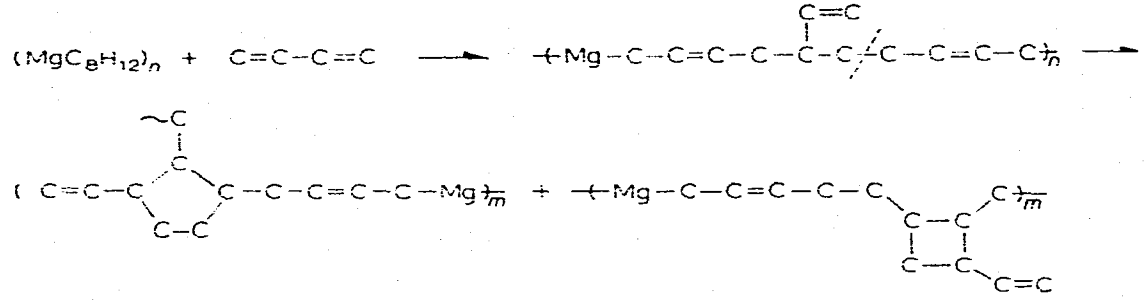
DISTRIBUTION (%) OF PROTOLYSIS PRODUCTS FROM $(MgC_4H_6)_n$ AND $(MgC_8H_{12})_n$ IN THF

Protolysis agents	$(MgC_4H_6)_n$ system			$(MgC_8H_{12})_n$ system					
	1-Butene	2-Butene		1,7-Octadiene	1,6-Octadiene		2,6-Octadiene		
		trans	*cis*		*trans*	*cis*	*trans*–*trans*	*trans*–*cis*	*cis*–*cis*
$(C_6H_5)_3COH$	96	2	2	44	43	10	1	1	1
$t\text{-}C_4H_9OH$	87	2	11	49	41	9	1	0	0
$i\text{-}C_3H_7OH$	84	2	14	45	38	15	1	1	0
H_2O	69	2	29	25	24	30	1	13	7
Piperidine	36	14	50	7	11	34	3	20	25
Pyrrolidine	12	11	77	1	4	14	3	27	51
$(CH_3)_3NO/H_2O$ [a]	4	14	82	0	1	1	11	44	43

[a] The trimethylamine oxide complex was hydrolyzed at 0°C.

tained also in this case. This decrease in reactivity of the magnesium compound III may be ascribed to the form of the carbon skeleton of the butadiene trimer in III. The hydrolysis products of III, $C_{12}H_{20}$, are cyclic compounds. Those are 1-methyl-2-vinyl-5-(*trans*-2′-butenyl)cyclopentane, 1-methyl-2-vinyl-5-(*cis*-2′-butenyl)cyclopentane and 1-methyl-2-vinyl-4-(*cis*-3′-pentenyl)cyclobutane, which have been identified by NMR, IR and mass spectroscopy. The ring closure can be depicted by the sequence of steps as follows.

Similar ring formation has been reported by Richey [19] and Lehmkuhl [10]. When the reaction of III with 5 molar equivalents of butadiene was carried out

