and its MR effect was very large even under low magnetic field which is the desired feature for application of MR devices. Although unclear at this moment, this paper demonstrates that high MR materials under low magnetic field are possible by controlling the doping level of a certain system.

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Dimerization of β-Iodo-α,β-unsaturated Enones by Samarium(II) Iodide[†]

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Alkene-alkene coupling reactions mediated by an organometallic species have been a subject of intense research interests in organic synthesis.[1] A particular case is the dimerization reaction involving the bond formation between sp^2 carbon centers. Besides the classical Ulmann coupling, many methods of alkene-alkene dimerization using a copper species have been known. Methods using other metals including Ni, Pt, Pd, and Rh have also been reported. Some of the representative substrates used for these dimerization processes are alkenyl halides, alkenylboranes, alkenylmercury species, and alkenylstannes.

Since the pioneering investigation by Kagan and coworkers, samarium(II) iodide has been a useful reagent in synthetic organic chemistry because it promotes various organic transformations.[2] Kagan and other research groups have also reported the coupling reaction of acyl halides mediated by samarium(II) iodide to produce α-diketones or α-ketols.[3] In the presence of ketones and aldehydes, the addition of an acyl moiety to the carbonyl group has been also observed. An acylsamarium species, RC(O)-SmI₂, has been suggested as the key intermediate. This species, then, reacts with electrophiles such as acyl halides, aldehydes, and ketones.

Since the formation of an acylsamarium species as the key intermediate has attracted attention, we have been interested in the reactions of β-halo-α,β-unsaturated enones in the presence of samarium(II) iodide. These compounds can be considered as vinylogous acyl halides (eq. 1). The formation of a vinylogous acylsamarium species would be of interest with respect to the preparation of coupled products bearing an interesting structural unit.

$$(1)$$
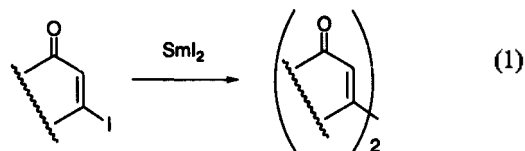
The necessary β-iodo-α,β-unsaturated enones are easily prepared by the methods reported in the literature.[4] Results of samarium(II) iodide-promoted reactions of β-iodo-α,β-unsaturated enones are summarized in Table 1.

As expected, the dimerization of the starting β-iodo-α,β-unsaturated enones occurred to give the corresponding conjugated 1,6-ketones (entries 1-6).[5] The six-membered ring cases are more efficient substrates than the five-membered cyclic compounds.[6] The exocyclic β-iodo-α,β-enones also provided the dimerization products efficiently (entries 7-9).

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Table 1. Dimerization of β-iodo-α,β-unsaturated enones[a]

Entry	Substrate	Product	Yield (%)
1			87
2			46
3			81
4			96
5			91
6			91
7			66
8			67
9			80

[a] 2.2-2.6 equiv. of SmI$_2$ were used.

All the reactions proceeded under very mild conditions (− 78 °C) and completed as immediately after the corresponding substrates were introduced to the reaction medium.

In order to gain more insight into the reaction mechanism and the reactive intermediates, we have performed the cross-coupling reactions, that is, two substrates were mixed (in equal amounts) and subjected to the reaction conditions. The corresponding coupled products were isolated. An equimolar mixture of 3-iodo derivatives of 2-cyclohexenone and 2-cyclopentenone generated approximately equal amounts of dimers of 2-cyclohexenone, 2-cyclopentenone, and the cross-coupled product (eq. 2). A similar experiment has been performed with a mixture of 2-iodomethylenetetralone and 3-iodo-2-cyclohexenone to give the expected cross-coupled and the dimeric products (eq. 3). As regards the rate of generation of the corresponding reactive species (either a radical or organosamarium species), the yields of the dimeric products and the corresponding cross-coupled products indicated that the rate for the formation of the cyclohexenone dimer appeared to be faster than for

the dimerization of cyclopentenenone or exomethylenetetralone.

(2)

30%   24%   29%

(3)

19%   33%   26%
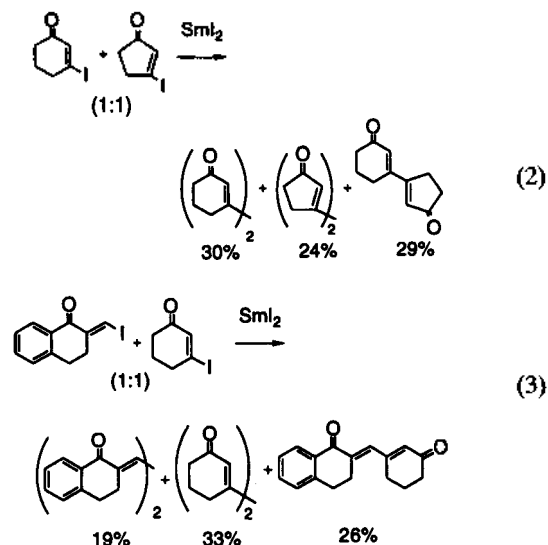
Our efforts to obtain the coupled products of these enones with electrophiles, such as carbonyl groups of aldehydes, epoxides, or alkyl halides have met with failure so far and only the dimerization products were observed under the reaction conditions described. Several observations are worth mentioning. First, approximately 2 equiv. of samarium(II) iodide are required for the optimum yield of the dimerization of 3-iodo-2-cyclohexenone (81%). With less than 2.2 equiv. of samarium(II) iodide, decreased dimerization yields with recovered starting materials were observed. Consequently, 2.2-2.6 equiv. of samarium(II) iodide were used throughout the reactions shown in Table 1. Use of more than 3 equiv. of samarium(II) iodide also decreased the yield. The addition of HMPA was required to achieve better results. In the absence of HMPA, usually lower yields of the desired dimerized products were obtained or decomposition of the starting materials was observed. Performing reactions with or without a proton source such as t-BuOH did not make any appreciable difference to the outcome of the reactions. This could support the view that radical types of the reactive intermediate are involved in the reaction. We presume that the key intermediates such as a radical species are involved in the course of the reactions, although involvement of the organosamarium species as the reactive intermediates cannot be ruled out and more studies are needed to understand the details of the reaction mechanism.

The dimerization reaction under the conditions described here appear to be specific to the case of cyclic enones as shown in Table 1. Preliminary studies on this coupling reaction with other types of substrates such as β-iodo-α,β-unsaturated esters (either cyclic or acyclic) and acyclic α-iodo-α,β-unsaturated ketones were not successful.

In conclusion, the dimerization of the β-iodo-α,β-unsaturated enones by samarium(II) iodide has been shown to be very facile to give the conjugated 1,6-dicarbonyl compounds which are not easily accessible by other synthetic routes. The products obtained from the samarium(II) iodide-promoted reaction here can be useful as interesting sub-

strates or key intermediates for many synthetic applications. Further studies on the reactions are in progress.

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5. Typical procedure: Dimerization of 3-iodo-2-cyclohexenone (entry 3, Table 1). A solution of 3-iodo-2-cyclohexenone (222 mg, 1.00 mmol) in THF (10 mL) was added to a SmI_2 solution (0.1 M) in THF (22 mL, 2.2 equiv.)-HMPA (2.2 mL) under nitrogen atmosphere at −78 °C. After the reaction was completed (monitored by TLC and the color of the solution which changed to brown immediately after the addition), saturated NH_4Cl (5 mL) was added. After most of THF was removed *in vacuo*, water (10 mL) was added and, the products were extracted with benzene and ether mixture (4 : 1, 15 mL × 3). The organic layer was separated, washed with saturated NaCl, dried ($MgSO_4$), and concentrated. Flash chromatography (hexane : ethyl acetate=2 : 1) provided the desired dimerization product as a pale yellow solid (77 mg, 81%). ^1H NMR and ^{13}C NMR data of the product matched those reported in the literature.[6] IR (KBr) 1650 (C=O) cm⁻¹; MS (m/e, rel intensity) 190 (M⁺, 100).

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Synthesis of Cephalosporin Derivatives Utilizing the Cephem Triflate. 2.[1] Introduction of 3-Position Substituents by the Reaction with Enamines[†]

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Cephalosporins have been a subject of synthetic efforts due to their antibacterial activities against many infectious diseases. For the synthesis of cephalosporin derivatives, introduction of substituents at the 3-position has attracted much attention.[2] Although 7-aminocephalosporanic acid (ACA) has been used extensively as a key starting material for preparing cephem derivatives *via* the bond formation at

the 3'-position (*i.e.*, carbon adjacent to the 3-position), direct introduction of the substituent by a wide variety of ways has also been developed. The 3-cephem triflate has been a useful substrate for introducing substituents to the cephems. If the carbon atom of the 3-position of cephems is bonded to a heteroatom, such as oxygen, sulfur, or nitrogen, the cephalosporin derivatives are easily prepared by the reaction between the corresponding heteroatom nucleophiles (for example, thioheterocycles and *N*-heterocycles) and the cephem sulfonates.[3,4] The cephem triflate can be used extensively