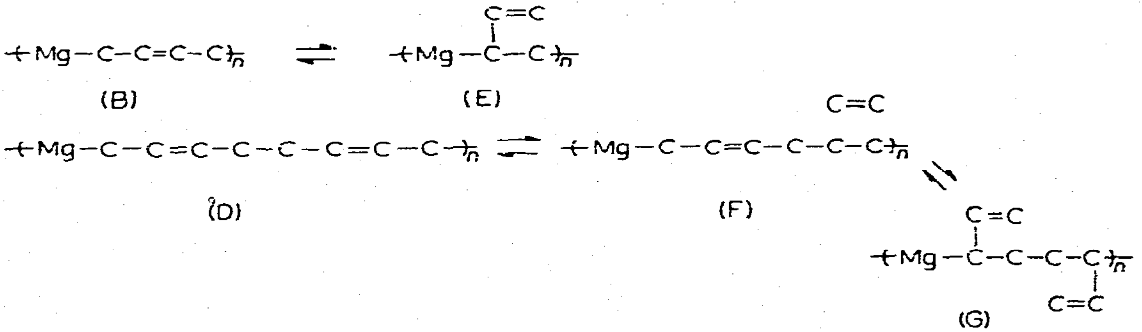


at 120°C, a mixture of butadiene tetramers $C_{16}H_{26}$ was obtained from the hydrolyzate of the resulting $(MgC_{16}H_{24})_n$ (IV). Hydrogenation of the tetramer on palladium charcoal afforded $C_{16}H_{30}$ isomers; only two C—C double bonds exist in the tetramer. This means that the ring closure, like that described above, again occurred during the formation for butadiene tetramer from III. No active allylic carbon—Mg bonds remained in the system. Compound IV thus obtained was not reactive toward butadiene even at high temperatures. These results may be explained on the basis of known chemistry: allylic carbon—Mg bonds are reactive with respect to insertion of olefins [10,22,23] but alkyl carbon—Mg bonds are not. The decrease in reactivity of III and the lack of reactivity of IV for insertion of butadiene can be ascribed to the interconversion of the allylic carbon—Mg bond to an alkyl carbon—Mg bond by the ring closure. The exact structure of the butadiene tetramer cannot be determined without some ideas as to the separation of the four isomers.

Protolysis of the magnesium—butadiene compounds

The distribution of the hydrolysis products derived from crotylmagnesium bromide is known to be dependent on the acidity [24] of hydrolysis agents and also on the polarity of solvents [25]. This dependency was observed also for I and II. Organic protolysis agents used here had a large effect on the variation of the product distribution relative to the hydrolysis agents reported in the past [24,25] (Table 2). The protolysis of I and II with a strong base such as piperidine or pyrrolidine led to the exclusive production of 2-butene and 2,6-octadiene, respectively. In contrast, the addition of tertiary butyl alcohol to I or II resulted in the formation of 1-butene or a mixture of 1,6- and 1,7-octadiene, respectively. This behavior is the same, in principle, as that of crotylmagnesium bromide and dicrotylmagnesium, as Table 3 shows. These variations in distribution of products may be explained by considereing an equilibrium between B and

E for I or D, F and G for II. In order to obtain information about the configurational change of II with the coordination of a strong base, *N*-methylpiperidine was utilized as a model compound of piperidine. The NMR spectrum of the *N*-methylpiperidine complex is assigned to the primary σ-bonded structure D. The chemical shift is the same within ±0.1 ppm as that of II itself in THF. No separate resonances attributable to the species F and G were detected. The hydrolysis of this complex resulted in the exclusive production of 2,6-octadiene (76% yield). The use of a stronger base gave a more typical example for this. Compounds I, II and crotylmagnesium compounds coordinated with one mol of trimethylamine oxide gave *cis*-2-butene or 2,6-octadiene (*cis*-rich) exclusively on hydrolysis (Tables 2 and 3). Thus, the linkage between the α-carbon and Mg atom in the complex is cleaved by hydrolysis in preference to the cleavage of γ-carbon—Mg bonds. The fact that these complexes with strong bases resulted in the exclusive production of *cis* isomer may be ascribed to the ionic character of the organomagnesium compound; i.e., the formation of *cis* isomer can be explained by the hydrolysis of ionic species derived from B and D, which are perhaps in equilibrium with covalent species B and D, respectively. The ionic species derived from B will be also in equilibrium with ionic species from E, and the ionic species from D will be in equilibrium with those of F and G. On the other hand, when acids or weak bases attack the compound II, the formation of *cis* isomer decreased relatively. This behavior is possible to explain by the hydrolysis of covalent species F and G which will be in equilibrium with D; i.e., the species D may convert to F or G by rapid 1,3-shifts which cannot be detected on the NMR times scale. The pathway of the *cis*—*trans* interconversion described in Scheme 1 may be explained by estimating the species F and G to be intermediates as was suggested for crotylmagnesium bromide [18].



Alkylation of I and II with alkyl mono- and di-halide

The alkylation of I and II with an alkyl halide can be explained by assuming structures E and G as intermediates. Compound I gave 3-methyl-1-pentene quantitatively by the reaction with methyl iodide, and II gave 3,6-dimethyl-1,7-octadiene and 3-methyl-1,6-nonadiene in 70 and 30 mol % yields. Thus, an alkyl group from an alkyl halide attacks the γ-carbon of I and II. The result is in good agreement with the conclusion about the alkylation of crotylmagnesium bromide and dicrotylmagnesium compounds studied by Young [24] and Prévost [25,26]. The alkylation reactions provide a novel route to cyclic compounds. The reaction of I with dibromomethane, dibromoethane, dibromopropane and

TABLE 3

PROTOLYSIS OF DICROTYLMAGNESIUM (AND CROTYLMAGNESIUM BROMIDE) IN THF

Protolysis agents	Product distribution (%)		
	1-Butene	*trans*-2-Butene	*cis*-2-Butene
$(C_6H_5)_3COH$	79 (76)	11 (14)	10 (10)
t-C_4H_9OH	90 (86)	4 (6)	6 (8)
i-C_3H_7OH	77 (84)	10 (7)	13 (9)
H_2O	65 (73)	12 (11)	23 (16)
Piperidine	44 (42)	17 (12)	39 (46)
Pyrrolidine	36 (34)	15 (12)	49 (54)
$(CH_3)_3NO/H_2O$	2 (16)	19 (11)	79 (75)

dibromobutane gave vinylcyclopropane [27], vinylcyclobutane [28], vinylcyclopentane [27] and vinylcyclohexane, respectively, in 20—25% yields. The reaction residue was a polymeric compound formed by intermolecular reaction. The reaction between II and dibromomethane afforded a 1/1 mixture of 5-vinyl-1-cycloheptene and 1,3-divinylcyclopentane [29] in 15% yields, respectively. A mixture of 5-vinyl-1-cyclooctene and 1,4-divinylcyclohexane was obtained from a reaction of dibromoethane with II. All these cyclic compounds were identified by NMR, IR and mass spectroscopy partly using authentic samples. This method for the synthesis of such cyclic compounds is rather convenient and widely applicable compared to the methods used in the past, but an improvement in their yields remains as a future problem.

Experimental

General comments

All experiments were carried out under argon atmosphere in a high vacuum system. The inside of the two-necked reaction tube (thickness 2 mm, 35 × 150 mm) dried under vacuum was filled with argon. It was sealed after the reagents had been added and then installed in a temperature-controlled water bath equipped with a vibrator. The resulting solution was transferred using a syringe equipped with a needle (0.8 × 300 mm). THF, benzene and toluene were dried over a sodium/potassium alloy and were distilled. Gas-liquid chromatographic analysis and separation of the reaction products were made with Yanagimoto Model G-80 and Varian-Aerograph Model 700 gas chromatographs using a column packed with 20% Silicone DC-500 on 40/60 mesh Celite 545. The purity of the product was checked with a Hitachi Model K-53 gas chromatograph using a capillary column (HB-2000, 90 m). Infrared spectra were recorded on a Hitachi Model EPI-2 spectrophotometer. The Nujol mull of I was sandwiched by KBr plates in a dry box. The spectrum of II was collected in THF with a JASCO K-III type liquid cell (KBr). The data were collected by compensating the spectrum with that of solvent. ^1H NMR spectra were recorded on a Varian Model A-60 instrument. The mass spectra were obtained using Hitachi RM-5 and RMU-7HR spectrometers.

Preparation of magnesium—butadiene compound I

To 6.08 g (0.25 g-atom) of magnesium turnings in 80 ml of THF cooled to —78° C was added 6.75 g (0.125 mol) of butadiene (dried over Molecular sieves 3A) by distillation and then 0.28 ml (1.0 mol% of magnesium) of iodobenzene as a catalyst. The reaction tube was sealed and the mixture was shaken for 15 h at 40° C. After the tube had been opened, the resulting white precipitate dispersed in THF was removed from the residual magnesium chips using a syringe and washed three times with anhydrous THF to give I. Resulting I was dried under vacuum (0.1 mmHg) at 70° C for 3 h. Typical yield of the solid was 51% based on butadiene. The chemical constitution, $MgC_4H_6 \cdot 2\,C_4H_8O$, of I was determined by the quantitative analysis of the magnesium according to the method of Gilman [30] and of butenes and THF by gas chromatography. (Found: C, 64.40; H, 9.81; Mg, 10.57. $C_{12}H_{22}O_2Mg$ calcd.: C, 64.75; H, 9.95; Mg, 10.92%.)

Preparation of magnesium—butadiene compound II

In essentially the same way as described above, the reaction of 13.50 g (0.25 mol) of butadiene with 3.04 g (0.125 g-atom) of magnesium turnings in 80 ml of THF was carried out at 40°C for 48 h in the presence of 0.08 ml of methyl iodide. The resulting yellow solution was separated from unreacted magnesium chips and then cooled to —78° C to induce the precipitation of II. Three reprecipitations were necessary to remove the contaminating I and III from the precipitated solid II, m.p. —5—0° C. The yield of II was 69%. The chemical constitution, $MgC_8H_{12} \cdot 2\,C_4H_8O$, of II was determined in the same way as described for I. (Found: C, 69.01; H, 9.88; Mg, 8.43. $C_{16}H_{28}O_2Mg$ calcd.: C, 69.46; H, 10.19; Mg, 8.87%.)

Preparation of magnesium—butadiene compound III

A mixture of 20.25 g (0.375 mol) of butadiene, 3.04 g (0.125 g-atom) of magnesium turnings and 0.08 ml of methyl iodide was heated in 80 ml of THF at 70°C for 50 h. After separation of the solution from unreacted magnesium, the solution was cooled to —78° C to remove compound II by precipitation. The upper layer removed from the precipitated II was evaporated to dryness under argon atmosphere, giving III as an oily compound in 62% yield. (Found: C, 72.25; H, 10.25; Mg, 7.18. $C_{20}H_{34}O_2Mg$ calcd.: C, 72.63; H, 10.35; Mg, 7.35%.)

Preparation of magnesium—butadiene compound IV

To 17.15 g (0.05 mol) of III in 90 ml of THF cooled to —78° C was added 13.50 g (0.25 mol) of butadiene by distillation. After sealing the reaction tube, the mixture was heated to 120° C for 12 h. Hydrolysis and deuterolysis of the resulting solution gave butadiene tetramer $C_{16}H_{26}$ and $C_{16}H_{24}D_2$, respectively, in 28—30% yields based on III. The tetramer was isolated with a preparative gas chromatograph, but the isolation of IV and separation of butadiene tetramer (composed of 4 isomers in gas chromatography) to each isomer are unsuccessful at the present stage. Hydrogenation of $C_{16}H_{26}$ (mass: M^+, *m/e* 218) on palladium charcoal afforded $C_{16}H_{30}$ (mass: *m/e* 222) in 99% conversion.

Deuterolysis of the compounds I, II, III and IV

To 1.11 g (5 mmol) of dried solid I in a reaction tube (thickness 2 mm, 25 × 100 mm) was added 10 ml of toluene. After the dispersion was cooled to —78° C, 0.5 ml of deuterium oxide was added and the tube was sealed. Deuterolysis was carried out at 0° C keeping the tube sealed. The tube was again cooled and opened. From the toluene soluble fraction, a mixture of 3,4-dideuterio-1-butene, 1,4-dideuterio-*trans*-2-butene and 1,4-dideuterio-*cis*-2-butene was obtained in 69, 3 and 28 mol % yields, besides the 2 mol of THF which had been coordinated to the magnesium atom. The yields were determined by gas chromatography and calibrated using calibration curves for 1-butene, 2-butene and THF. Deuterated butene isomers were isolated with a preparative gas chromatograph (the trap was cooled to —78° C). The position of deuterium in each isomer was determined by ^{1}H NMR spectroscopy from the proton peak area ratios. The purity (>98%) of the dideuterio-butenes was determined by comparing the parent peaks (M^+, *m/e* 58 for $C_4H_6D_2$) with those of standard C_4H_8 isomers (*m/e* 56).

Deuterolysis of II was carried out in benzene and gave 3,6-dideuterio-1,7-octadiene 3,8-dideuterio-1,6-octadiene and 1,8-dideuterio-2,6-octadiene in 25, 54 and 21 mol % yields, respectively. 2 mol of THF were obtained also in this case. ^{1}H NMR($CDCl_3$, TMS internal standard) and IR(neat) data are as follows. 1,7-Octadiene-d_2, IR (cm^{-1}): 1642 m(ν(C=C)), 980 m(δ(CH_2=CHR)), 908 s(δ(CH_2=CHR)). NMR τ (ppm) 4.7 (m, 2H, CH=C), 5.5 (m, 4H, CH_2=C), 8.4 (m, 2H, CHD—C=C), 9.0 (m, 4H, CH_2). *trans*-1,6-Octadiene-d_2, IR (cm^{-1}): 1642 m(ν(C=C)), 980 m(δ(CH_2=CHR)), 965 s(*trans* δ(CHR=CHR)), 910 s(δ(CH_2=CHR)). NMR: τ (ppm) 5.0 (m, 3H, CH=C), 5.5 (m, 2H, CH_2=C), 8.4 (m, 3H, CHD—C=C and CH_2—C=C), 8.8 (m, 4H, CH_2D and CH_2). *cis*-1,6-Octadiene-d_2, IR (cm^{-1}): 1640 m(ν(C=C)), 981 m(δ(CH_2=CHR)), 910 s(δ(CH_2=CHR)), 705 m(*cis* δ(CHR=CHR)). NMR: τ (ppm) 5.0 (m, 3H, CH=C), 5.5 (m, 2H, CH_2=C), 8.4 (m, 3H, CHD—C=C and CH_2—C=C), 8.8 (m, 4H, CH_2D and CH_2). *trans*—*trans*-2,6-Octadiene-d_2, IR (cm^{-1}): 1655 m(ν(C=C)), 965 m(*trans* δ(CHR=CHR)), 910 s(δ(CH_2=CHR)). NMR: τ (ppm) 5.0 (m, 4H, CH=C), 8.4 (m, 4H, CH_2), 8.8 (m, 4H, CH_2D). *trans*—*cis*-2,6-Octadiene-1,8-d_2, IR (cm^{-1}): 1655 m(ν(C=C)), 965 s(*trans* δ(RCH=CHR)), 705 m(*cis* δ(CHR=CHR)). NMR: τ (ppm) 5.0 (m, 4H, CH=C), 8.4 (m, 4H, CH_2), 8.8 (m, 4H, CH_2D). *cis*—*cis*-2,6-Octadiene, IR (cm^{-1}): 1656 m(γ(C=C)), 715 s(*cis* δ(CHR=CHR)). NMR: τ (ppm) 5.0 (m, 4H, CH), 8.4 (m, 4H, CH_2), 8.8 (m, 4H, CH_2D). The purity of these dideuteriated octadienes was confirmed to be >99% from the relative intensities of M^+, *m/e* 112 for $C_8H_{12}D_2$ and *m/e* 110 for C_8H_{14} in the mass spectra. The results of hydrogenation of these $C_8H_{12}D_2$ on palladium charcoal leading to the formation of $C_8H_{16}D_2$(M^+, *m/e* 116) supported above conclusion.

Deuteriolysis of III in benzene at 5° C gave dideuteriated butadiene trimers (DBT), 1-deuteriomethyl-2-vinyl-5-(*trans*-2′-butenyl-4′-deuterio)cyclopentane (DBT-1), 1-deuteriomethyl-2-vinyl-5-(*cis*-2′-butenyl-4′-deuterio)cyclopentane (DBT-2) and 1-deuteriomethyl-2-vinyl-4-(*cis*-3′-pentenyl-5′-deuterio)cyclobutane (DBT-3) in 28, 52 and 20 mol % yields, respectively. The parent peaks of these DBT, *m/e* 166, in the mass spectra corresponded well to $C_{12}H_{18}D_2$ and the M^+, *m/e* 164, of hydrolysis products to $C_{12}H_{20}$. Hydrogenation of DBT afforded $C_{12}H_{22}D_2$ as proved by mass spectroscopy (M^+, *m/e* 170). DBT-1, IR(neat) (cm^{-1}): 980 m(δ(CH_2=CHR)), 965 m(*trans* δ(CHR=CHR)), 910 s(δ(CH_2=CHR)). NMR($CDCl_3$): τ (ppm) 4.6 (3H, CH=C), 5.1 (2H, CH_2=C), 7.6 (1H, CH—C=C in the ring), 8.1 (2H, CH in the ring), 8.4 (8H, CH_2D—C=C, CH_2—C=C and CH_2 in the ring), 9.2 (2H, CH_2D). DBT-2, IR (cm^{-1}): 980 m(δ(CH_2=CHR)), 908 m(δ(CH_2=CHR)), 705 and 696 (*cis* δ(CHR=CHR)). NMR: τ (ppm) 4.6 (3H, CH=C), 5.1 (2H, CH_2=C), 7.6 (1H, CH—C=C in the ring), 8.1 (2H, CH), 8.4 (8H, CH_2D—C=C, CH_2—C=C and CH_2 in the ring), 9.2 (2H, CH_2D). DBT-3, IR (cm^{-1}): 981 m(δ(CH_2=CHR)), 910 m(δ(CH_2=CHR)), 705 (*cis* δ(CHR=CHR)). NMR: τ (ppm) 4.6 (3H, CH=C), 5.0 (2H, CH_2=C), 7.4 (1H, CH—C=C in the ring), 8.0 (2H, CH in the ring), 8.5 (8H, CH_2D—C=C and CH_2), 9.2 (2H, CH_2D). Deuterolysis of IV was undertaken in a similar manner. The mol. wt. of the product was determined by mass spectroscopy (M^+, *m/e* 220 corresponding to $C_{16}H_{24}D_2$). IR: τ (ppm) 981 s and 910 s(δ(CH_2=CHR)). Hydrogenation of $C_{16}H_{24}D_2$ gave $C_{16}H_{28}D_2$ (M^+, *m/e* 224) quantitatively.

Protolysis of I, II and crotylmagnesium compounds

To 11.13 g (0.05 mol) of I or 13.83 g (0.05 mol) of II in 80 ml of THF was added at —78° C 0.1 mol of a protolysis agent in 10 ml of THF. Protolysis was completed during the tube was allowed to warm to 0 ± 1°C in an ice bath. The tube was again cooled to —20° C and opened. The yields of butenes and octadienes were determined by gas chromatography. Crotylmagnesium bromide was prepared according to the method of Prévost [25]. Dicrotylmagnesium was prepared by isomerization; 200 ml of 1,4-dioxane was added to 7.96 g (0.05 mol) of crotylmagnesium bromide at 10° C and the precipitate of $MgBr_2$ was separated by filtration (yield, ca. 70%). Protolysis of these crotylmagnesium compounds were carried out in the same way as described above.

Alkylation of I and II

To a suspension of 22.25 g (0.1 mol) of I in 120 ml of anhydrous THF, a solution of 15.6 g (0.2 mol) of methyl iodide in 20 ml of THF was added dropwise over 30 min at 0° C. The mixture was stirred at 30° C for 12 h, yielding a white precipitate of MgI_2. The resulting solution was filtered and then distilled to give 3-methyl-1-pentene in 90% yield. In a similar way, a mixture of 13.8 g (0.05 mol) of II and 7.8 ml (0.1 mol) of methyl iodide in 80 ml of THF was heated at 40° C to give dimethylated octadiene derivatives in 82% yield. The reaction of I and II with dihalides were carried out in a similar manner. A typical example is as follows: To a suspension of 22.25 g (0.1 mol) of I in 120 ml of anhydrous THF, 17.38 g (0.1 mol) of dibromomethane in 40 ml of THF was added dropwise at 0° C. After the mixture had been stirred at 30° C for 20 h it was filtered, and the solution was distilled. Resulting vinylcyclopropane was finally separated from THF with a preparative gas chromatograph. In the preparation of vinylcyclobutane, toluene was used in place of THF, as the retention time overlaps with that of THF in gas chromatography. Vinylcyclopropane, vinylcyclobutane and 1,3-divinylcyclopentane were identified with authentic samples prepared by known methods [27—29]. Vinylcyclopentane and vinylcyclohexane were identified with commercial samples (Aldrich Chem. Co., Ltd.). Characterizations of other products were made by ^1H NMR, IR and mass spectroscopy. 1,4-Divinylcyclohexane, IR(neat) (cm^{-1}): 1641 m(ν(C=C)), 995 m and 910 s(δ(CH_2=CH)). NMR($CDCl_3$): τ (ppm) 8.7 (8H, CH_2), 7.9 (2H, CH), 5.4 (4H, CH_2=C) 4.5 (2H, CH=C). Mass spec.: M^+, *m/e* 136. 5-Vinyl-1-cycloheptene, IR(neat) (cm^{-1}): 1640 m(ν(C=C)), 994 m and 910 s(δ(CH_2=CH)). NMR($CDCl_3$): τ (ppm) 8.7 (4H, CH_2), 8.2 (4H, CH_2—C=C), 7.8 (1H, CH), 5.3 (2H, CH_2=C), 5.1 (2H, CH=CH), 4.5 (1H, CH=C). Mass spec.: M^+, m/e 122. 5-Vinylcyclooctene, IR(neat) (cm^{-1}): 1641 m(ν(C=C)) 994 m and 910 s(δ(CH_2=CH)). NMR($CDCl_3$): τ (ppm) 8.8 (6H, CH_2), 8.4 (4H, CH_2—C=C) 7.9 (1H, CH), 5.3 (2H, CH_2=C) 5.2 (2H, CH=CH), 4.6 (1H, CH=C) Mass spec.: M^+, m/e 136.

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